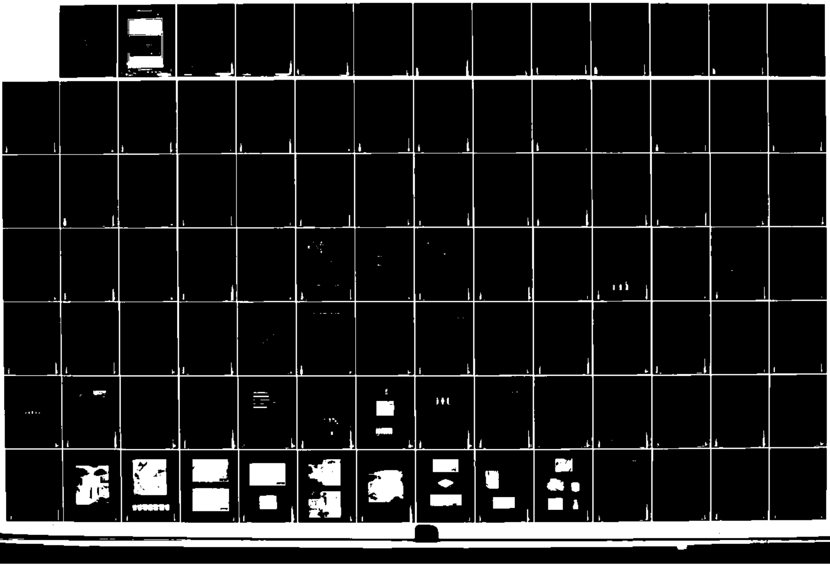
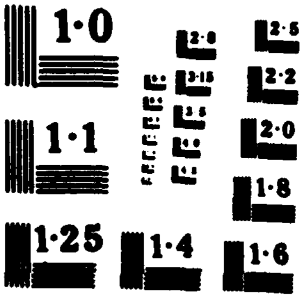
AD A148 598 MATERIALS SUBSTITUTION AND RECYCLING PROCEEDINGS OF THE 1/4
MEETING OF THE ST..(U) ADVISORY GROUP FOR AEROSPACE
RESEARCH AND DEVELOPMENT NEUILLY.. APR 84 AGARD CP-356
UNCLASSIFIED F/G 15/5 NL




1.0
2.8
2.5
3.2
2.2
3.6
1.1
4.0
2.0
1.8
1.25
1.4
1.6

[redacted]

3

AGARD-CP-356

AGARD-CP-356

ADVISORY GROUP

AD-A148 598

AGARD CONFERENCE PROCEEDINGS No.356

Materials Substitution and Recycling

This document has been approved for public release and sale; its distribution is unlimited.

DTIC
ELECTE
NOV 7 1984
S D
A

FILE COPY

[illegible]

COMPONENT PART NOTICE

THIS PAPER IS A COMPONENT PART OF THE FOLLOWING COMPILATION REPORT:

(TITLE): Materials Substitution and Recycling. Proceedings of the Meeting of the Structures and Materials Panel (57th) Held at Vimeiro, Portugal on 14-19 October 1983.

(SOURCE): Advisory Group for Aerospace Research and Development, Neuilly-sur-Seine (France)

TO ORDER THE COMPLETE COMPILATION REPORT USE AD-A148 598.

THE COMPONENT PART IS PROVIDED HERE TO ALLOW USERS ACCESS TO INDIVIDUALLY AUTHORED SECTIONS OF PROCEEDINGS, ANNALS, SYMPOSIA, ETC. HOWEVER, THE COMPONENT SHOULD BE CONSIDERED WITHIN THE CONTEXT OF THE OVERALL COMPILATION REPORT AND NOT AS A STAND-ALONE TECHNICAL REPORT.

THE FOLLOWING COMPONENT PART NUMBERS COMPRISE THE COMPILATION REPORT:

AD#:	TITLE:
AD-P004 211	The Nature of the Critical and Strategic Materials Problem.
AD-P004 212	Factors Affecting the Supply of Strategic Raw Materials with Particular Reference to the Aerospace Manufacturing Industry.
AD-P004 213	Measures for Materials Conservation in Aero-Engine Construction.
AD-P004 214	Towards a Cycle without Loss: Cobalt in the Aircraft Industry.
AD-P004 215	Gas Turbine Engine Design Considerations as Related to Alloys of High Critical Element Content.
AD-P004 216	Understanding the Roles of the Strategic Element Cobalt in Nickel Base Superalloys.
AD-P004 217	Oxide Dispersion Strengthened Alloys.
AD-P004 218	Substitution and Conservation Technology for Chromium.
AD-P004 219	Potential of Metal-Matrix Composites as Superalloy Substitutes.
AD-P004 220	Manufacturing Developments to Reduce Strategic Materials Usage.
AD-P004 221	Practical Implications of the Use of Aluminide Coatings for the Corrosion Protection of Superalloys in Gas Turbines.
AD-P004 222	Coatings for Fuel Economy or Materials Substitution.
AD-P004 223	The Navy Program to Develop Replacements for Critical and Strategic Materials.
AD-P004 224	Ceramics as Substitutes for Scarce Materials.
AD-P004 225	New Developments in Materials Recycling by the US Bureau of Mines.
AD-P004 226	Coating Developments to Restrict Strategic Materials Usage.
AD-P004 227	Trace Elements in Superalloys and the Implications for Recycling.
AD-P004 228	Trace Elements and Residual Elements in Superalloys.
AD-P004 229	Recycling Conform Design.

Accession For
NTIS GRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Dist Avail and/or Special
A/1

COMPONENT PART NOTICE (CON'T)

AD#: **TITLE:**

Accession For
NTIS GRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Avail and/or
Dist Special
A-1

AGARD-CP-356

NORTH ATLANTIC TREATY ORGANIZATION

ADVISORY GROUP FOR AEROSPACE RESEARCH AND DEVELOPMENT

(ORGANISATION DU TRAITE DE L'ATLANTIQUE NORD)

AGARD Conference Proceedings No.356

MATERIALS SUBSTITUTION AND RECYCLING

Papers presented at the 57th Meeting of the Structures and Materials Panel in Vimeiro, Portugal, 19–14 October 1983.

THE MISSION OF AGARD

The mission of AGARD is to bring together the leading personalities of the NATO nations in the fields of science and technology relating to aerospace for the following purposes

Exchanging of scientific and technical information.

Continuously stimulating advances in the aerospace sciences relevant to strengthening the common defence posture.

Improving the co-operation among member nations in aerospace research and development.

Providing scientific and technical advice and assistance to the North Atlantic Military Committee in the field of aerospace research and development.

Rendering scientific and technical assistance, as requested, to other NATO bodies and to member nations in connection with research and development problems in the aerospace field.

Providing assistance to member nations for the purpose of increasing their scientific and technical potential.

Recommending effective ways for the member nations to use their research and development capabilities for the common benefit of the NATO community.

The highest authority within AGARD is the National Delegates Board consisting of officially appointed senior representatives from each member nation. The mission of AGARD is carried out through the Panels which are composed of experts appointed by the National Delegates, the Consultant and Exchange Programme and the Aerospace Applications Studies Programme. The results of AGARD work are reported to the member nations and the NATO Authorities through the AGARD series of publications of which this is one.

Participation in AGARD activities is by invitation only and is normally limited to citizens of the NATO nations.

The content of this publication has been reproduced
directly from material supplied by AGARD or the authors.

Published April 1984

ISBN 92-835-0352-X

Printed by Specialised Printing Services Limited
40 Chigwell Lane, Loughton, Essex IG10 3TZ

PREFACE

Le caractère de rareté de certaines matières premières est longtemps resté un concept un peu abstrait pour les sociétés occidentales, et il a fallu, pour qu'elles en prennent conscience, qu'elles aient eu à faire face à des événements économico-politiques de première grandeur comme le premier choc pétrolier de 1973.

En matière de matériaux métalliques aéronautiques, l'événement majeur a sans doute été la crise Zaïroise de 1979, qui provoqua l'envolée des prix du cobalt. A partir de là apparaissait en pleine lumière un phénomène antérieurement bien identifié : la grande sensibilité de l'approvisionnement en un certain nombre de matériaux – chrome, cobalt, tantale, niobium, mais aussi dans une moindre mesure nickel, tungstène et molybdène – à la fois rares, et pour la plupart d'entre eux guère disponibles dans des pays sûrs.

En outre, l'évolution actuelle de l'industrie aéronautique en matière de moteurs – recherche de consommations spécifiques réduites, entrainant des températures de fonctionnement et des vitesses de rotation accrues – conduit à s'intéresser en matière de superalliages à des formulations nouvelles, dans lesquels la place des matériaux réfractaires figurant dans l'énumération précédente se trouve étendue.

Tous ces facteurs conduisent désormais les instances politiques, les constructeurs aéronautiques et les producteurs de matériaux, chacun pour leur part, à considérer les problèmes de stockage, de conservation, de substitution et de recyclage de matériaux métalliques, comme nécessaires à la fois sur le plan stratégique et sur le plan économique.

Le présent ouvrage, qui rassemble les communications présentées à une Réunion des Spécialistes du SMP de l'AGARD, est focalisé sur deux des sujets précédents : substitution et recyclage. Ont été abordées d'une part toutes les techniques susceptibles, en matière de superalliages, de réduire l'emploi des matières premières métalliques les plus sensibles, mais aussi toutes les solutions alternatives faisant appel à des matériaux d'une autre nature (intermétalliques, céramiques).

Par ailleurs ont été répertoriés les divers problèmes relatifs au recyclage des superalliages dans l'industrie d'élaboration : identification des problèmes provoqués en particulier par l'accumulation d'impuretés, et recherche des solutions correspondantes.

En outre ont été présentés, à titre de synthèse, deux documents introductifs sur les problèmes de géographie économique auxquels se réfère la réunion, ainsi qu'une revue sur les techniques économes en matières premières (métallurgie des poudres par exemple).

Une table ronde a eu lieu en clôture, comportant quelques communications brèves et une discussion générale sur chacun des deux thèmes retenus. Elle sera éditée sous la forme d'un opuscule complémentaire.

P. COSTA
Président du Sous-Comité
"Substitution et Recyclage de
Matériaux Hautes Températures"

Partial CONTENTS.

SESSION I – INTRODUCTION

SESSION II – SUBSTITUTION

SESSION III – RECYCLING

THE NATURE OF THE CRITICAL AND STRATEGIC MATERIALS PROBLEM

by

John B. Wachtman, Jr
Director, The Center for Ceramic Research
Rutgers, The State University of New Jersey
Piscataway, New Jersey 08854, USA

AD-P004 211

ABSTRACT

The economies and national defense systems of the industrialized, market-economy countries depend on many imported raw materials. Some of these materials are vital to the performance of advanced weapons or to basic production capacity such as machine tools. While no present shortage exists, the potential of supply interruptions requires national preparedness as a form of insurance. Adequate preparedness requires a multi-faceted strategy including the capability of short-term response, such as stockpiling, and longer term responses such as emergency substitution. Development of substitutes occurs normally only when a price or performance advantage is foreseen. Some substitutes are being developed through this natural economic process, but in other cases no direct economic motivation exists. Technically promising substitution development which could reduce vulnerability may require more deliberate and better organized government support.

1. INTRODUCTION: IMPORT DEPENDENCE

Substitution and recycling in relation to critical and strategic materials, the topic of this meeting, need to be considered in a broader context. What are critical materials and which of them are strategic? To whom? What are the actual or potential strategic problems? What can be done to solve these problems? What is the role of substitution and recycling within the overall set of solutions? What are the present and potential possibilities of substitution from a technical viewpoint? To what extent are these technical possibilities likely to be realized through normal market forces and current government programs? Is there a need for additional programs? In this paper we attempt to deal broadly with these questions, providing a background and setting the stage for the detailed technical papers to follow.

A vast literature exists on the subject of strategic and critical materials, especially with respect to the United States. Much of this literature is in the form of reports with limited availability. In this paper the author seeks to give a purely personal viewpoint supported by references which are far from a complete set but which are among the more accessible. Two forthcoming references of special merit were available in draft form (references 1,2) and have been used for a general update.

The highly industrialized, market-economy countries import more than half of many of the raw materials which they require. Table 1 gives percentages imported for 12 essential commodities. The United States, the European Economic Community, and Japan are each heavily dependent on imports. In contrast, the COMECON countries supply most of their own needs for these commodities with the exception of cobalt. Even for cobalt they supply about one-third of their needs and so would be able to come much closer to meeting their most essential needs from their own production than the EEC which imports 97 percent of its needs.

Concern over a possible interruption in supply is intensified by the fact that for some materials the supply comes primarily from a few countries. Moreover, some of these countries are thought to be politically unstable. Table 2 lists the primary source countries having the greatest reserves for the materials of Table 1 (references 3,4). Belgium-Luxemburg, listed as a source of cobalt, is of course not a primary source. This example suggests the difficulty of tracing supply to its ultimate source, for example, finding the true source of chromium during the embargo a few years ago. Caution and expert advice are appropriate in using such data.

2. CRITICAL MATERIALS

Concern with the economic and security aspects of materials shortages has a long history. In the United States this concern goes back to World War I and led ultimately to the establishment of the United States' strategic stockpile which exists today. Import dependence alone was not the concern. Rather the concern was and is with materials which are critical to a country's well-being and are strategic in the sense of being imported and being thought to be vulnerable to reduction of supply. Opinions as to which materials are "strategic and critical" have varied greatly. Sixty one commodities (some in several forms) are still held in the U.S. Stockpile but many are there for historic reasons rather than current views of their importance. Generally attention centers on a list of ten to fifteen minerals as shown in Table 3 (references 5,6).

A recent systematic evaluation of the degree of strategic metal vulnerability in the United States deserves special mention (reference 7). A committee of the Metals Properties Council chaired by K.W. Stalker examined 18 important metals. They used a new index which takes into account needs (in peace or war), reserves (World, North American, and USA), production (World, North American, and USA; each in peace and war), US consumption (in peace or war), reliability of source (in peace or war), state of US stockpile relative to goal, cost in $ per pound, ability to recycle (in peace and war), and probability of cartel formation (in peace and war). The results fell into three groups as shown in Table 4.

This result for the most critical metals corresponds closely to the current general view at a policy level in the United States Bureau of Mines concerning the most critical materials to the U.S. As shown in Table 5, these are chromium, cobalt, manganese, and the platinum-group metals (reference 8).

There is, in fact, no consensus on which are the most critical materials because different groups have different interests as well as different perceptions of vulnerability and therefore arrive at different lists of critical materials. Perhaps a more important difference of opinion concerns the question of the form of materials to consider critical. We shall return to this question in Section 13.

3. POSSIBLE PROBLEMS

Clearly there are differences in the strategic and critical materials problems of different countries among the industrialized, market-economy countries, but their problems seem increasingly similar. Much of the existing analysis refers to the United States and will be drawn upon as increasingly representative of the general situation.

Fischman has classified possible problems with minerals supply into two categories, long-term and short-term, as shown in Table 6 (reference 9). He views the former as arising out of persistent conditions, or trends, and the latter as arising out of large deviations from trend or other transitory occurrences. Most of the classifications of Table 6 are self-explanatory but a few may require clarification. Long-term exposure to short-term supply contingencies occurs when there is physical concentration of supply in areas (such as southern Africa with respect to chromium) that are unusually subject to politically motivated supply interruptions. Some of the price-driven problems classified by Fischman are primarily problems to producing countries rather than to users, and may even benefit users for a while but can lead to longer term problems for users if some suppliers are driven out of business.

From the point of view of this audience the above classification may seem over elaborate. Probably most of those present here would prefer to concentrate on items 2 and 9. That is, on living with the continuing potential of a politically-motivated supply restriction or the actuality of one. Before concentrating on this type of problem it is well, however, to reflect for a moment on some implications of the above complex classification. Mineral supply and demand is generally an economic question and becomes something else only when distorted by politics or war. Mineral resources are distributed unevenly among nations. There is an inevitable process of seeking economic advantage which market-oriented economies should presumably leave to the market to settle. In practice this economic truism is not completely followed by any government if the economic consequences become severe. Thus a discussion of critical materials is inevitably a political discussion whose ramifications may divide allies in some cases. We cannot pursue this subject here, and will concentrate on the types of emergency (2 and 9) in which this audience presumably can find common cause. That is, we will consider dealing with an existing emergency or a long-term threat of an emergency which is clearly of the nature of a war or a major political activity and clearly outside the normal market process even when the latter is modified somewhat by a moderate level of intervention by governments.

4. IMPACT AND LIKELIHOOD OF SUPPLY PROBLEMS

The impact of a supply problem depends, of course, on the uses on the material and would vary greatly among the critical materials. Let us briefly examine the major uses and the major sources of supply for the four most critical materials.

The major uses of chromium in the United States are shown in Table 7 (reference 10). Metal production dominates and within metal production stainless steel dominates. Superalloys, which are often cited as a vulnerable area, require only 2.5 percent of the chromium used in metals or less than two percent of all chromium used. Table 8 gives the distribution of known ore reserves and shows the well-known dependence on southern Africa. Table 8 also shows that despite the concentration of known chromium reserves in one part of the world there is an immense amount of it, more than a two hundred years supply at current use rates. The great utility of chromium, its relatively modest price as a speciality metal (less than a dollar per pound of contained chromium in ore), and the large reserves indicate that it will continue to be used in large amounts. Indeed, the development in South Africa of a new family of weldable, corrosion-resistant alloys (termed 3CR12 by Middleburg Steel and Alloys Ltd.) containing 12 percent chromium suggests that a considerable increase in the use of chromium may occur, possibly a 50 percent increase.

The use, distribution and price patterns for cobalt are quite different (reference 11). Table 9 shows that the use of cobalt is indeed concentrated in high technology applications: superalloys, magnets, and tools. Southern Africa is again an important source but does not overwhelm the picture to as great an extent. Substantial reserves exist in Oceania and the United States has a substantial amount of uneconomic resources which could be mined in an emergency. The immense potential of the seabed nodules should also be noted. The price of cobalt has varied from $5 to more than $25 per pound in recent years.

Manganese presents a quite different situation than either chromium or cobalt (reference 11). About 90 percent of all forms of manganese consumed in the United States is used in the manufacture of iron and steel. It is used for deoxidation, desulfurization, and control of morphology of sulfides and carbides in iron and steel products. Its effects on strength, toughness, hardness, and hardenability are also important. Steelmaking without the use of manganese, although possible, would adversely affect steelmaking costs. Fortunately, the distribution of manganese reserves is relatively widespread. The principal free-world sources of manganese are the Republic of South Africa, Gabon, India, Australia, and Brazil. Mexico could become a significant supplier in the future (reference 12).

The world production of platinum-group metals in 1978 is summarized in Table 11 (reference 13). Table 12 gives the major categories of use in 1977 and a forecast for yearly consumption beyond 1988. Without taking time to go into detail about palladium, rhodium, and iridium, let us note that they have some specialty uses (e.g. as components in certain catalysts or as crucibles for crystal growth) for which platinum alone cannot substitute. The platinum-group metals present a complex picture of specialty uses dominated by the requirements for catalysts for pollution control for vehicles. Despite great efforts, substitute catalysts have not displaced them yet. It is noteworthy that substantial deposits of platimum and palladium are known in Stillwater in the United States so that emergency mining would be possible.

5. POSSIBLE RESPONSES TO SUPPLY PROBLEMS

With these facts about critical and strategic metals in mind let us turn to a consideration of how a country might respond to a supply interruption. A useful classification of responses is given in Table 13 (reference 14). Let us recognize at once that the responses listed there do not fit with complete comfort into the boxes shown. Nevertheless, this classification does properly emphasize the most important aspects of these types of response in terms of whether they are primarily short-term or long-term and whether they are primarily aimed at modifying supply or modifying performance.

What can be done as a short-term response to a shortage of a critical material? Stockpiled material can be disbursed. Production from the remaining sources of supply can be allocated; i.e. government can override market allocation of the remaining short supply in the interest of national security considerations. Recycling can be increased beyond the normally economic level. All of these responses aim at providing alternate supply of the shortage materials. In contrast, the fourth type of short-term response is to substitute in situations where the technology of substitution is known and available.

What can be done to respond on a longer time scale? International relations can be cultivated to assure supply from remaining foreign sources. Domestic production from normally uneconomic sources can be subsidized. Research and development can be conducted to develop new substitutes. Substitution which has succeeded at the laboratory level can be pushed through the generally expensive and time-consuming process of establishment in commerce.

In the brief time available let us give some consideration to each of these responses.

6. STOCKPILING

In the United States, the Strategic and Critical Materials Stockpiling Act provides for "the acquisition and retention of stocks of certain strategic and critical materials and to encourage the conservation and development of sources of such materials within the United States and thereby to decrease and to preclude, when possible, a dangerous and costly dependence by the United States upon foreign sources for supplies of such materials in times of national emergency" (reference 15). The Act defines "strategic and critical materials" as "materials that (A) would be needed to supply the military, industrial, and essential civilian needs of the United States during a national emergency, and (B) are not found or produced in the United States in sufficient quantities to meet such need". It is interesting to note that the Act speaks of industrial and essential civilian needs as well as military needs and that it speaks of national emergency rather than more narrowly of war. However, the stockpile is clearly intended to be used only as a last resort and not for intervention in the economy except in extreme circumstances. The Act allows release of material only for "purposes of the national defense".

The status of the stockpile with respect to the four materials currently considered to be most important is summarized in Table 14. The goals are set by the Act's requirement that "The quantities of the materials stockpiled should be sufficient to sustain the United States for a period of not less than three years in the event of a national emergency". In practice, a complex set of political and budgetary considerations affect the holdings; for example, sale of excess material such as silver is often resisted by the producers. The situation differs greatly within the four materials; the goal is greatly exceeded for manganese, substantially met for chromium, and is less than half met for cobalt and the platinum group metals. Such a broad statement omits consideration of detailed considerations. For example, declining capacity for ferrochrome production could make the United States unable to use the stockpiled chromite at an adequate rate. On the other hand, certain other metallurgical furnaces might be capable of rapid conversion to ferrochromium production. A similar concern is whether the older stockpiled cobalt is of sufficient grade to be used directly for modern superalloys.

Whatever its shortcomings, the U.S. stockpile is a strong insurance policy which would provide priceless time to put other responses to an emergency into effect.

7. ALLOCATION

Under the Defense Production Act of 1950 the President of the United States is given broad powers to give priority to contracts and to allocate production involving strategic and critical materials when he finds that it is essential to do so in the national defense. This function is carried out primarily through the Department of Commerce. The authority has occasionally been used in peace time; for example, in connection with building the trans-Alaska pipeline.

8. RECYCLING

Recognizing that recycling will be treated in detail later, we shall confine ourselves to two points here. First, recycling of scrap within a plant or of between plants at different locations but belonging to the same firm is very different from recycling of scrap produced by diverse consumers. In the latter case collection and separation are serious problems. Second, the latter type of recycling brings into play additional institutional factors. In both cases the interplay of technical and economic factors controls how much recycling is done. In the latter case such institutional factors as the ownership of municipal refuse by numerous highly diverse types of local government units, which are subject to other overriding concerns, makes recycling post-consumer refuse for recovery of strategic materials difficult except for pulling out the most expensive items such as the platinum group metals.

9. SHORT-TERM SUBSTITUTION

A basic problem with substitution is that if the substitute were as good and as cheap as the material in use, substitution would occur without the pressure of the threat of strategic materials vulnerability. This statement must be modified by recognizing the large inertia in the use of materials caused by the investment in capacity to use the current material and the barrier which standards may cause. In many situations it is easier to write a standard in terms of a material rather than in terms of performance. Qualifying a new alloy for use in critical components of an aircraft is an expensive and time-consuming task.

Another crucial aspect of substitution is that it involves not just the properties of a material but the whole sequence of process involved in the manufacture and use of goods with the substitute material. Thus there are strong barriers to use of a substitute material unless the economic advantage is great enough to justify all the costs of new capital investment, new standards development, and user education. Sometimes the benefits of these investments cannot be captured by the person making them so that the real beneficiary must help with these costs if substitution is to occur.

Here is a situation where a certain amount of judicious investment by government seems an appropriate part of a balanced program of national security. While no clear action plan has evolved there is a continuing discussion on what should be done so that existing substitution technology could be rapidly deployed when needed. One proposal is for an "information stockpile" which would contain information on substitution technologies including all the associated process and use changes (references 16,17). It has been proposed to establish an international program to develop standards to facilitate the use of advanced materials (reference 18); a logical extension would be to develop standards for substitute materials for emergency use.

10. INTERNATIONAL RELATIONS

Since World War II a much more liberal trading system has evolved among the free world nations as a result of the recognition that protectionism had failed in the interwar period (reference 19). Three decades of relatively high growth rates took place in the industrial countries. In recent years the developing world has called for a new international economic order, heavily emphasizing the stabilizing of raw materials prices and seeking to raise them by means of international commodity agreements. This is a major challenge to the free trade, market-oriented system favored by most industrialized nations, at least in theory. Another challenge concerns off-shore minerals (including petroleum, manganese nodules, and the newly discovered sulfides) and the impact of the Law of the Sea.

11. ENHANCED DOMESTIC PRODUCTION

Domestic production of many minerals has declined in industrialized nations. The common explanation involves declining grades of domestic resources in contrast to good grades and cheaper labor in certain developing nations. However, some commodities can still be produced domestically from lower grade ores (e.g. copper in the United States) so that technology, organization, capital, and proximity to markets can sometimes overcome a resource disadvantage. Industrial, free-world nations generally do not find it advantageous to subsidize uneconomic mining, but support for minerals research and development and a favorable climate for domestic industry can be an important part of reducing vulnerability when marginally economic domestic resources exist. Discovery of new domestic ores would be very important yet, as Yoder (reference 20) points out, there is no major basic research effort in the U.S. specifically designed to provide the fundamental knowledge needed to explore for elements in minerals not now exposed at the earth's surface.

12. RESEARCH AND DEVELOPMENT FOR SUBSTITUTION TECHNOLOGY

Considering that substitution technology is one of two main themes of this conference and will be dealt with in many papers to come, we shall address only a few principal points.

First, substitution can be taken in a broader sense to include process substitution and to include coatings technology. Since some of the most important possibilities for savings in critical materials use would be excluded by a narrow definition of substitution, the broader sense is taken here. We have noted that two-thirds of chromium usage is in alloys. A recent study of the steel industry (reference 21) discusses several technical innovations which are being introduced in steelmaking which may act to reduce average alloy use in steel production. These include continuous casting, new melting and refining practices, quality control through sensors and computers, and improved shape control. Surface modification is a major opportunity for further reduction in critical materials use.

Possibilities for reduction by year 2000 in chromium and cobalt required by the aerospace industry are given in Table 15. The wide band between the high and low estimates indicate the great uncertainty of such estimates, but the results show that very important reductions in vulnerability are possible through technical advances in substitution and near net shape processing. Good technical opportunities exist for the substitution of ceramics for high temperature alloys, for cutting tools, for wear surfaces, and as components in composites (reference 22).

In view of these potential reductions, how much is being done to achieve them? The answer appears to be that relatively little is being done in a purposeful way with the exception of a few fine activities such as NASA's COSAM program (reference 23). The reason is apparent. Private industry has little incentive to invest in research and development solely to produce substitutes which would be used only in an emergency; they have little hope of reaping a financial benefit from such investments. Their work on improving performance and lowering cost does lead to replacement materials and does appear to be leading to reduced vulnerability through the development of alternate materials but this result is a spinoff rather than a primary goal. It is well to remember, however, that developments of new materials could also lead to increased rather than decreased use of critical materials as may be the case with the new 3CR12 steel mentioned earlier.

Government, as part of its role in seeking to assure national security has a good reason for supporting research on substitute materials. A survey of federally supported materials research and development in the United States in 1980 attempted to assess the amount of work being done on substitute materials (reference 24). Out of a total of 1, 103,683 thousand $ spent on federal materials R&D, 9,648 thousand $ was spent of work directly related to substitution and an additional 13,960 thousand $ was spend on work related to substitution. The total of 23,608 thousand is only about 0.2 percent but is even less impressive when it is realized that the projects are scattered in many agencies and are subject to pressure from other priorities which make stability of work difficult. Table 16 lists the total federal funding for all forms of research related to critical materials. The amount totals 7.4 percent of all federal materials R&D.

13. STRATEGIC AND CRITICAL ENGINEERING MATERIALS

Certain special manufactured materials can be critical and strategic because of the nature of the manufacturing process rather than the raw materials required. Our discussion so far has concentrated on raw materials. The implied assumption is that a country can process these raw materials into the vast number of engineering forms required. We briefly noted one case, ferrochrome versus chromite ore, for which an interruption of ferrochrome imports into the United States might cause a serious problem despite the large chromite stockpile because of declining capacity for ferrochrome production. Many other examples exist.

The case of ceramic substrates used as microelectronic chip carriers illustrates several points. The material itself, which is primarily aluminum oxide, is available from many sources and is not considered critical per se. However, the special form needed requires specialized manufacturing and stringent quality control. Japanese manufacturers supply about two-thirds of the substrate requirements. It is said that U.S. users of these substrates typically have an inventory sufficient only for a few days manufacturing requirements. An interruption in supply would probably have very rapid and serious consequences, both military and economic. In the case of Japan, interruption of supply to the United States seems very unlikely. However, this example does illustrate how specialized manufacturing capacity for critical engineering materials may be concentrated in a few countries for economic reasons.

On contrast to the extensive analysis and established set of responses for critical raw materials, relatively little has been done to provide insurance against vulnerability for special engineering materials. The balance of appropriate policy options is different. Stockpiling is much less attractive because the stockpiled material is likely rapidly to become obsolete and almost valueless. In the case of electronic substrates the next generation may involve much greater use of other ceramics, for example. In responding to a cutoff, greater reliance on allocation of domestically manufactured substrates plus expansion of domestic capacity would be needed. The critical importance of having a domestic manufacturing base from which to expand is clear. In another case, that of high grade silicon carbide fibers for advanced structural composites, the United States has no domestic supply considered equal to the quality of the Japanese fibers. The Department of Defense Advanced Research Project Agency recently moved to fill this gap by contracting with the Dow Corning

Company and other subcontractors to develop a domestic source.

Further detailed discussion of critical engineering materials is beyond the scope of this paper and is apparently not the purpose of this conference. However, growing use of high technology materials makes future consideration of this class of materials increasingly important for both economic and military reasons. In the United States there is a rising level of concern and a growing discussion of the need for a so-called "national industrial policy" (reference 25). Providing an insurance policy against shortages of critical engineering materials is recognized as an important component of this policy. Further development of specific ideas is needed.

14. SUMMARY

In conclusion the following summary points are offered as the personal viewpoint of the author:

(1) There is no shortage of strategic and critical raw materials today. None is foreseeable in the next few decades as a result of any physical limitation of reserves and resources. However, geographical distribution and political factors make man-made shortages a sufficiently real possibility that the industrialized, market-economy countries should be prepared to deal with emergency shortages.

(2) A reasonable national plan requires many components balanced between short and long-term and between supply and technically-oriented responses.

(3) The costs of preparedness must be born primarily by government because the private sector cannot expect to recover an investment in preparedness in normal circumstances so that a firm which makes such an investment will be at a competitive disadvantage.

(4) Within the total preparedness plan there is a strong role for research and development for substitution and recycling. Not only is their potential great for increasing preparedness but they have the chance of producing spinoff benefits of important commercial value to a country as a whole.

(5) To be effective, the substitution and recycling portion of a preparedness program need to be augmented with a program on standards development and a stockpile of information of the entire technology of protection and use.

(6) Present federal programs, at least in the United States, appear to be at a low level and to lack stability. The standards and information stockpile components are in an especially weak state.

(7) The whole topic of special manufactured materials which are critical because of the distribution of manufacturers rather than the distribution of raw materials is growing in importance. A different mixture of responses is needed. These involve sensitive issues of national industrial policies. Analysis is at a less advanced stage than for raw materials vulnerability.

REFERENCES

1. "Substituting Non-Metallic Materials for Vulnerable Metals", National Science Foundation, Division of Policy Research and Analysis. Report in preparation based on workshop held June 27-28, 1983.

2. "Technologies to Reduce U.S. Materials Import Vulnerability", study in progress by the Office of Technology Assessment of the United States Congress. Update of progress on the assessment presented to the ASM Government and Public Affairs Committee at its March 10, 1983 meeting.

3. "Mineral Commodity Summaries 1983", Bureau of Mines, United States Department of the Interior.

4. "Minerals in the U.S. Economy: Ten-year Supply-Demand Profiles for Mineral and Fuel Commodities (1966-75), Bureau of Mines, United States Department of the Interior.

5. "Special Report - Critical Imported Materials", Council on International Economic Policy, December 1974.

6. "Interagency Review of Federal Nonfuel Minerals Policy", United States Department of the Interior, 1979.

7. "An Index to Identify Strategic Metal Vulnerability", C.C. Clark, J.A. Ford, P.M. Richmond, K.W. Stalker, and J.R. Stephens, Report of a Task Group of the Metal Properties Council.

8. "The Domestic Supply of Critical Minerals", Bureau of Mines, United States Department of the Interior, 1983, and Private communication with the author by Thomas A. Henrie, Chief Scientist, U.S. Bureau of Mines.

9. Leonard L. Fischman, "World Mineral Trends and U.S. Supply Problems", Resources for

the Future, Inc. Research Paper R-20, 1980.

10. "Contingency Plans for Chromium Utilization", National Materials Advisory Board, National Research Council, 1978.

11. J.K. Tien, "Cobalt Availability and Superalloys and NASA's Activities in the Conservation of Strategic Aerospace Materials", published in National Bureau of Standards report NBSIR 81-2305, "Proceedings, U.S. Department of Commerce Public Workshop on Critical Materials Needs in the Aerospace Industry", February 9-10, 1981.

12. "Manganese Reserves and Resources of the World and Their Industrial Implications", National Materials Advisory Board, National Research Council, 1981.

13. "Supply and Use Patterns for the Platinum-Group Metals", National Materials Advisory Board, National Research Council, 1980.

14. Bruce W. Steiner, Center for Materials Science, National Bureau of Standards. Private communication with the author.

15. "Stockpile Report to the Congress, October 1981 - March 1982", Federal Emergency Management Agency.

16. "Conservation and Substitution Technology for Critical Materials", Proceedings of Public Workshop sponsored by the U.S. Department of Commerce/National Bureau of Standards and U.S. Department of the Interior/Bureau of Mines, held June 15-17, 1981 at Vanderbilt University, Nashville, Tenn. Published April, 1982, Department of Commerce, 1981.

17. "Critical Materials Requirements of the U.S. Aerospace Industry", Department of Commerce, October, 1981.

18. E. Hondros, National Physical Laboratory, United Kingdom. Private communication with the author.

19. "Raw Materials and Foreign Policy", International Economic Studies Institute, 1976.

20. Hatten S. Yoder, Jr. "Strategic Minerals: A Critical Research Need and Opportunity", page 229-241, Proceedings of the American Philosophical Society, Vol. 126, No. 3,1982.

21. "Critical Materials Requirements of the U.S. Steel Industry, U.S. Department of Commerce, March, 1983.

22. John B. Wachtman, Jr. "National Materials Policy: Critical Materials and Opportunities", American Ceramic Society Bulletin, Vol. 61, No. 2, pp 214-220, February, 1982.

23. "COSAM Program Overview - Conservation of Strategic Aerospace Materials", NASA Technical Memorandum 83006, October, 1982.

24. "Survey: Materials Life Cycle Research and Development in the Federal Government Fiscal Year 1980", Prepared for the Committee on Materials (COMAT), National Bureau of Standards, September, 1981.

25. "Seventh Biennial Conference on National Materials Policy", Conference sponsored by the Federation of Materials Societies, Report transmitted to the Committee on Science and Technology, U.S. House of Representatives, U.S. Government Printing Office, March, 1983.

Table 1. Net imports as a percent of consumption in 1977

Material	U.S.	E.E.C.	Japan	COMECON
Manganese	98	100	99	3
Cobalt	97	100	100	68
Bauxite	91	97	100	28
Chromium	91	100	98	2
Asbestos	85	90	98	1
Nickel	70	100	100	13
Zinc	57	91	74	9
Iron Ore	48	82	100	5
Silver	36	93	71	10
Copper	13	100	97	4
Lead	13	76	78	3
Phosphate	Export	99	100	23

Source: Bureau of Mines data.

Table 2. Major foreign sources of the U.S. supply during 1974-1977

Material	Countries
Manganese	Gabon, Brazil, South Africa
Cobalt	Zaire, Belg.-Lux., Zambia, Finland
Bauxite and Alumina	Jamaica, Australia, Surinam
Chromium	S. Africa, U.S.S.R., Zimbabwe, Turkey
Asbestos	Canada, S. Africa
Nickel	Canada, Norway, New Caledonia, Dom. Republic
Zinc	Canada, Mexico, Australia, Belg.-Luxemburg
Iron Ore	Canada, Venezuela, Brazil, Liberia
Silver	Canada, Mexico, Peru, United Kingdom
Copper	Canada, Chile, Peru, Zambia
Lead	Canada, Mexico, Peru, Zambia
Phosphate	U.S. is a major exporter

Source: Bureau of Mines data.

Table 3. Selected lists of critical materials

Material	1974 Council*	1977 Review **
Aluminum	X	X
Chromium	X	X
Cobalt	X	X
Columbium	X	-
Copper	X	X
Fluorspar	X	-
Iron Ore	X	-
Lead	X	X
Manganese	X	X
Mercury	X	-
Natural rubber	X	-
Nickel	X	-
Phosphate	X	-
Platinum	X	-
Tin	X	-
Titanium	X	-
Tungsten	X	-
Vanadium	X	-
Zinc	X	X

*Council on International Economic Policy
**Interagency Review of Federal Nonfuel Minerals Policy

Table 4. Analysis of materials critical to the United States in 1983 by the Metals Properties Council

Most Critical	Middle	Least Critical*
Tantalum	Vanadium	Aluminum
Chromium	Rhenium	Copper
Platinum	Titanium	Molybdenum
Columbium (Nb)	Tungsten	Magnesium
Manganese	Silver	Iron
Cobalt	Nickel	
	Gold	

Table 5. The four most important strategic and critical metals to the U.S. according to the U.S. Bureau of Mines

Chromium
Cobalt
Manganese
Platinum group

Table 6. Possible problems in mineral supply as classified by L.L. Fischman

Long-term problems (persistent, or trend problems)

1. Monopolistic control of prices
2. Long-term exposure to short-term supply contingencies
3. Declining domestic processing capacity
4. Steep price rises
5. Depressed prices
6. Price instability
7. Physical supply stringency

Short-term contingencies

8. Actions by foreign governments or other entities intended to disrupt supplies or raise prices
9. Actions or events that might incidentally disrupt supplies
10. Generalized demand surges
11. Natural disasters

Table 7. Chromium consumption in the U.S. by use

Use	Percent
Metal production	69
Chemicals	18
Refractories	13
Metals Use Breakdown	
Stainless steels	69.8
Other steels	22.5
Superalloys	2.5
Other	5.2
Total use in the U.S. in 1976	358 thousand tons contained Cr.

Source: National Materials Advisory Board based on Bureau of Mines data.

Table 8. World chromium ore resources and potential reserves

Country	Known Ore Reserves	Known Potential Ore
South Africa	62.4	76.5
Zimbabwe	32.7	20.5
USSR	1.2	0.8
Phillippines	0.3	<0.05
Turkey	0.1	0.2
All others	3.3	2.0
World total in million short tons	1,914	3,049

Source: National Materials Advisory Board based on Bureau of Mines data.

Table 9. Cobalt uses in the United States

Use	Percent
Super Alloys	30
Magnetic materials	20
Tool bits and dies	15
Catalysts	15
Driers	15
Other	5

20 million pound per year total

Source: J.K. Tien et al.

Table 10. Estimated 1979 world cobalt production, million pounds

Country	Mine Production	Reserves	Resources
U.S.	0	0	1,700
Canada	2	66	546
Cuba	3.6	40	2,340
U.S.S.R.	4.4	460	500
Zaire	29	1,000	1,500
Zambia	6	250	770
Oceania	19.2	1,130	
World Total	71.6	3,272	9,456
Seabed Nodules	----	-----	500,000

Source: J.K. Tien, et.al.

Table 11. World production of platinum-group metals in 1978

Country	Troy Ounces	Percent
U.S.S.R.	3,050,000	48.0
South Africa	2,950,000	46.5
Canada	279,000	4.4
Colombia	26,000	0.4
United States	8,300	0.1
Other	37,000	0.6

Table 12. Recent and forecast annual consumption by application

Application	1978		Beyond 1988	
	Troy Oz.	%	Troy Oz.	%
Automobile/ Truck	354,000	48.6	500,000	29.2
Electrical/ Electronic	90,000	12.3	238,000	13.9
Petroleum Processing	75,000	10.2	25,000	1.4
Glass/Glass Fiber	60,000	8.2	85,000	5.0
Ammonia Oxidation	58,000	8.0	62,000	3.6
Jewelry	35,000	4.8	225,000	13.1
Dentistry/ Medicine	27,000	3.7	45,000	2.6
Chemicals Processing	26,000	3.5	25,000	1.4
Off-the-Road Vehicles	3,000	0.4	5,000	0.3
Fuel Cells	1,000	0.1	340,000	19.8
Total	729,000		1,466,000	

Table 13. A classification of the range of responses to problems of minerals supply

Purpose	**Time Scale**	
	Short-term	**Long-term**
Alternate Supply	**1. Stockpiling** **2. Allocation** **3. Recycling** **4. Information stockpile**	**5. International Relations** **6. Domestic Production** **7. Research & Development**
Performance by alternate materials		**8. Dissemination of Substitution Technology**

Table 14. U.S. national defense stockpile inventory of the four strategic and critical metals taken to be most important in this paper

Commodity	Unit	1980 Goal	Inventory
Chromium, Chem. & Met. Grade	ST Cr metal	1,353,000	1,324,921
Chromite, Ref. Grade Ore	SDT	850,000	391,414
Cobalt	Lb Co	85,400,000	40,802,305
Manganese, Dioxide Battery Grade	SDT	87,000	212,136
Manganese, Chem & Met. Group	ST Mn	1,500,000	1,970,000
Platinum Group			
Iridum	Tr Oz	98,000	16,990
Palladium	Tr Oz	3,000,000	1,255,003
Platinum	Tr Oz	1,310,000	452,642

Table 15. Estimated possible levels of reduction by year 2000 in aerospace requirements for selected critical materials through technical developments

Possible percent reduction in fly weight per typical advanced aircraft:

	Cr	Co
High Reduction	50	80
Low Reduction	0	20

Possible percent reduction in buy weight, for a given fly weight, through reduced processing losses by using near net shape processing:

High Reduction	30	50
Low Reduction	10	25

Possible increase in the percentage recycled:

Current	56	59
High Possible	66	74
Low Possible	61	66

Table 16. Distribution of R & D funding for critical materials by technology goal

Technology Goal	Funding in $1000		
	Direct	Related	Total
Substitution	9,648	13,960	23,608
New Sources	10,258	2,523	12,781
Reclamation	560	1,850	2,410
Life Extension	28,010	3,060	31,070
Conservation	1,585	2,400	3,985
Total, all Technology	50,061	23,793	73,854

FACTORS AFFECTING THE SUPPLY OF STRATEGIC RAW MATERIALS WITH PARTICULAR REFERENCE TO THE AEROSPACE MANUFACTURING INDUSTRY

by

E.W.ANDERSON
Department of Geography
University of Durham
Durham DH1 3LE
England

SUMMARY

The study analyses the political and strategic factors affecting the supply of certain raw materials critical to the European NATO aerospace industry. For various reasons, including potential political instability, concentration of sources, small scale of production and technological-industrial problems, chromium, cobalt, hafnium, manganese, niobium, titanium, tungsten and vanadium are all considered to a degree at risk.

1. INTRODUCTION

Much simplistic polemic has appeared on the subject of strategic raw materials, but it is in reality a complex topic involving aspects of many substantive fields, including particularly, geology, technology, economics and politics with geopolitics (Fig 1).

Definitions

With regard to raw materials, the term 'critical' has normally been taken to imply a high degree of need within the defence industry. However owing to the wide ranging nature of that industry, allied to the fact that national power involves the total economic base, criticality has been applied more broadly.(1) In the present context the term is related to one specific industry (Fig 2).

The term 'strategic' has been used to denote a high level of import dependence and therefore geopolitical vulnerability.(2)

Recent literature has tended to combine all aspects of vulnerability and dependence in the one term 'strategic'. In the present study, for a raw material to be thus designated the following conditions must obtain:

(a) there must be a marked degree of import dependence;
(b) there must be a very limited number of significant suppliers;
(c) the material must be critical for the aerospace and directly associated industries.

All the criteria can be qualified. For example rather than a total geological absence of a raw material, import dependence may only imply that the costs of domestic recovery are at present uneconomic. Again, import dependence may result from a lack of technology, energy sources or sufficient market incentive. For these reasons many countries import partly processed ores and ferro materials.

Vulnerability clearly results when there is concentration on only a few sources which between them supply a high proportion of the raw material (Fig 3). In general terms the fewer the sources the greater the vulnerability although obviously the reliability of each must be taken into consideration. When there are only limited world producers of a particular mineral, there is no escape from concentration but in other cases, reliance on a few sources may occur for other reasons such as historical connections or the quality of the product. At a stage further removed, the known pattern of world reserves may dictate that at least in the short to medium term there is no alternative to concentration. Furthermore there may be indirect dependence when imports are taken from one country which itself obtains supplies from another. For example cobalt may be obtained directly from Belgium - Luxembourg but the true reliance is upon Zaire, the original source. Moreover the picture can be altered radically by substitution and recycling.

A further element to be considered is the scale of world production since if a raw material is scarce and also only available in small quantities it is far more vulnerable.(2) Not only can supplies be comparatively easily interdicted but investors can affect the market. On the other hand, transport can perhaps be by air and stockpiling is a more reasonable proposition. Conversely if an industry uses very large amounts of raw material, speculation is unlikely to affect supplies but stockpiling presents far greater problems.

In some ways advancing technology reinforces dependence. For example, once a particular metal has been accepted within an alloy, the time required for substitution together with all the testing militates against changes. Furthermore any substitute is unlikely to be completely congruent in all the characteristics required. A further point of significance is that most of the strategic raw materials have a range of uses, many of which are not connected directly with sensitive industry. Therefore the approximate percentage of use which can be validly labelled strategic, needs to be ascertained. If of course this is only a minor percentage, then other supplies can, if the expertise is available, be converted in time of stress. If on the other hand most of the raw material is used in strategic industry this renders the situation even more acute. There is also the question of relative cost in that the cost of the strategic may be very limited compared with the overall cost of the equipment. Therefore a large price rise would have little effect on usage. On the other hand of course, the materials used in bulk are very much more sensitive to price rises.

Political pressures

If a raw material comes from basically one foreign source, no matter how close that source geographically or ideologically, there must always be some vulnerability. Political change may occur, local events such as strikes may affect supplies and perhaps, more obviously, the country may require the material for itself and limit exports. Thus even supplies from within European NATO itself cannot be considered totally safe.

The same problems apply to sources in the USA and Canada with the additional problem of the 'Atlantic Bridge'. The difficulty of shipping raw materials across the Atlantic will depend of course upon the length of time during the build-up to any conflict. With a period of increasing tension, it is possible that sufficient strategic raw materials could reach Europe, but on the other hand, the sudden war scenario precludes such movements.

Several neutral countries such as Finland, Sweden and Austria provide strategic materials and during a period of tension, it is more difficult to foresee their reaction. Finland in particular enjoys close relations with the USSR and is clearly susceptible to Russian pressure.

European NATO is also dependent upon materials from Australia, South-east Asia, Japan and China. These very extended sealanes of communication, impossible to protect other than at particularly sensitive points, indicate a further source of vulnerability. With a transit period of more than four weeks, the time factor becomes especially important.

Furthermore European NATO depends to a certain extent upon supplies from Centrally Planned Economies (CPEs), particularly the USSR and China. These of course represent a different order of vulnerability in that, in the event of increasing tension, it can be assumed that supplies would be denied. However at present it seems highly improbable that the two main suppliers would act together. Other CPEs involved in such trade include Yugoslavia, Albania and a number of African states, notably Gabon. In the case of the latter group, the fear must be that Soviet pressure could lead to a change of trading practice. However such developing countries are particularly dependent upon revenues from their raw materials and the USSR is generally unable to supply economic aid other than that involving arms.

Nonetheless the importance of a particular raw material within the export trade of a country must be considered. For example if it accounts for only some 1% or 2% of the total value, supplies to consumers might be reduced or halted with only very modest effects internally.

Finally, southern Africa (3) needs to be treated separately. Not only is it a highly volatile area with the USSR and its surrogates involved, but it is a long way from Europe and South Africa itself of course poses a number of moral problems (Fig 4).

Thus in the case of all the major suppliers: USA, Canada, Australia and South Africa, there are potential difficulties. For example even in the case of the USA, titanium supplies were stopped at one stage and the total output was diverted for domestic consumption. The nickel supplies from Sudbury were affected by an eighteen month long strike while in Australia industrial relations problems are also a potential hazard. In contrast to these, South Africa is a consistent and regular supplier but, some would say, at what cost? The long term outlook for South Africa must cause some alarm. (4) These are of course all peace time scenarios and in the event of war the maintenance of supplies could only be guaranteed through stockpiles.

A further potential difficulty has resulted from the development in the supplier countries of refining, beneficiation and further stages of manufacturing. Thus the materials appear in trade in semi-processed form and processing facilities become redundant in the consumer countries. They therefore become dependent upon the producers not only for the ore but also for the further stages involved. This in turn of course affects the form in which materials can be stockpiled and poses problems of stockpile conservation and maintenance.

In conditions short of an incipient superpower conflict, supply problems can be looked at over a number of time spans. In the very short to short term, price changes are likely to exercise the major influence. These could be generated by anything from a natural catastrophe to trade union activity or stock market neurosis although for various reasons the development of cartels is judged unlikely. In the short to medium term local conflicts or extreme industrial action are likely to exercise the greatest influence. The problems of maintaining cobalt supplies from Shaba province, Zaire, in 1978 and the prolonged strike at Sudbury in 1969 are examples. The most obvious long term blockage would probably result from the actions of the USSR in South Africa. In peace time the most likely problems would seem to be those caused on a local level over a short to medium time span. These might involve: normal market fluctuations, industrial action, civil unrest, local conflict or sabotage.

However, it must be stated that in attempting to construct any model which might be applied to identify which raw materials can be considered strategic, the geopolitical input is as yet more speculative and less sophisticated than for example the geological (Fig 1).

The aerospace industry

According to a recent survey (5) the following European NATO countries are concerned with production in different areas of the industry:

(a) Multinational aircraft: Italy, France, the UK and West Germany;
(b) Military aircraft: France, the UK, Italy, the Netherlands and West Germany;
(c) RPVs and Drones: Belgium, the UK, France, Italy and West Germany;
(d) Surface effect vehicles: France and the UK;
(e) Spacecraft: France, European Space Agency (ESA) and NATO;
(f) Research rockets: France and the UK;
(g) Missiles: France, the UK, Norway and West Germany;
(h) Gas turbine engines: France, the UK, Italy and West Germany;
(i) Rotary wing aircraft: France, the UK, Italy and West Germany.

Thus European NATO is well represented in all branches of development and research in the aerospace industry although four countries are particularly dominant.

In investigating the raw materials considered strategic for the aerospace industry (Fig 2), the vast range of products must be borne in mind. Apart from this the machine tools and a wide variety of other equipment required to construct them must be considered. Thus if the line of production is followed back, many other materials not directly involved in the actual manufacture of aircraft could be designated strategic. A further example of the variety of components involved can be given if the control systems are considered. The operation of the engine and other vital units is often controlled by computer and electronic systems. Thus the whole field of semi-conductors becomes vital to the aerospace industry and this of course has its own strategic requirements.

Raw materials

Problems with the collection and anlysis of world-wide data on the production and reserves of raw materials together with the pattern of trade, have been well rehearsed elsewhere. However the points particularly relevant to the materials under consideration in the present study need to be stressed. Several strategics are produced through comparatively small companies in Third World countries and there must always exist some doubt as to the reliability of production data. Furthermore in any country where only one or two firms are involved there is often a problem of confidentiality. This may result in no figures being listed or a broad estimate being included. Then the materials themselves may come in a variety of grades and beneficiated states, and equating these causes problems. Furthermore increasingly, recycled sources are coming into play, frequently in countries not concerned with ore production, and assessment of the magnitude of production particularly of new scrap, may again be conjectural. This obtains particularly when both old and new scrap are concerned. As was shown earlier, the scale of production has a very great bearing upon problems of vulnerability and dependence.

With regard to reserves the definition itself depends upon the current technological state within a specific country and upon the economics of world trade in that particular material. It is therefore often a gross estimate based on a number of assumptions, especially about the consistency of the ore bearing body. Reserves, or economic resources, are defined within the Institute of Geological Sciences as those mineral resources which are workable under present socio-economic conditions. With the development of offshore mining with its attendant law of the sea problems, and possibly the exploitation of Antarctica, difficulties of estimating resources are likely to increase.

While the raw materials specified (chromium, cobalt, hafnium, niobium, tantalum, manganese, molybdenum, titanium, tungsten, vanadium, yttrium) have formed the basis of the study, it has been possible to identify others which are considered strategic within the industry. Even iron, one of the most commonly occurring of all elements, could be considered strategic in that production tends to be concentrated in a few areas and there is a tendency towards dependence on one or two countries for supplies. However since there has never been any question of its being in short supply, iron has not been included. Nickel, also abundant, is even more concentrated in its source of supply and difficulties could be foreseen. Among the other metals identified as important or potentially important are: beryllium, germanium, lithium and zirconium.

While some of the metals, for example tungsten, are vital by themselves most are important in the formation of alloys. The major alloys in the aerospace industry are those based on aluminium, nickel, steel and titanium. In engine production nickel, steel and titanium are used respectively for the hot end, centre and the cold end. When combined with these basic metals, often in small quantities, the other strategics confer a variety of properties on the alloy. The major necessities are resistance to high temperature, corrosion and wear. These strategics thus provide hardness, strength, stiffness, oxidation resistance and a number of more specialised properties such as stabilisation and grain size control. Within any one alloy there is therefore a very sophisticated and complex balance and this militates strongly against substitution over any but a medium time space. Normally for a key engine alloy, with all the re-testirg required this might extend to five years. Certain of the strategics are also used externally as coatings or sprays or in a way to confer certain properties on the surface molecular layers. To try alternatives or reduce levels of a particular metal thus requires acceptance trials. The leaner compositions might operate as efficiently but this means long term evaluation. Furthermore since the length of service expected is a vital element there will be an even greater time lag in adoption. In the aerospace industry there is of course research and development to minimise need for particular metals without sacrificing quality. However designs are produced without the factors of mineral economics in mind. It is clearly vital to have flexibility of design consistent with technology. Since the market price is likely to fluctuate, it would be impossible to design for known economic circumstances. Such rapid price changes have been seen over the recent past in the cases of cobalt, with the Shaba province conflict, titanium with the Russian withdrawal from the market and tantalum.

The aerospace industry thus uses low volumes of high quality and high price alloys. The main consideration must always be the characteristics of the metals not their costs or availability. The thrust of development is to improve the maximum power:weight ratio and to extract the optimum performance at minimum weight. Furthermore the element of reliability is always pre-eminent and in the case of military aerospace equipment, this might be described as ultra-reliability. As the criticality of a particular alloy is related so closely to its usage, there must always be major problems when substitution is contemplated. The properties of a potential substitute may be compared with that of its rival and clearly the two can never be entirely congruent. Thus difficulties may arise not in long term performance or resistance in hot corrosive environments but in terms of simple engineering. Furthermore the increased concentration on another element may not only affect the design but may make a change in strategic vulnerability.

The question must be asked as to what is the true economic value. It may well be that the cost of certain raw materials is very small compared with what is at stake, particularly in military fields. With the development of technology, the requirements for the construction of a particular piece of equipment will diminish as the buy:fly ratio improves. Indeed with the use of powder alloys and pressure moulding the amount of waste has decreased significantly. However overall the need for strategics is likely to increase as a result of the broadening range of products and costs overall will show an increase through price increases.

Thus substitution in so sophisticated an areas as the aerospace industry is very complex. As higher thrust is achieved, the environments in which the equipment has to operate become increasingly hostile, the requirements become more specific and the possibility of using alternative materials diminishes. At present for type testing, engines require 150 hours' running time before being sealed and certified. Any changes require a further type test to prove the new alloy. At a minimum this would take several months, costing perhaps half a million pounds. Therefore before any change could be seen in the consumption pattern, between four and five years might be required. Complete changes could take up to ten years although obviously in times of war standards would be changed and these time spans would have to be greatly reduced.

Furthermore, apart from the scientific and technological problems, substitution may be constrained by:

(a) difficulties such as inertia and investment provision within the industrial structure itself;

(b) social factors ranging from employment provision to pollution;

(c) psychological problems particularly those concerned with resistance to change.

Recycling also of course affects supply problems and can lead to diminished vulnerability. In the case of alloys containing only a very small percentage of the particular metal there are obvious problems but the recovery industry is itself developing a new range of techniques. Of particular interest is the recovery of germanium from flue dust and other minerals such as vanadium may be recovered from pulverised ash. Since the material requires little in the way of transport costs and is already in a form amenable to mineral extraction, far lower concentrations than those obtaining in ore can be considered potentially viable.

Commercial aspects

In examining potential blockages and even the amount of any mineral in transit between the mine and the aerospace industry, the various stages in the commercial pipeline need to be taken into account (Fig 5). In most cases there is an elemental supplier who imports the mineral and then despatches it to the alloy manufacturer. From there it goes for fabrication before finally appearing at a particular unit of the aerospace industry. Thus there may be four or five stages in the cycle since it would normally be considered prohibitively expensive for the manufacturer to deal directly with the raw material supplier. However to guard against potential problems certain companies in the aerospace industry have entered directly into long term contracts with the suppliers. This has been the case with particularly vulnerable metals such as cobalt and titanium. This development may become more common as with economic recovery in the West prices are bound to rise and there could be more industrial unrest. It must always be remembered in this context that the smallest gap between supply and demand can lead to a very large price rise.

The amount of a mineral in the pipeline, awaiting processing, etc. can be considered part of the stockpile. With the current recession and cash flow problems, most companies hold only minimal stocks but clearly a national stockpile under government co-ordination and control could alleviate at least short term stoppages in supply. Government subsidised private stockpiles might also provide an answer, but there would need to be clear guidlines about when the material could be used. Furthermore for any stockpile the form and quality of the raw material is crucial. With reduced refining capacity for certain metals it would be necessary to stockpile in beneficiated or even semi-manufactured form. Since it is the practice for aerospace procurement to plan for up to five years ahead, the stockpile requirements could be reasonably assessed. Information on European stockpiles is thin but it is known that France has fairly substantial provision which will be worth some £400 million by 1985 while the UK has spent £40-45 million to stockpile cobalt, chromium, manganese and vanadium. Besides Japan and South Korea, Spain, Sweden and Italy all operate stockpiles or are considering them. (3) With regard to stockpile maintenance there is the crucial problem of deterioration since many minerals need to be stockpiled in a highly specific form. The answer would be to store the material at one stage further back in the manufacturing process, but this presupposes that there is plant available to effect the final conversion. If such plant is not present and could not be economically established for the amount of material used, there must be a dependency upon a country possibly totally different from the original source. For example, Japan processes a range of materials such as silicon wafers and provides for them a major world repository. An important addition to any stockpile would be a data bank containing details of researched projects on such vital topics as substitution, conversion within the economy and recycling.

When supplies are limited and particularly where the usage is highly specific, investors may affect the commercial flow of the market. In general investment in strategic minerals is not a common way of building a portfolio but there are several brokers specialising in the field (9) As yet there has been little if any experience of selling under incipient conflict conditions to manufacturers. A strategics portfolio is of course a private stockpile and in the USA tax relief through the so-called 'Blue Sky' fund is planned. The recipient would agree to sell at a particular price, thus removing the major potential blockage in the system and indeed providing useful buffer stocks. However when problems of strategic mineral supply are considered the activities of investors must be taken into account, although experience shows that price manipulation may be successful in the very short term, but in the longer term it has always failed.

Quoted market prices refer to only very specific forms of each raw material and accordingly their use as a guide to changing strategic status has been criticised. Nonetheless there is generally a relationship between them and the materials in what may be their more commonly used forms. Further, they are readily obtainable and they do encapsulate a range of factors, geological, political and economic. In this context therefore it is interesting to note the peak price period during 1978-80 which affected all the major strategics (Fig 6). This of course coincided with the effective start of the resource war scare. (10) The subsequent fall in prices has caused a temporary lull in anxiety but has obviously provided a good time for stockpile purchases. As Western economies recover investment interest can be expected in cobalt, chromium, molybdenum, niobium, tantalum and titanium. Additionally and possibly of more importance in the long term strategic argument, hafnium and yttrium will come under consideration.

Strategic considerations

The following key points therefore emerge for detailed attention and were investigated through interviews and literature surveys:

(a) the major uses for the aerospace industry of each raw material;

(b) possible substitution;

(c) the geographical sources of each raw material, the scale of production and the extent of reserves; (11-16)

(d) the trading patterns leading to an assessment of dependence by European NATO countries;

(e) the vulnerability of major supply sources.

RAW MATERIALS

Chromium

Chromium is a critical component of many alloy steels and is irreplaceable at anything approaching the same price. It is particularly vital in all heat-resistant stainless steels and no suitable substitute exists for it in high pressure, high temperature, corrosive environments. Furthermore in most of the alloys in which it is found, chromium is the major metal occupying between roughly 20% and 25%. For corrosion resistance a level of below 12% results in markedly decreasing effectivness. With developing technology its use in the chromising alumina treatment of the surface layers of alloys, giving them a higher oxidisation resistance, is becoming increasingly important. In the aerospace industry therefore chromium is one of the major metals used, particularly for the production of steel-and-nickel based alloys. For its other uses in less exacting environments, substitutes may be found although frequently at higher cost and lower performance.

Sources

While there would seem to be potential elsewhere, notably in Brazil, Sudan and China, chromium in workable quantities has a comparatively limited distribution. Only eight countries each produce more than 2%. Output is dominated by South Africa (32%) which has shown a notable increase in proportion over the recent past and the USSR (27%). Other important producers are Zimbabwe (6%), Turkey (6%) and the Philippines (4%) all of which have shown a general decline, and Albania (13%) which has shown an increasing production. Within Europe only Albania, Turkey and Finland are of significance. Despite the range of smaller sources, the dependence upon only one major producer outside the CPEs represents long term vulnerability.

This dependence is seen to be even more acute when world reserves are considered. They are virtually completely concentrated in southern Africa with South Africa (68%) and Zimbabwe (30%). In fact the figure for South Africa is somewhat arbitrary since reserves to a depth of 300 m are estimated at over 3,000,000,000 tonnes, a figure higher than that quoted on most lists of world reserves. Furthermore South Africa has consolidated its pre-eminent position through the development of first class technology. The argon-oxygen-decarbonisation process has been developed so that low grade ores can be used to produce stainless steel at very competitive prices. Thus while Zimbabwe has higher grade ore, the thin seams and comparatively inefficient production methods render it increasingly less competitive.

Chromium increasingly enters world trade as ferro-chrome, which itself varies in degree of beneficiation. However taking it as basically one commodity, it can be seen that South Africa again plays a dominant role. In 1980 some 800,000 tonnes of ferro-chrome were produced amounting to 60% of the ferro-chrome entering world trade and 30% of total world production. South Africa in fact stockpiles in the form of ferro-chromium since this is more immediately usable and a number of varieties can be retained. The recovery rate is about 9%.

At present the market for chromium is depressed and the supply of ferro-chrome currently exceeds demand. However as research and development programmes bear fruit and particularly governments implement stockpile programmes, the outlook could change.

Indeed the United States Bureau of Mines expects demand to increase from the 1978 base at an annual rate of about 3.2% up to 1990.

European NATO Trade

Imports of chrome ore and concentrates into NATO Europe are dominated by South Africa which accounts for about 50% and is by far the major supplier to all the main importers. Other important sources are Turkey, Albania and Madagascar, while Finland and Greece provide supplies on a much smaller scale, and the USSR has varied considerably in importance over the recent past. The Netherlands and Germany are re-export sources. For ferro-chrome, Zimbabwe, South Africa and Sweden are all important, other sources being Turkey, Albania and Finland with Germany the major re-export supplier. The movement of unwrought and wrought chromium is very small and sources are mainly within NATO Europe, although some supplies are received from the USA and Japan.

Thus the vulnerability of European NATO is all too evident with only one NATO country, Turkey, of any importance as a source of chromium. There is a very heavy dependence on southern Africa, particularly South Africa itself while Albania as a CPE and Finland and even Sweden as neutral countries could pose problems of reliability.

Strategic considerations

Chromium illustrates a clear case of strategic vulnerability with very heavy reliance upon one source outside the CPEs. Furthermore with suppliers and particularly South Africa becoming more involved in beneficiation, low priced ferro-chrome can be produced, underpricing the industries of the consumer countries. As a result, plants for example in the USA and Japan have been closed. Thus there is increasing reliance upon South Africa which is supplying at present some 45% (by metal content) of requirements and selling not only the raw material but also power and technological expertise. Moreover this is compounded by the fact that the consumers seem reluctant to diversify sources even within the limited range available. This undoubtedly results from the reliability and quality of South African supplies. Also in the obvious country for development, Zimbabwe, the future appears rather uncertain.

Cobalt

Cobalt has a wide ranging significance as it is increasingly used with nickel and chromium alloys for parts of the air frame manufacture while being of specific importance in engine construction. It is also vital for the machine tools used to produce the various parts and also in a number of other aspects such as thrust rings for propellers and engine bearings. It is thus a high consumption metal the chief uses for which can be summarised as follows:

(a) a solid solution strengthening agent in nickel based alloys and some steels;

(b) a base for, in particular, wear-resistant alloys.

For its strengthening properties there are alternatives such as nickel, although others are much scarcer than cobalt itself. For wear-resistance there are no satisfactory substitutes. It would therefore be possible to build aero engines without cobalt but they would be more expensive in a number of ways. Following the world cobalt shortage in 1978 the use of cobalt was reviewed in the aerospace industry and while the range of uses has increased there is a trend towards a reduction of the metal in alloys. Possible substitutes include alloys containing nickel, vanadium, chromium and tungsten.

Sources

Cobalt is mostly recovered as a by-product of copper and nickel mining but world production is highly localised. Total annual production is approximately 30×10^3 tonnes, but there has been a decline recently. Only eight countries each produce more than 1% of the total, and production is dominated by Zaire (40%) and Zambia (9%). Zaire's predominance has tended to decline recently but it is still obviously the key source. The only European production is in Finland (4%). Of the CPEs, Cuba and the USSR produce about 6% each.

With regard to reserves, nine countries have over 1% of the total but again Zaire (38.5%) and Zambia (12%) are dominant. There are no reserves of this order in Europe, Finland having only 0.6%. There has been something of a glut on the market recently and producer stocks may be as high as 20,000 tonnes. Furthermore recycling techniques have been improved and it is possible that 12% of the market is in fact secondary cobalt. Zaire has therefore been cutting production but Zambia, with a view to the future, has commissioned a new plant at Kitwe which when its second phase is complete, will virtually double Zambia's production capacity.

Seabed nodules contain an estimated 225 million tonnes of cobalt or over seventy times the current world reserve. However the necessary large scale investment for production from these seems at least ten and more probably twenty years away.

Over the next year or two there would seem to be no difficulty with supplies of cobalt but with the increasing interest in stockpiles and the long overdue re-equipment of civil airlines, the picture could change rapidly.

European NATO Trade

Bearing in mind the political problems in southern Africa and also the fact that a high proportion of Zairian cobalt passes through Belgium, it is hardly surprising that reliable data are hard to collect. Indeed there is a certain reticence in publishing cobalt returns in national statistics. This doubtless results partly from lack of information but also from a desire for confidentiality and as a consequence, aspects of the movement of cobalt in world trade cannot be stated with certainty. The main, indeed the only stated source of ore and concentrates listed for Europe is Morocco. Cobalt is traded most commonly in unwrought, ferro and waste forms while there is some movement of wrought metal. The major sources are Zaire, Zambia, Norway and to a much smaller extent, Finland. Secondary sources are Sweden, the USA and the United Kingdom. This pattern emphasizes again the very strong dependence upon very few primary sources, with Zaire, which supplies approximately 65% (by metal content) completely predominant.

Strategic Considerations

Cobalt is medium scale in production and at present the consumption is well below production. However, it can be confidently predicted that the two will match again in the near future at which time the activities of investors may prove important. However the major source of vulnerability is the dependence upon one key less developed country with something of a history of instability. Cobalt accounts for 15% of the value of exports from Zaire but only 2% of those from Zambia, but such figures offer both producers some scope for manipulation. The coincidence of very limited sources in a geopolitically unstable area means that the problems of cobalt supply are potentially acute.

Hafnium

While hafnium is not used in the manufacture of air frames, it is quite important in the production of special alloys for jet engines since it control grain size in casting alloys and can confer ductility. It therefore governs the structure of parts which are under severe stress. However it is in the densifying of castings that hafnium is probably unique. As a result, for example, it promotes high creep strength and therefore lengthens the life of blades. The amount used is very small but there are no long term alternatives.

Sources

Hafnium production comes almost entirely from the mineral zirconium which usually contains about 1% of hafnium. It is recovered as a by-product in the production of hafnium-free nuclear grade zirconium-based alloys. It is therefore available at reasonable cost while the demand for reactor grade zirconium lasts. Statistics for world primary hafnium production are not available but the main source is concentrates from beach sands in the USA, Australia and India. South Africa also has extensive but lower grade beach deposits. There is no adequate source of zirconium in Europe. The scale of production is very small and the number of companies involved very limited. Therefore statistics tend to be confidential. Hafnium is produced as sponge and crystal bar, the USA producing 45 tonnes annually of the latter.

World reserves, judging by the distribution of zirconium, exceed 500,000 tonnes. Thus it can be concluded that potential hafnium supplies far exceed current demand.

Since there are no substitutes for hafnium in its major applications, prospects for hafnium look sound so long as the zirconium market remains healthy. At present recycling is insignificant.

European NATO Trade

Owing to its mode of production hafnium is only quoted in the trade statistics in its unwrought form. Furthermore few countries include it within their statistics. Imports into Europe are virtually all recorded as from the USA although it is known that some supplies come from Australia.

Strategic considerations

Since hafnium is unique and also produced on a very small scale there is some obvious vulnerability. Despite the variety of sources, dependence upon the USA could also present problems, not only with regard to maintaining the 'Atlantic Bridge' but also if American demand should rise. Furthermore it seems likely that investors will increasingly take an interest in hafnium.

Manganese

Manganese is an essential ingredient for all alloy steels 91% of it being used in the metallurgical industry. Its properties are to strengthen the steel in its own right and to desulphurise it. Nickel would provide some substitute but is expensive, while effective desulphurising agents are available but are themselves scarce.

Sources

Production at about 28 x 10^6 tonnes is very much greater than that of all the other strategics considered. It is dominated by the USSR (39%) and South Africa (22%) but six other countries each produce more than 1% of the world total. Included among them are: Brazil (8.5%), Australia (7.5%), Gabon (7%), India (7%) and China (6%). Altogether some 45% of production is within CEPs. Thus although there is rather wider choice of source, the pattern is not unlike that of chromium, with heavy dependence upon South Africa. *There is no manganese production in Europe.*

With regard to land based reserves the position of South Africa (53%) is even more dominant. The USSR possesses about 26%, Australia 9%, Gabon 5.5%, Brazil 3% and India 1.5%. Thus if CPEs are excluded South Africa possesses almost 75% of the world reserves. However reserves of seabed nodules are estimated at 2 x 10^{10} tonnes, and when these become available the picture will alter very considerably.

Since conditions are so closely related to those of the iron and steel industry, the market has been depressed recently. The production of ferro-manganese has also been at a level well below capacity and this has posed a number of problems. Basically ferro-manganese production is still considered of sufficient strategic importance for major investment even though the market is presently adverse. Therefore the question arises as to whether to maintain a strategic industry in an increasingly uncompetitive environment. As the steel industry recovers, so the tendency for all producing countries to beneficiate is almost certain also to increase. This will clearly affect alloy producing companies in the consumer countries and lead to even greater dependence upon the producers. *In this of course the trend is for manganese* to parallel chromium. As the capacity to smelt ferro-manganese declines so countries become more vulnerable to supply interruptions and less capable of processing ores held in a stockpile. Figures for recovery rates are not available.

European NATO Trade

Of all the strategic minerals under consideration the trade figures for manganese are much the most difficult to interpret. Manganese as ore, by far the most significant quantity, and in its ferro form is listed under a range of different grades. For ore and concentrates South Africa is by far the most important source for all the countries of NATO Europe apart from France, supplying 50% of imports. Next in order of significance are: Gabon (20%), Brazil (11%) and Australia while supplies are also obtained from Congo, Ghana and Morocco. The main sources for re-export are Belgium and Germany. Ash and waste are re-exported within Europe, but primary producers significant in the ferro-manganese trade, are South Africa, the USSR and Brazil. However re-export within Europe is more important and the leading countries are: Norway, Spain and Sweden. Manganese unwrought and wrought occupies a comparatively modest position in the trade statistics, the leading primary producer being by far South Africa. Thus South Africa dominates the manganese trade, supplying over 40% (by metal content). However the contribution of easily the leading secondary supplier, Norway, must be added since South Africa is its primary source, and the figure then exceeds 52%. Gabon provides approximately 15% (by metal content).

Strategic considerations

The scale of production is large and at present there is a surplus of manganese. *While there is a limited range of sources,* it is the reliability and quality of product which inclines the European countries towards South Africa. Gabon is a less developed country but manganese accounts for some 18% of the value of its exports. In the slightly longer term the lack of beneficiation facilities could pose further problems, but then other sources, such as Brazil, may supply relief.

Molybdenum

Approximately 80% of molybdenum is used in the iron and steel industry and the production of super alloys. In the manufacture of air frames molybdenum is critical for all low alloy steels and cannot be replaced. For engines it is used as an inter-metallic compound and also with tungsten for spray coatings. Molybdenum is further required for bearings and thrust rings. Within the aerospace industry molybdenum is a comparatively high usage metal, the amount being possibly half that of cobalt. The main properties are implanting strength, hardness and corrosion resistance to steel. It is also important in nickel-based alloys.

Sources

Molybdenum is a relatively common element, recovered from the working of many porphyry copper deposits. As copper capacity is now far beyond requirements, molybdenum should not be in short supply. However only five countries each produce more than 1% of the world total which is about 100,000 tonnes. The USA (60%) is completely dominant, the other major producers being Chile (14%), Canada (11%), USSR (9%) and China (2%). While the number of sources is therefore limited the fact that almost 75% of the production occurs within developed countries, lessens vulnerability.

World reserves are rather more widely spread although the USA (54%) and Chile (25%) still predominate. Other countries with significant reserves are: USSR (7%), Canada (6.5%). Peru (2.5%), China (2.5%), Iran (1.5%) and Mexico (1.5%). With regard to vulnerability the pattern of reserves parallels that of production.

There was a sharp increase in demand and production in the late 1970s but by 1980 a decline had set in. In fact the surge of 1979 is still being felt with new capacity being opened as late as 1981. While the main implications for molybdenum are closely tied to the steel industry and must wait for its recovery, conditions are favourable for the development of a new range of high technology uses. In particular research into high temperature steel has shown the benefits of including molybdenum. Therefore it is possible to forecast a modest increase in the market over the near future.

European NATO Trade

For ores and concentrates, much the most important trading form, the chief suppliers are the USA and Canada followed by Chile. While there is some re-export from the Netherlands, Germany and the United Kingdom. Ash and waste presents a most complex picture since there is re-export between the NATO countries but there are also imports from Austria, the USA and Niger. The ferro-molybdenum trade is dominated by Austria and Sweden although the main NATO countries apart from the United Kingdom are all involved. Again with unwrought and wrought molybdenum several countries are concerned but Austria and the USA are dominant. The molybdenum trade is very much dominated by the USA which provides about 65% (by metal content), Canada (18%) and Chile (12%), although the importance of non-NATO European countries particularly Austria and to a lesser extent, Sweden, must be born in mind. Problems of supply would therefore be concerned mainly with the 'Atlantic Bridge'.

Strategic considerations

The scale of production is within the medium range and at present there is no shortfall. There is a range of sources but the consumers tend to rely very heavily upon the USA. However should supplies be endangered Canada and Chile would seem to provide reasonable alternatives. From the trade lists it would appear that most of the European NATO countries retain sufficient beneficiation capacity.

Niobium (Columbium)

Niobium is important in the production of a range of steels, alloy steels and super alloys. In the aerospace industry it is used to stabilise stainless steel for air frames and also for welding. It is also used extensively in engine production for minor alloying, stabilising stainless steel, precipitation hardening, in nickel-based alloys and in wear coatings. There is also some interchange with titanium for corrosion inhibition in steel. The amount used is small but the properties are vital particularly in nickel-based, steel and titanium alloys.

Sources

Workable niobium sources are very highly concentrated and excluding the CPEs for which no figures are avaialble, there are only three countries each producing more than 1% of the world total. These are completely dominated by Brazil (87%) although Canada (11.5%) is also important. There are very small sources of niobium in Portugal and Spain. Reserves display a similar distribution with Brazil (70%) by far the most important, followed by the USSR (15%) and Canada (2.5%). The statistics thus reveal an extremely high degree of dependence on basically one source.

Despite the general economic decline, the demand for niobium remains relatively strong although increased stocks have accumulated. In fact during 1981 world niobium capacity increased through developments in both Brazil and Canada. Recovery is insignificant at about 2%.

European NATA Trade

For ore and concentrates niobium and tantalum are generally grouped together and this therefore rather obscures the pattern. The major suppliers of niobium are Canada and Brazil. The USA is predominant in other forms but the amounts are insignificant. The statistics reveal that Canada still dominates the trade supplying over 30% (by metal content) but more detailed investigation shows, at least for parts of the aerospace industry, total dependence upon Brazil.

Strategic considerations

While the scale of production is medium and at present probably exceeds demand, there is some room for investors in the market. The major strategic problem occurs when the range of sources is considered. Canada has only limited reserves and if not at present, at least in the future, there will be very heavy reliance upon one mine in Brazil.

Tantalum

In the aerospace industry tantalum is not used in air frames but in engines it is employed as an alloy strengthening element either by itself or with niobium. For this the amount is very small, a maximum of about 10%. Its major importance is as a strengthener in nickel-based alloys but it has been used as pure tantalum in for example the production of the RB211 heat shield. However even where it is important the use of higher performance powders has allowed economies to be made.

Sources

Total world production is about 440 tonnes and has shown a decline since 1979. There are five significant producers with Brazil (24.5%) and Canada (24%) the major sources. Others are Thailand (15.5%), Australia (12%), Nigeria (7%) and Mozambique (6%). If production from tin slags is added the world total is virtually doubled, with the greatest production being in Thailand, Malaysia, the USSR and to a lesser degree, Zaire. Thus although production is very small and this in itself could lead to problems should demand rise, the sources are widely spread. Furthermore there are very limited supplies within Europe, in Portugal and Spain.

Eight countries each have more than 1% of world reserves although dominant by far is Zaire (48%). Australia has 17.5%, Nigeria 9.5%, Thailand 6%, the USSR 6%, Malaysia 4.5%, Brazil 4% and Canada 1%. Although the Third World predominates, reserves are reasonably spread within the developed world and the CPEs.

Owing to substitution the more economical use of the metal and the general economic recession, demand for tantalum has fallen considerably. This contrasts sharply with the supply gap evident in the recent past and alleviated largely by the development of Australian sources. Recovery rates average about 8%.

European NATO Trade

For ore and concentrates the main sources are Canada and Brazil, followed by Malaysia (largely from tin slags) and Nigeria. Tantalum in other forms is important mainly from the USA although one or two European countries do use Australia as a source. While there is a strong dependence upon Canada the range of options is comparatively large and does not appear to pose strategic problems.

Strategic considerations

The potential difficulty lies in the scale of production which is small. At present there is insufficient demand even for this amount, but should the situation change, prices could rise sharply and supply difficulties could result. The present range of sources within the developed and less developed world militates against problems of concentration.

Titanium

The bulk of titanium ore, both ilmenite and rutile, is used for the production of titanium dioxide, the major pigment in nearly all white paint. This accounts for approximately 92% of the ore. Of the remainder the bulk is used for metal production and of this 60% is used for the aircraft and aerospace industries and a further 20% for steel and other alloys.

Within the aerospace industry titanium is one of the major metals used and is considered vital. It has a very high specific strength and specific stiffness and the modulus is between that of steel and aluminium alloys. It is used for precipitation hardening in nickel-based alloys and for corrosive inhibition in stainless steel. Because of its high strength it is a major component at the cold end of engines, for example for fan discs. Typically the alloy used for fan blades contains 90% titanium, 6% aluminium and 4% vanadium. The major ore is rutile, ilmenite being more for the commercial side of the market.

Titanium is also being used for highly stressed components in missiles, rockets and space capsules, as well as armour plating for airborne military equipment. Increasingly titanium carbide is becoming important in the machine tool industry in providing both coatings and complete tool tips. With such versatility, substitution for titanium is likely to lead to a loss of efficiency. For example carbon fibre composites may replace it, but they are very expensive. Furthermore a new aluminium alloy containing lithium, copper and magnesium is under test. For corrosion resistance there can be an interchange with niobium. However the range of applications for titanium is increasing all the time and it seems highly unlikely that it will ever be less vital for the aerospace industry.

Sources

Titanium is widely distributed and in fact of the structural metals only aluminium, iron and manganese are more abundant. The major problem is the process of extraction, smelting and fabrication, all of which are expensive. Since titanium is obtained from ilmenite, rutile and slags and production is measured in sponge and pigments, the interpretation of statistics is more complex than for the other strategics. World production of ilmenite is about 5,000,000 tonnes the dominant producer being Australia (28%). The other leading producers are: Norway (15.5%), Canada (15%), USA (12%), USSR (9%), South Africa (7%), Malaysia (4%), India (3.5%) and Finland(3%). Both Canada and South Africa produce from slags. The world production of rutile is about 400,000 tonnes of which Australia produces about 70%. The other main producers are: South Africa (11%), Sierra Leone (8%) and Sri Lanka (4%). Thus with rutile there is a very heavy dependence upon Australia, and Europe has no production. Canada is the dominant producer of slags followed by South Africa. The production of titanium metal is almost equally divided between the developed countries and the CPEs, with a world total of just under 110,000 tonnes of sponge. Only five producers are listed: the USSR (43%), USA (28.5%), Japan (26%), United Kingdom (2.5%)and China.

World resources of ilmenite are fairly widely spread but only eight countries each possess more than 1% of the world total. These are: India (23%), Canada (22.5%), Norway (18.5%), South Africa (15.5%), Australia (8%), USA (7.5%), USSR (2%) and Finland (1.5%). Rutile reserves are also widely distributed, although Brazil is dominant with 78.5%. Other leading countries are: Australia (8%), South Africa (4%), Italy (3.5%), Sierra Leone (2.5%), USSR (2%) and USA (1.5%). For rutile then while there are supplies in Europe there is a heavy dependence upon one country, Brazil.

Both the production and consumption of titanium sponge have continued to show increases but the markets for both ilmenite and rutile have continued to remain depressed, despite the fact that in 1981 the USSR became an instant buyer. The increasing range of applications would seem to ensure the health of the metal market, and indeed titanium is one of the few strategics in the production of which aerospace companies have invested directly.

European NATO Trade

Tables for ore and concentrates contain ilmenite and titanium, the major sources being: Australia, Norway, Canada and South Africa with more minor quantities from India, Sierra Leone and Sri Lanka. In other forms of the raw material, the trade is very small. Ash and waste is imported from the USA, Canada and South Africa, while for the ferro-alloy, Norway is the leading source. Titanium unwrought and wrought comes principally from the USA and Japan although the USSR is also a supplier. The range of sources is therefore comparatively wide with Australia supplying about 36% (by metal content), Norway 34% and Canada 27%. There could be difficulties with the maintenance of the 'Atlantic Bridge', the length of sealanes and the limited dependence upon the USSR. However NATO Europe is clearly well placed with regard to beneficiation.

Strategic considerations

Although rutile is produced on a fairly modest scale it is difficult to contemplate problems of ore supply. Much more of a limitation is the production of sponge which is more sparsely distributed both in amount and geographically. All three key suppliers, Japan, the USA and the USSR could reduce exports as a result of rising home demand. Furthermore Japan presents problems of distance and clearly under certain conditions supplies from the USSR would not be expected.

Tungsten

Tungsten has a range of unique properties and is also largely resistant to corrosion, imparting great hardness, strength and resistance to wear. Its main uses are in the production of tungsten carbides and alloy steels. Tungsten carbides are vital in the production of equipment requiring extreme wear resistance but substitutes, in all cases inferior, are generally available for uses other than rock drilling. Similarly for alloy steel there may be other possible replacements but none entirely satisfactory and no acceptable substitutes are currently available for the electrical uses.

The aerospace industry is a medium user of tungsten. In air frame construction there are no alternatives and for engines, tungsten is vital, by itself, with carbides for tooling etc. and in wear applications. It is also used for wear, erosion and oxidisation resistance when plasma-or-flame sprayed. Tungsten is further used in bearings and thrust rings. Overall its major use is in strengthening cast nickel-based alloys and with the drift from wrought to cast alloys its importance will increase.

Sources

World production is about 51,500 tonnes and is very widely spread. The leading producers are China (29%) and the USSR (18%). Other producers of note are: Australia (6.5%), Bolivia (6.5%), Canada (6%), USA (5.5%), South Korea (5.5%), North Korea, (4%), Thailand (3.5%), Portugal (3%), Austria (3%) and Turkey (2%). Within W. Europe, France, Portugal, Spain and Austria all produce moderate amounts of tungsten. With such a wide spread of sources and, particularly with tungsten in Europe, there does not seem to be a major problem of vulnerability.

World reserves are also widely spread although again China is dominant with 52.5%. Other countries with major reserves are: Canada (10.5%), USSR (8%), USA (4%), North Korea (4%), Turkey (3%) and South Korea (3%). The pattern of reserves is therefore similar to that of production except that China is relatively under-producing while the USSR is over-producing.

Tungsten has retained its demand despite the world-wide recession although there have been some cutbacks. With a variety of new tungsten projects planned there would seem to be a more than adequate supply of the metal for the future. Furthermore recent emphasis on foreign trade by China will greatly influence the amount available. Recycling is also important with a recovery rate of about 23%.

European NATO Trade

The major source of ore and concentrates is China, followed by Portugal, Bolivia and Australia. There is little trade in other forms of tungsten, the main sources being Austria and South Korea, with Sweden and the USA involved to a lesser extent. Thus there is no distinct pattern of dependence although there is clear dominance by China (about 10% by metal content) which is likely in future to increase. However a wide range of European countries maintains the capacity to produce ferro-tungsten even though China is again important.

Strategic considerations

Although the tonnage required is comparatively small, there must be disquiet about the increasing dependence upon China. Given the pattern of world reserves, there would seem, at least in the medium term, to be little alternative.

Vanadium

Vanadium is chiefly important as an alloying agent in armoured steel and in the production of titanium alloys. In the aerospace industry it is important as a toughener in cobalt-vanadium tool steels and for this there are no alternatives. It is also vital in providing strength at high temperature in steel and nickel-based alloys. Its importance in the 6:4 titanium alloys (aluminium 6%: vanadium 4%) has already been mentioned. The aerospace industry is thus a small user but vanadium is vital.

Sources

World production is about 35,000 tonnes and is dominated by South Africa (33%) and to a lesser extent, the USSR (29%) and the USA (13%). Other producers are China (11%) and Finland (8%). Thus there is production in Europe but for the developed countries there is dependence upon South Africa. The pattern with regard to reserve reinforces the position of the two leading producers, South Africa having 49.5% and the USSR 46%. In fact the only other country with more than 1% is Australia. However since vanadium is generally recovered as a by-product or co-product reserves are not fully indicative of available supplies. At present prices though, South Africa is clearly the dominant source. Recovery rates are about 8%.

With an increased availability particularly as a result of Chinese intervention in the market and the decline of world steel production, the market has been rather depressed. However world consumption still rose and there are plans for development not only in China but also in Venezuela and New Zealand. Therefore it can be concluded that while the range of applications will probably increase the actual supply will remain sufficient.

European NATO Trade

Vanadium ore is of no significance as a raw material and therefore trade in ore and concentrates is generally not listed except in the case of Belgium which receives supplies from Norway. With ash and residues the main source is given as secret but others listed include Mozambique, China and South Africa. The sources of ferro-vanadium are principally Austria and Noway while vanadium, unwrought and wrought, is imported on a comparatively small scale from Japan, South Africa and the USA. However vanadium imports in chemical form are particularly important and are dominated by Finland and South Africa, followed by Austria. Despite European supplies therefore there is a clear dependence upon South Africa, which supplies approximately 27% (by metal content).

Strategic considerations

Despite being a commonly occurring mineral the installed capacity for extraction is important and this leads to a marked dependence upon South Africa. With the South African domination of world reserves, this position is likely to be reinforced in the future.

Yttrium

The use of yttrium in the aerospace industry is extremely small and there seems to be little concern about supplies. It is used with magnesium and is a constituent in some blade alloys. It is a constituent of both nickel-based and cobalt-based super alloys giving resistance to erosion and also as a coating for turbo blades in engines. The other potential use within industry is in the production of lasers in which in the form of yttrium-aluminium garnet, it can give very fast pulses of the order of a few pico-seconds.

Sources

Statistics for yttrium production are incomplete since those for the USA are withheld for reasons of confidentiality and those for Canada are not available. However the total is probably between 515 and 600 tonnes. The major producer is Australia (approximately 30%) while India and Malaysia are also important.

With regard to reserves India is dominant with over 52%. Australia (15.5%), USA (4%), Brazil (6.5%) and Canada (6%) are also significant.

As improved technology and research lead to increasing demands there seems little doubt that these can be met. It is probable that the world's undiscovered resources are large relative to any expected demand. At present recycling does not occur.

European NATO Trade

Yttrium appears separately in the trade statistics which show that Austria, Belgium and Germany are sources for other parts of Europe. Presumably the yttrium originates mostly in Australia with possibly some import from Canada and the USA.

Strategic considerations

These must revolve mainly around the small scale of production since the range of sources is comparatively wide. Clearly, should demand rise and prices increase, investors could well affect the market.

3. THE COUNTRIES OF EUROPEAN NATO

While elements of the aerospace industry are represented in all the countries of European NATO except Iceland, the industries of West Germany, Italy and the UK are quite clearly the most important. Since it has been associated in many European projects and since it is all so closely integrated into NATO although not a member, France must also be included.

For all the raw materials described, the countries of European NATO, with only minor exceptions, are 90% import dependent, the figure varying from approximately 91% (cobalt and tantalum) to 100% (titanium). The only raw material for which this does not obtain is tungsten, for which the dependence is 58% (UK 56%). In the case of five materials, the dependence of France is rather lower than that of the other countries. None of the major aerospace countries has deposits of strategic minerals on any scale. In fact the only significant production is chromium (Turkey), clearly the most important, ilmenite (Norway) and tungsten (Turkey and Portugal).

An examination of the trading patterns reveals that three European neutral countries, Sweden, Finland and Austria, exercise a significant influence. Firstly in a period of increasing tension between West and East, their attitudes towards trading strategic minerals with NATO must be considered. Furthermore although it is one stage removed, there is still the basic dependence upon the original source of the mineral together with the vulnerability resulting from reliance upon processing abroad. All three countries trade in a restricted range of strategic minerals but all are important in the area of ferro materials.

Among the developed countries the major sources of strategic minerals for European NATO are: USA, Canada and Australia. All three suffer to a certain extent from the problem of distance, the first two with difficulties of maintaining the 'Atlantic Bridge' and Australia with very long sealanes to be protected. Apart from this the main difficulty with the maintenance of supplies from the USA could well be that the particular minerals are required for internal consumption. Developing countries, at different states of development, but important for the supply of strategics present rather different problems. Since many are highly dependent upon the export of raw materials for their economic wellbeing and since in any case this may be controlled by multinational corporations, there appears to be little coincidence between political and economic instability. In general, supplies do not appear to be disrupted by political change, a point shown vividly recently by continuing supplies of chromium from Zimbabwe. However in each there are possibilities of supply disruption through civil unrest, sabotage, local conflict, government expropriation and possibly the activities of Soviet surrogates.

In many ways for European NATO the most important country, neither developed nor developing, is South Africa. Apart from the various threats to its stability, particularly in the medium to long term, South Africa also poses a basic moral dilemma. For chromium and manganese and to a lesser extent vanadium and titanium, South Africa is a major producer and also possesses great potential for further development. Despite the current depressed state of the market there is great underlying strength resulting from:

(a) the enormous scale of reserves;

(b) the highly developed infrastructure;

(c) the abundant powers of beneficiation;

(d) the political and commercial stability; and above all

(e) the technological expertise.

Furthermore through its infrastructure South Africa controls most of the mineral exports from the developing countries of southern Africa

4. STRATEGIC CONCLUSIONS

The term 'strategic' when applied to a raw material implies a range of factors, geological, economic and political. Some of these can be quantified others are largely conjectural. Therefore to attempt a weighting is a particularly complex problem, and forcasts far into the future extremely hazardous.

(i) Raw materials

(1) Most at risk through the potential instability of sources are cobalt, chromium and manganese. In the longer term, offshore mining could alleviate the problem for cobalt and manganese.

(2) Most at risk through the concentration of sources are the above with the addition of, particularly, niobium. There could also be short term problems with nickel.

(3) Most at risk through reliance upon a CPE producer is tungsten.

(4) Most at risk through the small scale of production is hafnium.

(5) Most at risk through the reduction or lack or installed extraction or beneficiation plant are vanadium and titanium. Increasingly chromium and manganese in particular could also be affected.

(6) Most at risk overall are chromium, niobium and cobalt

(ii) European NATO countries (Fig 7)

(1) All are, with very minor exceptions, highly import dependent, with France rather less so than the others.

(2) There is a high degree of dependence upon southern Africa and in particular South Africa.

(3) There is a marked secondary dependence particularly on neutral European countries.

(4) There is a tendency to rely on a restricted range of sources. The neutral countries and Japan show that this may be rather less necessary than is commonly supposed.

(5) There is little dependence on Warsaw Pact sources.

REFERENCES

(1) James, D. (Ed.) 1981 Strategic Minerals: A Resource Crisis Council on Economic and National Security, Washington. pp 105.

(2) Anderson, E.W. and Blake, G.H. 1981 Selected Non-Fuel Minerals Ministry of Defence, London. pp 67.

(3) Anderson, E.W. 1982 The Need to Safeguard the Supply of Strategic Raw Materials to the West In: Stewart-Smith, G. Global Collective Security in the 1980s. Foreign Affairs Publishing Company Ltd. pp 67-79.

(4) Anderson, E.W. and Blake, G.H. 1982 The Republic of South Africa: a Stable Supplier? Ministry of Defence, London pp 83.

(5) Aviation Week and Space Technology, March 8, 1982 pp 8-280.

(6) House of Lords Select Committee on the European Communities 1982 Strategic Minerals HMSO.

(7) Statistical Office of the European Communities 1982 Analytical Tables of Foreign Trade NIMEXE 1980 *Office for official publications of the European Communities.*

(8) Marsh, P. 1983 The West Builds up its Metal Mountain New Scientist, 3rd March 1983 pp [illegible].

(9) Sinclair, J and Parker, R. 1983 The Strategic Metals War New York, Arlington House pp 18[illegible].

(10) Miller, J.A. Fine, D.I. and McMichael, R.D. 1980 The Resource War in 3-D - Dependency, Diplomacy, Defense World Affairs Council of Pittsburgh pp 109.

(11) Statistical office of the European Communities 1981 E C Raw Materials Balance Sheets 197[illegible]-1978 *Office for official publications of the European Communities* pp [illegible].

(12) Institute of Geological Sciences 1983 World Mineral Statistics 1977-81 HMSO pp [illegible].

(13) Crowson, P. 1982 Minerals Handbook 1982-83 Macmillan. pp 248.

(14) Spooner, J. et al 1983 Mining Annual Review 1982 Mining Journal Ltd.pp 568.

(15) US Department of the Interior, Bureau of Mines, 1983 Mineral Commodity Summaries 1983 US Department of the Interior pp 183.

(16) Packard, R. (compiler) 1982 Metal Bulletin Handbook Vol.II: Statistics and Memoranda Metal Bulletin Books Ltd. pp 579.

Fig. 1 THE PROBLEM

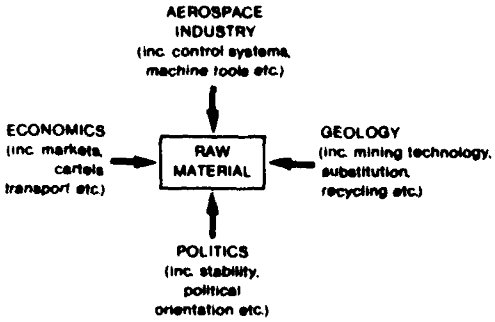


Fig. 2 CRITICALITY

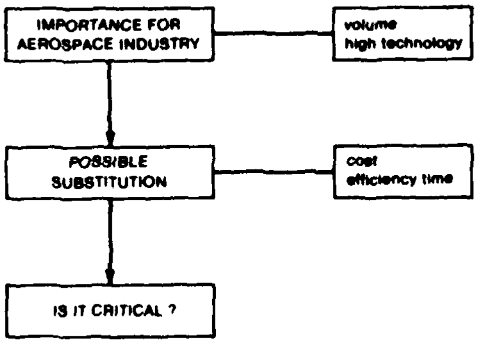


Fig. 3 SUPPLY CONCENTRATION

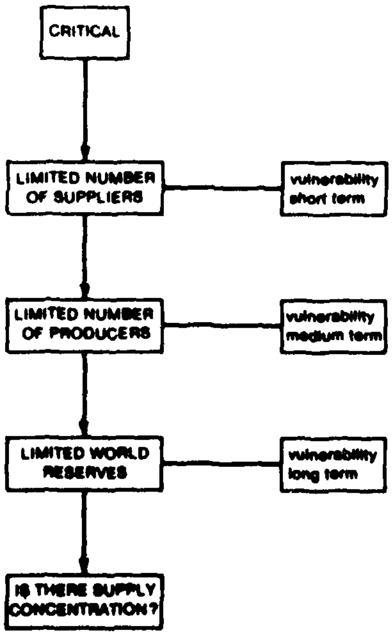


Fig. 4 POLITICAL VULNERABILITY

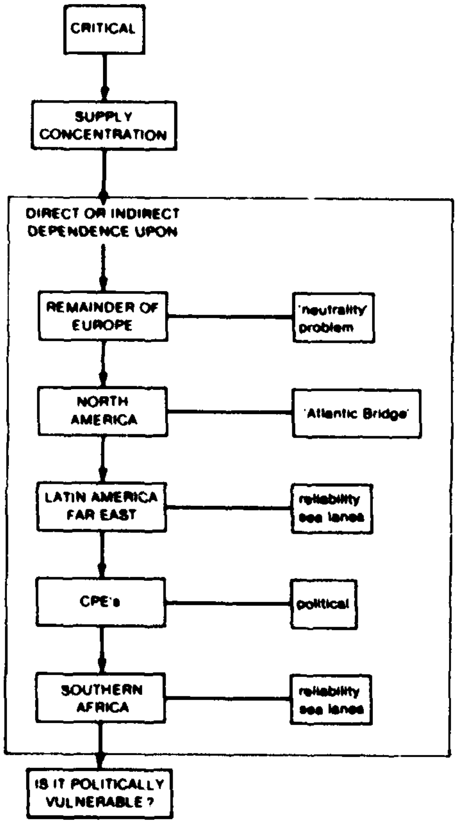


Fig. 5 STRATEGIC ALGORITHM

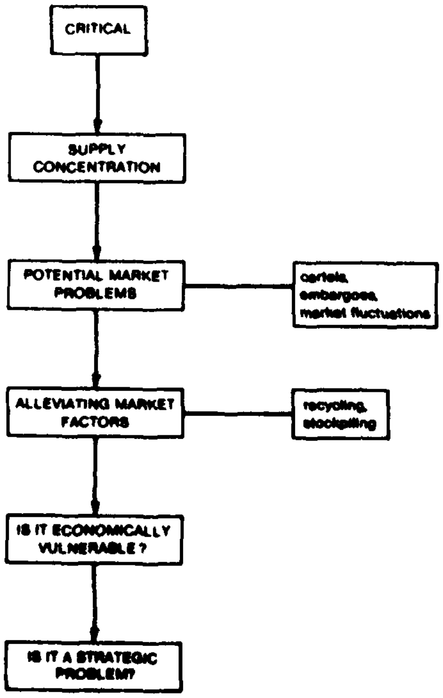


Fig. 6 PRICE FLUCTUATION

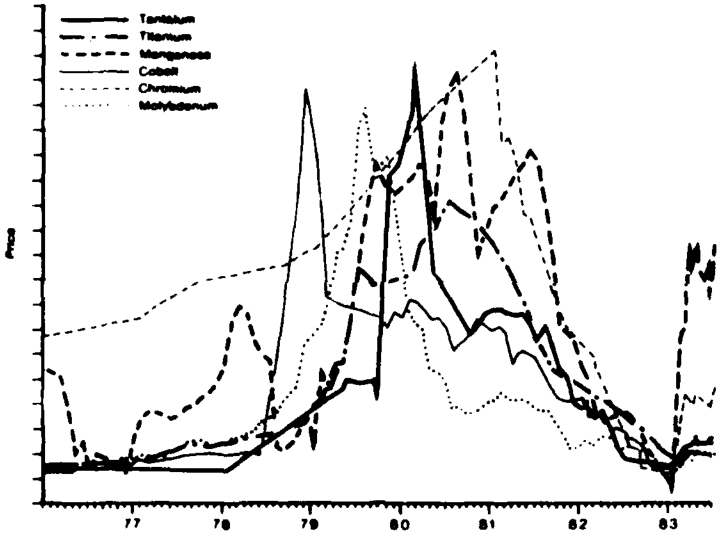
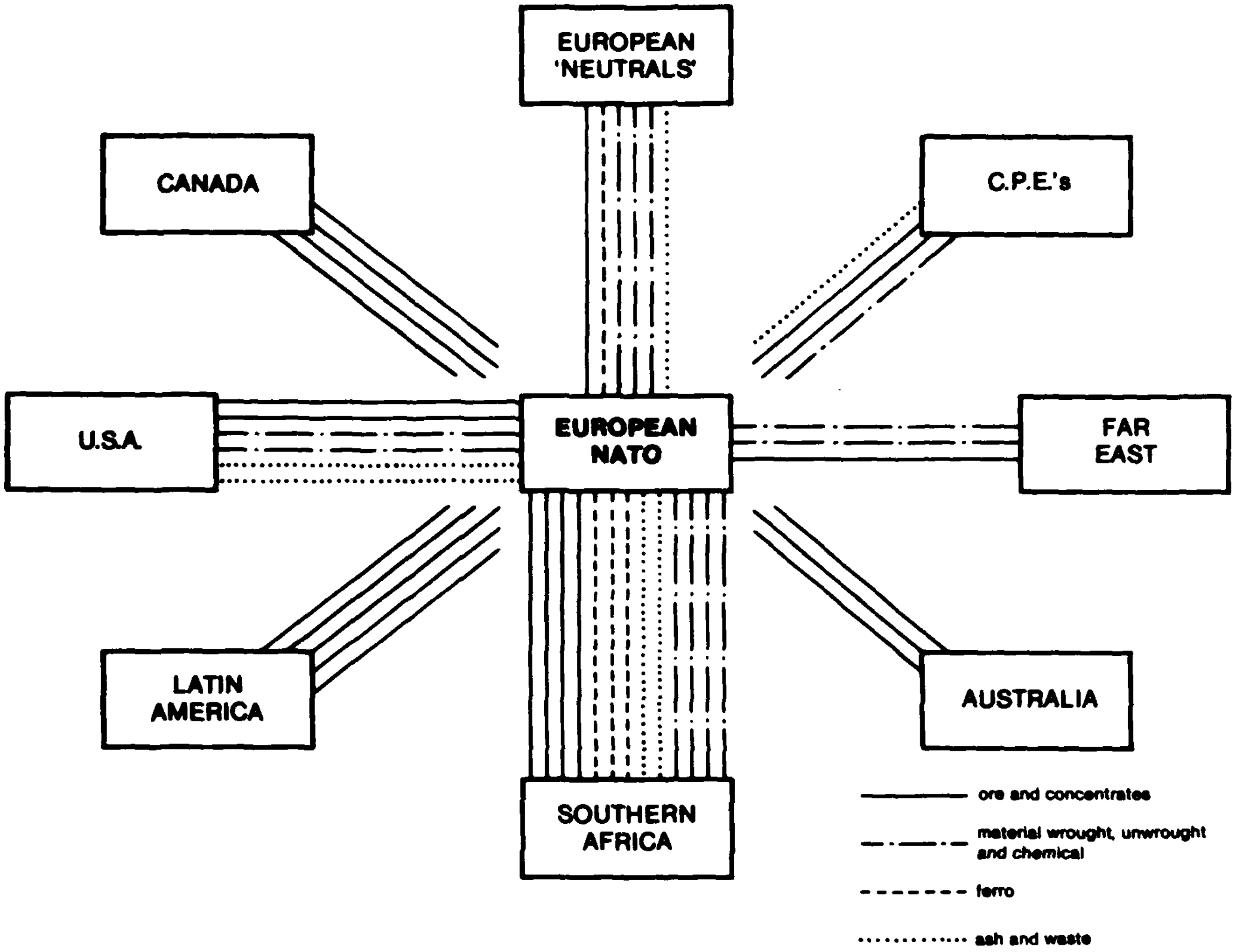


Fig. 7 EUROPEAN NATO: STRATEGIC MATERIALS DEPENDENCE



MEASURES FOR MATERIALS CONSERVATION IN AERO-ENGINE CONSTRUCTION

by

H. Huff, R. Gräter and R. Fröhling

MTU Motoren- und Turbinen-Union München GmbH
Postfach 50 06 40
D-8000 München 50, Germany

AD-P004 213

SUMMARY

Based on the following requirements

- Minimization of critical raw materials input
- Production of as little scrap (machining wastes, parts out of service) as possible

concepts for reducing the use of materials and the associated dependence upon raw materials imports are explained.

With reference to aero-engine components, the following possibilities are shown as examples:

1) Combination of very different materials by means of modern joining techniques. Components "built up" in this way contain expensive materials only where they are indispensable.
2) Approximation of the blank contour to the final contour of the component (thus reducing machining losses) by contour-forging, flow-turning and powder metallurgy.
3) Making run parts reusable.

It is shown that a considerable economy of materials is obtainable and has partly been achieved already. Attention is drawn to problems which may follow from the application; e.g. material deposition or joining of dissimilar materials results in a tendency to render the recycling of such engine components more difficult.

INTRODUCTION

To the aerospace industry the need to economize and preserve critical metals is very real. This involves metals (or the raw materials going into them) that are indispensable in the manufacture of aerospace equipment but the availability of which (at reasonable costs) is latently threatened as a result of economical or political uncertainties (high cost of exploitation, regional concentration in potential trouble spots, highly energy consumptive production). The critical metals used in aero engines are principally cobalt, chromium, nickel, titanium, tungsten and tantalum. While these raw materials may well have been in sufficient supply these past few years, with prices running relatively stable, long-term predictions are never safe (as witnessed by the performance of cobalt between 1978 and 1980).

Irrespective of the actual market situation, reasons of cost make a reduction in material investment an indispensable requirement. This applies in particular to aero-engine construction, where product material costs are high on account of the expensive alloying elements.

Conservation of critical metals or their raw materials is generally sought in a number of ways:

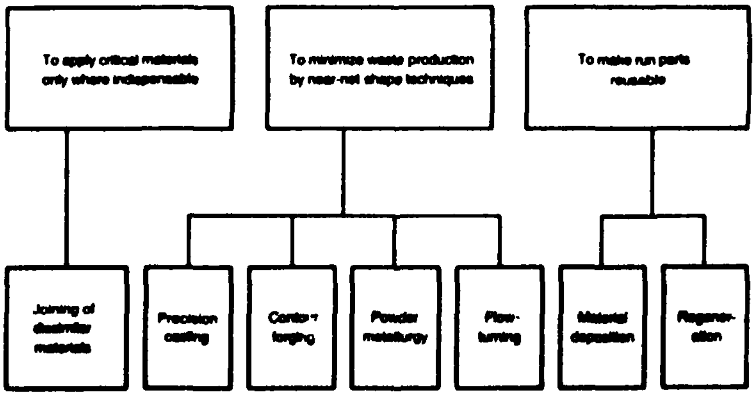
- by substitution, i.e., either by lowering the critical alloy content in existing materials (leaning) or by developing alternative materials from cheaper raw materials which are readily available on a long-term basis
- by the application of critical materials only where they are needed
- by the application of near-net-shape manufacturing processes
- by taking measures designed to extend the life of components
- by remelting scrap metal, accompanied by minimum possible downgrading.

Substitution and recycling are approaches in which the finishing industry (e.g. the aero-engine manufacturers) can assist - being mostly dependent on the good intentions and willingness to cooperate on the part of the material manufacturers. Whereas measures for reducing critical materials input and extending life can normally be planned and implemented by the finishing industry on its own.

The present paper discusses specific measures for reducing waste and for extending life as applied to engine components. Some of the methods and techniques used toward this end were evolved with other purposes in mind (e.g. light-weight construction). It is nevertheless shown that appreciable savings in materials or gains in life can be achieved for engine parts and that the concepts employed can also readily be transferred to other areas.

While the measures discussed below are representative of applications in engine construction, they do not claim to be complete.

MEASURES FOR MATERIALS CONSERVATION IN THE FINISHING INDUSTRY



Use of critical materials only where they are indispensable

In view of the fact that many engine components come under loads that vary considerably over the cross-section of the part, this requirement results in "tailored" components that may be composites of the most diverse materials ("multialloys"). These developments are made possible by highly advanced joining techniques. This is exemplified in Figs. 1 and 2. In either case the joint is made by electron beam (EB) or friction welding. It is exactly these joining techniques which permit the combination of the most dissimilar and sophisticated materials to produce these tailored components (whereas high-temperature brazing, for example, would be ill-suited for such joints, owing to the attendant heat transfer). Without suitable joining methods, the examples shown would be penalized by the added weight of screwed connexions or - if they are made from the solid - by a material cost that would be a multiple of that of the present solution.

Maximum reduction of machining waste by using near-net-shape technology

Investment casting, being the oldest and probably the most significant of near-net-shape manufacturing techniques, naturally finds wide use also in engine work. The limitations of the method are imposed not so much by its inability to meet geometry and tolerance requirements, as by the inherently inferior mechanical properties of the castings. To meet the exacting requirements of aero-engine service, drop-forged alloys are the material most widely used. Considering the complex geometries encountered in engines, this entails relatively large losses of material in machining (about 50% to 90%), unless suitable manufacturing techniques for economizing materials or for reducing the amount of waste are employed.

The potential savings offered by near-net-shape forging are illustrated by way of a rotor disk. Fig. 3 shows the forging in its normal shape, and Fig. 4 shows it in its leaned contour. For a nickel-base alloy disk, the relative weights would be:

Manufacturing stage	Normal version		Leaned version	
	Relative weight %	Actual weight kg	Relative weight %	Actual weight kg
Ingot	100	87.5	100	50.0
Billet	80	70.3	80	39.8
Forging	71	61.7	63	31.4
Finished part	11	9.5	20	9.5

This example indicates a possible reduction in material loss for a disk of the configuration shown of about fifty percent (from 78 kg for the normal version to 40.5 kg for the leaned version).

The method just described has its limitations where shapes grow difficult, or where very widely-varying degrees of deformation are involved. These difficulties are avoided by powder metallurgy, which will achieve the final contour without excessive loss of material even for components of less amenable shape. Fig. 6 illustrates a shaft made by a powder-metallurgy process. Compared with the forging (Fig. 5) it appreciably reduces the amount of material invested. The relative weights are:

Forging	100%
PM compact	60%
Finished part	7%

This method finds its limitations - as regards near-net-shape applications - mainly in the high cost of encapsulation. Fig. 7 shows qualitative relationships between cost and net-shape nearness.

It is especially with very thin-walled, axisymmetric components that flow-turning suggests itself for near-net-shape applications. Fig. 8 illustrates this by way of a compressor shaft sleeve (the figure shows the finished part contour together with the starting contour for flow-turning.) This extremely thin-walled tubular shape was originally machined from a solid forging (Fig. 8a). Material losses ran in the neighbourhood of 90%. This loss can be greatly reduced by flow-turning. The starting contour for flow-turning can be produced by machining either a bar section (Fig. 8b) or more advantageously a near-net-shape (referred to the starting contour for flow-turning) forging (Fig. 8c). Material investment would then be in the following relation:

8a : 8b : 8c : finished part ≈ 100 : 30 : 15 : 8

This process finds its limitation chiefly in the geometry of the component with application restricted to axisymmetric and thin-walled parts with simple shapes and smooth inner contours.

Making parts reusable

Measures for extending the life of components also will indirectly save substantial amounts of material. Considering that in engine work the components involved are generally expensive finished parts, every effort is taken in this area.

Distinction is made here between components whose life is spent as a result of fatigue or creep, and components made unserviceable by changes in dimensions (as a result of wear, fretting etc.)

Fig. 9 is a schematic arrangement illustrating the effect of regeneration on the lifetime of turbine blades. The hot isostatic pressing (HIP) process serves to heal creep voids and other flaws in the microrange, making the affected component reusable or giving it an additional life-span. This procedure is still in its infancy as regards material conservation.

The practice of restoring components suffering from wear (in its widest sense) to their specified dimensions, on the other hand, is finding wide use. This is where electroplating and chemical depositing processes especially, as well as thermal spraying methods, have proved their worth. The deposited materials are selected to meet specific requirements concerning properties such as thermal expansion and wear resistance. With a view to possible recycling, however, it should be taken into account that the deposited material ought to be compatible with the base material also from the metallurgical aspect. For nickel and cobalt alloys as base materials the deposit materials can be classified as follows:

Deposit materials the constituents of which are contained in the parent material	Deposit materials the constituents of which are considered contaminants in the parent material
Ni	NiP
Cr	$CoCr_2O_3$
NiCr	Ag
NiAl	Cu
NiCrAl	WCCo
NiAlMo	$NiCoCrAl_2O_3$
Mo	

Material-depositing processes have their limitations, primarily posed by the geometry of the components (e.g. accessibility to the surfaces to be built up, deposition thickness, etc.).

It is anticipated that processes still to come (such as low-pressure plasma spray deposition) will be able to deposit materials similar to the substrate material, to generally eliminate the problem of compatibility, i.e. the question of potential contamination. Expectations are currently directed toward nickel- and cobalt-base alloys only.

CONCLUDING REMARKS

Some of the material conservation measures described may involve considerable downgrading of scrap, loss of expensive alloying elements by dilution or costly separation of such elements in final recycling (reasons: union of materials that are incompatible with regard to recycling, carry-over of deleterious elements into the alloy). The problems discussed here may generally be reduced to the following alternative:

Decision (or approach)	Consequence
A) Use of "tailored" components of dissimilar materials. Dissimilar material deposition.	Initially savings in material or increase in lifetime, but possibly forgoing chance to recycle materials at full value
B) Use of uniform-material components having expensive materials also where they are not necessary.	Initially wider use of expensive materials, but possibly long-term chance to recycle (genuine closed-loop cycle)

With regard to universal long-term reduction of losses in the materials processing cycle, alternative "B" without question takes preference and "multialloys" should really not be permitted. However, for the aero-engine manufacturer and, almost certainly, for the metal-working industry in general, this does not represent a practicable solution as long as the cost of the blank is ten and more times as great as the value of scrap. Moreover, in many cases, repair procedures or lightness requirements tell against alternative "B".

Irrespective of such considerations, as well as from the costs point of view, the manufacturer will endeavour to sell off scrap (from machining, rejects etc.) at maximum possible prices. It cannot be absolutely excluded that unapproved scrap (i.e. that which may be contaminated) passes into the heat. Thus, this involves the risk of enrichment by harmful elements during recycling.

Manufacturers, who combine dissimilar materials, in their own interest, must bear in mind the compatibility question as early as the planning stage, short-term cost considerations notwithstanding.

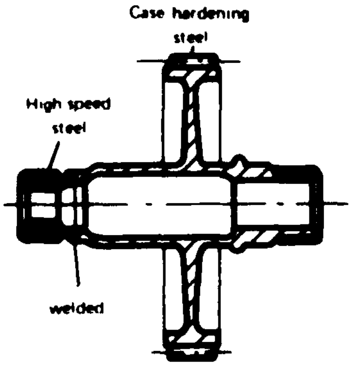


Fig. 1 GEAR SHAFT

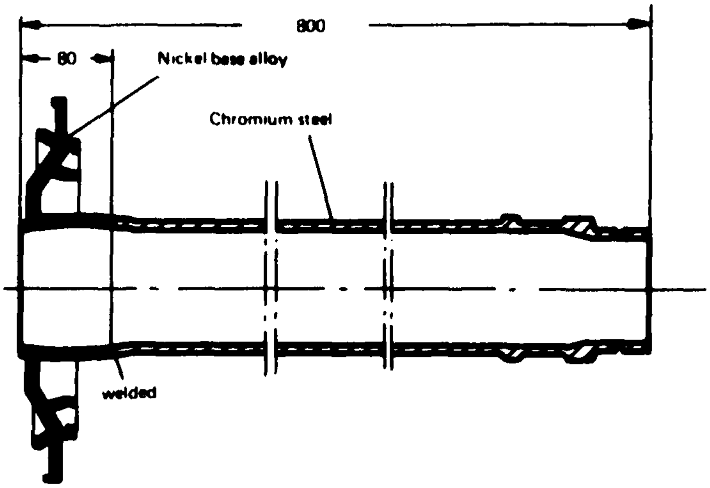


Fig. 2 TURBINE SHAFT

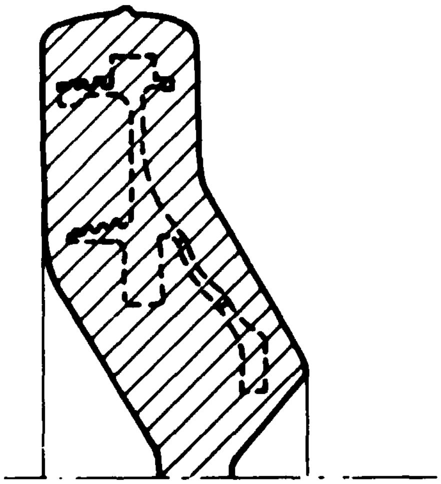


Fig. 3 FORGING CONTOUR NORMAL SHAPE

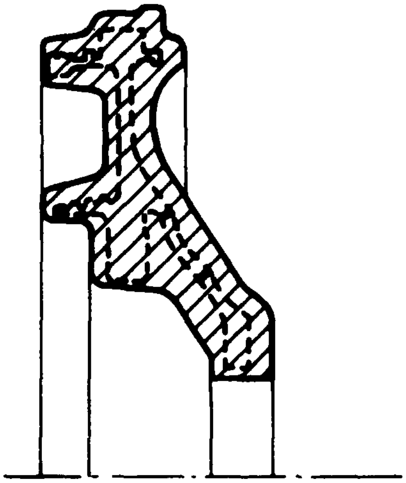


Fig. 4 FORGING CONTOUR NEAR-NET-SHAPE

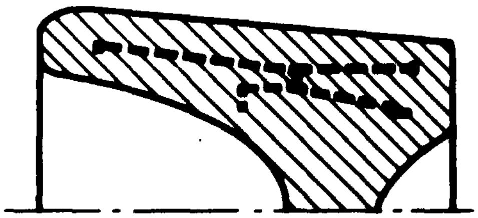


Fig. 5 FORGING CONTOUR

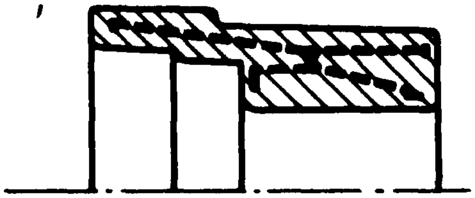


Fig. 6 PM CONTOUR

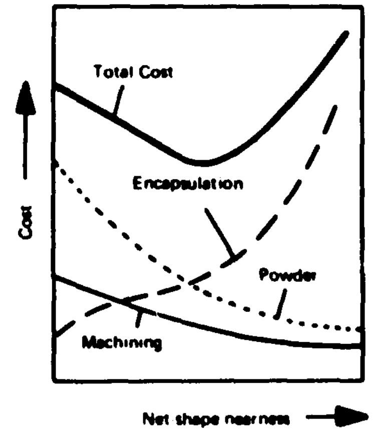


Fig. 7 ESTIMATED RELATIONSHIP BETWEEN COST AND NET-SHAPE NEARNESS

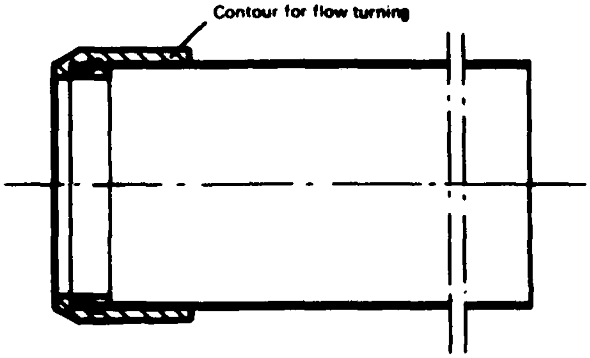


Fig. 8 COMPRESSOR SHAFT SLEEVE

8a SOLID FORGING FOR MACHINING

8b BAR SLICE FOR FLOW TURNING

8c FORGING FOR FLOW TURNING

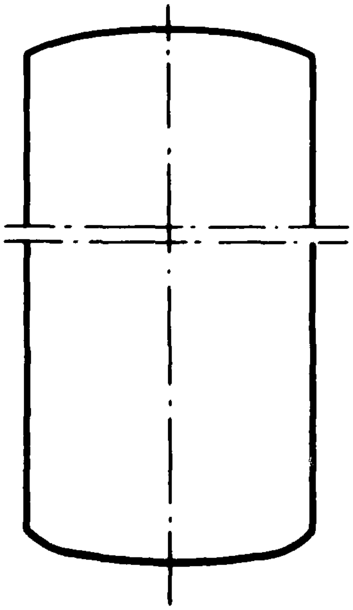


Fig. 8a

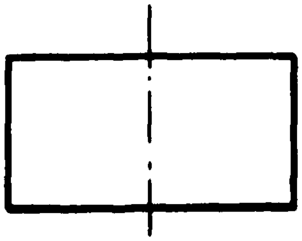


Fig. 8b

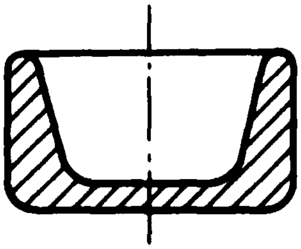


Fig. 8c

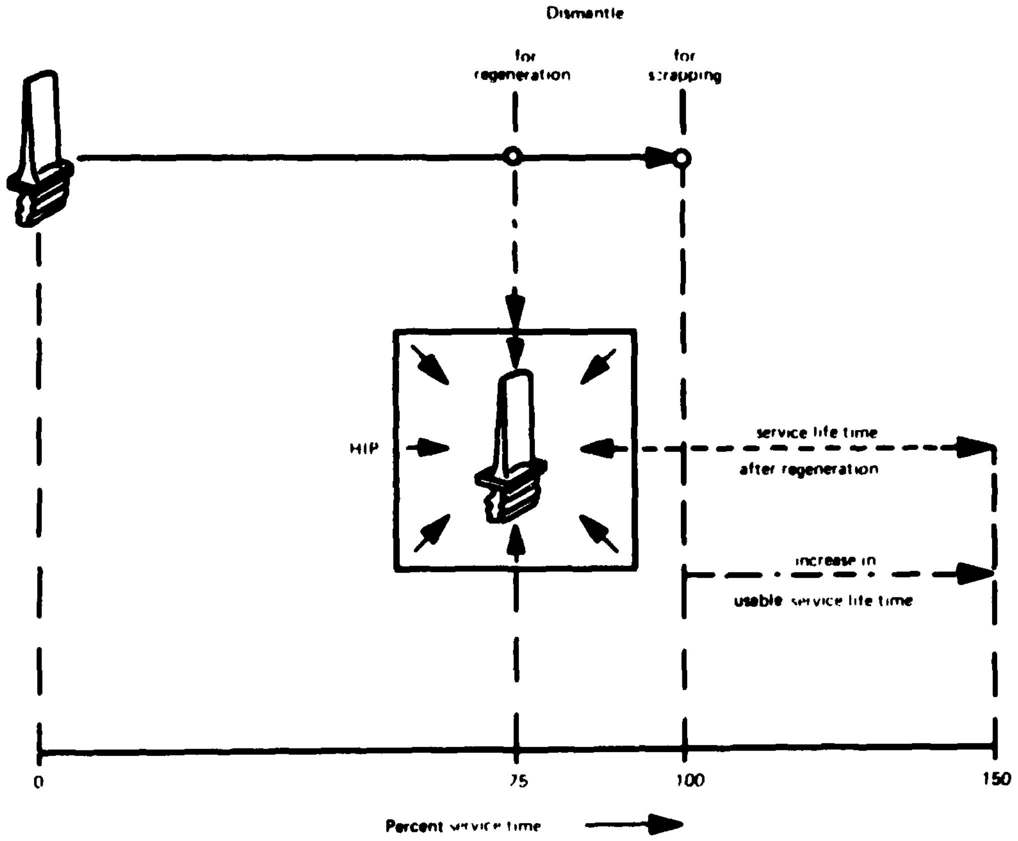


Fig. 9 SERVICE LIFE TIME OF TURBINE BLADES

AD-P004 214

TOWARDS A CYCLE WITHOUT LOSS: COBALT IN THE AIRCRAFT INDUSTRY

C. Voigt
Deutsche Forschungs- und Versuchsanstalt
für Luft- und Raumfahrt
Postfach 800320, D-7000 Stuttgart 80, Germany

SUMMARY

The flow cycle of cobalt in products used in the aircraft industry has been investigated. The manufacturing processes, uses and ultimate destinations of the materials containing cobalt (superalloys, ultra-high strength steels, tool steels and special alloys) have been quantitatively analyzed for the FRG. The ways in which cobalt is lost within the material cycle have been determined. Cobalt recovery rates for process scrap and obsolete scrap will be presented. It turns out that, ultimately, the dilution of cobalt in iron to a degree that it is of no value any more is the most important loss mechanism. A prime counter-action is improved scrap separation at all steps of the material cycle. The influence of no-scrap-technologies is discussed.

1. INTRODUCTION

The demand for primary metals produced from ore results from the demand for replacement of metals that have been lost and from the demand due to economic growth. Without loss and economic growth there would be no dependence on foreign ore production and the problems of strategic and critical elements would not exist. This demonstrates, in particular in a time of slow economic growth, the principal importance of a cycle with reduced or even zero loss.

There are, however, further advantages which make materials conservation desirable even if there were no problems of availability. First, every piece of material which is lost enters our natural environment, in many cases causing damage to nature. The health risk of lead lost in gasoline shows that one has to avoid material losses in order to preserve nature. Another consequence of materials loss leading to deterioration of the environment is the installation of new ore mines required for the production of material that replaces the loss. Second, the production of metals is in general less energy-consuming if one starts from scrap instead from ore [1], reuse instead of disposal of scrap contributes to the solution of the energy problem. Altogether, the reduction of material losses will be an important element in the development of our society.

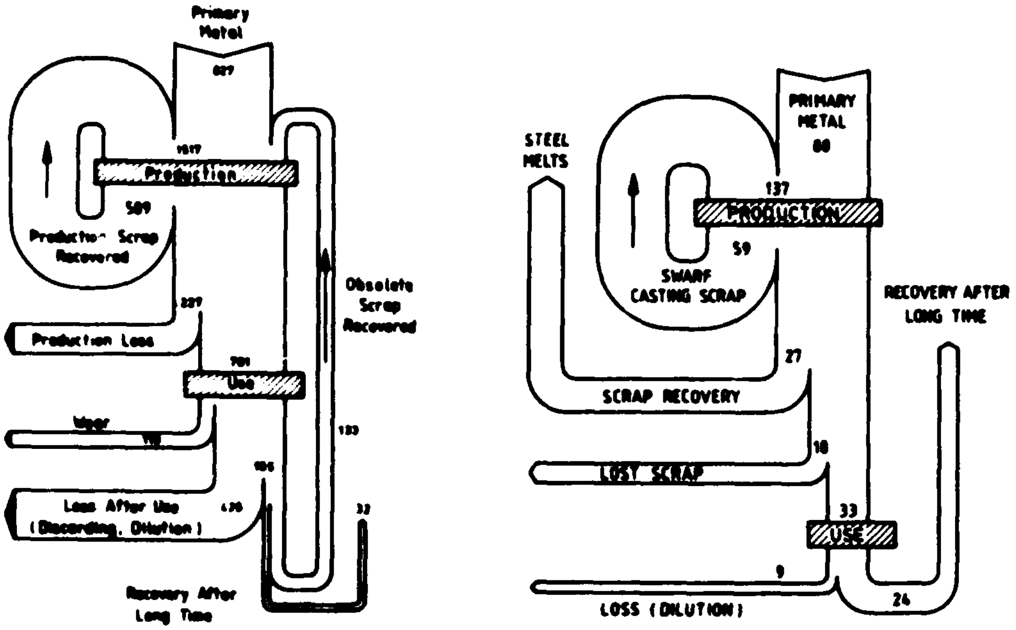
In this paper cobalt in metallurgical applications is taken as an example to investigate the ways in which a metal is lost in the material cycle and to propose measures how this can be avoided. Particular reference is made to cobalt used in the aircraft industry, i.e. for cobalt in high temperature materials, high-strength steel, hardmetal- and steel tools, magnets. The data which will be presented have been obtained from published statistics and informations from the cobalt consuming industry in the Federal Republic of Germany. Cobalt contained in imported semifinished products or alloys is not considered as being consumed in the FRG and is thus not included. Although the data refer to the FRG in 1981 it is believed that the conclusions are valid quite generally.

2. THE FLOW CYCLE OF COBALT

Fig. 1 shows the flow cycle of cobalt in metallurgical applications in the FRG in 1981. The production of finished products starts with the raw material which is composed of primary (granules, cathodes) and secondary metal (scrap). Scrap comprises scrap generated during production and scrap in the form of used parts and products (obsolete scrap). About one half of the raw material is converted to finished products. Three quarters of the cobalt contained in the production scrap is recovered, mostly as home scrap, i.e. scrap recycled without leaving the plant where it has been generated. One quarter of the production scrap is lost. As a rule, recovered scrap is used in the same area of application from which it originates. Exceptions exist for superalloy and stellite scrap which is used for steel melts.

Cobalt recovered from obsolete scrap amounts to 1/4 of all cobalt contained in finished products. The recycling rate is very high (50-75 %) for steel tools and superalloys, is lower for high-strength steel and hardmetals (10-30 %) and is zero for all the other groups. Most of the cobalt recovered is returned to the production cycle within one year, as an exception cobalt in superalloys and high-strength steel is recycled many years after the products have been put into service.

Fig. 2 shows the flow cycle of cobalt in high temperature materials (superalloys and high temperature steel).



FLOW CYCLE OF COBALT

Federal Republic of Germany 1981

Flow rates in t / a

Fig. 1. Metallurgical uses, total

Fig. 2. High temperature materials

3. COBALT USES

According to the amount of cobalt contained in finished products the cobalt containing materials can be divided into three groups of approximately equal size (Fig. 3).

Magnetic Material

Cobalt containing magnetic materials are essentially permanent magnets with Alnico-magnets (28 % Co) being the most important group. Magnets are produced with a high percentage of primary cobalt (80 %, Fig. 4), the amount consumed is somewhat less than one third of all primary cobalt.

Steels

High speed steel, hot work tool steel and high-strength steel are the biggest cobalt consumers, the cobalt content lies between 5 and 12 %. About one quarter of all primary cobalt is used for steels, the percentage (33 %) of primary cobalt at the raw material is much smaller than for magnets since large amounts of secondary raw materials are used. From all groups steels consume the by far largest fraction of purchased scrap and are therefore of great importance for the recovery of cobalt. Steels are the only group that uses scrap generated in other application areas.

Alloys

This group comprises alloys which are mostly iron-free and can contain up to 75 % cobalt and in addition nickel, chromium, tungsten and molybdenum as essential elements. Wear resisting alloys (stellites), superalloys, high-temperature steels and hardmetals are the biggest consumers of primary cobalt. Somewhat less than 50 % of all primary cobalt is required for the production, the percentage of primary cobalt in the raw material is in the average 66 %.

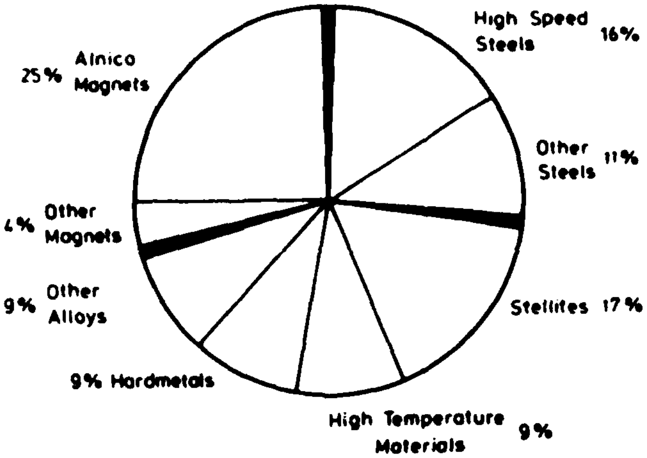


Fig. 3. Consumption of primary cobalt
Federal Republic of Germany 1981
100 % = 827 t/a

4. LOSS OF COBALT DURING PRODUCTION

During production, i.e. the conversion of raw materials to finished products, 227 t of Co are lost (one quarter of all cobalt imported). There are two main loss mechanisms with about equal magnitude. The first group comprises losses which are due to the

Mixing and Contamination of Solid Production Scrap.

A typical example is scrap in the form of turnings and chips generated when superalloy parts are machined. A direct reuse as a constituent of a superalloy melt requires an absolutely clean scrap handling due to the stringent specifications of superalloys. Any mixing with other scrap and any contamination with other metals has to be avoided. These requirements are difficult to achieve, as a consequence most of this scrap can only

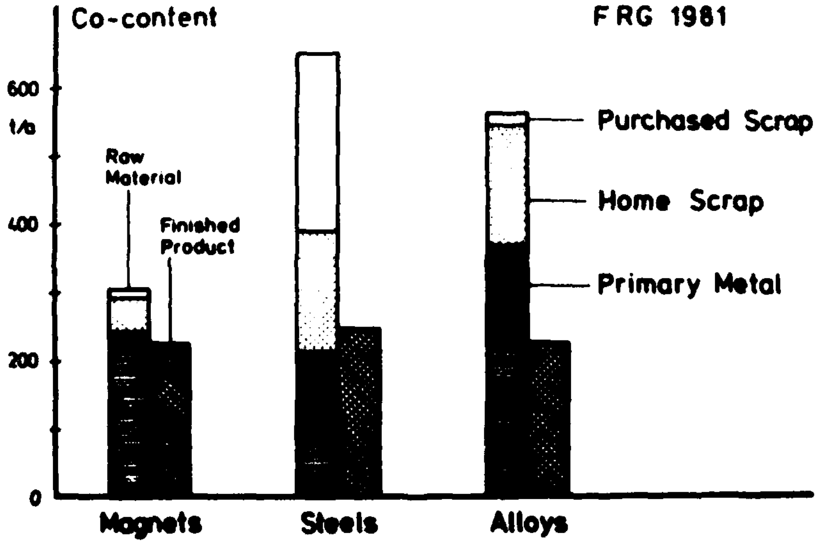


Fig. 4. Origin and amount of cobalt in the raw material and in finished products. Federal Republic of Germany 1981.

be used for the production of less valuable, less complex alloys or steels, i.e. the scrap is downgraded. However, even if scrap is handled as desired, present regulations for aircraft engine manufacture in Germany do not allow utilization of this material. A revision of these regulations towards a limited reuse of clean scrap in aircraft applications is in progress.

Although downgrading by itself does not mean that material is lost, loss of cobalt occurs, because it is very often an unwanted element in the melt charge in which it shall be used. By adding nickel or iron, cobalt is in such cases intentionally diluted to an extent that it is of no value anymore. Cobalt is a relatively ineffective alloying element in steels, compared for instance to nickel (the resp. consumptions in the FRG are 300 and 40 000 t/a), so the pressure to dilute cobalt is appreciable. The exact amount of Co lost through downgrading of superalloy production scrap is not known, it could be as high as 15 % of all primary cobalt needed for superalloy melts.

A similar situation exists in the steel industry. Mixed steel scrap with a cobalt content of only 3 % is generated in sizable amounts in the tool industry. A large fraction (~ 90 t/a) of this cobalt is lost by intentional dilution in iron.

Although it might be possible to improve the techniques for scrap cleaning and for sorting of mixed scrap into different fractions it appears to be much better to avoid mixing and contamination of scrap in the first place. A possibility would be to design machine tools with automatic separation of scrap according to composition. At some places production scrap is collected and classified by hand, this method is however expensive and does in the case of superalloys not always result in a high enough scrap quality. Consultations are underway in the FRG how an automatic scrap separation could be realized.

Lost Scrap

Whereas improvements in the recycling of cobalt contained in solid scrap appear to be technically and also economically feasible, it will be more difficult to reduce the other cobalt losses occuring during production. This group is called "Lost Scrap"*, typical examples are:

- Scale, dust and sludge collected without any classification so that cobalt is lost by intentional or unintentional dilution. As an example, all cobalt is lost which is contained in grinding and sawing dust generated in the process of investment casting of superalloys.
- Heavily contaminated production scrap which cannot be used anymore and which is therefore disposed of.
- Material lost in recycling processes.

Lost scrap is difficult to avoid. It is of particular disadvantage that it is often generated in small amounts so that one is easily inclined to pay not attention to it. The main burden to reduce these losses will rest on operating and organizing measures. It will be necessary to further integrate production steps and to change production processes in such a way that the scrap generated can easily be used again.

No-scrap-technologies

In principal, the most simple way to reduce losses of cobalt contained in production scrap is to generate little or no scrap at all. Well known no-scrap-techniques are powder metallurgy, continuous casting, forging and, as a special example, twist rolling of drills instead of machining.

Processes characterized by the removal of material start with an oversized metal piece which is worked to exact dimensions. The reverse procedure should in principal also be possible: To start with an undersized piece and to reach the desired dimensions by adding material thus avoiding the generation of scrap: deposition instead of removal.

Physical and chemical vapor deposition (PVD, CVD) and plasma-spraying are today successfully used for the manufacture of thin coatings. It should be rewarding to develop these processes towards the deposition of thick layers. Using plasma-spraying, tungsten layers of cm thickness have already been made.

Scrap is not generated if a product is made by applying a synthetic procedure, by putting parts together. Powder metallurgy, vapor deposition and also the manufacture of compound structures layer by layer are synthetic processes. Processes of this kind will be of great importance if a closed cycle technology shall be established.

---

* The terms used in this paper are similar, but not always identical to those defined in [2,3].

5. LOSS OF COBALT DURING SERVICE AND AFTER USE

Wear

The example of wear demonstrates that in practice it will not be possible to establish an ideally lossless material cyle. For this reason one has to avoid wear processes whereever possible. About one half of all cobalt wear losses occur for high speed steel and hard metal tools, mostly in machining processes. No-scrap-technologies making the use of drills and mills unnecessary would be very beneficial. If friction cannot be avoided wear parts should be built from materials with practically unlimited supply: Mg, Fe, Al, Ti, Si, C, N, O, H. These elements are not only plentiful, they are also not toxic [4], this too makes an increased use desirable. About 13 % of all primary cobalt imported is needed to replace cobalt lost through wear.

Mixing of cobalt-containing and cobalt-free obsolete scrap

The by far largest cobalt losses occur when cobalt containing used products are collected together with steel scrap leading to loss through dilution or when used products are disposed of as refuse. About 50 % of all imported primary cobalt is lost this way (Fig. 5).

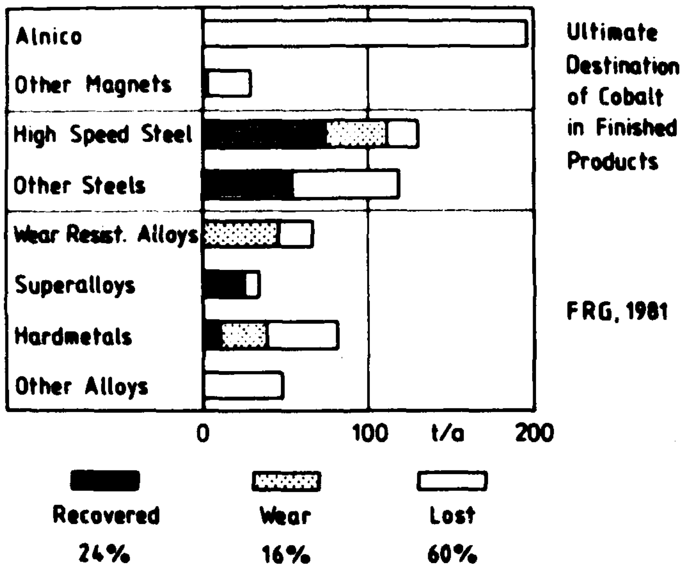


Fig. 5. Ultimate destination of cobalt in finished products
Federal Republic of Germany 1981

As an example cobalt in high-strength steels is considered which are used for instance for the manufacture of aircraft landing gear. After use these products are collected together with other alloy steel scrap. It can be assumed that due to the in general low effectiveness of cobalt in steels part of the cobalt is lost trough dilution in iron when the scrap is remelted. This problem is enhanced by the lack of a suitable recycling code on steel products which would facilitate the separation of obsolete scrap according to composition.

Obsolete hot work tool scrap (e.g. in superplastic forming tools) is classified according to the content of Cr, W, Mo, V and Ni, but not of Co, also in this case loss through dilution could be reduced with the aid of a suitable recycling code.

The end use area with the largest cobalt loss is that of magnetic materials. Magnets are nearly always part of a larger product, cannot be recovered separately because of the tight connection to this product and are therefore recycled together with large amounts of steel scrap. Practically all cobalt contained in magnets (25 % of all imported primary cobalt) is lost through dilution in iron, this includes all magnets in electronic aircraft equipment which have a cobalt content of up to 50 %.

The most important measure to reduce this loss is to design products differently as it is done now: design for eventual recycling. Products should be designed in such a way that after use they can be disassembled economically so that the parts obtained can be brought back in the production cycle with full use of all elements. It will be important to invent joining techniques allowing easy separation. Metal parts which cannot be separated because otherwise the product would not fulfill its function should have a composition that the remelted alloy can be used again (no copper in steel).

In the aircraft industry the possibility to recover cobalt from used products is much better than in most other end use areas. The reason is that most of the cobalt is contained in those parts of a jet engine which can easily be disassembled, i.e. design for recycling is already realized. Modular design, introduced to facilitate maintenance and repair, has been beneficial in achieving a high cobalt recovery rate.

Although standards of classifying and cleaning used engine parts are high, in the FRG remelted used superalloys are not allowed to be used again for the manufacture of jet engine parts. The main obstacle is to secure that remelted alloys are free of impurities which can be introduced for instance through coating materials or parts oxidized during service. Obsolete superalloy scrap is therefore downgraded whereby cobalt is lost through dilution if it is an unwanted element. The situation is nevertheless considerably better than in other end use areas, e.g. automotive applications, where present recycling methods lead to a complete loss of cobalt and other alloying elements such as nickel, tungsten or chromium.

The amount of cobalt needed in the aircraft industry in other than superalloy parts (magnets, tools, high-strength steels) is small. Since, however, the recovery rates are often not as high as for superalloys, cobalt losses cannot be neglected. It will be necessary to introduce design for recycling also in these areas.

6. CONCLUSIONS

Cobalt is lost in various ways and in all application areas, correspondingly a variety of counteracting measures will have to be applied. Nevertheless, two losses can be identified which are of particular importance because of their magnitude: The cobalt loss in used magnets and the loss through dilution in steel production scrap. Strong efforts to increase cobalt recycling in these fields is recommended. Improvements should be particularly easy in the case of steel scrap, whereas reclaiming cobalt from magnets will take a longer time to achieve.

In the aircraft industry cobalt is lost not only in those materials considered typical for this industry, i.e. high strength steels and superalloys. Cobalt contained in tools and magnets is also lost. It will be necessary to reduce losses in all these areas, and this will occur only in small steps. These efforts will not only be beneficial for cobalt, they will result in the saving of other alloying elements as well.

Looking at the loss mechanisms in a fundamental way one recognizes that most of the cobalt is lost because it is diluted in other materials such as iron or nickel. This applies to scrap generated during production as well as to obsolete scrap. Simple discarding (throw away) is, contrary to common belief, only rarely the cause of cobalt losses. Knowing the reason for cobalt losses one can specify the measures how they can be avoided.

Not to generate scrap is the most basic, principally most effective measure against loss.

For the production this means the development of no-scrap-technologies, in particular the invention of additive processes for the manufacture of products (deposition instead of removal). Growth, the process applied by Nature, can be looked at as a model, it is an ideal no-scrap-technology. It appears that the aircraft industry presents a large field for the application of no-scrap-technologies.

In the case of obsolete scrap the amounts of scrap generated can be reduced by

- Long product life (coating, corrosion resistant materials)
- Repair instead of replacement
- Design for material saving

Because of the direct economic advantages which can be obtained with these measures efforts in these fields are actively persued in the aircraft industry.

If scrap cannot be avoided, the next step is to avoid mixing of different scrap materials in order to minimize the possibility of loss through dilution. Scrap sorting is necessary at all steps of the material cycle. It could very likely most easily be achieved in the case of solid production scrap, one main reason that this is not always done is that people are unaware of the financial gain obtained through scrap sorting. Admittedly, the gain is small when primary raw materials are cheap as it is the case right now.

Collecting uncontaminated, unmixed obsolete scrap is more difficult. The most effective measure, design for recycling, is practiced today only on a small scale. A complete change or even reversal in design principles towards an attitude of thinking beyond the point where a product is sold will be necessary and will certainly be unavoidable in the long run.

In the aircraft industry downgrading of superalloy scrap can lead to loss of cobalt through dilution. In Germany downgrading will be reduced when new regulations for reuse of scrap will be introduced in the near future.

The last step to avoid cobalt losses comprises the recovery of cobalt from mixed and contaminated scrap by metallurgical or other methods and the refining of scrap which could otherwise not be used and would have to be dumped. Many recycling activities are presently concentrated in this field. These efforts together with those for scrap avoidance and scrap sorting, can contribute significantly to ease supply problems of strategic elements.

7. REFERENCES

1. C.L. Kusik and C.B. Kenahan, A.D. Little Inc., "Energy use patterns for metal recycling", 1978, NTIS-PB 284855.
2. LeRoy R. Curwick, W.A. Petersen and H.V. Makar, Inco Research & Development Center, Suffern, N.Y., "Availability of critical scrap metals containing chromium in the United States", 1980, United States Bureau of Mines Information Circulars 8821 and 8822.
3. J.J. DeBarbadillo, J.K. Pargeter and H.V. Makar, "Process for Recovering chromium and other metals from superalloy scrap", 1981, United States Bureau of Mines Report of Investigations 8570.
4. J.M. Wood, "Biological cycles for toxic elements" Science 183 (1974) 1049.

GAS TURBINE ENGINE DESIGN CONSIDERATIONS AS RELATED TO ALLOYS OF HIGH CRITICAL ELEMENT CONTENT

Robert A. Sprague
Manager, Engineering Materials Technology Laboratories
General Electric Company
1 Neumann Way, Mail Drop M82
PO Box 156301
Cincinnati, Ohio 45215-6301

AD-P004 215

The primary payoff in selection of wrought/cast alloys containing strategic elements is performance, not cost. For example, in commercial engines, the temperatures that parts are exposed to have increased steadily in an effort to improve specific fuel consumption. In military engines, higher operating temperatures are usually governed by efforts to improve thrust to weight ratio.

This paper will review the trade-offs that a designer must make in the selection of materials for specific component applications. Emphasis will be placed on discussion of what options are available in reducing the strategic material content of the engine system while still achieving performance and cost objectives.

Introduction

The primary payoff in selection of wrought/cast alloys for gas turbine engines is performance. In commercial engines the temperatures that parts experience have increased steadily in an effort to improve specific fuel consumption. In military engines (fighters) higher operating temperatures are also seen in the effort to improve thrust-to-weight ratios. The critical (1) strategic elements, cobalt, tantalum, columbium and chromium, are utilized in the hot section superalloys of these engines. These superalloys are used in the forged, cast and sheet forms. Highly loaded components such as turbine disks are typical of forged applications while cast applications are characterized by turbine airfoils such as rotor blades and stator vanes. While subject to lower steady state loadings than disks, the airfoils are subjected to higher thermal and vibratory loads as well as a more erosive and corrosive environment. The significant increase in temperature/strength capability of GE's turbine blade alloys is illustrated in Figure 1. Exhaust nozzle and combustor (rolled sheet metal) components are subject primarily to thermal, hoop and vibratory loads.

Considerations Involved

Apart from the foremost consideration of flight safety, there are many factors relating to design selection for gas turbine engines. Obviously, these considerations vary with the criticality of the component being designed. The acceptability of a materials change is therefore strongly dependent upon component loading environment, criticality and by the extent of the change. That is, if it is a change from a cast to a wrought alloy the change, while probably more costly, may be readily acceptable because of the higher reliability of wrought material in certain applications. However, a change from a wrought alloy to a cast alloy may imply lower design capability and therefore be more difficult to justify and verify. In general, the desirability of change is governed by the payoff. The payoff must be an initial cost benefit to the system, resulting in a mission life benefit directly applicable to reducing system ownership cost, or a sought after systems performance improvement. In any case, the state of technology is such that reasonably accurate cost estimates of the proposed changes effecting initial costs, ownership cost or performance payoffs are determinable to both manufacturers and users of gas turbine engines.

Beyond the cost benefit, the chances of developmental program success must be considered. In general, it is true that high cost benefit is obtained only through taking commensurate risks. It would be desirable if a large benefit could be realized with small risks. However, the near full maturity state-of-the-art gas turbine engine technology makes this opportunity rare. As opposed to cost benefit, the chance of developmental success is a more difficult criteria to assess. It must be remembered that technology advocates may not always fully understand the total criteria for application success associated with their advocacy. Therefore, it is mandatory that design engineers as well as materials and program managers, understand the cost benefit and more importantly the overall developmental risk analysis. Once positive agreement is reached, a material of high systems payoff will be developed and applied regardless of secondary factors such as development risk and strategic element content.

1)"A status review of NASA's COSAM (Conservation of Strategic Aerospace Materials) Program" - J.R. Stephens, Lewis Research Center, Cleveland, Ohio: NASA Tech.Memo 82852.

In gas turbine engines, very high durability is required for critical rotating components such as trubine disks. Durability is also a major factor for less critical parts such as turbine airfoils, although operating cost may be the reason for change. Similarly, the reliability of components such as combustors is a major consideration in terms of their durability and impact upon operating and maintenance costs. It should be noted that in many cases engine durability specifications and/or warranties drive engine producers toward using alloys of high strategic materials content. These requirements properly address the ownership cost issue and more than offset initial manufacturing cost concerns due to higher raw material cost.

The third consideration is that of component weight and size. Component weight in gas turbine engines is a major design consideration since a reduction in weight results in reduced fuel consumption. It should be remembered that in gas turbine engines, weight itself is compounded by the weight of the structure required to mount the engine and the structural carry-through members needed to transmit these mount loads to the main aircraft structural system.

Typical examples of engine weight reduction achieved without effecting engine diameter or length are the substitution of composites for metals in engine front frames, ducts and other areas where the low temperature composite materials now routinely available to engine designers is applicable to reliable flight safety systems. Other areas where engine weight has been reduced without dramatic changes in size is the application of titanium alloys to engine compressor sections. The high strength to weight ratio of titanium alloys has resulted in significant weight changes in many of today's commercial and military engines. From a design standpoint it should be noted that the high strength of titanium, together with its other balanced set of materials properties, was instrumental in making the large bypass ratio fan engine a reality.

Considering powerplant size, the case for weight reduction through size reduction at a constant thrust rating is often considered because this approach has a very large impact on overall systems weight reduction. When applying materials of increased specific strength to rotating components such as turbine disks and blades, the systems weight is dramatically reduced because rotor rim loads are reduced and allowable tip speeds are increased which then allows the diameter of the engine to be decreased without loss of performance. This is particularly true when such alloys can be applied throughout the rotating components or at least through major sections of the engine such as the high pressure compressor or high pressure turbine rotors. Therefore, the effect on engine weight reduction is magnified most through the application of high strength materials in rotating engine components. These high strength materials also permit more work per stage through increased wheel speeds with fewer stages for the same overall pressure ratio, resulting therefore in a shorter and lighter weight engine. The drive toward the use of composite materials in engines and perhaps, more importantly toward the use of high strength materials such as thermomechanically worked turbine disk alloys, becomes obvious when considering the escalating cost of fuel and the much needed objective to reduce fuel burn in both military and commercial systems.

A fourth area for consideration, although not necessarily directly related to design aspects, is that of reducing raw material input weight and of reclaiming expensive alloys containing the critical elements. (The present and proposed high strength wrought and cast alloys contain significant quantities of chromium and one or more of the other three critical strategic elements: cobalt, columbium and tantalum). Reducing raw material input weight is a key method to reduce cost and simultaneously conserve these strategic elements. An example of this is shown in Figure 2 where hot die forging of an Inconel 718 disk will reduce the quantity of billet required by as much as 70%. Two strategic elements, chromium and columbium, are therefore conserved. Reclaiming expensive alloys, i.e., the superalloys (particularly those containing the strategic elements) and titanium alloys, has become a major initiative of engine producers. Recycling these alloys into similar products is important, because when superalloy scrap is sold for non-aerospace revert purposes, its value is considerably reduced compared to its intrinsic value (which can be more easily realized by recycling the alloy scrap into the same or similar alloy). There have been many programs designed to more efficiently recycle gas turbine engine alloys and to maintain these alloys within the aerospace industry by recycling scrap into products similar to those from which the alloy scrap originated. In the case of alloys containing the strategic elements, it is not only imperative to reduce costs by recycling these alloys, it is also very important that they be recycled back to an aerospace product and not lost to their most critical national application.

Another major area of consideration is that of design criteria. The design criteria for gas turbine engine components varies considerably from component to component. Obviously, the design criteria for a cold section composite duct in the fan area of a large, high bypass ratio engine are considerably different from that of a cast turbine blade in the high pressure turbine section. The design criteria applicable only to metallic structures, and more specifically metallic structures which typically contain the strategic elements, will be considered in this report. The principle structures containing the critical strategic elements in gas turbine engines are turbine disks and airfoils. Additional uses of the four strategic elements in components such as combustors, certain case alloys and shafting, while important, utilize less of the strategic elements in volume consumed than high pressure turbine disks and airfoils.

Due to the flight safety criticality and, to a lesser degree, the extent of possible secondary damage caused by failure, much time and effort has been placed upon an improved understanding of turbine disk design criteria. Turbine disks are subjected to a wide spectrum of mechanically and thermally induced stresses during any given mission. The cumulative effect of these missions is to produce component degradation by several possible mechanisms, e.g., yield growth, creep growth, fatigue and environmental degradation. Further, the manufacturing process itself can have a major effect upon part life. To determine disk life, or more importantly, minimum disk life to a degraded but unfailed state, a complex set of interacting variables including design configuration, mission profiles, manufacturing sequence as well as alloy properties must, therefore, be properly assessed. While it is unlikely that an improper analysis can result in a flight safety problem, a conservative design, however, can result in decreased engine performance relative to actual system capability.

An understanding of the above criteria suggests the obvious...when an alloy and manufacturing process has been selected...only a major systems benefit provides sufficient incentive for change.

The disk alloy/process development cycle is shown schematically in Figure 3. There are three important things to note: 1) the process takes several years, 2) it is very expensive and, 2) the alloy development costs represent only a small fraction of this total cost

Figure 4 shows turbine disk raw materials cost relative to total cost. The major point here is that raw material cost per se is a small fraction of the component cost.

The overall conclusion is obvious...a major change in elemental material cost will not drive the designer toward alternate materials selection unless the designer has an established parallel alloy/process which he can readily adapt...generally an unlikely event. It should be noted, however, that the cobalt cost escalation of 1978 did produce this exact reaction, primarily because of the threatened unavailability of cobalt; readily adaptable alloy changes (i.e., 13.5% cobalt Waspaloy to 0% cobalt Inconel 718) were made by some engine producers.

What forces the designers to risk a new alloy system? The need for new disk alloys is established by mission requirements of performance or weight not achievable with any available material. To develop needed properties, metallurgists will first consider process alteration of current alloys. If this is found by an early judgment evaluation of limited effort to be impractical, the metallurgist will then turn to alloy development. The development process is directed toward achieving the goals on a schedule consistent with the product implementation needs with the lowest possible impact on resultant component cost. It should be emphasized that the alloy development and reduction to a practice time frame can be significantly reduced (up to 50%) in cases where an urgency such as competitive need is forecast.

Turbine Airfoils

While not as critical as disks from a flight safety viewpoint, the reliability of turbine airfoils is strongly related to operational cost as turbine airfoil failure can result in rather extensive secondary damage with resultant high engine removal and overhaul cost.

The design criteria for turbine airfoils necessitates a balance of environmental resistance and mechanical properties. Chromium, cobalt and tantalum, strategic elements utilized in turbine airfoil alloys, are important in achieving this balance. Reduction of the cobalt content of airfoil (and disk) alloys has been the goal of recent studies; the results to date indicate that the present cobalt content (usually 10-18%) could be reduced, but not eliminated. This reduction though, would require extensive laboratory evaluation and costly engine verification testing. The designer is not sufficiently motivated to consider this reduction without an offsetting technology benefit. Figure 5 depicts a typical turbine airfoil development plan and cost. Reducing cobalt content from 15% to 5% in a one-pound airfoil by substituting nickel would save .1 pounds of cobalt per airfoil. At a cost differential of $20 per pound, a cost savings of about $2 per airfoil would then be realized...little incentive for risk implementation or a large scale development effort in face of the component unknowns of coating compatibility, thermal fatigue life, etc. Therefore, again as in the disk case, the designer would be motivated for change only when a significant and marketable (needed) mission benefit can be achieved. This trend is evident when one realizes that the most recent changes in turbine airfoil technology are driven by alloy/process innovations such as directional solidification of tailored turbine airfoil alloys. In this case, a significant and desired technological benefit is gained. The introduction of directionally solidified airfoils has essentially eliminated the development/modification of equiaxed turbine airfoil alloys even though there has been concern for the critical element content of the widely used equiaxed alloys.

Conclusions

1. Current superalloys require two or more of the strategic elements, chromium, cobalt tantalum and columbium, and will continue to do so in the foreseeable future.

2. Readily adaptable superalloy system changes to conserve cobalt have already been adopted during 1978-80.

3. Results from research-in-progress indicate that a significant amount of cobalt in superalloys can be substituted for by non-strategic elements. Exploitation of these results require costly and time consuming alloy optimization and engine verification programs funded by both industry and government. These programs will begin only when they are warranted by sufficient economic incentive and by a high level of supply insecurity such as the sharp price rises and perceived supply problems that occurred in 1978.

4. The development of advanced high performance alloy systems can and should be directed toward strategic element conservation without jeopardizing the risk of application success.

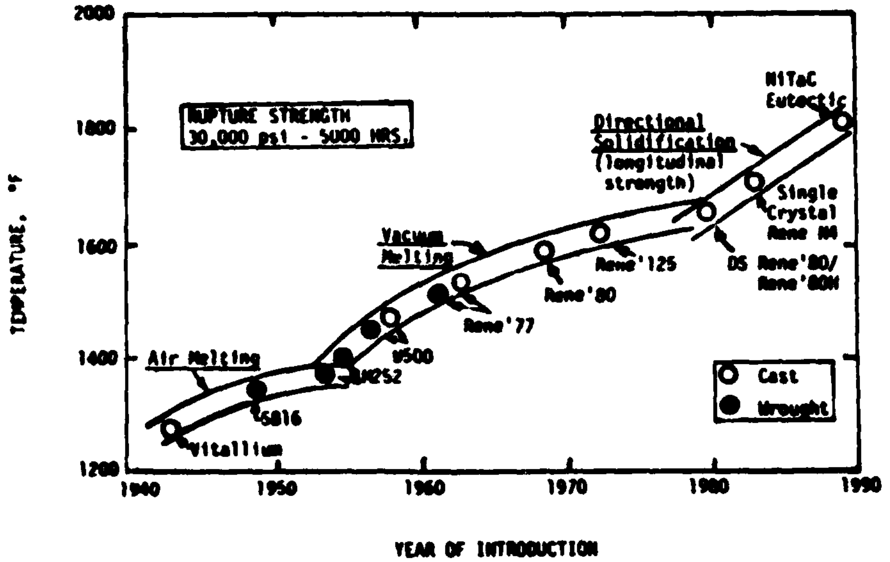


Figure 1. PROGRESS IN GENERAL ELECTRIC'S TURBINE BLADE ALLOYS

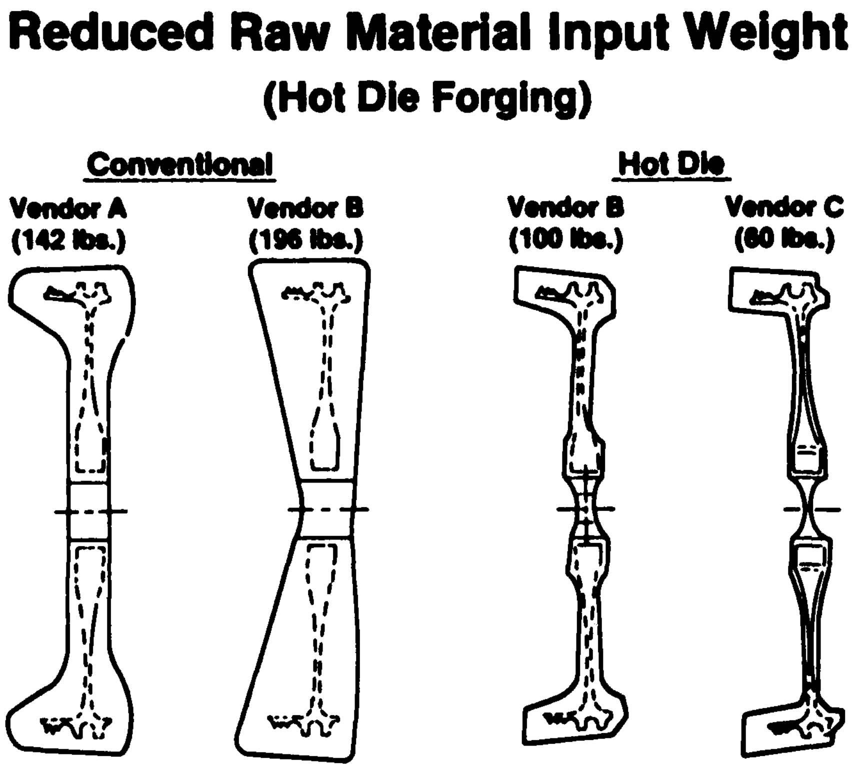


Figure 2.

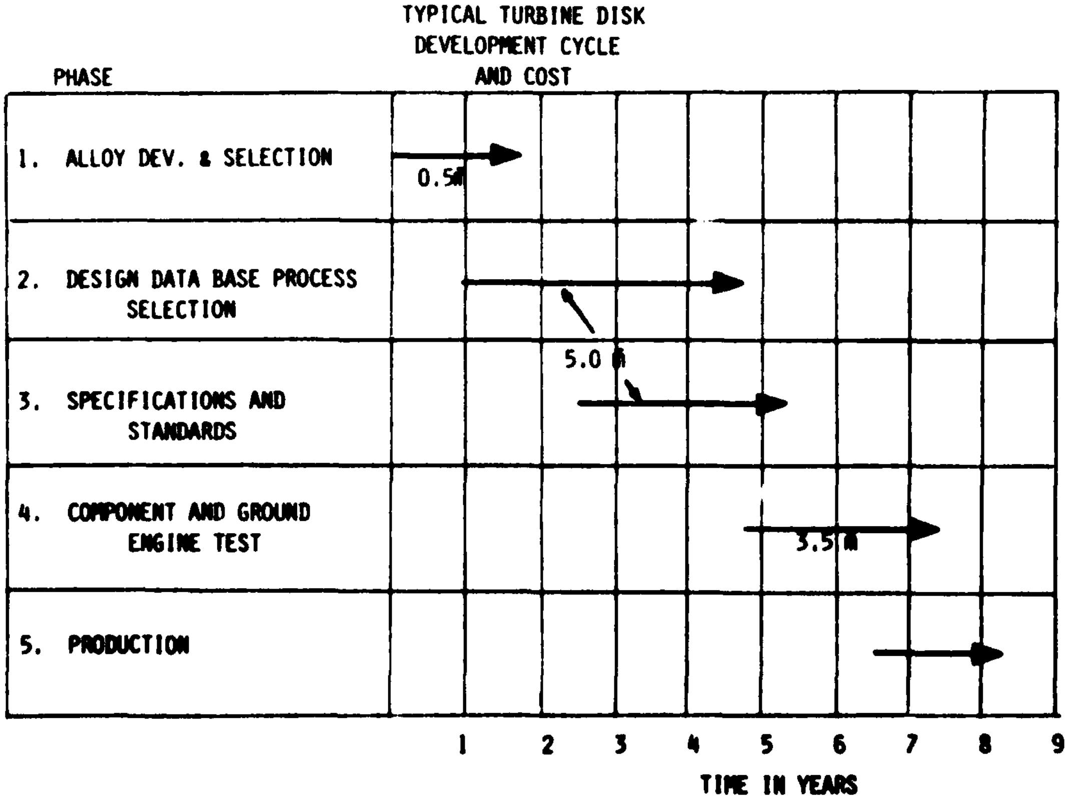


FIGURE 3.

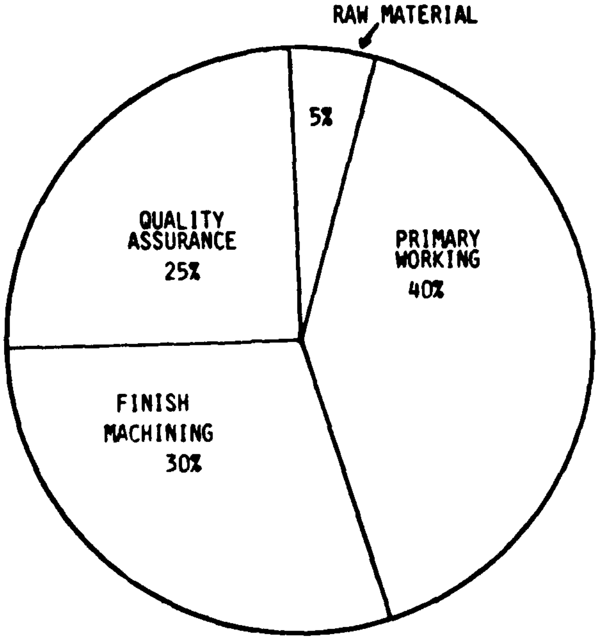


Figure 4. TYPICAL SUPERALLOY TURBINE DISK COST DRIVERS

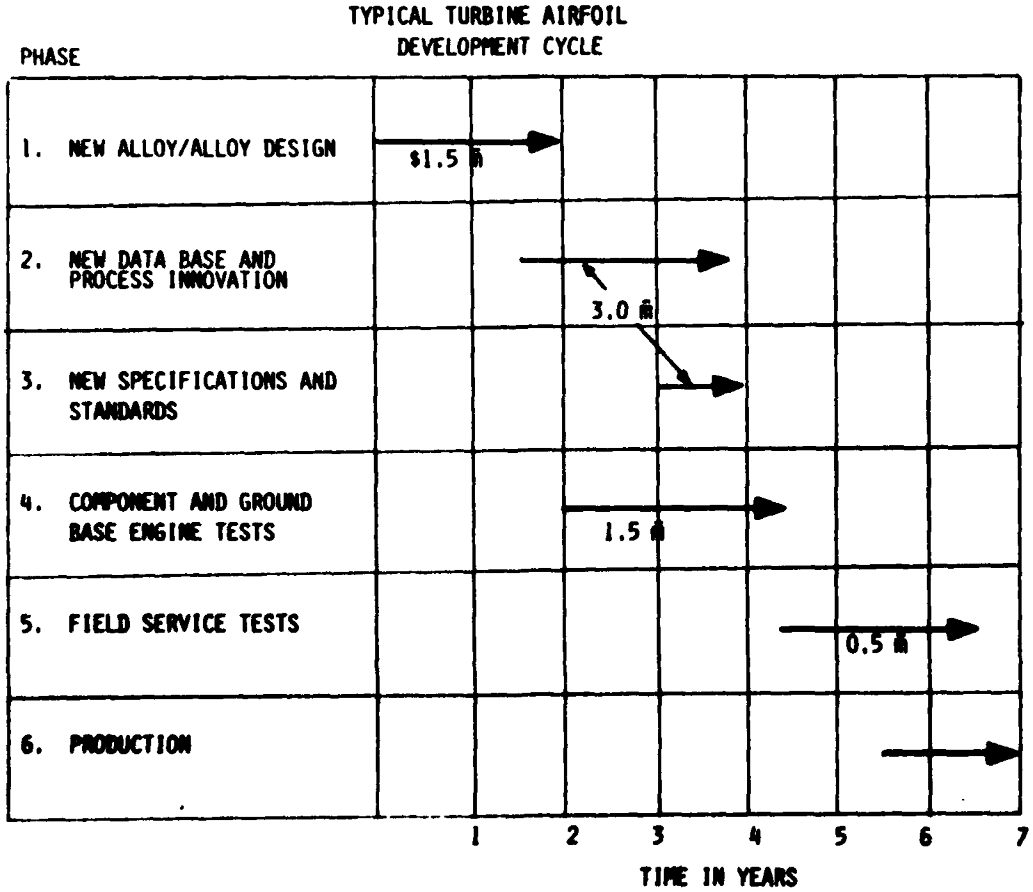


FIGURE 5.

UNDERSTANDING THE ROLES OF THE STRATEGIC ELEMENT COBALT IN NICKEL BASE SUPERALLOYS

Joseph R. Stephens and Robert L. Dreshfield
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

The United States imports over 90 percent of its cobalt, chromium, tantalum and columbium -- all key elements in high temperature nickel-base superalloys for aircraft gas turbine disks and airfoils. NASA, through joint government/industry/university teams, has undertaken a long-range research program (COSAM - Conservation of Strategic Aerospace Materials) aimed at reducing or eliminating these strategic elements by examining their basic roles in superalloys and identifying viable substitutes. This paper discusses research progress in understanding the effects of cobalt and some possible substitutes on microstructure, mechanical properties, and environmental resistance of turbine alloys.

INTRODUCTION

The United States is highly dependent on foreign sources for many materials required for its economic health. In the aerospace industry the four metals, cobalt, chromium, tantalum, and columbium have been identified as strategic materials. The United States imports in excess of 90 percent of each of these metals, and one country controls a major portion of the U.S. supply (ref. 1) for each metal. The National Materials and Minerals Policy, Research, and Development Act of 1980 (ref. 2) has helped to focus attention on this critical problem that faces not only the aerospace industry, but most other industries as well. Government agencies are responding to this Act by conducting research, holding public workshops and conferences, and coordinating efforts through various committees.

NASA Lewis Research Center has undertaken a long-range program in support of the aerospace industry aimed at reducing the need for strategic materials used in gas turbine engines (refs. 3 to 5). The program is called "COSAM - Conservation Of Strategic Aerospace Materials." This program has three general objectives; they are

(1) To contribute basic scientific understanding to the turbine engine "technology bank" so as to maintain our national security in possible times of constriction or interruption of our strategic material supply lines.

(2) To help reduce the dependence of United States military and civilian gas turbine engines on disruptive worldwide supply/price fluctuations in regard to strategic materials.

(3) To help minimize the acquisition costs as well as optimize performance of such engines so as to contribute to the United States position of preeminence in world gas turbine engine markets.

To achieve these objectives, the COSAM program is developing the basic understanding of the roles of strategic elements in today's nickel-base superalloys and will provide the technology base upon which their use in future aircraft engine alloys/components can be decreased. Technological thrusts in three major areas are underway to meet these objectives. These thrusts are strategic element substitution, advanced processing concepts, and alternate material identification. Based on criticality of need, initial efforts are concentrated on the strategic elements cobalt (97 percent imported), chromium (91 percent imported), tantalum (91 percent imported), and columbium (100 percent imported). This paper will focus on the major thrust of strategic element substitution and specifically on the roles of cobalt in commercial, nickel-base superalloys.

The strategic nature of cobalt in the U.S. arises not only because of the high import dependence, but also because of the location of the major sources, Zaire and Zambia in southern Africa, as illustrated in figure 1. The stability of the governments in these two countries is of major concern (ref. 6), and it was the invasion of Zaire in 1978 that led to the dramatic price increase and shortage of cobalt in the U.S. in 1978 through 1980. As a result of the price/supply situation for cobalt in 1978 through 1980, the United States has experienced a decline in cobalt usage (ref. 7). Figure 2 shows that 20 million pounds of cobalt were consumed in 1978, but by 1982 usage was down to an estimated 10.4 million pounds, a reduction of nearly 50 percent during the 4-year period. It should be pointed out that the stunted U.S. economy in 1981 and 1982 has undoubtedly contributed to this decline in cobalt usage. During this same period, the use of cobalt to produce superalloys, primarily nickel-base alloys for aircraft engines, increased from 4 million pounds in 1978 to a peak of 7.2 million pounds in 1980 before it declined to an estimated 3.8 million pounds in 1982. The decline in U.S. aerospace consumption of cobalt may be attributed in part to the economy, but concerted actions by the gas turbine engine manufacturers to reduce cobalt usage through efforts such as substitution and near net shape processing also have contributed to this downward trend.

Superalloys still remain the major user of cobalt within the U.S. economy as shown in figure 3. Of the 10.4 million pounds of cobalt consumed by the United States in 1982, 37 percent of it went for superalloy production used primarily for aircraft gas turbine engines (ref. 1). The dependence of gas turbine engines on the strategic material cobalt as well as the other strategic materials is illustrated in figure 4. The strategic metals cobalt, chromium, tantalum, and columbium are contained in superalloys, stainless steels, and steels that are used in engine manufacturing in such components as compressors, combustors, and turbines. The need for these metals has increased as the demands have grown for higher durability plus higher performance, fuel efficient aircraft turbine engines. For example, the strategic metal input requirement for an F100 turbofan engine is shown in figure 5 to be about 2500 pounds. Based on the essential nature of these metals and in order for the U.S. aircraft industry to maintain its competitive position, supplies must be readily available at a reasonably stable cost or conversely substitute material technology must be on the shelf which will allow engine manufacturers to use alternative materials in the event of a strategic material cutoff or price escalation such as occurred in 1978.

Because of the importance of cobalt to the aircraft engine industry several research programs were initiated as part of the COSAM program to determine the roles of cobalt in nickel-base superalloys which constitute the major use of cobalt in U.S. aircraft engines. A further objective of the programs was to identify less strategic substitutes for cobalt in a variety of nickel-base superalloys. Such research efforts could have long-term national benefits, and, in addition, the methodology developed in these programs could serve as a model for future efforts involving other strategic elements.

Three nickel-base superalloys were initially selected for the COSAM investigation on cobalt. The three alloys are listed in Table 1 with their typical applications in the aircraft engine industry, the forms in which they are used and remarks as to why they were selected for the COSAM activity. Applications include turbine disks as well as low- and high-pressure turbine blades. A variety of product forms are represented by the applications of the three alloys as noted in the table. The selection of the alloys was based primarily on the considerations given in this table. Waspaloy* was selected because it represented the highest tonnage of cobalt in commercial aircraft engines. Udimet*-700 was selected because it has a composition similar to many of the cobalt-containing nickel-base superalloys, and it is used in the as-cast, as-wrought ingot, as-wrought powder, and as-HIP powder metallurgy fabricated conditions. Thus, the composition versus processing study opportunities were great. The potential for determining the impact of cobalt on both conventionally cast and D.S. polycrystalline and single crystal turbine blades was the reason for selecting MAR-M*247. After initial evaluation of these three alloys, additional alloys Nimonic* 115 and Udimet 720 were added to the program to further illucidate the roles of cobalt in nickel-base superalloys.

The COSAM Program is constituted as a cooperative program involving NASA, universities and industry. Various research efforts are being conducted under the overall programmatic management of the NASA Lewis Research Center. Some of this work is being conducted in-house at Lewis. There are also cooperative projects under way involving Lewis with both industry and universities to optimize the expertise at each organization and to seek synergistic results from the combined efforts. This research cooperation is presented graphically in figure 6. Typical roles for each organization are shown. These roles, of course, vary from project to project. For example, one project can involve an industry contract or a university grant for the bulk of the effort with a range of supporting contributions from the other partners. Another project may be conducted mainly in-house at Lewis with a range of support from industry or a university. Universities involved in the cobalt substitution program include Columbia University, Purdue University, and Case Western Reserve University. Industry involvement on this program includes Special Metals Corporation, Battelle Columbus Laboratories, and IIT Research Institute.

RESULTS

Metallurgy

Central to the studies being performed under the COSAM Program are efforts to gain a basic understanding of the alloying effects of cobalt in nickel-base superalloys. A significant effort has therefore been directed toward studying the physical metallurgy of low cobalt derivatives of several commercial nickel-base superalloys. These studies will be reviewed here with regard to the $\gamma - \gamma'$ relationships and other microconstituents.

$\gamma - \gamma'$ Relationships. The effects of reducing cobalt content on liquidus, solidus and gamma prime solvus temperatures were determined for Udimet-700, Nimonic 115, Udimet 720, and MAR-M247 (refs. 8 to 11). The nominal alloy composition and γ' content of the alloys are listed in Table 2. As one might expect in systems with 4-7 components, no universal trends were observed. In these alloy systems, it was observed that reducing cobalt increased the γ' solvus temperature typically about 3° C per atom percent of cobalt. Jarrett et al., (ref. 8), have rationalized this behavior with findings of Heslop (ref. 12) and Mauer, et al., (ref. 13) in terms of a pseudo-binary phase diagram based on Heslop's work. Their diagram shown in figure 7 shows that at low levels of γ' formers (Al + Ti), reducing cobalt lowers the γ' solvus while at higher

---

*The trade names Waspaloy, Udimet, MAR-M, René and Nimonic are for United Technologies Corporation, Special Metals Corporation, Martin Marietta Corporation, General Electric Company, and the Inco family of companies, respectively.

levels, typical of modern superalloys, the behavior reverses. A cross-over point occurs at about 7 atomic percent Al + Ti, the composition of Waspaloy, where it is inferred that the γ' solvus temperature is independent of cobalt content.

Of interest for heat treating and working these alloys is the change in the solidus temperature as a function of cobalt content. For most compositions, reducing cobalt content appeared to raise the solidus temperatures, the exception being the small (5 wt. percent) cobalt content in the Udimet-700 alloy series (ref. 14), and in a single crystal derivative of MAR-M247 (ref. 11). The general trend however, is that while reducing cobalt increases the γ' solvus and solidus temperatures in higher γ' fraction alloys, the difference between the γ' solvus and solidus temperature decreases with removal of cobalt from the alloys.

In the alloys Waspaloy, Udimet-700, single crystal MAR-M247 and Nimonic 115 nickel substitution for cobalt had little effect on the amount of γ' formed. This would have been anticipated from the reported (ref. 15) average γ' partitioning ratio for cobalt of 0.37 (1.0 being equal partitioning to γ' and γ). For MAR-M247, however, decreasing cobalt decreases the amount of γ' (ref. 10). The independence of γ' content with cobalt level was previously reported (ref. 16) in the Russian literature for the cast alloy ZhS6K.

As one might expect, because the lattice parameter for face-centered-cubic cobalt is greater than nickel or Ni_3Al, as nickel is substituted for cobalt the lattice parameter for both γ and γ' phases tend to decrease. The lattice parameter of γ' in Waspaloy increased as cobalt content was reduced (ref. 13). However,the amount of γ-γ' mismatch tended to decrease for Waspaloy and increased for Udimet-700 with reducing cobalt content. It is thought that the effects on lattice parameter and mismatch result both directly from cobalt and indirectly from the influence that cobalt has on the relative solubility of the other elements in the γ and γ' phases.

Cobalt has been shown to affect the solubility of other alloying elements in nickel-base alloys by several investigators. Heslop (ref. 12) showed that 20 percent cobalt decreases solubility for titanium and aluminum in nickel - 20 percent chromium alloys. More recently in the COSAM Program, Jarrett et al. (ref. 8) and Nathal and Ebert (ref. 11) have shown that reducing cobalt also effects the relative solubilities of chromium and nickel in γ and γ' in Udimet-700 and MAR-M247. Similar results have also been reported by Maurer et al. (ref. 13) for Waspaloy.

Other microconstituents. The nickel-base superalloys normally contain significant amounts of intentionally added carbon and boron. Therefore in most compositions one finds a variety of carbide phases and borides. Further, after long time exposure, additional phases such as sigma, mu or terminal solid solution of the body-centered-cubic elements have been observed. The single crystal derivities of MAR-M247 studied in this program did not contain intentionally added carbon and boron - therefore their behavior is not included here.

Radavich and Engel (ref. 17) have reported that reducing cobalt in Udimet-700 has little effect on carbide mass, but causes the major carbide to change from TiC to chromium rich $M_{23}C_6$. The latter carbide further changes from a fine grain boundary morphology at intermediate cobalt levels to a massive morphology at 8.6 percent cobalt. A small decrease in the amount of M_3B_2 was also observed with decreasing cobalt amounts. After aging at 815° C for 1000 hours sigma phase was observed in compositions having 8.6 percent or more cobalt.

Nathal (ref. 10) observed that for MAR-M247 the weight fraction of carbide increased by 1 wt. percent and the morphology changed from discrete particles to a grain boundary film as the cobalt was reduced from 10 percent to 0 percent. The carbides were identified as MC types. Exposure to 982° C for 1000 hours caused the formation of M_6C needles, but no sigma or mu phases were observed at any cobalt level.

Observations by Radavich and Engle (ref. 17) for Nimonic 115 also showed a shift in carbide morphology with changing cobalt levels. At 10 percent cobalt the carbides are randomly distributed particles, while at 5 and 0 percent cobalt grain boundary films are observed in the as-rolled condition. They suggest that reducing cobalt decreases the solubility of the gamma for carbon and boron. A similar effect of cobalt on carbon solubility has been reported for MERL 76 (ref. 18).

Mechanical Properties

Of prime interest in the COSAM Program is the assessment of how much cobalt might be reduced from nickel-base superalloys, while still offering useful engineering alloys. The tensile, stress rupture and low cycle fatigue properties of low cobalt alloys will be discussed in this section. Readers are cautioned, however, the data were obtained from small heats and commercial size heats might result with differing properties.

Tensile properties. The room temperature tensile properties of cobalt modified Udimet-700 given either a partial or full γ' solution treatment are shown in figure 8 (ref. 8). The elevated temperature strength of cobalt modified MAR-M247 (ref. 19) are shown in figure 9. In all cases, it can be seen that cobalt has only little influence on the ultimate and yield strength of the alloys. Earlier work (ref. 16) by Lashko et al., also showed that additions of 10 percent cobalt changed the tensile and yield strength of ZhS6K only about 10 percent.

Stress-rupture life. The stress rupture behavior of Udimet-700 (ref. 14) was also studied in two heat treatment conditions. One heat treatment, typical of that which might be given to materials intended for low temperature service, for example disk applications, used a sub-solvus treatment, thus retaining a relatively fine grain size. The other treatment intended to maximize high temperature properties as required for blade applications, used a full γ' solution treatment. The stress rupture results are summarized in figure 10. For materials given partial γ' solution treatments, (fig. 10(a)) Harf's (ref. 20) results show that 0 percent cobalt and 17 percent cobalt alloys have about the same rupture life, with a maximum occurring at about 4 1/4 percent cobalt. Jarrett and Tien (ref. 14) however, show that the rupture life is independent of cobalt between 8 1/2 percent cobalt and 17 percent cobalt, but below 8 1/2 percent cobalt the stress rupture life decreases significantly. It can be seen that when the alloy is heat treated to fully solution the γ' (fig. 10(b)), that the stress rupture life at the low stress increases linearly with cobalt reduction in Udimet-700. This has been attributed by Jarrett et al., (ref. 8) to be due to formation of increasing amounts of fine γ' in the lower cobalt alloys. No explanation is offered for the behavior at the higher stress of 689 MPa where the life is independent of cobalt level.

If one examines the details of the heat treatments it is found that Harf used a partial solution temperatue about 40° C below the γ' solvus temperature for all of his alloys. Jarrett et al., on the other hand, used a partial solution temperature about 40° C below the γ' solvus between 8 1/2 and 17 percent cobalt, but used a constant temperature of 1129° C for the 0 to 8 1/2 percent cobalt alloys. That results in a solution temperature which is increasingly below the solvus for the alloys between 8 1/2 and 0 percent cobalt. At 40° C below the γ' solvus the amount of γ' changes about 1/4 percent (wt.) per degree C as the temperature changes (ref. 21). The γ' solvus increases at a rate of about 3° C per percent of cobalt removed. Thus one would expect that the 0 percent cobalt alloy studied by Jarrett et al., would contain about 6 percent less fine γ' than the 8 1/2 percent cobalt alloy. In fact they report 28.8 percent fine γ' in the 0 percent cobalt alloy compared to 34.2 percent for the 8 1/2 percent cobalt alloy or 5.4 percent less fine γ'. It seems that the loss in stress rupture life, with reduced cobalt observed by Jarrett et al., can be largely explained in terms of the reduced fine γ' available for strengthening.

Nathal et al., (ref. 19) reported decreased stress rupture life for reduced cobalt polycrystalline MAR-M247. This is shown in figure 11(a). They attributed the loss of rupture life to both reduced γ' amounts with decreasing cobalt levels and to the formation of a grain boundary carbide film at 0 percent cobalt. In contrast, Nathal and Ebert (ref. 11) reported an increase in rupture life with decreasing cobalt in stripped MAR-M247 single crystals as shown in figure 11(b). The absence of grain boundaries and hence carbide film formation may contribute to the reversal in behavior.

For the low γ' volume fraction alloy, Waspaloy, Maurer, et al. (ref. 13), reported decreasing stress rupture lives with decreasing cobalt levels. The slight decrease in the amount of γ' in the low cobalt alloys could not account for the loss of rupture life observed. They attributed part of the rupture life degradation to both a change in carbide partitioning at the grain boundaries and to increasing the stacking fault energy of the matrix with reducing cobalt content. Law, et al. (ref. 18), used similar reasoning to explain the reduced creep-rupture behavior of 0 percent cobalt MERL 76 and AF115 alloys.

Low cycle fatigue. Creep-fatigue tests were conducted on axially-loaded specimens of Waspaloy at 538° C and Udimet-700 at 760° C (refs. 22 and 23). Four different types of strain-controlled test cycles were performed on each composition of the reduced cobalt alloys. These cycles are listed below and the resultant stress-strain hysteresis loops are illustrated in figure 12:

PP - High frequency, 0.5 Hz triangular wave form.
CP - Same as PP, except with a 1-minute hold period at peak tensile strain.
PC - Same as PP, except with a 1-minute hold period at peak compression strain.
CC - Same as PP, except with a 1-minute hold period at both peak tensile and compression strains.

For direct comparison, the creep-fatigue test results were normalized by using a calculated life for an axial inelastic strain range of 0.0025 cm/cm, N_f.0025. The results of this analysis are shown in figure 13 for the two reduced cobalt content series of alloys. Examination of the Waspaloy data suggests that reducing the cobalt content of this alloy did not have an influence on fatigue life. The alloy with 0 percent cobalt exhibited fatigue lives equal to the standard 13 percent cobalt Waspaloy for most of the creep-fatigue cycles. Examination of the Udimet-700 data suggests that fatigue life is independent of cobalt content for PP and CP cycles. In contrast, the CC and PC cyles drastically reduced fatigue lives of the standard 17 percent cobalt Udimet-700 alloy while all the reduced cobalt content alloys exhibited longer lives for these two cycles. Based on these limited results, it is concluded that the reduction and/or removal of cobalt from Waspaloy and Udimet-700 is not detrimental to their short-time, creep-fatigue resistance.

Thermal fatigue. Effects of reducing cobalt content in Udimet-700 on thermal fatigue resistance were determined by fluidized bed testing (ref. 24). Triplicate test specimens of each alloy composition were heated by immersion in a hot bed for 3 minutes followed by immediate transfer to a cooler bed for an immersion time of 3 minutes. This cycle was repeated until specimen failure occurred. Specimens were examined after each 500 cycles. Failure was taken as the average of the number of cycles at the last inspection without cracks and the number of cycles at the first inspection with a crack. In this investigation, the fluidized hot bed temperature was increased at various increments to obtain cracking. A history of the test conditions is given in figure 14 for the Udimet-700 test results. Thermal fatigue lives are plotted as averages of the three test bars for each composition. Udimet-700 was evaluated in both the bare and coated (NiCrAlY overlay) conditions. The thermal fatigue results shown in figure 14 indicate that the best life (both bare and coated) was for the 8.6 percent cobalt content alloy. Interestingly, for the 4.3 and 8.6 percent cobalt alloys, the coated thermal fatigue life was less than that achieved by the bare material. Based on these thermal fatigue results, it appears that for both alloys the optimum cobalt content is about 8 percent, or at levels substantially lower than the alloy specifications of 17 to 19 percent cobalt for Udimet-700.

ENVIRONMENTAL RESISTANCE

Cyclic oxidation. The three nickel-base alloys, Waspaloy, Udimet-700, and MAR-M247 were tested in cyclic oxidation over the temperature range 760° to 1150° C for 1-hour exposure cycles for total times ranging from 100 to 1000 hours (ref. 25). Specimens were weighed and the surface X-rayed periodically throughout the duration of the test. Typical specific weight change data at 1100° C are shown in figure 15 for the reduced cobalt Udimet-700 and MAR-M247 alloys which represent the extremes in oxidation resistance. Reduced cobalt Waspaloy alloys exhibited oxidation behavior similar to the Udimet-700 alloys. Based upon specific weight change data, removing cobalt from Udimet-700 and Waspaloy substantially improves oxidation resistance and slightly improves oxidation resistance of MAR-M247. To compare the oxidation resistance of these alloys over the entire temperature range an oxidation attack parameter K_a was used. This was accomplished by fitting the weight change - time data to:

$$\Delta w/A = K_1^{1/2} t^{1/2} - K_2 t \qquad (1)$$

where $K_1^{1/2}$ represents an oxide growth constant and K_2 an oxide spalling constant. K_a is then defined as:

$$K_a = K_1^{1/2} + 10\ K_2 \qquad (2)$$

This K_a valve has been shown to correlate well with measured thickness changes (ref. 26). Figure 16 summarizes the oxidation behavior for the three alloy systems. The attack parameter is plotted on a log scale versus the reciprocal of absolute temperature. Only the 13 percent and 0 percent cobalt alloy data are plotted for Waspaloy and the 17 percent and 0 percent cobalt alloy data are plotted for Udimet-700. Based on extensive testing history at NASA Lewis, K_a values can be qualitatively rated as shown in the figure. "Excellent" implies a low growth rate with minimal spalling while "catastrophic" implies the test specimen is almost totally oxidized and converted to massive spall. It should be noted that the higher temperatures represent substantially accelerated testing compared to the normal use temperature of these alloys. At temperatures above 900° C the 0 percent cobalt content alloys of Waspaloy and Udimet-700 are clearly more oxidation resistant than their counterparts with the nominal 13 percent and 17 percent cobalt alloys, respectively. Cobalt content does not appear to affect oxidation resistance of MAR-M247 although the reduced 5 percent cobalt level alloy was on the lower side (better oxidation resistance) of the data band shown in figure 16.

X-ray diffraction data suggest an explanation for the oxidation behavior of these reduced cobalt alloys. Figure 17 schematically summarizes this behavior. In the Waspaloy and Udimet-700 alloys with Cr/Al ratios |1 (on an atomic basis), Cr_2O_3/chromite spinels and NiO form. Formation of NiO leads to excessive spalling and catastrophic failure. The presence of cobalt in the alloy accelerates this oxide breakdown process for the Waspaloy and Udimet-700 alloy series. In contrast, the Cr/Al ratio is 1 for MAR-M247 and Al_2O_3 and aluminate spinels are the chief oxides formed. These slower growing oxides are less prone to the formation of NiO in the scale which leads to accelerated spalling. In addition, the cobalt content does not appear critical in MAR-M247 suggesting that cobalt removal does not degrade oxidation resistance.

Hot corrosion. Both uncoated and coated specimens of Udimet-700 and uncoated MAR-M247 were evaluated. Wedge shaped test bars and the Mach 0.5 burner rig are shown in figure 18. Specimens were tested for 300 cycles. Each cycle consisted of holding the samples at 900° C for 1 hour followed by 3 minutes out of the flame during which time the samples cooled to near ambient temperature while in an air stream. The burner rig used jet A-1 fuel and pre-heated (~ 230° C) air which was seeded with a sodium chloride solution air aspirated into the combustor. Sodium level was maintained at 0.5 ppm in terms of fuel plus air and the sulfur content of the fuel ranged from 0.05 to 0.07 percent during the duration of the test. Photographs of the uncoated reduced cobalt Udimet-700 and MAR-M247 are shown in figures 19 and 20 (ref. 27), respectively. Based on appearance and weight change, hot corrosion resistance improves as cobalt is reduced in the alloys.

Data are currently being analyzed to quantitatively describe these results. In contrast, an aluminide coating applied to the reduced cobalt content Udimet-700 alloys indicated (fig. 21), that at 1100° C in a Mach 0.3 burner rig, optimum corrosion resistance was achieved at a concentration near 12.8 percent cobalt (ref. 28). These results along with the low-cycle thermal fatigue results where uncoated specimens gave better lives than coated specimens, suggest that coating composition must be tailored to the reduced cobalt nickel-base superalloys.

CONCLUSIONS

The COSAM Program, through the cooperative research efforts of NASA, industry, and academia, is providing insight into the roles of cobalt in today's advanced nickel-base superalloys. It is apparent that some generalities can be made as to the major effects of reducing cobalt in many of the alloys investigated in the COSAM Program and by others cited herein. For example, tensile properties and low-cycle fatigue resistance are essentially independent of cobalt content in the alloys investigated. Oxidation resistance and hot corrosion resistance have been shown to improve with decreasing cobalt content in the alloys normally used for high-temperature blades (Udimet-700 and MAR-M247). Stress rupture results gave mixed results with rupture lives both increasing and decreasing as cobalt was reduced in the alloys. These results could be related to the effects that reducing cobalt had on fine γ' content, carbide composition and morphology, and to stacking fault energy. In the case of Udimet-700, reduced rupture lives at cobalt contents of 4.3 and 0 percent were increased to values exceeding or equal to the standard 17 percent cobalt alloy by modifying the heat treatment for these low cobalt alloys. Thermal fatigue resistance and Mach 0.3 burner rig oxidation resistance of coated specimens indicated that best results were achieved in reduced cobalt content Udimet-700 alloys with 8.6 to 12.8 percent cobalt.

Based on the results obtained to date, it is concluded that a number of today's nickel-base superalloys used in gas turbine engines appear to contain more cobalt than is needed to meet engine requirements. Cutting the cobalt content in half appears to be readily feasible. The first generation of modified cobalt content alloys has been the result of substituting nickel for cobalt. Now that some insight has been gained as to microstructural and microchemistry changes that accompany mechanical and environmental resistant changes in the reduced cobalt alloys, alloying elements other than nickel may enhance the properties of low/no cobalt content nickel-base superalloys. Large scale heats of the reduced cobalt alloys will have to be produced and evaluated to assure reproducibility of findings to date on laboratory size heats.

The results from the COSAM Program are encouraging in that they hold the potential of reducing vulnerability of superalloys to cobalt in the event of future cobalt shortages or total cutoff of foreign supplies to the United States and other NATO nations.

REFERENCES

1. Bureau of Mines: Mineral Commodities Summary - 1983. Department of Interior, 1983.
2. National Materials and Minerals Policy, Research, and Development Act of 1980. GPO-84-714, 1981.
3. Stephens, J. R.: NASA's Activities in the Conservation of Strategic Aerospace Materials. NASA TM-81617, 1980.
4. Stephens, J. R.: A Status Review of NASA's COSAM (Conservation Of Strategic Aerospace Materials) Program. NASA TM-82852, May 1982.
5. Stephens, J. R.: COSAM Program Overview. NASA TM-83006, Oct. 1982.
6. Egypt's Technology Shift - Soviets Focus on Control of Oil Flow from Region. Aviat. Week Space Technol., vol. 115, no. 24, Dec. 14, 1981, pp. 48-54.
7. Bureau of Mines: Mineral Industry Surveys, Cobalt in 1978, 1979, 1980, 1981, and 1982. Department of Interior.
8. Jarrett, R.; et al.: Role of Cobalt in Nickel-Base Superalloys. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 37-50.
9. Sczerenie, F. E.; and Maurer, G. E.: Preparation of Low Strategic Metal Content Superalloys. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 21-36.
10. Nathal, M. V.; Maier, R. D.; and Ebert, L. J.: The Influence of Cobalt on the Microstructure of the Nickel-Base Superalloy MAR-M247. Metall. Trans. A, vol. 13A, Oct. 1982, pp. 1775-1783.
11. Nathal, M. V.; and Ebert, L. J.: Influence of Cobalt, Tantalum and Tungsten on the Microstructure and Mechanical Properties of Superalloy Single Crystals. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 107-116.
12. Heslop, J.: Wrought Nickel-Chromium Heat-Resisting Alloys Containing Cobalt. Cobalt, vol. 24, Sept. 1964, pp. 128-137.
13. Maurer, G. E.; Jackman, L. A.; and Domingue, J. A.: Role of Cobalt in Waspaloy. Superalloys 1980, J. K. Tien, et al., eds., ASM, 1980, pp. 43-52.
14. Jarrett, R.; and Tien, J. K.: Effects of Cobalt on Structure, Microchemistry and Properties of a Wrought Nickel-Base Superalloy. Metall. Trans. A, vol. 13A, June 1982, pp. 1021-1032.
15. Kriege, O. H.; and Baris, J. M.: The Chemical Partitioning of Elements in Gamma Prime Separated from Precipitation - Hardened, High Temperature Nickel-Base Alloys. Trans. Am. Soc. Met., vol. 62, Mar. 1969, pp. 195-200.
16. Lashko, N. F.; et al.: Influence of Cobalt on the Phase Composition of Some Heat-Resistant Alloys. Structure and Properties of Heat-Resistant Metals and Alloys, N. V. Pridantsev, ed., Israel Program for Scientific Translations, Ltd., Jerusalem, 1970, pp. 200-204.

17. Radavich, J.; and Engel, M.: Effect of Cobalt on Microstructure and Microchemistry of Nickel-Base Superalloys. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 51-62.
18. Law, C. C.; Lin, J. S.; and Blackburn, M. J.: Reduction of Strategic Elements in Turbine Disk Alloys. AFOSR-TR-81-0554, PWA-FR-14913, Pratt and Whitney Aircraft Group, May 1981. (AD-A102074.)
19. Nathal, M. V.; Maier, R. D.; and Ebert, L. J.: The Influence of Cobalt on the Tensile and Stress-Rupture Properties of the Nickel-Base Superalloy MAR-M247. Metall. Trans. A, vol. 13A, Oct. 1982, pp. 1767-1774.
20. Harf, F. H.: Effect of Reduced Cobalt Contents on Hot Isostatically Pressed Powder Metallurgy U-700 Alloys. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 63-70.
21. VanDerMolen, E. H.; Oblak, J. M.; and Kriege, O. H.: Control of γ' Particle Size and Volume Fraction in the High Temperature Superalloy Udimet-700. Metall. Trans., vol. 2, June 1971, pp. 1627-1633.
22. Halford, G. R.: Creep-Fatigue of Low Cobalt Superalloys. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 83-88.
23. Rungta, R.; Hopper, A. T.; Leis, B. N.; and Halford, G.: Considerations in Design Against Low Cycle Fatigue Damage in Superalloys, presented at "Designing with New High Temperature Alloys," AIME Fall Meeting, Philadelphia, PA, October 4, 1983.
24. Bizon, P. T.: Thermal Fatigue Resistance of Cobalt-Modified Udimet-700. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 77-81.
25. Barrett, C. A.: Oxidation of Low Cobalt Alloys. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 89-94.
26. Barrett, C. A.; and Lowell, C. E.: Resistance of Nickel-Chromium-Aluminum Alloys to Cyclic Oxidation at 1100° C and 1200° C. NASA TN D-8255, June 1976.
27. Stearns, C. A.: Hot Corrosion of Low Cobalt Alloys. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 95-98.
28. Zaplatynsky, I.; and Levine, S. R.: Coatings for COSAM Alloys. COSAM Program Overview, J. R. Stephens, ed., NASA TM-83006, 1982, pp. 99-106.

TABLE 1. SUPERALLOYS SELECTED FOR COBALT SUBSTITUTION STUDIES

Alloy	Typical engine application	Form	Remarks
Waspaloy	Turbine disk	Forged	Highest use wrought alloy in current engines
Udimet-700:	Turbine disk	Forged	Similar alloys used in various forms and applications
LC Astroloy	Turbine disk	As-hip-powder	
RENE 77	Turbine blades	Cast	
MAR-M247	Turbine blades and wheels	Cast	Conventionally-cast, D.S and single crystal

TABLE 2. NOMINAL COMPOSITIONS AND γ' CONTENTS OF NICKEL-BASE SUPERALLOYS SELECTED FOR COSAM PROGRAM

	Weight percent												percent
	Ni	Co	Cr	Al	Ti	Mo	W	Ta	Hf	B	Zr	C	γ'
Waspaloy	58	13.5	19.5	1.3	3.0	4.3	---	--	---	0.006	0.06	0.08	20
Udimet-700	53	18.5	15.0	4.3	3.5	5.2	---	---	---	.030	---	.08	45
MAR-M247:													
Polycrystalline	60	10.0	8.2	5.5	1.0	0.6	10.0	3.0	1.5	.020	.09	.16	55
Single crystal	62	10.0	8.2	4.4	1.0	0.6	10.0	3.0	---	---	---	---	63
Nimonic 115	59	14.8	14.6	4.9	4.0	3.5	---	---	---	.017	.001	.16	55
Udimet 720	55	14.7	18.0	2.5	5.0	3.1	1.26	---	---	.031	.031	.04	45

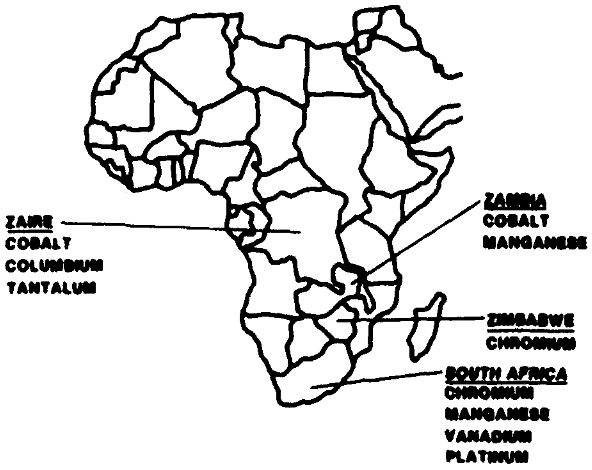


Figure 1. - Strategic material resources in Africa.

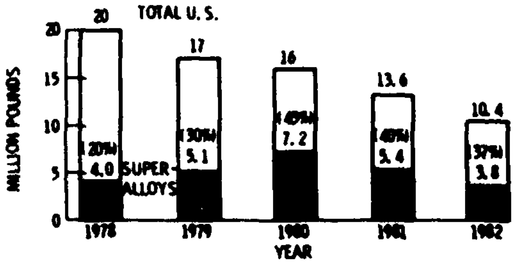


Figure 2. - Recent trends in United States and superalloy cobalt use.

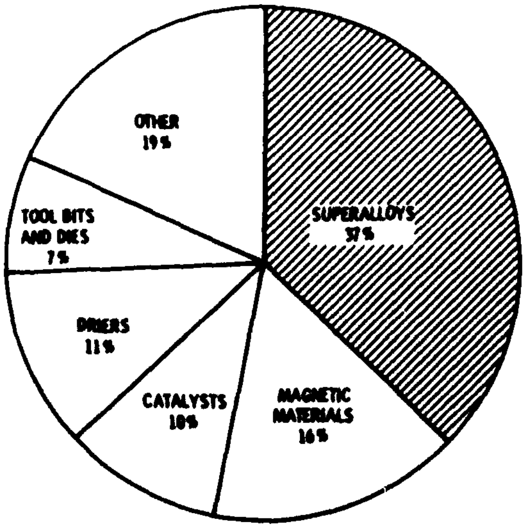


Figure 3. - Distribution of 1982 U. S. cobalt consumption-10.4 million pounds.

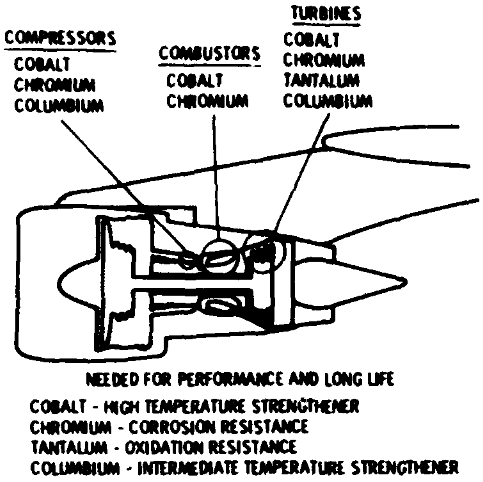


Figure 4. - Dependence of gas turbine engines on strategic materials.

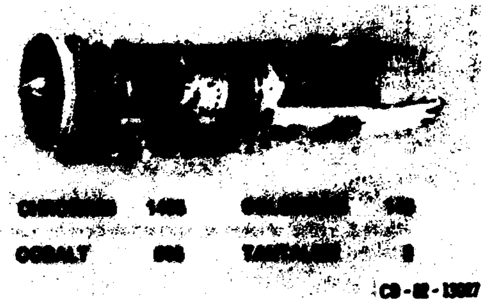


Figure 5. - F-100 engine input requirements in pounds.

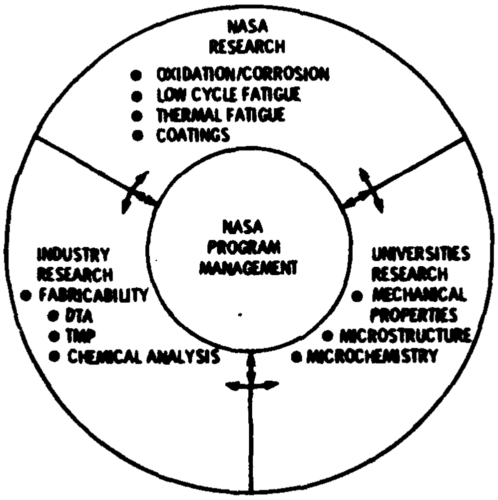
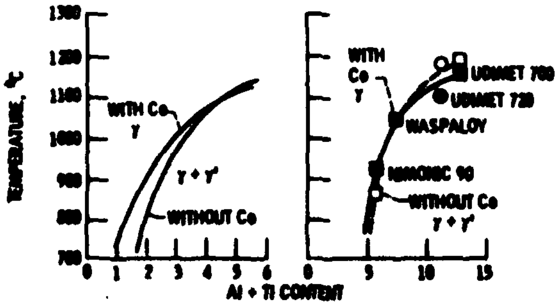


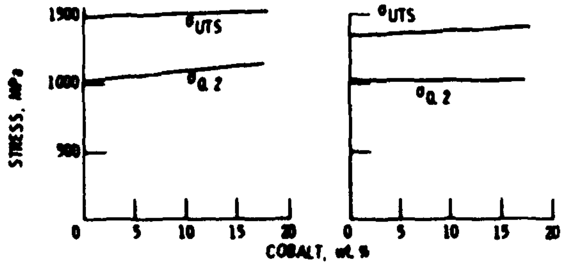
Figure 6. - Cooperative NASA-industry-university programs.



(a) w/o.

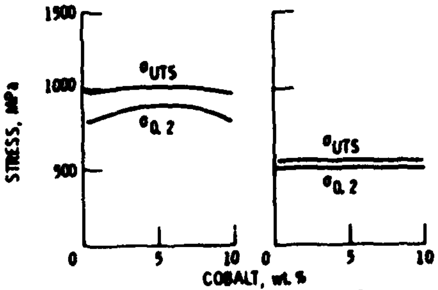
(b) a/o.

Figure 7. - Pseudo-binary phase diagrams after Heslop (ref. 13) for Ni-20Cr and Ni-20Cr-20Co and after Jarret et al. (ref. 8) for commercial wrought alloys.



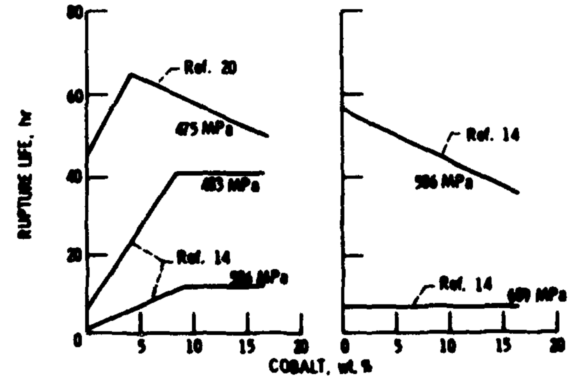
(a) Partial solution. (b) Full solution.

Figure 8. - Effect of cobalt on room temperature tensile strength of Udimet 700.



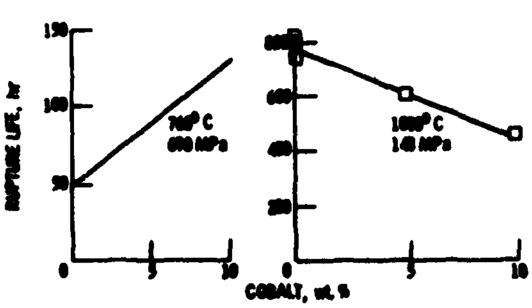
(a) 760° C. (b) 982° C.

Figure 9. - Effect of cobalt on elevated temperature tensile strength of Mar-M 247.



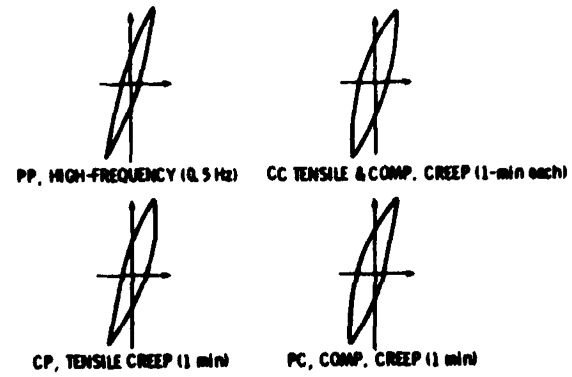
(a) Partial solution. (b) Full solution.

Figure 10. - Effect of cobalt on 760° C stress rupture life of Udimet 700.



(a) Mar M-247. (b) "Single Crystal" Mar-M 247.

Figure 11. - Effect of cobalt on stress rupture life.


PP, HIGH-FREQUENCY (0.5 Hz) CC TENSILE & COMP. CREEP (1-min each)

CP, TENSILE CREEP (1 min) PC, COMP. CREEP (1 min)

Figure 12. - Creep fatigue of low cobalt superalloys strain-controlled creep-fatigue cycles.

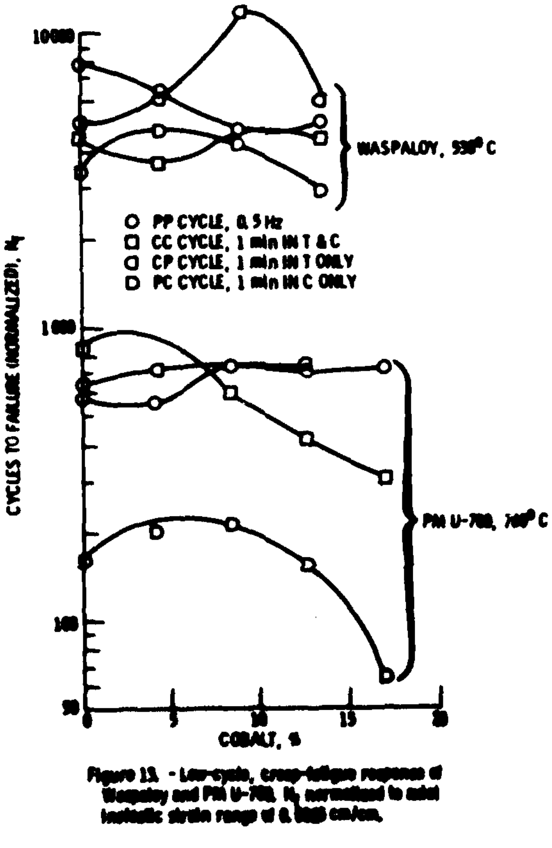


Figure 13. - Low-cycle, creep-fatigue response of Waspaloy and PM U-700. N_f normalized to axial inelastic strain range of 0.[illegible] cm/cm.

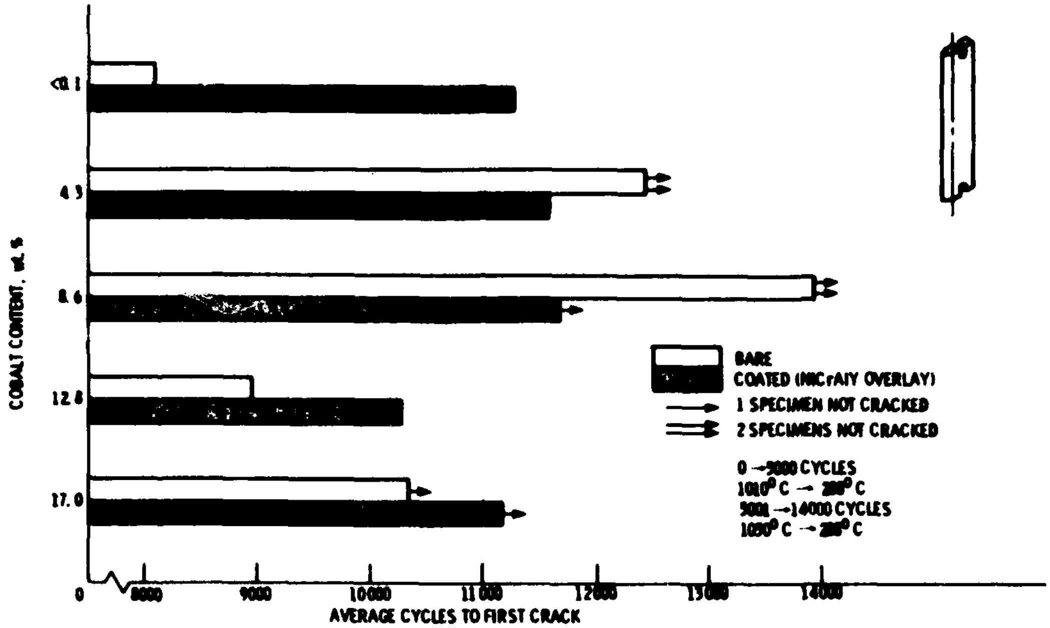
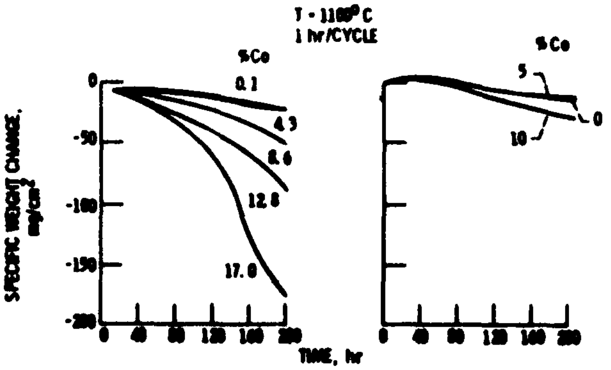


Figure 14. - Thermal fatigue resistance of reduced cobalt Udimet 700.



(a) Udimet 700.

(b) Mar-M 247.

Figure 15. - Cyclic oxidation behavior of reduced cobalt nickel-base superalloys.

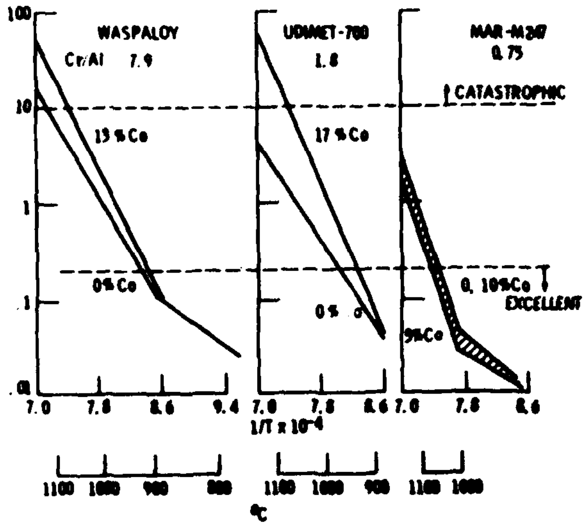


Figure 16. - Oxidation attack parameter, K_a, for reduced cobalt nickel-base superalloys.

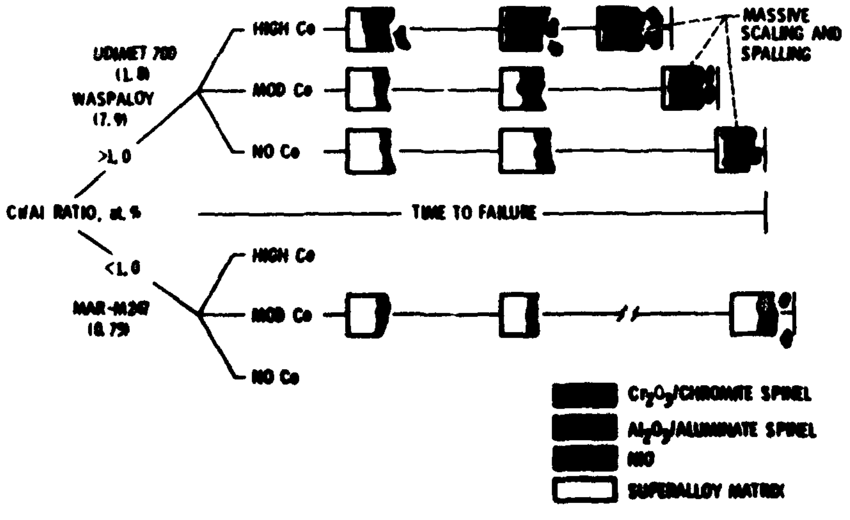
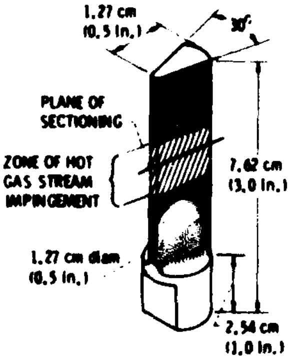


Figure 17. - Cobalt effect on nickel base alloy scaling protection and breakdown in cyclic oxidation.



Test bar

Burner rig.

Figure 18. - Hot-corrosion apparatus and test specimen.

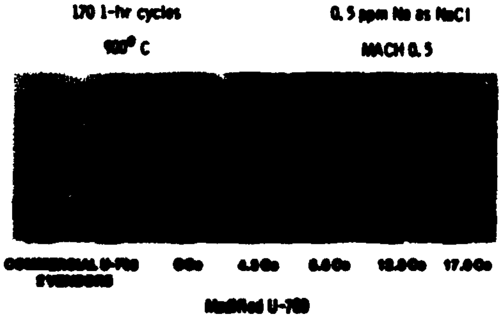
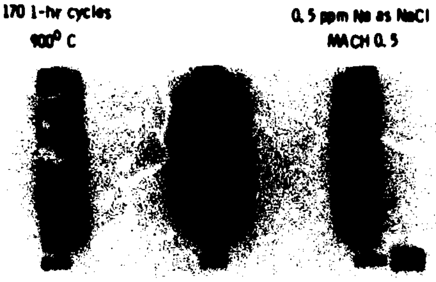


Figure 19. - Effect of cobalt on hot corrosion.

CD-82-12950



Modified MAR-M 247

Figure 20. - Effect of cobalt on hot corrosion.

CD-82-12951

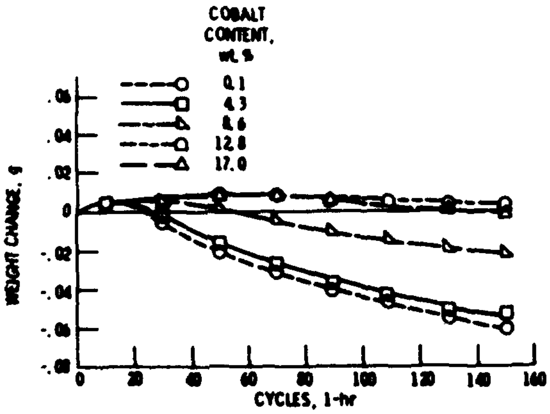


Figure 21. - Effect of cobalt on oxidation behavior of aluminized U-700 Mach 0.3 burner rig, 1100° C (front face).

OXIDE DISPERSION STRENGTHENED ALLOYS

by
G A J Hack
Wiggin Alloys Limited
Holmer Road
Hereford HR4 9SL
United Kingdom

AD-P004 217

SUMMARY

The principle of oxide dispersion strengthening has been applied to precious metals, nickel, ferritic steels, aluminium alloys and superalloys.

Conventional melting processes are unsuitable for the production of ODS alloys and alternative methods are required to incorporate oxides etc. into various base compositions. One of these methods, mechanical alloying is particularly appropriate to large scale commercialisation and can readily accommodate reactive alloying elements.

The commercial production, properties and applications of ODS superalloys are described. The strength contribution of the oxides gives the alloy designer more freedom to optimise for oxidation and sulphidation resistance or to minimise the use of strategic metals; for example, the alloys described are all cobalt-free.

INTRODUCTION

For more than a decade, oxide dispersion strengthened superalloys have been under intensive development to exploit their potential for exceptional creep resistance and stability at very high temperatures. This programme has culminated in the commercial availability of a range of ODS alloys and product forms manufactured by a technically sophisticated mechanical alloying process.

The development thrust which led to these alloys arose from the accepted limitations of conventional nickel base superalloys at temperatures of 1000°C and higher. At such elevated temperatures, the usual gamma prime strengthening phase present in nickel base superalloys loses its effectiveness as a barrier to dislocation movement. It was realised that if a more stable species of particle could be incorporated into the alloy matrix, then an entirely new class of superalloy would be possible, retaining significant strength even up to the solidus. Such an ideal particle species was identified during the development work as yttrium oxide, a readily available compound having many times the stability of gamma prime (Table 1.).

The mechanical alloying process has been developed as an acceptably economical and commercially feasible method of incorporating a refractory oxide into a superalloy matrix. Merely mixing the oxide with metallic powders does not achieve a sufficiently finely dispersed structure. Melting as an alloying method cannot be attempted, as the oxide forms an immiscible slag above the liquid metal. Other possible techniques using chemical reactions are uneconomic on a commercial scale and cannot be used to alloy the usual reactive elements such as aluminium and titanium.

Mechanical alloying has been proven commercially for many years and ODS alloys are now coming into widespread use for ultra-high temperature applications outside the gas turbine field where their application was originally pioneered. However, the largest proportion of ODS superalloys output is still sold to the gas turbine industry. Table 2 lists the chemical compositions of the three ODS alloys currently in commercial production.

Apart from superalloys, mechanical alloying is used to produce the oxide dispersion strengthened aluminium alloys(1) IN-9052 (Al-4% Mg-0.8% O-1.1% C) and IN-9021 (Al-1.5% Mg-4% Cu-0.8% O-1.1% C). These alloys have an excellent balance of tensile strength, fatigue resistance, toughness and corrosion resistance. IN-9052 is a solid solution type alloy having the strength of 7000 series aluminium alloys but the good corrosion resistance of the 5000 type. IN-9021 is an age hardenable high strength alloy having improved fatigue and corrosion resistance over the 7000 series alloys.

ODS nickel, dispersion strengthened with thorium oxide by a chemical process, is well known. However, where there are environmental objections to radioactive thoria, mechanical alloying has been used to replace thoria with yttria for those applications requiring a combination of strength and high thermal conductivity.

Platinum and its alloys can also be mechanically alloyed to incorporate yttrium oxide for ultra-high temperature applications where the high cost of platinum is justified by its extremely good resistance to corrosion in liquid glass.

MECHANICALLY ALLOYED POWDER PRODUCTION

The development of the mechanical alloying process has been reviewed in several previous papers by Weber and Benjamin et al. (2-5). Additional independent laboratory work on related processes has also been reported from time to time in the literature (6-8), and therefore the description in the present paper is limited to the commercial production of alloyed powder for the manufacture of superalloys.

Typical raw materials are listed in Table 3. Elemental metal powders, crushed master alloys and pre-alloyed powders are all suitable for use as feedstock.

Special analytical techniques have been developed to ensure that the high purity yttria powder lies within a narrow range of crystallite sizes suitable for use as a dispersoid strengthener. Previously reported work (9) has shown that optimum alloy strength is achieved with crystallite sizes less than 300 Å.

Yttria and metal powders are blended together to form a bulk feedstock for the mechanical alloying units. The chemical composition of this "pre-blend" is verified before allocation.

Mechanical alloying is carried out in production units of 34 kg and 1000 kg powder capacity. The larger units, (Figure 1) are being introduced to simplify quality control as commercial powder production levels now exceed 100t/year.

Figure 2 shows the powder raw material blend being transferred from a stainless steel container to one of the 1000 kg units. Both sizes of unit operate on the identical principle of a water-cooled high kinetic energy ball mill in which the raw material powders are milled together by through-hardened steel balls. Contamination from contact between the powder charge and the internal parts of the mill is prevented by a stable protective coating of the superalloy which accumulates on the steel balls and other surfaces, Figure 3.

A repetitive sequence of particle welding and fracturing occurs in the mill at a rate determined by the process kinetic energy, temperature and atmosphere, Figures 4, 5, 6. During the course of milling, an equilibrium particle size distribution is established and each individual particle acquires the alloying constituents in the correct proportions. Further milling continuously refines the powder structures and the process is considered complete when the composite particles have a finely layered sub-optical structure, Figure 7. At this stage the average spacing of yttria dispersoids at the layer interfaces is similar to the average layer thickness, resulting in an ideal random distribution of the oxide with an interparticle spacing of less than 0.5 micron. No further milling is necessary once this condition has been attained.

The mechanically alloyed powder is drained from the mill into further stainless steel containers specially reserved for processed powder, Figure 8. The powders from each production run are sieved on dedicated equipment, Figure 9, and evaluated by several techniques including sieve analysis, chemical analysis and powder metallography. Parts of several production runs may be blended together in a stainless steel container dedicated to one particular alloy, Figure 10. This blend is then subjected to a full chemical analysis, equivalent to a cast analysis in conventional alloy production. At all stages scrupulous cleanliness of the environment and handling equipment is observed to prevent contamination of the powder.

THERMOMECHANICAL PROCESSING

The aim of the thermomechanical processing is twofold. In addition to producing the required product form such as sheet, plate, bar, tube, etc., it is necessary to optimise the stored energy content of the product. If this is done correctly within narrow limits, it is possible to develop a coarse anisotropic grain structure during secondary recrystallisation heat-treatment which greatly enhances the elevated temperature mechanical properties. Studies have shown that the secondary recrystallisation response is dependent upon the entire processing history including the mechanical alloying stage and the powder consolidation variables.

Either hot extrusion or hot isostatic pressing may be used to compact the mechanically alloyed powder but subsequent hot working operations must be modified to compensate for the different levels of working involved with these consolidation methods. In most instances extrusion is preferred because it is less expensive than HIP and imparts a useful proportion of directional working necessary for anisotropic secondary recrystallisation.

Mild steel extrusion cans are filled from the "alloy blend". Cans up to 200mm diameter and 600mm long are presently used, containing up to 170 kg of powder. The wall thickness and end plug design of the cans are varied with both the alloy being produced and the product form in order to maximise yields. A minority of the filled cans are evacuated of air and sealed prior to extrusion but in most applications this has been found unnecessary.

Several hours soaking in a furnace at the extrusion temperature are required to ensure that the centre of the powder mass is heated thoroughly. During this time interdiffusion occurs which causes the highly strained composite powder particles to become chemically homogeneous with all the physical properties of a truly alloyed powder.

Extrusion is carried out in commercial 5000 and 6000 tonne presses at temperatures, ratios and speeds which are interdependent variables and which must be determined in conjunction with the subsequent remaining hot working parameters. A further complication is that the characteristics of individual extrusion presses have to be considered as part of the total thermomechanical working equation. It is not possible, for example, to scale-up exactly the required variables from experimental work with small laboratory presses, or even from experience with other large commercial units. Fortunately, once the operating parameters are established, the results are reproducible without difficulty.

In the as-extruded condition, ODS alloys have a very fine equiaxed sub-micron grain structure suitable for further hot working operations. However, some bar products are deliberately extruded under conditions designed to give a high thermomechanical work content which is sufficient to permit secondary recrystallisation to a coarse elongated grain structure without the need for further hot working operations. For example, the turbine blade alloy INCONEL alloy MA 6000 has been made experimentally by this method (10) and the iron base oxidation resistant alloy, INCOLOY alloy MA 956, can be made commercially in bar form by a similar route, Figure 11.

In the majority of production routes, the extruded bar is an intermediate stage which is normally followed by hot rolling. This is a highly controlled operation which is ideal for optimising the stored energy content and can be used in a sophisticated way to control texture. For example, the turbine vane alloy, INCONEL alloy MA 754, in the form of flat bar possesses exceptional thermal fatigue resistance which is derived from its (100) texture induced during thermomechanical working.

Another useful application of hot rolling occurs in the production of INCOLOY alloy MA 956 sheet. Isotropic mechanical properties and coarse "pancake" shaped grains are consistently produced in this product by a carefully controlled programme of hot cross-rolling of the extruded bar stock. Different cross-rolling schedules have been designed to achieve the best properties in sheet of various standard thicknesses.

Removal of the mild steel from the extrusion cans is carried out either by machining or by pickling, depending on the alloy and the product form. The latter factors determine the stage at which the can is removed, since the can may be beneficial in preventing excessive surface cooling during hot rolling an alloy such as INCONEL alloy MA 6000 which is thermally sensitive in the fine grain condition.

Following hot rolling, most products are ready for secondary recrystallisation heat-treatment. One obvious exception is INCOLOY alloy MA 956 intended for cold drawn wire, cold rolled sheet and even foil. Other exceptions are forging stock and products for hot fabrication, which generally respond more readily to deformation in the ultra fine grain condition. As with hot rolled products, the final major operation is the secondary recrystallisation heat-treatment.

SECONDARY RECRYSTALLISATION IN ODS ALLOYS

The most striking feature common to ODS superalloys is their remarkable capacity for secondary grain growth when annealed at very high temperatures following optimised thermomechanical working. Studies on bar have shown that the elevated temperature mechanical properties are proportional to the grain aspect ratio up to about 6:1, above which they are relatively independent (8). In practice, a minimum grain aspect ratio of 8:1 is normally considered acceptable.

INCOLOY alloy MA 956 and INCONEL alloy MA 754

Both these alloys respond readily to a static anneal at temperatures in the range 1300°C to 1380°C. When etched, INCOLOY alloy MA 956 extruded and annealed bar resembles directionally solidified turbine blade alloys in appearance, Figure 11, with single grains extending for lengths of half a metre of more and about a centimetre in cross-section. INCOLOY alloy MA 956 cold rolled sheet has a structure composed of a few large "pancake" grains through the section thickness, with the "pancakes" in the plane of the sheet. This structure images the thermomechanical history of the material.

Although nickel base INCONEL alloy MA 754 bar has a rather finer structure, the grain aspect ratio exceeds 8:1, Figure 12, and the elevated temperature strength is significantly higher than for INCOLOY alloy MA 956. This is believed to be an effect of the different relationship between the dispersoid and deformation mechanisms in fcc and bcc lattices. Fundamental research on this topic is currently being undertaken.

INCONEL alloy MA 6000 Bar

This alloy has a more complex composition, being strengthened with several solid solution additions, gamma prime for intermediate temperature strength and yttria for extreme elevated temperature creep resistance (11). Secondary recrystallisation to a coarse elongated structure has not been successfully achieved by static annealing, possibly because the relatively low solidus of approximately 1290°C prevents annealing at higher temperatures. However, a high aspect ratio grain structure can be produced over quite short distances in a sufficiently steep linear temperature gradient. Alternatively, extremely high aspect ratio structures can be developed over lengths of a metre or more by the application of a moving hot zone annealing techniques (12, 13). The effects of both static and moving temperature gradients are illustrated for the same length of bar in Figure 13.

In order to manufacture INCONEL alloy MA 6000 in commercially acceptable lengths of uniform structure, a moving zone technique must be used which is an integral part of the entire closely controlled thermomechanical processing sequence. This is necessary to optimise the final grain structures and maximise the resulting elevated temperature mechanical properties.

The final major step in the manufacture of INCONEL alloy MA 6000 bar is solution treatment and ageing to develop correctly the gamma prime structure for intermediate temperature strength. This heat-treatment is as follows:-

0.5 h/1230°C/AC + 2 h/955°C/AC + 24h/845°C/AC

PRODUCTION ZONE ANNEALING

The important parameters for zone annealing are maximum zone temperature, temperature gradient and linearity, bar section size, travel speed of the bar relative to the zone and the heating characteristics of the power unit. Experience with a small resistance heated zone annealer indicated that steeper longitudinal temperature gradients and faster production rates, in particular, would be highly desirable objectives, best achieved by using direct low frequency induction heating. A production zone annealer was therefore designed and built using this experience for the commercial zone annealing of INCONEL alloy MA 6000. Figure 14 shows the fixed induction heating coil on this production unit. Automatic temperature control is by optical pyrometer and the bar speed is stabilised electronically.

The maximum temperature of the hot zone forms part of the total thermomechanical working equation and must be selected from the limited temperature range in which secondary recrystallisation is possible in INCONEL alloy MA 6000. This range is bounded by the solidus at the upper end (1296°C) and a temperature slightly above the gamma prime solvus (1160°C - 1180°C) at the lower end.

The longitudinal temperature gradient has to be chosen in relation to bar speed and induction frequency in order to achieve through-heating of the bar and to avoid excessive thermal stresses during heating up to the zone maximum temperature. The relationship between the important parameter of bar speed and stress-rupture properties has been investigated in some detail as shown in Figure 15.

At very low speeds, a proportion of the stored energy in the bar is annealed out before directional recrystallisation can occur. Since this is equivalent to an under-worked condition, inferior stress-rupture properties are obtained. When very high speeds are used it is difficult to maintain a planar temperature profile through the bar section and shorter, curved grains result from growth away from the bar centreline in the direction of steepest temperature gradient. This structure again adversely affects the stress-rupture properties. Finally, at very high speeds, the centre of the bar may not even reach the lowest temperature possible for secondary recrystallisation and the mechanical properties fall to very low values.

It has been found that the best mechanical properties are associated with a characteristic "quadrant" structure which is seen in etched transverse bar sections. This is illustrated in Figure 16 and is believed to represent four families of grains, with almost identical orientations within each grouping. It is suspected that slight, symmetrical temperature gradients, superimposed on the principal overall linear gradient, are reponsible for these unusual grain orientation patterns.

Attempts have been made to produce INCONEL alloy MA 6000 as single crystal bar. Such a material could be more attractive as a turbine blade material than either existing single crystal alloys or ODS multicrystal materials. One of the main difficulties to be overcome is the favoured longitudinal grain growth mode which inhibits the amount by which lateral spreading of a selected crystal orientation can occur in a necessarily solid state process.

FABRICATION OF COMPONENTS FOR GAS TURBINES

INCOLOY alloy MA 956 cold rolled, annealed sheet is readily fabricated into complex components. However, as a ferritic steel, it has reduced ductility below its transition temperature and the normal precautions for this class of material have to be observed during fabrication. Thus simple sheet fabrications are possible at room temperature but more complex operations are best carried out by slightly warming the material to 100°C (14).

Most other product forms of INCOLOY alloy MA 956 are fabricated in the fine grain condition. Thus, rings can be readily rolled in INCOLOY alloy MA 956 and are being considered for both turbine casings and combustion chambers. Figure 17. shows the sizes which have been produced to date.

Both INCOLOY alloy MA 956 and INCONEL alloy MA 754 can be hot spun in the fine grain condition to make a range of components having circular symmetry such as combustor domes and swirler plates. Figure 18. demonstrates a selection of fabricated and forged components in both alloys.

INCOLOY alloy MA 956 may be welded using a near matching Fe-Cr-Al-Y filler wire for corrosion resistance but it is recommended that such welds are designed to operate under less severe conditions than for which the wrought sheet alloy is capable. Electron beam and laser welds have been shown to have useful high temperature properties (15), as have brazed joints. Rivetting, using INCOLOY alloy MA 956 rivet rod has also been effective in several commercial applications. Figure 19. shows a prototype combustion chamber made by rivetting a liner of INCOLOY alloy MA 956 sheet to an outer support of nickel base alloy (16).

In common with most high temperature superalloys, INCONEL alloy MA 754 cannot be welded easily but it does respond very well to standard high temperature vacuum brazing operations (15). The most common present commercial application is a brazed assembly of vanes and band segments, Figure 20.

Until forging techniques have been developed, the immediate applications for INCONEL alloy MA 6000 are for first stage turbine blades machined from solid bar. The alloy is no more difficult to machine than established blade alloys such as IN 738 and IN 792, and responds well to all the usual metal removing techniques.

The characteristics of INCONEL alloy MA 6000 make it ideal for increasing the metal temperature of turbine blades by 100°C or more in engines where the stresses are medium or low. This is because the intermediate temperature strength of the alloy is limited at the root end of the aerofoil section by the amount of gamma prime strengthening available. Studies have shown, however, that modification of blade mass and temperature distribution to fit the unique strength/temperature characteristics of the alloy can minimise this aspect (17). Figure 21 demonstrates a design study for a machined solid first stage blade in INCONEL alloy MA 6000.

CONCLUSIONS

Oxide Dispersion Strengthened alloys form a unique group with the properties of high strength and stability beyond those achievable with conventional materials. The commercial development of mechanical alloying as a process for producing ODS alloys on a large scale has allowed their special properties to be utilised in a large number of severe applications, especially in advanced aero engineering, but now increasingly in industrial high temperature environments such as fossil fuel burning, nuclear power generation, chemical plant and glass making.

REFERENCES

1. Bridges, P. J.: Conf. Proc. "1983 Powder Metallurgy Group Meeting", Edinburgh, Scotland, Publ. The Metals Society.
2. Benjamin, J. S.: 1970, Met. Trans. 1, pp. 2943-2951.
3. Benjamin, J. S. and Volin, T. E.: 1974, Met. Trans. 5, pp. 1929-1933.
4. Benjamin, J. S. and Larson, J. M.: 1976, AIAA Conf., Dallas, TX, USA, Publ. AIAA Journal.
5. Weber, J. H.: 1980, 25th Nat. SAMPE Symp., San Diego, CA, USA, Publ. Vol. 25, Sci. of Advanced Mat. and Proc. Eng. Series.
6. Wilson, G. G., Knott, B. R. and Desforges, C. D.: 1978, Met. Trans. 9A, pp. 275-282.
7. Coheur, L. and DeWilde, L.: 1975, 4th Eur. Symp. for Powder Met., 1, Grenoble, France, Publ. Soc. Francaise de Metallurgie.
8. Gessinger, G. H.: 1976, Met. Trans., 7A, pp. 1203-1209.
9. Benjamin, J. S. and Bomford, M. J.: 1974, Met. Trans. 5, pp. 615-621.
10. Merrick, H. F., Curwick, L. R. and Kim, Y. G.: 1977 NASA CR-135150 (NASA Contract NAS 3-19694), Cleveland, OH, USA.
11. Hack, G. A. J.: 1981, Met. Powder Report, 36-9, pp. 425-429.
12. Cairns, R. L., Curwick, L. R. and Benjamin, J. S.: 1975, Met. Trans., 6A, pp. 179-188.
13. Benn, R. C., Curwick, L. R. and Hack, G. A. J.: 1980 Conf. Proc. "High Performance Materials by Powder Metallurgy", Bristol, England, Publ. The Metals Society, published in Powder Metallurgy No. 4, 1981, pp. 191-195.
14. Robinson, M. L.: 1982, "Forming of INCOLOY alloy MA 956 sheet", IncoMAP publication.
15. Kelly, T. J.: 1982, "Joining procedures for MA products", IncoMAP publication.
16. NASA MATE Contract NAS3-20072, Project 3 report, Mar. 25 1981.
17. Benjamin, J. S.: 1976, Conf. Proc., Gas Turbine and Fluids Engineering, New Orleans LA, USA, Publ. ASME.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation for help, provided in the preparation of this paper, by IncoMAP (Inco Mechanically Alloyed Products) colleagues at the following locations within the Inco Organisation:-

Wiggin Alloys Limited, Hereford, England
(Production of ODS alloys).

Doncasters Monk Bridge Limited, Leeds, England
(Forging and fabrication of ODS alloys).

Huntington Alloys Inc., Huntington, West Virginia, USA
(Production of ODS alloys).

Inco Alloy Products Company Research Center, Sterling Forest, Suffern, New York, USA
(Development of ODS alloys).

TABLE 1

STABILITY OF STRENGTHENING PHASES

Phase	Approximate Free Energy of Formation at 1000°C (cal/mole)
γ'	- 25,000
Carbide	- 40,000
Y_2O_3	-220,000

TABLE 2

NOMINAL CHEMICAL COMPOSITION, Wt. %

	INCOLOY alloy MA 956	INCONEL alloy MA 754	INCONEL alloy MA 6000
Iron	74	1.0	-
Chromium	20	20	15
Aluminium	4.5	0.3	4.5
Titanium	0.5	0.5	2.5
Yttrium Oxide (Y_2O_3)	0.5	0.6	1.1
Nickel	-	78	69
Carbon	-	0.05	0.05
Tungsten	-	-	4.0
Molybdenum	-	-	2.0
Tantalum	-	-	2.0
Boron	-	-	0.01
Zirconium	-	-	0.15

TABLE 3.

TYPICAL RAW MATERIALS USED IN MECHANICAL ALLOYING OF INCONEL MA 6000

Powders	Particle Size (μ)
Type 123 Inco Nickel	4-7
Chromium	-150 +75
Molybdenum	-45
Tungsten	-11
Tantalum	-45
Ni-Al-Ti Masteralloy	-150
Ni-Al Masteralloy	-150
Ni-B Masteralloy	-150
Ni-Zr Masteralloy	-150
Y_2O_3	210-400 Å

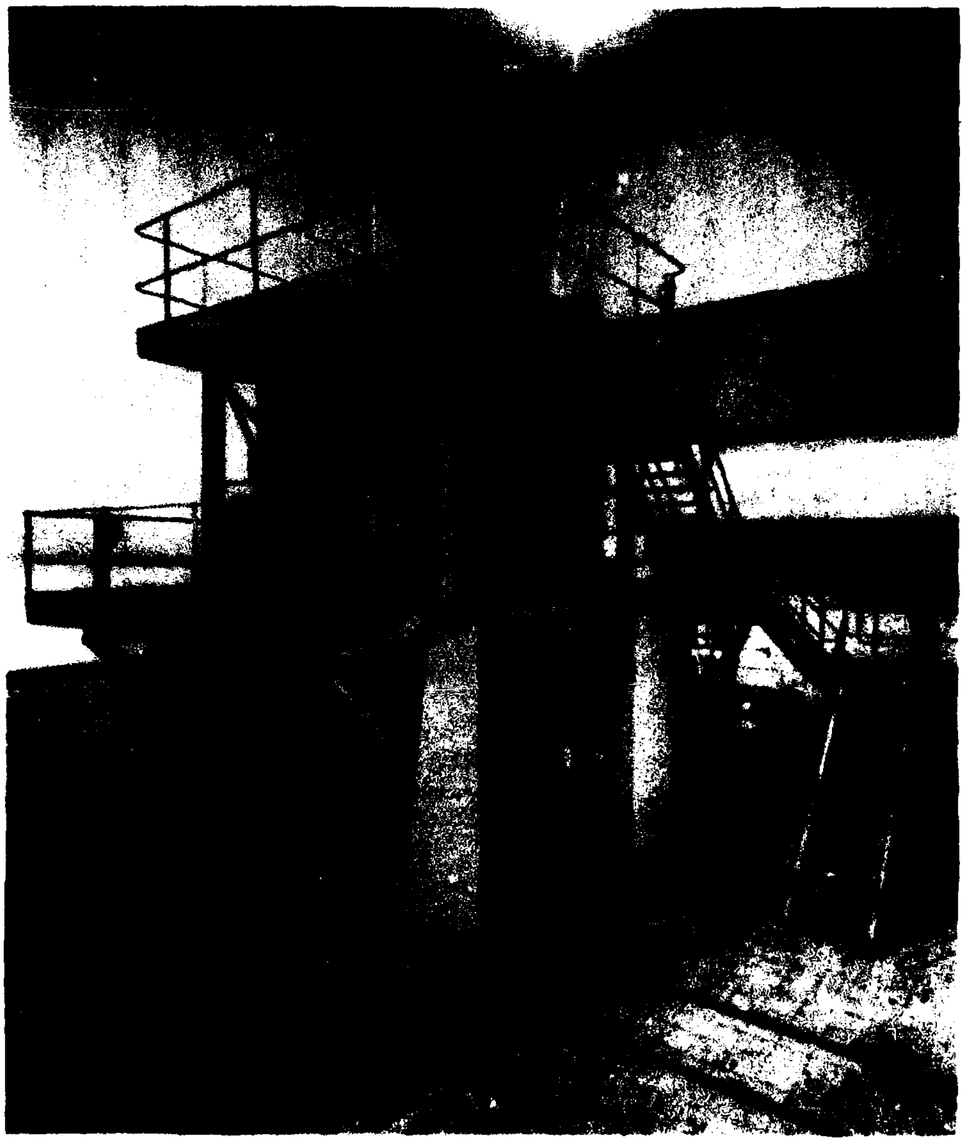


FIGURE 1: IncoMAP mechanical alloying facility. Each mill has a capacity of 50 tonnes/year oxide dispersion strengthened powders.

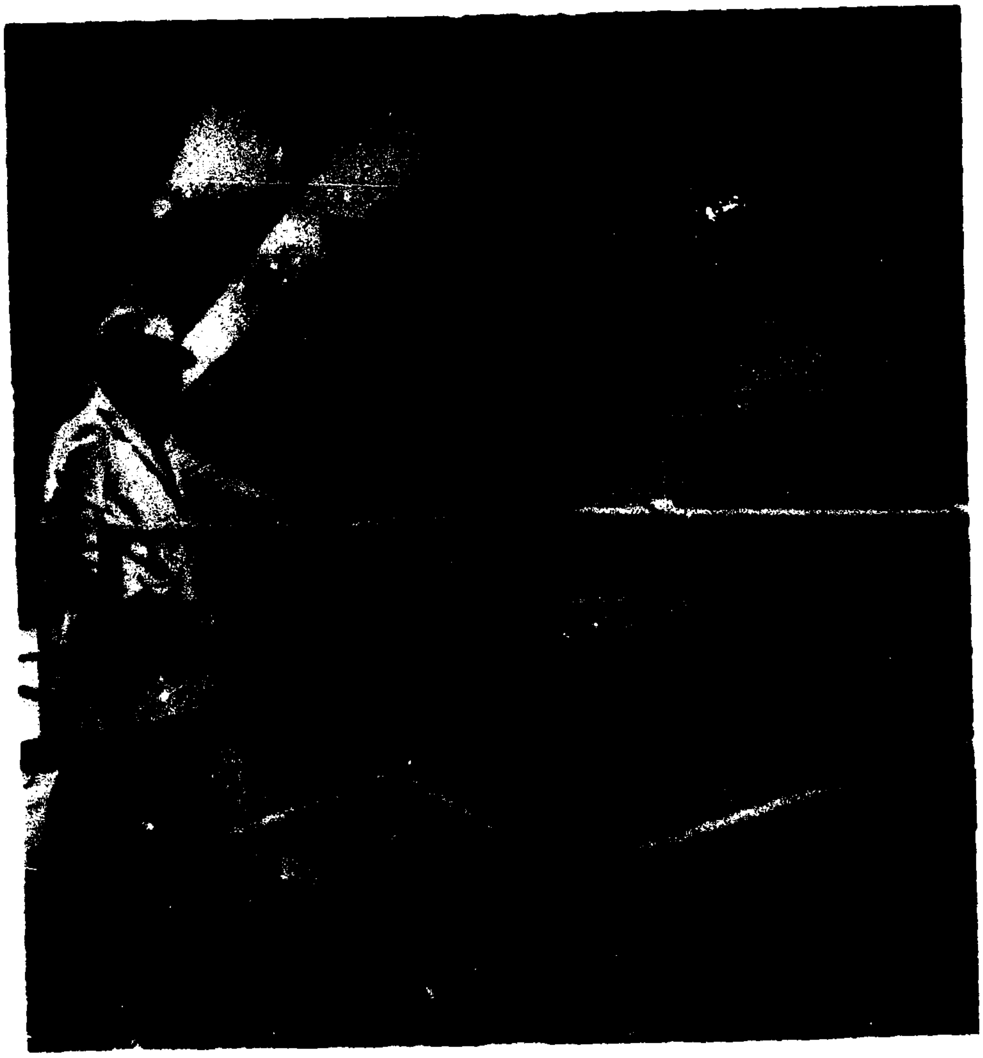


FIGURE 2: Mill about to be charged with alloy raw material powder blend.

FIGURE 3: Sequence showing accumulation of superalloy coating on process balls.

FIGURE 4: Raw materials comprising elemental powders and crushed master alloy. (Yttria powder is present but not visible).

FIGURE 5: Composite powder formation during processing.

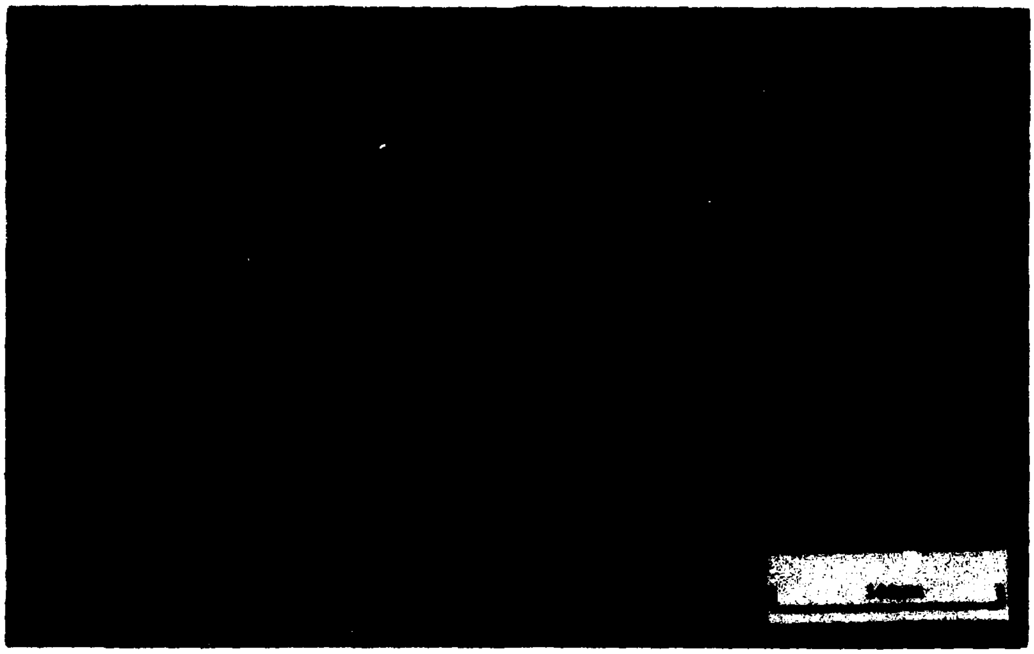


FIGURE 6: Fully processed powder.

FIGURE 7: Finely layered surface structure of processed powder. (SEM photo)

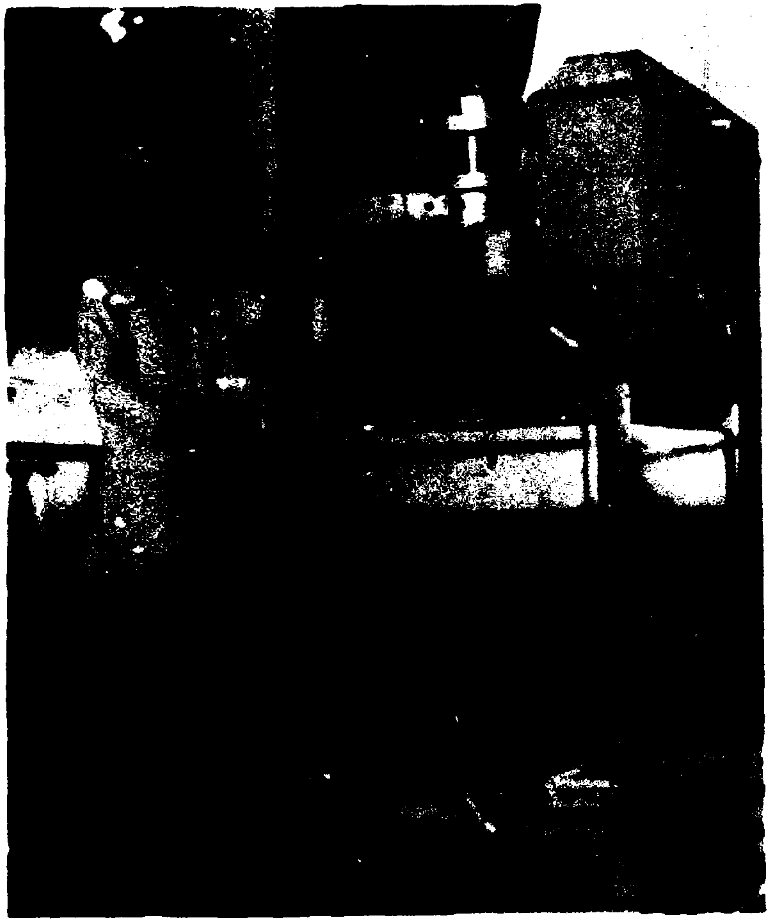


FIGURE 8: Discharging processed powder from mill into storage container.

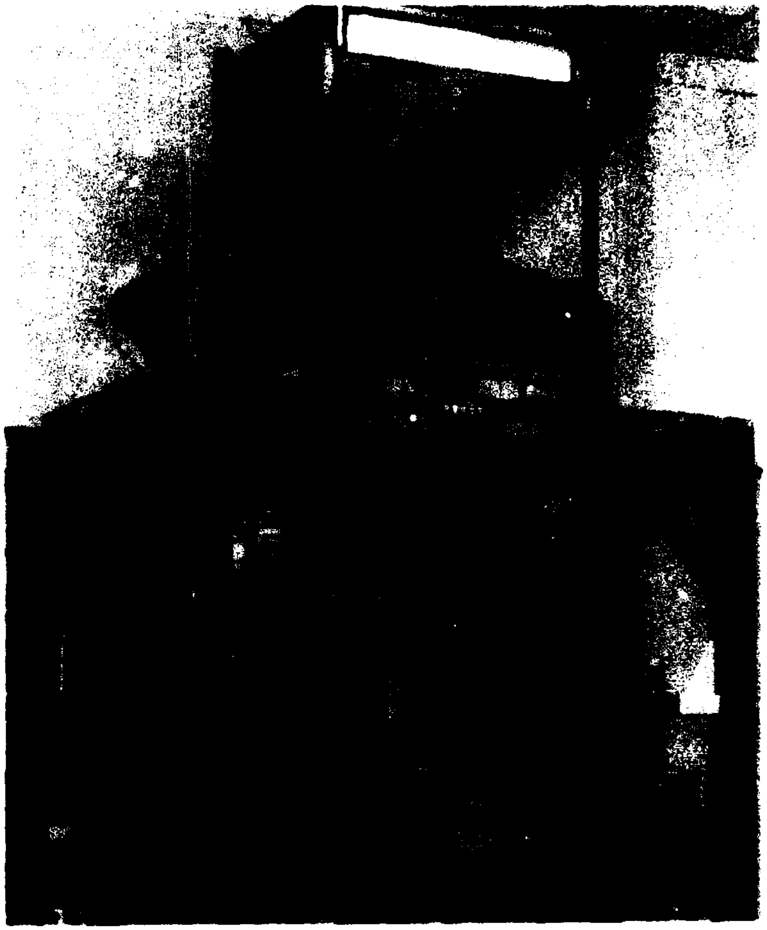


FIGURE 9: Sieving processed powder to remove oversize particles.

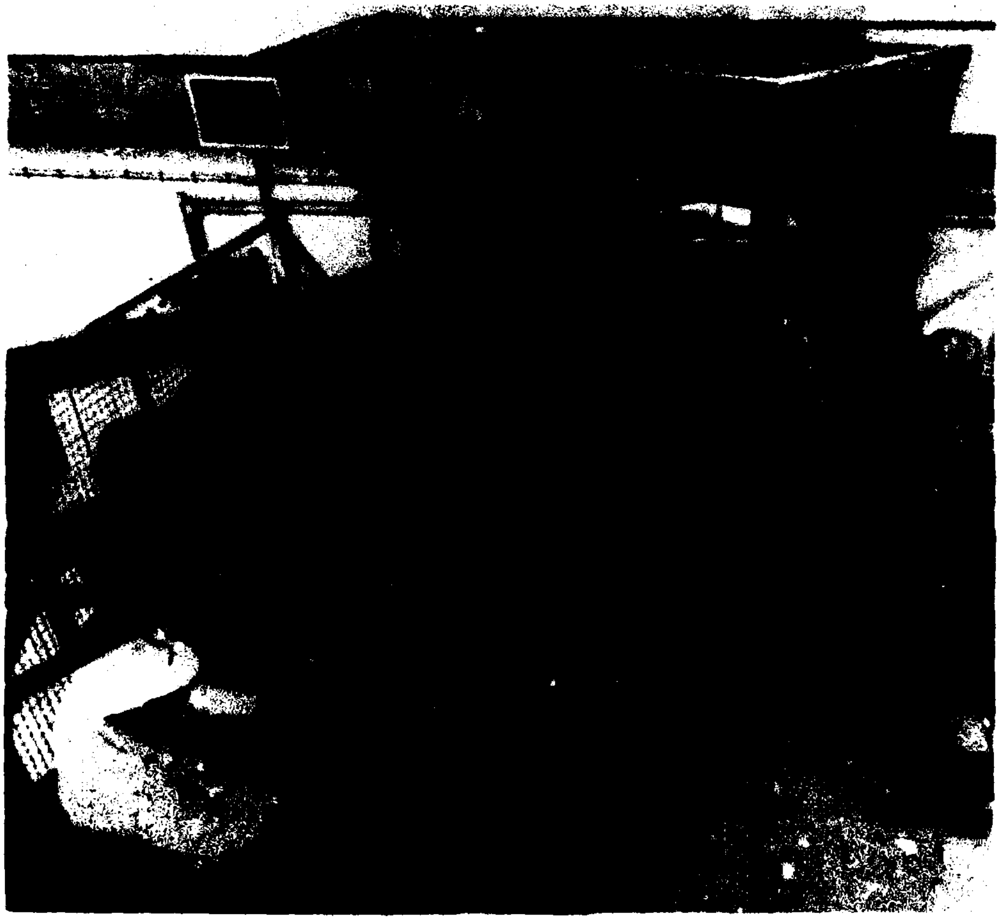


FIGURE 10: Powder container being loaded into frame of rotary blender.

FIGURE 11: Highly elongated grain structure of INCOLOY alloy MA 956 extruded bar after secondary recrystallisation.

FIGURE 12: Macrostructure of INCONEL alloy MA 754 bar.

FIGURE 13: Experimental gradient annealed structures in INCONEL alloy MA 6000 bar.

(a) Unaffected sub-micron equiaxed structure (as hot rolled).

(b) Limited region of static, steep temperature gradient above the secondary recrystallisation temperature.

(c) Coarse, nearly equiaxed structure annealed in static hot zone at maximum zone temperature.

(d) Coarse, highly elongated structure produced continuously in a steep moving temperature gradient by moving the bar.

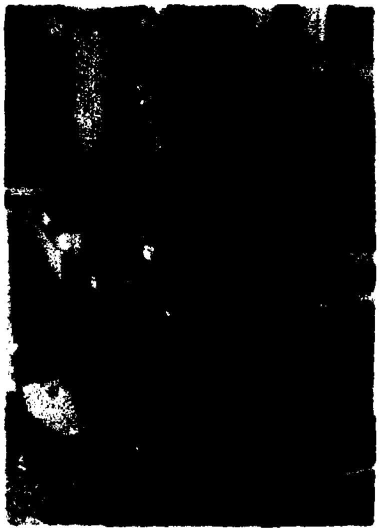


FIGURE 14: Zone annealer induction heating coil, pyrometer and bar grip mechanism.

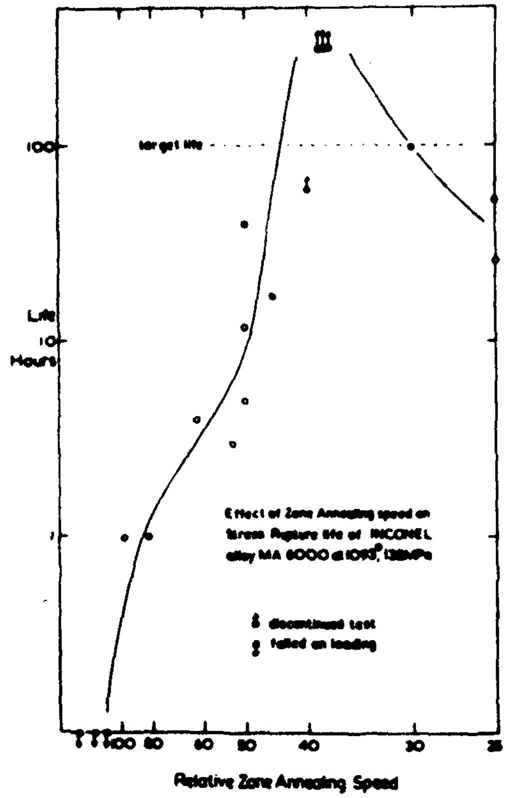


FIGURE 15: Determination of optimum zone annealing speed.

FIGURE 16: "Quadrant" grain orientation pattern in transverse section of INCONEL alloy MA 6000 bar.

FIGURE 17: Seamless rolled sections of INCOLOY alloy MA 956 intended for gas turbine rings.

FIGURE 18: Hot spun dish, sheet fabrications and forgings in INCOLOY alloy MA 956 and INCONEL alloy MA 754.

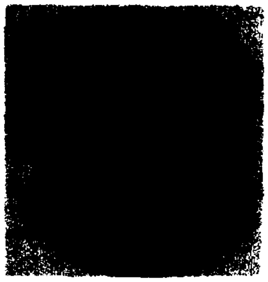


FIGURE 19: Prototype of an advanced high temperature combustion chamber using INCOLOY alloy MA 956.

FIGURE 20: Brazed turbine vane assembly currently in service and fabricated from INCONEL alloy MA754.

FIGURE 21: Solid turbine blade machined from INCONEL alloy MA 6000 bar.

Substitution and Conservation Technology for Chromium

AD-P004 218

By

Dr. Allen G. Gray
Adjunct Professor of Metallurgy and Management of Technology
Vanderbilt University Nashville, TN 37235
Past Technical Director, Presently Consultant
American Society for Metals
Metals Park, Ohio 44073

Summary

Chromium is a highly strategic and critical metal because of its significant import dependence and its essential uses for defense, energy and industrial products. It is used in such diversified applications as stainless steels and tool steels; alloy steels to provide hardenability in heat treatment, in air frames, and in landing gear; heat and corrosion resistant alloys; superalloys for jet engines; alloy cast iron; electroplating; and corrosion treatment for aluminum alloys. This paper presents information on application areas where substitution and conservation appear feasible in a supply crisis based on present available technology. Likewise, applications where research is needed to expand the substitution potential will be indicated. Opportunities for conservation and displacement with emerging technologies will be discussed. Finally, the value of an organized effort on "substitution preparedness" to gather and develop information on chromium substitution and conservation technology and have it ready as a contingency plan will be presented.

Chromium must be rated at the top of the priority list of critical and strategic metals because of its significant import dependence and its unique importance to defense, the aerospace industry, and modern industrial technologies. Its versatility as an alloying element is exemplified by its uses in many engineering materials including stainless steels, tool steels, alloy steels for hardenability in heat treatment, structural steels, heat and corrosion resistant alloys, superalloys, alloy cast iron and plated metal.

At the outset we should note that a significant factor contributing to the strategic importance of chromium is that many of its applications in essential alloy materials, particularly those used by the aerospace industry, are irreplaceable at present technology levels.

Because of its availability, effectiveness, and low cost, research in chromium alternatives has not been pursued as throughly as for other alloying elements. However a number of substitutes and technological options exist and implementation of these alternatives in a crisis would extend supply for the specific heat and corrosion resistant applications for which there are currently no viable substitutes for chromium.

In this presentation we will consider alternatives to chromium as an alloying element, both available technologies and opportunities for new technologies. Major points of emphasis are that technology for substitution, conservation and innovative displacement materials are among the most viable options for reducing vulnerability to a cut off of chromium and that now is the time to develop these technologies rather than after a crisis is upon us.

The issue of concern is vulnerability to disrupted supply and this suggests preparedness to adapt to a supply curtailment without serious consequences to national security, industry and commerce. It is prudent to have technology for alternatives tested, on the shelf, and an information system on their use ready for emergency preparedness. However, it should be recognised that the chromiumfree alternatives may not be economically viable at this time because of the low cost of chromium.

Chromium in Superalloys

Chromium is essential for elevated temperature oxidation and hot corrosion resistance of superalloys for aircraft jet engines. The chromium content of typical superalloys is given in Table 1. However, Prof. John K. Tien and his associates at Columbia University have pointed out that the high chromium content required for surface protection is not needed for the mechanical properties of superalloys and is often considered more deterimental than beneficial for these properties.

The possibility that over 90 percent of the chromium may not be needed opens the potential for conservation if methods can be developed to provide the surface requirements of chromium while eliminating the bulk of it from the alloys.

Surface alloying with chromium utilising ion implantation with controlled laser annealing of the implanted layer shows promise for conservation of chromium. With this method a high concentration layer of chromium near the surface can be built with a minimum number of implantation cycles.

Chromium Steel for Aerospace Applications

Other requirements for chromium consist of alloy steels and stainless steels for general aerospace applications as shown in Figure 1. The applications range from ultra high strength steels used in landing gear parts and structural fittings to stainless steels for tubing and ducting.

Not to be overlooked is chromium used in steels for forging dies and fabrication tooling. Estimated requirement for forging dies for a large transport made by one aircraft producer is 14 million pounds containing from 1 to 5 percent chromium.

Chromium containing ultra high strength steels, shown in the compilation below from Republic Steel Corp., are employed in forging applications for load bearing applications in engine mounts, tail section forgings, wing mounts, and landing gears. On a weight basis the largest use is landing gear.

Aircraft Landing Gear Steels

	Composition							
Alloy	C	Mn	Si	Ni	Cr	Mo	V	Other
98 BV 40	0.43	0.85	0.65	0.75	0.90	0.50	0.04	B
4330 M	0.30	0.95	0.27	1.80	0.85	0.40	0.08	-
4340	0.40	0.75	0.27	1.80	0.80	0.25	-	-
300M	0.40	0.75	1.65	1.80	0.80	0.40	0.80	-
HP 9-4-30	0.30	0.25	0.10	7.50	1.00	1.00	0.10	4.5 Co
HP 310	0.40	0.75	2.50	1.80	0.90	0.40	0.20	-

A workshop on chromium substitution held recently at Vanderbilt University brought out the fact that there is not any alloy research in progress which has as its goal the development of a chromium free steel for ultra high strength aircraft landing gear applications. As both military and commercial aircraft utilize the same alloys for landing gears this is an appropriate and vital area for alloy substitution research. This is in contrast with research work, that will be discussed subsequently, which has resulted in development of substitute chromium-free heat treatable steels and the establishment of a high technology base for chromium-free structural alloy steels.

The potential exists for displacement of high strength steels in new projects by titanium, and composite materials and by such alternate design approaches as illustrated by the hydraulic cylinder shown in Figure 2.

Substitution and Conservation options for Chromium In Stainless Steels for Corrosion and Oxidation Resistance.

There is a favorable trend toward substitution of precipitation hardening stainless steels with lower amounts of chromium in airframe applications. In some applications precipitation hardening bar, forging, and casting alloys of 17-4PH with 17 percent chromium are being replaced with 15-5PH containing 15 percent chromium and with PH 13-8Mo with 13 percent chromium. The vacuum melted PH 13-8Mo has improved mechanical properties without a compromise in corrosion and toughness characteristics.

Another trend affecting the use of chromium by aerospace is use of a higher chromium containing 21-6-9 alloy in place of AISI Type 321 stainless steel for hydraulic tubing. This is attributed to the superior cold worked mechanical properties of the 21 percent chromium alloy which results in significant weight savings over the 18 percent chromium 321 stainless alloy.

Titanium is an alternate material for hydraulic lines but its substantially higher cost, more difficult fabrication requirements and sensitivity to phosphate ester hydraulic fluids have limited its use. However it may be regarded as a viable alternative in the event of a chromium crisis.

Development of substitution and conservation options are evident in diverse engineering applications for stainless steels which can relieve some of the pressure on irreplaceable aerospace uses for chromium. There is increasing acceptance that although austenitic stainless steels contain 18 percent or more chromium for corrosion resistance, passivity is achieved with 12 percent and for many applications this amount will provide adequate corrosion resistance. Chemical industry applications may be exceptions.

The function of chromium as an austenite stabilizer in stainless steels can be fulfilled by nickel or manganese so that in an emergency the chromium content of replacement steels could be reduced to 12 percent. Austenitic steels with 14 percent chromium, compared with the traditional 18 percent chromium, have oxidation resistance and adequate strength for 1400° F service.

A 9Cr-1Mo steel modified with small additions of niobium and vanadium shows promise as a replacement for 18 percent chromium steel in steam power plant heat exchangers. New higher strength duplex stainless steels can lower total chromium demand by utilizing 50 percent reduced cross section although chromium content of these steels is higher. Research on an Fe-8Al-Mo alloy has demonstrated that a chromium-free iron base alloy can achieve high temperature oxidation resistance in air superior to that of AISI Type 304 stainless steel. Development of other new alloys without chromium is also underway: Iron-Manganese-Aluminum Alloys are being developed to substitute for austenitic nickel-chromium stainless steels in heat resistant applications at moderate temperatures and some corrosion resistant uses including the ocean environment.

Silicon Alloys Worthy of Development Efforts

High silicon molybdenum ductile cast iron is already in direct competition with high chromium steels in some high temperature applications on an economic basis. Si-Mo ductile is basically a standard ferritic nodular iron containing 4 percent silicon and 1 percent molybdenum. It is being used for turbocharger housings, exhaust manifolds, and furnace grates. It is probable that with minor design changes Si-Mo ductile iron could function in place of high chromium steels in numerous high temperature applications. A comparison of properties of the two materials is given in Figure 3.

While small additions of silicon, as noted above, enhance the oxidation resistance of materials, alloying with larger amounts (9-18 percent Si) provide excellent resistance to acqueous corrosion in many agressive acid media. Despite the excellent corrosion resistance of the high silicon alloys, the trend has continued toward more extensive use of chromium-containing stainless steels. This can be attributed to the limited mechanical properties, impractical fabricability, and poor weldability of the high silicon alloys.

It is evident that to expand the potential of these alloys as a viable chromium substitution option for corrosion resistant applications development efforts should be pursued to improve their mechanical properties and fabricability. Wrought, hot and cold-workable silicon containing alloys should be regarded as a goal to be achieved by recent advances in metallurgical processing declared A. I. Asphahani, Cabot Corp. at the Vanderbilt University workshop on Chromium Substitution.

In another approach, since many corrosion reactions occur on exposed surfaces, the high silicon alloys would be useful for weld overlaying, thermal spraying, and surface impregnation. A silicon impregnation process was developed in the early 1930's to provide components with excellent corrosion properties and to get around the brittleness and poor physical properties of high silicon alloys. The alloy surface containing 14 percent silicon had a thickness of 0.010 to 0.05 in. It is interesting to note that the developer of this process almost half century ago recognized the "strategic importance of replacing imported chromium with an element obtained from common sand." (Metal Progress, Oct. 1939)

Aluminides for Structural use at Elevated Temperatures

Both iron and nickel aluminides, as intermetallic alloys, have unique properties which make them attractive for structural applications at elevated temperatures. They are hard, stable, strong and resistant to elevated temperature oxidation and corrosion. The major difficulty, however, is their tendency to exhibit brittle fracture and low ductility.

Significant progress has been reported by Oak Ridge National Laboratory in improving the ductility of nickel aluminides (Ni_3 Al). The approach is based on addition of micro-alloying elements (Dopants) to control grain boundary chemistry and cohesion and reduce the tendency toward brittle intergranular fracture. Boron-doped nickel aluminides exhibit room temperature tensile ductility above 50 percent, the highest ductility ever achieved by polycystalline aluminides.

Unlike conventional alloys, the yield strength of microalloyed Ni_3Al increases at elevated temperatures, reaching a maximum around 600° C, as illustrated in Figure 4, showing test results for boron doped Ni_3Al and for advanced aluminides developed in recent research utilizing microalloying and thermomechanical treatment. The advanced Ni_3Al compositions have higher tensile strength at elevated temperatures than Waspaloy, an aircraft engine superalloy, as shown in Figure 5. These advanced aluminide alloys display at 600° C a yield strength of 120,000 psi (830 MPa) which is more than three times that of Hastelloy X, a ductile nickel base alloy. The resistance of aluminides to oxidation and sulfidizing atmospheres is a useful property for aerospace applications. Companies involved in production of aerospace alloys have expressed interest in the structural aluminides and plans are being made for preparation of large commercial heats for evaluation of properties.

Bearing Steels of AISI TYPE 52100 with Reduced Chromium

An alternate to standard AISI Type 52100 bearing steel, designated TBS-9 by its developer, the Timken Co., reduces chromium content from 1.5 to 0.5 percent. The low chromium alternate developed in anticipation of a possible chromium shortage satisfies all of the technical and bearing performance requirements of standard AISI 52100 bearing components. Because the new steel is more economical than 52100 it has received wide acceptance from users. The process was simply one of substitution of manganese and molybdenum for chromium based on prior work conducted on the influence of various alloying elements on hardenability of high carbon steels as shown in Figure 6.

User's experience has confirmed the equality of the substitute bearing steel and Timken reports that TBS-9 has replaced at least one third of its high carbon bearing steel orders, the best verification of its viability as an alternate ball bearing steel.

Bulk savings in chromium could amount to 910 tons annually in the U. S. if the TBS steel was substituted across the board in an emergency. It's likely that the producers of Type 52100 bearing steel have chromium-free proprietary compositions that could be brought forth in a crisis but are not being offered now because economics of applications are not favorable due to the low cost of chromium.

Heat treatable steels without chromium

About 17 percent of chromium consumed annually in the U.S. goes to produce constructional alloy steels where it used primarily for its effect on hardenability in heat treatment. While chromium is both highly efficient and cost effective in this application it can be replaced with alternative alloying elements.

Two grades of heat treatable carburizing steels widely used for gears and shafts are the AISI 8600 series containing nickel-chromium-molybdenum and the AISI 4100 series containing chromium-molybdenum. These two grades account for 60 percent of the chromium used in heat treatable alloy carburizing steels, which is about 10 percent of total U. S. requirements for chromium. Conservation by substitution of other elements for this chromium will reduce U. S. needs by 10 percent or extend the supply for those applications for which there is currently no viable substitute for chromium.

Research to develop new alloys to replace chromium in heat treated carburizing steels for gears and shafts was conducted at International Harvester Co. under sponsorship of U. S. Bureau of Mines and was reported at the workshop on "Conservation and Substitution Technology for Chromium" held at Vanderbilt University, October 1982. The chromium-free steels consist of a manganese-molybdenum substitute and a manganese-nickel-molybdenum substitute. The composition ranges for the replacement steels for AISI 4118 and AISI 8620 are given in Table 2. Tests conducted on experimental heats show that the chromium-free steels provide microstructure, heat treat response and mechanical properties equivalent to the 8600 and 4600 chromium containing grades. Hardenability bands for AISI 8620 and for AISI 4118 compared with the replacement chromium-free steels, given in Figure 7 and Figure 8, show an equivalent hardenability response.

Experience has shown that standard steels for applications requiring heat treatment can be replaced by new steels of different alloy composition provided the new steels exhibit the same hardenability, heat-treat response and mechanical properties. Thus by control of composition new chromium-free steels can be developed to replace standard steels in current parts without the need for redesign of the parts and with only nominal changes in process control parameters. Computer models for predicting hardenability, properties, and heat treatment requirements are now available to facilitate the development of new alloys. Basic assumption in the development of substitute heat treatable steels are:

- Engineering performance of a heat treated component is controlled by the carbon content, microstructure and residual stresses.
- The microstructure and residual stresses are governed by the carbon content, hardenability, and martensitic start-and-finish transformation temperatures.
- Alloy composition controls hardenability and transformation temperatures.

Thus opportunities exist to develop substitute steels composed of alternate non-strategic or less-strategic alloy elements provided the new steels have the same carbon content, hardenability, and martensitic transformation temperatures.

Chromium-Free Alloy Steels Ready when needed

Industrial research and development efforts by the steel industry in the United States have developed "on the shelf" alloy steels which conserve chromium, and are ready for use if the demand arises. Examples include a modified AISI 3120 alloy with chromium reduced from 1.50 percent to 0.60 percent. This alloy is already off the shelf and in use in automotive steering gear systems. Another alloy designated "2 Ni- 2 Mo" is being evaluated by Republic Steel Corp. for use in rock drilling bits and would reduce chromium content from 0.55 percent to zero compared with the currently used SAE-EX-55 steel.

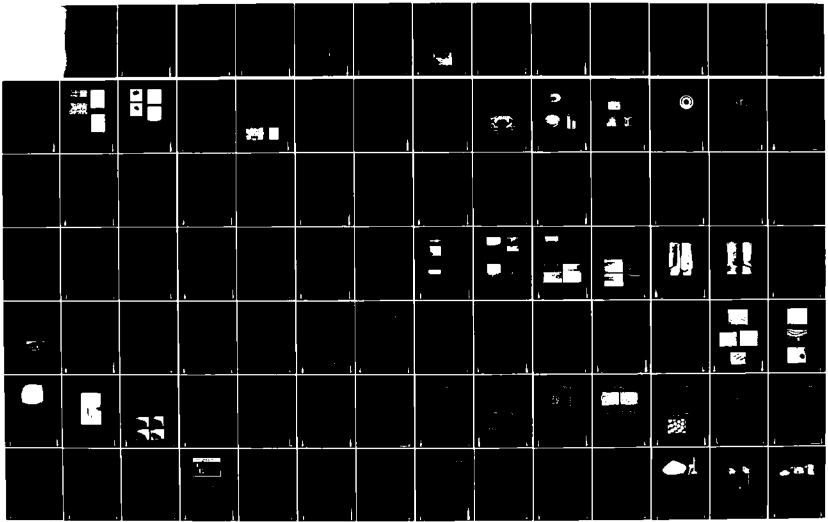
In terms of alloy bar steels, there would not be a serious problem. The technology is available to readily find alloy substitutes for chromium through the judicious use of molybdenum, boron, vanadium, manganese and nickel. Whether it is a carburizing steel, such as AISI 8620, or a through hardening steel such as AISI 4140 adequate non-chromium substitutes can be made available. Computerised hardenability prediction systems, previously noted, have proven to be accurate and fast and would shorten alloy development time for new steels to conserve chromium in a crisis.

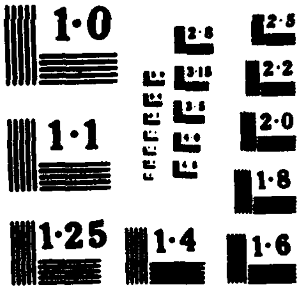
Carburizing Steels for Elevated Temperatures use

Additional research is necessary to determine the full potential of chromiumfree heat treatable carburizing steels for elevated temperature service in range of 600° F (315C) but prospects appear promising. To a large extent elevated temperature properties depend upon precipitation of alloy carbides during tempering at temperatures above the intended service temperature to form a strengthening dispersion stable at the operating temperature.

AD A146 598 MATERIALS SUBSTITUTION AND RECYCLING PROCEEDINGS OF THE MEETING OF THE ST..(U) ADVISORY GROUP FOR AEROSPACE RESEARCH AND DEVELOPMENT NEUILLY.. APR 84 AGARD CP-356 2/4

UNCLASSIFIED F/G 15/5 NL




1·0
2·8
2·5
3·2
2·2
3·6
2·0
1·1
4·0
1·8
1·25
1·4
1·6

The extent to which chromium enters into these various carbides is not well defined. However carbide precipitation and secondary hardening do occur in vanadium, molybdenum and tungsten alloyed steels without chromium additions, and such precipitation is the major prerequisite for good elevated temperature properties. A steel designated BC 1000 with about 1 percent chromium, as shown in Table 3, performed better than X-2M with almost 5 percent chromium in tests conducted by Climax Molybdenum Co.

Research on Pressure Vessel Chromium-Free Steels Needed

Chromium-free steels are available for most structural plate, an exception being pressure vessel plate. Annual consumption of ASTM A-387 steel grades used for pressure vessels, boilers and heat exchanges is 8,000 to 9,000 tons per year. The common grades contain either 1.25 percent or 2.5 percent chromium, which is required for high temperature strength, toughness and resistance to hydrogen. Pressure vessel steels are utilized in critically important applications and there is no research in progress to develop chromium-free alternate alloys for an emergency.

China Gear Steel Without Chromium or Nickel

What is described as a "Rare Earth Boron Steel" is being used in China for heavy duty carburized gears, and properties are reported to be better than those attained with conventional nickel-chromium gear steels. The steel used at the Nachang Gear plant has the following composition ranges in weight percentage: carbon 0.22-0.28; manganese 1.30-1.60; silicon 0.20-0.45; titanium 0.06-0.12; boron 0.001-0.004; Rare Earths 0.05. Chinese metallurgists attribute the improved rupture strengtn and toughness of the carburized gears to the rare earth additions.

High Strength Low Alloy Steels (HSLA)

HSLA steels constitute a new class of steels with high strength, toughness and formability achieved by applying advances in understanding of processing/microstructure/property relationships. The strength of these steels does not depend on traditional hardenability approaches and the majority do not contain chromium.

Properties are achieved by using microadditions, generally less than 0.1 percent of alloying elements, principally niobium, vanadium and molybdenum with controlled thermomechanical treatments. The use of these steels may be expanded to supplant chromium-containing heat treatable steels and low alloy steels in airframes.

Surface Modification and Alloying Systems

Metallurgical coating systems utilizing surface modification and alloying techniques such as ion implantation, laser and electron beam heating, ion bean mixing are currently undergoing rapid development. Coating techniques including electroplating, vapor deposition, sputtering, plasma spraying, and ion plating are currently in use in relevant applications.

From the technological viewpoint the use of all these techniques could be rapidly increased in the event of a severe chromium shortage. Certainly further technical progress and new capabilities will result from continual research in the area of surface modification. However, the potential for chromium conservation presented by advancement in coating systems should be pursued aggressively to develop these technologies into a viable option for emergency preparedness.

Established Coating Processes Conserve Chromium

Cladding with stainless steel is an important option for reduction in use of chromium where its primary function is to provide surface protection from corrosion, oxidation and/or wear. The technology for cladding carbon steels with stainless steel is well established and it is estimated that a substantial amount of the stainless steel plate used could be replaced by clad plate to conserve chromium.

Electroless nickel plate and nitriding are being used now where they are cost effective and could be used more widely for wear and corrosion protection if chromium was unavailable.

Alloying elements may be introduced by diffusion into the metal from a powder applied to the surface at elevated temperature. Chromium, diffusion bonded (0.002 in.) on low carbon steel sheet, may be used as an alternate to ferritic stainless steels in some applications. Alumnium diffusion coatings on steel are being employed in heat resistant applications.

Often surface treatments are effective in conserving instead of replacing chromium. An example is aluminized hot dip coated steel where the substrate instead of being a low carbon steel is a low alloy steel. Adding small amounts of chromium, aluminum, and titanium to the base metal increases the coated material's upper oxidation limit to 1500° F versus 1250° F. In times when low cost chromium is readily available, as it is today, for conservation to be effective a cost advantage inducement must be built-in. While material inertia holds back conservation in many existing applications, it's important that emerging high alloy applications be guided toward strategic material conserving alloys.

The Potential for Displacement Technologies

High performance ceramics offer many of the valuable properties that chromium contributes including high temperature strength, corrosion resistance, and hardness. Ceramics such as silicon carbide, silicon nitride and silicon alummium nitride have the potential for use in high performance aircraft engines and hot section components at temperatures comparable to those attainable with superalloys.

However to realize this potential major problems must be solved. The brittleness of ceramics is a major shortcoming. A better understanding of how to avoid flaws in the manufacturing process and the development of design approaches suitable for brittle materials are major challenges in the advancement of high performance ceramics as displacement materials for chromium containing high temperature alloys.

Composite technology is being pursued in all major areas of materials including polymers, metals and ceramics. Conservation of critical materials can result from direct displacement or from benefits due to a lighter aircraft. Composites represent one of the more promising technical possibilities for displacement of critical chromium by advanced materials.

Rapid solidification processing is another innovative materials technology which promises improved high temperature and high strength properties for engine and structural applications. This technology may lead to improved performance and to conservation of chromium and other critical metals. American jet engine manufacturers are devoting substantial research and development efforts to the process.

The Concept of Substitution Preparedness

In conclusion I would like to emphasize the value of an organized effort to gather and develop information on chromium substitution and conservation and have it ready as a contingency measure in event of a crisis.

As a spokesman for "substitution preparedness", which is how I referred to my recommendation, in testimony in the Congress of the United States, I pointed out that it is essential that appraisal and recording of substitution and conservation procedures in specific applications be as complete as available information allows. Thus, it is recommended that a plan be developed to "stockpile" this information. As research and development programs are developed to plug gaps and create new options for substitution and conservation, this technological know-how would be added to the information stockpile.

Needs for additional information on conservation options should be identified and defined so that research and development projects can be assigned to gather data required to expand capabilities in those areas which appear to be sound and achievable with available means.

It should be noted that leadtime is very short in an emergency situation. Thus a stockpile of information on substitution and conservation technology is also a stockpile of time, and a valuable, yet relatively low cost supplement to a strategic materials commodity stockpile.

Programs on substitution and conservation should be an important part of strategic planning for individual manufacturing firms. In presentations before company management groups I have encouraged an organized effort on strategic materials planning, including the development of substitution and conservation programs, pointing out that the objectives of a government initiative on substitution technology can be applied to company research and development programs on alternative materials for present and future products.

Acknowledgement:

Much of the information in this paper is gleaned from presentations and discussions at two industry/government/university/public workshops held at Vanderbilt University, Nashville Tennessee. The first workshop entitled "Conservation and Substitution Technology for Critical Materials" was held 15-17 June 1981 under sponsorship of U. S. Department of Commerce/National Bureau of Standards and U. S. Department of Interior/Bureau of Mines. The second workshop entitled "Conservation and Substitution Technology for Chromium" and "Trends in Critical Materials Requirements for Steels of the Future," was held 4-7 October 1982 under sponsorship of U. S. Department of Commerce/National Bureau of Standards, U. S. Department of Interior/Bureau of Mines and U. S. Department of Defense/Army Research Office. The writer served as organizer and general chairman of these two workshops.

TABLE 1. Chromium Content of Typical Superalloys

Wrought Ni-Base	Cr Content,
Waspaloy	19.5
Udimet 720	18.0
Udimet 700	15.0
Nimonic 115	15.0
Cast Ni-Base	
IN 738	16.0
Mar M200	9.0
IN 100	10.0
Alloy 713C	13.5
Iron-Base	
Inconel 718	18.5
Alloy 901	13.5
Incoloy 903	0.0
Cobalt-Base	
X 40	25.5
Mar M509	21.5
Mar M322	21.5

Waspaloy, Udimet, Mar M, and Nimonic, IN, Inconel and Incoloy are trademarks of United Technologies, Inc., Special Metals Corp., Martin-Marietta Inc., and International Nickel Company, Inc., respectively.

SOURCE Vanderbilt Workshop on Conservation and Substitution Technology for Chromium, October 1982

TABLE 2

CHROME-FREE REPLACEMENT COMPOSITIONS FOR STANDARD AISI 4118 AND AISI 8620 STEELS LADLE ANALYSIS RANGES

Chemistry Ladle Range, Percent	4100 TYPE STEEL*			8600 TYPE STEEL*		
	AISI-4118 Steel	Mn-Ni-Mo Replacement	Mn-Mo Replacement	AISI-8620 Steel	Mn-Ni-Mo Replacement	Mn-Mo Replacement
Carbon	.18 - .23	.16 - .21	.16 - .21	.18 - .23	.16 - .21	.16 - .21
Manganese	.70 - .90	1.00 - 1.30	1.00 - 1.30	.70 - .90	1.00 - 1.30	1.00 - 1.30
Chromium	.40 - .60	r	r	.40 - .60	r	r
Nickel	r	.20 - .40	r	.40 - .70	.40 - .70	r
Molybdenum	.08 - .15	.15 - .25	.25 - .35	.15 - .25	.25 - .35	.35 - .45
D_{IH}**, min, in	1.15	1.25	1.25	1.60	1.35	1.50
D_{IH}**, max, in	1.75	1.85	1.80	2.35	2.30	2.20
D_{IC}**, min, in	3.15	3.15	3.30	4.30	4.40	4.45

* The carbon content of the Mn-Ni-Mo and Mn-Mo replacements for the 8620 and 4118 steels is 0.02% lower than the standard grades. It is anticipated that this 0.02 % reduction in carbon content would be maintained throughout the entire replacement series.

** D_I values calculated from chemistry ±1/6 range.

r = residual level; Si range = .15-.35%; S = .05% max; P = .04% max.

SOURCE C. J. Keith and V. J. Sharma, Vanderbilt Workshop on Conservation and Substitution Technology for Chromium

Table III

CARBURIZING STEELS FOR ELEVATED TEMPERATURE SERVICE

Steel	Nominal Composition, Wt-%							
	C	Mn	Cr	Ni	Mo	W	V	Cu
CBS 1000	0.14	0.5	1.10	2.9	4.7	–	0.3	–
X-53	0.10	0.4	1.05	2.1	3.3	–	–	2.0
X-2M	0.15	0.3	4.80	–	1.4	1.4	0.4	–

Source Climax Molybdenum Co.
Vanderbilt Workshop on Conservation and Substitution Technology for Chromium

FIGURE 1

STEELS TYPICALLY USED IN AIRFRAME CONSTRUCTION

ALLOY STEELS	PRODUCT FORMS	APPLICATIONS
4130, 4140	BAR, FORGINGS, TUBING	FITTINGS, FASTENERS, WELDMENTS
4340, 300M, D6AC, 9Ni-4Co	BAR, FORGINGS	FITTINGS, LANDING GEAR STRUCTURE
H-11	BAR	FASTENERS
52100	BAR	BEARINGS
1085, 6150, 9254	WIRE	SPRINGS, CONTROL CABLE
STAINLESS STEELS		
17-4PH, 15-5PH	BAR, CASTINGS, FORGINGS	FITTINGS, HOUSINGS
PH13-8Mo, CUSTOM 455	BAR	FITTINGS, FASTENERS
17-7PH, AM350	SHEET, PLATE	DUCTING, FITTINGS, PANS, SPRINGS
3XX	BAR, SHEET, TUBING	FITTINGS, CABINETS DECORATIVE TRIM, DUCTING
21-6-9 (NITRONIC 40)	TUBING	HYDRAULIC LINES
440C	BAR	BEARINGS
A-286	BAR	FASTENERS

SOURCE Lockheed California Company, Vanderbilt Workshop on Conservation and Substitution Technology for Chromium

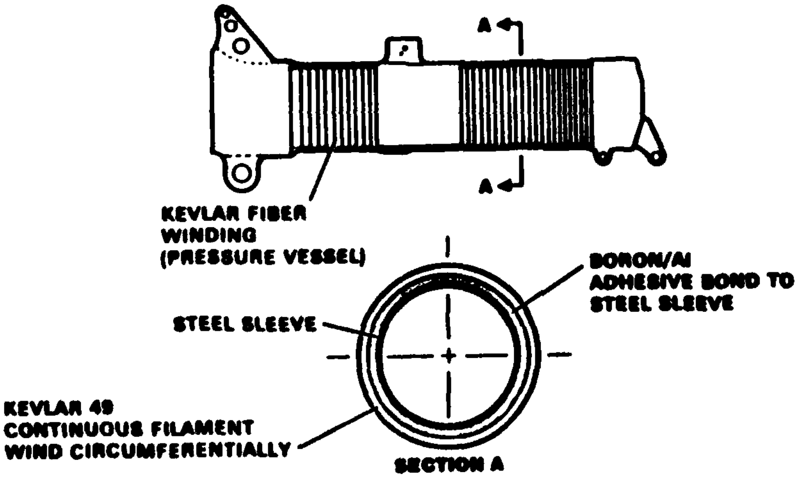
FIGURE 2

CONSERVATION OF CHROMIUM ALLOY STEELS

THROUGH

ALTERNATE DESIGN APPROACHES

CYLINDER



SOURCE. Lockheed-California Co., Vanderbilt Workshop on Substitution and Conservation Technology for Chromium

FIGURE 3.--Comparison of Properties of High-Chromium (HC) Steel and 4Si-1Mo Nodular Iron

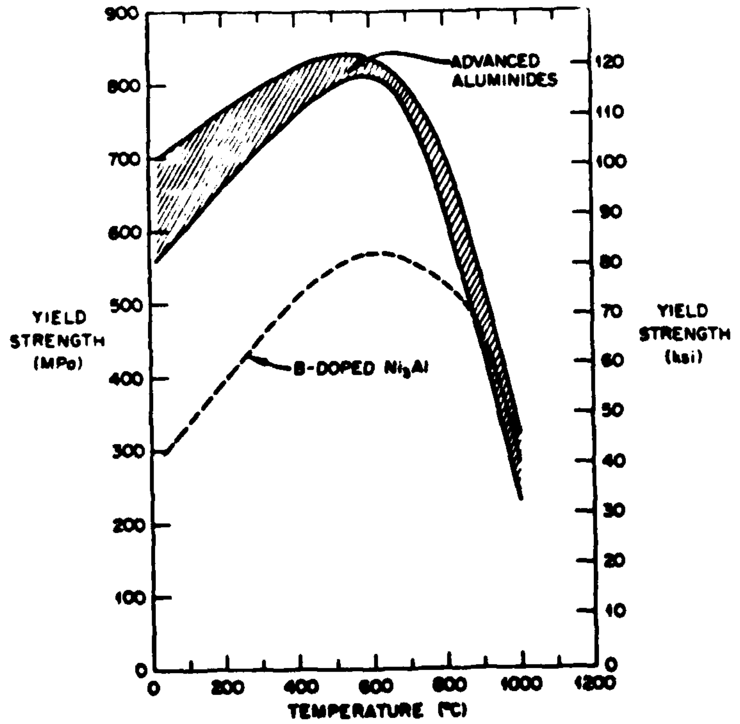
	HC STEEL	4 Si-1 Mo
Tensile Strength at Room Temperature	55,000 min.	80,000 min.
% Elongation at Room Temperature	2-19	8-19
Brinell Hardness No.	190-223	190-240
Load Bearing Service	up to 1200°F	up to 1500°F
Rupture Stress		
at 1300°F	–	3300 psi
at 1400°F	2300 psi	–

Source: Climax Molybdenum Co.

FIGURE 4

ORNL-DWG 83-13742

THE YIELD STRENGTH OF ALUMINIDE ALLOYS INCREASES WITH TEMPERATURE AND PEAKS AROUND 600°C



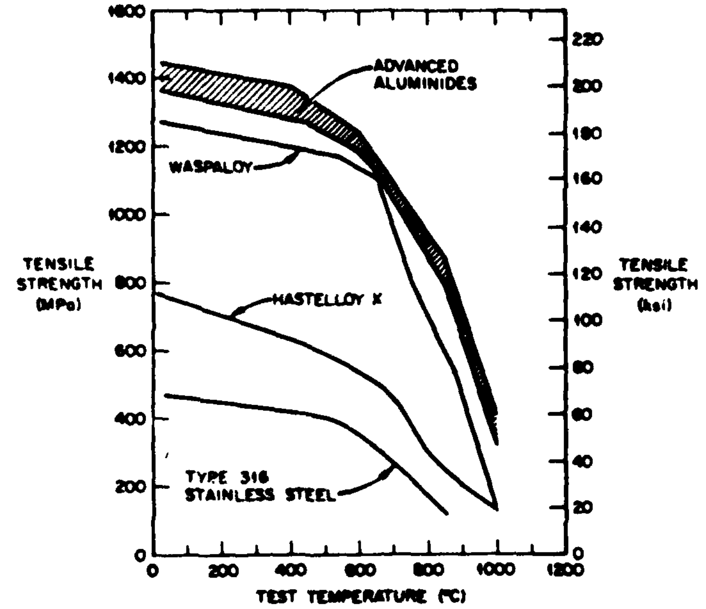
- THE STRENGTH OF Ni_3Al CAN BE SUBSTANTIALLY INCREASED BY MACROALLOYING WITH ALLOY ADDITIONS.

SOURCE: Dr. C. T. Liu, Oak Ridge National Laboratory

FIGURE 5

ORNL-DWG 83-13743

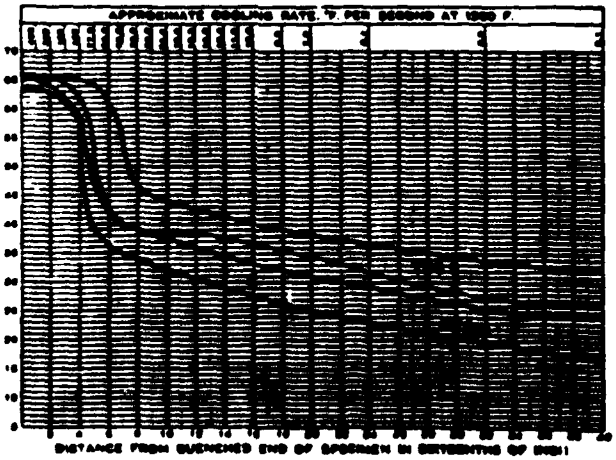
ADVANCED ALUMINIDE ALLOYS DEVELOPED AT ORNL HAVE HIGHER TENSILE STRENGTH THAN COMMERCIAL ALLOYS



SOURCE Dr. C. T. Liu, Oak Ridge National Laboratory

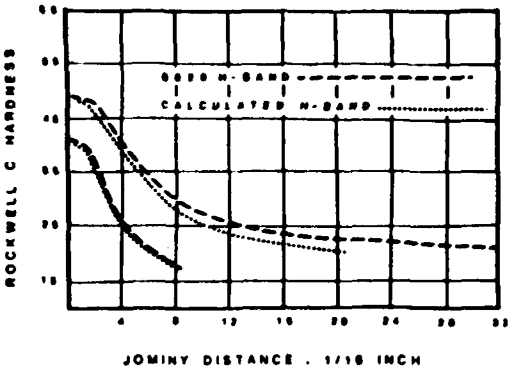
FIGURE 6 --Comparison of Hardenability of TBS-9, Low Chromium Bearing Steel With AISI 52100.

TYPE	HEAT NO.	C	Mn	Si	Cr	Mo	NORM. TEMP. °F	QUENCH TEMP. °F
52100	Avg 16 Hts.	.98/1.10	.25/.45	.20/.35	1.30/1.60		1650	1500
TBS-9	Avg 35 Hts.	.89/1.01	.50/.80	.15/.35	.40/.60	.08/.15	1650	1500



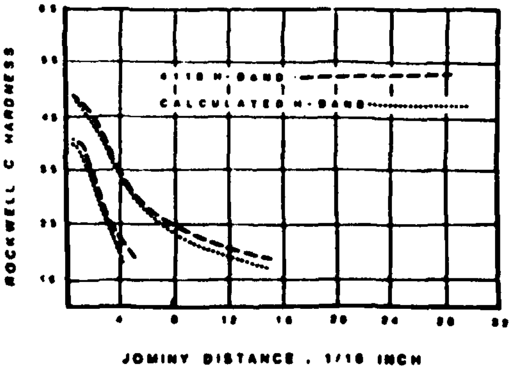
SOURCE C. F. Jatczak, Timken Company.

FIGURE 7.--Standard Jominy Hardenability Band for AISI 8620 Steel Compared to the Calculated Hardenability Band for the Chrome-Free Replacement Steels.



SOURCE: C. J. Keith and V. J. Sharma, International Harvester Co.

FIGURE 8.--Standard Jominy Hardenability Band for AISI 4118 Steel Compared to the Calculated Hardenability Band for the Chrome-Free Stels.



SOURCE: C. J. Keith and V. J. Sharma, International Harvester Co.

POTENTIAL OF METAL-MATRIX COMPOSITES AS SUPERALLOY SUBSTITUTES

by

M. McLean
National Physical Laboratory
Teddington, Middlesex TW11 OLW, UK

and

T. Khan
Office National d'Etudes et de Recherches Aerospatiales (ONERA)
BP72, 92322 Chatillon, Cedex, France

ABSTRACT

The potential of metal-matrix composites as gas-turbine blade materials has largely been judged on the increased temperature capabilities they offer over the strongest current superalloys. However, several composites that have been rejected on this basis are either independent of or have low concentrations of critical alloying elements. Consequently they should be reassessed as reserve materials matching the performance of existing widely used superalloys that depend on strategically vulnerable constituents. A review of metal-matrix composites for high temperature applications will be made in order to identify materials that are insensitive to the supply of critical elements.

An alternative approach might be to consider the potential of regenerating the original creep performance of certian monocarbide reinforced nickel based composites - such as Cotac 744 developed at ONERA - after service exposure. In this context the combination of perfectly elastic fibres in a creeping matrix would imply that high temperature deformation of these materials is almost completely recoverable. Hence, one should judge the potential of these materials in the light of total life expectancy through both the processing and regeneration conditions rather than from their simple creep behaviour alone.

INTRODUCTION

The principal motivation for the development of high temperature composite materials for gas turbine applications appears to have been to exceed the temperature capabilities of the very strongest superalloys. The aim has been to produce materials with an additional strengthening mechanism that remains operative after the usual hardening agent of nickel-base superalloys, viz γ' precipitate, has dissolved in the γ-matrix. Alloys have indeed been described that offer a clear technical advantage (1,2,3) over existing superalloys; however, processing difficulties affecting the economics of production have inhibited the exploitation of these materials. VerSnyder (4) has expressed the optimistic view that cost-considerations will only delay acceptance of these materials until the 1990's; however, there must be a danger that the advantages of these high strength composites will be superseded by developments in other materials (eg single crystals, oxide-dispersion strengthened alloys, ceramics).

The aim of this paper is to reassess the potential of high temperature composites in the context of the themes of the present meeting. Firstly, they will be considered as direct substitutes which match but do not necessarily exceed the performance of existing materials but which may offer significant advantages of reduced cost or reduced dependence on certain strategically vulnerable elements. Secondly, the response of composite materials to post-service rejuvenation procedures will be considered in order to assess the full potential service lives of components.

The emphasis will be on <u>in-situ</u>, rather than synthetic, composites since they are broadly compatible with existing investment casting and directional solidification technology and, consequently, are more likely to be accepted as direct substitutes for existing materials. It may be necessary to modify the processing conditions significantly (temperature gradient and solidification rate) and use different moulding materials in order to prevent mould-(or core-)melt interactions. However, the basic equipment and experience are available to allow commercial development of <u>in-situ</u> composites if an economic or strategic benefit warrants their exploitation.

CRITICAL METALS CONTENT

Analyses of import dependence of the US on critical metals have recently been published by Bradley (5) and by Metal Bulletin Monthly (6). These show that of the usual constituents of superalloys more than 90% of cobalt, chromium, tantalum, manganese and niobium originate from predominately Third World, South African and Eastern Bloc sources; consequently their supply is vulnerable to political and/or economic pressure. The situation is even more severe for the European industry which is dependent on virtually 100% of its raw materials so that nickel, titanium, tungsten, molybdenum and vanadium are also of strategic importance; the supplies of these elements, from ally nations, are perhaps politically assured but they are still subject to economic pressures. It would clearly be politic to have alternative materials less dependent on certain critical metals, available for use in important components in the event of disruption of supplies. It is unreasonable to consider the total elimination of all strategic elements in a metallic component; rather we shall describe the structure and properties of composites that have no or low concentrations of specific critical metals in relation to current materials. Their compositions are listed in Table 1.

CO-FREE ALLOYS

The mechanisms by which cobalt strengthens nickel-base superalloys have not been clearly established (7). Tien et al (7) have surveyed current evidence showing that the presence of cobalt can influence the volume fraction and solvus of the γ' precipitate, the stacking fault energy and the carbide chemistry which cumulatively lead to a large effect that makes cobalt an indispensible constituent of most advanced nickel-base superalloys.

While the benefits of Co have been incorporated in the development of the most advanced in-situ composites, such as the NITAC (2) and COTAC (1) series, some of the earlier versions were cobalt-free. However, the processing difficulties, low transverse ductilities and poor thermal fatigue resistance militate against any commercial exploitation of these materials. The γ-γ'-Cr_3C_2 alloy, developed at NPL (8), although not matching the high temperature strengths of the strongest in-situ composites is both cobalt-free and compares favourably with many current alloys.

a) Processing. Unlike many in-situ composites which must be directionally solidified very slowly (< 10 mmh^{-1}) in very high temperature gradients (~ 20 Kmm^{-1}), γ-γ'-Cr_3C_2 can be successfully prepared at high rates (up to 1000 mmh^{-1}) and in relatively low temperature gradients. This is similar to the conditions used in the directional solidification of superalloys. The alloy is relatively insensitive to the precise compositions acceptable microstructures being obtained from a range of casts made to commercial specifications (Figure 1). It would be necessary, however, to develop new mould and core materials since there are significant interactions between the melt and the conventional silica-base shell moulds (Figure 2). However, such a development may also be required to allow effective recycling of directionally solidified superalloys since silicon leached from the moulds can apparently weaken the longitudinal grain boundaries in directionally solidified components prepared from revert superalloys.

b) Physical properties. The density of 7.5 Mgm^{-3} is lower than that of most current superalloys (similar to IN100) and the melting temperature of 1320°C is as high as present superalloys.

c) Oxidation/corrosion resistance. The alloy has excellent cyclic oxidation resistance assessed by laboratory thermogravimetric tests and metallographic examination; this has been confirmed in burner rig tests performed by Rolls-Royce Ltd at 1323 K in an atmosphere containing 4 ppm NaCl. The results, shown as depth of attack as a function of time in Figure 3, compare favourably with previous data for typical stator and rotor blade alloys (C 1023 and MarMoo2 respectively). Indeed the uncoated γ-γ'-Cr_3C_2 has similar oxidation resistance to aluminised superalloys.

In the more severe corrosion rig test for 300 h at 850°C with fuel impurities of 0.15 sulphur and 50 ppm NaCl injected in the atmosphere there is no detectable loss of section although IN713 is severely affected in these conditions (Figure 4).

d) Mechanical Properties. The stress rupture data for γ-γ'-Cr_3C_2 are compared with those for currently available materials in Figure 5. The absolute comparison of 1000 h rupture stresses, relevant to stator blade applications, shows a substantial benefit over current stator alloys. A density compensated comparison, of interest in relation to rotating components, shows that γ-γ'-Cr_3C_2 matches most blading alloys in the appropriate stress range. In addition γ-γ'-Cr_3C_2 has adequate impact, fatigue, thermal fatigue, notch sensitivity and transverse creep behaviour.

FERROUS-ALLOYS

Although the NATO nations have a reasonably assured supply of nickel, there would be both cost and technical advantages if iron-base alloys could replace nickel-base superalloys for certain applications. As with γ-γ'-Cr_3C_2, the processing conditions for in-situ composites with M_7C_3 reinforcement in Ni, Co or Fe matrices are broadly compatible with current commercial directional solidification practice, economic solidification rates of ~ 30 mmh^{-1} being possible (9). A typical microstructure of an (Fe, Cr)-Cr_7C_3 in-situ composite solidified at 30 mmh^{-1} is shown in Figure 6. Several studies of such iron-base alloys have been reported (10,11,12) and the current status of these materials is summarised below.

a) Physical Properties. The alloys have low densities (~ 7.3 Mgm^{-2}) and melting temperatures of ~ 1200°C.

b) Oxidation/corrosion resistance. Iron based alloys containing aluminium and chromium together with minor additions of active elements (such as yttrium, cerium or lanthanum) have outstanding oxidation and corrosion resistance but are relatively weak. There has been considerable success in increasing the creep strengths of such materials, by incorporating carbide fibres, while retaining the excellent surface stability. The alloys with ferritic matrices tend to have better oxidation resistance than those with austenitic matrices although the latter have improved creep resistance. Figure 7 indicates the critical role that yttrium plays in improving the oxidation resistance.

c) Mechanical Properties. The stress rupture data are summarised in Figure 8 as plots of the stress to cause rupture in 100 h as a function of temperature. Information on current iron- and nickel-base superalloys are included for comparison. The ferritic in-situ composite (NPL A) shows a very substantial strength advantage over the single-phase FeCrAlY alloy which is finding increasing commercial application. However, the combination of strong fibre and weak matrix would be expected to lead to poor thermal fatigue resistance. Conversion of the matrix to the austenitic form has the dual effects of substantially increasing the rupture strength (Figure 8) and of giving better thermal fatigue performance. Two approaches have been taken to stabilizing the fcc form of the matrix by substituting nickel (11) (NPL B) or manganese (12) (UTRC) for iron. Both lead to similar stress rupture properties with about three times the rupture strength of the ferritic alloy. More importantly, they exceed the performances of advanced austentic ferrous alloys (CRM-6D) and of some nickel-base superalloys (Nimonic 80A, 90). Indeed with suitable density compensation these alloys are comparable to the strongest wrought superalloys (Nimonic 115).

CHROMIUM-FREE ALLOYS

Chromium is, perhaps, the most vital constituent of superalloys imparting the required oxidation/corrosion resistance; however, it is also among the most vulnerable to political or economic pressure. Rapid developments in coating technology, the subject of other sessions at this meeting, give the hope of using chromium-free or low-chromium alloys as the main structure of a component which can then be protected by a corrosion resistant coating. Several studies have been made of in-situ composites in the Ni-Al-Mo (3,13,14) system which show some promise. These range from alloys having superalloy-type γ-γ' matrices reinforced by α-Mo fibres (3,13) to γ'-α (14) eutectics.

a) Processing. These alloys can usually be directionally solidified at relatively high rates (up to 30 or 40 mmh^{-1}) but this requires very high temperature gradients. Thus exploitation of these materials would require substantial modifications to the current commercial directional solidification equipment and procedures. Also the dependence on coatings would introduce a substantial cost penalty.

b) Physical properties. This family of alloys has melting temperatures in excess of 1350°C and densities of about 8.5 Mgm^{-3}.

c) Oxidation/corrosion resistance. The total absence of chromium means that these materials have very poor intrinsic oxidation resistance. Some preliminary work has been carried out to determine their compatibility with coatings, but a great deal of further work would be required before such composite/coating systems could be exploited.

d) Mechanical properties. γ-γ'-α shows a substantial temperature advantage in stress rupture testing over all available directionally solidified and single crystal materials (Figure 9). Harf (13) has demonstrated that suitable heat treatments can give the material adequate shear creep performance and, like most in-situ composites the fatigue properties are very good.

ECONOMIC CONSIDERATIONS

The basic raw material costs of the various alloys described above, at 1980 prices, are listed in Table 2 together with similar information for current and projected rival materials. There is a clear potential cost advantage in all of these materials if they can be shown to be technically acceptable. The most advanced in-situ composites, such as COTAC 744 and NITAC 3-116A are presently much more expensive. However, one must consider the future usefulness of these materials both in terms of specific applications and the potential for savings through multiple service/rejuvenation cycles. Perhaps the most promising application of monocarbide reinforced eutectics is in small aeronautical engines ($\lesssim$ 1500 kW). Here the use of advanced cooling technology is extremely difficult due to the small dimensions and thin sections of high pressure (HP) blades. It is not surprising that even the most modern small engines generally use solid uncooled blades. The turbine inlet temperatures (TIT) can therefore not be increased substantially as in the case of large gas turbine engines which benefit from the latest cooling technology. However, the present trend towards higher TIT for achieving a higher specific thrust will either require cooling of these already very thin airfoils or use of materials capable of sustaining higher temperatures. Belaygue (15) has discussed and analysed in detail the various complications arising from an increase in TIT from 1050° to 1200°C which will necessitate the introduction of cooled blades in these small engines if conventional materials are used.

Since some advanced eutectic composites give a temperature gain of about 75°C over presently available DS superalloys and about 50°C over current single crystal alloys, the use of uncooled eutectic blades for such specialised applications may be viable. Examples of such components are shown in Figure 11.

COMPONENT RECYCLING

Another interesting property of certain monocarbide reinforced eutectics allows the original creep performance to be regenerated after service exposure. Therefore the overall economics of these basically expensive materials must take into account the life that can be achieved by multiple service/regeneration cycles.

The creep deformation of composites consisting of refractory fibres entrained in a relatively weak matrix is quite different from that in superalloys. When the fibres and matrix have widely different melting temperatures as, for example, NbC or TaC in nickel (eg in COTAC and NITAC alloys) it is unlikely that both phases will creep. Indeed transmission electron microscopy shows no carbide dislocations after creep at temperatures up to 1100°C. Rather, in service conditions the fibres, operating at very low homologous temperatures, will deform elastically gradually off-loading stress from the matrix to the fibres. The elastic deformation of the fibres is recoverable by heat treatment. This effect was first proposed and demonstrated by Khan et al (1) who designated it the "length memory effect".

Specimens of COTAC 744, whose microstructure is shown in Figure 12, were creep tested at various temperatures and stresses to about 1.2% strain in 200 to 300 hours. Previous work had shown that fibre fracture did not occur until about 1.3 to 1.6% strain. The specimens were re-heat treated without load (20 mins at 1200°C, AC + 16 hours at 850°C/ and observed to contract to virtually their original lengths as documented in Table 3. On re-testing, the material had similar properties to the virgin material. Consequentl the life expectancy of such materials can, in principle, be substantially extended by repeated rejuvenating heat treatments and an effective evaluation of the potential of advanced in-situ composites should take this into account. Clearly, the number of cycles that can be used in practice will depend on the dominance of other factors such as corrosion or fatigue crack growth.

Not all in-situ composites fully exhibit the length memory effect. For example, heat treatment of creep tested γ-γ'-Cr_3C_2 results in recovery of only part of the creep strain, the extent of recovery being greatest at low temperatures (Figure 10). This is probably due to the relatively high homologous temperature of Cr_3C_2, particularly at 825°C, resulting in creep of the fibres.

An important consequence of the stress carrying capacity of elastic fibres is that established extrapolation procedures, such as Larson-Millar plots, that have evolved for conventional engineering alloys, will always underestimate the long term properties of in-situ composites. In a recent theoretical treatment, McLean (16) has shown that for elastic fibres in a creeping matrix there is:

a) no steady state deformation

b) a decreasing creep rate that approaches zero when all of the stress is carried by the fibres

c) a break-down in the linear relationship between log (stress) and log (creep rate at 1% extension) or log (time to 1% extension) at low stresses where the creep performance is much better than indicated by data extrapolation.

CONCLUSIONS

Although in-situ composites have so far failed to meet the combined economic and technical targets for premier components such as HP1 turbine blades, at least some alloys appear to offer less direct benefits that could be of importance in the event of disruptions of supplies of critical metals

a) γ-γ'-Cr_3C_2 is a cobalt free alloy with good oxidation resistance and comparable strength to most existing superalloys.

b) Several iron-base composites with M_7C_3 reinforcement having no or little nickel, combine good oxidation resistance with the creep performance of many nickel-base superalloys.

c) γ-γ'-α is a high strength chromium-free alloy that may have uses in combination with protective coatings.

In addition, the potential of the most advanced composites, such as NITAC3-116A and

COTAC 744 (or their derivatives), may not be fully appreciated for the following reasons:

1) Time-dependent deformation in alloys with highly refractory fibres is totally recoverable so that the original properties can be re-established several times by heat treatment.

2) Extrapolation of short-term data always provides a pessimistic estimate of the long term performance of in-situ composites.

3) Introduction of cooled HP blades in small engines (< 1500 kW) may not be a practical way of increasing the overall engine efficiency and consequently the higher temperature capabilities of some eutectic composites may offer an attractive solution.

REFERENCES

1. T. KHAN, J.F. STOHR and H. BIBRING in Superalloys 1980, pp 531-540, edited by J.K. Tien et al, American Society of Metals, Metals Park, OH 1980.

2. C.A. BRUCH, R.W. HARRISON, M.F.X. GIGLIOTTI, M.F. HENRY, R.C. HAUBERT and C.H. Gay, Proc. of Conference "In-Situ Composites III, pp 258-267, edited by J.L. Walter et al, Ginn and Co, Lexington, Mass., 1979.

3. M.F. HENRY and M.R. JACKSON, NASA report CR-159416 (1979).

4. F.L. VERSNYDER in "High Temperature Alloys for Gas Turbines 1982". pp 1-50, edited by R. Brunetaud et al, Reidel Publishing Co., Dordrecht, Holland (1982).

5. E.F. BRADLEY, "Critical Metals - Conservation, Recycling and Substitution", AGARD discussion paper, 1982.

6. Metal Bulletin Monthly, "How Strategic are Strategic Metals?" pp 43-60, August 1982.

7. J.K. TIEN and R.N. JARRETT, in "High Temperature Alloys for Gas Turbines 1982", pp 423-446, edited G.R. Brunetaud et al, Reidel Publishing Co., Dordrecht, Holland (1982).

8. E. BULLOCK, P.N. QUESTED and M. McLEAN, Proc. of Conference "In-Situ Composites III", pp 420-430, edited by J.L. Walter et al, Ginn and Co., Lexington, Mass (1979).

9. V.W. HILDEBRANDT and P.R. SAHM, J. Mater. Sci., 13, 1031 (1975).

10. J. VAN DEN BOOMGAARD and A.M.J.G. VAN RUN, Proc. of Conf. on In-Situ Composites, p 161, edited by F.D. Lemkey and E.R. Thompson, NMAB Report 308-II, National Academy of Sciences, 1973.

11. P.N. QUESTED, D.E. MILES and M. McLEAN, Metals Technology, 7, pp 433-440 (1980).

12. F.D. LEMKEY, E.R. THOMPSON, J.C. SCHUSTER and H. NOWOTNY, Proc. of Conf. "In-Situ Composites IV", pp 31-50, edited by F.D. Lemkey et al, North Holland, NY (1983).

13. F.H. HARF, Proc. of Conference "In-Situ Composites III", pp 399-409, edited by J.L. Walter et al, Ginn and Co, Lexington, Mass 1979.

14. D.D. PEARSON, Proc. of Conference "In-Situ Composites III", pp 389-398, edited by J.L. Walter et al, Ginn and Co, Lexington, Mass 1979.

15. P. BELAYGUE, AGARD Conference Proceedings 229, High Temperature Problems in Gas Turbine Engines, 1977.

16. M. McLEAN, "Directionally Solidified Materials for High Temperature Service", Book 296, The Metals Society, London, 1983.

Table 1. Compositions of <u>in-situ</u> composites (wt%)

Alloy	Ni	Co	Cr	Al	C	Fe	Mo	W	Ta	Nb	Mn	Y	V	Re
a) γ-γ'-Cr_3C_2	bal	-	12.3	6.9	1.8	-	-	-	-	-	-	0.5	-	-
b) Fe-base														
NPL A (ferritic)	-	-	33.2	3.2	2.6	bal	-	-	-	-	-	0.8	-	-
NPL B (austenitic)	15.0	-	18.2	3.2	2.6	bal	-	-	-	-	-	0.8	-	-
UTRC (austenitic)	-	-	20.0	-	3.2	bal	-	-	-	-	10.0	-	-	-
c) γ-γ'-α	bal	-	-	6.0	-	-	32.0	-	-	-	-	-	-	-
γ'-α	bal	-	-	2.2	-	-	21.0	-	35.9	-	-	-	-	-
d) COTAC 744	bal	10	4	6	0.47	-	2	10	-	3.8	-	-	-	-
NITAC 14B	bal	3.7	1.9	6.5	0.24	-	-	-	8.2	-	-	-	4.2	6.3

Table 2. Raw material costs of <u>in-situ</u> composites and conventional high temperature alloys. (1980) prices.

<u>Alloy</u>	Cost <u>£/Kg</u>	
γ-γ'-Cr_3C_2	5.3	<u>in-situ</u> composites
Fe-base		
NPL A NPL B UTRC	1.5 - 4.0	
γ-γ'-α	9.5	
γ'-α	53.7	
COTAC 744*	12.5	
NITAC 14B*	>20	
IN 738LC	11.3	superalloys
IN939	14.0	
IN 100	11.4	
Mar M002	16.3	
X-40	25.2	

* The low yield of COTAC and NITAC alloy components due to slow processing rates and the small number of blades produced per cycle may lead to a substantial premium on the processing stage over the cost of DS and single crystal superalloy castings.

Table 3. Improvement in stress rupture life of COTAC 744 after repetitive heat treatments

Creep test conditions		Gauge length mm					Time to rupture, h	
Temp °C	Stress MPa	Initial	1st creep	Heat treat	2nd creep	Heat treat	cumulative	un-interrupted
850	400	30.02	30.40	30.06	30.42	30.10	1040	700
900	310	29.98	30.36	30.08	30.35	30.08	1303	700
1000	220	30.00	30.36	30.06			302	200

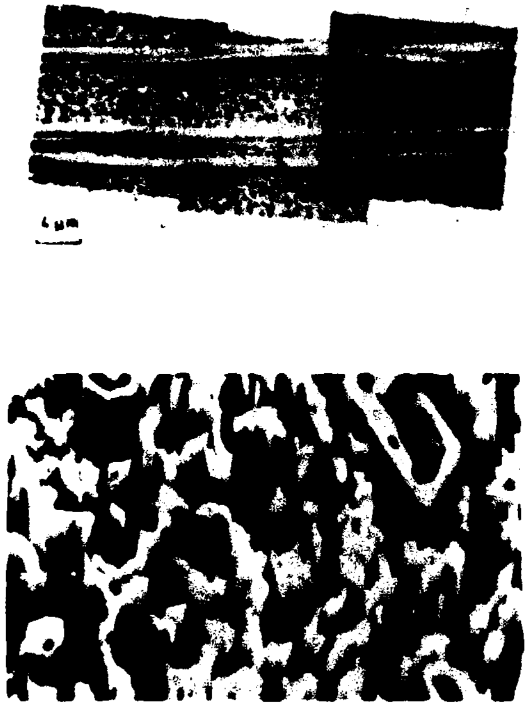


Figure 1. Micrographs of (a) longitudinal and (b) transverse sections of γ-γ'-Cr_3C_2 directionally solidified at 300 mm h^{-1} in a temperature gradient of ~ 13 Kmm^{-1}.

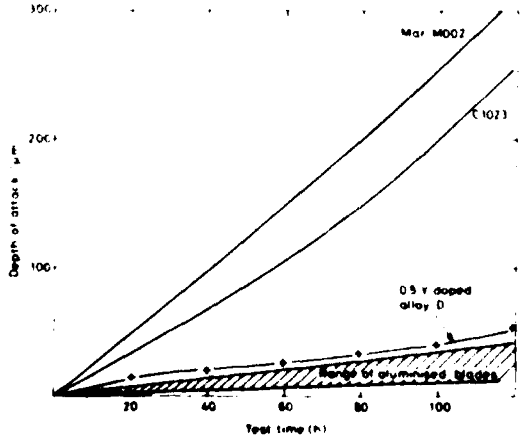


Figure 3. Depth of penetration of corrosion products during burner rig tests at 1323 K with 4 ppm salt.

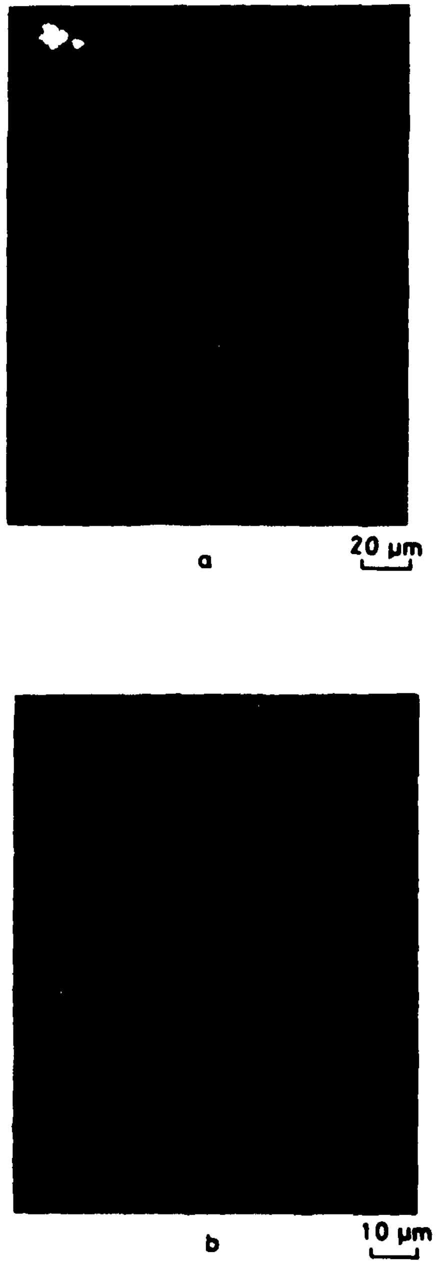


Figure 2. Transverse sections of γ-γ'-Cr_3C_2 directionally solidified in (a) a conventional silica-bound shell mould and (b) recrystallised alumina.

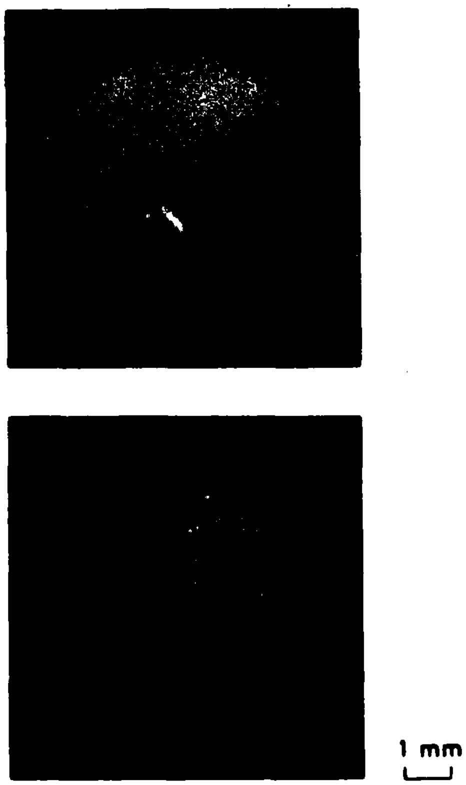


Figure 4. Comparison of sections of (a) γ-γ'-Cr$_3$C$_2$ and (b) IN713LC after burner rig tests at 850°C for 300 h.

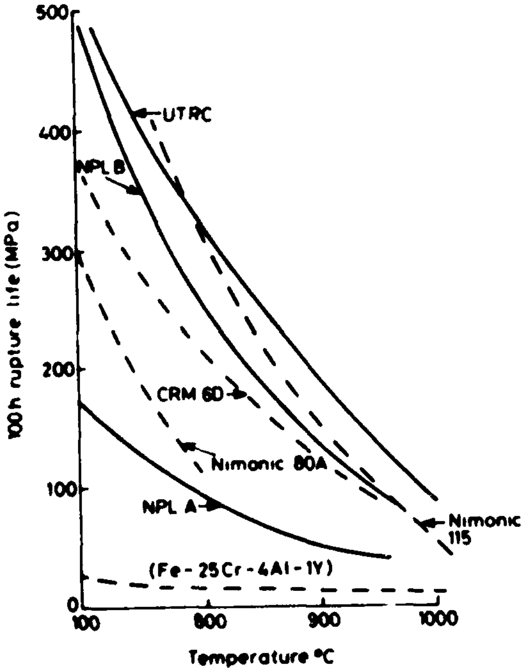


Figure 8. Stresses to cause rupture in 100h as a function of temperature for ferrous *in-situ* composites. Data for conventional iron- and nickel-base alloys are included for comparison.

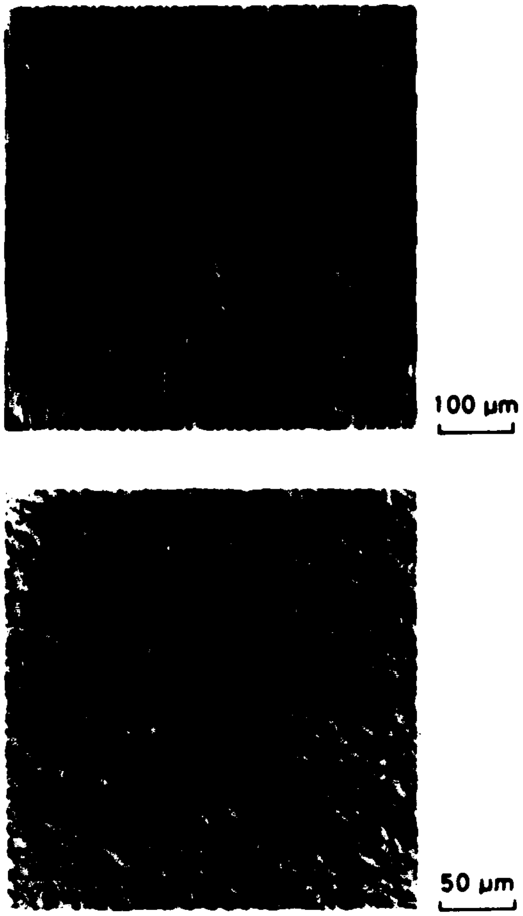


Figure 6. Micrographs of (a) longitudinal and (b) transverse sections of the FeCrAlY-Cr$_7$C$_3$ *in-situ* composite (NPL A) directionally solidified at 300 mmh^{-1}.

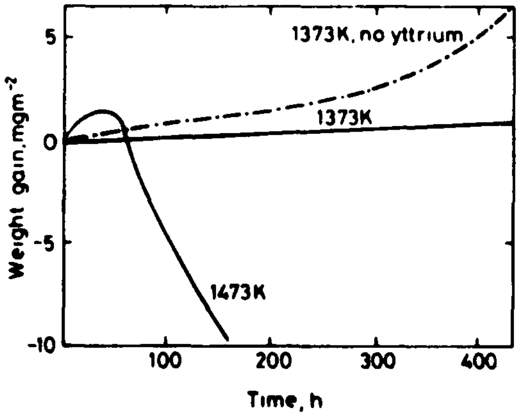


Figure 7. Comparative weight changes during cyclic oxidation testing of ferrous *in-situ* composites.

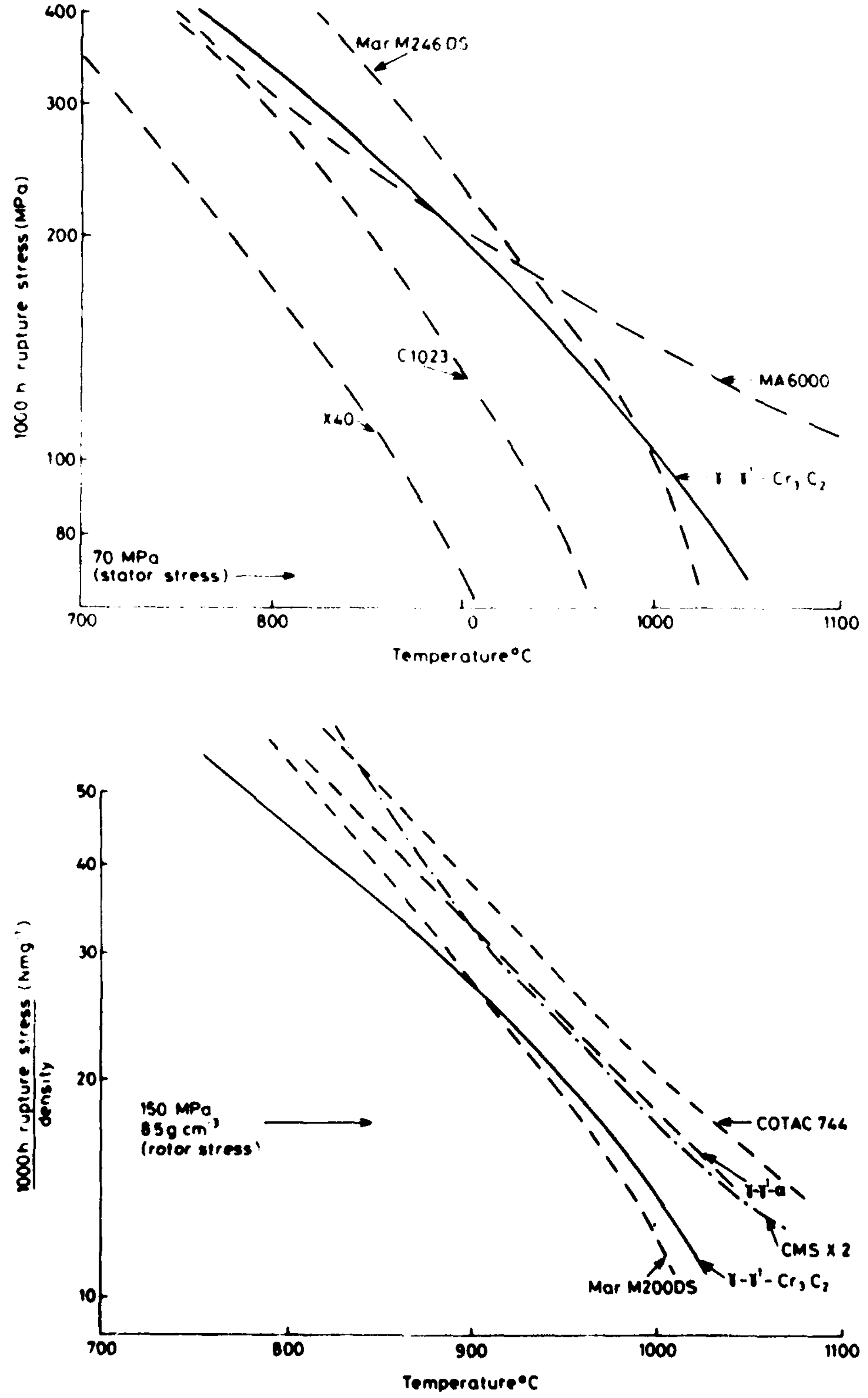


Figure 5. Stresses to cause rupture in 1000 h as a function of temperature for γ-γ'-Cr_3C_2. Data are shown for rival superalloys and in-situ composites for comparison (a) absolute stresses (b) density compensated stresses.

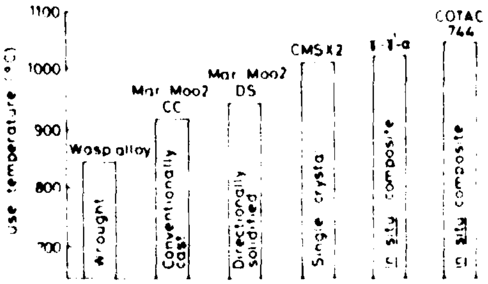


Figure 9. Potential rotor operating temperature for γ-γ'-δ in relation to rival alloys.

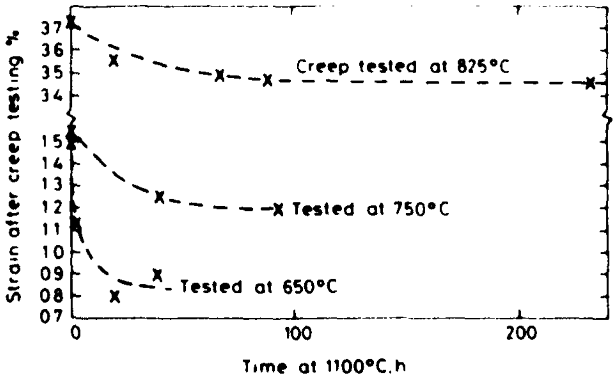


Figure 10. Change in length with time of creep specimens of γ-γ'-Cr_3C_2 during unloaded heat treatment at 1100°C after different prior test conditions.

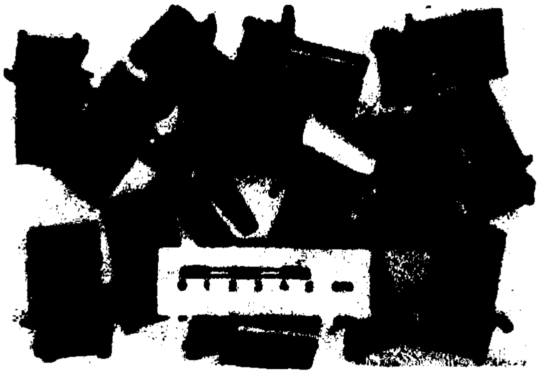


Figure 11. **Finished uncooled blades of the COTAC 74 in-situ composite.**

Figure 12. **Typical microstructure of a γ-γ' monocarbide reinforced COTAC eutectic (transverse section of COTAC 74 showing NbC fibres embedded in a γ-γ' matrix).**

MANUFACTURING DEVELOPMENTS TO REDUCE STRATEGIC MATERIALS USAGE

by

M. M. Allen, D. S. Halfpap, M. A. Siegel

Pratt and Whitney Aircraft Group
Government Products Division
P. O. Box 2691
West Palm Beach, Florida 33402
U. S. A.

AD-P004 220

ABSTRACT

The worldwide shortages and price escalations of cobalt, titanium, tantalum and other key elements in the late 1970's instigated manufacturing development programs to reduce their usage in gas turbine engines. This paper describes several programs which provided significant results in reducing raw material requirements, that have been reduced to practice. The programs include forging and casting complex parts to near net shape, recycling of machining scrap and used parts, repair and refurbishment of damaged or worn parts, and component retirement for cause. In addition to reduction of strategic material usage, these programs have resulted in lower cost parts due to reduced material input requirements and less machining.

INTRODUCTION

The spectacular growth of the aerospace industry in this century has been, in no small way, made possible by the accompanying growth in materials and process technology. In the span of a lifetime, we have been witness to the growth in aircraft capabilities from the wood and canvas aircraft with their piston engines made from off-the-shelf iron, steel and aluminum alloys, to the modern gas turbine powered aircraft of today. These advances required the development of specialized titanium, aluminum, and superalloy materials with high strength-to-density ratios, and very high temperature capability. To achieve these levels of performance, alloying elements such as cobalt, chromium, nickel, tantalum, titanium, and columbium were required. These elements are highly import dependent, as can be seen in Figure 1, being mined in some areas of the world which have been highly volatile over the years. Their importance to modern aircraft production coupled with their high import dependence has led to their classification as "strategic materials." Table I shows the amount of strategic materials that are required to make an F100 engine.

The first non wartime connected disturbance in the availability of strategic materials occurred in 1977 when civil disturbance in Zaire interrupted the mining of cobalt containing ore and resulted in allocation of supplies to users. This was accompanied by severe escalation of price ranging from 500% for producer cobalt to as high as 1000% for free market material. At the same time production requirements for civil and military aircraft and engines was high which aggravated the problem. Accompanying the cobalt problem were shortages in other key elements such as tantalum and titanium. The titanium shortfall was not due to a shortage of raw material (rutile) but rather was caused by insufficient equipment required to convert rutile to sponge.

MANUFACTURING DEVELOPMENTS

These shortages, which lasted for several years, resulted in programs at aircraft and engine manufacturers to reduce the usage of strategic materials. The programs initiated at Pratt and Whitney Aircraft at that time consisted of five basic elements. First, efforts were initiated to substitute alloys with less strategic material content, or to develop new alloys with less strategic material content. Second, a major manufacturing technology program was initiated to reduce input material requirements for forgings and castings and to revert scrap material. Third, programs were started to repair and restore damaged or worn parts. Fourth, a major effort to extend the cyclic life of rotor components was undertaken in the USAF Retirement for Cause program, and fifth, advanced technology engine designs were initiated with greatly reduced parts count. This paper will primarily address the reductions in strategic materials achieved through manufacturing technology, component repair and rejuvenation and retirement for cause.

It should be recognized that there are no basic strategic materials problems at this time. Cobalt is available at 1976 prices, and titanium sponge production capacity is more adequate. But, it should also be recognized that the primary source of relief from strategic materials problems has been the worldwide recession in the aircraft industry, with credit also to the strategic materials programs started in 1977. The potential for strategic material shortages and price escalations still exists particularly as new aircraft and engine orders increase.

In the area of manufacturing technology, two generic parts categories offered the promise of significant savings. Fan, compressor, and turbine disks have traditionally involved significant scrap in machining to final shape from conventional forgings. The advent of GATORIZED® superplastic forging of superalloy and titanium disks resulted in considerable savings in input material due to the inherent capability of forging closer to net shape. The GATORIZING process developed by Pratt and Whitney Aircraft takes advantage of the phenomenon of superplasticity of certain alloys, where the amount of energy needed to deform the metal diminished by producing the right structure and grain size. Figure 2 shows greater than 50% raw material savings in a typical F100 engine disk from conventional hammer or press forging compared to GATORIZING.

Refinements to the GATORIZING process were made to further reduce input material and reduce cost. Figure 3 shows a 40% reduction in input material for nine F100 components progressing from prototype GATORIZED forgings to today's production. Much of this technology was developed by Pratt and Whitney Aircraft under U.S. Air Force Materials Laboratory sponsorship.

The second area that has historically required very high quantities of raw material is large structural engine cases. Typically these cases are made from forged rings and struts which require extensive machining and joining. Under U.S. Air Force sponsorship, Pratt and Whitney Aircraft initiated a manufacturing technology program to apply and scale up conventional casting techniques to large cases. Initially, individual struts and rings were cast and tested for structural adequacy, and finally entire cases were cast in one piece as shown in Figures 4 and 5. The results of this technology are being incorporated in production engines. To date a reduction of 50% has been achieved, with potential for even further reduction as the technology continues to mature.

In 1977 when the pinch of cobalt and titanium shortages were first felt, an immediate action that was recognized was to utilize scrap material more effectively. Traditionally, aerospace scrap had been sold to dealers and downgraded for uses in less critical applications. To keep scrap material within the industry, it was necessary to segregate scrap material to prevent cross contamination and maintain chemistry control, and to develop processes for degreasing and removal of cutting tool material. Several government/Pratt & Whitney Aircraft sponsored programs involving both cast and wrought titanium and cobalt containing superalloys were initiated and carried through successfully. As an example, high volume IN100 chips from F100 engine disks were kept segregated from other scrap, were degreased and cleaned, packaged and returned to melters for reuse. After laboratory and engine testing, eighty percent of the chips ended up in new disks with as much as 100% revert. Figure 6 shows the revert cycle that was developed and put into production.

Another key technology area that was identified to have significant potential for reduction in strategic materials requirements was component life extension through rejuvenation and repair. Programs were initiated under U.S. Air Force Materials Laboratory sponsorship and Pratt and Whitney Aircraft to rejuvenate and restore to service previously scrapped parts. This not only reduced the need for new parts and raw materials, but also provided significant cost savings to customers. Two typical examples of parts that have been rejuvenated are a first stage turbine vane and a large structural case. Both parts are of superalloy construction, the vane being cast and the case fabricated from sheet-metal and forgings. Vanes with platform cracks, leading edge erosion, and airfoil cracks in Figure 7 were subjected to hot isostatic pressing (HIP), and weld repair. The successful repair procedure was implemented in the field early in 1982 and is saving 35,000 pounds (15,910 kg) of cobalt containing alloy a year as well as an annual cost savings of 10 million dollars.

The cases have been resolutioned, weld repaired, reaged and returned to service. The rework cost on a typical case is less than 10% of the cost of a new case. Figure 8 shows that 4,288 pounds (1,950 kg) of input alloy are saved for each set of three cases which can be rejuvenated. The largest part, a diffuser case, requires 2,820 pounds (1,280 kg) of superalloy to produce.

Potentially the most significant single program for conserving strategic elements short of complete engine redesign is extension of the useful life of critical rotating parts through the use of Retirement for Cause (RFC) methodology. The PWA/USAF RFC effort started in 1979 and could be implemented as early as 1985 in engine overhaul centers. Traditionally, cyclic life limited gas turbine engine components have been retired from service when they reach an analytically determined lower bound life where the first fatigue crack per 1,000 parts could be expected. Be definition, 99.9% of these components are being retired prematurely as they have (as a population) considerable useful life remaining. RFC is a procedure which would allow safe utilization of the full life capacity of each individual component. Since gas turbine rotor components are prime candidates and are among the most material intensive of engine components, adoption of a RFC maintenance philosophy could result in substantial material savings. A study conducted on 21 F100 rotating parts showed that 3,050 short tons (2,775 MT) of strategic materials could be saved over the life of the system through the implementation of RFC methodology (Table II). A major technical area being worked to achieve the potential savings is automated non-destructive evaluation. Computer driven systems such as that shown in Figure 9 are being developed to enhance flaw detection reliability and reduce inspection costs.

Finally, the greatest savings in strategic materials will be accomplished when improved engine designs are implemented with 50% fewer parts. These advanced technology engines will utilize new materials including non-metallic composites which are designed to minimize our dependency on foreign sources. Near net casting and forgings will be extensively utilized. Facilities such as the PWA disk facility under construction will be designed to more effectively handle scrap and reduce recycling cost. Components will be designed to meet stringent durability goals to maximize component life. Table III compares the F100 engine strategic materials to an advanced engine of the 1990's and shows an overall reduction in strategic material utilization of 60%.

While most of these efforts were initiated during the period of strategic material shortages, their worth is still apparent in cost savings even though strategic materials are sufficiently available today. In the event of future interferences in the flow of materials, they will greatly reduce the impact.

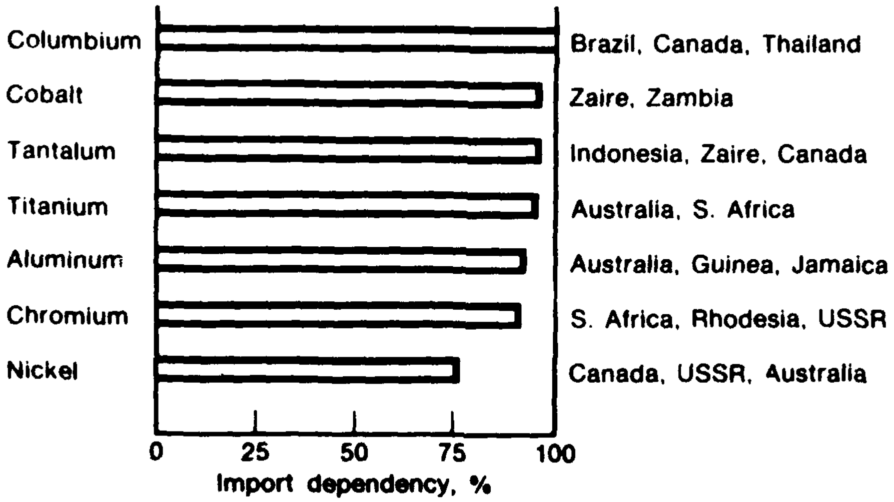


Figure 1. Import dependency and sources of seven elements termed strategic

	Input (lb)	Finished parts (lb)
Titanium	5440	798
Aluminum	670	121
Tantalum	3	0.5
Columbium	145	31
Cobalt	885	142
Chromium	1485	217
Nickel	4504	619

Table I. Amount of strategic materials required for an F100 engine

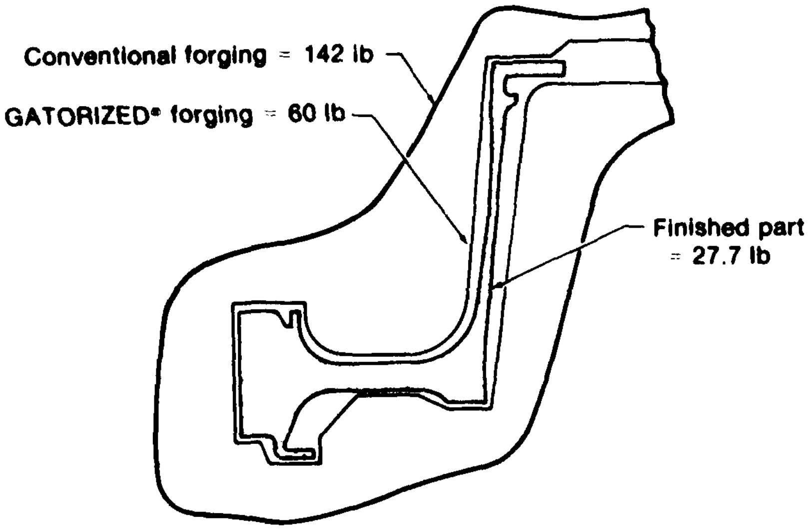


Figure 2 Cross sectional comparison illustrating greater than 50% material savings achieved by application of the GATORIZING forging process to a typical F100 engine disk

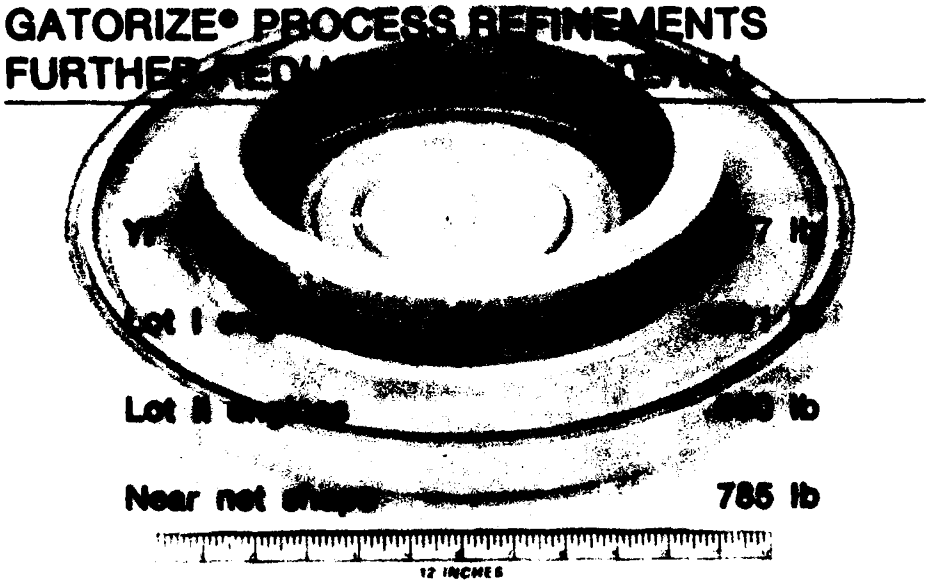


Figure 3 Refinements to the GATORIZING process allow a 40% reduction in input material on a set of nine F100 engine parts

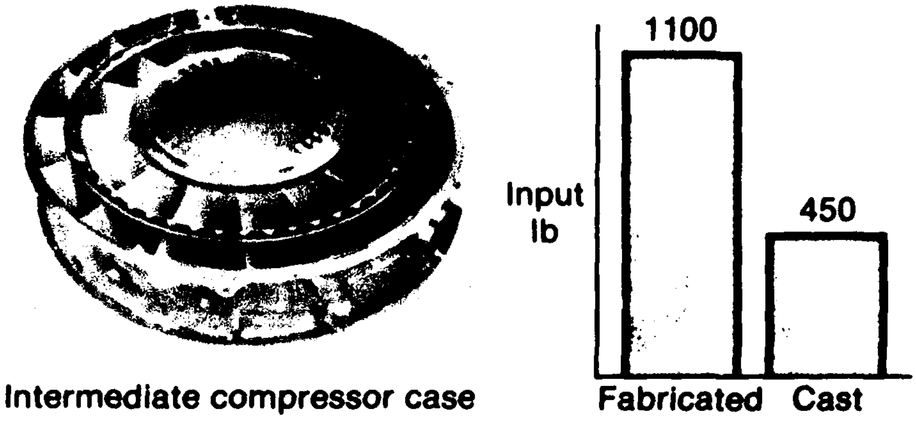


Figure 4 Large precision titanium castings save greater than 50% input material relative to cases fabricated from forgings

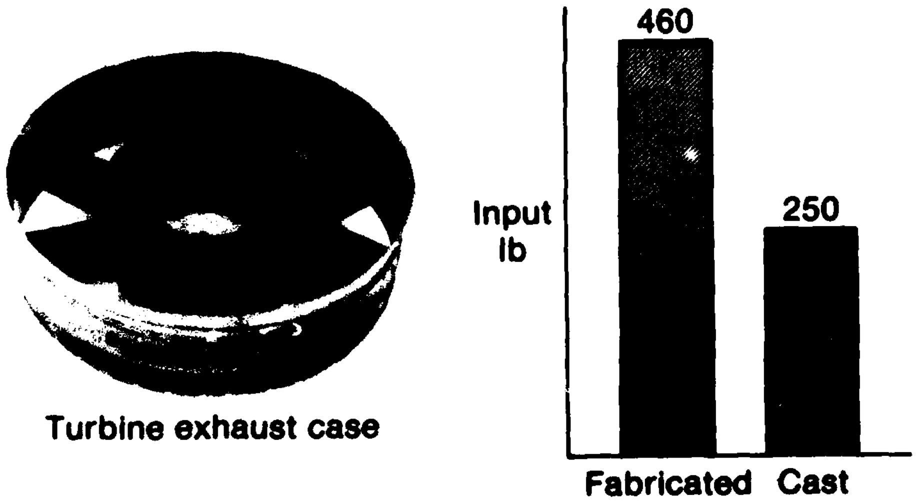


Figure 5 Large precision nickel base superalloy castings use 50% less input material than cases fabricated from forgings

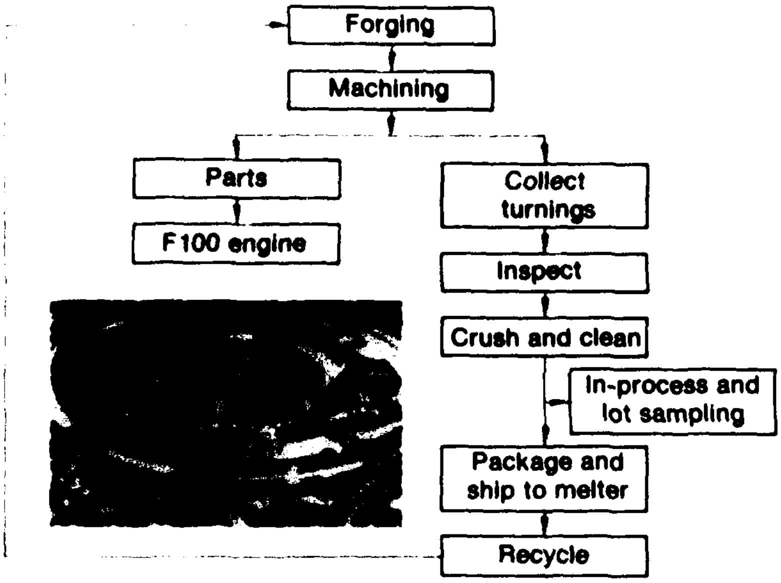
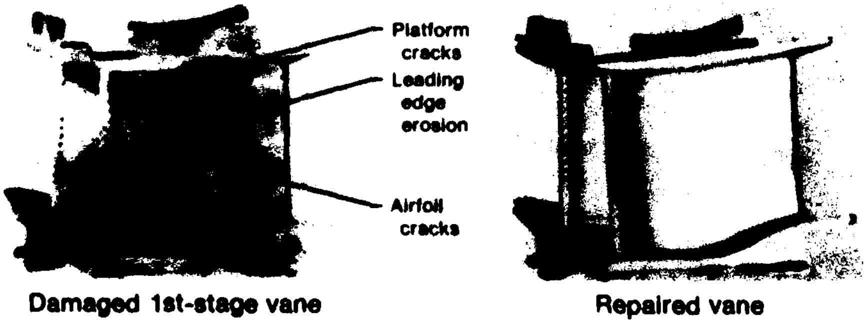


Figure 6 Schematic of machining chip reclamation process used in the production of F100 engine disks

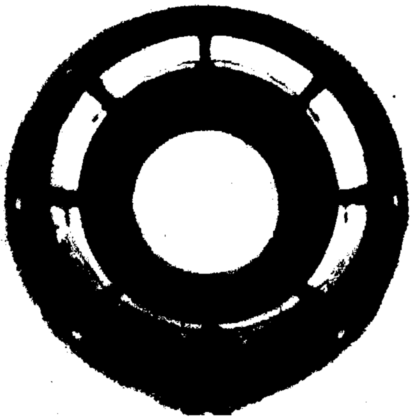


Damaged 1st-stage vane **Repaired vane**

- **Repair cost - 30% of new part cost**
- **Annual alloy savings - 35,000 lb**
- **Annual cost savings - $10M/yr**

Figure 7 Turbine airfoil repair conserves strategic materials and reduces cost ownership

Part	Input Superalloy lb
Diffuser case	2820
Turbine exhaust case	2400
Transition case	1068
Savings/engine set	4288



Diffuser case

Figure 8: Rejuvenation and repair of large nickel base superalloy engine cases conserves strategic materials

Material	Tons saved					
	Al	Co	Cr	Ni	Ti	Cb/Ta
Ti 6-2-4-6	37	—	—	—	505	—
Waspaloy	9	81	120	355	18	—
Astroloy	24	102	90	333	21	—
IN100	70	262	175	787	61	0.5
Total	140	445	385	1475	605	0.5
Total, all elements				3,050		

Table II: Strategic materials conservation potential for F100 engine rotor part Retirement for Cause Program

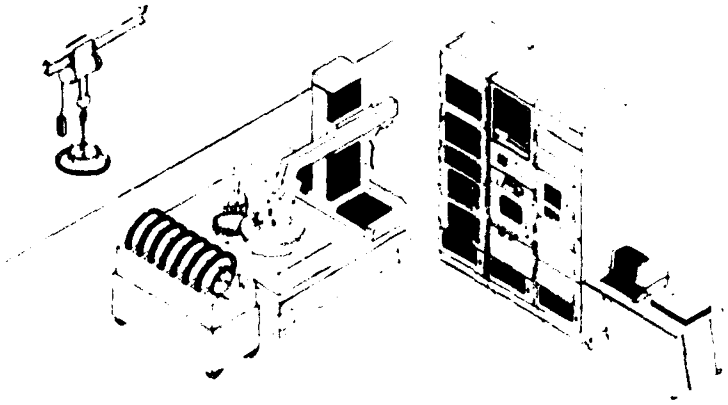


Figure 9 Advanced non-destructive evaluation systems are key to part life extension

	Today LB	1990's LB	% saved
Titanium	798	300	62
Aluminum	121	75	38
Tantalum	0.5	10	—
Columbium	31	2	94
Cobalt	142	20	86
Chromium	217	85	61
Nickel	619	275	56
	F100	Advanced engine	

Table III Fewer parts and advanced materials and manufacturing methods reduce strategic materials by 60% in advanced engines

PRACTICAL IMPLICATIONS OF THE USE OF ALUMINIDE COATINGS FOR THE CORROSION PROTECTION OF SUPERALLOYS IN GAS TURBINES

by

A. Strang

Central Metallurgical Laboratories.
GEC Turbine Generators Ltd.
Cambridge Road.
Whetstone.
Leicester.
LE8 3LH
United Kingdom.

E. Lang

Commission of the European Communities
Joint Research Centre.
Petten Establishment.
P.O. Box 2
1755 ZG Petten.
Netherlands.

& R. Pichoir

ONERA
Direction des Materiaux.
92322 Chatillon Cedex.
France.

SUMMARY

Aluminide coatings have been in use for some considerable time as a means of protecting nickel and cobalt based superalloys from oxidation and hot corrosion attack in both aero and industrial gas turbines. Their practical usage however has not been achieved without problems. In examining the overall role of coatings in achieving or prolonging component life, their advantages and disadvantages have to be considered most carefully, especially as the diversity of potential substrate alloys increases. The primary objective of this paper is ~~therefore~~ to consider in some detail the nature of the difficulties incurred in the pack aluminising of superalloys, especially in terms of prolonging component life without prejudice to performance, integrity and safety of the engine.

In considering this, the paper will first of all review the objectives and requirements of using aluminide coatings, the processes currently commercially available, the compatability of aluminide coatings with various superalloys substrates as well as the more general question of overall quality control of both the coating and the coated component. The properties of coatings themselves will be considered in terms of their corrosion resistance, overall thermal and structural stability, and effect on the mechanical properties of the substrate. Finally, the problems of long term corrosion protection will be examined in terms of the practicalities of reclaiming and recoating of ex-service turbine parts with view to extending component life and conservation of critical materials.

INTRODUCTION

Modern aero and industrial gas turbines are expected to function for prolonged periods under a wide variety of operational and environmental conditions with the maximum degree of reliability. Additionally, both operators and utilities expect extended engine and component lives at progressively higher power outputs in a climate where increased engine firing temperatures and decreasing fuel quality are becoming the rule rather than the exception. As a result of such demands, current engine development is aimed at improving efficiency and reliability as well as extending component life and reducing operating costs. The use of higher component stresses and engine firing temperatures in combination with progressively poorer grade fuels leads to severe metallurgical problems in the selection of suitable materials for prolonged and reliable hot component operation.

Historically, the demand for improved component life at higher stresses and operating temperatures has been met by alloy developments which, while leading to significant improvements in strength, have invariably been associated with poorer corrosion resistance. Whilst in the age of pure fuels this did not constitute a serious problem, the poorer corrosion resistance of these high strength alloys could lead to significant reductions in component lives in turbines which are run on low grade fuels, or in environments where agressive species may be present in the turbine air intake supply.

During the past decade further alloy developments have taken place in an attempt to improve corrosion resistance without loss of properties mainly by introducing higher chromium levels. In the case of wrought nickel base alloys, corrosion resistance variants of Nimonic 80A, 90 and 105 have emerged, viz. Nimonic 81, and 101, while in the field of cast alloys IN738 and IN939 are notable in having similar strength but improved corrosion resistance to the well known workhorse alloy IN713. Some improvements have also been achieved in the field of cobalt based alloys, FSX414 being a weldable, corrosion resistant derivative of X40. Althought such developments are highly desirable from the point of view of improving component lives in agressive environments, components tend to be much more expensive to produce. This is due to the corrosion resistant alloys being richer in expensive alloying elements particularly chromium, as well as often requiring more sophisticated and costly heat treatments to develop their properties. As a result of this, and in an attempt to conserve strategic materials, there has been a movement to resort to the use of corrosion resistant protective coatings on less sophisticated and hence less expensive alloys. Whilst the cost of coating can be significant in itself, it is often the case that in combination with a cheaper basic alloy the required component life and performance can be achieved at an overall lower cost to the user. In situations where an improvement in life is achieved the overall financial benefit to the user is further improved.

During the past decade extensive developments and improvements have also been made in the field of corrosion resistant coatings. As a result commercial coatings are currently available in a wide variety of compositions and forms which are applied to the substrate concerned by an equally wide variety of processes. Essentially these coatings can be divided into two groups which have been designated as reaction or diffusion type coatings and overlay coatings. In the first type, the coating is produced by a controlled chemical reaction with the surface of the component to be protected. Overlay coatings on the other hand are produced by deposition of the protective covering by a variety of techniques such as sputtering, physical vapour deposition (PVD), argon shrouded plasma spraying (ASPS), and low pressure plasma spraying (LPPS) before being partially diffused into the substrate by means of a suitably chosen heat treatment. Whilst the use of coatings is clearly advantageous from the point of view of protection of components from agressive species in the turbine, there are features of the processes involved which, if not suitably accounted for, could lead to reductions in component lives. Whilst, as already noted above, there are a great number of commercially available coatings and coating processes currently available for the protection of hot gas turbine components, it is the intention of this paper to concentrate on those produced by reaction or diffusion type processes, in particular the aluminides.

Aluminide protective coatings have been in use on nickel and cobalt based superalloys in gas turbines with a considerable degree of success since the 1950's. As a result a considerable amount of experience has been gained in service applications. Initially this was primarily in the aero engine field where short lives and high temperatures prevailed, the presence of the coating enabling the design life to be achieved in situations where oxidation and hot corrosion was life limiting in the engine. As operating temperatures increased in industrial applications, the use of aluminide coatings also became necessary in order that blade design lives could be achieved and in certain circumstances even extended. In these situations blade lives of 20,000 hours or greater were expected compared with up to 1000 hours in the case of the aero engines. Whilst the use of aluminide coatings in these applications was generally advantageous a number of problems emerged in their use. In considering the use of aluminide type coatings in practice both the advantages and disadvantages have to be considered for each particular service application.

As far as advantages are concerned, the following points are relevant:-

1. The use of coatings potentially prolongs the life of the component in the engine and as such conserves both materials and resources. This means that in the long term fewer engine sets of blading should be required over the total life of the turbine.

2. The use of coatings allows cheaper and less corrosive resistant materials to be used thus conserving strategic materials.

3. The use of coatings permits the use of cheaper fuel without any penalty to the life of the component.

4. The use of coatings permits the recovery and/or recycling of parts, by limiting corrosion damage to the top part of the coating only.

5. All in all, the use of coatings results in significant economic savings in materials, resources and fuels as well as limiting the exploitation of strategic materials, i.e. their use is cost effective.

Whilst the above indicates that there are clear economic and technical advantages in using coatings, there are a number of potential disadvantages:-

1. The coating process adds to the cost of producing the final component in terms of the coating process used, e.g. platinum aluminide coatings are significantly more expensive than simple aluminide coatings. Whilst there is initially an added cost, this may be more than recovered by the expected extension in component life.

2. The coating process may prejudice material properties leading to a reduction in component life.

3. The use of coatings necessitates the use of expensive reheat treatment of components to achieve the required specified properties.

4. The presence of defects in the coating can affect component and hence turbine integrity.

Considered as a whole, however the advantages generally outweigh the disadvantages since most disadvantages can largely be overcome by the use of suitable post coating heat treatments and quality control measures.

The overall aim should therefore be to use the cheapest and most effective process appropriate to the particular turbine application being considered consistent with achieving the maximum degree of protection without compromising the mechanical properties of the component or prejudicing the overall component life expectancy. An awareness of the various coating processes and their effect on material properties is therefore important. This will be considered in this paper particularly from the point of view of aluminide coatings.

COATING PROCESSES

The commercial processes currently most widely used for the application of aluminide coatings to superalloy substitutes are those of chemical vapour deposition (CVD) and pack cementation (PC).

Chemical Vapour Deposition (CVD)

In the classical CVD technique the aluminide deposits are generally produced in reactors into which an appropriate gas mixture is introduced and where only the components to be coated are heated to the required temperature. Both gas pressure and flow rate are controlled to ensure that the desired coating is obtained and that the reaction by-products are carried away from the vicinity of the components being coated. The actual coating is produced by either chemical decomposition (pyrolysis) of the gaseous phase or chemical reactions between the gaseous phase and the component substrate. The composition of the gas phase used depends largely on the type of coating required but can be composed of metal halides, metal carbonyls, metal hydrides or complex organic-metallic compounds. In the CVD process adequate control of parameters such as substrate temperature and gas compositions, pressure and flow rate are clearly essential if suitable coating thicknesses are to be achieved on different superalloy substrates. In practice the CVD technique is widely used for well defined applications and series production of similar pieces such as coatings on turbine blades, cutting tools etc.

Pack Cementation (PC)

In the pack cementation process the components to be coated are placed in semi-permeable boxes filled with a powder mixture containing the metal or an alloy of the metal to be deposited and a suitable halide which is volatile at the temperature at which the coating is formed. During this process the container pack and components embedded in the pack are held at the same temperature, surrounded by an atmosphere of hydrogen to minimise oxidation. Unlike CVD, the gas flow rates in the pack cementation process are almost zero. In one particular variation of this process coating occurs exclusively through the vapour phase with no direct contact between the pack and the component.

Although the chemistry of the coating process is complex, the essential processes which occur are as follows. At the coating temperature interaction occurs between the metal and halide in the pack, resulting in the formation of of a metallic halide which in turn reacts with the surface of the component being coated. The metal resulting from this reaction diffuses into the substrate with a consequential lowering of its activity at the substrate/pack interface. This transfer reaction between the pack and the substrate continues during the coating cycle, with an equilibrium condition between the gaseous phase in the pack and the substrate being established. Coatings produced by this process may be based on packs containing silicon, chromium or aluminium or in certain cases a combination of these elements (1). In the case of aluminide coatings produced on nickel and cobalt based superalloys, interaction between the metal applied and the substrate is a necessary part of the production of the coating, this consisting essentially of NiAl and CoAl respectively on these alloys.

ALUMINIDE COATING OF SUPERALLOYS

Nickel and cobalt based superalloys currently used in advanced gas turbine plant often operate in agressive environments and as such require to be protected from oxidation and hot corrosion attack in service. This is achieved by the use of coatings, often of the aluminide type (eg NiAl or CoAl), these being applied using various pack cementation processes similar to that described above. The morphology of the coatings produced is dependent on a number of factors the most important of which is the type of process, the composition of the pack and the composition and structure of the substrate material. Apart from variations in the process type and substrate material, the overall formation of the coating is largely governed by the aluminium activity of the pack, (2,3).

In processes where the aluminium activity of the pack is low, the base element of the alloy, viz nickel or cobalt depending on the superalloy substrate, diffuses preferentially through the coating being formed. This outward diffusion is a characteristic of a low activity pack cementation process. On the other hand, when the aluminium activity of the pack is high preferential diffusion of aluminium from the pack through the aluminide layer being formed and into the substrate occurs. This type of inward diffusion is thus a characteristic of a high activity pack cementation process.

Aluminide coatings produced on superalloy substrates by these processes do not exhibit the same resistance to oxidation and hot corrosion attack. In consequence, it may be necessary to carefully select the optimum aluminising process/substrate combination for specific turbine service environments. In this respect the overall coating/substrate stability is important especially in applications where extended periods of operation are envisaged, viz > 20,000 hours. A comparison of the potential problems encountered in the aluminisation of nickel and cobalt based superalloys using low and high activity processes is detailed below. Specific problems pertaining to the aluminisation of carbide fibre reinforced and oxide dispersioned strengthened (ODS) alloys as well as directionally solidified and single crystal materials are also discussed.

NICKEL BASE ALLOYS

Low Activity Aluminide Coatings

As previously described, the formation of aluminide coatings on nickel base superalloys in pack cementation processes in which the aluminium activity is low, occurs as a result of the outward diffusion of nickel. In consequence, the original substrate surface is finally located within the coating itself. As a result, the coating which is formed at between 1000°C and 1100°C, exhibits a two zone structure, each zone lying on either side of the original substrate surface as shown in Fig. 1a.

The outer zone consists of NiAl, containing various alloying elements in solid solution which have diffused together with nickel from the substrate alloy during formation of the coating. The internal zone, on the other hand, consists of NiAl containing various precipitates formed from those elements in the substrate material which are insoluble or incompletly dissolved in NiAl. As a result of diffusion of nickel from the substrate to the coating, the underlying zone becomes denuded in nickel and enriched in various other substrate alloying elements, especially aluminium. This leads to the formation of NiAl -phase. A further characteristic of these coatings is their low aluminium content, which varies by very little across the whole of the NiAl coating thickness. Due to this latter factor these coatings are held to be particularly structurally stable in service. Whilst the low activity aluminide coatings are generally succesful in protecting components from oxidation and high temperature corrosion attack, certain problems can arise which may affect their potential performance. Foreign particles on the surface of the component to be coated will, as described above, be incorporated into the coating in the position of the original metal surface. These will not generally affect the performance of the coating provided that they do not occur in quantities which might result in local delamination of the coating between the first and second zone. It is therfore important to ensure that the substrate material is as clean as possible prior to the coating operation. Contamination of the coating can also result from the cementation pack itself. This generally occurs in the external zone of the coating and in the case of contamination due to metallic inclusions from the pack, the oxidation/corrosion behaviour of the coating may be considerably modified (4). Finally in alloys which are particularly rich in chromium and certain other alloying elements, the internal coating zone may become excessively brittle leading to delamination of the coating during service.

High Activity Aluminide Coatings

In the high activity pack cementation processes, the nickel aluminide coating is formed by diffusion of aluminium into the component substrate. As a result of this the coating is formed below the original surface of the component. Furthermore this aluminisation process is carried out at a lower temperature than in the low activity process, usually in the range 700°C to 950°C. Initially the coating consists of Ni_2Al_3, the desired NiAl structure being formed by a post coating diffusion treatment carried out in the temperature range 1050°C to 1200°C. The coatings thus obtained exhibit a high aluminium gradient through the NiAl layer and are reported to degrade during high temperature utilisation due to interdiffusion effects with the substrate, (5).

The Ni_2Al_3 layer formed during the aluminising process contains all of the elements in the substrate material either in solid solution or as precipitates, pre-existing in the alloy or which have formed during the aluminising treatment. Transformation of the initial Ni_2Al_3 coating to the final NiAl form during the post coating diffusion heat treatment is a complex process involving inward diffusion of aluminium in the outer coating layers and outward diffusion of nickel from the substrate through the inner coating layer, Fig. 1b. This process results in the coating exhibiting three distinct zones. The outer zone consists of NiAl which contains various precipitates either from the original substrate or which have formed during the coating and subsequent diffusion treatment, together with elements from the substrate material held in solid solution. The internal region formed by aluminising of the subjacent alloy, consists of two regions: one close to the alloy similar to the internal zone of the low activity process, and the other corresponding to the low activity outer coating zone.

Since the composition of the external layer of high activity coatings is strongly dependent on the substrate composition, so must be the oxidation/hot corrosion characteristics. In certain instances the corrosion resistance may in fact be unsatisfactory, particularly if the substrate material contains titanium carbides (4,6). Problems may also result from the use of high activity coatings on substrate material containing massive carbide precipitates, particularly of the MC-type, Fig. 2. The presence of such features not only affects the coating continuity but may also provide sites for preferential oxidation and/or corrosion attack (4). Unlike low activity pack processes, the presence of contaminants on the component surface prior to coating or due to pick up from the pack, are less problematical in high activity aluminide coatings.

Finally, whilst Kirkendall porosity is a significant feature of pack aluminised nickel, no effect has been observed in pack aluminide coatings on superalloys produced by either high or low activity pack cementation processes.

COBALT BASE ALLOYS

In the case of cobalt base superalloys aluminide coatings can in principle be applied by both high and low activity processes. The thermal cycles associated with the aluminising treatments are, on the whole, generally longer in duration or conducted at higher temperatures than those used for nickel base alloys.

The protective coating in this class of alloys is the cobalt aluminide CoAl. As in the case of the nickel base alloys described above the CoAl will contain substrate elements both in solid solution as well as in the form of precipitates. The significant difference in the structure of aluminide coatings on cobalt-base alloys is the presence of a more or less continuous layer of large chromium and/or tungsten-rich carbides between the substrate and coating itself, Fig. 3. This may lead to spalling of the coating in thick deposits or under thermal fatigue conditions in service. In certain commercial processes such as CODEP D11, packs with relatively high aluminium contents are used which minimise the formation of the intermediate carbide layer by permitting a considerably reduced thermal cycle to be used during coating. In general however low activity processes are preferred for the aluminide coating of cobalt base alloys.

SPECIAL CASES

Directionally Solidified and Single Crystal Alloys

No significant problems have been encountered in the pack aluminising of directionally solidified superalloys, since in general the substrate compositions are similar to their equiaxed counterparts. In the case of alloys containing hafnium additions some reduction in the oxidation/corrosion resistance of high activity coatings may occur due to the presence of hafnium-rich precipitates in the outer coating zone.

The absence of major segregation effects and coarse carbide precipitates is a positive advantage as far as aluminide coating of single crystal superalloys is concerned. This advantage is realised irrespective of whether the coatings are applied using high or low activity processes.

Directionally Solidified Carbide Fibre Reinforced Eutectic Superalloys

In principle, the aluminide coating of fibre reinforced eutectic superalloys is only possible using low activity pack cementation processes, Fig. 4. The use of high activity processes would lead to very unsatisfactory aluminide coatings due to the very poor oxidation/corrosion resistance of the HfC, TaC or NbC fibres in the outer zone of the coating (6).

Oxide Dispersion Strengthened Superalloys

The improved high temperature properties offered by oxide dispersion strengthened superalloys are of particular interest in gas turbine applications where extended component life times are required at very high temperatures. It is anticipated however that protective coatings will be necessary if the full potential of these materials is to be achieved. However serious problems have been encountered with regard to the chemical and mechanical stability of coatings on alloys containing fine oxide particle dispersions.

In early tests on aluminide and duplex chromium coatings, void formation and rapid substrate interdiffusion effects led to premature coating spallation and failure. This type of premature failure mode has continued to persist despite the introduction of new coating systems such as overlays and duplex overlay/diffusion systems. Glasgow and Santoro (7) noted that the substrate composition was clearly important in that the tendency amongst oxide dispersion strengthend alloys to become porous, decreased with the alloys' increasing oxidation resistance. Boone et al (8) have recently investigated this in further detail arriving at the following conclusions:

1) The thickness and structure of aluminide coatings, particularly the inner coating zone on ODS alloys, is a strong function of the composition of the substrate alloy. Increased aluminum levels and possibly refractory strengthening elements appear to be beneficial.

2) The structure and stability of aluminide coatings on ODS alloys are functions of both the coating type and deposition process.

3) Coating void formation and the resulting spallation occur in the inner coating zone and are delayed but not prevented by the larger more dispersed zone produced by low activity coatings on alloys with a high aluminium content.

4) For all ODS alloys and aluminide coatings studied, the coating systems appeared to have insufficient protectivity to match the available mechanical properties. The lack of stability was manifested both by void formation in the coating and resulting spallation and by aluminum diffusion into the substrate (8).

Clearly there are significant problems associated with the coating of the oxide dispersion strengthened superalloys which must be overcome if the full potential of these materials is to be realised.

Alternative Processes

In addition to the pack cementation and chemical vapour processes described above a variety of other methods are available for producing aluminide coatings on superalloys.

Slurry

In this process a mixture of powders of suitable composition is applied to the component surface by painting, spraying or dipping. The components are then subjected to a suitable heat treatment during which the protective surface coating is produced by:-

1. Melting of the powder mixture accompanied by superficial dissolution of the substrate with the consequential formation of a multiphase coating by diffusion.

2. Chemical reactions in the slurry occurring concurently with interdiffusion with the substrate.

This latter process is known as the reactive slurry process.

Dipping

This process consists of dipping the components to be coated into a liquid metal bath containing the elements to be deposited. The desired coating is formed by diffusion either in the bath itself or during a subsequent heat treatment cycle.

Electrolysis in Fused Salts

In this process the component to be coated is immersed in a bath of molten alkali flourides held at between 500°C and 1200°C under an inert atmosphere. Coating is effected by electrolysis in the molten bath with the metal to be deposited acting as the anode and the component to be coated as the cathode. During deposition the metal from the anode interacts with the component to form the coating required.

Whilst the above processes can be used to produce aluminide and other metallide coatings on nickel and cobalt base superalloys they are not as widely used as the high and low activity pack cementation processes already described in detail above.

COMMERCIAL PROCESSES

Coating Types

Apart from the high and low activity pack cementation variants already discussed, commercial pack aluminising processes can be divided into two basic categories, viz single stage or direct aluminising processes and the more complex two stage aluminising processes.

Direct Aluminisation

Direct aluminisation treatments were amongst the earliest processes developed for the corrosion protection of superalloy components. Amongst the low activity types commercially available were the CODEP and HI-15 processes introduced between 1964-66 while high activity aluminising processes, such as PWA73 were introduced in 1969. Recently a new single stage pack cementation process has been developed involving the simultaneous codeposition of chromium and aluminium (1,9).

Two Stage Aluminisation

Two stage aluminisation processes represent a more recent development in the corrosion protection of gas turbine components, essentially consisting of a pretreatment or predeposition process conducted prior to the final aluminising stage.

Typical pretreatments used prior to pack aluminising include chromising, particularly of low chromium containing substrate alloys such as IN100 i.e. typical alumina formers. Other chromising treatments are also used, such as HC12 and PWA70, these being designed to avoid the formation of -chromium precipitates in the final coating. Some chromising treatments such as DP24 and Elcoat 240 actually lead to the formation of a layer of -chromium. Finally, pretreatments are also known in which other elements such as tantalum are co-deposited with chromium prior to the final pack aluminising treatment (10).

In the case of predeposition prior to pack aluminising, pure metals such as platinum and/or rhodium have been used as well as deposits of certain nickel or cobalt based aloys. Perhaps the best known of the commercial processes making use of the predeposition of platinum prior to pack aluminisation are LDC2 and RT22 (11). In these coatings an electrodeposited platinum layer, 5 to 10 microns in thickness, is often partially diffused into the substrate at a temperature in the range 1000°C to 1050°C prior to the final pack aluminising treatment. Depending on the thickness of the platinum deposit and the aluminising conditions applied the final coating structure may consist of either

1) a continuous external zone of $PtAl_2$ approximately 10 microns in thickness overlaying a 70 to 80 micron thick zone of β-phase (NiPtAl).

2) a basic coating of β-phase the outer part of which contains $PtAl_2$ precipitates

3) a coating consisting solely of β-phase containing platinum in solid solution.

The oxidation and corrosion resistance of these platinum aluminide coatings has been shown to be markedly superior to that of the simple aluminides (12). This together with the fact that they exhibit excellent structural stability makes their application in industrial turbines particularly attractive where components lives in excess of 30,000 hours are required (13,14).

Studies are currently in progress on coatings in which corrosion resistant nickel and cobalt based alloys are predeposited using sputtering, PVD and plasma spraying techniques prior to final pack aluminising (15). Whilst tests on some of these combinations are providing interesting and promising results, there are no commercial coatings of this type currently available.

PRACTICAL PROCESSING PROBLEMS

Whilst there are many practical problems associated with the aluminide coating of gas turbine components two of particular importance are considered here, viz, (a) selective coating of specific areas of components (masking) and (b) coating of cooled blades.

Masking

The masking of areas of gas turbine components which are not to be coated during the aluminising treatment is effected by simply painting the areas concerned with a refractory slurry e.g. ZrO_2. This process is most successful in high activity packs where the aluminising treatment is carried out at relatively low temperatures.

In low activity packs successful masking of components is much more difficult to achieve due primarily to the higher temperatures required by this process. Interactions occur between the refractory powder slurry, the superalloy substrate and the pack powder with the result that some aluminide coating occurs in the masked areas. Efficient masking systems have however been developed, for use with the low activity aluminide process, using neutral alloy powder mixtures tailored to match the composition of the superalloy to be coated. The actual details of the masking procedures differ from one processor to another and may have to be modified to suit the particular component being coated.

One process is based on a system of building up successive mask-coatings by repeated dipping to obtain a protective shell. In this process the first layers consist of a mixture which is neutral with respect to the composition of the superalloy. The final layers are almost pure chromium which, when sintered, become the mechanically resistant part of the protective shell.

Another commonly used comercial process consists of placing turbine blade roots in a can filled with an appropriate masking agent and then placing the whole assembly into the pack for the aluminising treatment. In processes making use of vapour phase aluminisation masking can readily be achieved by covering the areas required with a metallic sheet.

Coating of Cooled Blades

It has been well establised that in turbines using cooled blades in agressive environments, the long small diameter (<0.5mm) holes of the internal cooling passages must also be protected. The use however of conventional pack cementation processes in meeting this objective faces several serious problems. Not only are there great difficulties in feeding the reactants through the cooling channels but also in removing the pack mixture after the coating treatment. Obstruction of the cooling holes must be avoided at all costs since it can lead to blade failures in service due to local overheating effects. This is most likely to arise in the case of low activity pack cementation processes where the high pack operating temperature will favour sintering of the pack powder. Furthermore in this process the formation of the NiAl layer by the outward diffusion nickel from the substrate favours the embedding of pack particles in the coating, as well as leading to a reduction in the diameter of the cooling holes themselves.

In high activity processes, such as PWA73 the pack temperature is much lower and as such sintering of the pack powder in the blade cooling passages would not be a problem. Moreover the formation of the coating by the inward diffusion of aluminium is less likely to lead to entrapment of pack particles in the coating itself. Whilst there are clear advantages in using the high activity processes from the cooling passage blocking point of view this process is no better as far as efficient coating of these cooling passages is concerned. Aluminide deposition by a vapour or vacuum pack cementation may lead to more efficient corrosion protection of blade cooling channels.

A process has recently been developed in which the substrate to be coated is isolated from the powder mixture. During the treatment the powder generates a metal carrying gaseous species within the coating chamber. These species then reach the substrate by gaseous diffusion. The characteristic of the gaseous transport agent required by this type of process is called "throwing power". It is related to the ability to deposit aluminium on internal surfaces which then interacts with the base material to form the required aluminide coating. Various transport agents have been evaluated and their relative deposition rate measured. It has been found that complex halides of aluminium such as aluminium fluoride and alkali metals such as sodium, have sufficient throwing power (16).

A novel method of simultaneously metallizing the internal and external surfaces of turbine blades has been developed by the National Gas Turbine Establishment and Fulmer Research Institute, (17, 18). In this technique the components to be coated are placed in a retort separate from a near-conventional coating pack which consists of an aluminium source, a halide activator and an inert diluent. The retort is heated to 850°C and the pressure is then cycled by evacuating and re-filling with argon. Pressure cycle frequency may be in the range of up to about ten times per minute. Using this technique the coatings on the external surface of a blade aerofoil are typically 50 microns in thickness while the internal surface coatings are nearer to 25 microns thus minimising the danger of blocking the narrow cooling channels. The method has also been shown to be suitable for the generation of graded composition coatings where the final stage in the coating operation may include pulse aluminising, chromising or siliconising designed to seal microcracks or other defects in the surfaces of overlay coatings deposited by plasma-spray or other methods (19).

The coating of cooled blades has also been extensively investigated by G.E. Aluminide coatings were first obtained by the thermal decomposition of a metalorganic liquid (trisobutylaluminum - TIBA) at about 200°C (20). The aluminium deposit is produced either by dipping the pieces into the liquid or by circulating the liquid throughout the blades. A heat-treatment of a few hours at 1050°C is then carried out in order to form the aluminide coating. Other metallic deposits have also been produced by similar processes: nickel from nickel carbonyl at 150 to 250°C and chromium from liquid dicumenylchromium at 350 to 450°C. The deposition of successive layers of Ni, Cr, and Al allows the formation of alloy coatings. More successful methods have since been developed to coat internal surfaces: electroless deposition of nickel and slurry with a halide activator for chromium and aluminium deposition (21).

Quality Control of Coatings

The existence of coating defects has been recognised as a problem from the earliest days of using protective coatings in turbines, Fig. 5. Not only are defects undesirable from the point of view of potentially negating the value of the coating as regards corrosion protection but also due to certain forms of them acting as sub-critical defects which can lead to premature blade failure. In order therefore to ensure high reliability in coated components, careful quality control procedures must be excercised before, during and after coating (22). Such procedures are not only desirable but necessary if the life of the component is to be achieved and the integrity of the turbine during its operating life is to be guaranteed.

Most defects in coatings can be readily detected using a number of well establised techniques. There are however no generally accepted standards of testing nor standards of defect acceptance or rejection of coated parts. The final control measures are currently exercised by the turbines makers or the end user, where component refurbishing is involved, and generally defined in the specification laid down for the coating concerned. Apart from the usual quality audits of commercial coating producers and the routine monitoring of the coating process itself, the quality of coatings is generally determined on the basis of test coupons and/or randomly sampled component cut up tests. In cases where the components are large and expensive, such as high power industrial gas turbine blades the coating quality may be largely assessed on the basis of cut-up tests on test coupons alone.

Evaluation of Test Coupons

The homogeneity of a coating is greatly dependent on the manner in which the components being coated are distributed within the pack cementation box. This being the case it is necessary to sensibly distribute test coupons of the substrate material throughout the box in order that adequate checks on the quality can be made after coating. Whilst the increase in mass of these testpieces is the first valid indication of the coating quality, other tests may be necessary to establish the final coating quality, such as

1) metallographic determination of the coating thickness and assessment of its structure by comparison with established standard microsections

2) determination of the surface aluminium content (or platinum in the case of LDC2 or RT22 types) by X-ray fluorescence or β -backscattering techniques.

3) assessment of coating integrity using fluorescent dye penetrant, ultrasonic, eddy current, radiographic, infra-red emission or other appropriate techniques,

and

4) static and/or dynamic oxidation tests followed by visual and metallograhic examination.

Evaluation of Coated Components

It is equally and arguably more important to carry out the quality control tests described above on actual aluminised components randomly selected from each batch being coated. Whilst there is a considerable degree of merit in this approach, there is a danger of overkill, not to mention the increased commitment of resources with a subsequent increase in costs. A compromise must therefore be reachwd with respect to adequately assessing the coating process from the point of view of achieving the required quality control standards without resorting to unjustifiable commitment of resources and consequent expenditure, all of which will reflect itself in the final cost of the component. In other words, the proper and most efficient use of resources must be exercised without compromising the quality of the end product. This is especially important in the assessment of actual coated components since, as is the case in large industrial turbines, they can individually cost several thousand pounds each. In this case the assessment of quality must largely rely on the use of non-destructive tests of components in association with a more rigorous background of testing based on test coupons which have been coated in the pack at the same time.

In assessing the quality of coated components two principal sources of defects have to be considered, viz. (a) those originating from the component and (b) those originating from the actual coating process.

With regard to defects arising from the substrate being coated, it is necessary to distinguish between new (virgin) components and those which have undergone repair. The latter being more complex are dealt with below in the section dealing with repair and recovery of ex-service components. In the case of new components, certain defects detected after coating are generally associated with residues from the precision casting moulds which have not been adequately removed from the component surface by sand-blasting after casting. In practice only 0.3-0.5% of all pieces tested are rejected on this basis and these are generally recoverable by stripping and recoating. Defects arising from surface porosity in investment castings are relatively rare since these would be dressed out prior to coating. Some defects may also arise due to large carbide outcrops in the substrate. Again these are relatively rare.

Defects arising from the coating process itself include various types of cracking, porosity, entrapment of inclusions, compositional variations, thickness variations and interfacial separation, Figs. 5 & 6. Whilst many of these defects can be detected by visual and/or other non-destructive testing techniques, others may depend on the destructive examination of test coupons and indeed actual components themselves. Defects may also arise during the finishing of the coated parts such as locally too severe sand-blasting leading to overthinning of the coating. This can often be reclaimed by use of a supplementary coating treatment without resorting to stripping of the part concerned. In the case of the other defects described above a complete recycling of the component is necessary to recover the part.

Repair and Recovery of Coated Turbine Parts

In order to conserve both materials and energy, and prolong the service life of hot section, stationary and moving gas turbines, repair and recovery procedures are becoming generally accepted practices (22, 23). These procedures include recoating of turbine parts, repair welding/brazing of cracks, replacement of aerofoils and hot isostatic pressing (HIP) to recover the effects of creep damage. In pursuing this philosphy however, the quality control procedures which must be exercised are even more vigorous than those imposed in new components. Not only must it be shown that the recovered part is indeed fit for service, but this must be done in a situation where extremely difficult technical problems must be overcome to ensure a sound part. The main problem to be overcome in attempting the recovery of used turbine blades is to ensure that they are sufficiently clean before the refurbishing operation is commenced. This will be highlighted in the discussion of the basic procedures outlined below.

The recoating of turbine components may be necesary due to a number of causes such as

1) faults which have developed during the original coating treatment, Fig. 5.1)

2) general or local corrosion attack whereby after a period in service the coating can no longer fulfil its protective function, and

3) local damage to the component by impact etc.,

Recoating may also be carried out as part of an overall refurbishing programme on a component in association with brazing and welding repair work. In each case the original coating has to be effectively stripped from the component before recoating can proceed. This is generally achieved using a combination of abrasive blasting and chemical stripping procedures. Great care is necessary to ensure that the old coating is effectively stripped down to the unimpaired base material and in the case of corrosion damaged parts, below any effects the corrosion attack may have had on the substrate. This means that the dimensions of the component will be reduced after each stripping operation, thus reducing the effective load bearing cross section of the aerofoil. Stripping and recoating can therefore only be carried out a limited number of times expecially in blading where the aerofoil wall sections are thin, e.g. high performance cooled aircraft blades. For example, if a 60 micron thick aluminide coating which has penetrated the base material by 25 microns is stripped from a blade having a wall thickness of 0.5 to 1mm, a 2 to 5% reduction in the cross section of the aerofoil will occur with a corresponding increase in the nett section stress (24).

It has been suggested that the problems associated with the reduction in aerofoil cross section can be avoided by simply removing the corrosion products without stripping the coating as a whole (24, 25). This means that the effective substrate being recoated will have a higher aluminium content than the original substrate alloy. Lehnert and Meinhardt (24) have however shown that this technique can successfuly be applied to LDC2 coatings and that the recoated product exhibits the normal chemical composition and structure expected in this platinum aluminide coating. Further work has suggested that low activity pack cementation processes are the most suitable for coating repair using this procedure (25). If the original coating however is not removed the risk of spallation after recoating is likely to increase due to the new coating thickness being increased by a factor of approximately 2, (23).

The success of any recoating operation will be largely dependent on the availability of stripping and cleaning techniques which can remove both the corrosion products and remaining coating without undue damage to the turbine parts (26). Whilst stripping and cleaning procedures must be effective in order to ensure a successful end result they must not be too vigorous. Grain boundary attack or preferential dissolution of the substrate alloy must be avoided or at least minimised especially in thin walled components such as cooled aerofoils. In such components it is particularly difficult to remove oxides and sulphides from internal cavities and narrow cooling channels. In such cases it has been found to be advantageous to subject the parts, after chemical stripping, to an additional cleaning step in hydrogene. Even more efficient cleaning of these difficult areas is achieved by treatment in gaseous fluorine or using the Fluor Carbon Cleaning process (26). These procedures significantly reduce the reject rate after recoating. In the case of chemical stripping a reject rate of approximately 5% is experienced compared with 1-2% using the additional fluorine cleaning step. However, a reject rate of 5% on recoating is poor when compared with the 0.3-0.5% recorded in the coating of new components. Finally, should the stripping procedures described above have been unsuccessful in fully removing all traces of sulphur penetration in the substrate, 'sponge-like' features may occur on the component surface after recoating.

Following stripping and cleaning the new surface to be coated may differ in chemical composition and structure from that of the original alloy, primarily due to coating/substrate interdiffusion effects which have occurred during service. In consequence, both the structure and composition of the 'new' coatings are likely to differ from those produced on virgin substrates. Currently relatively little is known regarding the behaviour of recoated components in service, particularly with regard to their long term corrosion protection capability. Nevertheless reliable coatings appear to be generally achieved with records of both blades and vanes in aero engine applications having been recoated up to 12 times (25).

Successful repair of coatings which have been locally damaged due to impact etc., has been reported using the Sermalloy I procedure, in which a powder containing 88% aluminium and 12% silicon is applied to the surface. Coating repair is effected by a thermal treatment of approximately 15 hours duration at 1000°C, this being often incorporated into the quality heat treatment cycle required by the component alloy. Certain users however automatically reject impact damaged components on the basis that the coating crack may have extended into the substrate. These become candidates for stripping and inspection before resorting to possible salvage by recoating.

If repairs by brazing or welding are necessary, stripping and cleaning of the component has to be meticulously controlled since the presence of any coating or contaminant will seriously affect the repair procedures, as has recently been shown by Haafkens, (26). Repair welding is usually effected using a TIG process with a filler wire which may differ considerably in composition from the original component material. The differing compositions of the filler weld materials will result in a zone in which the final coating may be significantly different in both its composition and hence potential corrosion resistance. It has been reported that these compositional differences are more marked when high activity rather than low activity processes are used during recoating. A further complication is the formation of Kirkendall porosity during recoating, particularly when simple filler metals such as IN62 are used in the weld repairs. Amongst other problems encountered in the use of simple weld metals, such as 80Cr20Ni, is the formation of chromium rich layers at the coating/weld metal interface which might lead to spallation of the coating, (22, 23).

Recoating of components after brazing repairs may lead to problems associated with coating composition and integrity, due to the formation of complex low melting point ternary eutectics such as M-Al-Si or M-Al-B. In the case of cobalt-base alloys repaired using nickel base braze metals, the coating in the brazed areas is much thicker and of a different composition to that on the rest of the component. This may lead to a reduction in the anticipated life expectancy of the coating in service either due to differential corrosion effects or thermal fatigue damage at compositional interfaces in the coating itself.

The repair of thin walled sections associated with cooled components create complex problems in their own right. Not only is there a limited availability of adequate material to support the repair but in many cases the repaired areas will effectively prove to be non-load carrying and even less so due to further reductions in load carrying area resulting from diffusion effects associated with the recoating process.

Finally should hot isostatic pressing be used as part of a component refurbishing programme to recover creep damage or other microstructural defects, it is essential that any coating present is completely stripped beforehand. In the case of aluminide coatings, rapid diffusion of aluminium into the substrate would occur at the high temperatures associated with the process (>1200°C) resulting in a significant loss in surface ductility.

It is clear from the points made above that repair and refurbishment of high temperature gas turbine parts is not only feasable, and cost effective but also desirable from the point of view of conservation of energy and materials. Great attention to achieving and maintaining the quality of the refurbished parts must be exercised if the safety and integrity of the turbine is to be assured. The user has the final say in this respect, since should components exhibit defects after repair, they can be rejected, reprocessed or, if not too serious in nature, life-limited in engines operating under less demanding conditions.

CORROSION BEHAVIOUR

Severe hot corrosion attack and degradation, particularly of components in the hot sections of marine and stationary gas turbine may occur due to deposition of sulphate/chloride salts originating from the presence of sulphur and chlorides in the fuel or in the ingested air. This degradation principally occurs as follows.

During the course of a short incubation period, a protective scale develops on the surface of the component, which is comparable to that observed under conditions of pure oxidation. In the case of components protected by aluminide coatings a protective layer of Al_2O_3 will be formed during this stage. After this incubation or initiation period, rapid attack occurs by hot corrosion, the rate of this being controlled by the actual composition of the coating. For example, the presence of chromium prevents basic fluxing of the Al_2O_3 scale during the incubation period while yttrium and platinum prevent access of agressive salts to the subadjacent coating by reducing the risk of cracking and spallation of the surface protective oxide (27). Besides basic fluxing, other mechanisms such as acid fluxing may be induced by certain substrate elements or gas contaminants, leading to further hot corrosion degradation. In addition to this, the rate of coating degradation is considerably increased if the surrounding environment periodically fluctuates from oxidising to reducing conditions. Under these conditions pure -phase nickel aluminide coatings have been found to provide better corrosion protection than those containing noticeable amounts of chromium (28).

Assessment of the corrosion resistance of coatings and determination of the mechanism of the degradation process has been the subject of extensive laboratory based studies (29). These include a variety of hot corrosion studies conducted on salt coated material exposed in SO_3/SO_2 environments under both isothermal and thermally cycled conditions. Similar tests have also been conducted in ash-mixtures the composition of which are based on deposits removed from ex-service turbine blades. Electro-chemical methods using molten salt baths have also been used in an attempt to ascertain the conditions under which breakdown of the protective scale on the coating may occur. Tests have also been performed using burner rigs where a closer approach to 'real' gas turbine conditions can be simulated in terms of gas pressures and velocities as well as thermal fluctuations. In addition, various of these tests have been performed on coated materials under stress in order to determine the penalty that this additional factor has on the overall likely performance and hence life expectancy of a coated component (30, 31). All of these approaches are valuable from the point of view of selecting the most likely coating/substrate combination to succeed in a particular turbine application, as well as enabling some of the fundamental processes of the corrosion process to be studied. In the final analysis however, it is the performance in the turbine which will be the ultimate determining factor in deciding whether the correct selection has been made in terms of achieving improvement in overall reliability and life expectancy.

Degradation and Corrosion Behaviour of Alumninide Coatings.

The primary objective in using coatings is to provide protection of the component substrate from corrosion due to agressive species in the turbine environment for as long a period as possible. It therefore follows that the coating composition and thickness are of significant importance since it is these which determine the availability of protective scale forming elements during the life of the coating. Furthermore the overall integrity of the coating is vitally important since once it becomes breached, either due to cracking or chemical attack, it is at the end of its useful life in terms of protection of the component. Another factor which may lead to a reduction in the effectiveness of the coating as far as protection of the substrate is concerned, is its overall thermal stability. Due to coating/substrate interaction effects the chemical composition of the coating may be changed such that its overall corrosion resistance may be reduced to even less than that of the substrate material it is designed to protect (13).

During service, two basic coating degradation mechanisms have been observed on aluminide coatings.

1) outward diffusion of nickel in combination with inward diffusion of aluminium leading to an effective increase in the overall coating thickness with consequential reduction in the aluminium content of the outer coating zone, and

2) consumption of aluminium due to Al_2O_3 scale formation and spallation at the outer surface of the coating. This can lead to significant consumption of aluminium in the coating resulting in the β-NiAl being converted to the less oxidation resistant γ'-phase (Ni_3Al).

This process occurs progressively with service exposure until γ' fingers penetrate throught to the outer coating surface after which rapid failure of the coating occurs, (32, 40). These effects are noticeably accelerated by other processes such as hot-corrosion, erosion and thermally or mechanically induced spallation damage to the coating during its service life.

The joint effect of the two basic processes described above leads to an initial increase in coating thickness followed by a decrease which can be described by the equation

$$\frac{dh}{dt} = A\ e^{-Q/RT}$$

where h, is the coating thickness, Q is the activation of energy of nickel diffusion in NiAl.

Substrate composition also plays an important role with regard to the overall potential corrosion resistance of the coating, due primarily to coating substrate interaction effects such as those described above. This has been amply demonstrated for a number of different coating/substrate combinations, Fig. 7, (32).

Aluminide-coatings were originally developed for protection against oxidation (i.e. enhanced formation of Al_2O_3) in aero-gas turbines. Under hot corrosion conditions, such as that typically encountered in stationary gas turbines, such aluminide coatings can only provide limited protection since by interaction with molten sulphate deposits, the Al_2O_3 is being converted into unprotective aluminates (basic fluxing). However, it has been shown that even under corrosive conditions some noticeable extension of service lives can be achieved, Fig 8.

As already described, the presence of chromium in aluminide coatings promotes and sustains the Al_2O_3 formation and therefore reduces the effect of basic fluxing. However due to the limited solubility of chromium (and other elements) in the β-phase there is also only limited potential to improve the hot corrosion resistance of the simple aluminides.

A significant advance in the field of aluminide coatings has been the development of the two stage processes utilising electrodepostion of platinum. In these systems the improved oxidation and corrosion resistance is associated with the formation of $PtAl_2$ in the outer zone of the coating together with the presence of platinum in solid solution in the β-phase. The presence of $PtAl_2$ results in the retention of aluminium at the coating surface and as such promotes Al_2O_3 scale formation with the minimisation of spallation. Furthermore the $PtAl_2$ acts as an aluminium resevoir, also reduces the rate of inward diffusion of aluminium towards the substrate. Finally extensive studies by Strang and Cooper (32) have demonstrated that the thermal stability of the platinium aluminide coatings is markedly superior to that of the simple aluminides, the presence of platinum suppressing the transformation of β-phase to the less corrosion resistant Ni_3Al observed in simple aluminide coatings. The overall improvement in thermal stability exhibited by the platinum-aluminide coatings has been particularly exploited in industrial gas turbine applications, where component lives in excess of 30,000 hours in agressive environments is expected.

EFFECTS OF COATINGS ON THE PROPERTIES OF SUPERALLOYS SUBSTRATES

One of the most significant difficulties associated with the use of pack cementation coating processes is that their associated and often protracted thermal cycles are generally imcompatable with that which is required to develop the desired mechanical properties, particularly creep strength of modern superalloys.

The presence of a coating can also affect other important properties, e.g. high cycle and low cycle fatigue. Care must therefore be taken to ensure that the choice of coating is optimised with respect to the corrosion protection, mechanical property and hence life requirements of the component. The application of a coating may therefore affect the properties of the substrate and hence, of the basic component in a variety of different ways. These are now considered in detail.

CREEP AND TENSILE PROPERTIES

Coating Thermal Cycle

The prolonged periods of exposure at high temperature and slow cooling rates associated with pack aluminising processes are generally incompatible with the heat treatments required to develop the required properties in modern superalloys. In particular the creep properties of nickel base alloys are likely to be severly reduced due to an unsatisfactory distribution of ' being produced during the coating thermal cycle. Unsatisfactory grain boundry carbide distributions may also occur, resulting in poor high temperature ductility in the material. If coating of gas turbine parts is necessary, it is therefore important to eliminate any deleterious effects on material properties arising from the coating process. This can generally be achieved by implementing the full quality heat treatment for the alloy after the coating process has been carried out, (32). In certain alloy systems, coating can be carried out with the material in the as-cast or fully heat treated condition without the properties being unduly affected, Fig. 9. In other alloy systems deleterious changes in the microstructure of the substrate due to the coating process can only be reversed using the normal quality heat treatment for the alloy, Fig. 10. Certain other cases exist where it is possible to guarantee the substrate alloy properties by combining the coating thermal cycle within the quality heat treatment cycle required by the alloy.

In certain situations minor modifications to the substrate alloy composition can make the application of a coating feasable where previously no success was possible. This is well illustrated in the case of the commercial alloy CoTac744, which requires the following quality heat treatment.

Solution treatment	30 mins. @ 1220°C AC
Ageing	16 hours @ 850°C AC

As already discussed high activity pack aluminising processes are unsatisfactory for coating carbide fibre reinforced eutectic superalloys. The alternative low activity processes whilst being more suitable can still be detrimental due to the effect of the slow cooling rate associated with the coating thermal cycle. In work conducted by ONERA, (33) the creep rupture life of CoTac744 was found to be reduced by a factor of 3 at temperatures between 850°C and 900°C, when aluminide coated according to the following process;

30 mins. @ 1220°C AC - solution treatment stage
10 hours @ 1050°C slow cool - low activity aluminide coating
16 hours @ 850°C AC - ageing stage

At temperatures of 1000°C and greater no loss in properties were recorded due to the fact that at these high temperatures the creep properties are dictated by the properties of the carbide fibres, while at lower temperatures the strength of the matrix dominates.

A significant improvement in creep strength and transverse ductility in the temperature range 900°C to 1000°C can be achieved by modifying the composition of the alloy (CoTac784) and utilising a modified 3-stage quality heat treatment, viz.,

Solution treatment	30 mins. @ 1220°C - 1240°C AC
First ageing treatment	16 hours @ 1050°C AC
Second ageing treatment	16 hours @ 850°C AC

By combining a low activity pack aluminising process with the first high temperature ageing step it is possible to coat the modified alloy without affecting the creep properties, provided that the cooling rate after the coating cycle is not unduly slow. The improvements described are due to an increase in the γ' stability resulting from an increase in the γ'-solvus temperature brought about by the modified alloy composition.

The quality heat treatment for monocrystalline alloys such as CMSX2 normally consists of a 3-stage process, viz.,

Stage 1	2-3 hours @ 1280°C to 1320°C AC		
Stage 2	15 hours @ 1050°C, AC	or	4-6 hours @ 1100°C, AC
Stage 3	15-24 hours @ 850°C, AC		

Low activity or high activity aluminising processes can be incorporated into the quality heat treatment cycle for this alloy without detriment to the creep properties provided the cooling rate from the stage 2 cycle is fast enough. Should, in the case of a low activity process, the post coating cooling rate prove to be too slow, the microstructure can be restored by incorporating an additional 4 hour treatment 1050°C, followed by a rapid cool, into the total heat treatment cycle. This procedure is also valid in the case of the coating procedure adopted for the modified CoTac744 alloy. The above example clearly illustrates how coating processes can be incorporated into the normal quality heat treatment cycle for the component material, as well as indicating the need to ensure that both the coating and quality heat treatment procedures are compatible.

Reduction of Cross-section

Aluminide coatings are normally assumed to be non-load bearing. Furthermore as a result of their application a certain portion of the substrate is consumed thus effectively reducing the cross-sectional area of unaffected substrate material. This means that the nett section stress in a coated component, such as a turbine blade will be effectively higher than in the same component in the uncoated condition. This effect has been recognised in the study of the effects of coating on the creep rupture properties of superalloys, stress correction factors having to applied in the case of coated testpieces, (32, 34).

For example, the formation of a 60 micron thick aluminide coating on IN100 will result in the consumption of approximately 40 microns of substrate material. In the case of thin walled component 1mm in thickness, the load bearing section after coating on both sides will be reduced to 0.92mm. The corresponding 9% increase in stress at a constant load implies a reduction in creep rupture life by a factor of two times, vis 500 hours instead of 1000 hours at 850°C. According to Hauser et al (34), the creep rupture life would be reduced by more than 60% for a wall thickness of 0.5mm.

Practical considerations such as this are clearly important in the case of thin wall sections associated with cooled gas turbine blades, Fig. 11. It should be noted that thin section materials are already known to exhibit reduced rupture lives when compared with normal thickness materials, and that application of a coating would reduce this further (35). As a result of such factor the repeated coating of thin wall blades is clearly limited.

Finally, the additional weight of the aluminium in the coating may, in the case of very thin walled blades, lead to increase in the overall section stress and hence a significant reduction in component life, Fig. 12, (36).

Coating/Substrate Interdiffusion

In various studies on the effects of coatings on the high temperature properties of nickel and cobalt based superalloys, significant coating/substrate interdiffusion effects have been observed. This is hardly surprising since the composition of the coatings are substantically different from the substrate upon which they lie and as such, strong chemcial interdiffusion effects during high temperature exposure in service would be expected. These not only lead to changes in the structure of the coatings, which in time may change their effective corrosion resistance, but also to substantial modifications to the microstructure of the alloy zone adjacent to the coating. In this respect Strang has reported the presence of extensive σ-phase precipitation at the coating/substrate interfaces of both simple and platinum aluminide coatings on IN738LC. (37,38,39). In studies conducted on creep rupture testpieces exposed for up to 40,000 hours duration at 750°C and 850°C platelets of σ-phase were shown to extend from the coating/substrate interface for up to 100 microns into the substrate itself. Under certain conditions the σ-platelets were also observed to offer an easy path for crack propagation from the coating into the substrate material, (39). Lang and Tottle have made similar observations on coated IN738LC specimens exposed for various periods at temperatures up to 1000°C, (40). In these studies R-phase was detected at the coating substrate interface in addition to the -phase already reported, Fig 13.

Whilst the presence of these plate-like phases in the subcoating zone has so far not been found to be detrimental to either the creep or low cycle fatigue life of super-alloys, (14,38,41) no studies have so far been reported on thin section material. Their potential effect on the high cycle fatigue properties of a number of nickel based superalloys is currently under investigation in a number of laboratories, (42,43). Whilst no detrimental effects on basic high temperature properties have been reported due to σ-platelets in the sub-coating zone of aluminised nickel base alloys, Strang has suggested that they may be potentially dangerous on the basis of sub-critical crack growth considerations. In the case of a normal aluminide coating a through thickness crack or defect may be 75 to 100 microns in depth. Should however extensive σ-phase precipitaton occur during service in the subscoating zone, say up to a depth of another 100 microns, then the total defect to be considered is now 200 microns in size. Under certain circumstances such a defect may extend by sub-critical growth processes such as thermal and/or high cycle fatigue and thus lead to failure of the component.

It can generally be concluded that provided that all of the necessary precautionary steps are taken, the application of aluminide coatings should not lead to a deterioration in the basic creep rupture or tensile properties of the substrate alloys. On the other hand, since the presence of a coating does not confer any strength to the substrate, any benefit can only be expected under conditions where environmental effects are likely to be life limiting. A useful coating will therefore, by appropriate protection scale formation, effectively seal the substrate off from ingress of any agressive species likely to reduce component life by grain boundary attack (44) or reduction of load bearing cross section due to corrosion, Fig. 14, (45).

COATING DUCTILITY

Survival of the coating, in terms of its mechanical integrity, will be critically dependent upon its inherent strain tolerance capability or ductility. Strains imposed upon the coating during operation of the turbine will be due to the thermal and mechanical stress cycles experienced by the components concerned. As a result of this, the strains generated will be a combination of those resulting from thermal expansion mismatches between coating and substrate as well as those transmitted by mechanical deformation of the substrate itself. The ability of the coating to accommodate such strains will be dependent not only upon their magnitude and frequency ofapplication but also on other factors such as coating type, thickness and the temperature range over which the maximum strains have to be tolerated. Due consideration of these factors is especially important if premature mechanical failure of the coating is to be avoided.

A certain disadvantage of aluminide coatings in this context is that while at high temperature they possess fairly high ductility, below a certain temperature, known as the ductile/brittle transition temperature (DBTT), their failure strain drops to less than 0.2%, i.e. they are effectively brittle. While the ductility behaviour of MCrAlY overlay coatings can now be adjusted by compositional modifications, the ductility of aluminides however varies only slightly with composition, CoAl being generally more brittle than NiAl, Fig. 15. To a minor extent aluminide coating ductility is also dependent on the substrate alloy composition, coating process route, straining rate and on coating thickness. However this typical behaviour of aluminides need not be detrimental provided that proper actions are taken to ensure that (thermal) strains are minimized, particularly at temperatures below DBTT so that the maximum strain range level experienced by a coated component does not exceed the failure strain of the coating. This can generally be achieved in practice by careful control of turbine start-up and shut down cycles.

FATIGUE PROPERTIES

Varying results have been reported concerning the effect of aluminide coatings on the low cycle, high cycle and thermal fatigue properties of superalloys. Since fatigue failure is generally (in the absence of internal flaws and porosity) initiated at the surface, and affected by the environment the application of a coating on the surface may potentially affect fatigue properties of coated components. Whether it does or not will depend on the relative intrinsic mechanical and physical properties, and their temperature dependence, of both the coating and substrate alloy, respectively. These properties include yield strength, elastic modulus, thermal expansion coefficients, ductility and DBTT. If the relevant properties of the coating are worse than those of the substrate then cracks can be generated in the coating, whereby the coating will lose its prime function to provide corrosion protection. Furthermore such cracks may propagate into the substrate by subcritical crack growth process and lead to premature failure of the entire component (see above). On the other hand, if the coating (fatigue) properties are better than those of the substrate, then an improvement of the overall behaviour can be anticipated, in air and even more so under corrosive environment.

For the fatigue behaviour of coated parts residual (or intrinsic) stresses in the coating will also be of vital importance to its behaviour under cyclic loading (47). It is know that such stresses will increase with thickness of the coating, however little is known about their relative magnitude for the various coating/substrate combinations. Betz et al.(48) have reported some results on how coating ductility and LCF-endurance decrease with increasing coating thickness, Fig. 16.

Low Cycle Fatigue

Relatively few studies have been conducted on the low cycle fatigue properties of coated nickel and cobalt-based superalloys, and variable results have been obtained, this being mainly due to differences in testing technique, coating type, test temperature range and so on.

Wells and Sullivan (41) have demonstrated that significant improvements in the low cycle push-pull fatigue properties of U700 can be achieved by pack aluminising this alloy. In tests conducted at 927°C, the cyclic strain tolerance of coated material was up to 50% higher than that of the uncoated alloy. Although crack initiation resistance was improved by the use of a standard pack-aluminising treatment followed by the normal quality heat treatment for the alloy, further benefits resulted by the inclusion of an intermediate coating diffusion treatment, Fig. 17.

The effects of pack-aluminide coatings on the push-pull low cycle fatigue characteristics of Rene 80 have been evaluted using a strain range partitioning analysis technique by Kortovich and Sheinker (48) and Halford and Nachtigall (49), Fig 18.

In tests conducted at 871°C and 1000°C under ultra high vacuum conditions, Kortovich and Sheinker indicated that whilst the fatigue life was significantly affected by the strain cycle type, the introduction of a creep factor reducing the life considerably, there was little or no effect of the coating or test temperature on the fatigue properties. In a parallel programme, Halford and Nachtigall demonstrated that there were no significant differences between uncoated and pack-aluminised René 80 in push-pull low cycle fatigue tests conducted in air at 1000°C.

A comparison of these data on Rene 80, however, indicated that whilst there is a significant effect due to environment, viz the fatigue strength is higher in vacuum than in air, there is no difference between material in the coated and uncoated conditions within a particular environment, Fig. 18.

Although this situation would be expected to be maintained in long-term tests conducted in vacuum, a progressive weakening of uncoated material compared with coated might be expected to occur in high temperature, long-term tests conducted in air. This would be especially true in thin section material. In the Rene 80 work the coating treatment was incorporated into the normal quality heat treatment schedule for the alloy.

The effects of various aluminide and platinum-aluminide coatings on the reverse bend low cycle fatigue properties of IN738LC and FSX414 have been reported by Strang (39). In tests which incorporated a 30 minute dwell period between each cycle, at various temperatures between 500°C and 900°C, no significant differences between coated and uncoated material were found for durations of up to 700 hours and 1500 hours in the case of FSX414 and IN738LC respectively (Figs. 19 and 20). In all of these tests the full quality heat treatment appropriate for IN 738LC and FSX414 was carried out after coating.

In practice the actual coating response will be the result of the strain cycle imposed by a combination of mechanical and thermal effects. As a result of this there has been a move towards achieving tests which are more representative of actual turbine blade operating conditions by carrying out programmed thermo-mechanical fatigue tested on coated material. Whilst relatively little work has been reported in this area, the data reported indicates that cracking is likely to occur in the coating in relatively few cycles if a sufficiently high strain level occurs below the coating transition temperature. Conversely, should the peak strain be imposed above the transition temperature, crack initiation may take many thousands of cycles to occur, and be in the substrate below the coating rather than in the coating itself.

On the basis of the work reported to date it can therefore be concluded that there appears to be no significant negative effect due to coating on the low cycle fatigue properties of nickel and cobalt superalloys, although premature cracking of the coating can occur, if it is is too thick, or is excessively strained below its DBTT.

High Cycle Fatigue

The effects of coating on the high cycle fatigue properties of nickel and cobalt-based superalloy blading material have not been comprehensively reported to date. Various workers have reported the results of limited studies indicating that the application of coatings can have both positive and negative effects. The wide variance in coating influence is due to factors such as variations in testing techniques, viz push-pull, rotating bend, cantilever bend and so on, as well as variations due to other factors such as type of coating, method of application, coating thickness, use or otherwise of a post-coating heat treatment.

In a general way, the high cycle fatigue response can be favorably influenced if the coating provides a surface that is fatigue resistant, especially at low stresses, if favorable residual stresses are introduced as a result of the coating deposition, or if the coating protects the substrate from the environment. On the other hand, the fatigue lives could be reduced if the coating is less fatigue resistant than the substrate, if the diffusion zone which usually exists between the coating and the substrate significantly reduces the load bearing capability of the coating/substrate composite, or if unfavorable residual stresses are introduced during coating deposition.

Bartocci (50) found that aluminide coatings lowered the 10^7-cycle fatigue strength of the alloy SEL 15; the thicker the coating the greater the effect. In tests performed at 815°C, 25 and 50 micron thick coatings reduced the 10^7 cycle fatigue strength by approximately 8% and 15% respectively, even though a post-coating heat treatment had been carried out. Similar reductions in the fatigue strength of aluminide coated U500 have been observed by Betts (51) in tests conducted at 734°C.

Pack aluminising was also reported by Llewelyn (52) to lower fatigue strength of Nimonic 105 tested at 900°C, but use of a corrective post-coating heat treatment improved the fatigue strength beyond that of the uncoated alloy. Belgaew et al. (53) reported that protection of the nickel base alloy ZhS6U with aluminide coatings did not reduce fatigue strength at 950°C and 1000°C and led to improved properties at RT provided coating thicknesses were controlled to between 40 and 60 microns. At thicknesses of greater than 60 microns premature failure occurred primarily as a result of cracking in the less ductile aluminide layer. Improvements in the room temperature fatigue properties of aluminide coated nickel and cobalt based alloy have also been reported by Puyear (54) as well as by Lane and Geyer (56).

A more comprehensive study of the effects of pack aluminide coatings on the high cycle fatigue properties of nickel based alloys has been reported by Paskeit, Boone and Sullivan (56). In studies conducted on U700 in the temperature range RT to 900°C, using reverse bend specimens, they were able to demonstrate that application of a 75 micron thick aluminide coating could lead to improved properties in the temperature range RT to 500°C and impaired properties at temperatures between 500°C and 900°C, Fig. 21. The enhancement of properties in the lower temperature range was attributed to the aluminide coating having a higher crack initiation resistance than the substrate. This was based on data indicating that the room temperature yield strength of NiAl is greater than 689MPa at strain rate equivalent to that achieved in these tests. A room temperature endurance limit of approximately 448MPa is therefore not inconsistant for a material consisting principally of NiAl phase. It is of interest to note that in spite of the substrate strength being lower than that of the coating, initiation is reported to occur at RT in the coating. As the temperature increases the endurance limited for NiAl decreases while that for the substrate increases, at least up to 800°C. A cross over in properties therefore occurs with the result that above 550°C the coated material is marginally weaker. This occurs in spite of a post-coating corrective treatment being carried out and is a reflection of the relative properties of coating and substrate. At 900°C the fatigue properties of coating and uncoated U700 are the same and it may be that at still higher temperatures, due to a further cross over effect, coated material is again superior, due to the substrate being protected from oxide fingering effects leading to the early failure of the material.

In more recent work the push-pull high cycle fatigue properties of platinum aluminide and plasma spray overlay coated IN738LC and IN939 have been evaluated by Grunling et al. (57) in collaboration with other COST 50 Round II workers (58,59,61). Tests on LDC2 and RT22 coated IN738LC conducted at 650°C and 850°C indicate that provided the appropriate quality heat treatment is carried out after coating there is no significant loss in the high cycle fatigue strength and in some cases an improvement. These data are supported by independent studies on RT22 coated IN738LC conducted at 750°C by Cooper (61).

In the studies described above, initiation of the fatigue crack always occurred in the substrate and not in the coating and as such it can be argued that the coating has no negative effect. This was however reversed when samples were aged prior to testing. This resulted in a lowering of the fatigue strength and the observation of initiation occurring in the coating. Whilst other evidence indicates that σ -platelets form below the diffusion zone, these play no part in reducing the fatigue strength in the section thicknesses considered here, viz appproximately 4mm. It must, therefore, be concluded that some reduction in the strength and/or ductility of the coating occurs and that may be in part responsible for effects observed.

Summarizing the effect of coatings under cyclic conditions, it may be suggested that in order not to degrade the fatigue properties of a substrate over the entire range of cyclic stresses, the coating must have not only the ductility of the substrate at high stess levels (LCF) but must also have the strength of the substrate at low stress levels (HCF), i.e. high yield strength or low elastic modulus. In addition, the coating must protect the substrate from oxidation during high temperature exposure. A coating with optimum properties, therefore will have to be tailored to the substrate by controlling the composition, ductility, and strength.(46)

Thermal Fatigue

In many respects the thermal fatigue behaviour of coated superalloys might be expected to be similar to that observed in low cycle fatigue studies on these materials. The overall observations on the effects of coating thickness, coating ductility, control of the applied strain cycle, and so on, are all equally applicable, as are the remarks made regarding coating integrity. Additionally, however, as has been demonstrated by Strangman (62), the degree of thermal expansion mismatch between the coating and substrate must be considered since this is likely to be the major source of strain generated in the coating during thermal cycling. Large differences in thermal expansion coefficients between a coating and its substrate may lead to premature cracking in the coating, particularly if the coating is thick and peak strains occur below the coating DBTT. These cracks may in turn propagate into the substrate during further thermal fatigue cycles, ultimately leading to failure of the component.

Selection of coatings for each application must therefore be based not only on their corrosion resistance but also on their DBTT and compatibility with the substrate alloy in terms of their thermal expansion properties. In general terms it may therefore be considered that the most important overall mechanical property of a coating is its resistance to thermal fatigue cracking. In spite of such observations, however relatively few data on the thermal fatigue properties of coated superalloys have been published, which in addition are difficult to interpret due to the large variety of specimen shapes and testing cycles used as well as the varying definitions of what constitutes specimen failure .

Boone and Sullivan (63) have investigated the effects of aluminide coatings, produced by inward and outward diffusion processes, on the thermal fatigue properties of a number of nickel and cobalt-based superalloys, incl U700 and WI-52. The results indicated that in polycrystalline substrates inward-type aluminide coatings generally improved fatigue performace while the outward-type was detrimental. These differences are explained in terms of the microstructures of the coatings. The fine grained structure, characteristic of the outer layer of the inward-type aluminide, appears to inhibit crack initiation, while the coarse grained columnar-like structure of the outward type is less resistant.

Some other results of thermal fatigue testing of coated and uncoated superalloys are summarised in Fig. 22. It was further found (64,65,66) that coatings on DS-alloys generally did not improve the thermal fatigue resistance, but it should be recognised that DS-materials are already vastly superior to their polycristalline counterparts. It has also been observed that even where coatings led to an improvement of the thermal fatigue strength, once initiation had occurred, the crack growth into the substrate was faster than in the non-coated alloy (67) Fig 23.

Cycling coated and uncoated Glenny discs in IN738LC between 950° and 40°C showed that on discs giving rise, due to their geometry, to high strain levels during thermal cycling, a detrimental effect by LDC-2 coatings was observed while the same coating on discs involving smaller maximum strain levels induced a significant improvement of thermal fatigue resistance.(14)

CONCLUDING REMARKS

Whilst there continue to be a number of technical difficulties associated with the use of aluminide coatings on certain superalloy substrates, these are more than outweighed by the overwhelming advantages offered by this type of system for the protection of high temperature gas turbine components. The cheap and effective aluminide systems developed for the protection of aero engine components have been extensively developed to the extent that they are also currently finding applications in long life industrial gas turbine systems.

These coating systems are generally well understood, can be applied with confidence and efficiency to complex shaped components and provide protection for many thousands of turbine hours in agressive environments. Blade repair and recoating processes are now well developed and can be applied with a high degree of reliability and quality control, thus extending the potential lives of many gas turbine components. This approach is not only cost effective but also conserves energy as well as strategic raw materials.

Whilst the use of aluminide coatings is clearly cost effective care must be exercised in ensuring that they continue to be applied to superalloy systems without prejudice to their mechanical properties and hence life of the components. In this respect it is important to ensure that the coating system is properly matched to the alloy heat treatment in order that no losses are incurred in the basic mechanical properties of the material. Coating thicknesses should be optimised such that the required degree of protection is obtained without the risk of premature cracking due to high strain and/or thermal fatigue effects in the component. A continuing high standard of quality control should be exercised in order to ensure that defective coatings are not put into turbines, thus minimising the risk of component failure due to sub-critical crack growth processes during service.

As is evident from the above, the use of aluminide coatings as a cheap and efficient palliative to high temperature corrosion in gas turbines will continue well into the future. There is however need for further development work, not only in improving the coatings themselves, but also in their practical application. For example, ODS alloys and carbide fibre reinforced eutectic alloys are still difficult to coat effectively using aluminide systems. Improved processes are also required for protecting internal passages in cooled blades. The use of alloying additions or Al_2O_3 particles to aluminide coatings should be investigated in an attempt to improve their mechanical properties, in particular ductility. The effect of coatings on the mechanical properties of thin section superalloys is not yet fully understood. Finally whilst the quality control exercised in the production of commercial coatings is generally high there are no internationally accepted NDT and quality control standards for coatings. The development of such procedures could only improve the overall effectiveness and reliability of the most cost effective coating system developed to date.

ACKNOWLEDGEMENTS

The authors wish to thank the Directors of GEC and ONERA together with the Commission of the European Communities for permission to publish the paper.

REFERENCES

1) G. Marijnissen. Final Report COST 50 / II-NL3. "Study of Gas Phase Coating Mechanisms", 1981, see also ref. 9.

2) G.W. Goward, D.H. Boone and C.S. Giggins. Trans. Am. Soc. Met. 60, 1967, p. 228.

3) G.W. Goward, J. Metals 22, 1970, p. 31.

4) R. Pichoir. In : Materials and Coatings to Resist High Temperature Corrosion, Edit. P.R. Holmes and A. Rahmel, Appl. Sci. Publ., London 1982, p. 271.

5) J.L. Smith and C.E. Lowell. J, Electrochem. Soc, 121, 1974, p. 800.

6) C. Duret and R. Pichoir. In : "Coatings for HT-Applications", Edit, E. Lang, Appl. Soc. Publ., London 1983. p. 33.

7) T.K. Glasgow and G.T. Santoro. "Oxidation and Hot Corrosion of Coated and Bare ODS Superalloy HA-755E". Oxidation of Metals - to be published.

8) D.H. Boone, P.A. Crane and D.P. Whittle. Thin Solid Films, 84, 1981, p. 39.

9) C. Duret, A. Davin, G.H. Marijnissen and R. Pichoir, "Recent Approaches to the Development of Corrosion Resistant Coatings" in "High Temperature Alloys for Gas Turbines 1982". Proc, Conf. by Brunetaud et al., Reidel Publ. Co., Amsterdam, 1982, p. 78.

10) French Patent No. 1.589.365 (19.09.1967).

11) R.P. Seeling and R.J. Stueber. High Temperature - High Pressures 10 (1978), p. 202.

12) S. Shanker, D.E. Koenigh and L.E. Dardi, J. Metals, Oct. 1981, p. 13.

13) S.P. Cooper and A. Strang, In : "High Temperature Alloys for Gas Turbines 1982", ed. Brunetaud et al., Reidel Publ. Co., Amsterdam, 1982, p. 249.

14) E. Lang and E. Bullock. "The Effect of Coatings on the HT Mechanical Properties of Nickel-base Superalloys". Final Report COST 50/II-CCRI, CEC-Report EUR 8242 EN, 1982.

15) R. Pichoir, Chemcial Vapor Deposition - Fifth International Sumposium, ed. The Electrochemcial Society Inc. Princeton Univ. 1975, p. 298.

16) R.S. Bender and R.S. Parzuchowski. US Patent USC No. 661-903(25-2-76).

17) J.E. Restall and C. Hayman. British Patent No. 1.549.245. May 1979 and US Patent No. 4.156.042, May 1979.

18) J.E. Restall, B.J. Gill, C. Hayman and N.J. Archer. Proc. 4th Int. Symp. on Superalloys, Seven Springs Sept. 1980, p. 405.

19) J.E. Restall, British Patent Application 1.926.456 (1979) and Euro Patent No. 0.024.802 (1980).

20) D.A. Besen. US Patent GE No. 622-376(14-10-75).

21) P.L. Ahuta. Final Report "Internal Coating of Air-cooled Gas Turbine Blades". GE. Nov, 1979, NASA C.R. 159-701.

22) P. Mazars. Heurchrome, Private Communication.

23) G.H. Marijnissen, Elbar, Private Communication.

24) G. Lenhert and H.W. Meinhardt. Electrodepos. Surface Treat. I. (1972/73), p. 189.

25) High-Temperature Oxidation Resistent Coatings. Report National Academy of Science/Material Acadamy of Engineering, Washington 1970. p. 121.

26) M.M. Haafkens In : "High Temperature Alloys for Gas Turbine 1982". ed. R. Brunetaud et al., Reidel Publ. Cie. Amsterdam, 1982. p. 931

27) J.G. Fountain, F. Golightly, F.H. Stott and G.C. Wood. Oxidation of Metals 10. 1976. p. 341.

28) P. Steinmetz, B. Roques, B. Dupre, C. Duret and R. Morboili. Annual Meeting TMS-AIME High Temperature Protective Coatings, Atlanta, March 1983.

29) Ch. Just. In : "High Temperature Alloys for Gas Turbine 1982". ed. Coutsouradis et al., Appl. Publ. London 1978, p. 147.

30) J. Conde. AMTE, Private Communication.

31) H.W. Grunling. K.H. Keinenburg and K.K. Schweitzer. In : High Temperature Alloys for Gas Turbines 1982". ed. Brunetaud et al., Reidel Publ. Amsterdam 1982, p. 507.

32) A. Strang and S.P. Cooper. Final Report COST 50/-UK24, GEC Report W/CML/1983/3, 1982.

33) M. Rabinovitch/ONERA. Unpublished work.

34) J.M. Hauser, C. Duret and R. Pichori. "Influence des Traitements de Protection sur les Proprietes Mechaniques Pieces en Superalliage, AGARD Conf. Proc. No. 312.

35) High Temperature Oxidation Resistant Coatings. National Academy of Science/National Academy of Engineering, Washington 1970, p. 118.

36) G.W. Goward. "Materials and Coatings for Gas Turbine Hot-Section Components". Proc. Gas Turbine Materials Conf., Washington 1972, p. 85.

37) A. Strang. "The Effects of Corrosion Resistant Coatings on the Structure and Properties of Advanced Gas Turbine Blading Alloys". 13th CIMAC Congress, Vienna May 1982.

38) A. Strang, 4th Conference on Gas Turbine in a Marine Environment. Annapolis, Maryland. USA. 1976.

39) A. Strang. In : "Behaviour of High Temperature Alloys in Aggressive Environments". Proc. Int. Conf. Petten (NL) 15-18 Oct. 1979, The Metals Society, London 198, p. 613.

40) E. Lang and L. Tottle. "Some Observations concerning the Structural Stability of Aluminide Coatings on Alloy IN 738 LC, JRC Report on Special Activities P/COST/II 1.3, March 1981.

41) C.H. Wells and L.P. Sullivan. Trans. A.S.M. <u>61</u> (1968), p. 149.

42) S.R. Holdsworth, GEC Private Communications.

43) H.W. Grunling, BBC Private Communications.

44) D.A. Woodford. Met. Trans. <u>12A</u> (1981), p. 299.

45) K. Schweitzer and W. Track. "Pestigheitsverhalten von Turbinenschaufelwerkstoffen mit und ohne Schutzschichten unter Heissgaskorrosion", Final Report COST 50/II-D13, MTU June 1981.

46) D.E. Gramham and D.A. Woodford. Met. Trans. <u>12A</u> (1981), p. 329.

47) W. Betz, H. Huff and W. Track. Z. f. Werkstofftechnif <u>5</u>, (1975), p. 161.

48) C.S. Kortovich and A.A. Sheinker. AGARD Conf. Proc. No. 243, April 1978, p. 1-1.

49) G.R. Halford and A.J. Nachtigall. AGARD Conf. Proc. no. 243, April 1978, p. 2-1.

50) R.S. Bartocci. ASTM STP No. 421, September 1977, pp. 169-187.

51) R.K. Betts. GE Report R67FPD357, October 1967. (Reference 21 in Myers and Geyer, SAMPLE QUART Vol. 1, 1970, pp. 18-28).

2) G. Llewelyn. ASTM STP No. 421, September 1967.

53) M.S. Belgaev, N.D. Zhukov, M.P. Krivenko and V.V. Terekhova. Problemy Prochnosti, No. 11, November 1977.

54) R.B. Puyear. High Temperature Metallic Coatings, Machine Design, July 1962, pp. 177-183.

55) R. Lane and N.M. Geyuer. Journal of Metals, Vol. 18, February 1966, pp. 186-191.

56) G.F. Paskeit, D.H. Boone and C.P. Sullivan, Journal of the Institute of Metals, Vol. 100. February 1972, pp. 58-62.

57) A.W. Grunling, K. Schneider and H.V. Arnim. Final Report, COST 50/II-D2, BBC February 1981.

58) G. McColvin. Final Report COST 50/II, UK6, H.W. February 1982.

59) A. Strang. Interim Report. COST 50/II-UK24, GEC, May 1979.

60) P. Moorehouse and P.L. Miler, Final Report COST 50/II-UK11, IRD, October 1981.

61) S.P. Cooper. GEC Whetstone, UK Private Communication.

62) T.E. Strangman. Thin Solid Films Vol. 45, September 1977, pp. 499-506.

63) D.H. Boone and C.P. Sullivan, ASTM STP No. 520, June 1972, pp. 401-415.

64) J.E. Restall, National Gas Turbine Establishment, Farnborough, Hants, Private Communication, March 1982.

65) D.A. Spera, M.A.H. Howes and P.T. Bizon. NASA Tech. Reports, NASA TNX-52975 and NASA CR 72 738, 1971.

66) J.R. Rairden, Thin Solid Films, Vol. 53, 1978, p. 251.

67) A.J.Santhanam and C.G. Beck. Thin Solid Films, Vol. 73, 1980, pp. 387-395.

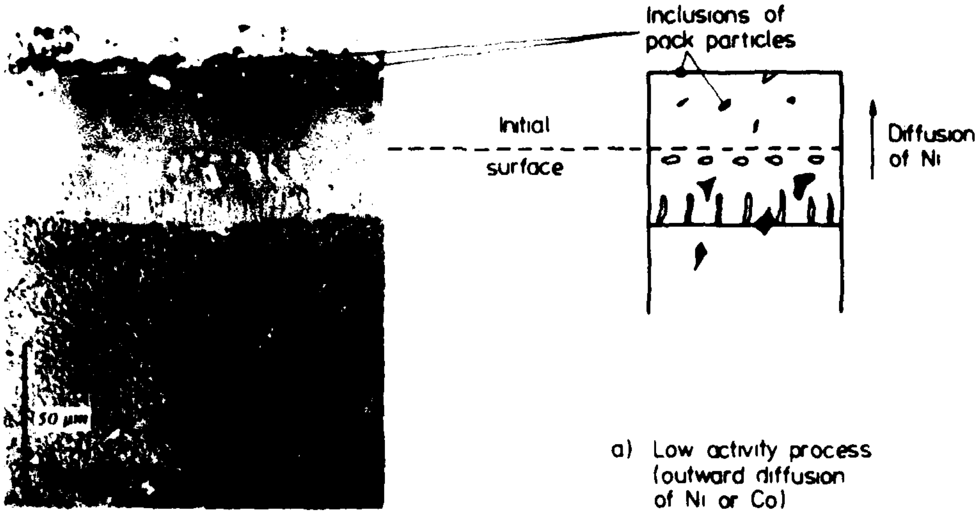
68) J.C. Galsworthy, J.E. Restall and G.C. Booth, In : "High Temperature Alloys for Gas Turbine 1982". ed. Brunetaud et al., Reidel Publ. Amsterdam 1982, pp. 207-235.

69) G.W. Meetham, Inst. of Metallurgist Spring Refresher Course, 1978, Cardiff U.K.

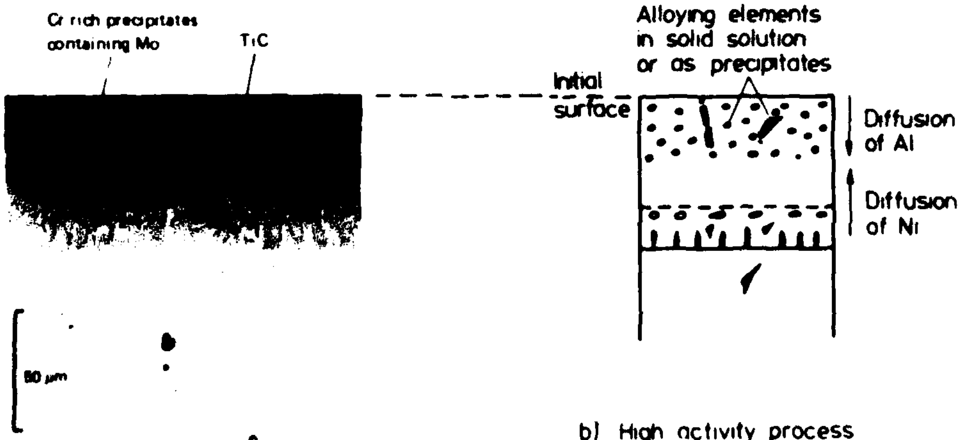
70) P.C. Felix and M. Villat, Sulzer Technical Review, Vol. 3, 1976.

71) C. Haywood, Admiraltyn Marine Technoology Establishment, Holton Heath, Dorset, U.K. Private Communication, June 1982.

72) J.E. Restall, National Gas Turbine Establishment Farnborough, Hants. Private Communication April 1982.



a) Low activity process (outward diffusion of Ni or Co)

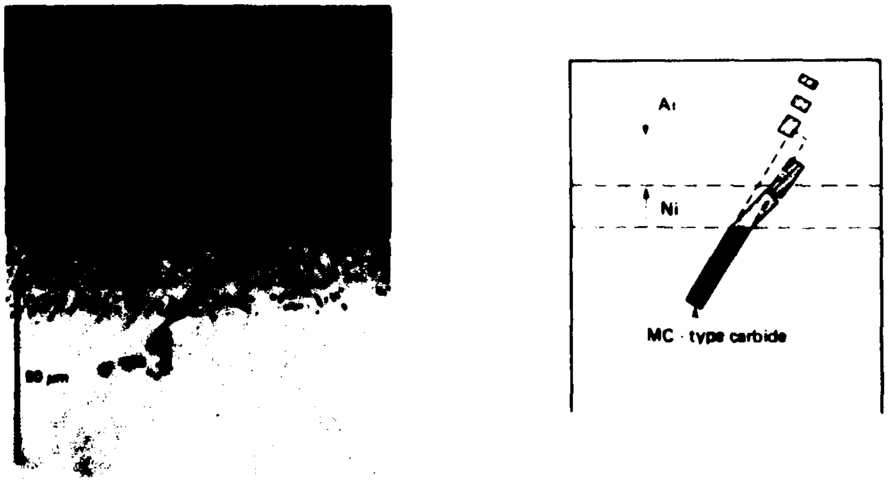


b) High activity process (inward diffusion of Al)

Fig. 1 – Comparison of the structures of two NiAl-type coatings.

a) NiAl type coating on IN 100 obtained by high activity aluminizing treatment and subsequent diffusion annealing

b) Local oxidation in the vicinity of a MC-type carbide (IN 100 treated by high activity aluminizing technique and subsequently oxidized 100 hours at 1100° C).



c) Cracking of a MC-type carbide during a high activity aluminizing treatment (MAR.M.004).

Fig. 2 – Behaviour of MC-type carbides in high activity aluminide coatings.

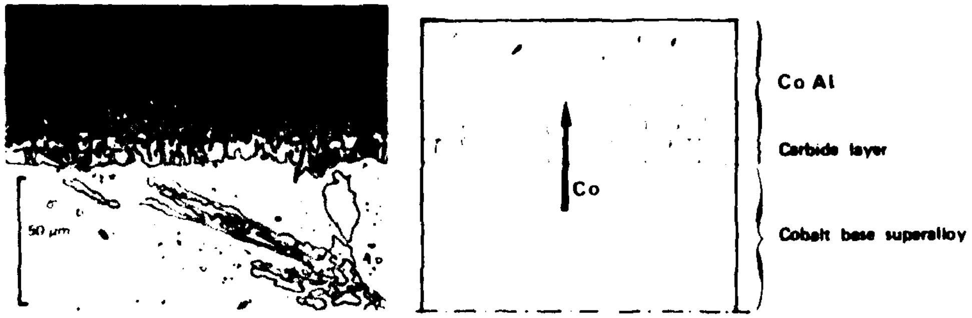
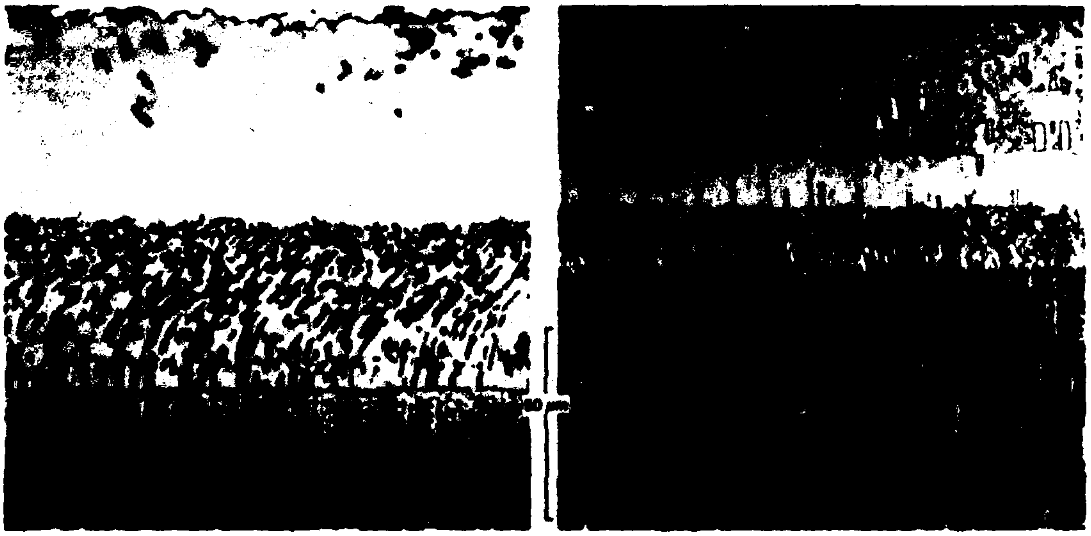


Fig. 3 – Low activity aluminide coating on Co-base superalloy X 40.



Low activity aluminizing treatment

High activity aluminizing treatment

Fig. 4 – NiAl-type coatings on COTAC 744 (γ/γ' – NbC eutectic).

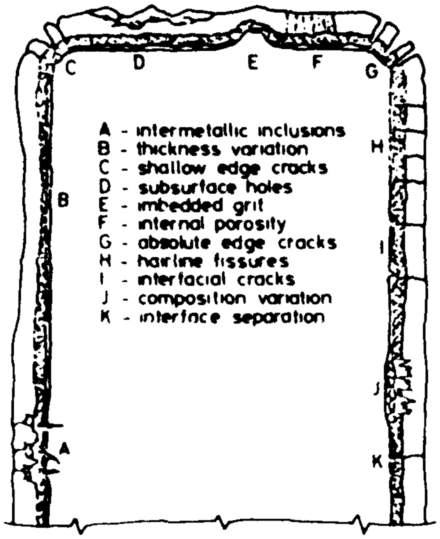


Fig. 5 – Representative random defects in coatings (from ref. 25).

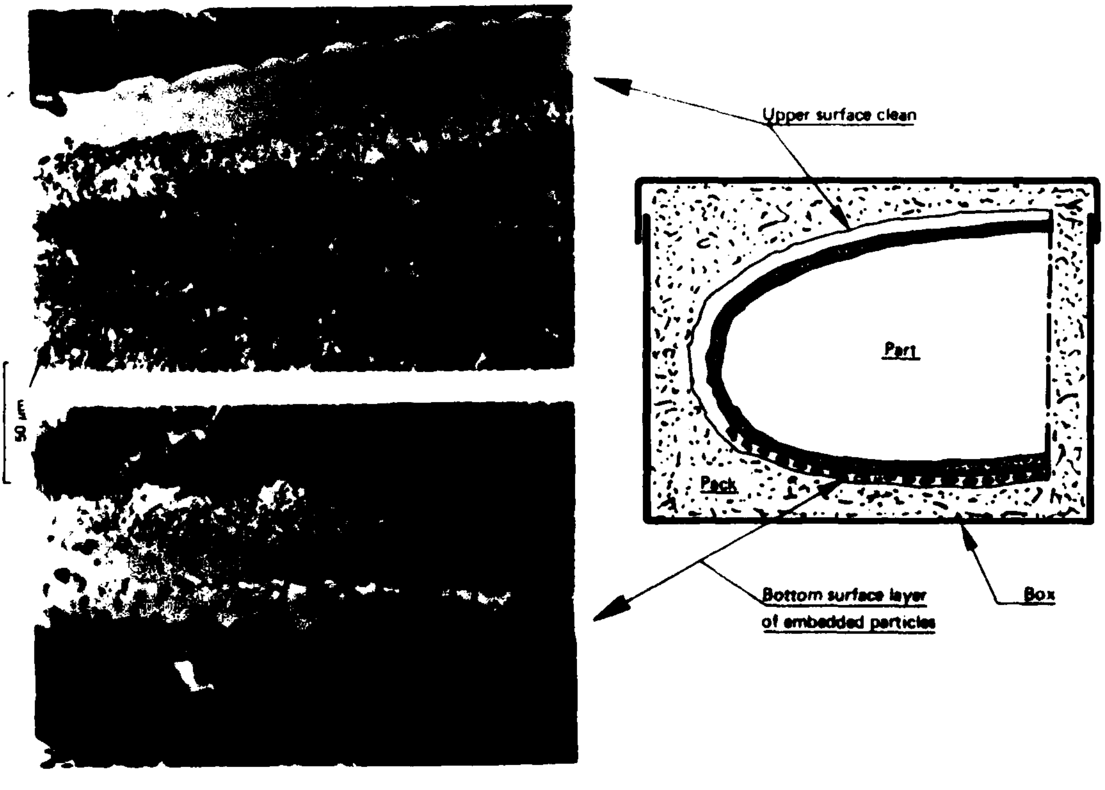


Fig. 6 – Variation of coating structure caused by positioning of the part in the cementation pack ; HI-15 on IN 738 LC.

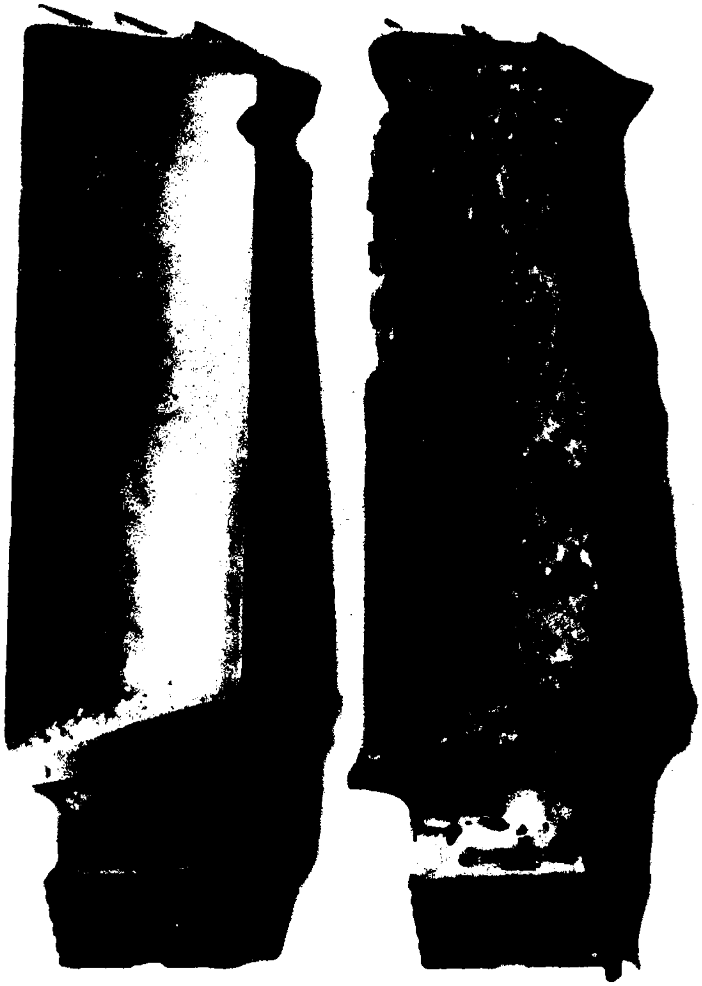


Fig. 7 – Industrial gas turbine blades from a desert location in the Middle East. Pack aluminised IN 738 blade after 12,000 hours service (left) and pack aluminised Nimonic alloy 115 blade after 2000 hours service (right) (from ref. 68).

a)

b)

Fig. 8 – (a) Uncoated and (b) aluminised Dart turbine blades after "inter-island" operation (from ref. 89).

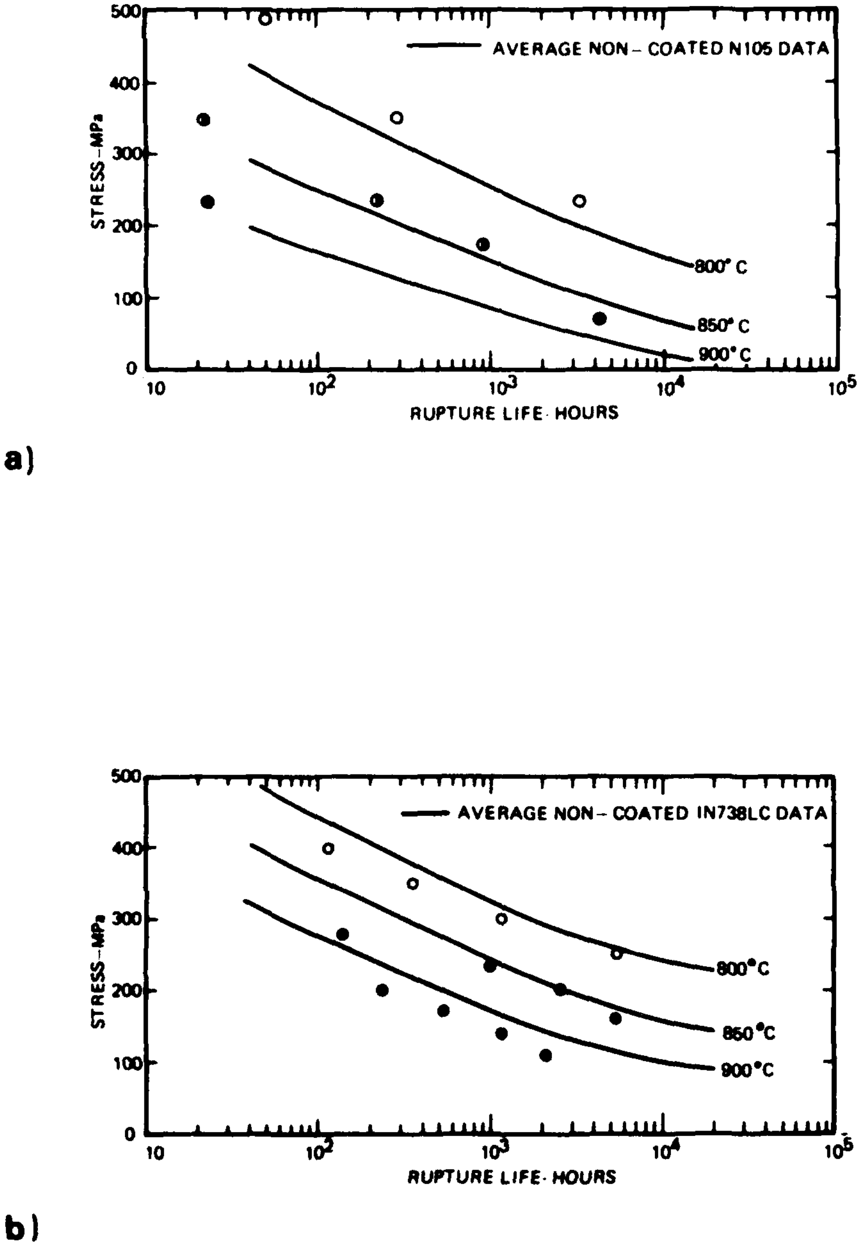


Fig. 9 – Effect of CVD Si-coatings on creep rupture life : no detrimental effect being observed on Nimonic 105, (a) ; while same coating leads to reduction of t_r for IN 738 LC, (b). (after ref. 70).

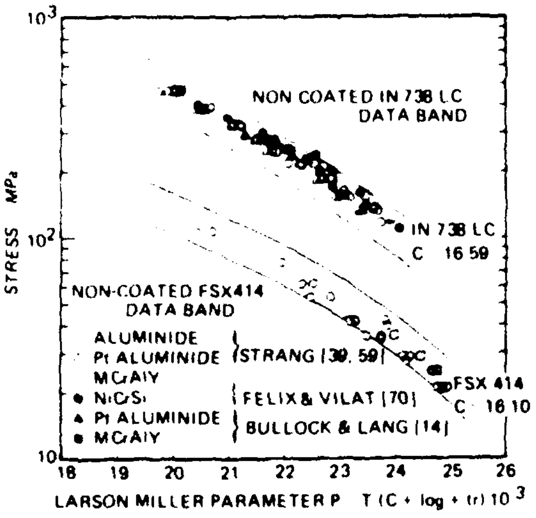


Fig. 10 – Rupture properties of coated and non-coated IN 738 LC and FSX4 14. (Quality heat treatment had been applied after coating process).

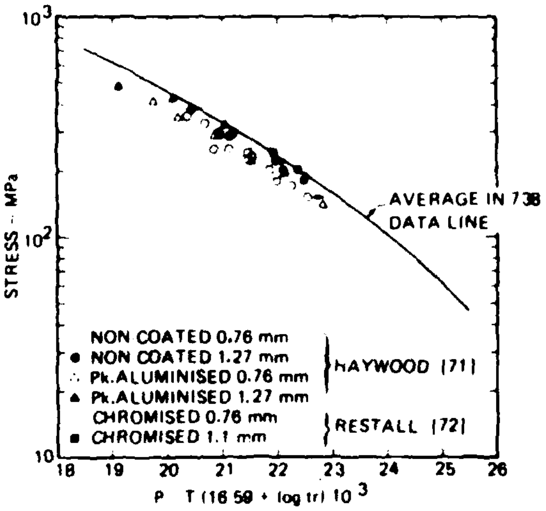


Fig. 11 – Rupture properties of thin section IN 738 C in the coated and non-coated condition.

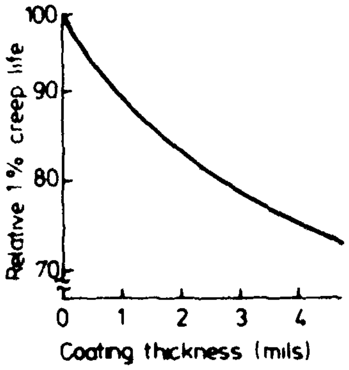


Fig. 12 – Effect of coating weight (thickness) on blade creep life (from ref. 3).

Fig. 13 – Platelike phases formed by interdiffusion of a Hi-15 coating on IN 738 LC creep-tested 10 375 h/750°C/ 320 N/mm².

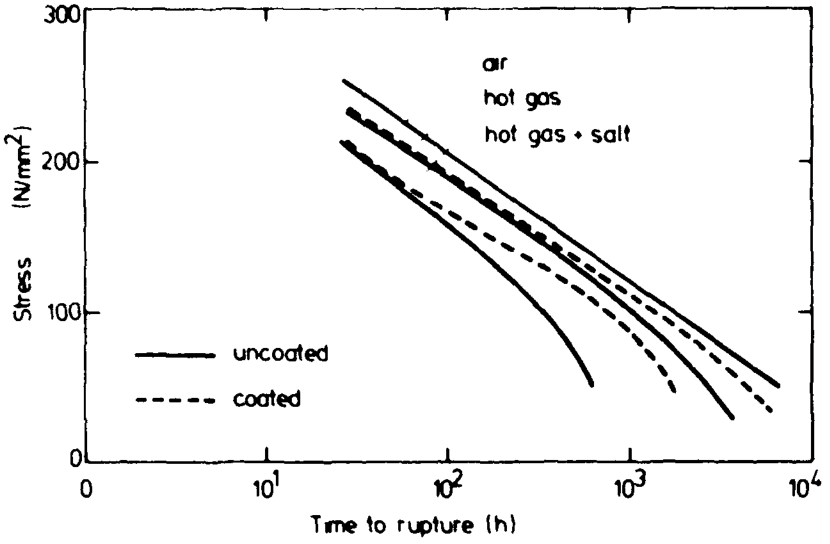


Fig. 14 – Influence of hot gas corrosion on creep rupture life of uncoated and coated turbine blade alloy : IN 100 (950° C) (after ref. 45).

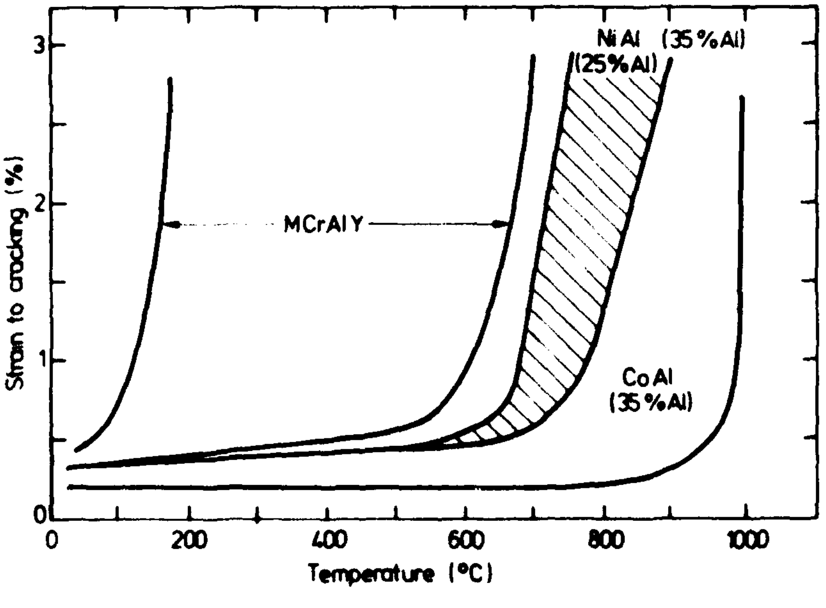
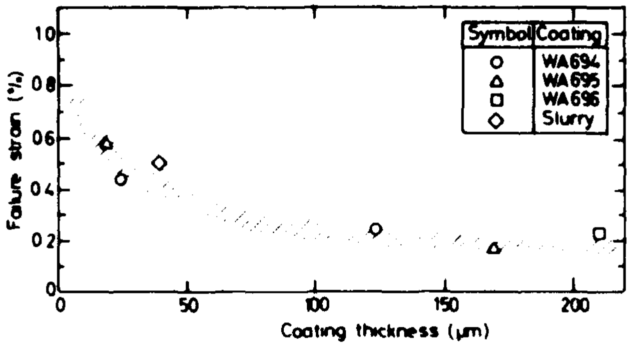
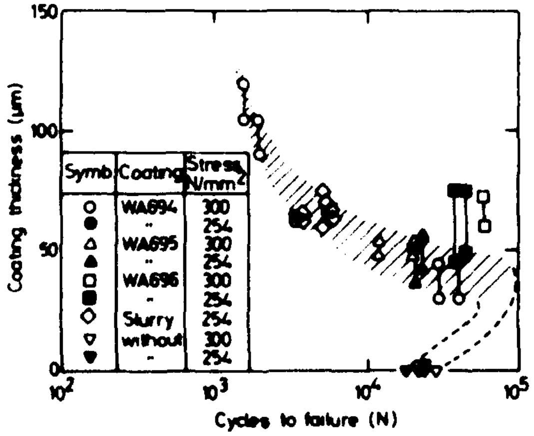


Fig. 15 – Relative brittle-ductile behavior of diffusion aluminide and MCr AlY coatings (after ref. 3 and 8).

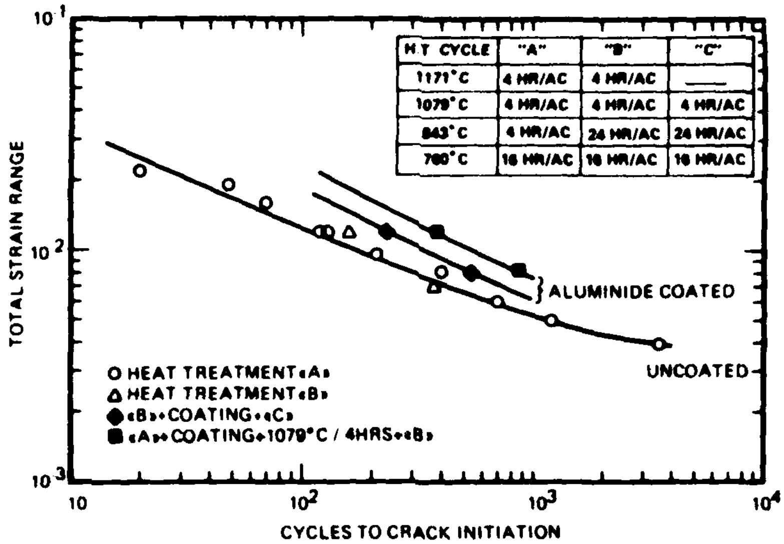


a) Ductility of coating versus thickness



b) LCF strength of nickel alloy IN 100 : stress cycles at fracture versus coating thickness at 960° C in hot gas atmosphere.

Fig. 16 – (from ref. 47).



H.T. CYCLE	"A"	"B"	"C"
1171°C	4 HR/AC	4 HR/AC	____
1079°C	4 HR/AC	4 HR/AC	4 HR/AC
843°C	4 HR/AC	24 HR/AC	24 HR/AC
760°C	16 HR/AC	16 HR/AC	16 HR/AC

Fig. 17 – Low cycle fatigue properties of coated and non-coated U700 at 927°C (from ref. 41).

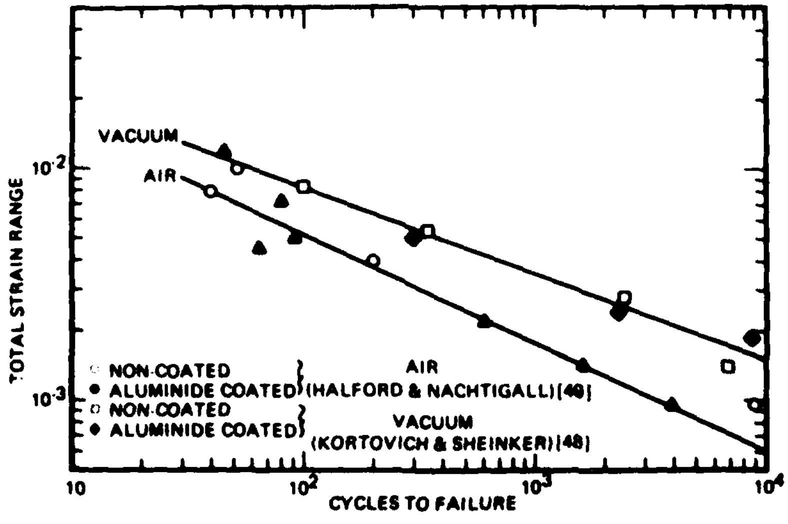


Fig. 18 – Low cycle fatigue properties of coated and non-coated René 80 at 1000°C.

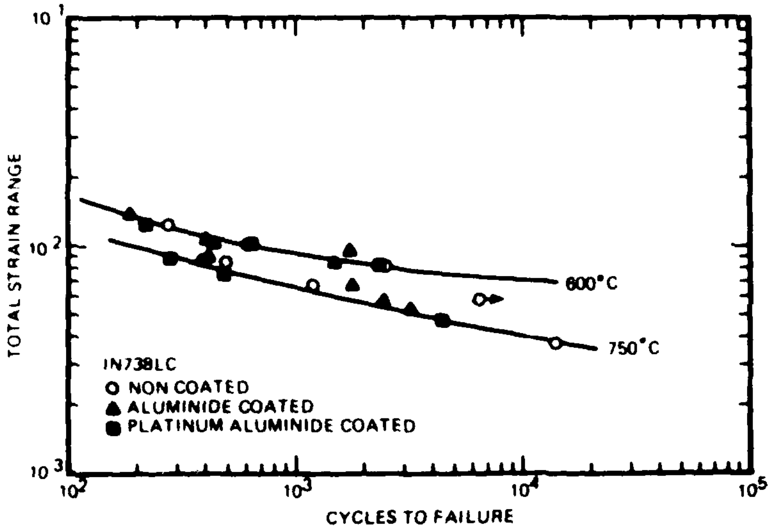
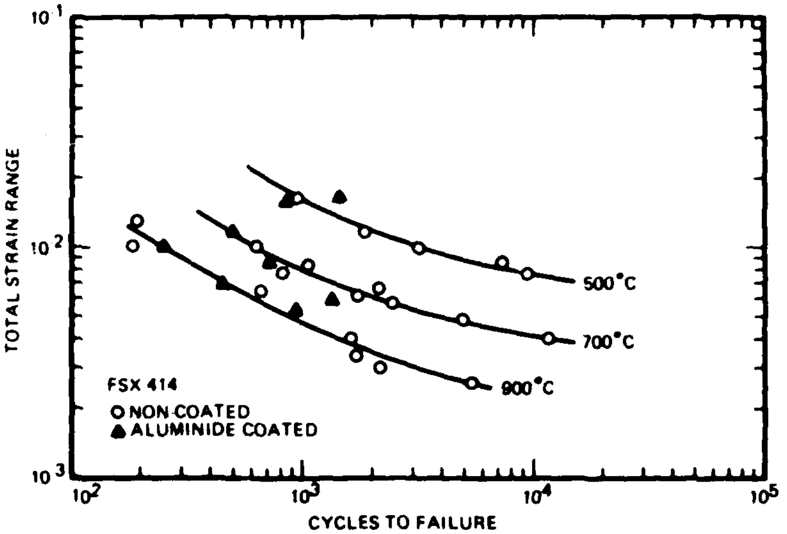


Fig. 19 – Low cycle fatigue properties of coated and non-coated IN 738 LC.

Fig. 20 – Low cycle fatigue properties of coated and non-coated FSX414



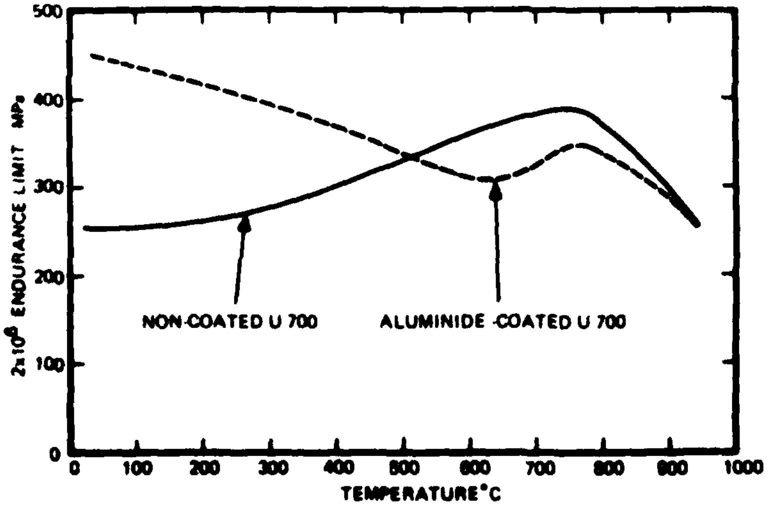


Fig. 21 – High cycle fatigue properties of coated and non-coated U 700 (from ref. 58).

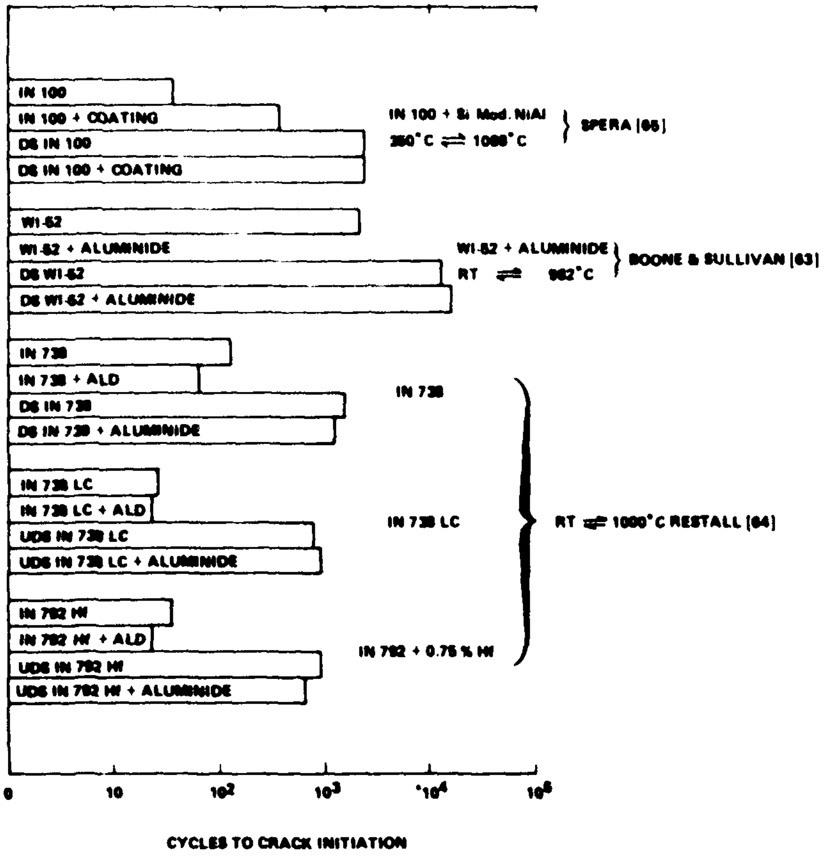


Fig. 22 – Thermal fatigue properties of polycrystalline and UDS superalloys in the coated and non-coated condition.

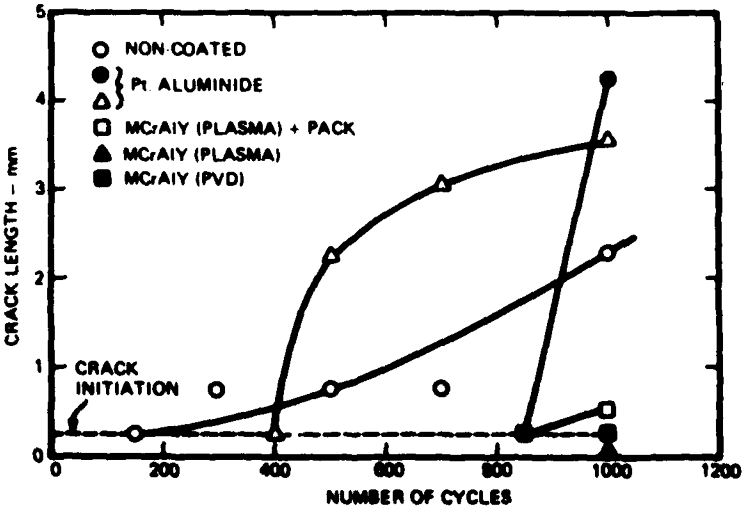


Fig. 23 – Effect of coating on thermal fatigue crack growth in U 710 (from ref. 67).

COATINGS FOR FUEL ECONOMY OR MATERIALS SUBSTITUTION

J.P. Coad and K.T. Scott
Materials Development Division
Atomic Energy Research Establishment
Harwell
Didcot
Oxfordshire
United Kingdom

ABSTRACT

The application of three coating techniques to problems of fuel economy or materials substitution is described. The coating techniques are plasma spraying, Sputter Ion Plating (SIP) and Plasma Assited Vapour Deposition (PAVD), and the applications range from thin coatings for nuclear and aerospace use to free standing furnace elements.

INTRODUCTION

Surface coatings are asssuming an ever increasing importance in many spheres of industrial activity especially when the use of relatively small quantities of high performance materials can significantly extend the operational range of inferior substrates. Thus, coating technology is particularly relevant for materials substitution and fuel economy. The objective of this paper is to present an account of three coating techniques that are being exploited at Harwell with examples of their application that are appropriate to this theme. The emphasis has been biased towards the applications and materials development rather than on the processes themselves. Two of the techniques, plasma assisted vapour deposition (PAVD) and sputter ion plating (SIP), deposit thin films, while the third, plasma spraying, produces thick coatings.

PLASMA SPRAYING

Plasma spraying is one member of a family of coating processes known generically as flame or thermal spraying. In the plasma process the heat source is an electric arc struck between two electrodes, the anode of which serves as a nozzle(1). Making the diameter of the latter smaller than that of the free-burning arc results in very high current densities which generate temperatures up to 20,000°K and force the ionised gases (i.e. a plasma) to be ejected as a jet with velocities up to and exceeding the speed of sound. Such arc-plasmas serve as efficient sources of kinetic and thermal energy. Most devices use argon or nitrogen as the main plasma gas, often with small additions of hydrogen and operate at power levels between 20 and 80KW.

The coating material, in powder form, is injected into the plasma at a position mainly determined by its thermal characteristics. Because of the high temperature and inert nature of plasmas and also since residence times for the particles are typically no longer than a millisecond almost any material can be sprayed provided it melts without significant dissociation or evaporation. Thus, many metals, ceramics and even some plastics can be sprayed. However, as far as the substrate is concerned plasma spraying is effectively a cold process and so it is possible to coat a wide range of materials including those of low melting point with minimum risk of oxidation or distortion. Substrate preparation usually consists of degreasing and blasting with alumina grit to provide a surface texture onto which the sprayed particles can quench and adhere.

Plasma spraying is a rapid process which can deposit thick coatings (0.1-2.0mm) and does not require the use of an inert chamber. Sprayed coatings have a unique anisotropic, lamellar structure (Fig. 1) built up from splat-quenched particles with an ultra-fine microstructure and often containing metastable phases(2). Their major limitation is residual open porosity which results from the rapid solidification, material shrinkage and gas entrapment. In some cases, if the economics allow, post-coating treatments such as sealing, shot-peening, hipping or laser-glazing are used to reduce this porosity. For the important class of MCrAlY overlays considerable claims are made(3) for the use of low pressure plasma spraying to produce metallurgically bonded coatings the microstructure of which is refined by annealing with the plasma in either the transferred or non-transferred arc mode.

An important pre-requisite for successful plasma spraying, especially with ceramic materials, is to have well characterised free-flowing powders. Single- or multi-component oxide coatings are frequently used and their spray powders are made conventionally by crushing the fused ceramic followed by selective milling and sizing, which for hard substances, can often be lengthy, dusty and energy-consuming processes. Improvements in coating quality are obtained from the use of small particle size (e.g. 5-25 μm) but this frequently results in bad flow properties.

Methods based on gel processing have been developed at Harwell to prepare a range of powders suitable for plasma spraying(4). Typcially a concentrated aqueous dispersion of an oxide or oxide mixture is gelled by some appropriate means to give spherical particles of the required size which are then calcined to yield free-flowing powders. More recent developments(5) have enabled a small quantity of a sol to be used as a "vehicle" into which relatively large amounts of ceramic powder can be carried as a "passenger" yielding non-sedimentary dispersions of even higher concentrations. The latter are added to an immiscible solvent and agitated to a predetermined degree to form spherical particles of the required size and simultaneously gelled by any one of several techniques.

The extremely small particle size (~150Å) in the sols and also of the passenger material (typically 2 µm) yields an active oxide powder which readily allows full reaction or sintering to take place at relatively low temperatures. For example, high density spheres of fully stabilised zirconia can be formed at only 900°C. Many homogeneous, multicomponent oxide systems have been prepared as free-flowing powders down to 5 µm diameter by either conventional sol-gel methods or by the gel vehicle route. Typical products are shown in figure 2. The principle advantages of gel processes over traditional powder fabrication routes are control of particle size (and shape), materials economy, energy saving (low temperature firing) and reduction of the dust hazards associated with crushing and sieving. The gel vehicle route offers further benefits through less use of expensive sol, low shrinkage on calcining the gel and substantial reduction in processing costs.

The scope of plasma spraying at Harwell has been further extended by developing it as a fabrication technique(6). If a plasma sprayed coating is deposited on a mandrel which is subsequently removed by some appropriate means then a discrete "free-standing" artefact remains which accurately reproduces the mandrel shape. The method is particularly suitable for preparing 'one-off' or prototype components. Its main advantages are (i) the preparation of items from materials which are difficult to machine or process by conventional routes but which can be sprayed, (ii) the processing of pure materials without the use of additives, (iii) the preparation of thin sections or complex shapes and (iv) the manufacture of high density components which can frequently be used without any subsequent heat treatment.

One of the earliest uses of Harwell plasma sprayed sol-gel materials was in the development of high temperature fuel cells using $16.9^{w}/o$ yttria stabilised zirconia as the electrolyte(7). The operating principle of such cells depends on the diffusion of negative oxygen ions through vacancies in the oxygen sub-lattice. Provided suitable electrodes are attached to either side of the ceramic the ions are transported from an oxygen-rich atmosphere to an oxygen-deficient atmosphere and an electric current can be drawn from the cell. Above 800°C the anion mobility is sufficient for useful power generation. Such cells are attractive because they have no moving parts, the electrolyte is invariant with a long life and they can operate at high electrochemical efficiency on a variety of hydrocarbon fuels and air without the use of the expensive precious metal catalysts required for low temperature fuel cells. To avoid power loss through internal resistance working units were composed of thin (~200 µm) spray formed tubes interconnected by an electronically conducting material compatible with both oxidising and reducing conditions. The latter-Nb_2O_5 doped TiO_2-was also produced by gel processing and deposited by plasma spraying. A third gel processed oxide, SnO_2 doped In_2O_3, served as the air electrode.

As fabricated the thin electrolyte tubes were slightly permeable to air and more so to hydrogen. The residual porosity reponsible for this was removed by sintering the components at 1800°C in a zirconia tube furnace. The elements for the latter were also fabricated by plasma spraying stabilised zirconia and could be operated as resistors or susceptors (a resistor version is shown in figure 3). The high purity of the sol gel materials enabled susceptors to reach 2400°C whereas comparable tubes spray formed from commercially available powders suffered serious loss in mechanical strength above 1700°C.

A combination of high temperature fuel cells and zirconia furnaces has been proposed recently for the production of hydrogen by the thermolysis of water(8). This could be an important development for a hydrogen based economy, piped hydrogen, for example, avoiding the high energy losses occurring during the conventional transmission of electrical power. Zirconia furnaces with elements made by the Harwell route are being used in the manufacture of optical fibres. The reliable production of a high quality fibre will play an important role in reducing the quantity of copper used in cable.

Fusion reactors are expected to play a vital role in the long term strategy of the developed nations. To achieve steady state operation in such reactors devices called 'limiters' are incorporated primarily to prevent unstable plasmas damaging their toroidal confinement. In an experimental reactor such as the Joint European Torus (JET) limiters must withstand energy impulses of at least $2KWcm^{-2}$ at 1500°C from intense proton bombardment. Conventionally limiters are constructed from copper faced with either molybdenum or tungsten but unfortunately contamination of the plasma by refractory atoms can have a cooling effect. However, materials of low atomic number could avoid this problem and some work has been carried out to evaluate whether plasma sprayed oxides could meet the requirement(9). Under carefully controlled conditions materials such as Al_2O_3, $MgAl_2O_4$ and TiO_2 have been sprayed onto copper. These have subsequently withstood repeated thermal cycling up to 800°C and irradiation by ion beams of $2KeVD_2^{+}$ ions without degradation. Figure 4 shows the surface of a TiO_2 coating after this treatment and it is indistinguishable from that of an as-sprayed coating.

The desirability of using cheaper but often more corrosive fuel together with increased operating temperature to achieve better efficiency from both turbines and reciprocating engines has resulted in higher levels of damage from corrosion and thermal stress. Corrosion arises from liquid salts formed on combustion from Na, S and V impurities commonly present in lower grade oils, while the higher temperatures are responsible for faster oxidation rates and stress cracking. The most vulnerable components are the blades and combustion cans in turbines, and pistons, valves and cylinder heads in diesel engines. Improvements in coating technology will be vital in combating these problems. For example, pack aluminising or the application of MCrAlY overlays by low-pressure plasma spraying(3) and other techniques have proved very effective in combating oxidation of turbine blades. Considerable effort is also being expended world-wide to develop thermal barrier coatings which resist the higher gas temperatures but keep the substrate temperature below the critical levels for oxidation and mechanical failure. Because of their low thermal conductivity (1-2 Wm^{-1} °C) plasma sprayed zirconia based ceramics are currently the most favoured materials. Their main disadvantage is inadequate resistance to thermal cycling and shock for realistic lifetime especially in aero gas turbine applications. Figure 5 shows a small turbine blade coated with .1mm of NiCrAlY and a 12^{w}/oY_2O_3-ZrO_2 (.4mm) derived from gel processed powder. The ceramic did not fail until some 2000 cycles (each of 10 minutes at 1100°C and 10mins in a cold fluidised bed) and considerably out performed commercially available coating materials subjected to identical tests. No oxidation of the substrate is apparent beneath the NiCrAlY even though this was air plasma sprayed. In contrast unprotected areas of the substrate suffered considerable oxidation during the test.

Kvernes and colleagues have developed thermal barrier coatings for diesel applications(10). In particular they found that a triplex coating of NiCrAlY-Cr-Y_2O_3/ZrO_2 (composition unspecified) showed no degradation after 6000 hours in service testing in large bore marine diesel engines. Figure 6 shows typical diesel exhaust valves coated at Harwell with a metallic bond and up to 2mm of various ZrO_2 materials. In laboratory tests such coatings have survived severe thermal testing with oxy-acetylene flames but their long term behaviour remains to be evaluated.

PAVD COATINGS

In Plasma Assisted Vapour Deposition (PAVD) the samples to be coated are either suspended or supported in a glass reaction vessel (normally silica) and the samples are connected to earth. The glass reaction vessel may be evacuated by means of a rotary pump, and a range of gases may be fed into the vessel from a gas handling manifold where their individual flow rates are accurately monitored by means of mass flow controllers. The pumping speed and rate of supply of gases to the reaction vessel are controlled so as to give a pressure in the reaction vessel of a few mbar. In the simplest form of apparatus, a helical RF induction coil is present around the glass reaction vessel level with the samples. When the coil is energised an axial magnetic field is produced which causes samples to be heated according to their magnetic susceptibility; in practice it is found that most metals are readily heated to at least 800°C in the system. If the sample temperature is raised to 800°C or above (depending on the reactive gases present in the system) then a thermally activated reaction is liable to occur: since the reaction occurs at the hot substrate this naturally results in a coating on the surface. This is the basis of chemical vapour deposition (CVD)(11) and deposition can occur at atmospheric pressure as well as at pressures down to a few mbar (where the technique becomes known as low pressure CVD (LPCVD)). However the energised RF coil also produces a radial electric field between the samples (at earth potential) and itself. In the pressure range 1-10 mbar this results in a glow discharge formed within the gas and a high excitation rate for the gas molecules present. These activated gas atoms and molecules are far more likely to react and since the greatest electric field exists at the surface of the samples, then a coating is likely to result. The region of high electric field close to the sample surface (the plasma sheath) follows closely the contours of the surface allowing uniform coating over complex surface geometries. This phenomenon was well illustrated by the original use at AERE of the PAVD process i.e. that of coating continuous tows of 7 μm diameter carbon fibres(12). Ten thousand of the carbon fibres were passed along the axis of the chamber together and a plasma sheath formed around each individual fibre and resulted in uniform coating(in this case of silicon carbide).

By suitable arrangements of the magnetic and electric fields, samples can be coated by PAVD at any temperature required and with a wide range of materials. Experiments at Harwell have been largely restricted to silicon-based coatings, and two applications of these coatings will be described in some detail.

Silicon carbide and silicon nitride coatings have been studied as wear resistant surfaces, and a particular example of relevance to the themes of the conference is the application to fibre heaters. Yarn is heated to thermally 'fix' a twist in the fibres by passing the fibres over a hot surface under tension, which requires a substrate material with good thermal properties and resistance to wear from the abrasive particles used as delustrants in the yarn. An ideal bulk material would be brass since it is inexpensive and has excellent thermal properties, but the wear resistant is inadequate. Hard-chromium-plated brass has been employed with some success, and the plating has the added advantage of producing an ideal surface topography for fibre contact; however, even with thick chromium deposits the component lifetime was limited. Brass heater shells (hard-chromium-plated) were coated by PAVD with silicon carbide (on which the favoured topography was faithfully maintained by the PAVD coating) and the resulting surface carbide proved to be far more resistant to wear by the fibres. A heater shell (which had been used prior to PAVD coating) is shown in Figure 7, after PAVD coating with silicon carbide at about 350°C.

PAVD is currently being used to develop silica coatings for applications to the British Advanced Gas-Cooled Reactor (AGR) programme(13). The fuel for the AGR is in the form of UO_2 pellets packed under pressure into a 15mm diameter 20%Cr/25%Ni niobium-stabilised stainless steel (20/25/Nb) can (termed the 'cladding'), the length of the sealed tube (or fuel 'pin') being approximately 1 metre. Chemical interactions between the cladding of the fuel pins and the carbon dioxide based reactor coolant can affect the performance of the fuel in two principal ways. In the first, oxidation of the cladding leads to a loss of section by general and localised attack which reduces the capability of the cladding to contain the fission gas pressure within the fuel pin in the event of a reactor depressurisation incident. The second effect is that the Fe and Ni constituents of the oxides formed on the pin surface catalyse the formation of carbonaceous deposits onto the pin, which impair its heat transfer characteristics. These deposits derive from the radiation and thermal induced degradation of the precursors formed from the methane and carbon monoxide, which are added to the coolant to limit the corrosion of the graphite moderator.

There is a considerable economic incentive to exploit the development potential of the AGR system by extending the target mean burn-up of fuel from the current 18 GWd/tU to at least 24GWd/tU and even possibly to 30 GWd/tU. This extended burn-up would reduce fuel cycle costs both at the fabrication and reprocessing stages. However any extension in the dwell time of fuel in-reactor obviously increases the extent of oxidation of the cladding. It is prudent therefore to investigate means of reducing the oxidation of the cladding and the use of protective coatings is one such technique. In addition, these coatings could inhibit the catalysed formation of carbonaceous deposits onto the fuel pin surface. They would allow, therefore, greater flexibility in the choice of coolant composition to limit moderator corrosion, leading to the use of less aggressive coolants in the reactor and hence to an increase in moderator life.

Silicon coatings deposited onto small sections of 20/25/Nb fuel can by PAVD have greatly reduced the extent of oxidation in CO_2, as can be seen in figure 8. The upper band represents the weight gains from a large number of 20/25/Nb control samples, whilst the band of low weight gains represents ten samples PAVD coated with SiO_2. In fact this data is biased against the coatings, since well over 90% of the weight gain that does accrue on the coated samples is from the unmachined internal surface of the drawn tube, whereas negligible oxidation occurs on the carefully machined outer surface (which is the only surface exposed to the reactor environment). The coatings have also been shown to prevent metal catalysed carbon deposition in tests in the DIDO reactor at Harwell, leaving only a thin pyrocarbon (which forms on all surfaces exposed to the AGR gas mix). Complete fuel pins have also been coated by PAVD and tested in the Windscale AGR, and the results were in line with the small-scale experiments described. Figure 9 shows a PAVD system being used to coat an AGR fuel pin; a larger system has now been developed to coat 12 fuel pins at each loading.

PAVD coatings such as the silica described above have potentially wider application to corrosion problems, and a programme in this area has been approved by the Commission of the European Communities. The programme entitled "silicon-rich metallic and ceramic coatings for substitution of chromium in high temperature technology", is being carried out in conjunction with the National Physical Laboratory (NPL), Teddington, London and Imperial College London, and also includes work on coatings based on sol-gel technology and laser glazing.

SPUTTER ION PLATING (SIP)

SIP is a coating technique which employs atoms and ions sputtered from solid plates as the source material, and a negative bias on the samples during deposition to control the structure of the coating as described in a paper by Mattox and Macdonald(14). A schematic diagram of the equipment which indicates the main features is shown in Figure 10. Samples are suspended within a stainless steel cylinder and are surrounded with plates of the source material; electrical connections are made (separately) to the samples and to the plates. The stainless steel vessel can be heated with external heaters and its temperature is monitored. Purified argon, or other gas, is passed continuously through the coating chamber at a pressure of about 10/d mbar, where d is the chamber dimension in mm. A mechanical pump is sufficient to maintain the working pressure, provided a vent on the coating compartment is designed with a high aspect ratio such that back diffusion of external contaminating or reactive gases cannot take place: for a related reason no condensible vapour within the enclosure can escape. The general procedure is as follows. A flow of high purity argon at reduced pressure is established and further purified by passing it through a continuously working titanium getter. The coating compartment and its contents are then heated to about 300°C to outgas all the exposed surfaces and to establish a very pure atmosphere, which is important for good adhesion of the coatings. In many cases, the samples are then cleaned by ion bombardment to remove thin oxide layers and further promote adhesion, but if the naturally occurring oxide is tough and well adhered to the parent metal ion cleaning may not be necessary. In order to produce a coating a large negative voltage (typically 1000V) is applied to the plates of source material which causes a glow discharge to form in the vessel and argon ions bombard the inner surfaces of the plates. Atoms and ions of the source material are sputtered from the plates, and move in a random manner through the chamber with a short mean free path. Much of the material is redeposited on the plates, but material arriving at the sample surface (or exposed parts of the chamber) settles to form the coating. A relatively small bias voltage on the samples (0 to 100V) results in "ion polishing" of the nascent coating(14) to form a dense structure without significant re-sputtering. The use of a DC bias limits the technique to conducting coatings, but the substrates may be either insulating or conducting, since once the coating commences the surfaces rapidly become conducting and the bias effective. Sputter Ion Plating has been used to deposit a wide range of metals and metallic alloys, as well as the carbides and nitrides of many metals, and further details may be found elsewhere(15). Applications of the technique include materials conservation (longer lifetimes), materials substitution and greater fuel efficiency, and an example of each will indicate the versatility of the sputtering method.

An area where coating development is extremely active at the current time is coating of tool steels for wear resistance. It has been shown that for many different cutting processes the lifetime of the cutting tool can be increased by a significant factor if it is first coated with a hard layer of low coefficient of friction. Widespread use of such tooling would then result in a reduced consumption of tool steel, which is taking an increased amount of strategic materials as compositions become more complex. By far the most common coating applied to tool steel is titanium nitride, and in SIP this is done by sputtering titanium targets with a partial pressure of nitrogen added to the argon gas. Drills coated with TiN by SIP have shown a factor of ten improvement in useful cutting life, and a range of other tools have also given encouraging results. When directly compared with an uncoated tool, a coated tool also requires less energy to maintain a given cutting rate than the uncoated tool. Because TiN is relatively straightforward to deposit and works well in many cases, there has so far been little work on alternative coatings which may outperform TiN in certain instances. It may also prove possible in the future to combine a wear resistant coating with a simpler (and cheaper) substrate material. However, the current emphasis is on improving existing tools with TiN on an economic scale; the latest SIP system coats approximately 1000 small components (e.g. drills), per loading and further development is continuing.

There is frequently a desire to use a particular bulk material for which the surface properties are unsatisfactory. For example, lightweight alloys such as aluminium or titanium alloys might provide adequate strength and fatigue properties, but have inadequate wear or corrosion resistance, and coatings are being assessed in a number of these situations. One such case concerns the increased use of components made from titanium alloys in aircraft engines, where the primary limitation on the use of such components is the rate of oxidation at increasing temperature. If the maximum allowable temperature can be increased by 100°C by using coated titanium alloys, then very useful savings in engine weight can be made. It is possible that SIP could be an appropriate method for tackling this problem.

Whilst lightening a gas turbine engine improves the effective efficiency by facilitating a commensurate increase in payload, the turbine efficiency may be directly improved by either running the turbine at higher temperature, or reducing the percentage of air used for blade cooling. In order to achieve these improvements in efficiency, it is inevitable that components in the turbine (notably the first stage rotor blades) will run at higher temperatures. First stage rotor blades already use highly sophisticated bulk materials together with a surface treatment such as pack aluminising to reduce oxidation but further improvements in temperature capability can be achieved using surface coatings to prevent oxidation at higher temperatures (i.e. overlay coatings such as the M-Cr-Al-Y alloys, where M is Ni, Co, Fe or a mixture of these elements) or as a thermal barrier. SIP has been used to deposit a range of overlay coatings (16) and the results compare well with coatings deposited by more capital-intensive equipment such as electron-beam evaporation and low-pressure plasma spraying (LPPS). Figure 11 shows a series of micrographs of an CoCrAlY coating of nominal composition Co-20Cr-9Al-0.3Y on a wrought superalloy turbine blade. The four micrographs show the coating as received and after 250, 500 and 1000 hours at 1000°C in air; in each case the part of the aerofoil shown is the trailing edge, which is the region where defects in a coating are most likely to appear. In the early stages at 1000°, the as-coated structure transforms into a fine two-phase structure, the lighter phase being a Co-Cr solid solution and the darker phase β-CoAl which coarsens with increasing time at temperature. A uniform region depleted in Al is formed at the outer surface of the coated blade due to outward diffusion of Al to form the protective alumina scale. The Al level near the coating/substrate interface is also reduced due to inward diffusion of Al to form regions of nickel aluminide within the inconel substrate. It can be seen from Figure 10 that the extent of the inward diffusion increases with time, as also does the outer region of depletion though this is not very evident in this particular series of micrographs. SIP overlay coatings have been included in a series of corrosion rig tests which also examine the use of such coatings for resisting hot corrosion with very encouraging results (16).

CONCLUSIONS

Harwell has a wide range of coating facilities of which just three have been discussed in this paper; plasma spraying, plasma assisted vapour deposition (PAVD) and sputter ion plating (SIP). All the techniques are engaged in a wide variety of experimental programmes, many in collaboration with industrial companies, which concentrate on applications of coatings rather than development of the coating techniques. All the examples chosen in this paper have some connection with materials conservation/substitution, indicating that there is widespread interest in this topic, and that coating technologies have a fundamental role to play therein.

ACKNOWLEDGEMENTS

A number of the coating programmes described in this paper have been carried out under contract from the Procurement Executive, MOD, and the authors wish to thank them for their support and encouragement. The experimental help of co-workers at Harwell is also kindly acknowledged.

REFERENCES

1. R.F. Smart and J.A. Catherall, "Plasma spraying", Mills and Boon, London, 1972.
2. S. Safai and H. Herman, Proc. Advances in Surface Coating Technology, London 1978. The Welding Institute Cambridge p.1.
3. R.W. Smith, W.F. Schilling and M.M. Fox. Proc. 9th Int. Thermal Spraying Conf. The Hague, 1980, p.32.
4. R.L. Nelson, J.L. Woodhead, K.T. Scott, L.L. Wassell and A.G. Cross, Proc. 7th Int. Metal Spraying Conf. London 1973, Welding Institute, Cambridge 1973 p.96.
5. K.T. Scott and J.L. Woodhead, Thin Solid Films 95 (1982) p.219.
6. K.T. Scott and A.G. Cross. Energy and Ceramics. P. Vincezini (ed). Proc. 4th Int. Meeting on Modern Ceramic Technology, 1979, Elsevier, Amsterdam, 1980, p.596.
7. T.L. Markin, Power Sources No. 4 Brighton 1972, p.583.
8. A.M. Anthony, Advances in Ceramics Vol.3 Science and Technology of Zirconia Ed. A.H. Heuer and L.W. Hobbs, p.437.
9. K.T. Scott and J.P. Coad Thin Solid Films 80 (1981) p.279.
10. I. Kvernes, P. Fartum and R. Henrikson, U.S. Government Printing Office 1979 0-281-704/1033.
11. See for example Hinterman, H.E. Thin Solid Film 84 (1981) p.215.
12. K. Linger, Proceedings of IPAT 77, Edinburgh June 1977, CEP Consultants.
13. P.L. Allen, D.A. Moore, M.J. Bennett, J.A. Cairns, J.P. Coad, J.B. Sayers and A.W.P. Newbigging, BNES Conf. on Gas-Cooled Reactors Today, Bristol, Sept. 1982.
14. D.M. Mattox and J.E. Macdonald. J. Appl. Phys. 34 (1963) p.2493.
15. J.P. Coad and R.A. Dugdale, Proceedings of IPAT 79, London July 1979, CEP Consultants, p.186.
16. J.P. Coad and J.E. Restall, Metals Technology 9 (1982) p499.

Fig. 1 Cross-section of a plasma sprayed titanium dioxide coating showing the typical lamellar structure and a shrinkage crack.

Fig. 2 (a) 17 $^{w}/o$ Y_2O_3 - ZrO_2 powder made by sol gel processing.
(b) TiO_2 powder produced by the gel vehicle route.

Fig. 3 A zirconia resistor furnace with the element fabricated from a gel processed powder by plasma spraying

Fig. 4 Surface of a TiO_2 coating after irradiation with 2 KeV D_2^+ ions at 500°C.

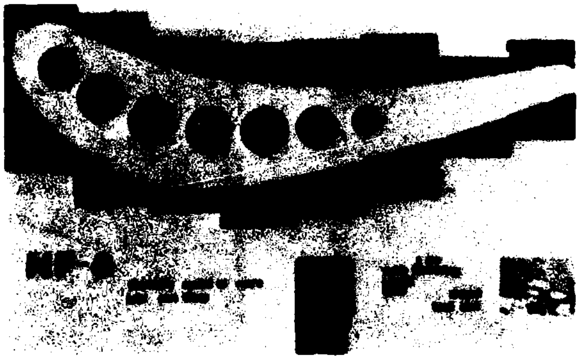


Fig. 5 A small turbine blade coated with 0.4mm of 12 $^w/o$ Y_2O_3-ZrO_2 over 0.1mm NiCrAlY after extensive thermal cycling to 1100°C.

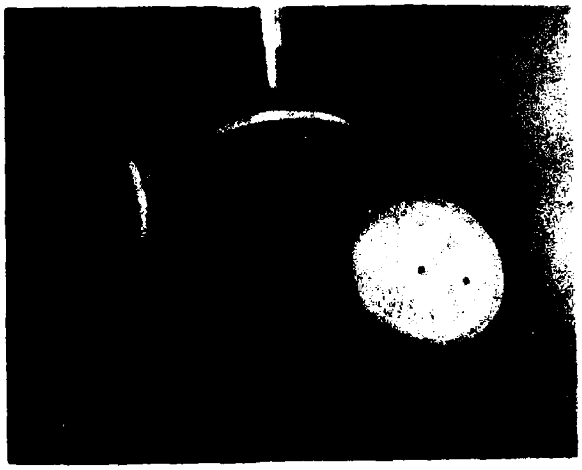


Fig. 6 Diesel exhaust valves coated with up to 2mm of stabilised zirconia over a bondcoat.

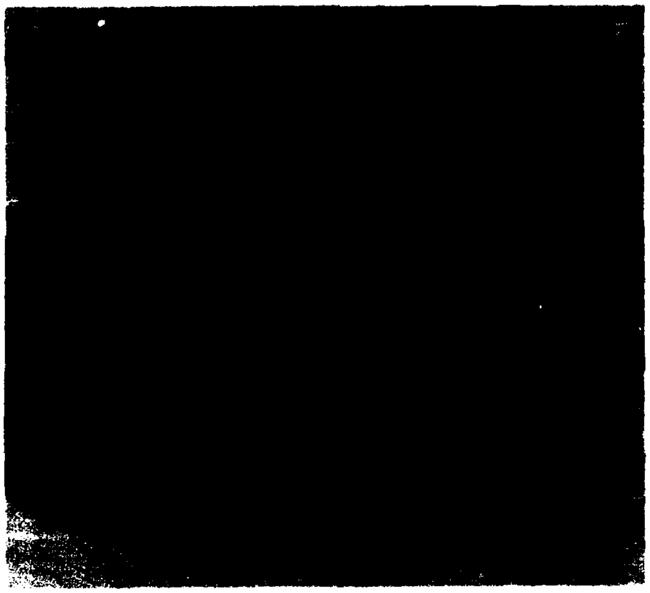


Fig. 7 A chromium-electroplated brass heater shell coated with SiC by PAVD.

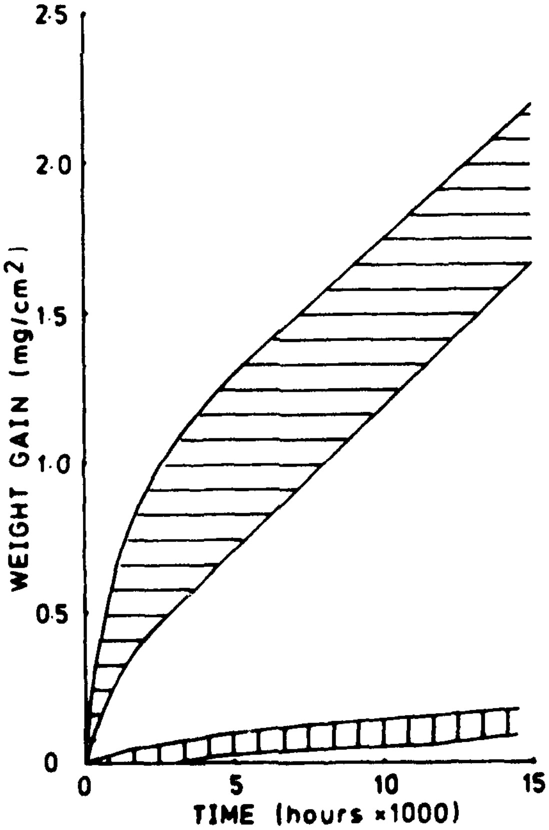


Fig. 8 A comparison of the oxidation rates of SiO_2 coated (vertical hatching) and uncoated (horizontally hatching) 20/25/Nb samples.

Fig. 9 A PAVD system used for coating AGR fuel pins.

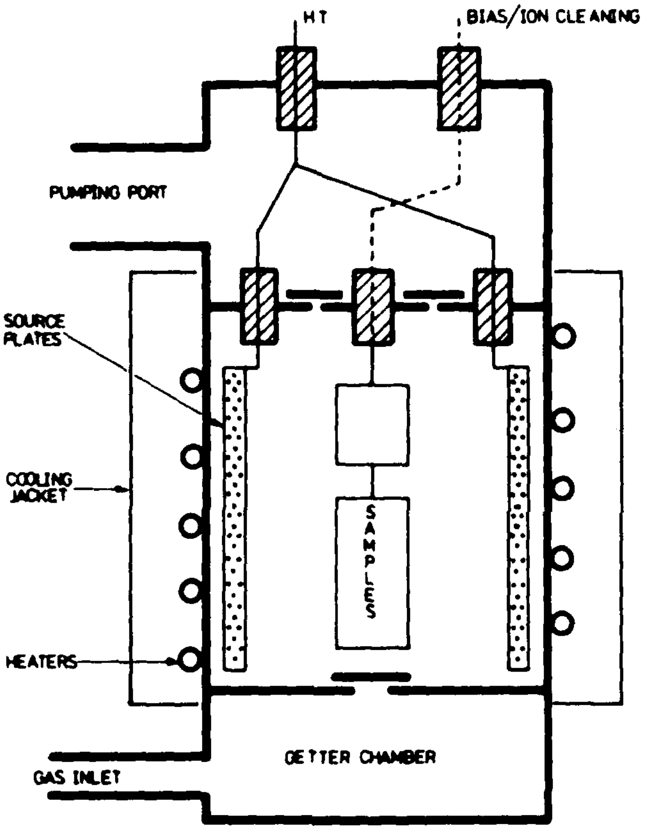


Fig. 10 Schematic view of the Sputter Ion Plating system.

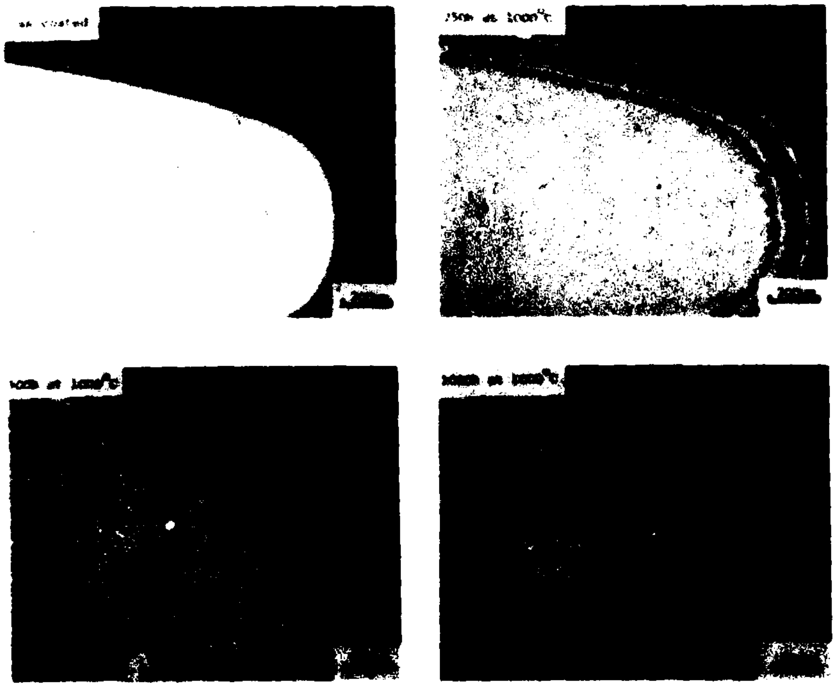


Fig. 11 CoCrAlY coatings on a turbine blade as-coated, and after periods of 250, 500 and 1000 hours at 1000°C in air.

THE NAVY PROGRAM TO DEVELOP REPLACEMENTS FOR CRITICAL AND STRATEGIC MATERIALS

by
Mr. James J. Kelly
Program Element Manager for Materials
Naval Material Command
Washington, DC 20360
&
Mr. Marlin A. Kinna
Materials Technology Administrator
Naval Sea Systems Command
Washington, DC 20362

In response to the United States President's endorsement of research and development on critical and strategic materials (CSM), the Navy has initiated a program to develop design options for CSM in future weapon and platform systems. Key objectives of the program are: development of a data base, fabrication of materials and components, demonstration of hardware, and establishment of manufacturing processes to provide reproducible materials and components. Four materials thrusts are addressed. They are: utilization of domestically abundant materials, development of domestic high temperature materials, evaluation of new materials and alloys, and conservation of critical materials.

The President of the United States and the Congress recently endorsed and emphasized the role of research and development to decrease U.S. dependence on imported materials used in advanced defense systems. This endorsement motivated the U.S. Department of Defense (DOD) to formulate a research and development plan for satisfying potential critical and strategic materials (CSM) requirements.(1) The Navy, in response to the intent of the DOD Plan, initiated a program aimed primarily at development of design options for CSM in future Navy weapons and platform systems. The philosophy of the program is outlined in this paper and selected examples of possible design options are presented.

The Navy's program is not limited to consideration of imported materials; it also addresses certain domestic materials believed critical to the performance of future systems. An example of such a material is beryllium, whose availability may be limited by U.S. environmental protection standards or worker health safety considerations. Figure 1 presents the objective of the critical/strategic materials program, and defines the Navy's concept of critical and strategic materials. Research and development studies will include, but are not limited to, the strategic and critical materials listed in Figure 2. The selection of these materials was based on documentation from the U.S. Congress(2), the DOD General Accounting Office (GAO)(3), the U.S. Bureau of Mines(4), and independent nonprofit corporations, such as the Institute for Defense Analysis (IDA). Note that aluminum oxide is identified. While there are domestic sources of bauxite in the U.S., economics have favored importing this material and it is listed by the GAO as a critical/strategic material. Also note that the Navy Research and Development Program is confined in scope to structural and thermal protection materials.

As previously stated, the Navy program goal is to provide substitutes and design options for critical and strategic materials. Since resources are limited, it has been necessary to devise a program that will maximize the probability of successfully developing the necessary design options. The intent of the program, therefore, is to develop specific substitute materials and design options, and to encourage their use in selected systems applications. This will be accomplished by the methodology shown in Figure 3. Key elements of the effort to encourage systems utilization are: (1) establishing a sound data base, (2) conducting hardware demonstrations and "in use" tests, and (3) developing proven manufacturing technology that will provide reproducible component hardware. A detailed flow chart for development of substitutes and design options is shown in Figure 4. It should be noted that, while manufacturing technology is shown following component demonstration and evaluation, these program functions may have to be reversed if facility scale-up is required in order to produce components for demonstration. Although Figure 4 shows systems integration as the final step in the development process, it actually occurs concurrently with all the activities. However, the systems designer must make the final materials choice, basing his decisions on performance comparison, mission cost, and long range availability of the strategic material.

A number of Navy systems have been analyzed, both for quantity of CSM required, and for potential as test beds for substitutes or design options. The results, summarized in Figure 5, lead to the conclusion that ordnance systems are most attractive for introduction of alternatives to critical and strategic materials. The decision is based on the findings that: (1) almost all of the CSMs are utilized in ordnance, (2) weight savings, valued at $2,000 per pound for almost all systems can be realized, and (3) because they are nonman rated, early introduction of alternate materials into systems use is possible.

The organization of the Navy program is based on the requirements shown in Figure 6. Of the four program requirements, a definable systems advantage resulting from use of the new material/design option is most important. It is the systems advantage that will justify qualification of the design option for actual use, and convince the systems program manager to provide the necessary funding support. Based on these requirements the decision has been made to emphasize utilization of composites as substitutes and design option materials. Composites which will be considered include organic, metal, carbon and ceramic matrices reinforced with graphite, boron, glass and silicon carbide fibers.

How can composites be used to conserve critical/strategic materials? Consider the hypothetical case where aluminum is in short supply. With appropriate technology development, some of which is currently ongoing, aluminum can be diluted through the use of either continuous fibers (graphite, boron, SiC) or discontinuous reinforcement (whiskers or particles of SiC, B_4C, etc.). Because many properties will be significantly improved by the fiber additions, less material will be needed to meet system requirements. This, combined with the "dilution" effect, can reduce the amount of matrix required by 50% or more. To continue with the aluminum example, Figure 7 shows an example of a "hybrid" composite containing both graphite and boron fibers, with graphite being used for maximum specific modulus in one direction and boron used to provide specific strength in the direction transverse to the graphite fibers. Even more complex composites have been shown to be feasible, using both boron and graphite fibers in aluminum and particulate silicon carbide added to meet system requirements for shear strength. Such a composite material not only conserves the base metal but, through system-specific design, can be used to replace structural steel containing high percentages of chromium, cobalt, etc.

Another composite material which offers strong incentive for development is reinforced copper. Copper is a domestically abundant material with a relatively high melting point (1083°C), but it has not been used extensively for high temperature applications because of high density and poor mechanical properties. The potential as a composite matrix, however, is outstanding because of its chemical compatibility with a wide range of reinforcements. Figure 8 lists some continuous and discontinuous candidate reinforcements. Fabrication feasibility of several of these has already been shown. Figure 9 is a photo-micrograph of copper reinforced with continuous graphite fibers. Excellent translation of mechanical properties was obtained. Moreover, mechanical properties are quite attractive at temperatures up to 800°C. Strength as a function of temperature is shown in Figure 10. Clearly, the effect of reinforcement on high temperature strength retention is worthy of note. In the same manner, modulus characteristics are markedly improved, as shown in Figure 11. It can be concluded that selection of low density reinforcements makes copper competitive with stainless steels and Inconel in the 500-800°C temperature range on the basis of specific mechanical properties. For some applications, the extremely high thermal conductivity provides another major advantage. Figure 12 is a photomicrograph of continuous silicon carbide fibers in copper. These fibers have extremely high compressive strength in comparison with graphite. Property translation is excellent at room temperature but additional high temperature data is required in order to show the potential of this system.

The Navy program to develop alternates for critical/strategic material is summarized in Figure 13. As shown, the effort is divided into four categories, i.e., evaluation of domestically abundant materials, development of domestic high temperature design options, fabrication of new materials and alloys, and conservation of critical materials. Tasks within each category are summarized in the remainder of this paper.

A. Utilization of Domestically Abundant Materials

Three programs in this category, will be oriented specifically toward future systems applications. The objective of the first program will be to replace CSM components in a generic tactical missile design with components constructed entirely of domestically abundant materials. Missile operational requirements will be selected, materials design concepts and tradeoffs will be identified, and a data base on selected materials test specimens will be generated. Promising design options will be selected for scale-up and evaluation. The second program will address secondary structural components of aircraft. Alternate materials and designs will be selected, fabricated and tested. The objective of the third program will be to provide a metal matrix composite alternate as a second source for beryllium components. Preliminary work has shown potential for selected composites in this application.

B. Development of Domestic High Temperature Materials

There are numerous high temperature domestic metals which, when reinforced with graphite or silicon carbide fibers have excellent potential as a design option for high temperature strategic metals and superalloys. Under this task, metal matrix composite samples will be prepared and evaluated to determine maximum feasible operating temperatures. A thermal and mechanical properties data base will be generated on selected matrix alloys, fiber reinforcements and fiber volume composites. An effort will also be carried out to extend the objectives of the metal matrix composite task by addition of high temperature metal foils to the basic composite material. Effects of the foil on physical, mechanical and thermal properties of the resulting "hybrid" design options will then be determined for selected combinations.

C. Evaluation of New Materials and Alloys

The development of ceramic composites is in its infancy in the United States. Although there has been extensive work to develop high performance carbon-carbon composites (one class of ceramic composite) little else has been done to advance the state of technology of reinforced ceramics. A program will be started to identify materials property requirements which may be met by ceramic composites, define promising composite constituents, and conduct laboratory evaluation of selected fabricated materials. Under another task, an analysis of the potential for using zirconium as an alternate material will be conducted. Zirconium, although domestically abundant in the U.S., has been underutilized for many years. If the analytical results are positive, a program to introduce zirconium into a few selected applications will be organized and initiated. In the final task planned for development of new materials and alloys, a thorough literature search to determine the feasibility of developing a corrosion resistant magnesium alloy will be carried out. Magnesium, also abundant in the U.S., corrodes readily, particularly in the range of operational Navy environments. It is believed that corrosion may be significantly reduced by alloying the base metal with appropriate domestic alloy metals. If results of the literature search are positive, a materials fabrication and evaluation plan will be developed.

D. Conservation of Critical Materials

Work has been conducted to develop a near-net shape casting process for subcomponents of a post-boost propulsion system. The sub-components are currently machined out of billets of columbium, resulting in most of the starting material being reduced to scrap. The proposed casting process will reduce material requirements by more than 80 percent, and result in significantly reduced labor and machining costs. An exploratory task is also under way to develop a pressure casting process which will eliminate the "pipe" formed during recrystallization. Utilization of the entire cast billet is thus achieved.

In conclusion, the Navy has responded to the Department of Defense plan to satisfy potential strategic and critical materials problems. A program to develop design options based on exploitation of advanced composite materials has been generated, and particular attention will be given throughout the program to transition of the new technologies into advanced systems applications. It is believed that, by concentrating on the development of new composites and design options based on domestically abundant materials early on, major problems resulting from our inability to import strategic and critical materials can be avoided in the future.

(1) Research and Development Plan for Satisfying Department of Defense Critical/Strategic Materials Requirements, 1 July, 1981.

(2) Hearings Before the Subcommittee on Science, Technology and Space of the Committee on Commerce, Science and Transportation, U.S. Senate, Serial No. 96-122, P. 406, July 1, 1980.

(3) Statement of Dr. Michael Markels, Jr., President, Versar Inc., "Metal Matrix Composites as Substitutes for Critical Materials", Before the Subcommittee on Economic Stabilization of the Committee on Banking, Finance and Urban Affairs, U.S. House of Representatives.

(4) Conference on DOD Responsibilities Under the National Materials and Minerals Policy Act, Ft. McNair, Washington, D.C., May 5-7, 1981.

FIGURE 1

DESIGN OPTIONS FOR STRATEGIC/CRITICAL MATERIALS

OBJECTIVE: TO DEVELOP MATERIALS AND DESIGN OPTIONS, BASED ON DOMESTICALLY ABUNDANT MATERIALS, WHICH WILL DECREASE DEPENDENCE ON POTENTIALLY STRATEGIC AND CRITICAL MATERIALS

DEFINITION:

STRATEGIC MATERIAL — ONE IN WHICH THE PROBABILITY EXISTS FOR SUDDEN SUPPLY DISRUPTION OR SHARP PRICE INCREASE

CRITICAL MATERIAL — ONE WHICH IS ESSENTIAL FOR THE APPLICATION—AFFECTS U.S. DEFENSE POSTURE

SCOPE: RESTRICTED TO STRUCTURAL AND THERMAL PROTECTION MATERIALS. RUBBER SUBSTITUTES ARE NOT CONSIDERED IN THIS PROGRAM

FIGURE 2

REPRESENTATIVE CRITICAL/STRATEGIC MATERIALS (CSM)

TANTALUM
CHROMIUM
COBALT
BERYLLIUM
MANGANESE
COLUMBIUM
PLATINUM GROUP METALS

OTHER POSSIBLE CANDIDATES
TUNGSTEN
GOLD
ALUMINUM OXIDE

FIGURE 3

METHODOLOGY FOR DEVELOPMENT OF SUBSTITUTES FOR CSM

- SELECTION OF CSM FOR SUBSTITUTION
- DEFINITION OF DEVELOPMENT PROGRAM
- FABRICATION FEASIBILITY DEMONSTRATION OF SUBSTITUTE
- SUBSTITUTE DATA BASE DEVELOPMENT
- COMPONENT DEMONSTRATION AND EVALUATION
- MANUFACTURING TECHNOLOGY
- SYSTEMS INTEGRATION

FIGURE 4

DEVELOPMENT OF SUBSTITUTES/DESIGN OPTIONS FOR CSM

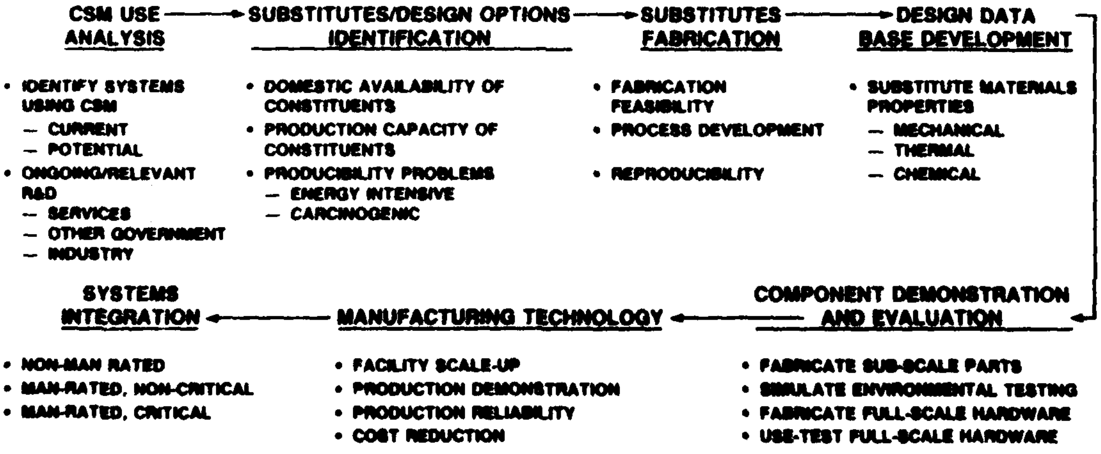


FIGURE 5
SUMMARY OF CHARACTERISTICS OF NAVY SYSTEMS

CHARACTERISTIC	SPACE	ORDNANCE	AIRCRAFT	SHIPS
MAN-RATED	NO	NO	YES	YES
VALUE OF 0.45 KG (1 lb) OF WEIGHT SAVED	$20,000	$2,000	$200	$20
OPERATIONAL LIFETIME	VERY LONG	VERY SHORT	LONG	VERY LONG
TIME FOR SYSTEMS UTILIZATION OF NEW MATERIALS*	5 YR	5 YR	10 YR	20 YR
AMOUNT OF CSM REQUIRED	LOW	HIGH	HIGH	VERY HIGH

* TIME FROM LABORATORY DEMONSTRATION OF PROPERTIES TO ACCEPTANCE INTO A NEW SYSTEM

FIGURE 6
REQUIREMENTS FOR DEVELOPMENT OF SUBSTITUTES/DESIGN OPTIONS

- DOMESTIC AVAILABILITY OF PROPOSED SUBSTITUTE MATERIAL
- NEAR-TERM SYSTEMS APPLICATIONS RECEIVE PRIORITY
- DESIGN OPTION MUST OFFER A DEFINABLE SYSTEMS ADVANTAGE, SUCH AS:
  - REDUCED LIFE CYCLE COST
  - REDUCED PROCUREMENT COST
  - IMPROVED SYSTEMS PERFORMANCE
- A COMMITMENT MUST BE MADE TO CARRY SUCCESSFUL DEVELOPMENT THROUGH SYSTEMS QUALIFICATION; AVAILABLE FUNDING MUST INCLUDE:
  - TECHNOLOGY BASE
  - MANUFACTURING TECHNOLOGY
  - SUPPLEMENTAL FUNDS FOR QUALIFICATION AS REQUIRED

FIGURE 7

PREDICTED AND ACTUAL TENSILE TEST DATA FOR CROSS-PLIED Gr/B/Al HYBRID COMPOSITE

SAMPLE ORIENTATION	(graphite)	ULTIMATE STRESS (M Pa × 10^{-6})	MODULUS (G Pa × 10^{-9})	ELONGATION
0°	PREDICTED	474.4	169.6	~0.40%
	TEST	544.7	160.6	0.42%
90°	PREDICTED	233.0	80.3	~0.40%
	TEST	235.8	59.1	0.49°

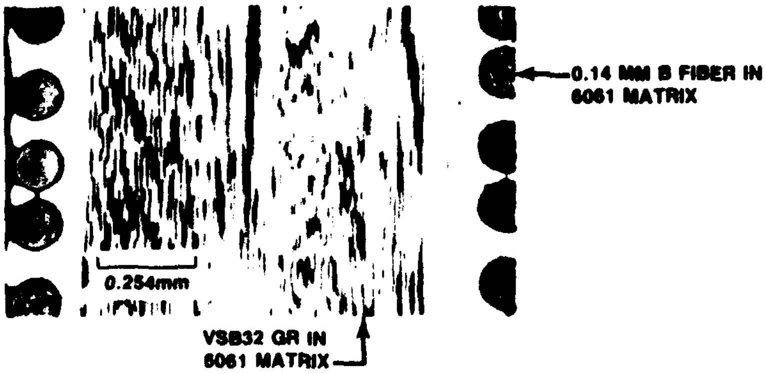


FIGURE 8

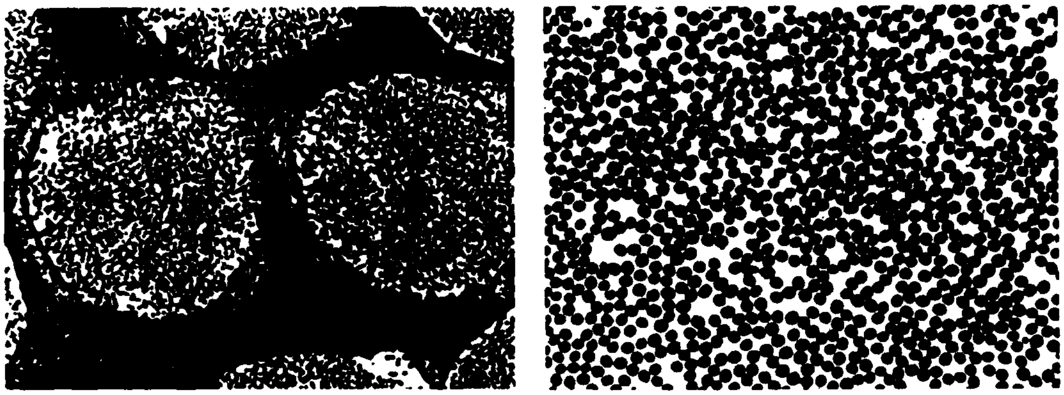
POSSIBLE REINFORCEMENTS FOR COPPER

CONTINUOUS	DISCONTINUOUS
GRAPHITE	TiC
SiC	TiN
BORON	SiC
Al_2O_3	Si_3N_4
TUNGSTEN	B_4C
MOLYBDENUM	TiB_2

SELECTION WILL BE BASED ON FIBER-MATRIX COMPATIBILITY AT MAXIMUM FABRICATION TEMPERATURE AND/OR MAXIMUM USE TEMPERATURE

FIGURE 9

MICROSTRUCTURE OF GRAPHITE REINFORCED COPPER WIRES



75X

250X

FIGURE 10

EFFECT OF GRAPHITE REINFORCEMENT ON ULTIMATE TENSILE STRENGTH OF 113 COPPER

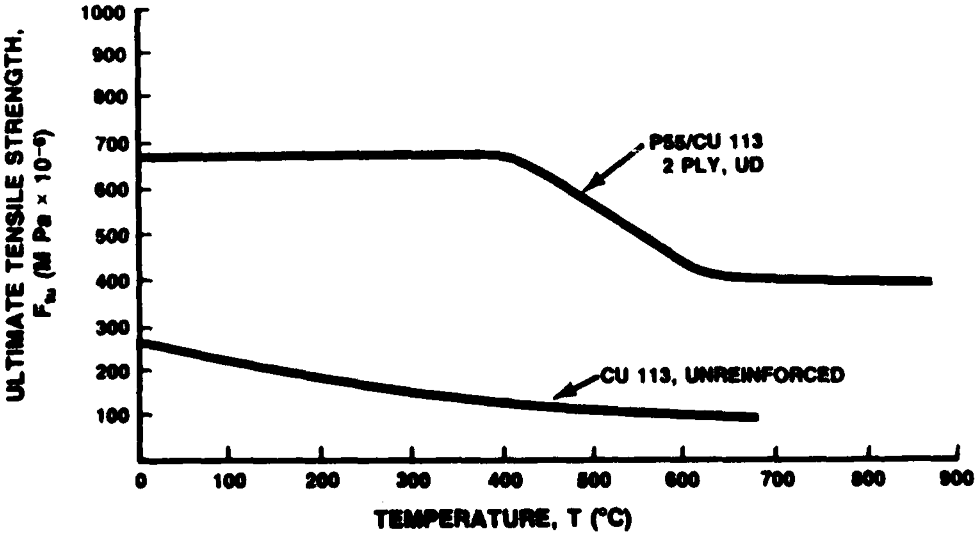


FIGURE 11
EFFECT OF GRAPHITE REINFORCEMENT ON TENSILE MODULUS OF 113 COPPER

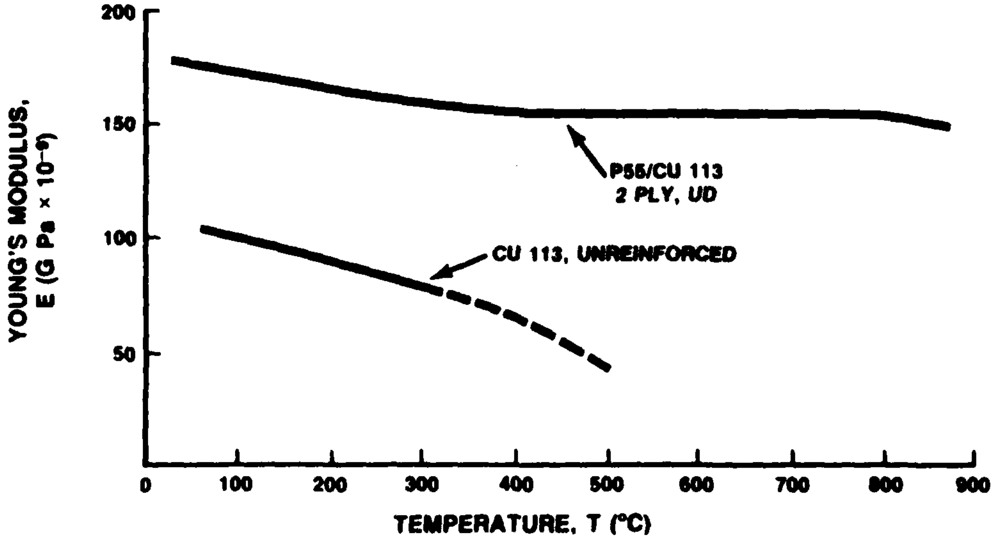


FIGURE 12
CROSS SECTION OF SILICON CARBIDE COPPER (0.14 MM DIAMETER FIBERS)

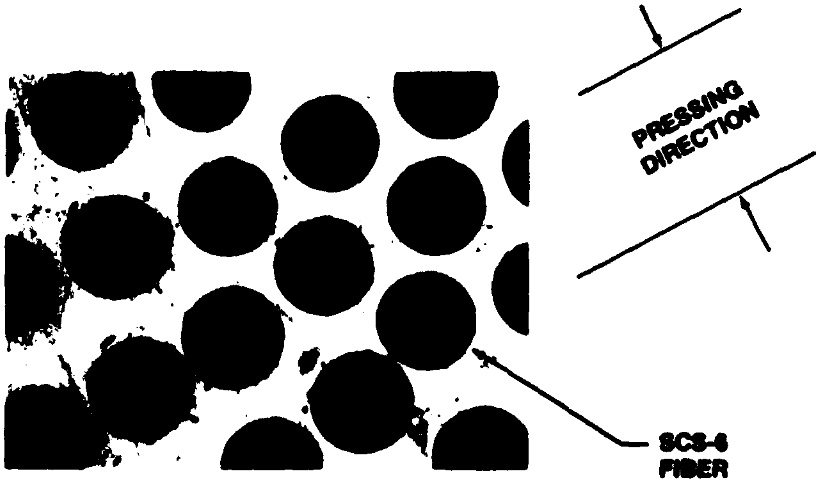


FIGURE 13
NAVY DESIGN OPTIONS PROGRAM (PRIMARY CATAGORIES/PERCENT OF EFFORT)

- UTILIZATION OF DOMESTICALLY ABUNDANT MATERIALS (40%)
  - TACTICAL MISSILE SYSTEM COMPONENTS
  - AIRCRAFT SECONDARY STRUCTURAL COMPONENTS
  - GUIDANCE SYSTEM COMPONENTS
- DEVELOPMENT OF DOMESTIC HIGH TEMPERATURE MATERIALS (30%)
  - FABRICATE AND EVALUATE GRAPHITE REINFORCED COPPER
  - INVESTIGATE STABILITY OF HIGH TEMPERATURE METAL CLADDING FOR METAL COMPOSITES
- EVALUATION OF NEW MATERIALS AND ALLOYS (20%)
  - CERAMIC COMPOSITES
  - ZIRCONIUM — POTENTIAL FOR UTILIZATION
  - CORROSION RESISTANT MAGNESIUM
- CONSERVATION OF CRITICAL MATERIALS (10%)
  - NEAR-NET SHAPE PROCESSING
  - PRESSURE CRYSTALLIZATION

Ceramics as Substitutes for Scarce Metals

R. Nathan Katz
Army Materials & Mechanics Research Center
Watertown, MA 02172

AD-P004 224

Abstract

Lack of domestic availability of critical industrial metals, such as chromium and cobalt make the U.S. economy vulnerable to supply disruption, or cartel inspired price manipulation. These critical metals are primarily used as high temperature, corrosion resistant or metal cutting alloys. Modern high performance ceramics are attractive substitutes for critical metals in many of these applications. This paper will explore opportunities for the use of ceramics as substitutes in several example applications.

Introduction

The U.S. economy has become increasingly dependent upon imported minerals and fuels during the past few decades. In the case of oil, this was dramatically brought home to the general public by the post 1973 energy crisis with its attendant gasoline lines and increased transportation and utility costs. Less obvious to the public, but equal in it's potential for economic disruption, is our heavy (and growing) dependence on imports for many vital industrial metals. Various studies over the past ten years have dealt with this issue.[1] Table I lists several industrially important metals and the extent to which the U.S. relies on imports to satisfy its national requirements. This paper will focus on chromium and cobalt, because they top most lists of "critical" materials and serve as typical examples of the critical materials problem in general.

Table I. IMPORTS OF STRATEGIC MATERIALS

METAL	DOMESTIC PRODUCTION %	PERCENT IMPORTED % (1980)
COLUMBIUM	0	100
MANGANESE	0	97*
COBALT	0	97*
TANTALUM	0	97*
CHROMIUM	0	91*
PLATINUM GROUP	NEG	87*
NICKEL	9	73

*DIFFERENCE IS DUE TO SALES FROM FEDERAL STOCKPILE
DATA FROM REF. 1

TABLE I

Before addressing the question of how ceramic technology can help reduce the severity of the "critical" materials problem with respect to chromium and cobalt, and Ni, we need to have some perspective on several issues. First, why are these metals industrially important? Second, is it really a problem that they are imported? Once we have some perspective on these issues we are in a position to ask the third, and key question, namely, what is required of those materials which might substitute for chromium and cobalt. A fourth important question that one might ask is "Are there different types or categories of substitution?"

This paper will briefly address the above questions and then proceed to provide illustrations of how various high performance ceramics are currently contributing to the industrial world's technical options for materials substitution. In several of these cases the potential for conservation of "critical" materials is accompanied by major opportunities for energy savings or productivity enhancement.

The Industrial Importance of Chromium and Cobalt

Chromium and cobalt each play significant roles in the metallurgy of high temperature and/or corrosion resistant structural alloys. These alloys are the backbone of a modern, industrial society. The superalloys used in gas turbine and jet propulsion engine technology are critically dependent on these two metals. Thus, their availability is key to our civil air transportation system, our military aviation, and in many locations, the availability of adequate electrical peak load generating capacity. Chromium is essential for stainless steels. Aesthetics aside, food processing, high temperature chemical processes, and several fuel processing technologies are dependent on this metal. Cobalt is also heavily used in superalloys (45% of the U.S. consumption of cobalt goes into superalloys). Cobalt is a major constituent of the "stellite" family of high hardness, high temperature alloys used where wear resistance at high temperatures is required. Cobalt also plays a major role in magnetic alloys and high performance magnetic compounds such as the AlNiCo's and SmCo. Indeed, one sixth of the free world's cobalt usage is for magnetic materials. This element also is important as a liquid phase sintering aid for WC cutting tools or wear components (in oilwell drilling equipment for example). Many more examples could be cited, but the central point is clear, the availability of chromium and cobalt is essential to the maintenance of an industrial economy as we now know it.

The Problem

Simply stated, while U.S. economy is critically dependent upon these two elements, we import virtually 100% of our needs. Moreover, the sources of supply are vulnerable to disruption either in the event of civil or regional war, or as the result of adverse political decisions of unfriendly governments (see Table II). In addition, the possiblity of an OPEC-like cartel cannot be ignored. If all of this seems a bit melodramatic it is well to recall that in 1978 one result of civil war in Zaire's Shaba Province was the brief interruption of cobalt production and the price of cobalt on the spot market jumped from ~$10 to ~$40. Even if supplies are not actually cut off or interrupted, such price turbulence is not conducive to economic stability.

CRITICAL INDUSTRIAL ELEMENTS

ELEMENT	RESERVES (% WORLD)	PRODUCTION (% WORLD)
Cr	•REP. S. AFRICA - 69	•REP. S. AFRICA - 35
	•ZIMBABWE - 30 (CHROMITE)	•USSR - 25
		•ALBANIA - 11
		•PHILIPPINES - 6
		•ZIMBABWE - 6
Co	•ZAIRE - ~30	•ZAIRE - 50
	•USSR - ~20	•ZAMBIA - 10
	•NEW CALEDONIA - ~18	•USSR - 8
		•CUBA - 7
		•CANADA - 5

TABLE II

Requirements For Substitutes

What is required of substitute materials for chromium and cobalt? The answer follows directly from a consideration of the applications of these two metals as just discussed. A primary requirement is the ability to function as a structural material at high temperature. This implies high temperature strength, strength retention as a function of time (i.e., good stress rupture behavior), and reasonable fracture toughness. Chemical inertness is of particular importance for applications in severe environments such as chemical processing, gas turbines, industrial heat exchangers, or metal cutting tools. Thus, corrosion and erosion resistance of possible substitutes will be important. These are all rather obvious considerations, there are several others which are less obvious. When one is presented with an opportunity to make a materials substitution one should also ask:

> Is it possible to use a material which will require less energy to produce and utilize throughout the material's life cycle?
>
> Is it possible to use a domestically available as opposed to an imported raw material?
>
> Is it possible to use a raw material which would minimize environmental impacts?

As we shall see in the next section, the modern high performance ceramics (silicon carbide, silicon nitride, transformation toughened zirconia, and ceramic matrix composites) have potential to satisfy most, if not all, of the above requirements.

High Performance Ceramics As Substitutes

High performance ceramics, for the most part, exhibit outstanding strength at room temperature. With the exception of transformation toughened zirconia (TTZ) these materials retain their strength to 2000°F, and beyond (see Table III). As shown in Figure 1, SiC, and Si_3N_4 offer significantly better stress rupture performance at 2200°F than the high temperature Ni and Co containing superalloys at 2000°F. The significant differences in thermal expansion and conductivity, Young's Modulus, and density between the ceramics and metal shown in Table III mean that one cannot, in general, simply substitute a ceramic component for a metallic one. As a result of these differences, incorporation of a ceramic substitute will usually result in large changes in temperature and stress distributions, moments of inertia, component deflections, and weight distributions. Therefore, the entire system must be re-analyzed and redesigned to accommodate the ceramic substitution.

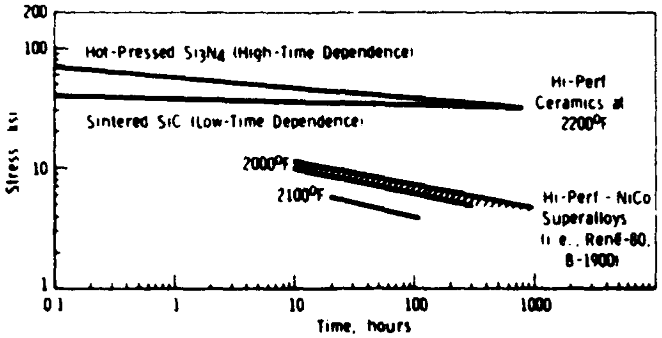


FIGURE 1

MATERIALS OF INTEREST - PROPERTIES COMPARISON

MATERIAL	STRENGTH (R.T.)	STRENGTH (2000°F)	SPECIFIC GRAVITY	THERMAL CONDUCTIVITY (BTU/hr ft °F)	THERMAL EXPANSION (in./in./°F)
VARIOUS SINTERED SiC's	50 to 80 ksi (FLEXURE)	SAME	3.2	50 to 100 (R.T. to 2000°F)	2.5 to 3.0 (R.T. to 2000°F)
VARIOUS SINTERED Si_3N_4's	30 to 100 ksi (FLEXURE)	SAME	2.7-3.2	10 to 35 (R.T. to 2000°F)	1.25 to 2.0 x 10^{-6} (R.T. to 2000°F)
TRANSFORMATION TOUGHENED ZrO_2 (TTZ)	50 to 90 ksi (FLEXURE)	? NOT WELL KNOWN	5.8	1 to 2 (R.T. to 2000°F)	4 to 8.5 x 10^{-6} (R.T. to 2400°F)
SiC/LAS COMPOSITES	95 to 120 ksi (FLEXURE)	70 to 130 ksi	2.6	NOT AVAILABLE	3 to 4 x 10^{-6} (R.T. to 2000°F)
STEELS (4100, 4300, 8600, 9800 SERIES)	150 to 200 ksi (TENSILE YIELD)	USELESS (100 to 150 ksi, 1000°F)	7-8	25 (R.T.) 18 (1200°F)	6 to 8 x 10^{-6} (R.T. to 1200°F)
CAST IRONS	30 to 80 ksi (TENSILE YIELD)	USELESS (25 ksi, 900°F)	7-7.5	80 (R.T.)	10 to 17 x 10^{-6} (R.T. to 1960°F)
ALUMINUM ALLOYS	60 to 130 ksi (TENSILE YIELD)	USELESS (20 ksi, 600°F)	2.5	80 to 130 (R.T.)	12 to 14 x 10^{-6} (R.T. to 600°F)

TABLE III

Silicon nitride and SiC have demonstrated outstanding corrosion and erosion resistance in such aggressive environments as gas turbine engines, heat exchangers and a variety of seal and bearing applications. Zirconia is one of the few materials which can endure the rigors of contact with molten steel for significant times.

Concerning the energy input for making a ton of superalloy versus making a ton of high performance ceramic, Davidge, has performed some interesting calculations. Comparing the energy input to win the elements required to produce a ton of a typical Ni-Cr-Co alloy with that to produce a ton of silicon nitride, he calculated 36,000 vs. 19,000 kWh/ton, a nearly two to one advantage for the ceramic.[3] After this point, comparisons became very imprecise, but if a near net shape sintered or HIP'ed ceramic part could be substituted for a metallic one which required significant machining, it is likely that the energy advantage of the ceramic can be maintained. However, the main energy savings which will accrue *from* ceramic substitution are to be gained through improved systems efficiency as illustrated in Table IV. The author has calculated that such fuel savings[4] would be in the neighborhood of ~ $17 billion per year for the U.S. economy alone.

Table IV. EXAMPLES OF PROJECTED ENERGY SAVINGS FROM USE OF CERAMIC TECHNOLOGY

TECHNOLOGY	SYSTEMS CONFIGURATION	REDUCTION IN FUEL USE (%)
GAS TURBINES		
AUTOMOTIVE	~150 hp, REGENERATED, SINGLE-SHAFT ENGINE, 1370°C TURBINE INLET TEMPERATURE	27
TRUCK	~350 hp, REGENERATED, TWO-SHAFT ENGINE, 1240°C TURBINE INLET TEMPERATURE	17
INDUSTRIAL/SHIP	~1000 hp, SIMPLE-CYCLE, THREE-STAGE ENGINE, 1370°C TURBINE INLET TEMPERATURE	10
DIESEL ENGINES		
TRUCK	~500 hp, ADIABATIC-TURBOCOMPOUND, 1210°C MAXIMUM COMPONENT TEMPERATURE	22
INDUSTRIAL HEAT RECOVERY		
RECUPERATORS	SILICON CARBIDE RECUPERATED SLOT FORGING FURNACE OPERATING AT ~1300°C	42

TABLE IV

The use of high performance ceramics is likely to be minimally disruptive of the environment. Many commercially exploited metal ores yield only 1% or less metal. Thus, to obtain a ton of metal, one may have to mine 100 tons of ore, crush and leach it, and then have to put 99 tons of comminuted ore back into the excavation. Comminuting a solid (ore) into a powder approximately doubles the original volume. This accounts for the mountains of tailings surrounding most mining sites. Since high performance ceramics depend upon N_2, C, O_2, as well as Si or Zr (from sands), no such unsightly environmental distruption as tailings will be created. Of course, one of the most important benefits of the N_2, C, O_2, or Si based ceramics is that they are universally, abundant and potentially cheap.

The one drawback to the use of high performance structural ceramics is their inherent brittleness. In order to successfully utilize these materials[4-6], one must deal with this by using the appropriate design methodology. In a previous paragraph, the term "reasonable toughness" was cited as being an important structural requirement. A material can be brittle, and at the same time be tough enough for structural use! Figure 2 gives the range of several metals and polymers commonly used as engineering materials, it is important to note that the high performance ceramics possess fracture toughness in the same range of values. This strongly infers that structural design with ceramics can be successfully executed. As we shall see later in this paper, that is indeed the case.

Substitution Models

In order to devise a successful strategy for materials substitution, it is important to know what type of substitution you are trying to affect. Figure 3 lists two major types of substitution, reactive and proactive, with examples of each. Reactive substitution is sub-divided into two classes, replacive and displacive. Replacive substitution is done for purely economic reasons. Material A is getting too costly so use material B. No increase in, or benefit to, systems performance is sought. In displacive substitution, Material B may or may not be less costly than Material A, but using it enhances systems performance to such an extent that it will displace Material A. We are all familiar with this type of substitution from the current displacement of copper telephone lines by optical waveguides (SiO_2). The concept of proactive substitution is rather new. Briefly, it is to have a viable technological alternative to the application of scarce materials sufficiently developed so that the scarce materials will not have to be utilized in the first place.

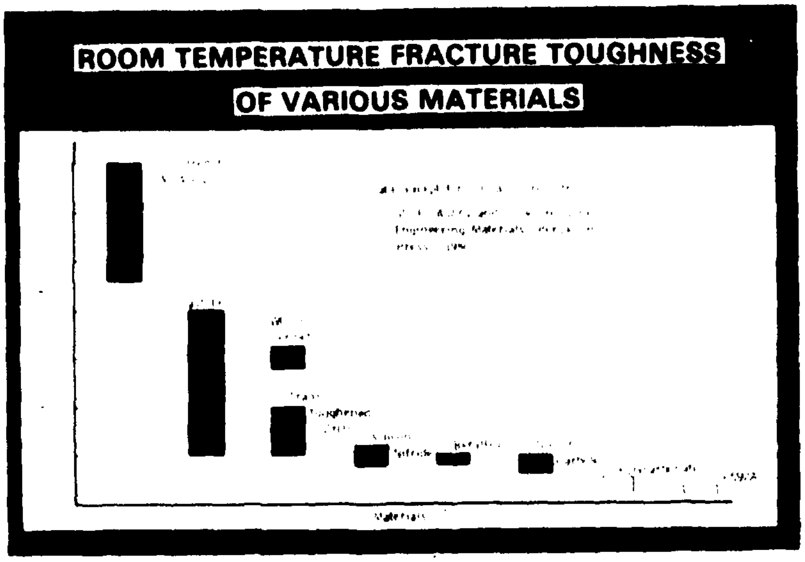


FIGURE 2

The balance of the paper will give examples of ceramic technology applied to each major category of materials substitution shown in Figure 3 and discussed above.

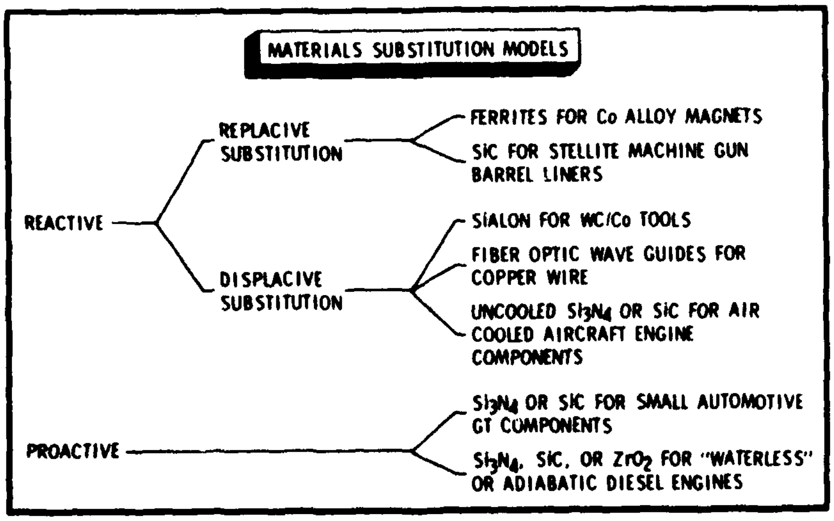


FIGURE 3

A Ceramic 50 Cal. Gun Barrel Liner

The application of high performance ceramics to substitute for the current stellite (~60% Co) 50 cal. barrel liner in the M-2 machine gun, is a good example of a potential replacive material substitution. The driving force to initiate feasibility studies for such substitution was economic; the previously cited quadrapuling of the price of Cobalt due to the civil war in Zaire. No significant gain in performance was anticipated.

Figure 4 lists the properties that one would desire of a ceramic to be utilized as a small caliber gun tube liner. Based on these properties, sintered SiC, sintered Si_3N_4, transformation toughened zirconia, and a glass matrix composite were selected as viable candidates. Availability of material led to investigating sintered α-SiC first. Bunning, et. al.[7], have previously reported on a successful 1000 round, single shot smooth bore feasibility demonstration. Wong[8] has recently demonstrated that rifling of such inserts is feasible and should not be excessively expensive in production. Recent tests have shown that graphite reinforced glass composites can survive single shot firing tests, but erode excessively[8]. However, the limited success indicates that a wider latitude in material properties exists than previously thought. Also, as improved matrix materials are developed ceramic matrix composites might be very well suited for this application.

DESIRED PROPERTIES FOR CERAMIC GUN BARREL LINERS:

MELTING POINT	$\geq 2600^{o}$F
MOR (RT)	≥ 50 ksi
α	$\approx 15/^{o}$C
E (RT)	$\geq 30 \times 10^{6}$ psi
H	HIGH
K	LOW
ρ	LOW
ΔT_c	HIGH

FIGURE 4

Before SiC or alternative high performance ceramics are deemed acceptable for use as small caliber gun barrel liners, more testing of durability under single and burst firing conditions and rifled as well as smooth bore testing must be carried out.

Si_3N_4 Cutting Tools

The recent introduction of Si_3N_4 based cutting tools into the marketplace will make an interesting case study of displacive substitution vis-a-vis cemented WC. In this case the substitution will be displacive since significant enhancements in productivity are attained. Figure 5, based on a recent press release from the Ford Motor Co., shows the major potential for increased productivity in machining cast iron. Similar gains have been cited by Jack,[9] Lumby,[10] and promotional literature from Kennametal and GTE. Several of these sources also indicate that Si_3N_4 based tools provide enhanced rates of metal removal for Ni based superalloys.[3]

As noted in Figure 5, researchers at Ford have found that Si_3N_4 based cutting tools do not fail catastrophically, they become dull and can be resharpened and reused (as a smaller size tool). This is an interesting illustration of a ceramic possessing a "reasonable toughness" in a most aggressive application.

CERAMIC CUTTING TOOLS FOR PRODUCTIVITY ENHANCEMENT

FORD S-8 (SILICON NITRIDE) CUTTING TOOL DEMONSTRATED:

- LONGER LIFE
- 220% PRODUCTIVITY ENHANCEMENT
  ESCORT CLUTCH CYLINDER MACHINED IN 18 sec
  VERSUS 58 sec STANDARD
- CAN BE RESHARPENED AND REUSED
  (SOURCE - FORD MOTOR CO., CORPORATE NEWS
  DEPT. RELEASE, 11/22/82)

FIGURE 5

Ceramics for the Adiabatic Diesel Engine

The diesel engine is capable of considerable development via the turbo-compounded "Adiabatic Diesel," which runs hot, eliminates the water cooling system (and consequently the heat lost to that system), and extracts useful heat from the higher temperature exhaust gas via a turbine. Use of such an engine can reduce specific fuel consumption by 35 percent and simultaneously increase specific power. As a consequence of eliminating the water cooling system, a 50 percent increase in engine reliability is projected.

In order to obtain such gains, very efficient insulation of the combustion and exhaust portions of the engine system is required so that the exhaust gases will have the highest energy content to transfer to the turbocompound system. Therefore, the two potentially contending technologies would appear to be insulated high temperature metals or self insulating high temperature ceramics. Thus, the adiabatic, turbo-compound diesel engine provides our first example of a potential proactive substitution. And in fact, proactive substitution by opting for ceramic technology is what is occurring.

Even casual readers of the business or popular scientific press have become aware of the world wide race to develop a ceramic based, waterless or "Adiabatic" diesel engine. While it appears that the Japanese may be leading at the moment in the area of light duty diesels for passenger car use, the U.S. appears to have the lead in the development of the adiabatic engine for heavy trucks. The world's most fuel efficient (.285 lb/hp-hr specific fuel consumption) engine is a joint development of the U.S. Army's Tank and Automotive Command (TACOM) and the Cummins Engine Co. A recent paper by Bryzik and Kamo (11) provides an in depth status report on this engine.

Briefly, an early version of this engine utilizing ZrO_2 based coatings in the combustion and exhaust areas, has been installed and successfully run in a 5 ton truck. On the road fuel economy exceeded expectations going from ~ 6 to ~ 9 mpg (in a lightly loaded condition). Over 3000 miles of successful testing has been carried out. This engine has demonstrated reduced emissions and enhanced multi-fuel capacity. The engine has no radiator, hoses, fan, or associated belts. In fact, this version of the Adiabatic engine has 361 fewer parts than the standard cooled engine from which it was derived.

Presently, the piston, cylinder liner, cylinder heads, exhaust, and intake parts are coated with a ZrO_2 based coating. Future versions of the engine will utilize more ceramic coated or even monolitic ceramic components.

The fact that a viable ceramic materials option (ZrO_2 based coatings) was available, has enabled the TACOM/Cummins design team to take a proactive materials substitution position eliminating the need for extensive use of critical materials to provide the worlds most fuel efficient vehicular engine technology.

Summary

1. It is becoming increasingly apparent that high performance ceramics can function in many of the industrial roles now filled by chromium or cobalt containing alloys.

2. Replacive, displacive, and proactive substitution of critical materials by high performance ceramics are currently under development.

3. Major areas where structural ceramics are likely to substitute for "critical" metals in the near to mid-term future include: heat engine components, cutting tools, and small caliber gun barrel liners.

REFERENCES

1. Hurlich, A., "Strategic Materials - Technological Trends", Mechanical Engineering, July 1982, p 44.

2. Polk, D.E. "Permanent Magnet Materials: An Opportunity to Reduce Cobalt Consumption", Naval Research Reviews, Office of Naval Research, Four/1982, p 24.

3. Davidge, R., "Economic and Energetic Considerations in Nitrogen Ceramics", Nitrogen Ceramics, Noordhoff International Publishers, Leyden, 1977, p 653.

4. Katz, R.N., "High Temperature Structural Ceramics", Science, 280, 23 May 1980, p 841.

5. Mueller, J.I., Kobayashi, A.S., and Scott, W.D., Design with Brittle Materials, University of Washington Press, Seattle, WA, 1979.

6. Ceramics for High Performance Applications II, eds., Burke, J.J., Lenoe, E.M., and Katz, R.N., Brook Hill Publishing Co., Chestnut Hill, MA; (available through MCIC, Battelle; Columbus, Ohio), 1978.

7. Bunning, E.J., Claxton, D.R., and Giles, R.A., "Liners for Gun Tubes - A Feasibility Study", Ceramic Eng. & Science Proceedings, July-August 1981, p 509.

8. Wong, P., "Ceramic Materials for Lightweight Guns", to be published in the proceedings of the 1982, Tri-Service Gun Tube and Erosion Symposium.

9. Jack, K.H., unpublished comments made at the second NATO-ASI on Nitrogen Ceramics, U. of Sussex, UK, August 1981.

10. Lumby, R.J., "The Preparation, Structure, and Properties of Commercial SiALON Ceramic Materials", Ceramic Eng. and Science Proceedings, January-February 1982, p 50.

11. Bryzik, W. and Kamo, R., "TACOM/Cummins Adiabatic Engine Program", in The Adiabatic Diesel Engine, SAE SP-543, February 1983.

NEW DEVELOPMENTS IN MATERIALS RECYCLING

BY THE U.S. BUREAU OF MINES

by Robert C. Horton, Director,
and
Charles B. Kenahan, Chief, Division of Materials and Recycling
Technology, Bureau of Mines, U.S. Department of the Interior
2401 E Street, NW Washington, D.C. 20241

ABSTRACT

The U.S. Bureau of Mines has been a strong advocate of materials recycling for over 50 years and has emerged as a world leader in the development of innovative recycling technology. Because recycling conserves mineral reserves, the Bureau considers the mineral-based waste products generated by industry and the consuming public as potential secondary mineral resources. This paper presents promising technical solutions to complex recycling problems such as recovery of cobalt, nickel, and chromium from superalloy scrap; the separation, recovery, and reuse of nickel and chromium from stainless and specialty steel wastes; precious metal recovery from electronic scrap; an environmentally acceptable method for recycling lead-acid batteries; recovery of nonferrous metals from scrap automobiles; and rapid scrap identification methods suitable for today's modern alloys.

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	L	liter
cm	centimeter	lb	pound
ft	foot	m	meter
g	gram	nm	nanometer
gal	gallon	oz	ounce
h	hour	pct	percent
in	inch	s	second
K	Kelvin	t	short ton
kg	kilogram	yr	year
kW	kilowatt		

INTRODUCTION

The mission of the U.S. Bureau of Mines is to help ensure the continued viability of the domestic minerals economy and the maintenance of an adequate minerals base so that the Nation's economic, social, strategic, and environmental needs can be met. As part of that mission, the Bureau conducts research programs to provide new and improved technology for recovering and recycling metals and minerals from a variety of waste materials. The recycling program addresses the basic objective of recovering for reuse the metal and mineral values contained in wastes. This recovery and reuse will lessen U.S. import dependence on strategic and critical metals (Cr, Co, and Ni), as well as other economically important commodities (Pb, Al, Zn, Cu, and precious metals). The Bureau of Mines views recycling as an important and valuable means of conserving mineral reserves and considers the mineral-based waste products generated by industry and the consuming public as potential secondary resources.

Authority for this research is derived from the Organic Act of 1910 (30 U.S.C. 1-11), which established the Bureau of Mines. It was later reinforced by the Mining and Minerals Policy Act of 1970, Public Law 91-131, which states in part "***it is the continuing policy of the Federal Government in the national interest to foster and encourage ***the use and recycling of scrap to promote the wise and efficient use of our natural and reclaimable mineral resources***." The most recent legislation affecting the Bureau, the National Materials and Minerals Policy, Research and Development Act of 1980, Public Law 96-479, specifically directs it to increase the level of metallurgical research in the area of strategic and critical materials. Current recycling program emphasis is on recovery of Co, Ni, and Cr from superalloy, stainless steel, and specialty steel scrap and wastes.

The Bureau of Mines has been involved in recycling research for over 50 years, and in the 1970's was recognized as a world leader in the field by the Bureau International de la Recuperation, a worldwide organization of recyclers. That organization presented its first gold medal to the Bureau in April 1979, in recognition of its outstanding achievements in recycling technology over the years.

As a result of its extensive research efforts in recycling, the Bureau has trained and developed a cadre of scientists and engineers who use their metallurgical and minerals processing training and experience to solve the complex recycling problems created by modern metallurgical technology. The Bureau's Minerals and Materials Research activity, which is composed of over 600 employees at 7 research facilities located across the United States, is well equipped to address modern recycling problems and has made many significant contributions to recycling technology.

In the late 1950's, Bureau scientists developed the technology needed to dispose of 9 million surplus Cd-Mg casings produced for World War II bombs. A vacuum distillation and selective condensation process was devised that allowed the surplus casings to be refined into marketable Cd and Mg products (1). A more recent achievement was the development of a practical method to recover Co and refractory carbides from cemented carbide scrap. The Bureau patented process (2) involves heating the carbide scrap in molten Zn, which breaks down the Co matrix. When the Zn is removed by vacuum distillation for reuse, the carbide and Co remain in a brittle mass that can be ground to reusable powder. At least seven companies are now using this process to recover carbide scrap that was previously discarded. Another Bureau patented process (3), for separating and recovering the metal, mineral, and energy values contained in municipal solid waste, has been adopted in whole or in part by many municipalities in the United States and abroad. A $50 million recycling plant based on this technology was constructed in Monroe County, New York, and is capable of processing about 1.8 million kg (2,000 t) of municipal waste daily.

This paper presents some examples of recent Bureau research that show promise for solving complex recycling problems. Topics discussed include recovery of Co, Ni, and Cr from superalloy scrap; separation, recovery, and reuse of Ni and Cr from stainless and specialty steel wastes; precious metals recovery from electronic scrap; a hydrometallurgical method to recycle scrap Pb-acid batteries; recovery of nonferrous metals from scrap automobiles; and development of scrap identification methods suitable for today's modern alloys.

To accomplish its research effectively, the Bureau, through formal and informal agreements, consults and cooperates with such prestigious U.S. recycling organizations as the National Association of Recycling Industries, the Institute of Scrap Iron and Steel, the Aluminum Recycling Association, the American Iron and Steel Institute, and the American Foundrymen's Society, as well as with many individual companies involved in handling and recycling ferrous and nonferrous scrap. This mutual cooperation ensures that the Bureau's recycling program addresses real problems of national significance and enhances technology transfer to users.

SUPERALLOY SCRAP (SAS)

Bureau of Mines interest in finding an efficient and economical method to treat SAS dates back to the early 1960's. Techniques for recycling Ni- and Co-base alloys had been devised but were complex, costly, and/or inefficient in recovering both the major and minor components of scrap alloys. One early Bureau scheme to treat SAS involved a sulfation and leaching treatment of oxidized alloy to remove Co and Ni sulfates with Mo, W, and Cb remaining in the residues. Electrolysis in H_2SO_4 was used to dissolve the alloys (4). A [illegible] Bureau technique consisted of a combined solvent extraction-electrolytic method for producing high-quality Ni and Co from NiO_2 containing 76 pct Ni and 0.8 pct Co as well as other metals (5). Still another method involved chemical reclaiming of SAS turnings, borings, and grindings in a chlorinated acid solution with separation and recovery of each component metal by a series of operations comprising carbon adsorption, solvent extraction, and selective precipitation (6). Several electrochemical techniques also were developed using diaphragm-type cells. One was a combination solvent extraction procedure to remove and separate Co and Fe from Ni followed by electrodeposition of pure Ni and Co from chloride-based purified electrolyte (7). The other employed a diaphragm-type electroytic cell that was 80 pct efficient in recovering Co and Ni. However, no satisfactory method was developed for reclaiming Cr from the scrap (8).

Recently a comprehensive study (9) of the domestic availability of Cr from six classes of SAS was conducted and published using 1976 data. (See Table 1.) The six alloy classes in this availability study were as follows:

1. Investment cast Ni- and Co-base,
2. Hardfacing cast Ni- and Co-base,
3. Wrought Ni- and Co-base,
4. Wrought Ni-Fe-base,
5. Heat-resistant alloy castings,
6. Corrosion-resistant alloy castings.

Table 1 - U.S. availability of six classes of SAS containing Cr

Category	10^6 kg	10^6 lb	Pct
Remelted	189.0	416.8	72
Downgraded	47.6	104.9	18
Exported	8.9	19.7	3
Lost	17.9	39.5	7
Total (1976 data)	263.4	580.9	100

The lost material was primarily oxide contaminated and not economically recoverable. The downgraded and exported categories, however, contained 10 million kg Cr (22.1 million lb), 2.7 million kg Co (5.9 million lb), and 24.0 million kg Ni (53 million lb). Based on this information, the Bureau of Mines initiated several research projects to develop economical methods to recover the Cr, Ni, and Co from some of this material.

A scheme for recovering Cr and other metals from SAS is described in detail in a Bureau publication (10). As in other processes, a blended scrap charge is melted and partially oxidized, resulting in Ti, Al, Zr, and Hf, but little Cr is segregated to the slag. The bath is then sulfidized to form a partial matte, a mixture of molten metallic sulfides. When solidified, the matte contains three major components: nickel sulfide (Ni_3S_2), chromium sulfide (Cr_2S_3), and a Ni-rich metal phase. The sulfur content of the matte is critical.

At the optimum sulfur level, virtually all of the Cr is contained in the Cr_2S_3, and a good separation is possible. Subsequent separation of the metal and sulfides can be achieved by conventional magnetic separation and froth flotation or by other mineral processing techniques. The essentially Cr-free, Ni-rich components are then given a hydrochloric acid-chlorine leach ($HCl-Cl_2$) that leaves elemental sulfur as a recoverable residue. The Fe and Mo are removed by hydrolysis. Solvent extraction and electrowinning steps then produce pure electrolytic Ni and Co. The Cr_2S_3 contains some dissolved Ni that can be removed by leaching. However, since a Cr metal product containing Ni would probably be acceptable for the superalloy industry, further separation was not extensively investigated. The preferred process involves roasting to a low-sulfur oxide product in a fluidized-bed converter, followed by aluminothermic reduction that produces a Cr-Ni metal ingot.

The basic process was tested in a series of laboratory experiments. In some cases, modifications of the basic scheme were defined, and limited testing was conducted. Based on the results of the experimental work, a pilot plant was designed to treat 45 kg (100 lb) of scrap feed per hour. A simplified flowsheet for the proposed plant is presented in Figure 1.

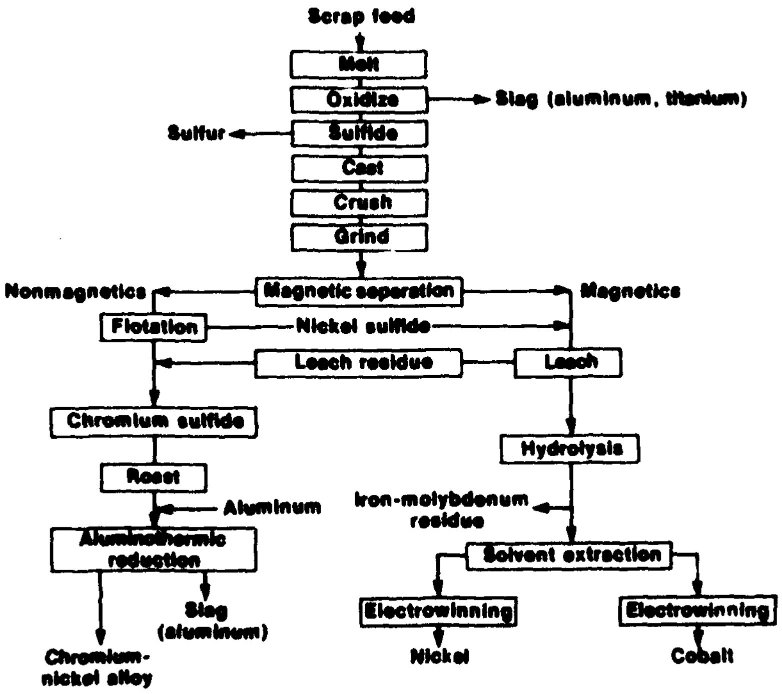


Figure 1 - Proposed flowsheet for recovery of Cr and other metal values from SAS.

Another study conducted for the Bureau (11) reports on a conceptual pyrometallurgical flowsheet that demonstrates the key process steps for recovery of Cr from a variety of SAS as a ferrochromium product in a batch process. The selective oxidation of Cr into a Cr-rich slag had been shown to be feasible by previous Bureau research (4). Chromium-bearing SAS was melted and the Cr oxidized to the slag by blowing the melt with O_2-N_2 gas mixtures. Following tapping of the slag, the contained Cr_2O_3 can be reduced with C, Al, or ferrosilicon to produce a ferrochromium product. Figure 2 shows a simplified flowsheet of the proposed pyrometallurgical method for recovering the Cr, Ni, and Co. Four commercial grades of SAS were used to conduct the experiments and test the viability of the flowsheet. Besides SAS samples, other materials charged to the furnace included fluxing agents and reductants. Two induction furnaces, a 50-kW furnace with a capacity of 9.0 kg (20 lb) and a 20-kW, 0.45-kg (1-lb) capacity furnace, were used in the experimental work. The furnaces were arranged to allow top-blowing with mixtures of nitrogen and oxygen onto the surface of the molten baths for oxidation purposes. Bottom-blowing with nitrogen was achieved through a tuyere. Reduction was accomplished by adding a weighed amount of reductant (graphite, ferrosilicon, or aluminum) onto the surface of a molten Cr-bearing slag produced during an oxidation experiment.

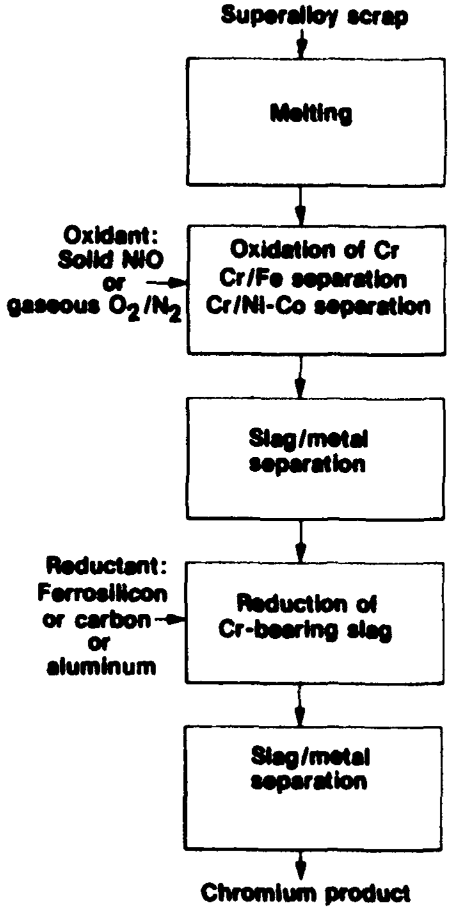


Figure 2 - Unit operations of proposed process for recovering Cr, Ni, and Co from SAS.

Data obtained from the experimental work indicated that Cr removals from the Cr-bearing SAS exceeded 99 pct regardless of the presence of other alloying elements. As expected from commercial practice, no difficulty was experienced in reducing Cr_2O_3 (in a slag phase) to Cr metal. There was no evidence of Ni or Co oxidation while Cr oxidized. It was possible using ferrosilicon to recover up to 95 pct of the Cr initially present in a slag phase. Sufficiently good Fe-Cr separation to produce a ferrochromium product suitable for steelmaking also was achieved by bottom-blowing. Comparison of top-blowing and bottom-blowing experiments with melts having similar levels of Cr indicate that with bottom-blowing, Cr can be oxidized with little or no Fe oxidation occurring. This could not be achieved with top-blowing. Using synthetic slags, that is, slags that were not produced in an oxidation experiment, a ferrochromium product was produced that contained 65 pct Cr at a recovery of 95 pct of the Cr. Additional work needs to be conducted using an electric arc furnace to insure a high-temperature slag to promote fluidity. Oxygen lancing onto the top surface of the melt is also proposed as the simplest way to achieve Cr oxidation. Although appropriate Cr-Fe ratios have been obtained, the ultimate purity of the ferrochromium product with respect to alloying elements such as W, Mo, and Ta, which report to the slag, needs further investigation.

Current Bureau research on treatment and recovery of SAS includes investigations of improved methods to recover critical alloy metals from grindings and oily contaminated sludges as well as bulk alloy scrap. One promising technique involves reacting bulk scrap with molten Al or Zn to form an easily crushable and readily dissolvable intermetallic compound. Another scheme is based on melting mixed SAS into anodes followed by electrolytic recovery of a Ni-Co alloy by controlled-potential electrolysis.

The objective of the Bureau's current work on grinding wastes is to devise a method for separating and recovering Co, Ni, and Cr as well as associated metal values from hardfaced grinding sludge wastes that result from industrial grinding of valves and valve seats (Figure 3). To increase engine durability, hardfacing is applied to steel valves and ground to finished size. Although the initial hardfacing alloy contains no Fe, the grindings contain as much as 30 pct Fe base metal contaminant from metal-finishing operations. Conventional mineral beneficiation techniques such as tabling, flotation, and magnetic separation were ineffective for separating metallics from troublesome grinding debris. Particles of Al_2O_3 became entrained in the metallic shreds and prevent the use of physical separation methods.

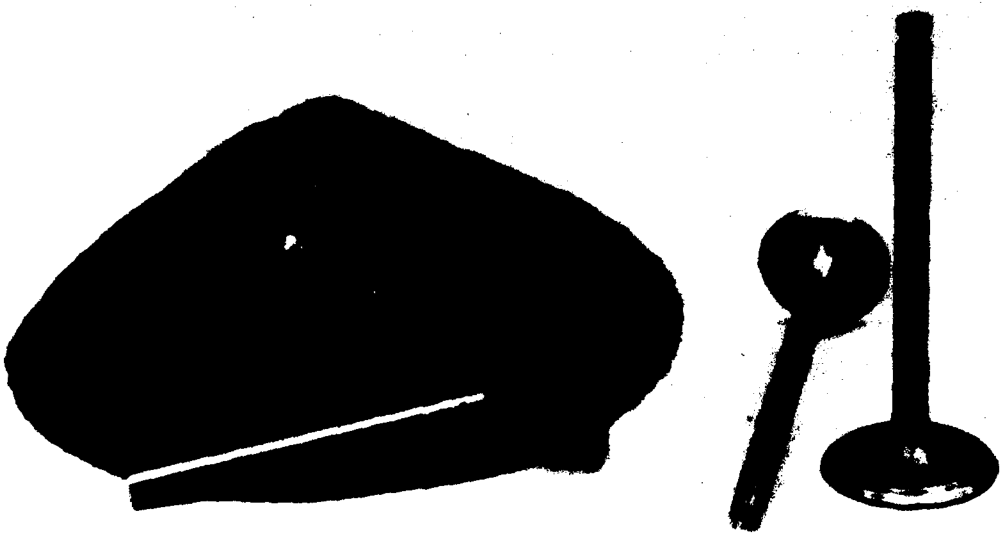


Figure 3 - Hardfaced valve before grinding and Co-rich grinding waste, (left); finished valves (right).

A conceptual flowsheet being examined to treat such wastes is shown in Figure 4. The grinding waste is usually contaminated with cooling oil and first requires degreasing before leaching. The degreased grindings contained in pct, 30.1 Fe, 20.9 Cr, 15.4 Co, 13.6 Ni, 3.9 Mn, 5.4 W, and 10.7 acid insoluble material, which was mostly abraded grinding media. Leaching results showed that HCl and aqueous chlorine were effective solvents for the grinding waste. Satisfactory metal extractions were readily achieved with both solvents in 6 h of leaching at boiling; however, with HCl W extraction was only 13.9 pct whereas with aqueous chlorine, it was 75 pct.

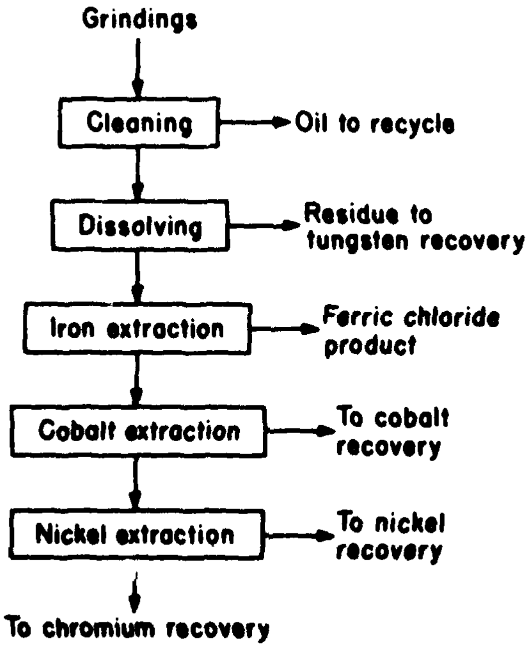


Figure 4 - Major conceptual operations for reclaiming metal values from hardfaced grinding wastes.

Research is currently in progress to separate and recover metal values from both the HCl and aqueous chloride leach liquors. Methods being considered are ion exchange, solvent extraction, adsorption and selective precipitation. Only when an appropriate metal recovery system has been developed will a compatible leaching procedure become apparent.

Another promising technique under study involves the formation of intermetallic compounds of SAS with Al or Zn. The key to this work is formation of a readily crushable intermetallic compound by melting offgrade scrap with Al or Zn in an inert atmosphere (Figure 5). It was determined that an Al content of 30 pct at 1,873 K (1,600° C) was optimum for obtaining an easily crushable alloy. Leaching alloys of this composition with 6N HCl or 6N H_2SO_4 at 368 K (95° C) resulted in dissolution of over 90 pct of the alloys tested in only 1 h.

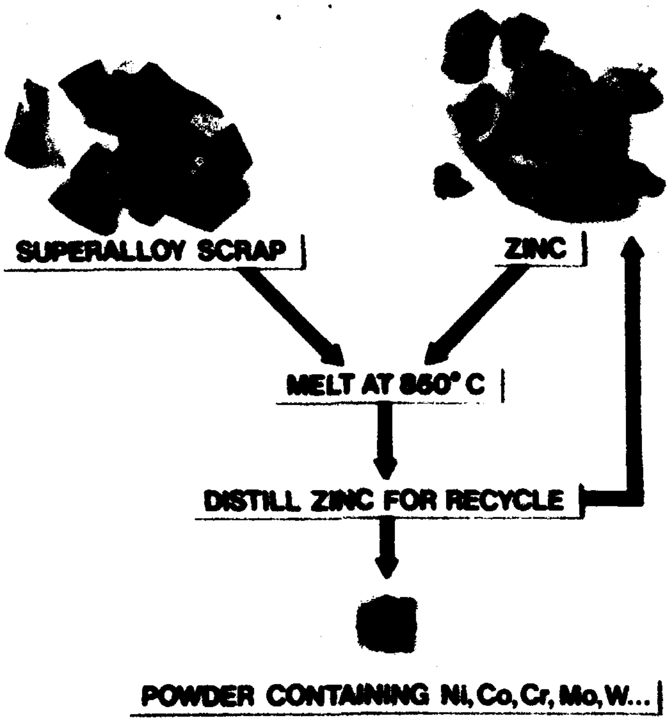


Figure 5 - Intermetallic compound technique for reducing bulk SAS to powder.

Table 2 shows the dramatic increase in dissolution rate for three commercial alloys using the intermetallic compound formation technique. Current studies are focused on using Zn in lieu of Al. At 1,123 K (850° C) molten Zn also will dissolve the superalloy material and produce the same friable, crushable characteristics obtained with Al, although more Zn is required than when using Al. However, the advantage of using Zn is that it can be vacuum-distilled from the reacted alloy material and recycled back to the process. Additional research is being conducted on precipitation of the component metals from the acid leachates with the addition of CaO or NaOH. Controlled potential electrolysis also will be investigated as a possible method to recover the individual metal values from the leach solutions.

Table 2 - Weight loss after leaching SAS with 6N HCl at 368 K (95° C), 1 h, percent

Scrap type	Alloy only	Alloy plus 30 pct Al
IN-738	0.24	98
Mar-M-509	.66	92
Rene-41	.08	90

Another scheme under investigation in Bureau laboratories involves melting SAS to form anodes for electrolytic processing. Figure 6 depicts the steps involved with treating deoiled, mixed contaminated machining chips in an induction furnace under a protective atmosphere, followed by casting into anodes. It should be noted that any new technology must be applicable to scrap mixtures of Ni, Co, and Fe-Ni base alloys with relatively high Co, Cr, and Ni contents. Mixture ranges of 10 to 20 pct Co, 15 to 25 pct Cr, and 50 to 65 pct Ni must be used in order to be effective.

Synthesized compositions of these mixtures have been cast into anodes and are being evaluated. Also, W, Mo, Cb, Ti, V, and Al must be recoverable in order for new technology to be efficient in materials conservation.

Figure 6 - Basic steps involved in producing a soluble anode from SAS for electrolytic recovery of Co and Ni.

Soluble anodes are being evaluated to determine the feasibility of using a controlled potential electrolytic method to effect Co-Ni deposition of sufficient purity for direct recycle as a master alloy. The controlled potential electrolytic method was primarily an analytical tool in the past, but is now considered a viable approach for complex scrap recycling technology. It involves control of the potential between the cathode and the reference electrode that is immersed in the electrolyte within the range of deposition potentials of the metal(s) being deposited, rather than direct control of the amperage between the anodes and cathode. The controlled potential results in variable control of the anode-cathode amperage and voltage to maintain the desired electrolyte-cathode voltage for continued selective deposition, in this case a Co-Ni product, with other metal ions remaining in solution or reporting to the sludge. Other options such as the use of anode baskets to contain the scrap, in lieu of remelted anodes, or electrowinning from solution also are under consideration.

STAINLESS STEEL (SS) WASTES

An availability study (12) was made of scrap metals containing Cr in the United States that covered wrought SS and heat-resistant alloys. This report concluded that the total SS scrap generated in 1977 as prompt industrial and obsolete scrap amounted to 781.0 million kg (861,000 t). A breakdown is shown in Table 3.

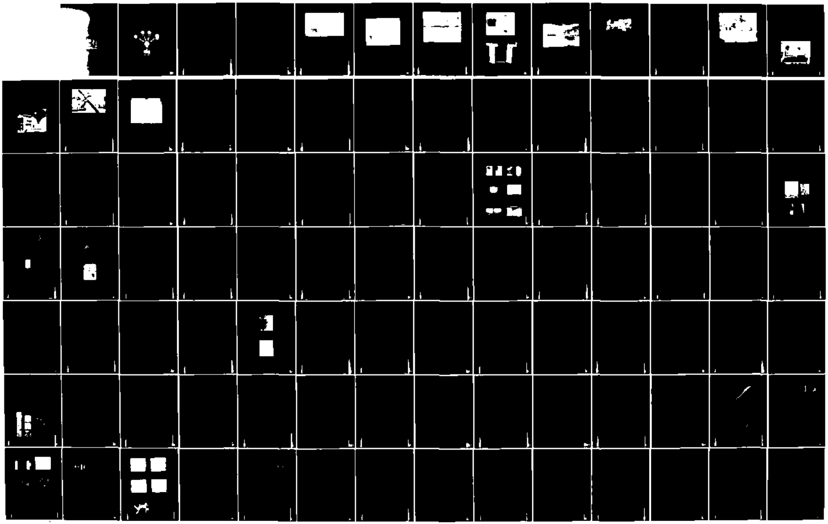
Table 3 - U.S. availability of prompt industrial and obsolete SS scrap

Category	10^6 kg	10^3 t	Pct
Collected, melted, exported	446.3	492	57.1
Downgraded	128.8	142	16.5
Unrecovered	205.9	227	26.4
Total (1977 data)	781.0	861	100

Based on an average Cr content of 16.7 pct, 56.2 million kg (62,000 t) of potentially recoverable Cr was lost in SS scrap alone in 1977. Much of this unrecovered scrap originated from appliances,

AD A148 598 MATERIALS SUBSTITUTION AND RECYCLING PROCEEDINGS OF THE MEETING OF THE ST..(U) ADVISORY GROUP FOR AEROSPACE RESEARCH AND DEVELOPMENT NEUILLY.. APR 84 AGARD CP-356 3/4

UNCLASSIFIED F/G 15/5 NL




2.5
2.2
2.0
1.8
1.6

utensils, and cutlery. A significant factor in the amount of SS available for reuse in the future will be the degree to which automobile catalytic converter shells made from type 409 SS are recycled. At a production rate of 10 million cars per year, the 16-kg (35-lb) converter shell could generate as much as 158.7 million kg (175,000 t) of SS scrap per year. Cars containing these catalytic converter shells are only now being retired in significant quantities from active service in the United States.

It is estimated that over 9 million kg (20 million lb) of Cr and 3.6 million kg (8 million lb) of Ni plus other metal values such as Mo and Mn are lost annually to furnace dusts, mill scale, and contaminated grinding swarfs in the U.S. stainless and specialty steelmaking industries. Recently the Bureau of Mines devised a promising pelletizing procedure (13) for treating and recovering 90 pct or more of the Cr, Ni, Mo, and Fe in these wastes. Manganese also can be recovered by this process.

The commercial feasibility of the pelletizing method was shown by a number of industrial-sized electric arc furnace heats, wherein the pelletized wastes represented as much as 19 pct of the furnace charge, replacing part of the normal SS scrap charge. Pelletized waste products used in the laboratory and commercial scale heats were electric furnace (EF) baghouse dust, argon-oxygen decarburization (AOD) vessel baghouse dust, centerless grinding swarf, and mill scale. Figure 7 shows a typical mixture of the four types of wastes used to produce the pellets and the final furnace product. Waste materials were supplied by a private company, and analyses of the principal components are given in Table 4.

Figure 7 - Simplified schematic showing four common SS wastes, pellets prepared from the wastes, and recyclable master alloy ingot made by smelting the pellets.

Table 4 - Partial chemical analyses of typical SS waste products, percent

Waste material	Cr	Ni	Mo	Fe	Mn	Pb	Zn
EF dust	9.3	2.2	1.1	27.8	3.6	0.8	4.9
AOD vessel dust . . .	11.1	3.8	.7	40.5	5.5	.6	.8
Grinding swarf	11.7	6.8	1.2	61.6	1.0	.1	<.1
Mill scale	8.6	3.9	.5	54.8	.8	.1	<.1

Pelletizing was selected as the most practical and economic means to agglomerate the wastes. The four steelmaking wastes were combined in approximately the same proportion originally generated at a commercial plant and mixed with coke breeze reductant and portland cement binder. For a plant collecting all four wastes, the typical composition of the pellets, in percent, was as follows: 20, EF dust and mill scale; 15, AOD dust; 45, grinding swarf; 10, coke breeze; and 4, portland cement. Figure 8 shows the flow diagram for laboratory agglomeration of the four wastes.

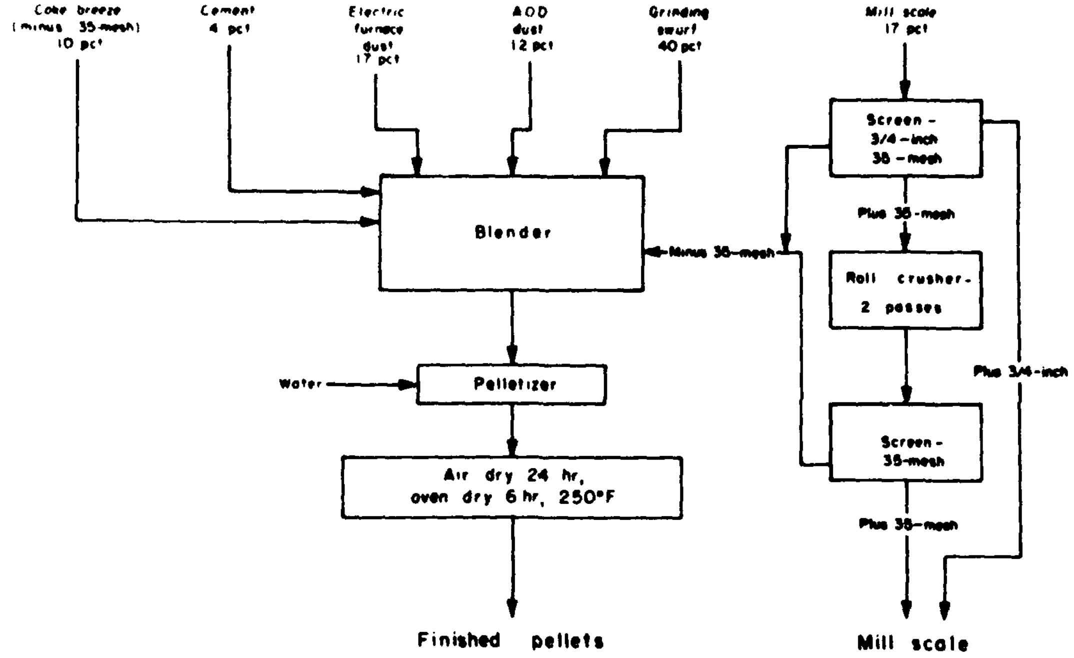


Figure 8 - Flow diagram for laboratory agglomeration of four common SS wastes by pelletizing with coke breeze reductant and cement binder.

Early laboratory tests in a 45-kg (100-lb) induction furnace indicated that a variety of combinations of pellet compositions could be used, and the carbon content of the coke breeze would reduce iron and nickel oxides and most of the chromium oxide. Ferrosilicon was added to the molten bath to scavenge the remaining Cr from the slag. The furnace was charged with 90 to 95 pct pellets and 5 to 10 pct loose mill scale. An all-pellet charge also can be used to reduce a backlog of wastes at a plant. However, it is anticipated that in normal commercial practice only 10 to 20 pct of the furnace charge would consist of pelletized wastes to replace a portion of the SS scrap charge.

Pellets containing as much as 55 pct mill scale from five different plants produced equally good results. Blending and pelletizing all four waste types represents the most complicated set of conditions. In those plants that generate only one or two of the four wastes, pelletizing is simplified.

Subsequently, 907-kg (1-t) heats of the pelletized mixture were conducted in a commercial plant. Chromium recovery was lower than experienced in the laboratory size tests, but still acceptable. The Ni reported to the ingot as expected. A 3,629-kg (8,000-lb) master alloy ingot from all-pellet heats made at a private plant was incorporated into a commercial 17,237-kg (19-t) heat of type 316 SS. The experimental ingot was completely compatible with the SS scrap and made up the balance of the charge.

At this point it was decided to assess the simpler, more economical method of substituting part of the scrap charge in the production arc furnace with pelletized waste. Five heats were made in which pelletized material constituted 14 to 19 pct of the charge. The pellets were added to the furnace with the SS scrap. All five heats met or exceeded the required specifications after processing through the AOD vessel and were marketed as commercial SS bar, rod, or forging ingot. With only a few exceptions, Cr, Ni, and Mo recoveries exceeded 90 pct.

The work was conclusive in showing that SS wastes such as flue dust, mill scale, and grinding swarf can be pelletized and charged successfully, along with scrap, into production heats of SS. This not only offers an opportunity to recover and recycle critical metals but also solves waste storage and disposal problems.

Additional tests on other specialty alloy wastes such as those generated in producing alloy 901 pipe for use in the gas and oil industry, electrochemical machining sludge from aircraft engine parts fabrication, and Cr-Zn hydroxide sludge resulting from the treatment of spent chromic acid plating solutions indicated that these and similar wastes can be converted into pellets for furnace charging with good results.

Other work on stainless and specialty steelmaking wastes in the early stages of investigation includes methods to recover Cr, Ni, and Co values from slags and spent SS pickling solutions. Tests on specialty steelmaking slags are being conducted to segregate and upgrade Cr-bearing fractions from crushed, ground, and sized slag samples. The slags are characterized as to composition and the various phases present. Chromium is present in the slags both as metallic particles and as complex oxide phases. Selective leaching and X-ray diffraction analysis indicate the presence of Cr-bearing spinel-type compounds in a number of the slags. By using selective sizing, magnetic separation, and tabling, the Cr-bearing constituents have been liberated and segregated into upgraded fractions. Recent tests have shown that net recoveries of about 60 pct Cr, 98 pct Ni, and 85 pct Fe can be achieved using conventional mineral beneficiation techniques. Efforts are now directed toward improving Cr recovery and the grade of separated fractions.

Bureau research on recycling and recovery of spent mixed acids and sludges from acid pickling operations is being conducted in cooperation with the American Iron and Steel Institute. Acid pickling is widely used in the metals industry for cleaning annealed and hot-worked SS. The most commonly used pickling bath for stainless and specialty steels is a mixture of HNO_3 and HF acids. It is estimated that at least 114,000 m^3 (30 million gal) of spent mixed acids are generated each year in the United States. This not only represents a significant loss in valuable metals, nitrate, and fluorine values, but also presents a disposal problem. Research on acid pickling is focused on electrogeneration of the spent acids with secondary efforts on other potential recycling or recovery technology such as selective crystallization, solvent extraction, and roasting.

In related research, the Bureau is studying the fundamentals of the acid pickling process used for cleaning annealed and hot-worked SS. Greater understanding of the effects of important bath parameters such as temperature, concentration of HNO_3 and HF, chemical complex formation, scale and alloy composition, agitation, aeration, immersion time, and dissolved metal concentrations could result in the selection of a set of operating conditions that would yield improved surface quality of the SS, reduce loss of critical metals, lessen the disposal problem, and extend the bath life. Initial studies are focused on two widely used SS types, 304 and 430, that have been subjected to cold or hot rolled-mill anneal treatments. The effects of solution temperature and composition on the rate of metal dissolution are being evaluated. Analyses also are being made to characterize the composition and structure of the surface and the bulk material of samples removed at selected times during the acid pickling process.

ELECTRONIC SCRAP (ES)

Several years ago, in cooperation with the U.S. Department of Defense, the Bureau initiated a research program to assess the precious metal content of obsolete ES and to develop a method to mechanically process ES generated by the military. Precious metals can be found in electronic equipment components such as pin connectors, contact points, silver-coated wire, terminals, capacitors, plugs, and relays. Some electronic equipment may have relatively high concentrations of precious metals, and some apparatus may have little or none. The problem is to determine which components contain high concentrations of precious metals and segregate those pieces mechanically from the less valuable Al, Cu, and Fe. Initially, 36 military surplus units were hand-dismantled, and the potential yield of base and precious metals from each was determined (14). More than half the units were radio receivers, transmitters, tuners, and power supplies; the remainder were miscellaneous navigation and communications equipment (Figure 9). All 36 units were produced prior to 1957 and did not contain any printed circuits. More recent samples of ES equipment did contain printed circuits.

After shredding and screening, ES can be treated as a complex ore from which the various components are concentrated in discrete fractions. In an effort to estimate the distribution of precious metals in obsolete electronic equipment and determine its fair market value, a minerals processing concept was first developed and demonstrated successfully on a laboratory scale. Based on the laboratory model, a small pilot plant was assembled for upgrading the scrap into metal concentrates at feed rates up to 0.063 kg/s (500 lb/h).

The pilot plant consists of a series of unit operations designed to take advantage of the physical properties of ES components to effect separation. As shown in the flowsheet (Figure 10), the sequence of principal operations is shredding, air classification, wire picking, magnetic separation, sizing, and finally eddy-current and high-tension separation (HTS). All of the equipment, with the exception of the eddy-current magnetic precleaner, is currently in use in the mining and recycling industries, and the flowsheet represents an "off-the-shelf" approach to the overall pilot plant design.

Figure 9 - Typical avionic ES before processing.

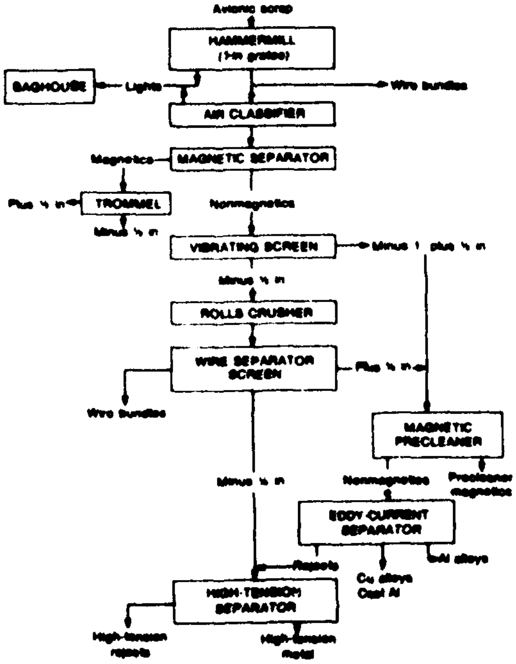


Figure 10 - Flowsheet for processing ES.

The pilot plant operations are continuous through the trommel and roll crushing steps. The eddy-current and high-tension separators are batch operations. An overall view of the continuous pilot plant operation is shown in Figure 11. Equipment, left to right, is the trommel, air classifiers with the curved discharge duct work, magnetic separator, screen, and roll crushers. The shredder is in the center background.

Figure 11 - Continuous portion of the 0.063-kg/s (500-lb/h) ES pilot plant.

Products from this process are an Fe-base fraction, an Al fraction, a mixed metal fraction, a wire fraction, air classifier lights, and a minus 0.006-m (1/4-in) nonmagnetic metal fraction. The latter is recovered by HTS. The HTS fraction represents only about 5 pct of the total input for certain types of mixed scrap, yet contains one-half of the total Au and Ag. Typical Au and Ag contents in the HTS fraction range from 0.6 to 1.2 and 9.4 to 18.7 g/kg (20 to 40 and 300 to 600 oz/t), respectively, depending on the age and type of electronic scrap processed. A typical precious-metals-bearing concentrate after HTS of mechanically processed circuit board assemblies is shown in Figure 12.

The small particle size of the HTS fraction makes it ideal for hydrometallurgical treatment to recover the base metals and further concentrate the precious metals. Precious metal toll refiners charge by weight of scrap treated, and shipping this material without extracting the base metals, even though it is acceptable as is, is an added expense. Typical feed material for hydrometallurgical processing (HTS fraction) is shown in Figure 12. Aluminum is extracted from the feed material in the first-stage ambient temperature NaOH leach, followed by incineration to remove organic matter. Nickel is extracted in the second-stage oxidative dilute H_2SO_4 leach at 363 K (90° C) and is removed from the spent leachate by cementation with the Fe-base magnetic fraction. The third-stage leach was conducted in concentrated H_2SO_4 at 423 K (150° C). The leach residue and leachate contained most of the precious metals.

Laboratory tests demonstrated the technical feasibility of treating the processed ES by a hydrometallurgical method to recover precious and base metals from an upgraded fraction of obsolete ES (15). The three-stage leach process produced a final residue amounting to only 12 pct of the initial feed to the leaching process, yet it contained all of the Au and 55 pct of the Ag. This residue is amenable to precious metal recovery by toll refining at a fraction of the cost required for the original feed material. The remaining 45 pct of the Ag is recovered from the third-stage filtrate. Copper was recovered as an 88-pct-grade cement Cu, and recoveries exceeded 90 pct.

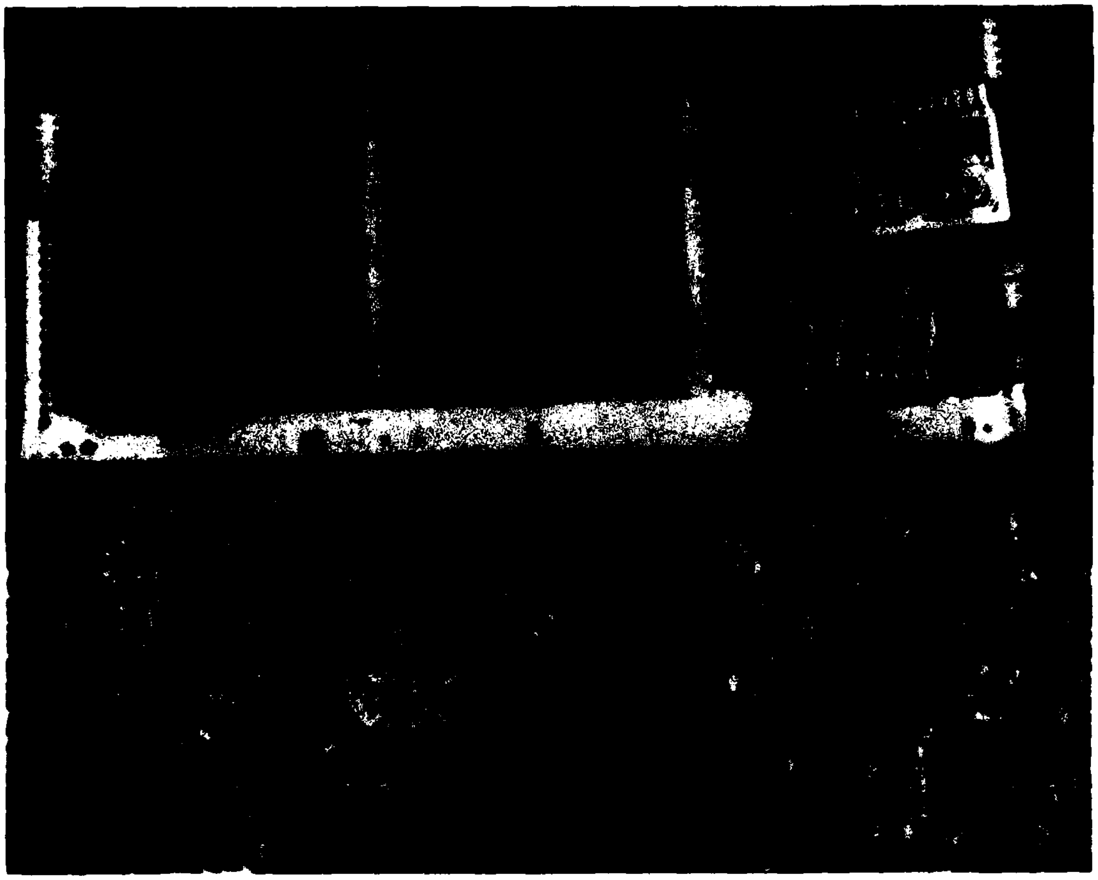


Figure 12 - Typical precious metal-bearing concentrate (lower right) after HTS of mechanically processed circuit board assemblies (non-metallic rejects on left).

SCRAP LEAD ACID BATTERIES

The secondary lead industry in the United States is the largest producer of Pb, accounting for about 45 pct of domestic production. Over 90 pct of the metal supplied to the secondary smelters is in the form of Pb-acid batteries. In current U.S. commercial practice, Pb metal and sludge are separated from the battery case and the acid and smelted in a reverberatory or blast furnace. Emissions of Pb and SO_2 fumes during smelting are difficult to control and present the industry with costly technical control options if it is to meet U.S. lead emission standards (16).

With this in mind, the Bureau investigated a combination electrorefining-electrowinning method for recycling Pb from scrap batteries with the dual objectives of eliminating the Pb and SO_2 emissions associated with the present pyrometallurgical smelting process and producing Pb pure enough for use in maintenance-free batteries (17).

The discarded metal and battery sludge used in the investigation was obtained from a large domestic secondary smelter and was typical of material charged to a commercial reverberatory furnace. A fully discharged auto battery contains 3.8×10^{-3} (1 gal) of 18 pct H_2SO_4 electrolyte, 4.5 kg (9.9 lb) of Pb metal in the grids and lugs, and 5.7 kg (12.6 lb) of Pb as sulfate-oxide sludge. After washing to remove adhering sludge, screening, and hand-picking to remove plastic and rubber, the material analyzed, in percent, 86 Pb, 9 sulfate-oxide sludge, and 5 plastic and rubber. The sludge analyzed, in percent, 60 $PbSO_4$, 21 Pb, and 19 PbO_2. The Pb metal grids and lugs were melted and cast into anodes for electrorefining. Lead was leached from the sludge by treating it with NH_4CO_3 and $(NH_4)HSO_3$, followed by dissolution in waste fluosilicic acid ($H_2SiF_6 \cdot H_2O$) for recovery by electrowinning (Figure 13). The $H_2SiF_6 \cdot H_2O$ used as electrolyte both for electrorefining and for leaching the sludge is a large-volume waste product generated during the production of phosphate fertilizer. Impure anodes were prepared for electrorefining by melting the Pb-Sb metal scrap and casting in a carbon mold. Patented (18) insoluble PbO_2-coated Ti anodes developed by the Bureau were used for electrowinning. Cathode starter sheets were made from commercial thick corroding-grade Pb sheet. Figure 14 shows the configuration of the anodes used for electrorefining and electrowinning.

Figure 13 - Depiction of combination electrorefining (top path) and electrowinning (bottom path) method for recycling Pb from Pb-acid batteries.

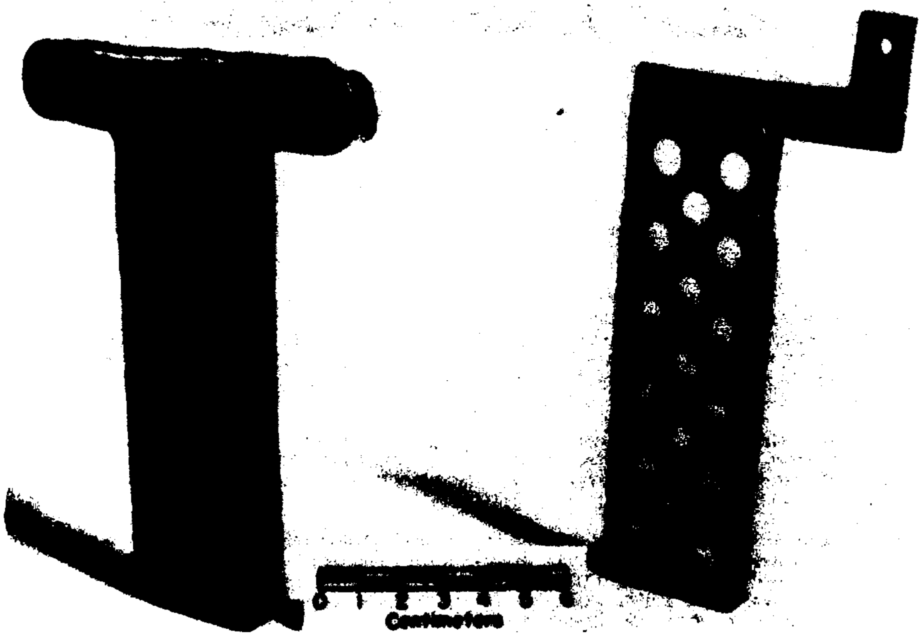


Figure 14 - Anodes used for electrorefining (left) and electrowinning (right) Pb from scrap Pb-acid batteries.

In past work, Pb electrowinning failed because much of the Pb in solution reported to the anodes as an insoluble PbO_2 compound, at the expense of metallic Pb deposition at the cathode. A major technical breakthrough was made with the discovery that PbO_2 formation can be prevented by having as little as 1.5 kg/m^3 (1.5 g/L) P in the electrolyte. The waste $H_2SiF_6.H_2O$ is particularly suited for electrowinning since it already contains the necessary P.

One- and two-liter plastic vessels were used initially for the electrolytic cells and later were replaced by the 0.02-m^3 (20-L) multielectrode cell shown in Figure 15. The multielectrode cell which consisted of 3 cathodes and 4 anodes in both the electrowinning and electrorefining sections produced about 45.4 Kg (100 lb) of Pb during a 7 day cycle in each electrolytic section. The bench-scale work described above shows a great deal of promise, and Pb of 99.99+ pct can be produced routinely. Preliminary economic and technical evaluations indicate potential for this process, but additional larger scale demonstration is needed to ensure its viability.

Figure 15 - Laboratory unit for electrorefining and electrowinning Pb. On the right, electronic control panel with process flow diagram. On the left, electrolysis section with 0.02-m^3 (20-L) multielectrode cell and ancillary equipment.

SCRAP AUTOMOBILES

The automotive industry is one of the largest consumers of metals and also one of the largest sources of new and old scrap in the United States. Eight to ten million motor vehicles are retired annually from active service. Developments and trends in the automotive industry are indicative of the nature of the changes that may occur in scrap car recycling technology. Automotive materials specification and design have been undergoing dramatic changes, especially since the energy crisis of 1974. The size of U.S. cars is being reduced, dimensions of components are being decreased, and lighter materials are being substituted for steel and cast iron parts. Changes such as a reduction in the use of plain carbon steels and cast iron and an increase in the use of low-alloy high-strength steels, aluminum alloys, and plastics have already occurred, and the recycling technology to deal with these changes must be developed now.

The Bureau of Mines has had an active research program on recycling ferrous and nonferrous values from scrap cars since the late 1960's. Some work also has been done on the effect of increased plastic content on automobile recycling (19-20). The initial work on scrap cars began with the design and development of a smokeless incinerator that served as an interim solution to the problem of burning nonmetallics from scrap cars (21). Later, Bureau researchers determined the composition of a typical automobile including ferrous and nonferrous metals, glass, rubber, and plastics. Fifteen U.S.-made automobiles were statistically selected and completely hand-dismantled and separated into ferrous, nonferrous, and nonmetallic fractions (22). From these data, the composition of a typical automobile, circa 1960, was postulated. Later, several 1972-73 and 1975 model U.S. cars were dismantled, and average compositions for these cars were determined. Bureau researchers also hand-dismantled four models of 1981-82 Japanese cars. Figure 16 shows the materials contained in a hand-dismantled 1982 Nissan Sentra. In addition, two identical Japanese cars from each manufacturer were shredded in a commercial automobile shredder, and all of the products were collected for analyses to compare metal recoveries with materials distribution. Table 5 summarizes the composition based on hand dismantling of the various domestic and foreign cars described above.

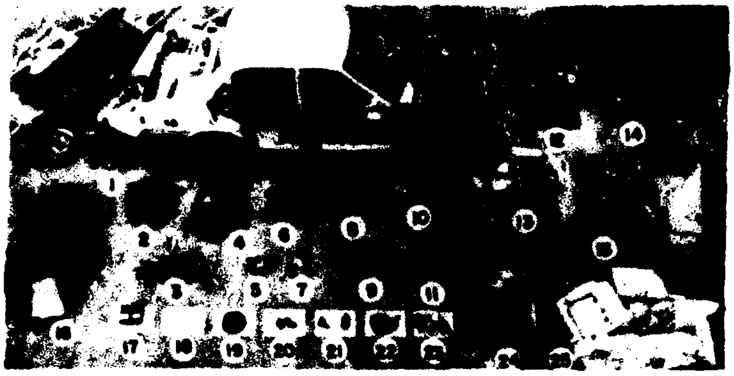


Figure 16 - Hand-dismantled 1982 Nissan Sentra automobile.

1. Light iron
2. Cast steel
3. Stainless steel
4. Heavy iron
5. Zinc
6. Spring steel
7. Chrome-plated steel
8. Hardened steel
9. Coated copper wire
10. Cast iron
11. Copper and brass
12. Aluminum
13. Vinyl
14. Plastic
15. Combustibles
16. Rubber
17. Battery
18. Lead
19. Carbon
20. Ceramic (magnetic)
21. Ceramic
22. Asbestos
23. Circuit board and electrical components
24. Glass
25. Polyurethane foam

Table 5 - Distribution of materials in automobiles as determined by hand dismantling

Material	Composite U.S. auto, circa 1960				Average of 1972, 73, and 1975 model U.S. autos				Average of 4 1981 and 1982 Japanese autos			
	lb	kg	Total of category, pct	Total auto, pct	lb	kg	Total of category, pct	Total auto, pct	lb	kg	Total of category, pct	Total auto, pct
Light steel	1,309.5	594.0	43.0	36.6	1,484.5	673.4	47.8	38.2	942.7	427.6	64.0	48.2
Heavy steel	1,222.4	554.4	40.2	34.2	1,146.7	520.1	36.9	29.5	407.8	185.0	27.7	20.9
Cast iron	511.4	232.0	16.8	14.3	475.7	215.8	15.3	12.3	122.4	55.5	8.3	6.3
Total	3,043.3	1,380.4	100.0	85.1	3,106.9	1,409.3	100.0	80.0	1,472.9	668.1	100.0	75.4
Copper	31.9	14.5	20.3	.9	43.2	19.6	23.1	1.1	24.9	11.3	18.8	1.3
Lead[1]	20.4	9.2	13.0	.6	24.0	10.9	12.9	.6	17.5	7.9	13.2	.9
Zinc	54.2	24.6	34.5	1.5	40.4	18.3	21.7	1.1	5.3	2.4	4.0	.3
Aluminum	50.6	23.0	32.2	1.4	79.0	35.8	42.3	2.0	84.6	38.4	64.0	4.3
Total	157.1	71.3	100.0	4.4	186.6	84.6	100.0	4.8	132.3	60.0	100.0	6.8
Rubber	145.0	65.8	53.3	4.1	178.7	81.0	38.8	4.6	116.6	52.8	42.3	6.0
Plastic	[2]	[2]	[2]	[2]	136.5	61.9	29.6	3.5	111.4	50.5	40.5	5.7
Combustibles	127.2	57.7	46.7	3.6	145.3	65.9	31.6	3.8	47.4	21.5	17.2	2.4
Total	272.2	123.5	100.0	7.7	460.5	208.8	100.0	11.9	275.4	124.8	100.0	14.1
Glass	87.2	39.6	85.5	2.4	100.1	45.4	78.1	2.6	67.4	30.6	93.1	3.5
Noncombustibles	14.8	6.7	14.5	.4	28.0	12.7	21.9	.7	5.0	2.2	6.9	.2
Total	102.0	46.3	100.0	2.8	128.1	58.1	100.0	3.3	72.4	32.8	100.0	3.7
Grand total	3,574.6	1,621.5	NAp	100.0	3,882.1	1,760.8	NAp	100.0	1,953.0	885.7	NAp	100.0

NAp Not applicable.

[1] Includes batteries.

[2] Combined with combustibles.

The dismantled 1982 Sentra contained about 12 pct high-strength, low-alloy steel that was not found in the other Japanese cars. Recovery rates for ferrous and nonferrous values of the Japanese cars after shredding were 88 and 60 pct, respectively. Comparable recovery rates for U.S. cars after shredding were 90 and 80 pct for the ferrous and nonferrous values, respectively. The lower recovery rate for the nonferrous values from the Japanese cars appears to have resulted from generation of large amounts of aluminum fines that are lost to the nonmetallic fraction during shredding and processing. There were no materials used in the foreign cars that would present secondary metal recyclers with handling or processing problems; however, the amount of rejects generated per ton of ferrous product recovered may be of future concern.

During the past 10 yr, over 80 pct of the cars scrapped in the United States have been processed in over 200 shredder operations in commercial scrap yards. With the advent of these shredders, the Bureau focused its attention on recovering nonferrous values contained in the nonmagnetic materials disposed of by these processors. Air classification methods used initially yielded concentrates of up to 90 pct metal. However, to obtain these higher purity concentrates, about 40 pct of the metals are lost in processing. Bureau researchers then adapted a water elutriation treatment technique to recover the metal values from the nonmagnetic shredded materials. A 0.45-m (18-in) diameter, 2.52-kg/s (10-t/h) column water elutriator (Figures 17 and 18) was designed, tested, and evaluated at a commercial shredding operation for recovery of mixed nonferrous metals from the nonmagnetic material and has proven to be efficient and economical.

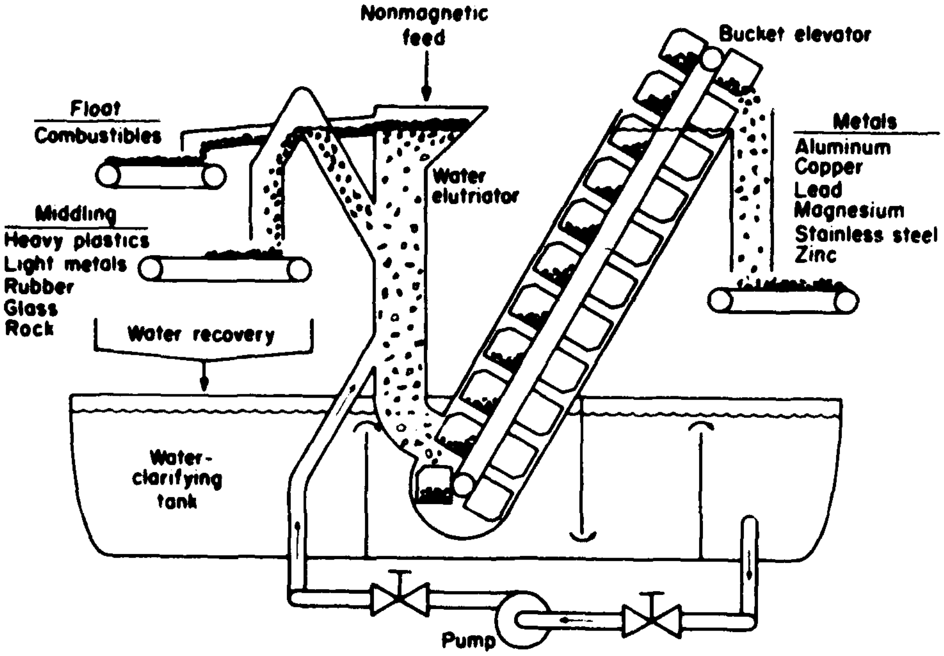


Figure 17 - Schematic of Bureau of Mines 2.52-kg/s (10-t/h) water elutriator system for separating nonferrous metals from scrap car shredding operations.

Operation of the water elutriator is simple and efficient. Nonmagnetic material from the automobile shredder is fed onto the surface of a column of rising water. Dense materials fall through the rising water and are collected as a sink product at the bottom of the column; medium-density materials are removed as an intermediate product in a water flow through a discharge port located between the overflow and sink; and light materials are carried out in the overflowing water at the top of the column as a float product.

Nearly 99 pct of the mixed metals were recovered in the water elutriator system from the shredded nonmagnetic material as a 70-pct-metal concentrate. Optimum operating conditions have yielded a 93-pct-pure metal product resulting in a 93-pct metal recovery. The elutriator float product consists of combustibles, light plastics, foam rubber, and minimal amounts of coated and uncoated Cu wire. The middling discharge is made up of medium-density rubber, plastics, glass, rock, coated and uncoated Cu wire, thin sheet SS, and wrought Al.

Records kept at a commercial shredder operation show a 34-pct increase in nonmagnetic metals recovery during 1 yr of operation of the Bureau water elutriator, compared with recoveries from a previously used air classification system. Detailed information on size, analysis, and distribution of the products can be found in reference 23.
]

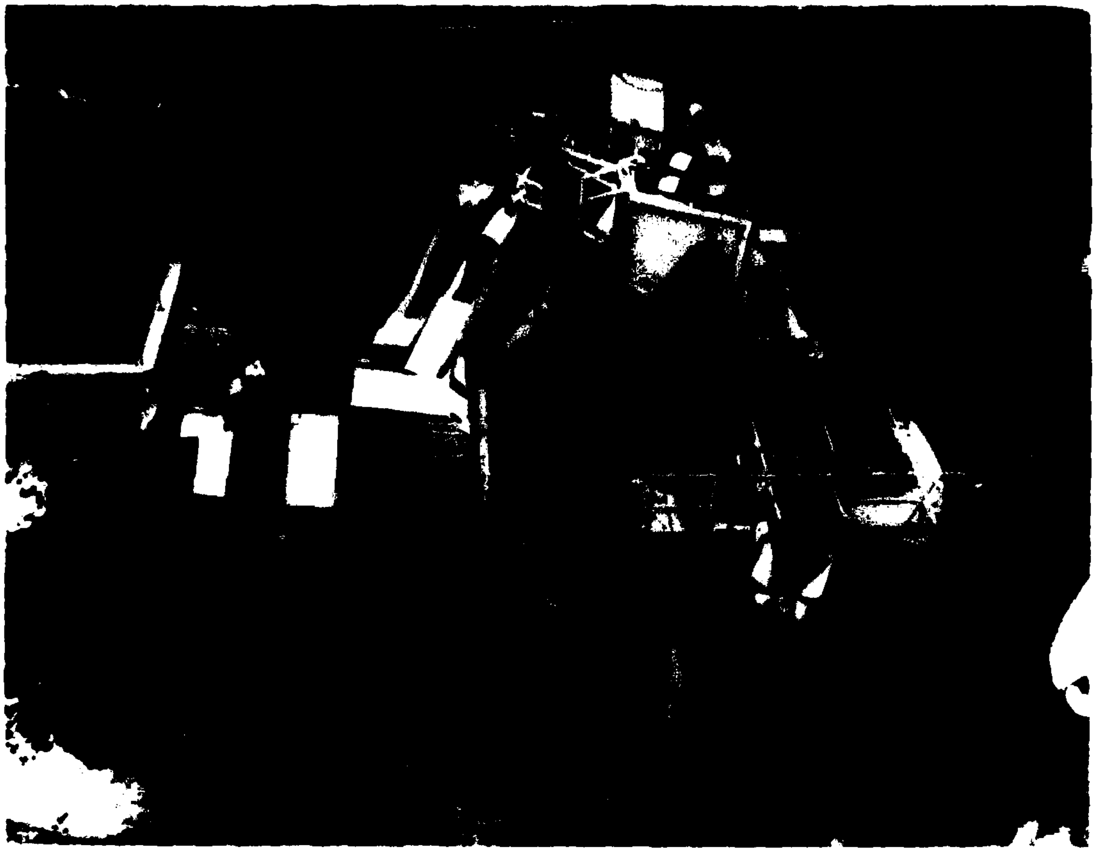


Figure 18 - Water elutriator in operation at commercial scrap yard.

After proving the commercial viability of the water elutriator in recovering nonferrous metals from scrap automobile shredding operations, Bureau researchers now are investigating the use of heavy-media techniques to separate the nonferrous metals from each other. Low-cost barite was selected as the medium, which is prepared by mixing it with water to the desired density. The barite remains in suspension in densities (specific gravities) above 1,700 kg/m^3 (1.7 g/cm^3), and the medium is easily pumped at densities to above 2,600 kg/m^3 (2.6 g/cm^3). The metal separations are determined by the terminal velocity of the particles and the density of the medium. Total separation and recovery of Mg from a mixed metal concentrate is accomplished using a medium density of 1,900 kg/m^3 (1.9 g/cm^3); a 96-pct separation with 94-pct recovery of Al is achieved at a medium density of 2,350 kg/m^3 (2.35 g/cm^3). Seventy-five percent Cu and Zn base metal concentrates have been obtained of the respective metals; however, because of overlapping alloy densities, distinct separations have not yet been achieved.

The barite-medium metal separation is conducted in a trough with the medium flowing through and overflowing at the end of the trough as shown in Figure 19. Barite medium is pumped through the trough at a flow rate that varies with the density and the separation desired. Metal being separated is carried from the trough in the overflow, while the other metal or metals sink through the medium. The 1.83-m (6-ft) trough shown in Figure 20 separates 1.26 kg/s (5 t/h) shredded automotive nonferrous mixed metal concentrate containing Mg, Al, Cu, and Zn. The Mg is recovered in the first-stage trough and Al in the second. The Cu and Zn are presently hand-sorted.

Barite is recovered for recycling by shaking the sink and float products on a vibrating screen and then rinsing with a water spray. The barite recovered by shaking is immediately recyclable. The water-washed barite will not remain in suspension at a density less than 1,700 kg/m^3 (1.7 g/cm^3) and is recovered for makeup from the bottom of the washing settler circuit. Periodic screening of the overflowing barite through a 100-mesh screen removes the fines that could inhibit separation. Barite seems to have an unlimited recycling life, and 99-pct recovery appears practical.

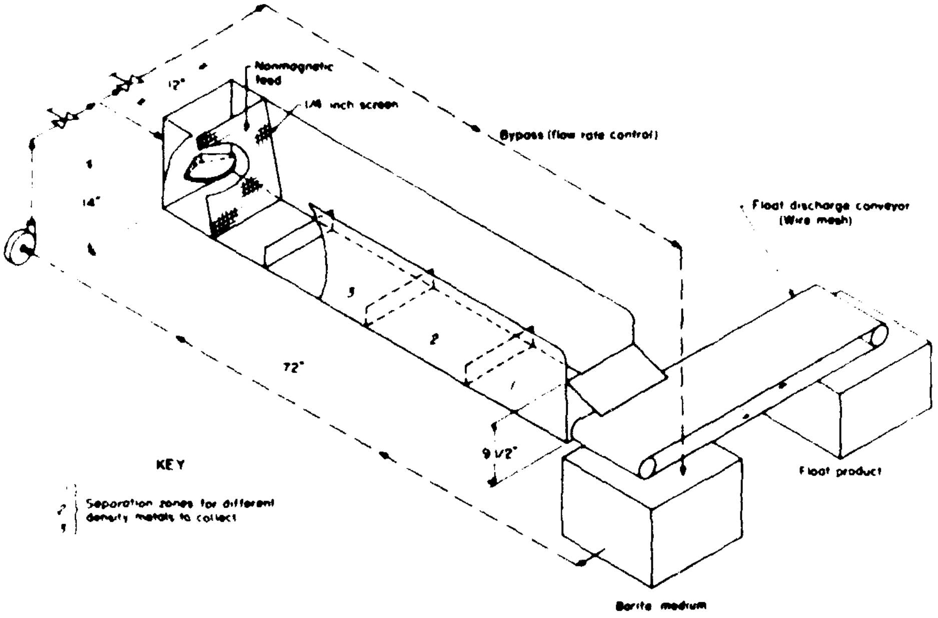


Figure 19 - Diagram of barite trough for separating nonferrous metals from scrap cars.

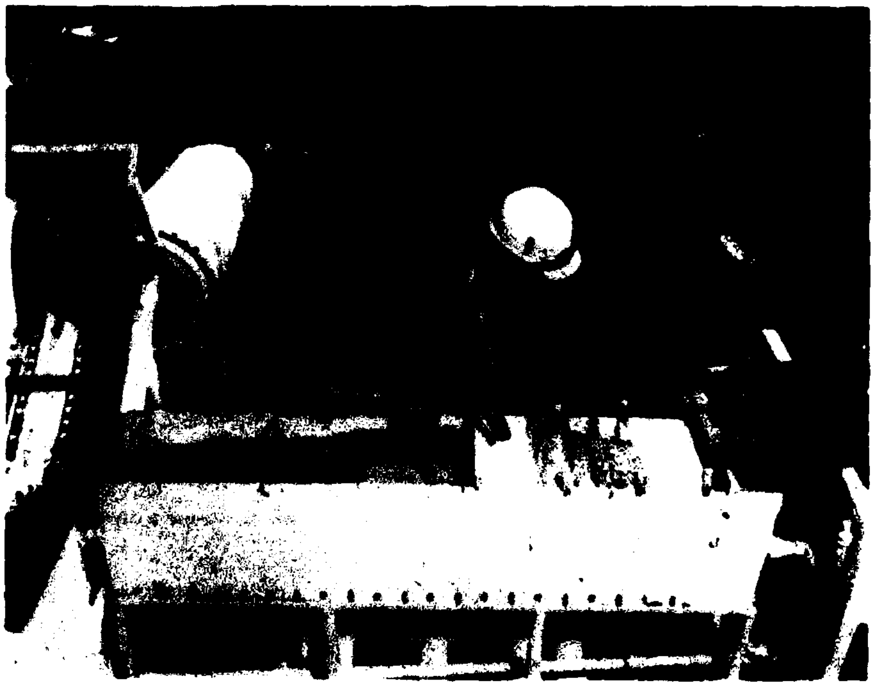


Figure 20 - Laboratory model 1.26-kg/s (5-t/h) barite separation trough for separating nonferrous metals from scrap cars.

Another problem that has an impact on recycling nonferrous shredded material from scrap automobiles is the Al alloy mix recovered from the scrap. Present-day U.S. cars contain about 45 kg (100 lb) of Al, and projections show that this may increase to about 90 kg (200 lb) by 1990. This could represent an Al scrap resource of over 907 million kg (2 billion lb) annually. A significant portion of this increase in Al will be in wrought grades. The typical mix in future cars will be 50:50 wrought and cast alloys. The secondary foundry industry in the United States is unable to absorb all of this scrap for casting alloys, and high levels of Si, Fe, Cu, and Zn in the cast alloys make the unseparated scrap unsuitable for wrought alloy production without the addition of large amounts of primary Al for dilution purposes.

Bureau researchers investigating the problem of separating cast and wrought Al alloys discovered that wrought alloys remained ductile above 873 K (600° C), whereas the high-Si casting alloys exhibited considerable loss of ductility above 773 K (500° C). This property behavior of the two alloys was exploited by the Bureau in a patented hot-crush method for separating wrought from cast alloys (24).

Laboratory experiments consisted of heating mixed scrap to 833 K (560° C) in a small rotary electric furnace and then fragmenting the hot mixture in a crusher or small hammer mill (Figure 21). After screening, the fragmented cast alloys were recovered as an undersize faction, while the oversize wrought alloys were collected from the top of the screen. Figure 22 shows a typical separation achieved by this method. Magnetic separation is normally required after the crushing step to remove any loose ferrous items. Feasibility tests showed that the method can be adapted to a single-step operation in a heated rotary furnace that would heat and fragment in a single operation through repeated lifting and dropping in the furnace.

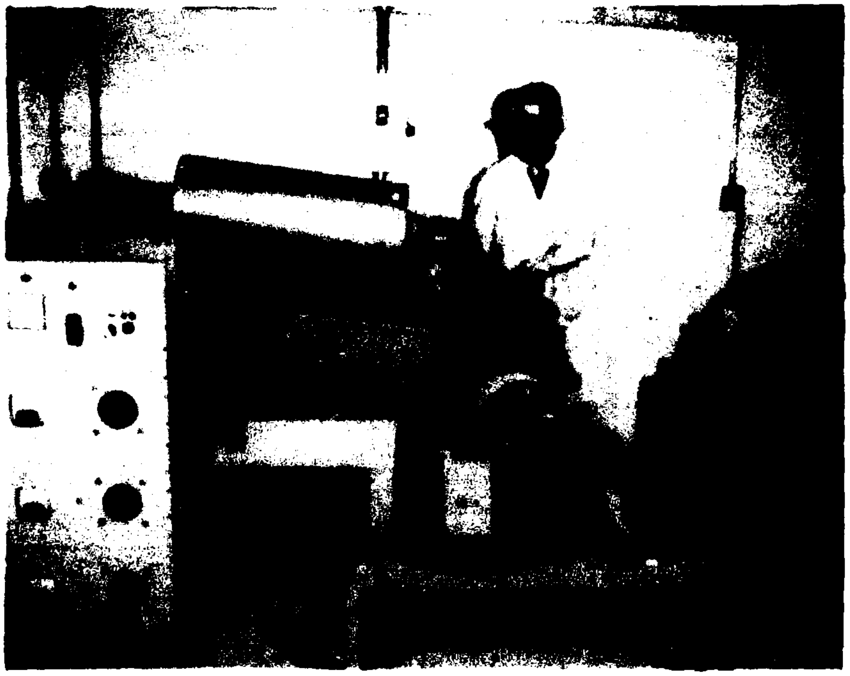


Figure 21 - Furnace, hammer mill, and drum magnet used to separate wrought and cast Al scrap alloys.

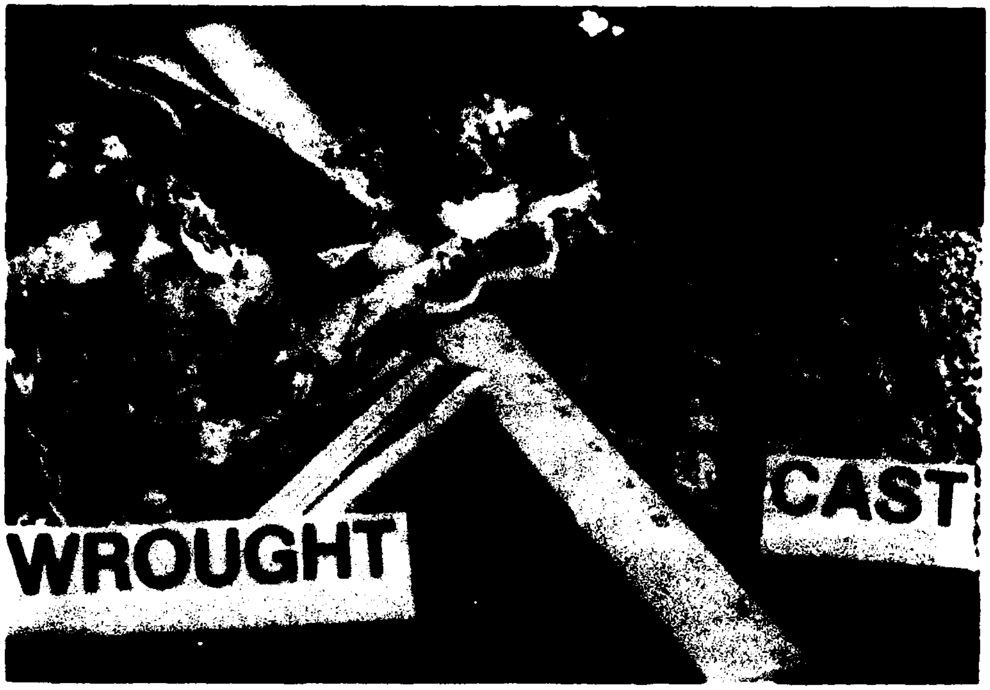


Figure 22 - Separated wrought and cast Al products obtained by the hot-crushing process.

SCRAP METAL IDENTIFICATION

The National Association of Recycling Industries and the Institute of Scrap Iron and Steel, as well as many individual scrap processors, have indicated that many alloy groups require new or improved identification and sorting techniques. In fact they have identified this as one of the most serious problems in scrap processing. More than 205.9 million kg/yr (227,000 t/yr) of SS scrap is not recovered owing to lack of rapid and accurate identification methods. An additional 128.8 million kg (142,000 t) is downgraded to lesser value materials. Wrought SS and heat-resistant alloy scraps alone account for a loss of 56.2 million kg (62,000 t) of Cr annually in the United States (12). Effective recycling is of vital concern in the United States because of both the strategic and critical element content of many alloy groups as well as the potential energy savings associated with recycling them.

For scrap metals to be returned to operations where they can be recycled effectively, they must be sorted and segregated into lots that contain similar materials. Identification of these metals or alloys is the first and most critical phase in this operation. In routine operation of a commercial scrap yard, identification and segregation of scrap metals are carried out by experienced sorters. The degree of separation the scrap metals receive at the scrap yard depends on the ability of these sorters to identify alloys and on the value of the materials. Identification of scrap may be accomplished by object recognition and by considering color, apparent density, magnetic properties, nature of sparks resulting when a metal or alloy is touched to a grinding wheel, and chemical spot tests. When highly accurate analyses are needed, more time-consuming methods, such as chemical and spectrographic analysis, are used. New alloys now entering the scrap market are making recognition increasingly difficult, even for experienced sorters. The problem is compounded by the decreasing number of available, skilled scrap sorters. This skill in recognition can be achieved only through years of day-to-day, hands-on experience in the scrap yard or plant.

To alleviate this problem, the Bureau has been conducting the following studies:

1. Determine areas requiring new or improved sorting technology,
2. Evaluate and develop new and improved identification and sorting methods,
3. Test problem alloy groups, such as Ni- and Co-base alloys, to determine the most promising rapid identification methods,
4. Track trends in new alloy development in order to better predict their impact on scrap recycling.

Early work involved identification and analyses of copper-base alloys by fluorescent X-ray spectrography (25). Recently a comprehensive survey of the methods used for identifying scrap metals has been made (26). Current methods that have been reviewed and evaluated include object recognition; density determination; magnet, spark, and chemical spot testing; thermoelectric and eddy current measurements; and various analytical techniques.

Figure 23 shows an apparatus being used by Bureau scientist to obtain reproducible spark patterns to measure the spatial radiance of sparks. It consists of a grinder and a sensor that is connected by fiber optic cable to a spectrophotometer that measures the intensity of the light rays characteristic of the alloy used to generate the spark.

Figure 23 - Laboratory apparatus consisting of a grinder, optical sensor, and spectrophotometer used to obtain reproducible spark patterns.

Spectra of spark patterns have been recorded for several alloys including mild steels; high-strength, low-alloy steels; 200, 300, and 400 series SS; Inconels; Incoloys; Haynes 20 MOD; and Hastelloy B-2. Between 500 and 700 nm, the spectra show differences except in the case of 300 series SS and their low carbon analogs; e.g., 304 and 304L SS and 316 and 316L SS.

In general, as the Ni content of an alloy increases, the intensity maximum is shifted to a higher wavelength. It is expected that the observed differences will make it possible to separate alloys not amenable to separation using conventional spark testing.

In addition, a flowsheet for separating Ni-base alloys and SS has been designed (Figure 24). This flowsheet, which uses thermoelectric response and optical emission spectroscopy techniques, requires less than half the operations present in a conventional separation scheme based on chemical spot tests. This methodology begins with thermoelectric measurements to make the first separation into alloy groups, followed by use of a portable emission spectroscope to narrow the identification to more specific groups or individual alloys. The cost for both of these instruments is quite low, making them available to the small scrap processor. Plans call for testing this flowsheet in an operating scrap yard.

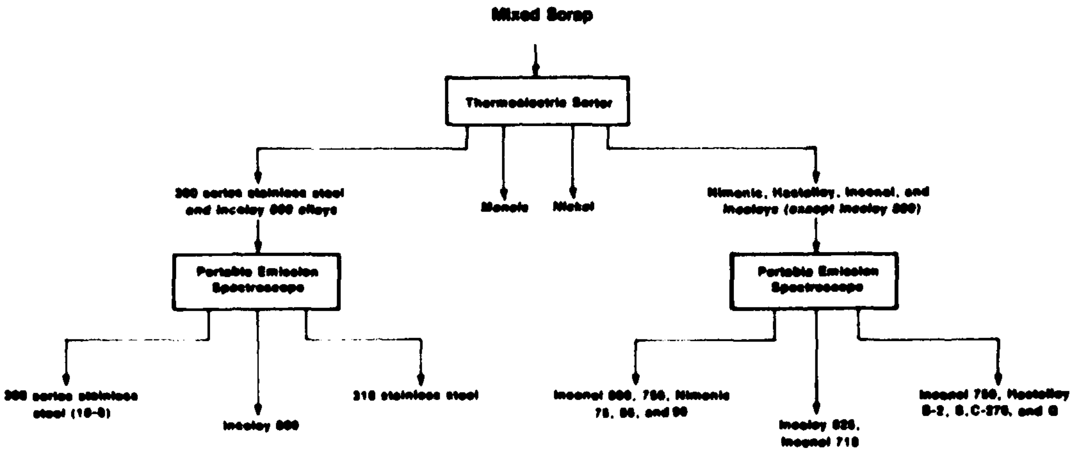


Figure 24 - Proposed instrumental technique for sorting high-value scrap.

It should be noted that the research described in this paper represents only a cross section of the type of work the Bureau of Mines is conducting on the recovery and recycling not only of strategic and critical materials, but also economically important commodities such as lead, aluminum, zinc, copper, and precious metals. The current Bureau of Mines research program in recycling consists of 41 inhouse projects dealing with a broad spectrum of problems on metal- and mineral-based waste products, as well as work on mineral tailings, slimes and process waterwater.

REFERENCES

1. Caldwell, H. S., Jr., and M. J. Spendlove. Recovery of Magnesium and Cadmium From Incendiary Alloys by Vacuum Distillation. BuMines RI 5476, 1959, 17 pp.

2. Barnard, P. G., A. G. Starliper, and H. Kenworthy. Reclaiming Refractory Carbides and Cobalt From Cemented-Carbide Scrap. Secondary Raw Materials, v. 7, No. 9, September 1969, pp. 19-21.

3. DeCesare, R. S., F. J. Palumbo, and P. M. Sullivan. Pilot-Scale Studies on the Composition and Characteristics of Urban Refuse. BuMines RI 8429, 1980, 32 pp.

4. Kenworthy, H., V. A. Nieberlein, and A. G. Starliper. Experimental Extraction of Strategic Components From S-816 Alloy Scrap. BuMines RI 5786, 1961, 27 pp.

5. Brooks, P. T., and J. B. Rosenbaum. Separation and Recovery of Cobalt and Nickel by Solvent Extraction and Electrorefining. BuMines RI 6159, 1963, 30 pp.

6. Brooks, P. T., G. M. Potter, and D. A. Martin. Chemical Reclaiming of Superalloy Scrap. BuMines RI 7316, 1969, 28 pp.

7. Brooks, P. T., and G. M. Potter. Electrochemical Recovery of High-Purity Nickel and Cobalt From Crude Nickel and Ferronickel. BuMines RI 7402, 1970, 25 pp.

8. Hayashi, M., D. R. Peterson, and D. W. Bridges. Electrochemical Recovery of Cobalt-Nickel From Superalloy Scrap. BuMines RI 6445, 1964, 35 pp.

9. Curwick, L. R., W. A. Petersen, and H. V. Makar. Availability of Critical Scrap Metals Containing Chromium in the United States: Superalloys and Cast Heat-and Corrosion-Resistant Alloys. BuMines IC 8821, 1980, 51 pp.

10. deBarbadillo, J. J., J. K. Pargeter, and H. V. Makar. Process for Recovering Chromium and Other Metals From Superalloy Scrap. BuMines RI 8570, 1981, 73 pp.

11. Kusik, C. L., K. Parameswaran, D. J. Kinneberg, and H. V. Makar. Pyrometallurgical Recovery of Chromium From Scrap Metals: Laboratory Studies. BuMines RI 8571, 1981, 41 pp.

12. Kusik, C. L., H. V. Makar, and M. R. Mounier. Availability of Critical Scrap Metals Containing Chromium in the United States: Wrought Stainless Steels and Heat-Resisting Alloys. BuMines IC 8822, 1980, 51 pp.

13. Higley, L. W., Jr., R. L. Crosby, L. A. Neumeier. In-Plant Recycling of Stainless and Other Specialty Steelmaking Wastes. BuMines RI 8724, 1982, 16 pp.

14. Dunning, B. W., Jr., and F. Ambrose. Characterization of Pre-1957 Avionic Scrap for Resource Recovery. BuMines RI 8499, 1980, 20 pp.

15. Hilliard, H. E., B. W. Dunning, Jr., and H. V. Makar. Hydrometallurgical Treatment of Electronic Scrap Concentrates Containing Precious Metals. BuMines RI 8757, 1983, 15 pp.

16. Chemical and Engineering News. EPA Issues Final Air Quality Standards for Lead. V. 6, Oct. 9, 1978, p. 6.

17. Thrash, J. H. Maintenance Free Batteries, Effects on the Recycling Industry. Recycling Today, v. 16, No. 5, May 1978, pp. 36-40.

18. Smith, L. L., R. G. Sandberg, and E. R. Cole, Jr. Method of Producing a Lead Dioxide Coated Electrode. U.S. Pat. 4,159,231, June 26, 1979.

19. Dean, K. C., J. W. Sterner, and E. G. Valdez. Effect of Increasing Plastics Content on Recycling of Automobiles. BuMines TPR 79, May 1974, 14 pp.

20. Valdez, E. G. Separation of Plastics From Automobile Scrap. Proceedings, Fifth Mineral Waste Utilization Symposium, IITRI, Chicago, Ill., Apr. 13-14, 1976, pp. 386-391.

21. Chindgren, C. J., K. C. Dean, and J. W. Sterner. Construction and Testing of a Junk Auto Incinerator. BuMines TPR 21, February 1970, 8 pp.

22. Dean, K. C., and J. W. Sterner. Dismantling a Typical Junk Automobile To Produce Quality Scrap. BuMines RI 7350, 1969, 17 pp.

23. Steele, D., and J. Sterner. A Water Elutriation System for Recovering Nonmagnetic Metals From Automobile Shredder Rejects. BuMines RI 8771, 1983, 21 pp.

24. Montagna, D., and H. V. Makar. Method for Wrought and Cast Aluminum Separation. U.S. Pat. 4,330,090, May 18, 1982.

25. Campbell, W. J., and H. E. Marr. Identification and Analyses of Copper Base Alloys by Fluorescent X-Ray Spectrography. BuMines RI 7635, 1972, 30 pp.

26. Newell, R., R. Brown, D. Soboroff, and H. Makar. A Review of Methods for Identifying Scrap Metals. BuMines IC 8902, 1982, 19 pp.

EFFET DES TRAITEMENTS SOUS VIDE SUR L'EVOLUTION DES TENEURS EN ELEMENTS TRACES DANS LES SUPERALLIAGES

par
J.P. WADIER
Etudes et Recherches
et
J. MORLET
Directeur Technique
IMPHY SA
Aciéries d'Imphy
Imphy
58160
France

RESUME

Le recyclage des superalliages procède d'une nécessité économique et stratégique. Deux voies privilégiées de recyclage sont examinées tant au point de vue thermodynamique que technologique :

- Fusion oxydante intermédiaire pour éliminer le Titane et l'Aluminium afin de débuter l'élaboration sous vide avec un bain oxydé ;
- Fusion inerte sous vide de riblons reconditionnés.

Le texte passe successivement en revue l'action du vide sur la réaction Carbone/Oxygène, la désulfuration et la dénitruration éventuelle ainsi que la distillation des métaux lourds.
L'effet ultérieur de la refusion sous vide (VAR) et sous laitier (ESR) sur la qualité du produit final est pris en compte.

VACUUM RECYCLING EFFECT ON MINOR ELEMENTS IN SUPERALLOYS

Superalloy recycling is an economical and strategical necessity. Two different ways of scrap recovery are examined from a thermodynamical and technological point of view :

- Air melting with oxygen blowing to remove Titanium and Aluminium before Vacuum treatment ;
- Non reactive melting of conditionned scraps in VIM.

This paper examines in detail the vacuum effect on Carbon/Oxygen reaction, desulfurization and Nitrogen removal as well as heavy metal distillation.
Further reactions during remelting in VAR or ESR are taking account to assure the quality of the final product.

INTRODUCTION

La bonne économie de la production des superalliages passe par le recyclage des chutes générées tout au long du processus de fabrication. Cet aspect du métier est important du fait du coût et de la rareté croissante des matières premières, mais aussi parce que les quantités de chutes produites sont particulièrement élevées.

Selon une enquête (ref. 1) réalisée aux ETATS-UNIS en 1976 mais dont les éléments techniques restent d'actualité, sur 140 000 tonnes de superalliages issues des fours d'élaboration, seulement 40 000 tonnes ont été mises en oeuvre dans des ensembles (cf. figure 1). En d'autres termes, sur 100 tonnes coulées, 28 tonnes seulement sont effectivement utilisées et elles-mêmes sont recyclées en grande partie après un temps de service compris entre 5 et 10 ans.

Selon les mêmes auteurs, on estime que les lits de fusion sont constitués en moyenne par 41 % de matières neuves et 59 % de matières recyclées. Ce dernier chiffre représente une moyenne fluctuant en fonction des conditions économiques et des disponibilités avec des variations de cycle. On observe aussi une grande disparité suivant les nuances, leur utilisation et les modes de mise en oeuvre ; le taux de matières recyclées pouvant être très faible pour les alliages pour aubes de turbine type IN 100 et pouvant atteindre 80 % pour des pièces forgées après double fusion sous vide (VIM + VAR).

1- CHOIX DES CONDITIONS D'ELABORATION EN FONCTION DU TYPE DE MATERIAUX A RECYCLER

Les matériaux à recycler doivent être considérés a priori comme des matières premières comme les autres. Ils se distinguent cependant des matières neuves car ils sont à la fois plus purs en volume et plus pollués en surface :

- Ils ont déjà subi une double élaboration sous vide (VIM + VAR) qui en fait des matières premières de très bonne qualité ;
- Ils se présentent sous des formes variées avec un degré de contamination en surface qui s'aggrave lorsque l'on passe des chutes massives aux chutes légères et enfin aux tournures et autres produits divisés.

L'utilisation qui en est faite et en particulier le mode de mise en oeuvre dépend de la présentation de ces matériaux (charge massive ou divisée), du degré de pollution et de la nature de celle-ci, des possibilités technologiques de purification à l'état solide et aussi de la destination de l'alliage.

Du point de vue présentation physique, il est commode de distinguer :

- Les chutes massives, bien identifiables, plus ou moins oxydées en surface qui peuvent être nettoyées par

meulage ou grenaillage avant le recyclage. Elles représentent (ref. 1, tableau 1) 68 % du total des chutes réutilisables ;
- Les chutes légères et tournures (25 % du total des chutes) qui sont dans un état plus divisé et dont le nettoyage relève de techniques adaptées : broyage puis traitements par voie humide, décapage et dégraissage, visant à éliminer en particulier les huiles de coupe et d'une façon générale les apports de Carbone. Elles constituent un métier en soi qui n'est pas l'objet de cet exposé. Seule une sélection et un conditionnement rigoureux permettent le recyclage dans les super-réfractaires ;
- Le solde (7 %) est déclassé et utilisé dans des nuances plus courantes telles que les aciers inoxydables.

L'efficacité des traitements dépend évidemment de l'état physique et le mode de mise en oeuvre est adapté en fonction de la nature des chutes reconditionnées :

- Recyclage direct au four à induction sous vide (VIM) des chutes massives qui ont un pédigree et qui ont subi un nettoyage approprié ;
- Affinage préliminaire au four à arc avec traitement complémentaire (AOD ou VOD) pour purifier les chutes les plus polluées. On obtient ainsi une matrice, contenant les éléments les plus intéressants du point de vue économique Nickel, Cobalt Chrome, Molybdène et, sauf cas particulier, sans Titane, ni Aluminium.
  Cette matrice entre comme élément de charge au four à induction sous vide.

RECYCLAGE DIRECT AU FOUR A INDUCTION SOUS VIDE

Le recyclage direct des chutes au four à induction sous vide est la solution la plus évidente du point de vue économique puisqu'il permet d'utiliser la totalité des matières premières par la voie la plus courte et partant avec les meilleurs rendements matière et la plus faible consommation d'énergie.
Toutefois, les matériaux à recycler contiennent des éléments réactifs tels que le Titane et l'Aluminium qui les rendent agressifs vis-à-vis des réfractaires et de l'environnement. De ce fait, les risques de dégradation du bain par des réactions parasites sont importants et la stratégie d'élaboration vise à conserver la qualité des matières enfournées en minimisant ces réactions. L'examen ultérieur des cinétiques de désoxydation et de dénitruration justifiera l'orientation vers une fusion aussi inerte que possible. On sait, en effet, que le four à induction sous vide est un réacteur chimique peu performant, aux possibilités de purification limitées particulièrement sur bains aussi complexes que ceux des superalliages.

Sous ces réserves et avec les précautions supplémentaires qu'il requiert, le recyclage direct ne doit pas être considéré comme une voie de rattrapage. Il suffit pour s'en persuader de rappeler que c'est la technique utilisée dans les Fonderies de précision, en particulier celles de moulage en cire perdue des aubes de turbines. Le haut niveau de qualité requis est satisfait moyennant des précautions qui, si on les transpose dans la technologie d'élaboration d'alliages, constituent des contraintes. Elles sont reprises ici car elles illustrent bien et de façon simple la démarche conduisant aux techniques de recyclage des chutes massives :

- La charge est constituée par une seule pièce cylindrique, nettoyée par meulage ou tournage pour éliminer la surface polluée ;
- Un creuset neuf étuvé à haute température est utilisé à chaque fusion pour éviter toute contamination par les restes de la coulée précédente.;
- La fusion est rapide et la coulée se fait dès mise à température du bain ;
- La masse à fondre est faible (au plus quelques dizaines de kilos) et la surface de contact avec l'atmosphère est réduite.

Les conditions de recyclage dans un four VIM de plusieurs tonnes avec des chutes de différentes tailles et un creuset, où subsistent toujours des restes de la coulée précédente, sont différentes mais ce sont les mêmes principes qui guident la définition du processus.

PREAFFINAGE AU FOUR A ARC

Si du fait des pollutions ou de l'aspect physique des chutes, les techniques de nettoyage évoquées plus haut sont insuffisantes, il est préférable d'avoir recours à une opération de purification préalable au four à arc suivie éventuellement par un traitement en poche ou au convertisseur. Ainsi, au prix d'un coût énergétique non négligeable et de la perte des éléments oxydables comme le Titane et l'Aluminium, on récupère et purifie une part importante de chutes non directement utilisables en jouant à la fois sur les possibilités d'affinage pneumatique et sur les échanges métal-laitier.

- La fusion au four à arc permet :
  . de reconstituer à partir de nuances compatibles des compositions homogènes de matrice ;
  . d'éliminer par oxydation et échange métal-laitier les éléments : Chlore, Sodium, Plomb et Soufre, provenant des produits de combustion (ref. 2) ou des revêtements des aubes de turbine.

- Le traitement hors du four (AOD, VOD), sous pression partielle d'Oxygène assure la décarburation en sauvegardant le Chrome. On traite ainsi des chutes carburées par des huiles de coupe ou des produits de combustion.
  . l'injection d'Argon et le brassage dû aux bulles de CO favorisent le dégazage de l'Hydrogène, de l'Azote et des éléments volatils
  . la désulfuration par le laitier se pratique dans les conditions habituelles après réduction du bain métallique.

  Les cinétiques de réaction sont rapides et conduisent à des états proches de l'équilibre ; ce qui n'est pas toujours souhaitable. En particulier, il est difficile de protéger le métal liquide à forte teneur en Chrome contre la réoxydation et la renitruration, lorsque le bain liquide est exposé à l'atmosphère, spécialement pendant la coulée.
  Le prétraitement au four à arc offre aussi la possibilité de choisir le niveau d'Oxygène en fin d'élaboration : le bain est soit semi-calmé, soit bien désoxydé avec une teneur élevée en Aluminium.

Ainsi, la réutilisation des matières à recycler au four à induction sous vide se fait avec deux types de charge très différents, l'un avec une charge semi-calmée qui se rapproche des matières neuves, l'autre contenant du Titane et de l'Aluminium avec une composition proche de la composition finale. La conduite de l'élaboration et le contrôle des éléments résiduels qui en découlent sont donc différents dans les deux processus qui, chacun, visent à minimiser les teneurs finales en Oxygène, Azote, Soufre et oligoéléments. Le choix parmi les options possibles résulte d'un examen des comportements, qui est fait dans la suite élément par élément, mais qui dans la pratique est orienté par un souci de compromis indispensable.

2- EVOLUTION DE L'OXYGENE

Lors d'une élaboration au four à induction sous vide, l'affinage Carbone, Oxygène constitue une part essentielle de l'opération. Sous vide, le Carbone est un puissant désoxydant qui présente l'avantage de donner un produit de réaction gazeux qui s'élimine facilement et qui entraîne avec lui d'autres impuretés telles que l'Hydrogène et l'Azote. On utilise cette possibilité avec des charges en matière neuve contenant de l'Oxygène et des refusions semi-calmées car un bas vide est favorable au dégagement d'oxyde de Carbone. Le Titane et l'Aluminium sont ajoutés après l'affinage dans un bain qui contient peu d'Oxygène, ce qui minimise la quantité d'inclusions oxydées qui doivent décanter (figure 2, ref. 3).

Les charges préélaborées qui contiennent du Titane et de l'Aluminium sont beaucoup plus réactives vis-à-vis de l'Oxygène et de l'Azote, et déjà, au cours du chauffage, la surface portée au rouge agit comme un piège pour fixer les traces de gaz qui subsistent même à faible pression du fait de la désorption des poussières ou des fuites résiduelles. A l'état liquide, non seulement l'Aluminium et le Titane ne permettent pas la désoxydation par le Carbone sous vide, mais lorsque leur concentration est élevée (supérieure à 1 %) ils ne jouent plus leur rôle habituel de désoxydant.

Par exemple, dans le cas d'un alliage Fe-Al (cf. figure 3), on montre que la concentration de l'Oxygène soluble passe par un minimum de 4 ppm pour une teneur en Aluminium de 0.075. Au-delà de cette concentration, la solubilité de l'Oxygène augmente très vite et il en est de même avec le Titane. L'accroissement de la solubilité de l'Oxygène dans le métal liquide favorise les réactions avec le réfractaire et l'atmosphère résiduelle. L'Oxygène en solution ne pouvant pas être éliminé sous forme de CO, précipite sous forme d'oxyde aux basses températures, c'est-à-dire pendant la solidification (ref. 4 et 5).

En présence de Titane et d'Aluminium, l'approche est donc inverse de celle adoptée pour les matières neuves ; on cherche à éviter les réactions vers l'équilibre ou à en contrôler la cinétique. En pratique cela signifie : contrôler la propreté et l'étanchéité du four mais aussi la qualité des réfractaires et limiter la durée de l'élaboration.

- Les réfractaires, pisé, brique et ciment, ne doivent pas contenir des oxydes susceptibles d'être réduits par Aluminium et Titane, en particulier l'oxyde de Fer et la silice. Cependant, même les pisés les plus inertes du type spinelle alumine-magnésie réagissent partiellement avec le Titane et la remontée d'Oxygène qui en résulte ne peut être limitée qu'en réduisant la durée d'élaboration.
- Si dans le cas des matières neuves un très bas vide est nécessaire pour favoriser la désoxydation par le Carbone, pour dégazer l'Hydrogène et l'Azote et pour éliminer les métaux lourds volatils comme le Plomb et le Bismuth, il n'en est pas de même avec une charge recyclée. La présence de Titane et de l'Aluminium empêche la formation d'oxyde de Carbone et, quant aux gaz et métaux lourds, ils ont déjà été éliminés lors de l'élaboration primaire VIM + VAR. Il est préférable de rechercher un vide moyen d'environ 50.10^{-2} Torr qui est obtenu rapidement par les pompes mécaniques et les Roots afin de réaliser une fusion inerte rapide.

DESOXYDATION DE L'ALLIAGE IN 718

La figure 4 compare l'évolution de l'activité et de la teneur totale en Oxygène au cours de l'élaboration de l'alliage IN 718 à partir de matières neuves sous vide profond de 10^{-2} Torr et de matières recyclées sous vide moyen de 50.10^{-2} Torr.

Pour les charges en matière recyclée, on notera en fin de fusion que l'activité de l'Oxygène mesurée à l'aide d'une jauge électrolytique et la teneur totale mesurée par chimie sont toutes les deux bien groupées (de l'ordre de 5 ppm pour l'activité et de 40 ppm pour la concentration). Du fait du raccourcissement du temps d'élaboration, la reprise d'Oxygène reste faible, jusqu'à la mise des additions correctrices. Le niveau final n'est abaissé que lors des ajouts d'alcalinoterreux, Calcium et Magnésium. Dans le cas de charge du type matières neuves, l'Oxygène en fin de fusion est plus dispersé du fait d'états initiaux non "normalisés", mal définis au sens physico-chimique et des difficultés à contrôler la réaction C-O pendant la fusion. Pendant l'affinage sous vide profond du bain qui s'est progressivement homogénéisé pour se rapprocher de l'équilibre, le Carbone réduit l'Oxygène, et les résultats des mesures sont bien groupés.

L'addition d'Aluminium ne fait abaisser ni l'activité, ni la teneur en Oxygène et ce sont encore le Calcium et le Magnésium qui permettent d'atteindre des concentrations de 10 à 20 ppm d'Oxygène résiduel.

En résumé et à ne considérer que les éléments Carbone et Oxygène, pour les produits qui sont destinés à l'élaboration de lingots électrodes, il n'y a possibilités réelles d'élimination de ces éléments qu'en l'absence de Titane et d'Aluminium. Dans ce cas, un affinage sous vide profond de matrices reconditionnées par fusion préalable permet comme pour les matières neuves une purification très complète.

Dans le cas contraire, il est préférable de rechercher une opération relativement rapide qui minimise les réactions parasites en particulier avec le creuset et qui de ce fait attend du vide essentiellement un effet de protection des éléments réactifs et pour laquelle on se contente du niveau de pompage moyen. Cette pratique est d'autant plus efficace que le four a un taux de fuite faible.

La possibilité de réaction étant très limitée, cette technique est réservée aux matières recyclées bien identifiées et où les sources de Carbone et d'Oxygène non contrôlées ont été éliminées.

3- EVOLUTION DE L'AZOTE

Les bains métalliques constitués à partir de matières recyclées sont en général hors d'équilibre en ce qui concerne la teneur en Azote et la pratique industrielle vise d'abord à maintenir un niveau aussi bas que possible car les phases de dénitruration au four à induction sont lentes et de conduite délicate.

En effet, le Chrome et l'Aluminium confèrent au bain une grande affinité pour l'Azote (cf. figure 5) qui rend difficile la dénitruration par le vide alors que la précipitation et l'élimination des nitrures solides TiN ne conduisent pas à des niveaux aussi bas que souhaités (ref. 6).

PRECIPITATION DES NITRURES

Les nitrures de Titane qui précipitent au sein du bain liquide peuvent être éliminés par décantation et piégeage sur les parois du creuset.
A titre d'exemple pour une matrice type :

Ni	Cr	Co	Mo	Ti	Al
54	18	18	4	3	3

Le produit de solubilité s'exprime sous la forme :

$$\log a_{Ti}.a_N = -\frac{10\ 350}{T} + 2.5$$

Avec des coefficients d'activité : $f_{Ti} = 3.8$ et $f_N = 2.8\ 10^{-3}$, la teneur en Azote, à 1420 °C, en équilibre avec 3 % de Titane est de 60 ppm, ce qui signifie que l'on ne peut pas espérer obtenir des valeurs inférieures par précipitation et décantation des nitrures. On constate (cf. figure 6 et tableau 2) que si la teneur en Azote des chutes est faible (< 60 ppm) et que si la fusion est conduite dans de bonnes conditions d'étanchéité, il n'y a d'évolution du niveau d'Azote au cours de l'élaboration ni par action du vide, ni par précipitation.

EFFET DU VIDE

Avec une charge sans Titane, la dénitruration peut s'accomplir par l'effet du vide. La cinétique de réaction est du premier ordre et l'étape limitante est constituée par le transfert en phase liquide. Les vitesses de dénitruration ont été mesurées dans trois fours à induction sous vide de tailles différentes : 6 tonnes, 1.5 tonne et 50 kg (cf. figure 7 et tableau 3).

Dans un four de laboratoire de 50 kg, on peut éliminer sous vide environ 200 ppm d'Azote par heure (cf. tableau 3) mais au fur et à mesure que le rapport Surface d'échange / Volume des différents fours diminue, la vitesse de dénitruration diminue elle aussi. Elle n'est plus que de 20 $ppm.h^{-1}$ dans un four de 1.5 tonne et de 10 $ppm.h^{-1}$ dans un four de 6 tonnes.
En pratique, on vérifie, tableau 2, que le traitement sous vide entre la fin de fusion et la fin d'affinage permet seulement de passer de 120 à 110 ppm en moyenne, et que c'est l'addition de Titane et la précipitation de TiN qui abaisse la concentration en Azote à moins de 60 ppm, valeur prédite par le calcul du produit de solubilité. D'où l'intérêt d'éliminer autant que faire se peut l'Azote avant élaboration au four sous vide.

TRAITEMENT AU FOUR A ARC

Au four à arc, l'évolution de la teneur en Azote de ces charges chromées résulte de réactions ayant des effets inverses. Pendant la fusion à l'air, la charge se nitrure (cf. figure 8), puis le soufflage d'Oxygène et la formation d'oxyde de Carbone favorisent la dénitruration, le bain gardant par ailleurs son avidité pour cet élément. Dans ces conditions, de légers écarts de pratique conduisent inévitablement à des teneurs dispersées.
Dans l'exemple de la figure 8, pour des alliages type U 500, la teneur en Azote de fin d'affinage est comprise entre 10 et 40 ppm, mais dès que le laitier qui joue un rôle protecteur est éliminé, le bain qui contient 18 % de Chrome entre en contact avec l'atmosphère et il y a une renitruration que l'on peut plus ou moins limiter.

L'obtention de basses teneurs en Azote passe par un affinage poussé du bain par l'oxyde de Carbone ou par un bullage par gaz neutre avec une coulée à l'abri de l'air. Si la coulée a lieu à l'air, il y a une renitruration supplémentaire qui explique le niveau élevé (120 ppm) choisi pour l'exemple de la figure 6 et la dispersion de la teneur en Azote de ces charges refondues au four VIM.

4- EVOLUTION DU SOUFRE

L'absence de laitier au four à induction sous vide ne permet pas de désulfurer par la méthode traditionnelle d'échange d'Oxygène et de Soufre entre métal et laitier, la seule voie envisageable est la précipitation de sulfures insolubles de Calcium ou de Magnésium résultant d'un traitement par Calcium, Magnésium, Terres Rares. (cf. figure 9).

En indexant la mise de désulfurant sur la teneur en Soufre, on peut éliminer jusqu'à 200 ppm de Soufre et obtenir un résiduel de l'ordre de 10 ppm. L'excès de Calcium et de Magnésium s'élimine rapidement sous vide mais les sulfures déposés sur les parois du creuset sont très oxydables et le Soufre se redissous dans la coulée suivante. On observe alors un enrichissement graduel en Soufre, coulée après coulée (cf. figure 10) qui impose à chaque fois d'augmenter la dose de désulfurant. Face à une telle évolution, il faut considérer la désulfuration au four à induction sous vide comme un moyen de réparer un accident local mais non comme une procédure à utiliser systématiquement.
La voie normale de désulfuration des chutes sulfurées passe par le traitement par un laitier basique d'un bain bien désoxydé au four à arc. Le bas Soufre va de pair avec un bas Oxygène et un résiduel plus ou moins important en Aluminium. Le métal ainsi réduit s'apparente aux chutes de la nuance et, comme elles, relève d'une gamme type recyclage direct.

5- OLIGOELEMENTS

La valeur d'usage des superalliages, correspondant aux utilisations les plus exigeantes, suppose la mise sous contrôle de 67 éléments dont 39 reconnus nocifs à l'état de traces (moins de 25 ppm pour chacun et une somme inférieure à 400 ppm). Trois éléments Pb, Ag, Se doivent être inférieurs à 5 ppm, Tl et Te étant inférieurs à 1 ppm et Bi inférieur à 0.5 ppm. Le tableau 5 donne les résultats de quelques analyses. De par leur réactivité, les éléments se différencient sommairement en deux catégories (ref. 7 et 8) :

- Certains As, Sn, Sb, P ne sont pas volatils et ne s'éliminent pas au cours de l'élaboration et de la refusion sous vide. On constate un enrichissement progressif dû au recyclage qui contraint à procéder à des dilutions ou à un déclassement pour maintenir les teneurs à un niveau acceptable ;
- D'autres éléments sont volatils, c'est le cas en particulier de Te, Bi, Pb, Ca, Mg, Zn, Cu, Se qui sont éliminés au moins en partie par les traitements sous vide car les cinétiques de distillations au four VIM sont

lentes, de l'ordre de 10 ppm par heure pour le Plomb au niveau de 20 ppm. La refusion VAR est beaucoup plus efficace pour déplomber puisqu'elle permet de garantir dans le lingot une teneur en Plomb inférieure à 5 ppm, même à partir d'une électrode qui en contiendrait 20 ppm.

6- EFFET DE LA REFUSION AU FOUR A ELECTRODE CONSOMMABLE

La refusion au four à électrode consommable est destinée à contrôler la solidification des lingots, c'est-à-dire à assurer une répartition homogène des phases secondaires et à minimiser le taux de ségrégation.
Du point de vue qui nous intéresse ici, elle permet aussi de compléter le traitement du four à induction sous vide.

- Au four VAR, l'éclatement des gouttes métalliques dans l'arc offre des possibilités d'échange avec le vide ; l'augmentation de surface accélère les cinétiques de mise à l'équilibre dans des conditions de température et de pression différentesde celles du four VIM. Les gaz résiduels (CO, H_2) sont désorbés et éliminés par le système de pompage. Les pertes en Azote ne sont pas négligeables puisque au niveau de 50 ppm, on a établi la relation empirique suivante :

  $$\Delta N = -0.74\, N_2(\text{initial}) + 5.8$$

  Les éléments volatils condensables se déposent sur les parois de la lingotière et se retrouvent en peau des lingots. Dans un cas extrême, on a pu doser dans le distillat jusqu'à 0.1 % de Soufre, 40 ppm de Plomb et 80 ppm de Zinc, alors que dans la matrice, le Plomb et le Zinc étaient à des concentrations inférieures à 5 ppm. La concentration des impuretés en peau des lingots représente cependant un risque élevé de fragilisation.
- La refusion ESR épure le métal par dissolution des oxydes dans le laitier et assure un complément de désulfuration. Pour des teneurs initiales de quelques dizaines de ppm, le taux de désulfuration est voisin de 50 %. Les concentrations en gaz et éléments volatils ne sont pas abaissés en ESR et le contrôle du Titane et de l'Aluminium n'est obtenu que par un ajustement précis de la composition du laitier.

En d'autres termes, la refusion vient compléter les purifications qui ont été opérées lors des phases précédentes. Les possibilités qu'elle offre contribuent à améliorer la valeur d'usage à la fois par réduction des teneurs moyennes et dispersion plus régulière des phases nocives. Néanmoins, cet aspect ne peut être considéré que comme secondaire devant l'objectif essentiel de cette opération qui demeure le contrôle de la structure de solidification.

CONCLUSION

Les chutes générées au cours du cycle de fabrication de pièces en superalliage et les pièces elles-mêmes après usage sont de plus en plus systématiquement réutilisées comme matière première. L'augmentation du taux de recyclage est liée à des progrès dans les techniques physico-chimiques de nettoyage des matières à recycler et par une meilleure compréhension et mise sous contrôle des opérations d'affinage en phase liquide et enfin une adaptation des modes de conduite de l'élaboration au four à induction sous vide.
A les considérer individuellement, les principaux éléments qui constituent la pollution peuvent être ramenés à des teneurs compatibles avec les exigences, mais c'est leur présence simultanée qui rend les opérations plus complexes et conduit à des recommandations contradictoires.
Lorsque la présentation physique des chutes et leur nettoyage préalable permettent une opération directe au four à induction sous vide, une gamme d'élaboration rapide assimilable par certains aspects à une fusion inerte conserve toute la qualité obtenue par l'élaboration d'origine. Ceci suppose que les précautions nécessaires à la conservation des chutes soient prises tout au long du cycle, depuis la fusion du métal jusqu'à l'usinage des pièces. De telles précautions sont à l'évidence coûteuses, mais l'enjeu est important devant le coût matière et énergétique des opérations de reconditionnement par pyrométallurgie.
Celles-ci offrent de plus larges possibilités de purification par affinage pneumatique et par échange métal-laitier, toutefois il est difficile d'agir simultanément sur tous les éléments à la fois pour les amener aux niveaux souhaités. D'autre part, les rendements matières sont moins favorables que dans le recyclage direct.

L'ensemble de ces mesures judicieusement combinées permet un taux de recyclage globalement élevé et à ce titre, on peut considérer, pour une part importante des alliages, que l'on a ainsi une source de matière première de qualité.

REFERENCES

1- CURWICK, PETERSEN, DE BARBADILLO - Superalloys Scrap - Generation and recycling - in Superalloys (1980) Seven Springs Conference, p. 21
2- WOULDS - Recycling of engine serviced superalloys, in Superalloys (1980), Seven springs Conference p. 31
3- PRIDGEON, DARMARA, HUNTINGTON, SUTTON - Principles and pratices of vacuum induction melting and vacuum remelting, in Metallurgical treatises TIEN, ELLIOT published by AIME (1981)
4- HONE, HOUOT, RIGAUD - on the minimum in the desoxidation equilibrium curve in liquid iron oxide Fe-O-M alloys Can. Met. Quart. 13,4 1974, p. 619
5- BARBURAO TARE, JANKE, FISCHER - Influence of Aluminum and Chromium on the activity of Oxygen in Nickel based Melts at 1600 °C, Met. Trans.9B, Sept. 1978, p. 399
6- BORSCH, TIEN, HOWSON - Progress in vacuum melting, Metal Progress, October 1982, p. 49
7- HOLT, WALLACE - Impurities and trace elements in Nickel base superalloys. International Metals Review, March 1976, p. 1-24
8- OLETTE - Elimination sous vide des oligoéléments - Mem. Scient. Rev. Metal. 1960, vol. 57, n° 6, p. 467.

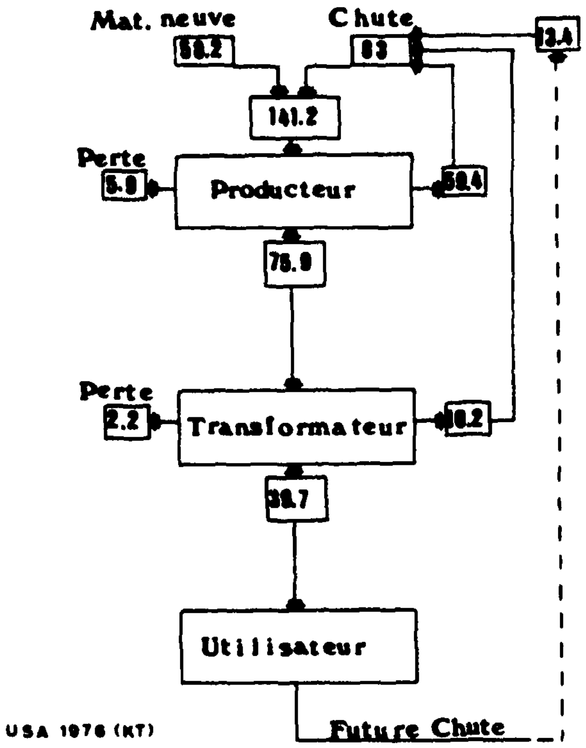


FIGURE 1 - Diagramme de la production des chutes et recyclage des superalliages aux USA 1976, en millier de tonnes (ref. 1)

Materials flow diagram for superalloy, 1976, USA in thousand metric tons (ref 1)

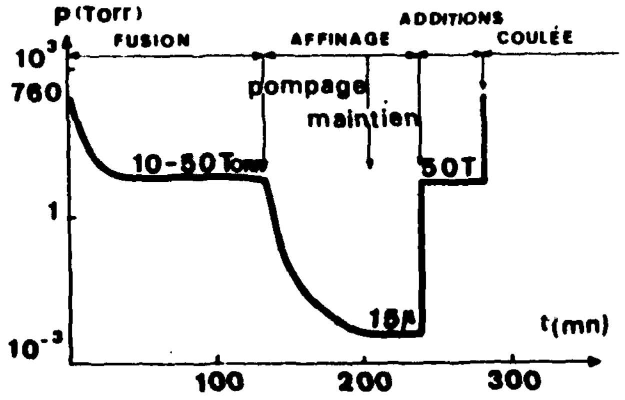


FIGURE 2 - Evolution de la pression en fonction du temps dans une élaboration au four à induction sous vide.

Pressure changes with time during a typical VIM heat.

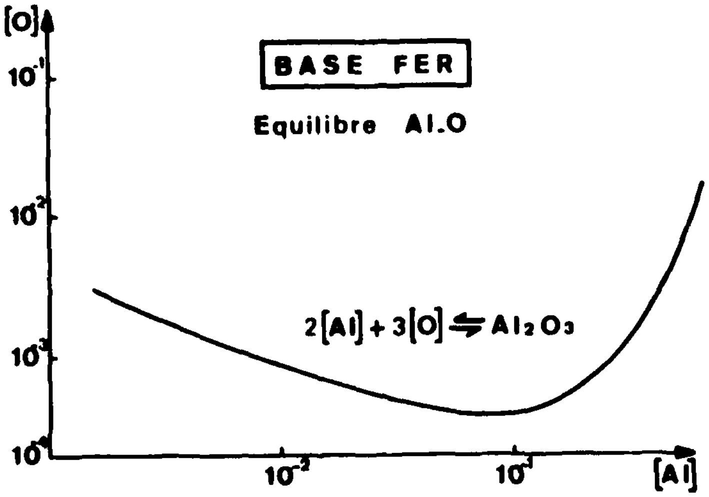


FIGURE 3 - Concentration en Oxygène en équilibre avec l'Aluminium dans un bain liquide Fe - Al

Oxygen in equilibrium with Aluminum in liquid Fe - Al alloy.

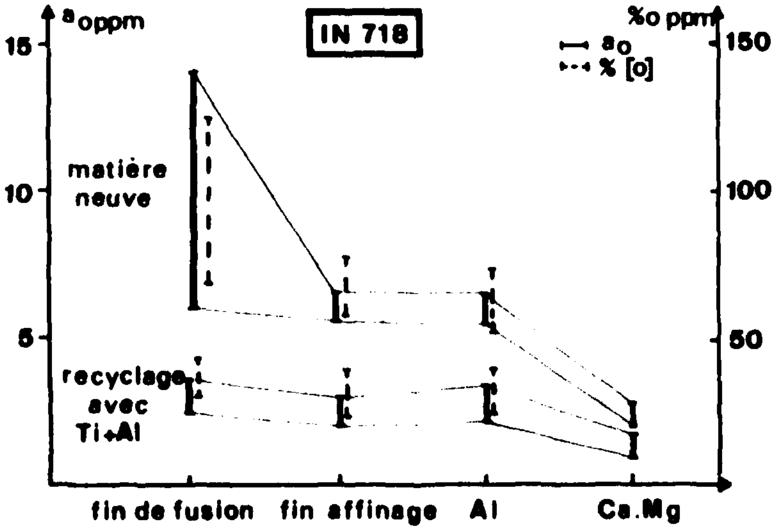


FIGURE 4 - Evolution de la concentration et de l'activité de l'Oxygène au cours de l'élaboration de l'alliage IN 718 au four à induction sous vide. Comparaison entre les charges en matière neuve et les charges avec Titane et Aluminium.

Oxygen activity and concentration during VIM of IN 718. Comparaison of the melting of revert and virgin materials.

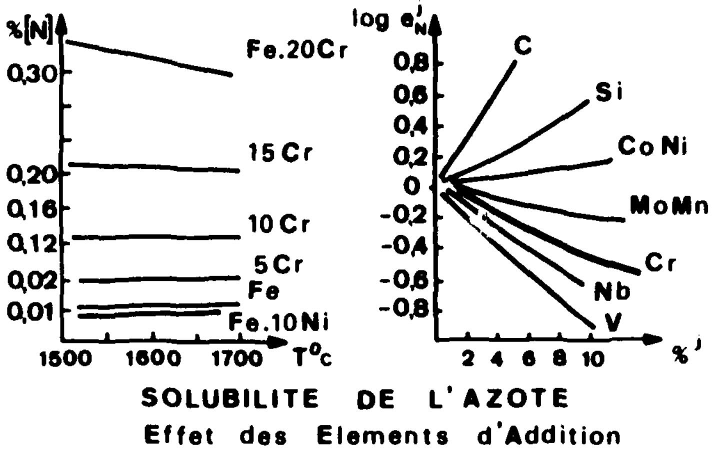


FIGURE 5 - Solubilité de l'Azote en fonction des éléments d'addition.

Nitrogen solubility as a function of alloying elements.

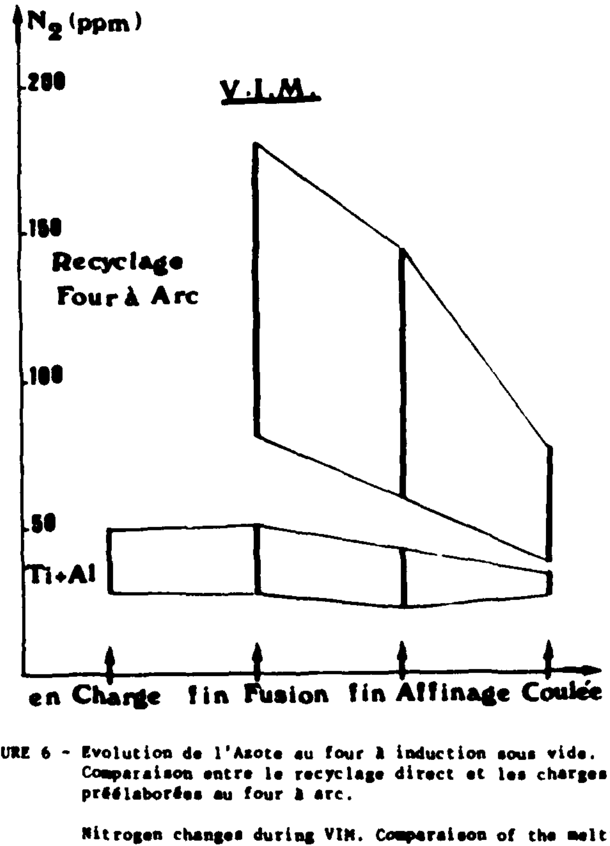


FIGURE 6 - Evolution de l'Azote au four à induction sous vide. Comparaison entre le recyclage direct et les charges préélaborées au four à arc.

Nitrogen changes during VIM. Comparaison of the melting of revert and Arc furnace pre-refined materials.

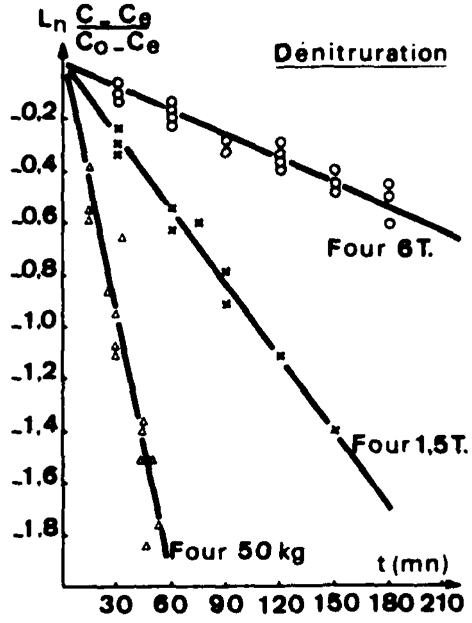


FIGURE 7 - Cinétique de dénitruration dans trois fours à induction sous vide 6 t, 1.5 t et 50 kg.

Nitrogen degassing kinetic in three different Vacuum Induction Furnaces 6 T, 1.5 T and 50 kg.

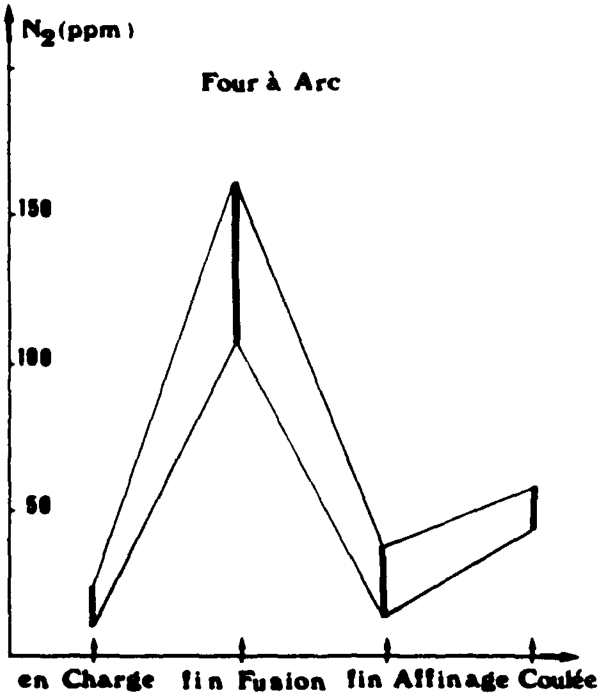


FIGURE 8 - Evolution de l'Azote au four à arc à l'air pendant la fusion de chutes.

Nitrogen changes during a melt of scraps in an Electric Arc Furnace.

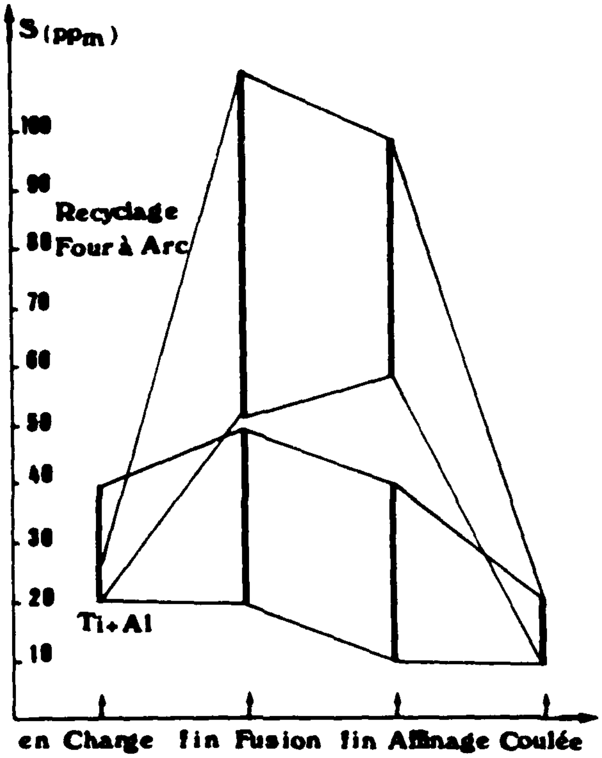


FIGURE 9 - Evolution du Soufre au four à induction sous vide. Comparaison entre le recyclage direct et les charges préélaborées au four à arc.

Sulfur changes during VIM. Comparaison between revert and Arc furnace pre-melted materials.

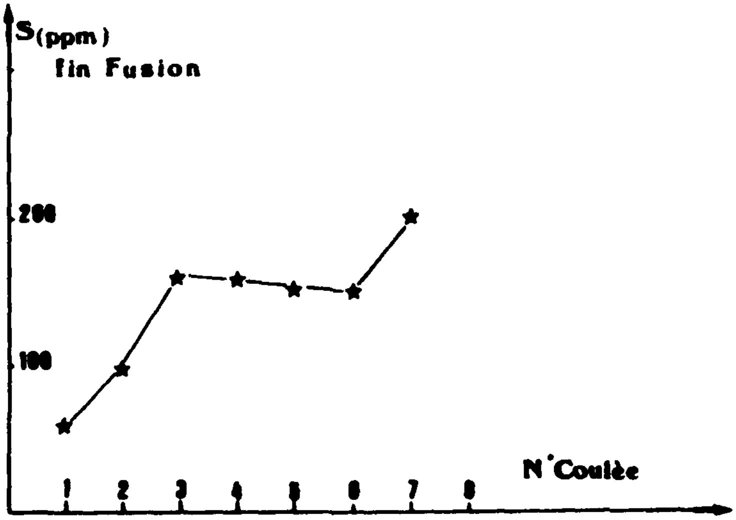


FIGURE 10 - Evolution du Soufre en fin de fusion au four à induction sous vide en fonction de l'ordre de coulée. Effet résiduel du traitement par des alcalinoterreux.

Evolution of the Sulfur content after melting as a function of melt number. Residual effect of Ca, Mg treatment.

	Massif	Léger	Perte	Total
Producteur	85	11	4	100
Transformateur	35	58	6	100
Total	68	27	5	100

TABLEAU 1 - Répartition des différents types de chutes générées en 1976 aux USA (en pourcentage).

Form and quantity of scrap generated in the USA in 1976 (in %).

	Fin Fusion	Addition	Coulée
Refusion	122	100	56
Chute Ti+Al	36	36	31

TABLEAU 2 - Evolution de la teneur en azote en ppm au cours de l'élaboration au four à induction sous vide - Alliage ATGW2A, moyenne de 10 coulées.

Nitrogen changes during VIM - Alloy type U 500 · Average value of ten melts.

Four kg	6000	1500	50
Ø cm	90	64	20
$S/V\ 10^3\ cm^{-1}$	6.8	22	70
$K \frac{S}{V} 10^5$	5	15	55
$K\ 10^3$	4	5	8
$\frac{dN}{dt}$ ppm/h	10	20	200

TABLEAU 3 - Comparaison des cinétiques de dénitruration dans trois fours à induction sous vide : 6 t, 1.5 t, 50 kg.

Comparaison of Nitrogen degassing kinetic in three different vacuum induction furnaces : 6 t, 1.5 t, 50 kg.

ANALYSE TYPIQUE IN 718

C	Mn	Si	S	P	Cr	Fe	Co	Mo	Nb	Ti
0.044	0.15	0.17	0.002	0.002	17.97	18.58	0.02	2.92	4.82	0.92

ANALYSE TYPIQUE IN 718

Al	B	Cu	Ni	Ca	Mg	Bi	Tl	Te	Pb	Ag
0.61	0.0060	0.0014	53.59	0.00017	0.0002	0.00002	0.00001	0.000075	0.0002	0.0002

ANALYSE TYPIQUE IN 718

Se	Sn	Zn	Rb	Pd	Li	As	Ga	F	Na	Sc
0.000025	0.0055	0.0013	0.0015	0.00013	0.0004	0.0025	0.0017	0.00003	0.0015	0.000012

TABLEAU 4 - Analyse typique de l'alliage IN 718
Typical analysis of a 718 Alloy

PROBLEMES POSES AUX MOTORISTES
PAR LE RECYCLAGE DES MATERIAUX METALLIQUES

Y.HONNORAT - J.NOUAILLES

Société Nationale d'Etude et de Construction
de Moteurs d'Aviation
2, Bld Victor
75724 PARIS CEDEX 15
FRANCE

RESUME

La fabrication des pièces principales de moteurs aéronautiques implique une garantie sur leur valeur d'usage qui n'est pas toujours complètement vérifiable par contrôle non destructif. Or, les rendements de fabrication sont souvent très faibles et le coût des pièces est très influencé par les économies de matière : le motoriste doit donc recycler les chutes de fabrication et ceci est d'autant plus rentable que le circuit de recyclage est plus court. Ce recyclage est susceptible de générer des problèmes de qualité vis à vis desquels il faut se prémunir.

Des exemples relatifs à la mise en oeuvre d'alliages de titane corroyés et de superalliages de nickel pour moulage en cire perdue illustrent les mécanismes par lesquels le recyclage des chutes est susceptible d'influer sur la qualité des pièces. Le rôle respectif des différents partenaires que sont l'aciériste, le fabricant de pièces brutes, le motoriste et le recycleur est mis en évidence. Les moyens que les techniques de contrôle de recette procurent au motoriste pour maitriser le problème sont explicités.

oOo-

La plupart des matériaux métalliques mis en oeuvre dans les turbines à gaz aéronautiques font l'objet, depuis l'origine de cette industrie, d'une production à partir de charges sélectionnées pour ce type d'application, dans des fours conçus à cet effet, chez des élaborateurs spécialisés.Ceci est particulièrement vrai pour les alliages à hautes caractéristiques à base de nickel ou de titane qui sont utilisés pour les pièces les plus sollicitées. Compte tenu de la rareté et des problèmes d'approvisionnement que posent certains métaux qui sont des constituants essentiels de ces alliages, et du relatif isolement des chaines d'élaboration et de transformation de ceux-ci dans l'ensemble de l'industrie métallurgique,le problème de la réutilisation des chutes s'est immédiatement posé.Or la présence simultanée de métaux difficilement séparables, dans ces alliages souvent utilisés presque exclusivement dans la construction des moteurs, rend très difficile la valorisation de leurs chutes dans d'autres classes d'alliages de la métallurgie spéciale. Il est donc vite apparu que les solutions qui puissent être satisfaisantes tant du point de vue économique que du point de vue technique, devraient être recherchées à l'intérieur du cadre de la métallurgie aéronautique.

NATURE DU PROBLEME POSE AU MOTORISTE ET DES ENJEUX

Le problème est d'autant plus aigu que, compte tenu de la complexité croissante de la forme des pièces, les rendements de production entre la pièce finie et le matériau produit par l'aciériste sont souvent faibles. Ainsi, il n'est pas rare de mesurer dans le cas de moteurs modernes, des rendements de mise en oeuvre de 15% pour des aubes de turbine coulées en fonderie de cire perdue, ou de 10% pour des disques de compresseur ou de turbine forgés en matrices fermées. Pour obtenir les rendements globaux de fabrication entre la pièce montée sur moteur et la charge d'enfournement de l'aciériste, ces proportions sont à multiplier par les rendements d'élaboration du matériau qui sont respectivement de l'ordre de 87% et de 55%.

On peut donc aisément calculer, sur la base de ces chiffres, que la fabrication d'un kilogramme d'aube de turbine génère 6.7 kg de chutes : la fabrication d'un kilogramme de disque génère 17.2 kg de chutes. (Curieusement les résultats de calcul de ce dernier chiffre sont très voisins, qu'il s'agisse de superalliages à base de nickel ou de superalliages à base de titane). L'incitation économique au recyclage des chutes est donc très forte. A titre d'exemple,on gagne 1% sur le coût de production d'un moteur civil comme le CFM.56 en abaissant de 10% le coût de fabrication des disques, et ceci peut être obtenu en gagnant 25% sur le coût de la matière mise en oeuvre. Dans le cas de l'alliage de titane TA6V PQ élaboré par triple fusion sous vide, utilisé pour les disques de compresseur basse pression, ce gain sur la matière peut être obtenu en remplaçant une charge de matière neuve par une charge mixte de 55% d'éponge et 45% de copeaux recyclés. De la même façon, on calcule que, malgré des fluctuations très fortes du prix des jets moulés en superalliage de nickel IN 100 élaborés à partir de matière neuve (les prix ont varié dans une proportion de 1 à 2 depuis deux ans), l'économie réalisée par le fondeur qui utilise des jets moulés élaborés à partir d'une charge mixte comprenant 50% de chutes de fonderie et 50% de matières neuves est constamment resté à l'intérieur d'une fourchette de 37 à 44% du prix de base. On peut ensuite remarquer que, puisque des techniques d'élaboration et de mise en oeuvre différentes président à la fabrication de ces deux catégories de pièces, la répartition des poids de chute en fonction de leur nature (chutes massives, copeaux, meulures, perte au feu, etc...) et l'endroit où elles sont créées (Aciérie, forge ou fonderie, atelier d'usinage, etc..) sont variables d'un cas à un autre.

La conception et la fabrication des moteurs étant gouvernées par des règlements très stricts destinés à garantir la sécurité des passagers d'avions et la fiabilité des machines, l'attitude des constructeurs vis à vis du problème de recyclage des chutes a été longtemps très conservatrice. En effet, le dessin de la plupart des pièces de moteur étant fondé sur le principe "Safe Life", par définition, la durée de vie des machines doit être garantie en tenant compte des endommagements naturels ou accidentels des pièces, et donc, pour les disques,de la capacité des matériaux à garder l'intégrité de leurs caractéristiques pendant toute la durée de leur utilisation; ou pour les aubes de la capacité des carters à retenir les débris des pièces rompues en service.

Or, s'il est facile de mettre en évidence les variations dans le comportement et l'endommagement des matériaux sous l'effet de la réintroduction des chutes dans leur cycle de fabrication, jusqu'à il y a dix ans, les facteurs influents de cette dispersion n'avaient pas pu être suffisamment cernés.

LES PARTENAIRES ET LES METHODES DU PROGRES

Des raisons de deux ordres peuvent être invoquées pour expliquer cela :

- une connaissance insuffisante des conditions de fonctionnement des outils d'élaboration,
- une méconnaissance des lois d'endommagement des matériaux, en particulier sous l'effet conjugué des différents types de sollicitations auxquelles les pièces peuvent être soumises en service.

Ce n'est que par des progrès parallèles dans ces deux domaines que l'on peut depuis quelques années s'affranchir peu à peu du principe selon lequel les matériaux doivent être élaborés à partir de matières neuves les plus pures possibles, et mis en oeuvre dans des pièces dessinées avec des coefficients de sécurité élevés pour se prémunir contre des mécanismes d'endommagement non modélisés. Les aciéristes ont effectué un travail considérable d'étude et de modélisation des processus d'affinage et d'évolution des inclusions dans les fours d'élaboration et de refusion. En même temps, les outils ont été diversifiés et dotés de moyens de plus en plus sophistiqués pour mettre sous contrôle leur fonctionnement. C'est sur ces bases que reposent les premières publications proposant des méthodes de recyclage des superalliages, et parmi celles qui ont permis de faire avancer le problème de façon significative, on peut citer la publication de CREMISIO en 1977 (1) qui fait une revue critique des techniques disponibles pour le traitement des chutes, et celle de WOULDS en 1980 (2), qui le premier, a donné des résultats d'essais industriels d'affinage de superalliages de fonderie en cire perdue.

De leur côté, les motoristes ont effectué des progrès sensibles dans l'identification des modes de sollicitations endommageants et de leurs effets séparés et combinés, les principaux étant la fatigue, le fluage et l'agression de l'atmosphère au contact de la pièce en service. Ces progrès reposent tout d'abord sur une large utilisation des théories de la mécanique de la rupture, qui a permis de quantifier la tenue à la propagation des fissures et la nocivité des petits défauts de qualité des matériaux. On a ainsi pu mettre en évidence le rôle de certaines impuretés nocives ou de certaines additions bénéfiques sur la vitesse de propagation des criques, et déterminer quantitativement le rôle néfaste des inclusions dans la tenue à l'amorçage des fissures. HERMAN et SENECHAL, dans une publication récente (3), ont analysé en détail les progrès réalisés à ce sujet dans la conception et la fabrication des disques de turbomachines.

Mais au delà des travaux de base effectués par l'aciériste et le constructeur, le recyclage des chutes requiert la participation active de recycleurs spécialisés qui regroupent et conditionnent les chutes dans des installations construites à cet effet, et selon des procédés spécifiques et des gammes figées. L'importance du rôle de ce partenaire intermédiaire découle de l'application nécessaire du système d'assurance de la qualité au recyclage des chutes, et depuis quatre ans plusieurs sociétés se sont développées tant en Europe qu'aux USA pour répondre à la demande de l'industrie des moteurs aéronautiques.

Par ailleurs, des travaux importants ont été effectués et se poursuivent pour la mise au point de méthodes de contrôle non destructif (4) et, d'analyse élémentaire (5-6) plus performantes ainsi que pour perfectionner les méthodes d'évaluation du comportement des matériaux au cours de leur mise en oeuvre. En particulier, en fonderie de précision, les travaux de l'ECOLE DES MINES de PARIS en concertation avec la SNECMA (7-8) sur la solidification des superalliages ont débouché sur des progrès importants dans le choix des qualités d'alliage difficiles à couler.

Afin de préciser la nature des difficultés à surmonter, des solutions adoptées et des résultats obtenus, nous allons passer en revue successivement des exemples d'application de la démarche décrite ci-dessus à deux catégories différentes de matériaux : les alliages de titane corroyés et les alliages de nickel pour moulage en cire perdue.

LE RECYCLAGE DES ALLIAGES DE TITANE CORROYES

Vis à vis du recyclage des chutes, les alliages de titane se distinguent des autres alliages utilisés dans les moteurs par le fait que leur cycle de fabrication ne comprend pas d'étape d'élaboration en masse à l'état liquide, et que l'on ne procède que par fusion et solidification locales et progressives. De ce fait la dilution des impuretés, et la séparation ou la réduction des inclusions ne peuvent se faire aussi complètement que pour les alliages des métaux ferreux.

Parmi les inclusions exogènes les plus nocives susceptibles de se trouver dans les alliages de titane figurent les carbures très difficilement solubles comme WC (cf figure 1).
De telles inclusions proviennent généralement de débris d'outils. Pour se prémunir contre les pollutions accidentelles de ce type, est tout d'abord nécessaire pour le motoriste d'établir un classement par catégories des chutes récupérables, tout en exigeant que les chutes recyclées proviennent exclusivement de de produits de qualité aéronautique, qu'elles soient triées par nuance et rassemblées en lots homogènes.

La SNECMA, dans son document DMR 24 qui définit les conditions de réception des billettes et barres en alliage de titane, a inséré une grille de classification des chutes qui distingue quatre catégories :

- les chutes massives dont la traçabilité est assurée et qui proviennent des fabrications de l'aciériste qui les recycle,
- les chutes massives, sans traçabilité, qui doivent être contrôlées unitairement,
- les chutes légères (poids < 500 g) sans traçabilité, contrôlées par prélèvement,
- les copeaux lotis avec un contrôle de la nuance sur un échantillon représentatif.

Dans chacune de ces catégories sont distinguées les chutes usinées avec des outils en carbure,qui nécessitent un tri et un contrôle particulièrement soignés de celles usinées avec des outils en acier rapide, pour lesquelles l'expérience a montré que les risques de persistance d'inclusions nocives au cours des refusions successives étaient négligeables. Les chutes massives ne doivent pas présenter à leur surface de traces d'insertion accidentelle de morceaux d'outils. Les contrôles les plus rigoureux sont exigés sur les copeaux dont le plus grand état de division accroit les risques de pollution. Certains recycleurs ont mis récemment au point des chaines de conditionnement spécialisées dans le traitement des copeaux de titane, qui combinent des méthodes de tri fondées sur plusieurs particularités physiques des matériaux à réparer (densité, magnétisme, opacité aux rayonnements etc...) et un contrôle final à 100% par radiographie X. Ces chaines de tri ont considérablement diminué le risque d'inclusions exogènes dans les lingots, et les plus petites particules de carbures triées avec une quasi-certitude par de telles installations ont un diamètre qui s'échelonne selon les cas de 0.20 à 0.60 mm., et qui en moyenne est de 0.40 mm.

Compte tenu des niveaux de sollicitations des pièces, qui sont en particulier en fatigue oligocyclique, de l'ordre de 500 MPa, les facteurs d'intensité de contrainte correspondant aux défauts les plus nocifs de cette taille de 0.40 mm sont de l'ordre de $K = 10\ \mathrm{MPa}\sqrt{m}$. Dans ces conditions, les vitesses de fissuration en fatigue restent très faibles, soit environ 10^{-5} mm/cycle, et les inclusions de cette taille ne sont pas susceptibles de réduire sensiblement la durée de vie escomptée des pièces.
Cependant le forgeron n'a pas toujours en l'état actuel des techniques de contrôle disponibles en atelier, la possibilité de vérifier la propreté inclusionnaire des produits livrés par l'aciériste à un niveau de résolution équivalent. C'est ainsi qu'à la SNECMA les billettes meulées sont contrôlées par ultra-sons avec une fréquence de 5 MHZ. Avec le niveau de sensibilité courant B 40, la taille du plus petit défaut détectable sans tenir compte des atténuations liées aux facteurs d'impédance et de forme de l'inclusion, est de 0.85 mm (diamètre du trou à fond plat équivalent). Avec le niveau A 20, à la limite des impositions possibles sur ce type de produit, cette dimension se réduit à 0.60 mm. Sur des barres à aubes où la structure est plus perméable aux ultrasons, on peut atteindre un seuil de 0.35 mm en contrôle US par immersion.

En résumé, on peut donc estimer que, dans le cas qui nous préoccupe, les résultats atteints par les recycleurs sont cohérents avec les exigences actuelles des constructeurs de moteurs. Cependant, les possibilités de contrôle des demi-produits se révèlent insuffisantes et il faut procéder ensuite à des contrôles plus onéreux (radio à haute sensibilité en particulier) sur pièce pour garantir leur durée de vie. Ainsi la réduction de coût de la matière est en partie consommée par l'augmentation du coût des contrôles.

En dehors des inclusions dures de carbure, de nombreux autres types de contamination sont susceptibles d'accompagner le recyclage des chutes de titane, tels que des oxydes, des débris d'électrodes de soudage, ou des morceaux ou copeaux de métaux réfractaires. La figure 2 montre un cas de pollution de TA 6 Zr 5D (type IMI 685) par de tantale qui tire son origine d'un mélange de chutes.Il est remarquable de constater que, bien que l'inclusion puisse être moins dure que l'alliage qui la contient, elle entraine des déchirures en forge (figure 3). Ceci s'explique sans doute par le fait que la plastification d'une telle inclusion au cours du forgeage ne s'accompagne pas de sa recristallisation, la température de corroyage de l'alliage de titane étant trop basse. On comprend donc que le recyclage des chutes de titane pose des problèmes multiples qui relèvent de cas d'espèce très variés, et nécessite d'accumuler un volume suffisant d'expérience industrielle chez les différents partenaires avant de pouvoir prononcer l'agrément de nouvelles filières de recyclage.

LE RECYCLAGE DES SUPERALLIAGES DE NICKEL EN FONDERIE DE PRECISION

Pour ces matériaux qui participent d'un autre mode d'élaboration et d'une autre technique de mise en oeuvre, les origines des contaminations sont différentes et leurs manifestations éventuelles lors du recyclage des chutes se situent à une échelle de taille inférieure dans la structure.
Plus de 90% des chutes générées lors de la mise en oeuvre des jets moulés livrés par l'aciériste au fondeur se retrouvent sous la forme massive des alimentations de coulée. La figure 4 montre un exemple de telles chutes après tronçonnage des aubes coulées en NK 15 CADT (type RENE 77). On distingue immédiatement sur cette chute les premières causes de contamination que sont les réfractaires de coulée et la zone de retassure, où le métal reste liquide suffisamment longtemps pour qu'il soit difficile d'éviter les réactions avec l'atmosphère lors de l'ouverture du four de coulée. La figure 5 illustre des cas de réaction entre céramiques de fonderie et métal, et permet de comprendre que les nettoyages par grenaille ou attaque chimique qui sont systématiquement pratiqués par le recycleur puissent ne pas être toujours parfaitement efficaces. Cependant, les techniques de filtration à la coulée de jets qui se sont répandues depuis deux ans chez tous les aciéristes (9-10) résolvent semble-t'il convenablement le problème de la propreté inclusionnaire.

Par contre, les autres types de pollution, plus difficiles à combattre, ont conduit depuis longtemps à distinguer différentes classes de coulées-mères selon la constitution de la charge et à réserver leur utilisation chez le fondeur en fonction de la pièce à couler, plus ou moins sensible aux contaminants. On définit ainsi pour les alliages élaborés sous vide

- la classe A, élaborée à partir de matières neuves, où l'aciériste peut introduire une proportion de 12% de ses propres chutes,

- la classe B, dont la charge comprend de 40 à 60% de chutes de l'aciériste et du fondeur client,

- la classe C dont la charge est constituée à 100% de chutes de l'aciériste et du fondeur client.

L'expérience montre que la qualité du métal recyclé ne dépend pas seulement du soin apporté au tri et au nettoyage des chutes. C'est ainsi que pour une pièce donnée on constate des différences systématiques de caractéristiques lorsque l'on change la classe d'élaboration. La figure 6 montre, à titre d'exemple, l'abattement de la durée de vie en fatigue vibratoire d'aubes en NK 15 CADT (type RENE 77) constaté en coulant ces pièces avec un alliage de classe B au lieu de la classe A. En général, les chutes de caractéristiques s'accompagnent de modifications microstructurales mineures affectant principalement les espaces interdendritiques, qui sont donc à relier aux dernières étapes de la solidification (7-8).

Le contrôle radiographique par rayons X, effectué systématiquement sur les aubes coulées en fonderie de précision, permet, avec les améliorations obtenues récemment en utilisant des tubes à foyer fin et des écrans renforçateurs de contraste, de distinguer de petites variations du taux de porosité interdendritique auquel les propriétés mécaniques sont très sensibles. Sur la base de ce contrôle, la fonderie de la SNECMA classe systématiquement les lots d'alliages, et l'analyse statistique des résultats met en évidence les éléments en trace les plus nocifs: et les traces d'éléments carburigènes Hf et Nb, mais surtout l'azote, sont apparus comme les premiers responsables.

La figure 7 montre une différence sensible des teneurs en azote entre les approvisionnements des classes A et B du même alliage NK 15 CADT. L'analyse répétée de la distribution de cet élément par un de nos fournisseurs principaux (10) au cours du tri de descendants de coulée analogues à ceux de la figure 4, met en évidence des variations significatives 8 à 35 ppm selon le point de prélèvement,et la possibilité de séparer par tronçonnage les zones les plus polluées afin de différencier les procédures de recyclage et tenter de réduire cet écart.

Ceci est un exemple des améliorations successives apportées par l'aciériste à la teneur résiduelle en azote. D'autres travaux portant sur les procédures d'affinage au four à induction sous vide s'y sont ajoutés pour obtenir des résultats du type de ceux illustrés aux figures 8 et 9, où l'histogramme des teneurs en azote après ces améliorations apparaît décalé de façon significative vers des teneurs plus faibles dans le NK 15CATu (type IN 100).

Pour affiner le classement radiographique du taux de porosité à la coulée, le laboratoire de la SNECMA a mis au point une expérience de coulée en source au four à induction sous vide d'éprouvettes de microporosité. Une grappe de quatre éprouvettes cylindriques de diamètre 13 mm et longueur 100mm est coulée en source dans des conditions thermiques reproductibles et contrôlées. Une plaquette de 2mm d'épaisseur est ensuite prélevée par un découpage parallèle à l'axe des éprouvettes aux fins de caractérisation.

La mesure en micrographie optique des taux de porosité a permis d'étalonner les clichés de radiographie X par comparaison aux clichés-types de la norme ASTM et d'établir le tableau de correspondance de la figure 10. La validité de cet essai de microporosité a été établie par la caractérisation de lots matière utilisés en fonderie. C'est ainsi que l'on a obtenu, avec le NK 15 CATu par rapport à un lot de classe A de référence conduisant à un cliché ASTM 1, les résultats suivants avec des lots de classe B se différenciant par des traces de polluants :

- avec + 500 ppm de Hf un cliché ASTM 3
- avec + 200 ppm de Nb un cliché ASTM 4
- avec + 20 ppm de N un cliché ASTM 4

Ces résultats recoupent parfaitement l'expérience de l'atelier de fonderie. Ils ont conduit à adopter cet essai de microporosité pour la caractérisation de lots industriels. Le même essai permet de relier, de façon plus précise qu'à partir des dissections de pièce, les caractéristiques mécaniques à la distribution de la porosité et la figure 11 montre un exemple d'une telle corrélation établie par des essais de fluage à partir d'éprouvettes découpées dans les plaques prélevées pour la radiographie.

Un autre cas d'analyse structurale quantitative, utilisé pour le classement des lots de NK 15 CDAT est illustré à la figure 12 qui montre la fréquence cumulée des carbures en fonction de leur taille mesurée sur coupe polie au grossissement x 1500 à l'aide d'un analyseur d'image automatique. Ce type de mesure, effectué sur un grand nombre d'échantillons permet de rendre compte de façon plus fine des différences entre lots du type de celles illustrées à la figure 6. La conjugaison de telles études structurales avec des analyses thermiques différentielles conduit à identifier quantitativement les facteurs de contamination au recyclage des chutes à adapter en conséquence les spécifications et à réduire les causes de rebut en atelier.

CONCLUSION

Le recyclage des matériaux métalliques utilisés dans la construction des moteurs aéronautiques implique une collaboration étroite entre les différents partenaires que sont l'aciériste, le recycleur, le fondeur ou le forgeron et le constructeur de moteurs.

L'enjeu économique est important, mais les gains sur les quantités de matières neuves mises en oeuvre ne peuvent être obtenus que sur la base d'un système complet d'Assurance de la Qualité impliquant des documents spécifiquement aménagés, de procédures de tri et des procédés de recyclage bien établis avec des gammes figées, ainsi que des méthodes de contrôle adaptées. Il importe ensuite de vérifier par des audits périodiques la conformité des pratiques à ce système.
Le motoriste doit orchestrer les actions de ses fournisseurs et ne mettre ou faire mettre en oeuvre que celles dont l'inocuité sur la qualité des pièces a été démontrée par des dissections ou des essais partiels. Dans cette démarche, l'analyse structurale quantitative s'avère être un moyen particulièrement efficace, en ce qu'il permet d'identifier avec précision les facteurs influençant la valeur d'usage des pièces lesquels l'aciériste peut avoir prise, comme la propreté inclusionnaire ou les traces d'éléments résiduels.

REFERENCES

(1) - R.S.CREMISIO , L.M.WASSERMAN - Superalloy scrap processing and trace elements considerations. Vacuum Met. Conf. June 1977 - Krutenale Ed. Science Press - Publ. p. 353.

(2) - M.J.WOULDS - Recycling of engine service superalloys - Seven Springs 3rd Intern. Superalloys Conference, Sept. 1980 - J.K.TIEN ed. - ASM Publ. p. 31 -

(3) - C.HERMAN - P.SENECHAL - Tenue à l'endommagement par fatigue et fluage des disques de turbomachines en superalliages - 10ème colloque Aciers et Alliages Spéciaux dans l'Aéronautique - Le Bourget, Juin 1983 -

(4) - C.DEBONS, Y.HONNORAT, R.SCODELLARO, G.SANDIS - Contrôle non destructif des disques de turbine Détermination des conditions de limites de détection - Rapport SNECMA, Oct. 81-
Contrat DRET 7734558 -

(5) - Y.HONNORAT - P.BLANCHARD - Adaptation des méthodes de fabrication et de contrôle des demi-produits aux exigences de qualité de l'Aéronautique - 8ème Colloque Aciers et Alliages Spéciaux dans l'Aéronautique - Le Bourget, Juin 1979 - Revue Aciers Spéciaux n° 48,p.23 -

(6) - J. GAITTET - Contrôle de traces d'oligo-éléments par fluorescence X - 25ème Colloque de Métallurgie - Juin 1982 - Publ. INSTN, p. 217 -

(7) - E. BACHELET, G.LESOULT - *Quality of castings of superalloys* - 1st *Conference* High Temperature Alloys for Gas Turbines, Liège Sept. 1978 -R. BRUNETAUD, Ed. REIDEL Publ. p.665 -

(8) - L. OUICHOU, F.LAVAUD, G. LESOULT - Influence of the composition of nickel base superalloys on their solidification behaviour and foundry performance Seven Springs 3rd Intern. Superalloys Conference, Sept. 80 - J.K. TIEN ed. - ASM Pub. p. 235 -

(9) - J.R.MIHALISIN - Conservation of materials at the HOWMET Turbine Components Corporation Alloy Division TMS paper selection F.81-4 - Met. Soc. AIME Pub.

(10) - *W.HOLLAND - SPECIAL METALS Corp.* - Communication privée.

Figure 1

Figure 2

Figure 3

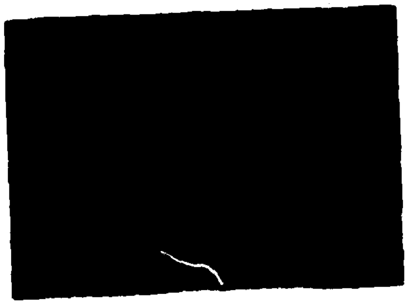


Figure 4

Figure 5

Figure 6

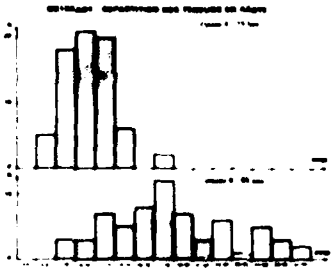


Figure 7

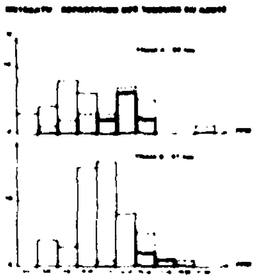


Figure 8

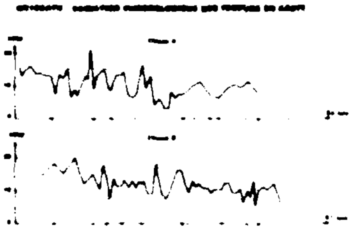
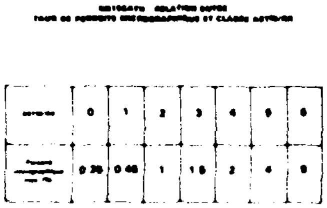


Figure 9



[illegible]	0	1	2	3	4	5	6
[illegible]	0.30	0.40	1	1.5	2	4	9

Figure 10

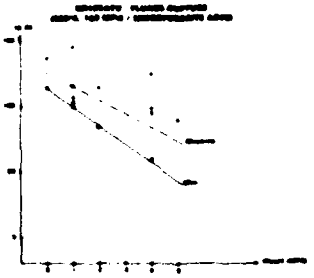


Figure 11

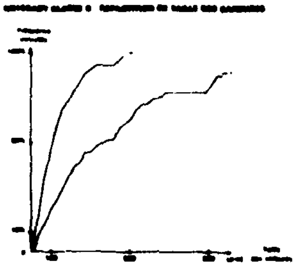


Figure 12

COATING DEVELOPMENTS TO RESTRICT STRATEGIC MATERIALS USAGE

R. J. Hecht and D. S. Halfpap

Pratt and Whitney Aircraft Group
Government Products Division
P. O. Box 2691
West Palm Beach, Florida 33402
U. S. A.

AD-P004 226

ABSTRACT

Hot section gas turbine engine components have relied on the use of superalloys which contain high percentages of strategic elements to attain an optimum compromise of high temperature strength, corrosion and oxidation resistance. Due to limited availability and price fluctuations of certain key alloying elements, such as cobalt and tantalum, selection and substitution of superalloys with lower strategic element content is being accomplished. The change in alloy often leads to the use of materials with less corrosion and oxidation resistance. This paper describes the development of protective coatings that have enabled the implementation of less environmentally stable alloys with no loss, and sometimes an increase, in component capability and life. Development of tailored MCrAlY overlay coatings, improved diffusion aluminides, thermal barriers, and alternate wear resistant coatings has enabled the coating corrosion and oxidation life to be more independent of the base superalloy composition and hence allow more latitude in alloy selection. The resulting coating developments and their effects on reducing strategic element use are presented.

INTRODUCTION

The limited availability of strategic elements that occurred starting in 1977, and the resulting price escalations, led to an increased awareness of the dependence upon key elements such as Co, Cr, Ni, Ta, Ti and Cb used in the manufacture of gas turbine engines. This situation led to the initiation of programs at Pratt and Whitney Aircraft to reduce the useage of these "strategic or critical" elements through the following efforts.

- Substitution and/or development of less strategic element containing alloys and composites.
- Reduction in the input material requirements in component manufacture.
- Repair and restoration of worn or damaged parts for extended service.
- Initiation of new engine design to reduce part count and/or extend component durability.
- Extension of component life through improved non-destructive evaluation (NDE) and retirement for cause (RFC) criteria.
- Substitution and/or development of metallic and ceramic protective coatings, that are not only lower in strategic material content, but also allow use of existing or new "strategic element lean" alloys.

The results of this initiative for the first five items have been previously described by Allen, Halfpap and Siegel.* This paper describes the work in coating development, processing and implementation that has and will continue to impact the reduction of strategic elements in Pratt and Whitney Aircraft engines.

COATING DEVELOPMENTS

Historically the major use of protective coatings or surface treatments has been to reduce the oxidation and/or hot corrosion (sulfidation) distress of hot section components in the combustor, turbine and afterburner (augmentor) and exhaust nozzle sections of the gas turbine engine. Of the strategic or critical elements used in an engine today, see Table I, the two most important elements impacting hot section coating usage are Co and Cr. These elements along with Ni are the backbone of the high temperature superalloys. The composition of typical Co and Ni base superalloys is given in Tables II and III. The chromium with aluminum and/or minor additions of refractory elements give these alloys their oxidation and corrosion resistance. The emphasis of coating developments has been to enrich the part surface, such that increased oxidation (temperature capability) and corrosion resistance is obtained. Hence, the thrust of coating efforts to reduce strategic element usage in the hot section has been focused at allowing the substitution of nickel base alloys for cobalt base alloys, use of lower cobalt containing coatings, and extending component durability to reduce scrappage and spare part inventory requirements. Four major coating developments have been responsible for meeting these objectives:

* Presented this Conference.

1) Development of the MCrAlY overlay class of coatings

2) Use of Pt modified diffusion aluminide coatings

3) Development and use of insulative "thermal barrier" ceramic coatings

4) Application of optimum wear resistant coatings

The greatest single contribution by Pratt & Whitney Aircraft to reduce strategic element dependence was the revolutionary development of the MCrAlY (M = Fe, Co, Ni) class of overlay coatings. These overlay coatings, applied by electron beam vapor deposition, plasma spray and sputtering techniques allow the coating composition to be designed independent of the substrate alloy, and to be optimized for the best compromise of oxidation resistance, corrosion resistance and mechanical properties, Figures 1 and 2. The development of MCrAlY overlay coatings has led to the availability of a family of coatings that provide 2-10 times the oxidation-corrosion resistance that of state-of-the-art diffusion aluminide coatings. Early developments led to a CoCrAlY (67% Co) series of coatings that still today are the most corrosion resistant coatings available in the gas turbine industry. These coatings have provided over a three-fold increase in corrosion life of 1st stage blades, see Figure 3, and allowed for the first time, substitution of higher strength nickel base superalloy vanes for cobalt base aluminide coated vanes in advanced Air Force engines. This sutstitution reduced Co usage by over 36 kg. (80 lb.) per engine.

To meet the demand for higher temperature capability, the NiCoCrAlY class of coatings was developed. The coatings offer higher ductility, and approximately the equivalent hot corrosion resistance to that obtained with CoCrAlY, while having approximately 45 percent by weight less cobalt. The NiCoCrAlY coatings (23% Co), now replacing CoCrAlY, reduced cobalt usage while still maintaining or increasing airfoil durability. Savings of 4,600-9,000 kg. (10,000-20,000 lb.) of cobalt are projected by this substitution. The largest benefit brought about by the NiCoCrAlY class of overlay coatings was the availability of higher temperature capability coatings that could be formulated independent of the substrate alloy, and optimized for the engine mission and environment. These coatings, when combined with less corrosion-oxidation resistant alloys lean in strategic elements, create an alloy/coating system that has no net loss in capability. With the use of advanced NiCoCrAlY coatings on newly developed essentially Co, Cr free nickel base superalloys, corrosion resistance commensurate with that of conventional nickel base superalloys has been achieved, see Figure 4.

With the cobalt shortage in 1978, the cost of CoCrAlY coatings approximately doubled in price; attention was focused on developing cobalt lean coatings. In applications where oxidation resistance was needed (over corrosion resistance) NiCoCrAlY coatings were substituted. Where corrosion resistance and not temperature capability (i.e., oxidation resistance) was life limiting, Pt modified diffusion aluminide coatings were substituted for the CoCrAlY overlay coatings. Although not giving the corrosion protection of CoCrAlY, these Pt aluminides did provide corrosion/oxidation protection to meet the needs of in-service engines, Figure 4. Although Pt is also considered a strategic element, its use in these coatings is low, approximately 0.01 gm/cm^2, or about 1/60 the Co used in CoCrAlY.

Along with MCrAlY coating developments, advances in "thermal barrier" ceramic coating developments have further lessened the dependence on strategic elements in gas turbine engines. Prior to the cobalt crises of 1977 cobalt base sheetmetal alloys, see Table III, were being used for the manufacture of combustors, augmentor and nozzle components. These alloys were selected over Ni base alloys for their improved creep/rupture strength and fatigue capability. The crisis caused the engine design community to revisit nickel base alloys in all areas. The development of a more spall resistant duplex $MgO.ZrO_2$ thermal barrier coating (Figure 5) was instrumental in the substitution of nickel base alloys for Co base sheet alloys. The improved coatings offer over 56°C (100°F) metal temperature reduction, see Figure 6. Implementation of nickel base alloys with these new coatings in plase of cobalt alloys is being accomplished in all Pratt and Whitney Aircraft engines. The estimated cobalt savings obtained on a typical engine combustor, is shown in Figure 7. This savings includes the effects of a seven-fold reduction in cobalt in the alloy plus improvements in manufacturing methods.

Beyond the combustor, augmentor and nozzle applications, the use of these thermal barrier coatings on turbine airfoils is also being investigated. Developments of more adherent thermal barrier coatings have yielded coatings that can withstand the higher airfoil heat fluxes and provide up to 167°C (300°F) in metal temperature reduction. With this insulation benefit, even less strategic element containing turbine airfoil alloys can be used, thus reducing further our dependence on strategic elements.

U.S. Air Force Retirement for Cause studies have pointed out that the most fruitful area for reduced strategic material usage, short of complete engine redesign, is through component life extension. The exhaust nozzle of a modern engine is a complex assembly of over 400 major parts which is subjected to extreme wear conditions, elevated temperatures, vibrations, and constant part-to-part movement, Figure 8. Selection of optimum wear coatings is not always straight forward because of the diversity of materials used; titanium, nickel base superalloys, cobalt superalloys, columbium alloys and composites. At Pratt and Whitney, extensive developments have been conducted to optimize thermal barrier and wear coatings for the exhaust nozzle. Figure 9 shows a comparison of wear rates experienced during testing of various coatings on a nozzle divergent flap bridge clamp. This work led to tripling the life of thirty of the nozzle components.

FUTURE EFFORTS

Advanced coating technology will continue to be a key element in reducing our dependence on strategic materials in gas turbine engines. U.S. Air Force sponsored programs are underway to develop coatings with increased resistance to oxidation and corrosion at higher temperatures as well as improved mechanical properties. Some of these coatings are void of cobalt content. When coupled with advanced superalloys essentially free of cobalt and chrome, these coatings provide higher turbine airfoil capability with less dependent on strategic materials. Development of thermal barrier coatings for sheet metal and turbine components will continue and provide increased capability to all hot section parts. Efforts to be in a "state-of-readiness" to rapidly implement these developments before a shortage or crisis occurs will remain a major part of Pratt and Whitney's overall effort to reduce strategic material usage in gas turbine engines.

	Input		Finished parts	
	Kg	(lb)	Kg	(lb)
Titanium	2473	(5440)	363	(798)
Aluminum	305	(670)	55	(121)
Tantalum	1.4	(3)	0.2	(0.5)
Columbium	66	(145)	14	(31)
Cobalt	402	(885)	65	(142)
Chromium	675	(1485)	99	(217)
Nickel	2047	(4504)	281	(619)

Table I Weight of strategic elements used in the manufacture of an F100 gas turbine engine

	wt %						
Alloy	Cr	Ni	Al	Ti	Ta	Cb	Co
Cobalt base							
MAR-M 509	23 4	10	-	0 2	3 5	-	55
MAR-M 302	21 5	-	-	-	9	-	58
WI-52	21	-	-	-	-	-	64
Nickel base							
B1900	8	65	6	1	4 3	-	10
IN100	9 5	61	5 5	4 7	-	-	15
MAR-M-200	9	61	5	2	-	1	10

Table II Strategic elements in cobalt and nickel base superalloys used for cast turbine vanes and blaces. (Composition given in weight percent.)

	wt %				
Alloy	Ni	Cr	W	Cb+Ta	Co
Cobalt base					
L605	10	20	15	-	53.5
Ha 188	22	22	14 5	-	41.4
Nickel base					
Hast X	Bal	22	0 6	-	1 5
IN 625	Bal	21 5	21 5	3 65	0

Table III: Strategic elements in cobalt and nickel base sheet alloy used in manufacturing combustor, augmentor and nozzle components. (Composition given in weight percent.)

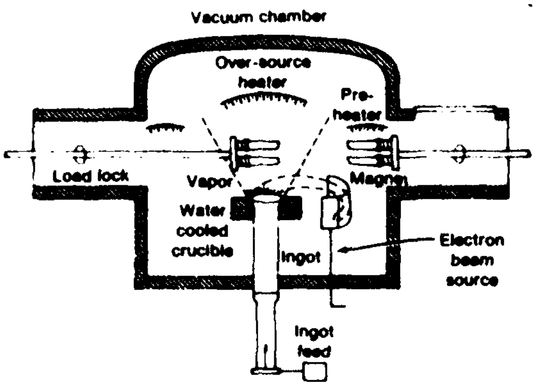


Figure 1 Schematic of electron beam vapor deposition process used in implementing MCrAlY overlay coatings to gas turbine vanes and blades

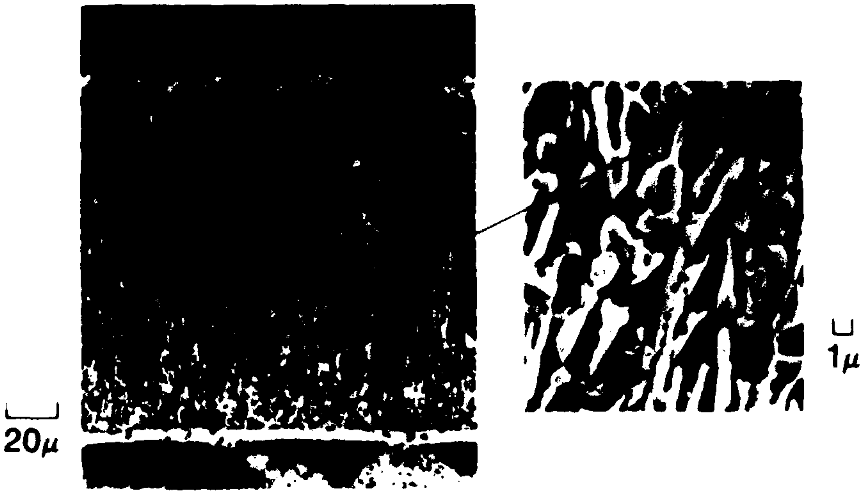


Figure 2 Microstructure of typical MCrAlY overlay coatings. Dark phase is β (CoAl or NiAl), light phase is γ (nickel or cobalt solid solution).

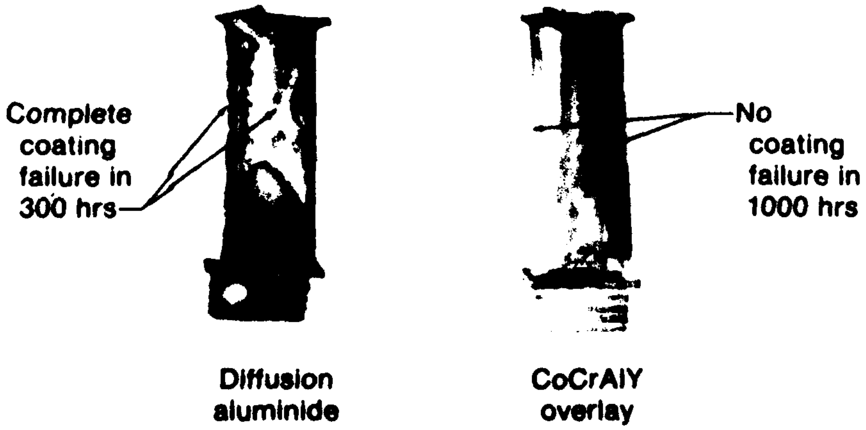


Figure 3 First stage blades after service evaluation illustrating over 3X life extension achieved with substitution of CoCrAlY overlay coating for standard diffusion aluminide coating

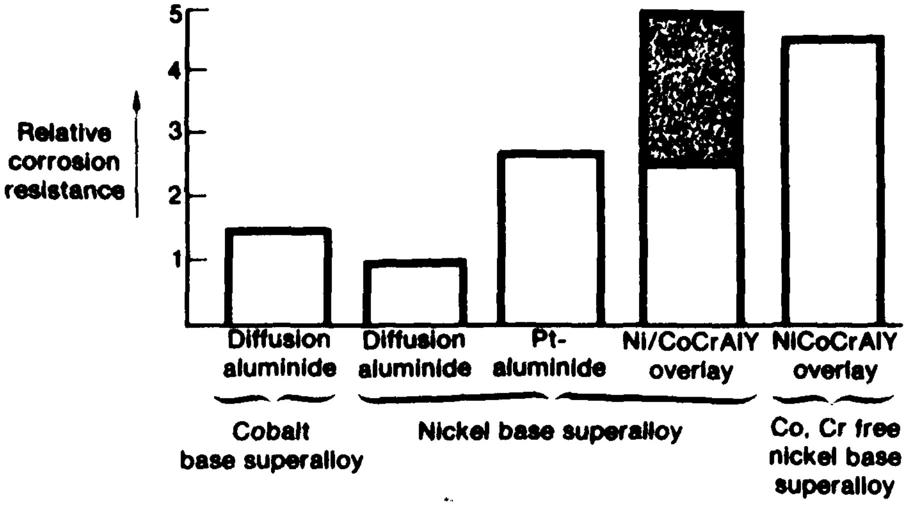


Figure 4 Hot corrosion life of diffusion aluminide, Pt-aluminide and NiCoCrAlY overlay coatings showing advantages of overlay and Pt modified diffusion coatings. Comparison based on 35 ppm salt, 995°C (1750°F) cyclic burner rig testing.

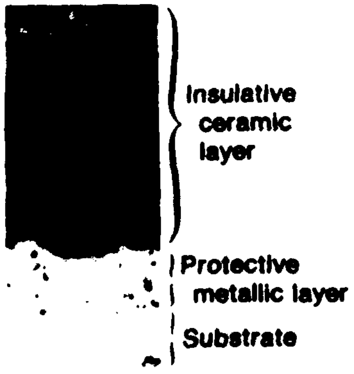


Figure 5 Microstructure of typical plasma sprayed thermal barrier coating used for protection of combustor, augmentor and nozzle components from thermal distress

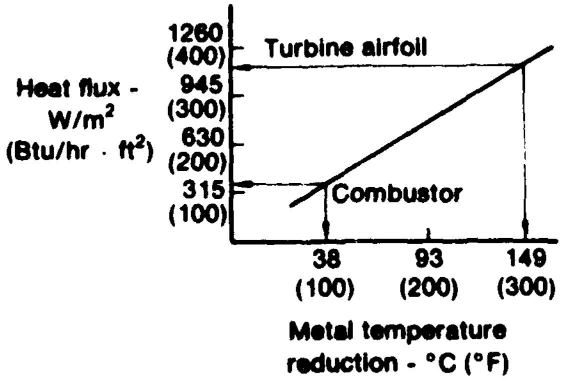


Figure 6: Potential metal temperature reductions possible with use of thermal barrier coatings. Temperature reduction increases with increasing heat flux.

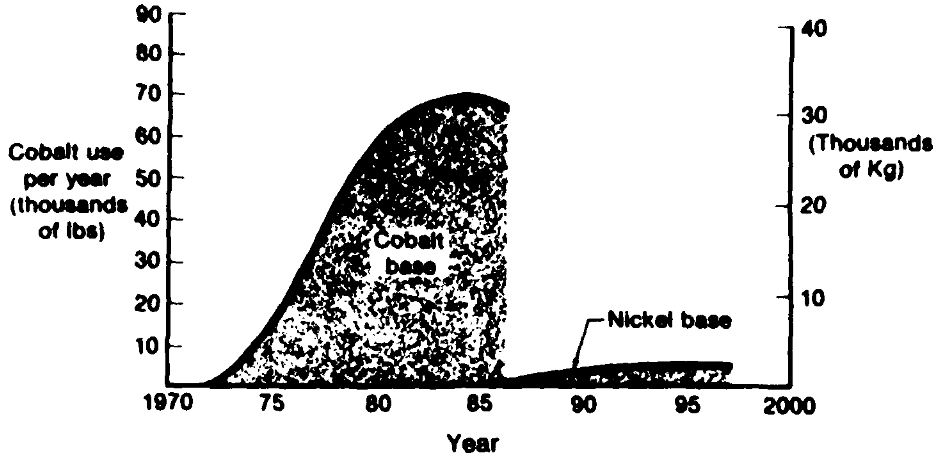


Figure 7 Cobalt savings achieved in advanced engine combustor by use of improved spall resistant thermal barrier coating and substitution of a Ni base alloy for the standard Co base superalloy

Figure 8 Overall view of typical advanced tactical fighter exhaust nozzle showing complex nozzle design

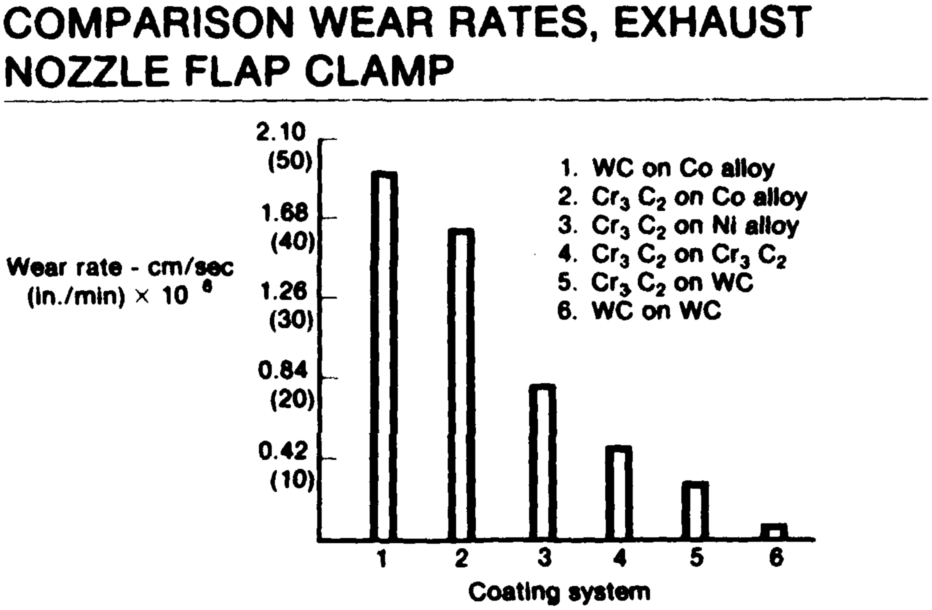


Figure 9 Comparison of wear rates of various coatings on nozzle divergent flaps showing life improvement by selection of optimum wear resistant coating

TRACE ELEMENTS IN SUPERALLOYS AND THE IMPLICATIONS FOR RECYCLING

by

P N QUESTED and T B GIBBONS
Division of Materials Applications
National Physical Laboratory
Teddington, Middlesex, UK. TW11 OLW

G L R DURBER
Glossop Superalloys Ltd
Glossop, Derbyshire, UK

AD-P004 227

SUMMARY

The more efficient use of recycled foundry scrap or revert alloy presents an alternative to substitution as a means of conserving strategic raw materials and represents more efficient utilisation of valuable resources. A major difficulty is the inferior foundry performance of revert alloy which can result in hot tearing or unacceptable levels of microporosity so that recycled material has generally been used for the less critical components in the turbine.

The present paper considers the general problem of control and specification of impurity elements with particular attention to the situation relevant to recycled alloys and considers the influence of certain impurities on microstructure and properties. It will be shown that there is scope for the improvement of specifications for impurity elements and that a better understanding of the relationship between casting conditions and microstructure is required for conventionally cast alloys.

INTRODUCTION

Uncertainties in the price stability and long-term availability of certain elements crucial to the high temperature performance of superalloys has led to increased interest in using larger amounts of recycled material to conserve these strategic elements (1,2). The general extent to which the USA and the countries of Europe depend on imports of elements such as nickel, chromium and cobalt, essential for high strength superalloys, is evident from Table 1. Although performance rather than price can be the major criterion for high strength superalloys a considerable amount of scrap (1) is currently recycled within the industry but this is largely used for less critical components. The need to recycle material arises because of the large amount of high quality scrap regularly produced by individual foundries. Thus, during the investment casting of blades only about 40% of the melt weight emerges in the final product and in the case of wrought alloys some complex machined parts may have a final product yield of approximately ten per cent. Generally it is estimated within the industry (4) that the weight of semi-finished products leaving the plant is less than 30% of the weight of alloy melted.

Although the major element concentration of recycled material is adjusted during reverting to meet the original specification it is generally agreed that the foundry performance of revert alloy is inferior to that of virgin. This inferiority, which can result in increased microporosity or in hot-tearing, may be due to small changes in the content of minor elements such as zirconium, silicon, nitrogen and oxygen etc as a result of contamination from the mould, cores and furnace environment. Thus some effort has been devoted to the determination of the influence of small differences in the trace element content on the foundry performance and the high temperature properties of Ni-Cr-base alloys to provide a basis for the control of elements found to have a detrimental effect on behaviour.

The purpose of this paper was to review certain aspects of the specification and control of trace elements during melting and casting with particular emphasis on the problems associated with recycled material and to consider the effect on microstructure and properties of the minor elements generally believed to influence the behaviour of revert alloys.

SPECIFICATIONS FOR TRACE ELEMENTS

The increased awareness of the harmful effects of elements such as Pb, Bi, Ag etc on the high temperature performance of superalloys led in the 1960's to the formulation of specifications agreed between customer and supplier fixing acceptable limits for the content of individual trace elements. These specifications have become more stringent in the intervening years as more data have become available and this trend is illustrated in Table 2 where the values currently specified by a typical customer are shown along with the limits fixed in earlier specifications. A further development has been the introduction of the concept of the lower reporting limits with the aim of indicating the presence of significant amounts of impurities within the limits set by the relevant specifications and current values have been included in Table 2. The downward trend in lower reporting limits which is largely a consequence of an improved analytical capability is illustrated in Table 3 where it can be seen that the limit for Bi for example has been reduced by a factor of 10 since 1975. Also, the limit for Ca, which it is claimed can sometimes have a beneficial and sometimes a harmful influence, is now 5 ppm but was 100 ppm in 1981. It is generally acknowledged that many of the elements in question are regularly analysed at concentrations above those of the lower reporting limits but, at the amounts usually detected, none even approaches the maximum specified value. Several of the elements viz Zn, Ga, and Sn are commonly agreed to be of little concern for control of product quality.

The measures described have provided the basis for the control of deleterious trace elements but with the important exception of SAE, AMS 2280 for military aircraft applications (Table 2), national specifications for superalloys do not, in general, include comprehensive limits for impurities. This is illustrated in Table 4a where specifications for minor elements from typical national standards for an IN100 type alloy are shown and the most comprehensive from the point of view of impurities which are generally recognised as harmful, viz AFNOR NK15CAT, gives limits for Ag, Pb and Bi only. The corresponding BS HC204 specification includes limits for only Ag and Pb and the latter is fixed at twice the AFNOR value. These specifications apply to both virgin and revert heats and the levels of elements such as Zr and Si can readily be met during reverting. Also it will be noted that no limits are laid down for control of gases eg nitrogen and oxygen and variations in nitrogen content in particular can seriously influence the performance of recycled Ni-base alloys. An important feature of each of the specifications in Table 4a is that stress-rupture tests are required for release purposes but only the LW 2.4674 standard includes a test at a temperature low enough (760°C) to indicate the presence of unacceptable amounts of nitrogen.

The specification for the Chinese alloy K17 which is similar in composition to IN100 provides an interesting comparison and it can be seen from Table 4b that in this case limits are indicated for a comprehensive list of trace impurities. However the lowest temperature for stress rupture testing for release purposes is 900°C.

IMPURITY CONTROL DURING MELTING AND CASTING

The impurity content of virgin melts can in principle be controlled by choice of raw materials and by suitable adjustment of melting practices (6,7,8,29). The typical content of impurities for the major raw materials used is shown in Table 5 and it can be seen that the chief source of impurities, particularly of sulphur and phosphorous, is chromium. Tin occurs in both Cr and Co but, apart from Ga, is the only metalloid present in any significant amount.

When typical impurity levels from several casts of certain superalloys with the nominal composition given in Table 8 are considered it can be seen (Table 6) that for about twenty casts of Mar M002 the impurities are for the most part, well below the specified limits (Table 2). A similar conclusion can be reached for the casts of virgin and revert IN713 LC. In this case only the analysis for Ga, Sb, and Mg approach the limits and interestingly the Pb content of the revert casts has dropped significantly while the Sn content has increased. This result is broadly consistent with the findings of work (9) to investigate the effect of vacuum processing on the selective removal of impurities from Ni-20% Cr which showed that Pb could be reduced to ~ 5 ppm in one hour at 1560°C whereas the Sn content was largely unaffected. Examination of the data available for about twenty casts each, of virgin and revert IN738LC shows that similar trends can be identified in this material also. Some of the differences in the trace element content in the various alloys can be attributed to the variations in major element compositions and for example the somewhat higher concentrations of sulphur in IN939 and IN738 can be related to the higher chromium content in these alloys.

The effect of melting practice on trace element content has been examined for certain wrought alloys and when electro-slag remelting (ESR) was applied subsequent to vacuum induction melting (VIM) for the alloys IN718 and C263 there was no noticeable reduction in trace element content (10). The use of a high fluoride slag increased the Pb content in alloy C263. However, as Table 7 shows, electron beam melting (EBM) following VIM significantly reduced the content of Pb and oxygen in Nimonic 80A (11) and had a similar effect on lead, bismuth, silver and oxygen in IN738 (12). There was however little effect on nitrogen content in the IN738 although some reduction occurred in Nimonic 80A and any loss of chromium was minimal.

Revert alloys are in general characterised by a higher content of nitrogen and in some cases silicon while, as has been shown, the amount of metalloids can frequently be reduced. Typical values of nitrogen analysis have been included in Table 6 for virgin and revert casts of the alloys shown and it should be noted that the higher Cr alloys viz IN939 and IN738 generally contain larger amounts of nitrogen. In the vacuum melting of virgin material nitrogen can be reduced by controlling the melting procedure ie by melting the nickel and chromium and allowing time for the nitrogen to be evolved before the strong nitride formers are added. However even under these conditions the nitrogen content is about an order of magnitude greater than the value calculated on the basis of Sievert's Law (13) for a 20% Cr-Ni binary alloy, with a 10 μm pressure of nitrogen, indicating that longer hold times would be required to reach equilibrium. Some control of the nitrogen level in reverted material is possible by careful selection of scrap and by removing the surface layer from recycled castings since nitrogen contents of greater than 100 ppm (10,29) have been measured near the surface of cast superalloys. Silicon contamination results from interaction with moulds and cores and appears to be associated with small components and with parts cast by directional solidification and is relatively insensitive to the melting procedure. As a result of improvements in analytical techniques allowing silicon to be determined to ~ 0.01 wt% (10), it has been shown that revert Mar M002 can contain at least six times as much silicon (0.06 wt%) as the virgin stock (<0.01 wt%)

THE EFFECT OF RECYCLING ON MICROSTRUCTURE AND PROPERTIES

A characteristic of castings produced from recycled superalloys is the higher levels of microporosity (14,28) compared with those normally obtained in similar castings from virgin heats. Typical data are shown in Fig 1 and, while the reasons for the high levels of microporosity have not been satisfactorily established, the stress rupture properties of material of this type are reduced. Consequently the tendency has been to restrict the use of revert to castings with good feeding characteristics or to use HIP to close the micropores. The effectiveness of this treatment is evident from Fig 2. In recent work (13) the deliberate addition of nitrogen to cast carrots of Mar M002 caused an increase in micrporosity and a drop in stress rupture performance, Figs 3 and 5, thus providing some evidence to link the high gas contents typical of revert alloys (Table 6) with the poor foundry performance. This investigation also showed that the increase in nitrogen content was accompanied by a change in the morphology of the MC carbides which became more blocky in appearance. Significantly it appeared that, in the high nitrogen alloys, the carbides had nucleated on smaller particles rich in Ti and probably TiN or TiCN, Fig 4. The results of subsequent experiments have shown that the stress-rupture properties of the alloys with high contents of nitrogen were largely restored to those of the undoped material by a HIP treatment, Fig 5. Taken together these results would appear to confirm that the inferior performance of revert alloy can be mainly attributed to the increased microporosity associated with the higher content of nitrogen.

Earlier work on virgin melts of IN100 (15,16) also showed that high nitrogen contents gave increased microporosity and that Ti reacted with the nitrogen to form nuclei of Ti(CN). From one of these investigations (16) it was proposed that contents of nitrogen and oxygen should each be limited to 15 ppm in IN100. Further evidence to indicate that nitrogen content can influence the morphology of MC carbides in IN100 has been provided by Lamberigts (17) and it was shown that in some cases the carbide particles were enriched in Ti. However, it should be noted that there is evidence that the shapes of the carbide particles in superalloys can also be influenced by cooling rate from the casting temperature (18,19). Also, while it is well known that carbon content can influence the amount of microporosity (20,21) there is no evidence ~~of significant~~ variations in content of this element between virgin and revert melts.

Revert material, especially that originating from the directional solidification process, often contains an increased amount of silicon within the specification limit (usually 0.2% max.) set for the individual alloys. At higher concentrations (5) Si is known to be deleterious to mechanical properties largely through the stabilising of Laves phases although it is claimed that high Si contents improve oxidation resistance and weldability. The influence of Si between 0.1 and 0.9% on the microstruture and properties of a high strength wrought alloy has been considered by Wang et al (22). Reductions in tensile strength and in ductility were attributed to changes in the amounts, types and morphology of carbides and in particular to the formation of a continuous film of M_6C at the grain boundaries. Study (13) of the effect of a deliberate addition of Si (0.16%) to Mar M002 showed a substantial decrease in porosity and an increase in the amount of a Ni-Hf intermetallic which also contained Si and Zr, Fig 6. This phase was taken into solution at 1100°C and it was suggested that the reduction in porosity was due to the feeding provided by this low melting-point constituent. It appears that the major influence of Si may be in increasing the volume fraction of the Ni-Hf intermetallic and in the work of Burke (24) the presence of larger amounts of this phase was correlated with the increased tendency to hot tearing during the directional solidification of revert Mar M200 + Hf. The formation and thermal stability of Ni_5Hf in some superalloys has been discussed in some detail by Yunrong and Yulin (23).

Although there is little evidence to suggest that the content of Zr is increased during recycling this element remains a potential contaminant in revert alloy. Recent work by Radavitch (25) has shown that deliberate addition of Zr to a complex Ni-base alloy resulted in a serious deterioration in stress-rupture performance. The life to rupture was reduced from 105h in the base alloy with no deliberate addition of Zr to 30h when 0.15% Zr was present and this was accompanied by an increase in microporosity and by changes in carbide morphology. Zr has traditionally been regarded as a beneficial addition in alloys (5) of this type and further work is clearly necessary to establish the generality of these findings. Preliminary work, by the present authors, with the deliberate addition of 0.1% Zr to Mar M002 shows little change in the stress rupture properties at 760°C compared to the base alloy. It should be pointed out that the use of recycled material in the casting of single crystal parts will give rise to particular problems since elements such as carbon, nitrogen silicon and zirconium which will be picked-up during processing are not present as deliberate additions in the virgin material (27).

IMPLICATIONS FOR FOUNDRY PRACTICE

There appear to be two principal alternatives available to enable recycled Ni-Cr-base alloys to be used effectively in the casting of complex parts for gas turbine applications. These are:

(i) the modification of the alloy composition during remelting to restore the minor element content to that of the virgin alloy;

(ii) control of the investment casting conditions to enable revert alloy to be used to produce castings matching in soundness and mechanical properties those obtained with virgin stock.

Bearing in mind the difficulties described in controlling the content of elements such as nitrogen and silicon, option (ii) above appears the more attractive. Some support for this view is provided by the observation that, despite the general difficulties encountered in using recycled superalloy material, there are certain foundries that claim to be able to cast with high revert ratios and produce sound castings in complex shapes. This experience encourages the belief that adjustment of features of the casting process itself can have an important influence on the soundness of components. It is well known that casting conditions can be controlled to yield products with low levels of microporosity and evidence has been presented to show that low mould temperatures can result in increased numbers of micropores (14,26). However microporosity can also be encouraged by slowing down the cooling process by using mould backing and increased pouring temperatures (26). Consideration of these apparently contradictory findings has led to the suggestion that optimum casting conditions will exist between fast and slow cooling rates which will give small amounts of evenly distributed microporosity. Other workers (14) have suggested, on the basis of creep test results, that pouring temperature has an influence on the performance of blades in Mar M002 cast from revert material. It appears that detailed studies of the relationship between casting conditions, solidification structure and microporosity have been carried out for directional solidification (26) but not for conventional casting, and information of this type would undoubtedly aid in determining the optimum casting conditions for recycled alloy.

The technique of "cross blending" as mentioned in a recent paper by de Barbadillo (4) may provide an opportunity for avoiding some of the foundry problems associated with the high nitrogen content of revert alloy. The example mentioned was the use of scrap IN713, which contains niobium but no cobalt, along with scrap IN100 which contains cobalt but no niobium to melt IN738 which contains both elements. The advantage from the point of view of nitrogen content is that, even in the virgin melts the amount of nitrogen present in the high-Cr alloy IN738 is substantially greater than that reported for revert IN100. In this way valuable scrap could be recycled without prejudicing foundry performance.

CONCLUSIONS

1. Specifications, agreed between customer and supplier are adequate for the control of metalloid - type impurities in recycled materials but improvements are required for elements such as oxygen, nitrogen and silicon.

2. National standards are generally inadequate for the control of impurities in superalloys and there is scope for revision to take account of available information.

3. Control of melting practice and selection of raw materials offer some opportunity for limiting the nitrogen and oxygen content in virgin melts whereas scrap selection and cross blending appear to be the best possibilities for revert alloy.

4. Increased nitrogen contents are associated with changes in microstructure and increased microporosity in Mar M002 but the number of micropores can be reduced and the creep performance restored by an increased silicon content or by a HIP treatment.

5. Further studies of the relationship between casting conditions, solidification structure and microporosity are required to provide a basis for optimising the casting conditions for revert alloys.

REFERENCES

(1) CURWICK, L R, PETERSEN, W A and de BARBADILLO, J J. Proceedings of the Fourth International Symposium on Superalloys, p 21, ASM, Metals Park, Ohio, 1980.

(2) STEPHENS, J R. NASA Technical Memorandum 82852, 1982.

(3) CROWSON, P C F. Proceedings of International Conference on Future Metal Strategy p 9 The Metals Soc, London, 1980.

(4) de BARBADILLO, J J. Met.Trans 14A, 1983, 329.

(5) HOLT, R T and WALLACE, W. International Metal Reviews, Review No 203, March 1976, 21, p 1.

(6) CREMISIO, R. Chapter 13 of "Superalloys" edited by SIMS, C T and HAGEL, W C. John Wiley & Sons, New York, 1972, p 373.

(7) HAMBLETON, R C. Chapter 7 of "The Nimonic Alloys", second edition edited by BETTERIDGE, W and HESLOP, J, Edward Arnold, London, 1974, p 115.

(8) FORD, D A. Chapter 6 of "The Development of Gas Turbine Materials" edited MEETHAM, G W. Applied Science Publishers, London, 1981, p 147.

(9) TURILLON, P P. Transactions of the Vacuum Melting Conference 1963 edited by BUNSHAH, R T. American Vacuum Society, Boston MA, 1964, p 88.

(10) DURBER, G L R unpublished results.

(11) GIBBONS, T B. Proc. of Int Comf on Electron Beam Welding & Melting, Paris 1970, p 545.

(12) TIPLER, H R and PECK, M S. Final Report COST 50 DMA(A)33 June 1981.

(13) DURBER, G L, OSGERBY, S and QUESTED, P N. Metal. Technol. in press.

(14) VIATOUR, P, COUTSOURADIS, D, HABRAKEN, L, and DRAPIER, J M from "High Temperature Alloys for Gas Turbines" edited by COUTSOURADIS, D et al p 875, Applied Science Publishers, London, 1978.

(15) WLODEK, S T. Trans. ASM. 1964, 57, 110.

(16) HARRIS, K, SCHWER, R E, BROWN, G W and VALENTINE, D C in "Vacuum Metalurgy" Proc. AVS Conference, Pittsburgh, 1977, p 389, Science Press, `Princeton.

(17) LAMBERIGTS, M, THERET, J M, and DRAPIER, J M in "High Temperature Alloys for Gas Turbines", p 747 edited BRUNETAUD, R et al. D. Reidel Publishing, Dordrecht, Netherlands, 1982.

(18) FERNANDEZ, R, LECOMTE, J C and KATTAMIS, T Z. Met.Trans. 9A, 1978, 1381.

(19) McLEAN, M. "Directionally Solidified Materials for High Temperature Service" Metals Society London, 1983.

(20) QUICHOU, L, LESOULT, G, LAMANTHE, G, HAMAR, R, THERET, J M and BACHELET, E in "High Temperature Alloys for Gas Turbines", p 955 edited BRUNETAUD, R, et al. D.Reidel Publishing Company, Dordrecht, Netherlands, 1982.

(21) EDWARDS, M R. Proceedings of the Fourth International Symposium on Superalloys, p 295, ASM, Metals Park, Ohio, 1980.

(22) WANG, Y S, GUAN, X M, YE, H Q, BI, J and XU, A S ibid p 63.

(23) YUNRONG, Z and YULIN, C ibid p 465.

(24) BURKE, J J, WHEATON, H L and FELLER, J R. Presented at 1978 Annual AIME Meeting in Denver, Colarado, February 1978.

(25) ANTONY, K C and RADAVICH, J F. Proceedings of the Third International Symposium on Superalloys p 137, ASM, Metals Park, Ohio, 1976.

(26) BACHELET, E and LESOULT, G in "High Temperature Alloys for Gas Turbines" edited by COUTSOURADIS, D, et al, p 665 Applied Science Publishers, London, 1978.

(27) STRANGMAN, T E, HOPPIN, G S, PHIPPS, C M, HARRIS, K and SCHWER, R E. Proceedings of the Fourth International Symposium on Superalloys, p 215, ASM, Metals Park Ohio, 1980.

(28) HOCKIN, J. Proceedings of the British Investment Casters Technical Association 13th Annual Conference, Paper 3, B.I.C.T.A, Sheffield, 1975.

(29) THIERY, J and VOELTZEL, J. Proceedings of the AGARD meeting on Advanced Casting Technology, Paper 18, AGARD-CP-325, 1982.

TABLE 1

Imports of major alloying elements for superalloys as a percentage of consumption after Crowson[3]

	UK	EEC	USA
Aluminium	62	62	85
Chromium	100	100	91
Cobalt	100	100	98
Nickel	100	100	72
Titanium	100	100	n.a
Tungsten	99.5	99	52
Niobium	100	100	100
Molybdenum	n.a	100	n.a
Tantalum	100	100	97
Vanadium	100	99	33
Zirconium	100	100	n.a

n.a = not available

TABLE 2

Specifications for trace elements in cast superalloys and current lower reporting levels ppm

Specification	Ag	Zn	Cd	Ge	In	Tl	Sn	Pb	As	Sb	Bi	Se	Te	Ca	Mg	Au	Hg	Ga	K	Na	Th	V
Typical requirements to 1975	5	-	-	-	-	-	-	10	-	-	1	-	-	-	-							
AMS 2280$^{(a)}$	50*	50*	50*	50*	50*	5	50*	5	50*	50*	0.5	3	0.5	-	-	50*	50*	50*	50*	50*	50*	50*
Typical current requirement	5	5	0.2	30	0.2	0.2	30	5	30	3	0.5	5	2	-	50							
Current lower reporting limits	0.1	1	0.1	10	0.1	0.2	5	0.25	5	1	0.1	1	0.5	5	5							

* Total content of all these elements must not exceed 400 ppm

(a) Trace Element Control Nickel Alloy Castings, AMS 2280, 1975

TABLE 3

Trend in Lower Reporting Limits (ppm) for trace elements

Year	Ag	Zn	Cd	Ga	In	Tl	Sn	Pb	As	Sb	Bi	Se	Te	Ca	Mg
1975 (DC arc emission)	5	-	-	-	-	-	-	5	-	-	1	-	-	-	-
1981 (Hollow Cathode)	2	2	0.1	10	0.5	0.2	10	2	20	3	0.5	5	3	100	5
1983 (Hollow Cathode)	0.1	1	0.1	10	0.1	0.2	5	0.25	5	1	0.1	1	0.5	5	5

TABLE 4A

Minor and trace element limits in specifications for IN100
(Weight per cent except where indicated)

	I BS HC204	II BS 3146 PART 3 Type VMA12	III LW.2.4674	IV AMS 5397A	V AFNOR NK 15CAT
Si	0.2 max	0.2 max	0.2 max	0.2 max	0.2 max
S	0.015 max	0.015 max	0.015 max	0.015 max	0.015 max
B max	0.01 - 0.02	0.01 - 0.02	0.01 - 0.02	0.01 - 0.02	0.01 - 0.02
Cu	0.2 max	0.2 max	0.2 max	ns	0.2 max
Ag	5 ppm max	n.s	n.s	n.s	5 ppm max
Zr	0.03 - 0.09	0.03 0.09	0.03 - 0.09	0.03 - 0.09	0.03 - 0.09
Bi	n.s	n.s	n.s	n.s	0.5 ppm max
Pb	10 ppm	n.s	20 ppm	n.s	5 ppm max

n.s = not specified

I British Standard: Aerospace Series Specification for Nickel base cobalt-chromium-aluminium-titanium-molybdenum alloy castings (Co 15.0, Cr 10.0, Al 5.5, Ti 4.8, Mo 3.0) HC204: February 1973

II Specification for Investment Castings in metal Part 3. Vacuum melted alloys, Type VMA 12. BS3146: 1976.

III Hochwarmfeste Nickel-Gu-Leigierung 0.2C-15Co-10Cr-6Al-5Ti-3Mo IV Werkstoff-Leistungsblatt 2.4674, March 1981.

IV Alloy Castings, Investment, Corrosion and Heat Resistant. 50 Ni-9.5Cr-15 Co-3.0Mo-4.8 Ti-5.5Al-0.015B-0.95V-0.6 Zr. Vacuum-melted, Vacuum-Cast. A.M.S. 5397A, issued 1965, revised 1977.

V AFNOR designation number NK 15 CAT, Association Francaise de Normalisation.

TABLE 4B

Minor and trace element limits in the specification for
the Chinese alloy K17.
(Weight per cent except where indicated)

Si	S	P	B	Zr	Bi	Pb
<0.5	<0.01	<0.01	0.01 -0.022	0.05 0.09	<1 ppm	<5 ppm
Sb	Sn	As	Mn	Fe	Ag	
<10 ppm	<10 ppm	<10 ppm	<0.5	<1	n.s	

Information courtesy of Zhuang-Qi Hu, Institute of Metal Research, Chinese Academy of Sciencies, Shenyang, China.

TABLE 5

Trace element content of major raw materials used in superalloy production (ppm)

Material	S	P	Ag	Zn	Cd	Ga	Ti	Sn	Pb	As	Sb	Bi	Se	Te	Mg
Nickel, Carbonyl	<15	<5	<1	<1	<.1	< 1	<1	<1	<1	<5	<1	<.2	<1	<1	<5
Elect A	< 2	<2	<2	5	<.1	<.1	<.1	<.2	1	<.5	<.5	<.2	<.5	<.2	<5
Elect B	<10		<1	5	<.1	< 1		<1	3	<2		<.5	<.5	<1	<5
Elect C	8	1	<1	2			<1	<1	<3	<2	<1	<1	<1	<1	
Elect D	<2		<.8	3		<.1	<.1	<.2	.7	<.5	<.5	<.2	<.5	<.2	
BMC PPT	40	2		<2			<.1	<.5	.4	<2	<1	<.1	<.5	<.2	
Cobalt, Elect A	20			13	18	<10		<10	<1		<5				
Elect B	2		.6	<2	<.1	<10		<10	<2	<.5	3		<.5		<5
Elect C	<2			1	<.5	<10			2	<.5					5
Elect D	20	<1	<2	<2	.2	<10	<.1	<10	<2						10
Elect E	6	<3	<2	13	.2	<10		<10	<2		3				<5
Chromium, Elect A	50	30	<2	<2		50		<10	2		3				<5
Elect B	80	20	<2	<2		100		15	<2		3				<5
Thermit A	50	40	<2	14		100		<10	2		4	<.5			<5
Thermit B	90	<100	<2	10		100		<10	<2		3	<.5			<5
Molybdenum	50	50	<2	5		<10		10				<.5			<10

TABLE 6

The range of impurity content and average values for about 20 casts for each alloy except for IN939 where the sample size was six in each case (ppm)

virgin/revert ratio Mix	Alloy	Pb range (mean)	Ga range (mean)	Sb range (mean)	Sn range (mean)	Zn range (mean)	N range (mean)	O range (mean)	[illegible] range (mean)	Mg (mean)
100% virgin	MM 002	r-0.3 (.25)	10 - 23 (15)	r	r - 8 5	1.5 - 4 2.5	5 - 13 10	6 - 23 (11)	1 - 4 (3)	12 - 26 (16)
"	738 C	r-0.6 (.4)	r - 23 (15)	r - 1.5 (1)	5 - 18 (10	r - 3 1.5	13 - 32 (21)	4 - 20 (12)	1 - 7 (4)	6 - 27 (15)
"	713LC	.3 - 1.9 (.8)	10 - 25 (17)	r - 3 (1)	r - 10 6	1.5 - 6 3.5	11 - 14 (12)	4 - 26 (11)	na	6 - 49 (12)
"	C1023	.4 - .6 (.5)	r - 23 (13)	r	6 - 13 9	r - 6.5 (3)	18 - 27 (22)	6 - 33 (13)	1 - 4 (2)	na
"	IN 100	r	r - 18 (11)	r	5 - 16 (11)	r - 2 (1)	5 - 16 (10)	4 - 23 (12)	na	na
"	IN 939	r - .4 (0.25)	15 - 23 (18)	r	r - 15 (12)	r	19 - 39 (30)	22 - 28 (24)	na	na
100% revert	MM 002	r	12 - 16 (14)	r	r - 7 (5)	r	12 - 21 (16)	8 - 15 (11)	2 - 5 (3)	na
"	738LC	r	r - 17 (12)	r	6 - 13 (9)	r	27 - 97 (53)	10 - 28 (16)	2 - 13 (7)	8 - 29 (17)
"	713LC	r	r - 19 (14)	r	r - 10 (5)	r	na	9 - 21 (14)	na	6 - 43 (17)
"	C1023	r	r - 14 (10)	r	7 - 13 (10)	r	19 - 28 (24)	12 - 27 (19)	2 - 6 (4)	na
"	IN 100	r	r - 15 (10)	r	6 - 12 (8)	r	14 - 17 (16)	5 - 19 (14)	na	na
50/50 virgin/revert	IN 939	r	11 - 20 (15)	r	10 - 16 (13)	r	28 - 50 (36)	13 - 22 (18)	na	na
Reporting limits		.25	10	1	5	1	5	5	3	5

r = below reporting limit

na = not available

Ag, Bi and As not normally found above reporting limits of .1, .1 and 5 ppm respectively.

TABLE 7

Effect of electron beam remelting on impurity content of a wrought and a cast Ni-base superalloy

(analysis in ppm)

Alloy	Pb	O	N	Mg	Si*	S*	Ag	Bi
Nimonic 80A **VIM**	14	27	56	86	0.32	.002	**na**	**na**
Nimonic 80A **VIM + EBM**	2	2	23	13	0.31	.002	**na**	**na**
IN738LC **VIM**	0.6	12	16	<10	<.05	.002	0.1	0.1
IN738LC **VIM + EBM**	<0.1	3	16	<10	<.05	.005	<0.1	<0.1

na = not analysed

* wt%

TABLE 8

Composition of high-temperature alloys listed in Table 6

(Composition weight per cent, balance nickel)

Alloy	C	Cr	Ti	Al	Co	Mo	B	Zr	W	Nb	Hf	Ta	V
Mar M002	0.15	9.0	1.5	5.5	10.0	0.5 **max**	0.02 **max**	0.05	10.0	-	1.5	2.5	-
IN 100	0.15 0.20	8.0 11.0	4.5 5.0	5.0 6.0	13.0 17.0	2.0 4.0	0.01 0.02	0.03 0.09	-	-	-		0.7 1.2
IN 713LC	0.3 0.7	11.0 12.5	0.4 1.0	5.5 6.5	1.0 **max**	3.8 5.2	0.005 0.015	•0.05 0.15		**Nb + Ta** 1.5 - 2.5			-
IN 738	0.18	16.0	3.5	3.5	8.5	1.75	0.008	0.08	2.5	0.7	-	1.6	-
C1023	0.16	15.5	3.6	4.2	10.0	8.5	0.006		0.2 **max**	0.25	-	-	-
IN 939	0.15	22.5	3.7	1.9	19.0	-	0.01	0.1	2.0	1.0	-	1.4	-

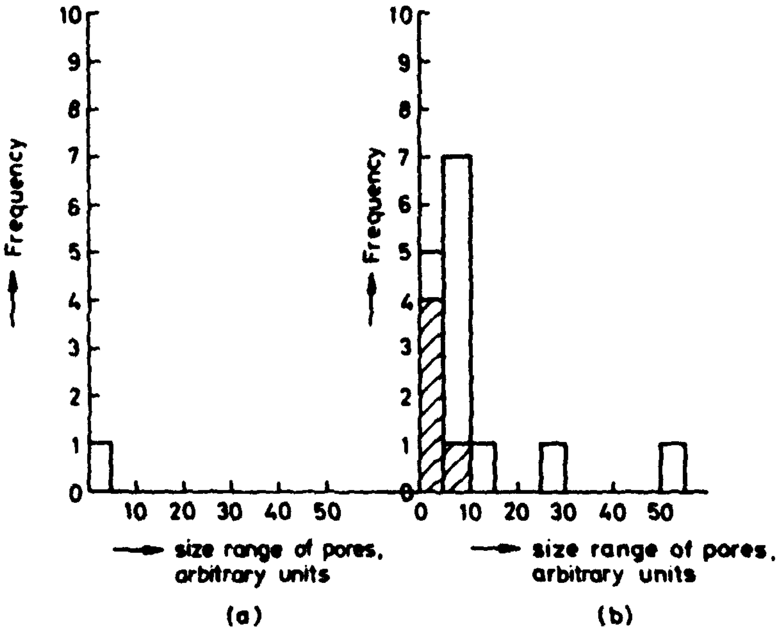


Figure 1 Microporosity in blades cast from (a) virgin and (b) revert Mar M002. Hatching shows the effect of H.I.P. (1200°C/4h/1000 atmospheres). No porosity was observed in the H.I.P. ped virgin material (after Viatour et al[14])

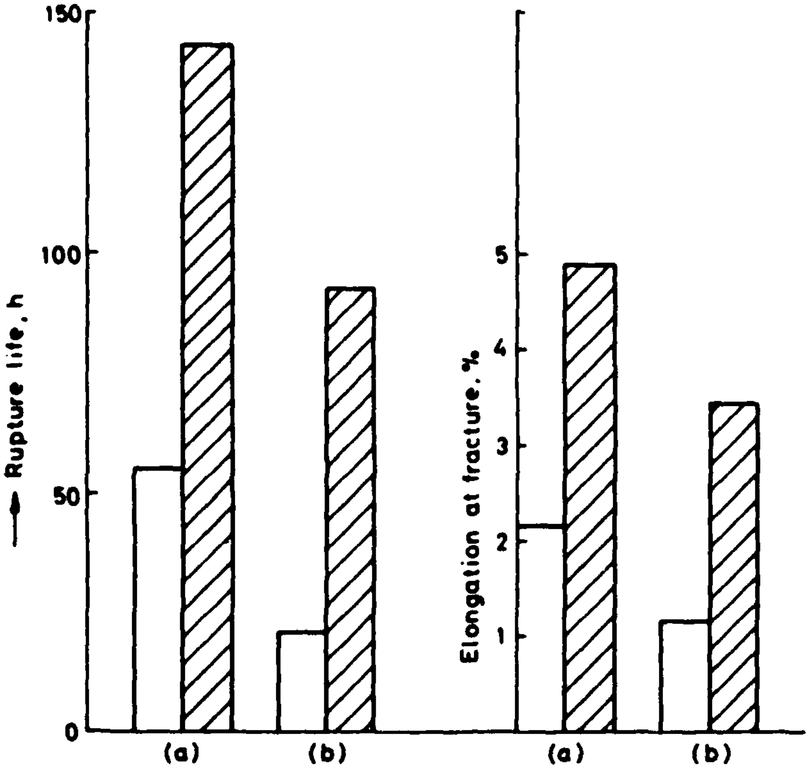


Figure 2 Rupture lives and ductilities for (a) virgin and (b) revert Mar M002 tested at 760°C with a stress of 695 MPa. Hatching shows the properties after Hot Isostastic Pressing (4h / 1000 atmospheres / 1200°C) (after Viatour et al[14])

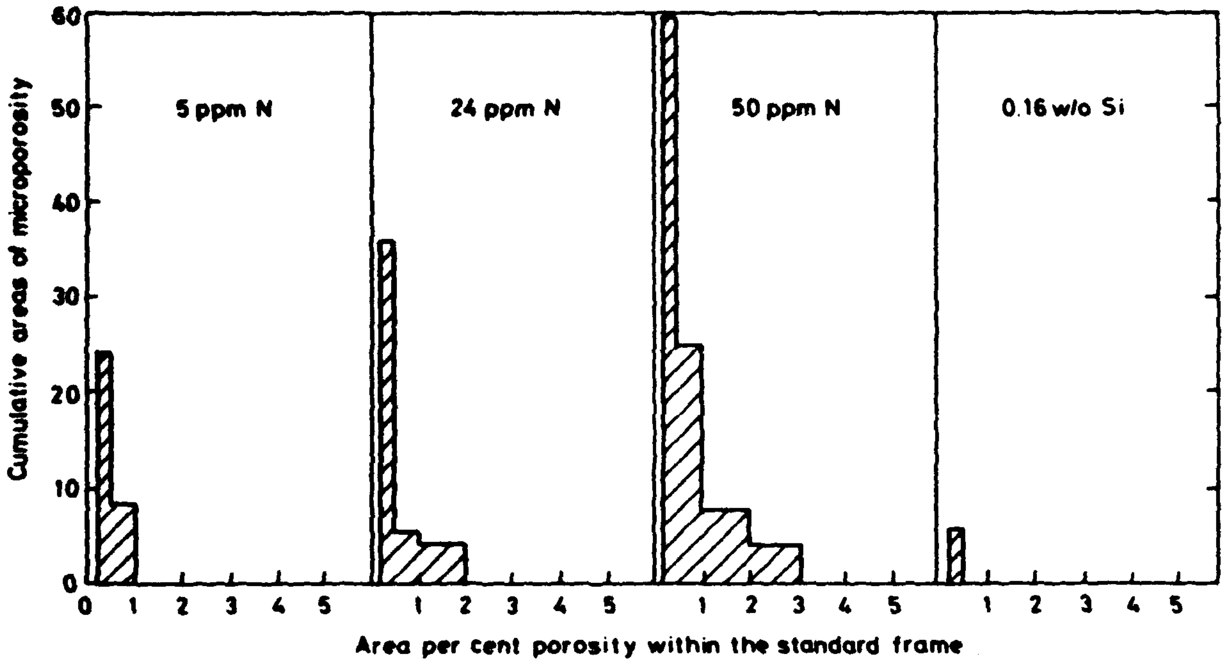


Figure 3 Comparison of the microporosity levels found *in* samples of Mar M002 with various additions

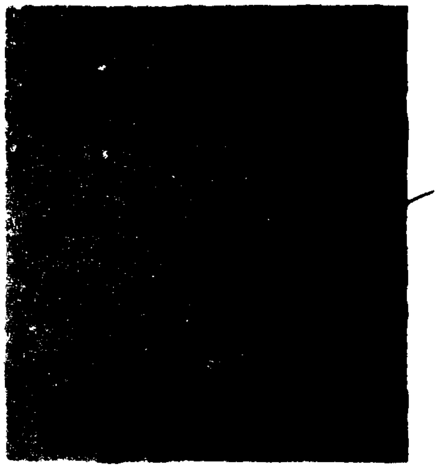


Figure 4. Titanium rich centres in the "carbides" of Mar M002 doped with 50 ppm nitrogen.

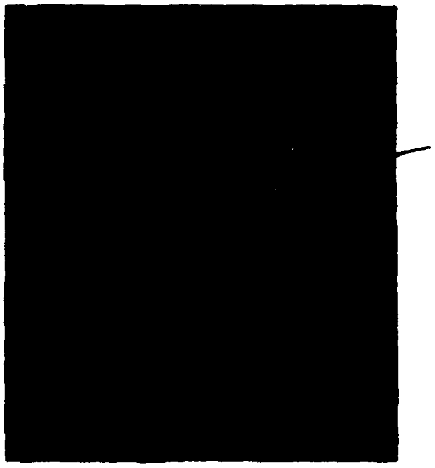


Figure 6. Nickel-Hafnium rich phase containing zirconium and silicon in Mar M002 with 0.16 wt % Silicon.

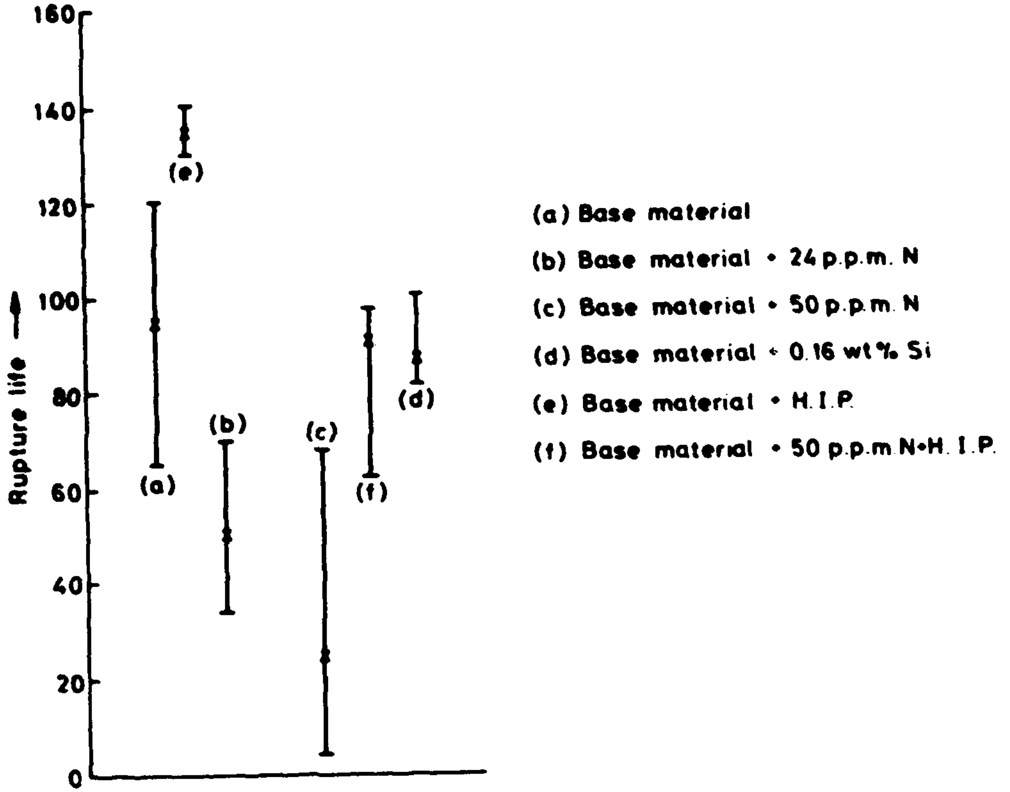


Figure 5 The variation of rupture life of Mar M002 tested at 760° C and 695 MPa with indicated levels of dopant and with and without hot isostatic pressing

EFFET DU RECYCLAGE SUR LES STRUCTURES DE FONDERIE
ET LA SANTE INTERNE DE L'ALLIAGE IN 100 : ETUDE DE LABORATOIRE

Sylvie RUPP, Jean MASSOL, Yves BIENVENU

Centre des Matériaux
Ecole des Mines de Paris
B.P. 87
91003 EVRY Cedex - France

Gérard LESOULT

Ecole des Mines de Nancy
Parc de Saurupt
54042 NANCY Cedex - France

RESUME : Des lots d'alliages IN 100 "vierge" et "recyclé" ont été sélectionnés par deux fonderies européennes de superalliages (recherche européenne concertée). L'étude de laboratoire vise à interpréter les tendances plus marquées à la microporosité notées par les fondeurs dans le cas des lots recyclés en terme de déroulement de la solidification.

L'analyse thermique différentielle ne montre pas d'écarts dans les températures caractéristiques de la solidification autres que celles imputables aux légères variations de composition.

La trempe en cours de solidification dirigée permet la mesure de grandeurs morphologiques régissant la circulation du liquide dans la zone pâteuse venant compenser le retrait de solidification. Des différences de cinétique de précipitation des phases solides sont observables entre alliages vierge et recyclé.

Les résultats préliminaires d'une étude concernant l'alliage Mar M 002 seront également présentés.

1 - INTRODUCTION

La microporosité est un défaut de fonderie dont l'origine est en général attribuée à un dégagement de gaz lors de la solidification ou à une alimentation insuffisante en liquide pour compenser le retrait de solidification.

Dans le cas des superalliages à base de nickel, la pratique du recyclage entraîne une augmentation de la microporosité |1| et une détérioration des propriétés mécaniques des pièces coulées. Les autres présentations de cette session sont d'ailleurs en partie consacrées à cette dégradation du matériau.

Les origines de cette dégradation sont souvent attribuées à l'augmentation de la teneur de l'alliage en impuretés et parmi celles-ci, c'est l'azote qui est le plus souvent cité. Le recyclage s'accompagne, en général, d'une augmentation de la teneur en azote de quelques ppm. La teneur critique permettant le recyclage serait de l'ordre de 20 ppm ; au delà, le taux de rebut deviendrait excessif [2].

Une étude comparative de laboratoire a été consacrée à la solidification de superalliages aéronautiques de type IN 100 et Mar M 002 vierges et recyclés. La sélection d'un "bon" alliage vierge et d'un "mauvais" alliage recyclé a été effectuée sur la base de contrôles micrographiques ou radiographiques de la microporosité ou sur la base d'essais de fluage-rupture à haute température. La présente étude s'inscrit dans le cadre d'une recherche concertée européenne COST 50 associant des industriels et des laboratoires anglais, belges et français.

Cette étude comparative fait essentiellement appel à deux techniques de laboratoire, l'analyse thermique différentielle et la trempe de la zone pâteuse solide/liquide en cours de solidification dirigée, pour mettre en évidence des différences au niveau du déroulement de la solidification et tenter d'interpréter la différence de tendance à la formation de microporosités constatée en fonderie.

Des deux origines les plus fréquemment citées de la microporosité : dégagement de gaz et difficulté d'alimentation en liquide du retrait associé à la solidification, c'est surtout la seconde qui a retenu notre attention. Les raisons de ce choix sont la localisation préférentielle des défauts dans des zones poreuses à texture dendritique pouvant atteindre près de 1 mm de dimension et les résultats d'une étude préliminaire sur le comportement thermochimique et sur l'analyse de l'azote contenu dans l'IN 100.

2 - ANALYSE ET COMPORTEMENT THERMOCHIMIQUE DE L'AZOTE DANS L'IN 100

La méthode analytique retenue est l'extraction de l'azote par fusion réductrice de l'alliage en creuset de graphite chauffé par induction et entraînement par un courant d'hélium suivi, dans une deuxième étape, par un dosage en chromatographie en phase gazeuse.

La variation en fonction de la température de la teneur analysée est importante *(Fig. 1)*. On peut estimer ainsi la teneur en azote emprisonné sous forme de gaz dans les pores à moins de 1 ppm, ce qui représente en terme de volume une faible proportion de la microporosité. L'extraction totale de l'azote (gazeux, dissous et combiné) n'est obtenue qu'à partir de 2000°C environ, mais elle peut être facilitée par l'addition de tiers éléments : du platine en l'occurence.

Les calculs thermochimiques préliminaires ont porté sur les équilibres

$$\underline{Ti} + \underline{N} = TiN\ (s) \qquad |1|$$

$$\text{et} \qquad \underline{N} = 1/2\ N_2\ (g) \qquad |2|$$

Ils conduisent à estimer la température de précipitation des nitrures TiN dans l'alliage IN 100 liquide à 2000 K et à proposer la relation suivante entre la pression d'équilibre d'azote et la teneur en azote dissous :

$$P_{N_2} = 3\,[\%\,\underline{N}]^2 \qquad |3|$$

Bien qu'obtenus à partir d'un ensemble de données thermochimiques très incomplet, ces résultats de calculs sont en bon accord avec la connaissance de la stabilité de l'azote combiné et dissous déduite des résultats expérimentaux. La faible valeur de la pression d'équilibre de l'azote dans les superalliages permet de comprendre la lenteur de la cinétique de l'extraction pendant la fusion réductrice.

Une étude thermochimique et cinétique de la dénitruration et la désoxydation des bains d'alliages à base de nickel est en cours à l'Ecole des Mines de Nancy et à l'Ecole d'Electrochimie de Grenoble pour déterminer avec plus de précision les données thermochimiques relatives à l'interaction de l'azote et de l'oxygène avec les éléments constitutifs de l'alliage liquide [3].

3 - CONSIDERATIONS THEORIQUES SUR LA POROSITE DE RETRAIT

Les superalliages se contractent à la solidification. Quand la fraction solide dépasse 0,7 environ, l'alimentation en liquide pour compenser le retrait ne peut se faire que de façon capillaire à travers le réseau interdendritique ou intergranulaire.

Un pore (vide ou contenant du gaz) peut se développer quand sa pression interne P_{int} est supérieure à la somme de la pression locale du liquide P_ℓ et la pression due aux forces capillaires P_γ.

$$P_{int} > P_\ell + P_\gamma \qquad |4|$$

La pression interne est, dans le cas du dégagement d'azote dans les conditions de l'équilibre, reliée à la teneur [% N] dans le liquide résiduel par l'équation |3|.

La pression locale est d'autant plus réduite que la perte de charge associée à la circulation du liquide dans la zone pâteuse, ΔP, est importante :

$$P_\ell = P_0 + P_m - \Delta P \qquad |5|$$

où P_0 désigne la pression extérieure et P_m la pression métallostatique.

Dans un milieu poreux, la perte de charge, dans la mesure où la loi de Darcy s'applique, varie selon la relation suivante :

$$\vec{\text{grad}}\,\Delta P = \frac{\mu}{k}\,\vec{v} \qquad |6|$$

où $\vec{v}$ désigne la vitesse d'écoulement du fluide, μ sa viscosité et k la perméabilité du réseau poreux.

La perméabilité du réseau est reliée aux paramètres morphologiques de l'interface solide/liquide : fraction f^ℓ et surface d'interface solide/liquide σ. Les relations déduites soit de modèles hydrodynamiques, soit de mesures sur des réseaux dendritiques métalliques ou organiques [4][7] sont du type : $k \sim (f^\ell)^2$ pour une densité de dendrites primaires donnée, et, de façon plus générale :

$$k \sim \frac{(f^\ell)^3}{\sigma^2} \qquad |7|$$

La vitesse d'écoulement du liquide $\vec{v}$ et la cinétique de formation du solide peuvent être reliées par l'expression locale du bilan de masse :

$$\frac{d\rho}{dt} + \text{div}\,\rho^\ell\,\vec{v} = 0 \qquad |8|$$

soit, dans la mesure où ρ^s et ρ^ℓ sont indépendants de la température et de la composition dans l'intervalle de solidification :

$$\beta\,\frac{df^s}{dt} + \text{div}\,\vec{v} = 0 \qquad |9|$$

où $\beta = (\rho^s - \rho^\ell)/\rho^\ell$ est la contraction lors de la solidification.

La cinétique de formation du solide est elle-même régie par le bilan thermique dont l'expression diffère de celle du bilan de masse à cause de la génération interne de chaleur latente de solidification, H :

$$\frac{dT}{dt}\left(1 - \frac{df^s}{dT} \cdot \frac{H}{c_p}\right) = a\;\nabla^2 T \qquad |10|$$

où a et c_p désignent respectivement la diffusivité thermique et la capacité calorique de l'alliage.

Les équations |9| et |10| permettent d'établir la relation suivante entre les divergences du flux thermique et du flux de liquide :

$$\text{div}\,\vec{v} = a \,.\, \beta \,.\, \frac{df^s}{dT}\left(1 - \frac{H}{c_p}\frac{df^s}{dT}\right)^{-1} .\nabla^2 T \qquad |11|$$

Le calcul du champ des vitesses, puis celui des pertes de charge, grâce à l'équation |6|, nécessite donc le calcul du champ des températures et la connaissance du déroulement de la solidification.

Le champ des températures pour une pièce de fonderie donnée peut être calculé par des méthodes numériques, aux différences finies ou aux éléments finis [7][8], ou par des méthodes analytiques dans le cas de la solidification dirigée [5][9].

Dans notre étude comparative de la tendance à la microporosité d'alliages vierge et recyclé, nous avons supposé que les légères modifications de compositions chimiques dûes au recyclage n'entraînaient que des modifications négligeables des champs thermiques à type de pièce de fonderie et conditions de coulée identiques. Nous nous sommes donc attachés à estimer avec précision les conséquences des modifications chimiques de l'alliage sur le déroulement métallurgique de sa solidification caractérisé par :

- un paramètre morphologique, la perméabilité $(f^\ell)^3/\sigma^2$
- un paramètre cinétique de retrait, $\beta \,.\, \frac{df^s}{dT} \,.\, \left(1 - \frac{H}{c_p}\frac{df^s}{dT}\right)^{-1}$ proportionnel à la contraction de la zone pâteuse et à la vitesse de refroidissement instantanée.

Ces deux grandeurs jouent en effet un rôle privilégié dans le contrôle de la circulation du liquide au milieu de la zone pâteuse comme le montrent respectivement les équations |6| et |7| d'une part, l'équation |11| d'autre part.

4 - TECHNIQUES EXPERIMENTALES

Un "bon" alliage vierge et un "mauvais" alliage recyclé ont été sélectionnés par les fonderies de superalliages partenaires dans le programme COST. Les matériaux se présentent sous forme de rondelles découpées au milieu de lingotins ou de "carottes".

Une étude macro et microscopique sommaire des alliages montre une *zone équiaxe* plus importante dans le cas de l'alliage recyclé, les grains étant plus fins que dans l'alliage vierge. Une étude métallographique plus fine de ces matériaux est réalisée par les autres laboratoires partenaires.

La teneur en éléments majeurs diffère peu et parmi les impuretés c'est surtout la teneur en azote qui augmente, en doublant pratiquement *(Tableau 1)*.

L'analyse thermique différentielle a été effectuée à différentes vitesses de chauffage ou de refroidissement *(Fig. 2)*. Les températures de précipitation sont obtenues par extrapolation à vitesse nulle des quatre ou cinq valeurs dans un diagramme température/vitesse *(Fig. 3)*. La validité de cette procédure a été établie sur le liquidus des métaux purs nickel et or.

La trempe de la *zone pâteuse* en cours de solidification dirigée est effectuée sous argon ou sous vide. Le métal contenu dans un tube d'alumine est chauffé par induction et refroidi à son extrémité inférieure par une circulation d'eau *(Fig. 4)*. La vitesse de tirage est constante et la trempe n'est déclenchée qu'après tirage d'une longueur suffisante. La vitesse de trempe (de l'ordre de 10 K/s) permet de figer l'interface solide/liquide.

Après trempe, le barreau est d'abord sectionné longitudinalement et poli. Le repérage des températures se fait à partir de l'enregistrement du profil thermique pendant la solidification. L'écart entre la température correspondant au sommet des dendrites et le liquidus (A.T.D.) est faible *(Fig. 5)*. La mesure de la fraction liquide f^l et de la *surface spécifique d'interface* σ sont obtenues à partir des sections transversales après polissage et attaque Kalling. Comme les analyseurs automatiques d'images ne peuvent pas différencier la structure de trempe de celle de la solidification, il est nécessaire de redessiner sur papier calque l'interface photographiée à un grossissement 25 *(Fig. 6)*. L'analyseur d'images du type T.A.S. calcule les grandeurs morphologiques f^l *et* σ *par une* succession d'opérations morphologiques sur image digitalisée. On estime à ± 0.05 la précision sur f^s et à 20 % la précision relative sur σ.

Il est certain que les structures basaltiques obtenues par trempe en cours de solidification dirigée ne sont pas directement comparables aux structures habituellement équiaxes observables dans les pièces obtenues en fonderie de précision. Il est certain par ailleurs que les conditions de *refroidissement* du métal sont différentes. *En fonderie équiaxe de pièces de type aube,* le gradient thermique est en général plus faible, alors que la vitesse effective de croissance du solide est plus forte (du fait du nombre élevé de grains) que les valeurs correspondantes imposées en solidification dirigée. Le temps local de solidification $(T_L - T_S)/(G.V)$, de l'ordre de 1500 s (pour l'IN 100) dans les conditions les plus *fréquemment* utilisées dans cette étude, est en général supérieur aux temps mesurés en fonderie [7]. Ceci se traduit au niveau de la microstructure des alliages solidifiés par une taille plus importante de l'espacement interdendritique secondaire et des carbures par rapport aux conditions industrielles. Malgré ces différences importantes entre la structure du métal coulé en fonderie et celle du métal trempé en cours de solidification *dirigée* (T.S.D.), la technique de T.S.D. permet de révéler des différences morphologiques (f^l et σ) et des différences cinétiques (df^s/dT) entre alliages à conditions de refroidissement identiques. Le postulat de cette étude est que les différences observées ici en solidification dirigée correspondent à des différences analogues, sinon identiques, *effectives* pendant la solidification équiaxe des pièces coulées en fonderie de *précision.*

5 - RESULTATS EXPERIMENTAUX

5.1. Analyse thermique différentielle

Les températures de liquidus, de formation des carbures primaires, de précipitation eutectique γ/γ' et de solidus sont reportées sur le *tableau 2*. Les faibles différences notées entre alliage vierge et recyclé peuvent s'interpréter en fonction des faibles différences de composition et des variations correspondantes de la température de liquidus, *estimées* empiriquement à partir de la formule de Cook et Guthrie [10](cette formule ne tient pas compte des teneurs en impuretés des alliages). L'intervalle de solidification $T_L - T_S$, est de l'ordre de 75 K pour l'alliage vierge et de 90 K pour l'alliage recyclé.

Les thermogrammes des alliages IN 100 montrent parfois deux pics carbures distincts, ce phénomène semble plus fréquent pour les alliages recyclés.

5.2. Microstructure de solidification unidirectionnelle

L'analyse morphologique de la structure dendritique a été effectuée sur trois barreaux (deux élaborés à partir de l'alliage vierge, un à partir de l'alliage recyclé).

L'évolution de la fraction liquide f^l en fonction de la température montre une rupture de pente correspondant à la précipitation des carbures environ 20 K sous le liquidus. Dans cette représentation, f^l est plus faible dans le cas de l'alliage *recyclé (Fig. 8)* : l'écart semble significatif au vu des précisions estimées.

La surface spécifique d'interface σ présente des évolutions très proches pour les trois alliages, avec un maximum à f^s = 0,65 *(Fig. 7)*, alors que la valeur idéale pour le contact des sphères serait de *0,7* environ.

Il découle de ces comparaisons que la perméabilité spécifique, $(f^l)^3/\sigma^2$, est supérieure pour un même écart de température à la température de liquidus dans le cas des alliages vierges *(Fig. 8)*. En fait, cette représentation conduit à tirer des conclusions hâtives et il est plus judicieux de comparer les alliages à un même "besoin thermique" donné. Le "besoin thermique" ou quantité de chaleur à extraire pour passer de f^s = 0 à f^s peut être exprimé par :

$$f^s H + c_p (T_L - T) \qquad |12|$$

Par la suite, nous avons adopté une valeur de 3000 cal/mole pour H et une valeur de 10 cal.mol^{-1}.K^{-1} pour c_p. En fin de solidification, c'est-à-dire pour des "besoins thermiques" de plus de 2000 cal/mole, la perméabilité de la structure dendritique de solidification à la circulation de liquide est légèrement supérieure pour les échantillons solidifiés à partir de l'alliage vierge *(Fig. 9)*.

La deuxième grandeur contrôlant la formation de la microporosité, celle liée à la cinétique de croissance du solide :

$$-\frac{df^s}{dT}\cdot\left(1-\frac{H}{c_p}\frac{df^s}{dT}\right)^{-1}$$

a été calculée à partir des courbes tracées sur la *figure 6*. Cette grandeur, qui permet de comparer le champ des vitesses d'écoulements du fluide, est en général plus élevée dans le cas de l'alliage recyclé *(Fig. 10)*.

Les comparaisons présentées sur les *figures 9 et 10* laissent prévoir une perte de charge plus élevée pour l'écoulement du liquide à travers la structure de solidification pour l'alliage recyclé. Ces résultats de laboratoire, bien que l'écart entre les valeurs expérimentales comparées soit souvent du même ordre que les incertitudes attachées aux mesures, semblent apporter une explication de la propension plus marquée à la microporosité pour l'alliage recyclé.

Il convient de répéter cette comparaison sur d'autres couples d'alliages et aussi de s'intéresser aux phases mineures qui précipitent à la solidification, les carbures essentiellement, avant de conclure à la généralité de l'approche proposée.

5.3. Observations sur la précipitation des carbures

Au cours de cette étude, la morphologie des carbures n'a pas été étudiée avec autant de détail que dans les travaux de nos partenaires du programme COST 50 qui concluent à une morphologie plus massive des carbures dans l'alliage recyclé (coulées industrielles).

Dans les solidifications dirigées (T.S.D.), la taille des carbures approche 10 µm et leur morphologie est "massive". La taille élevée des carbures dans les alliages solidifiés au laboratoire par rapport à celle mesurée dans les pièces de fonderie est une conséquence des différences déjà mentionnées entre la fonderie équiaxe et la solidification dirigée au niveau du gradient et de la vitesse du "front" de solidification (§ 4).

Dans le but de savoir si, dans les conditions du laboratoire, l'influence du recyclage sur la morphologie des carbures n'était pas masquée par l'influence d'impuretés apportées par l'argon au cours des solidifications unidirectionnelles ou par le choix d'une vitesse de tirage trop faible, de nombreuses T.S.D. ont été effectuées en variant la vitesse de tirage de 0,5 à 8 mm/mn sur l'alliage IN 100 vierge. Cela n'a pas fait sensiblement varier la fréquence de formation de carbures de forme élancée, dite en écriture chinoise *(Fig. 5b)*. Le passage de la solidification sous argon à la solidification sous vide n'a pas non plus d'effet sensible sur la microstructure des carbures. Une étude plus fine de la morphologie des carbures est en cours pour mettre en évidence une éventuelle corrélation entre densité de micropores et morphologie des carbures comme cela a été avancé par différents auteurs [11].

6 - RESULTATS COMPLEMENTAIRES AVEC D'AUTRES ALLIAGES IN 100 OU Mar M 002

6.1. Alliages IN 100

Une étude avec un autre couple d'alliages IN 100, vierge et recyclé, sélectionnés par une deuxième fonderie de superalliages montre les mêmes variations au niveau des courbes f^L (T) entre alliage vierge et recyclé *(Fig. 11)* que celle déjà mise en évidence sur la *figure 6*.

Ce deuxième ensemble de résultats conforte l'hypothèse que la tendance à la microporosité et la forme de l'évolution en fonction de la température de la fraction solidifiée sont liées. Il conforte donc l'interprétation théorique simplifiée qui a été donnée en terme d'écoulement du liquide dans la structure dendritique.

Quel est le mécanisme responsable du changement d'allure des courbes f^L (T) après recyclage de l'alliage ? L'azote est l'élément le plus "suspecté" : il est susceptible d'affecter la composition des carbures [12][13] et le partage des éléments entre solide et liquide. Une fois connu le coefficient de partage entre liquide et phases solides (γ, carbures) et la relation entre la température et la composition du liquide à l'équilibre, il est possible de calculer f^L (T) en faisant des hypothèses sur la diffusion des éléments dans le liquide et le solide [5][14]. De tels calculs sont en cours dans le cas du recyclage mais aucune conclusion ne peut encore être avancée.

6.2. Alliages Mar M 002

Des alliages, vierge et recyclé, ont été sélectionnés et ont fait l'objet d'études de laboratoire similaires à celles décrites pour l'IN 100.

Les deux alliages étudiés en A.T.D. et T.S.D. sont très peu différenciés, les courbes fraction liquide en fonction de la température en particulier sont très proches *(Fig. 12)*. Dans ce cas, on n'a pas de grande différence de tendance à la formation de microporosités associée au retrait de solidification entre alliages vierge et recyclé.

7 - CONCLUSION

Les techniques de laboratoire utilisées semblent capables de différencier le déroulement de la solidification d'un alliage recyclé dans le cas des IN 100, mais pas dans le cas des Mar M 002. En fonderie, l'expérience industrielle semble conclure à une meilleure adaptation du Mar M 002 que de l'IN 100 au recyclage.

Il semble donc que les études de laboratoire, en particulier celles de la morphologie d'interface s/l, fournissent un indice fidèle de la tendance à la microporosité pour deux alliages du même type, mais différents seulement par le fait d'avoir été recyclé ou non. L'interprétation apportée ici, en termes d'hydrodynamique dans la zone pâteuse en fin de solidification, complète celle proposée par d'autres auteurs [5][15]. Il importe aussi de tenter de rapprocher cette interprétation des corrélations microporosité/microstructure et des résultats d'analyse des carbures par une modélisation des réactions de solidification.

REFERENCES

1 **P. VIATOUR et al**
"Casting Conditions, Microstructure and Creep Properties of Mar M 002 Blades" in "High Temperature Alloys for Gas Turbines", Liège 1978, Ed. Coutsouradis et al., Applied Science Publishers (1978) p. 875-892.

2 **K. HARRIS et al**
"The Influence of Nitrogen and Oxygen on the Castability of IN 100". Publication de la Cannon-Muskegon Corporation (1976).

3 **D. ABLITZER, J. DRIOLE et al**
Rapport de fin d'étude COST 50 - Round III (à paraître en 1984).

4 **T.S. PIWONKA et M.C. FLEMINGS**
"Pore Formation in Solidification", Trans AIME 236 (1966) p. 1157.

5 **R. MEHRABIAN, M. KEANE et M.C. FLEMINGS**
"Interdendritic Fluid Flow and Macrosegregation ; Influence of Gravity", Met. Trans. 1 (1970) p. 1209-1220.

6 **R. MURAKAMI, A. SHIRAISHI et T. OKAMOTO**
"Interdendritic Fluid Flow Normal to Primary Dendrite Arms in Cubic Alloys", Acta Met. 31 (1983) p. 1417-1424.

7 **L. GUICHOU, G. LESOULT, G. LAMANTHE, R. HAMAR, J.M. THERET et E. BACHELET**
"Microporosity Formation in Investment Casting of Nickel Base Superalloys : Metallurgical Effects, Thermal Modelling and Foundry Assessment" in "High Temperature Alloys for Gas Turbine 1982", Liège 1982, Ed Brunetaud et al., D. Reidel Publ. Co. (1982) p. 955-973.

8 **T.W. CLYNE**
"Numerical Modelling at Directional Solidification of Metallic Alloys", Metal Science 16 (1982) p. 441-450.

9 **J. DAOXIN, J. LECOMTE-BECKERS et L. HABRAKEN**
"Modelling Micropore Formation During Directional Solidification", C.R.M. Report n° 59 (1982) p. 26-33.

10 **R. COOK, A.G. GUTHRIE**
"Factors Affecting Foundry Characteristics of Nickel-Rich Alloys for High-Temperature Applications", Foundry Trade Jl (May 1966) p. 686-689.

11 **M.S. DEAN**
"Porosity in IN 100, a Nickel Superalloy", Master of Science. University of Bristol (October 1977).

12 **Dr. P.N. QUESTED and K.M. RAINE**
"Phase Identification by Interference Film Microscopy", Metals and Materials (October 1981) p. 37.

13 **M. LAMBERIGTS, J.M. THERET, J.M. DRAPIER**
"Relations Between Chemistry, Solidification Behaviour and Microstructure in IN 100" in "High Temperature Alloys for Gas Turbines 1982", Liège 1982, Ed. Brunetaud et al, D. Reidel Publ. Co. (1982) p. 747-758.

14 **L. GUICHOU**
"Solidification et sensibilité à la microporosité d'alliages de fonderie à base de nickel" Thèse Docteur-ès-Sciences Physiques INPL (29 Avril 1983) Travaux réalisés au Centre des Matériaux de l'Ecole des Mines de Paris.

15 **L. GUICHOU, F. LAVAUD et G. LESOULT**
"Influence of the Chemical Composition of Nickel-Base Superalloys on their Solidification Behaviour and Foundry Performance" in "Superalloys 1980", Seven Springs (1980), Ed. J.K. Tien et al., A.S.M. Publ. (1980) p. 235-244.

REMERCIEMENTS

Les auteurs tiennent à exprimer leur gratitude au Ministère de l'Industrie et de la Recherche pour le soutien de cette étude, et leurs remerciements aux partenaires européens du programme COST 50 pour la fourniture des matériaux, les échanges d'informations et les discussions fructueux. Messieurs THERET et MORBIOLI de la S.N.E.C.M.A et Messieurs GUICHOU, POSTLETHWAITE, MIDDLETON et HALAGAN, chercheurs au Centre des Matériaux sont remerciés pour leur contribution à cette étude.

TABLEAU I : COMPOSITION CHIMIQUE DES ALLIAGES *

	IN 100 Première série		IN 100 deuxième série		Mar M002	
	Vierge	Recyclé	Vierge	Recyclé	Vierge	Recyclé
C	0,17 %	0,16 %	0,18 %	0,16 %	0,13 %	0,16 %
C_2	9,74	9,69	9,28	9,30	8,9	9,11
Mo	3,05	2,99	3,00	2,97	-	-
V	0,95	0,95	0,81	0,77	-	-
Ti	4,64	4,64	4,72	4,38	1,31	1,52
Al	5,49	5,39	5,54	5,59	5,59	5,54
Co	15,00	14,9	14,44	14,12	10,1	10,09
Ta	-	-	-	-	2,74	2,68
W	-	-	-	-	10,2	9,91
Hf	-	-	-	-	1,64	1,61
O_2	8 ppm	4 ppm	5 ppm	6 ppm	5 ppm	
N_2	4 ppm	10 ppm	7 ppm	17 ppm	6 ppm	13-16 ppm

* Les alliages IN 100 deuxième série et Mar 002 ont été utilisés pour les résultats complémentaires.

TABLEAU II : VALEURS MOYENNES ET ECART TYPE (3 ESSAIS) DES TEMPERATURES CARACTERISTIQUES DE L'IN 100 PREMIERE SERIE

Alliage	T_L °C	T_C °C	T_S °C
Vierge	1322 ± 2	1306 ± 2	1245 ± 2
Recyclé	1322 ± 2	1311 ± 2	1243 ± 2

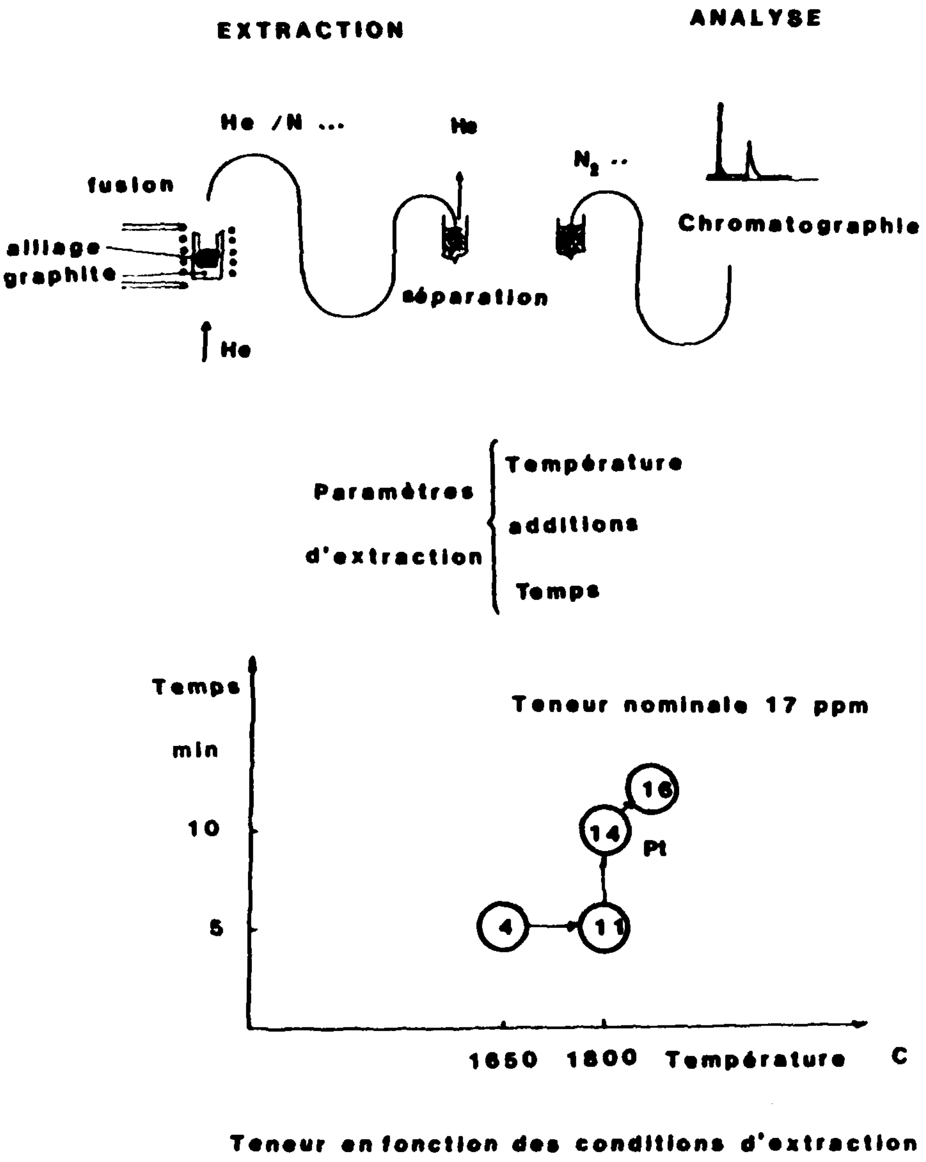
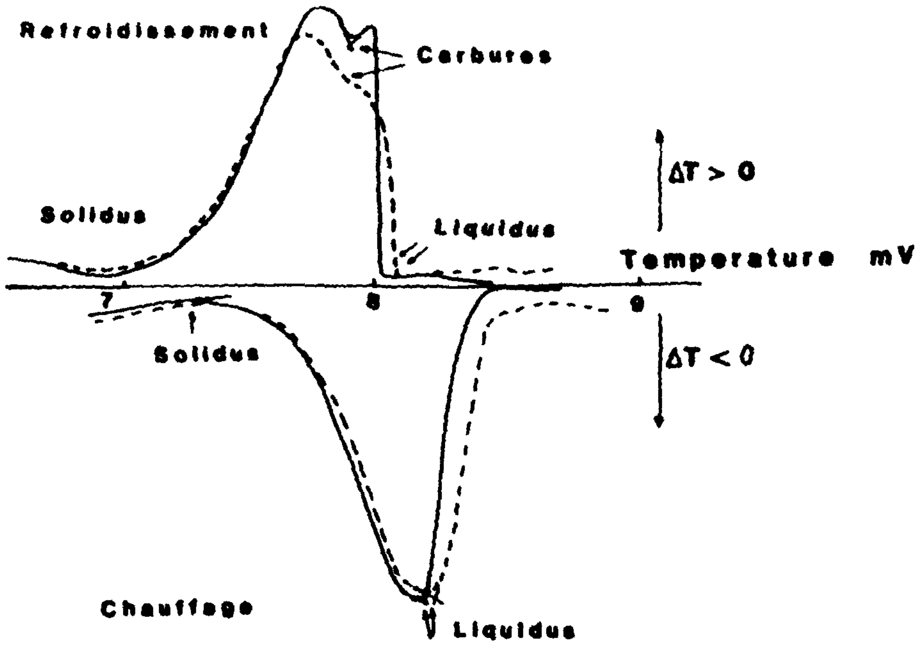


FIGURE 1 : Représentation schématique du dispositif expérimental d'analyse de l'azote et principaux résultats de l'étude.



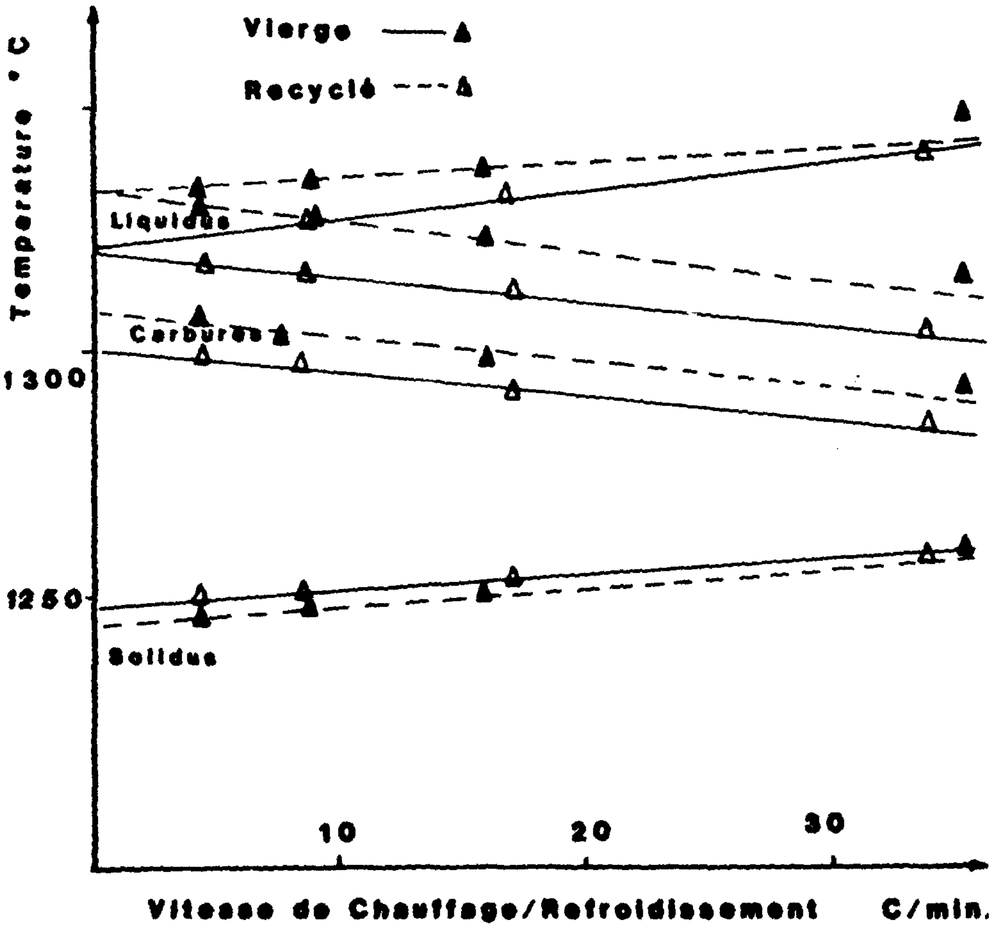


FIGURE 2 : Exemples de thermogrammes A.T.D.

FIGURE 3 : Exemple de la procédure d'extrapolation des temperatures caractérisiques à vitesse nulle.

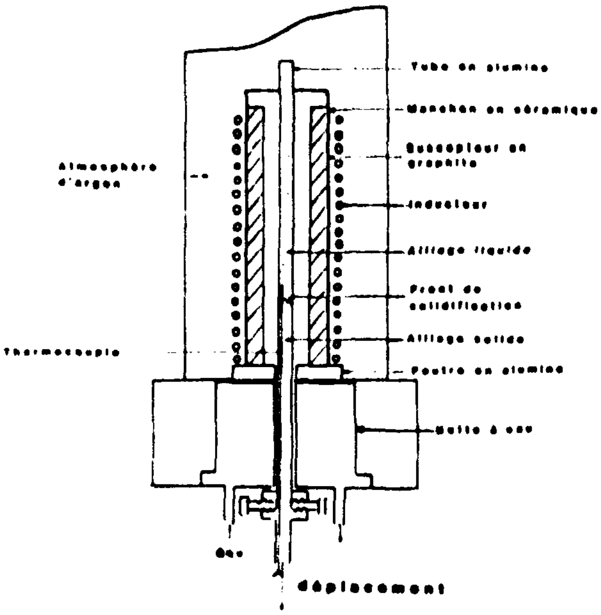


FIGURE 4 : Installation permettant de faire des trempes en cours de solidification dirigée (T.S.D.)

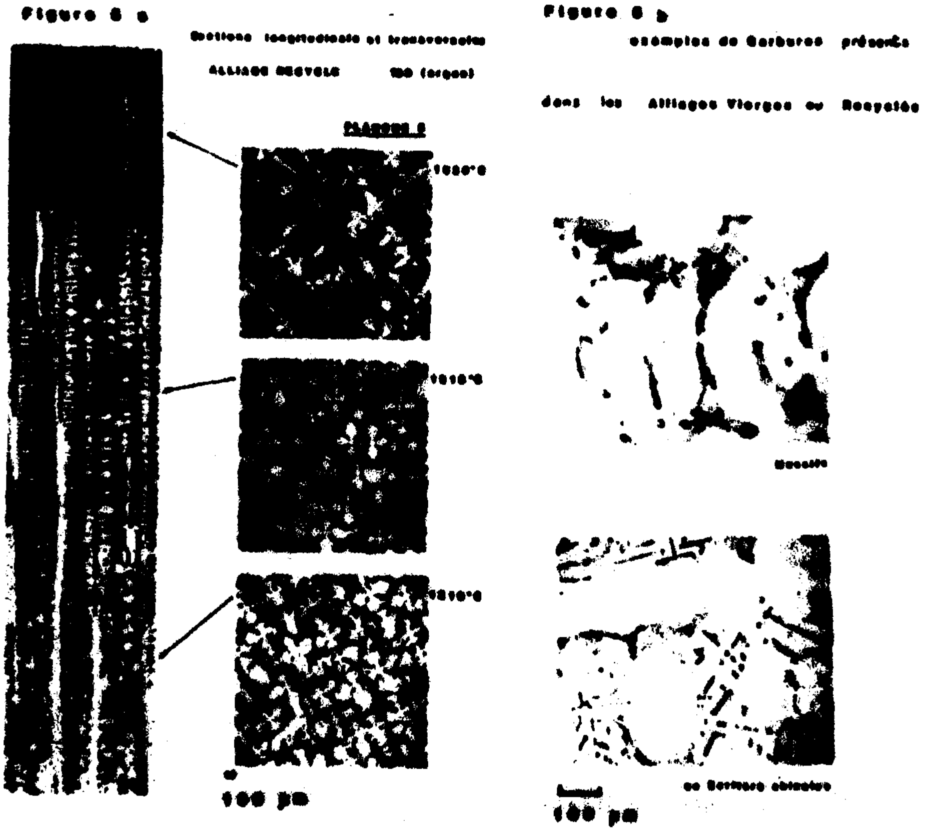


FIGURE 5 : Exemples de la microstructure d'alliages IN 100 trempés au cours de la solidification dirigée.

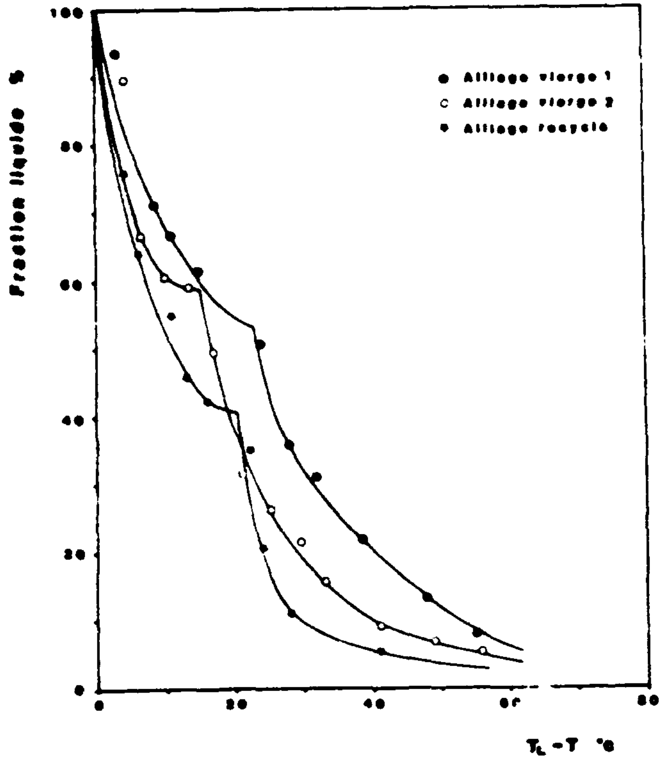


FIGURE 6 : Evolution de la la fraction liquide en fonction de la température. 2 élaborations T.S.D. avec alliage vierge - 1 avec alliage recyclé.

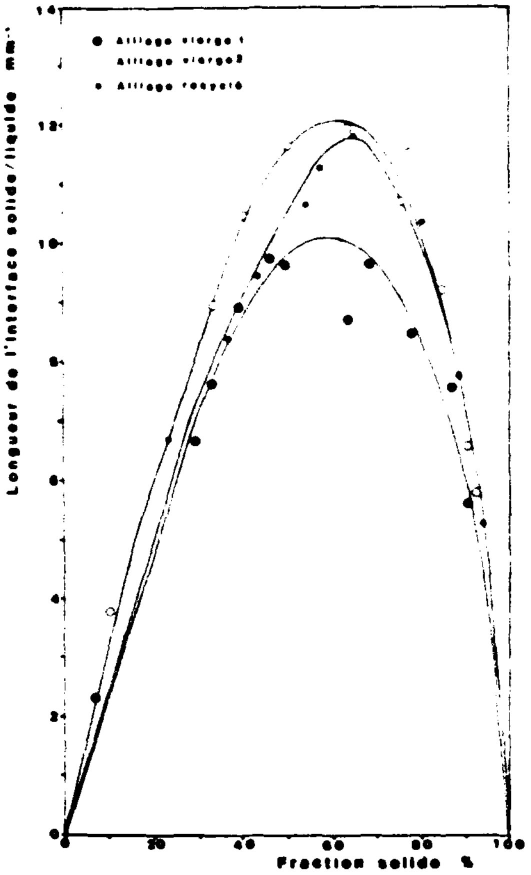


FIGURE 7 : Surface spécifique de l'interface solide/liquide.

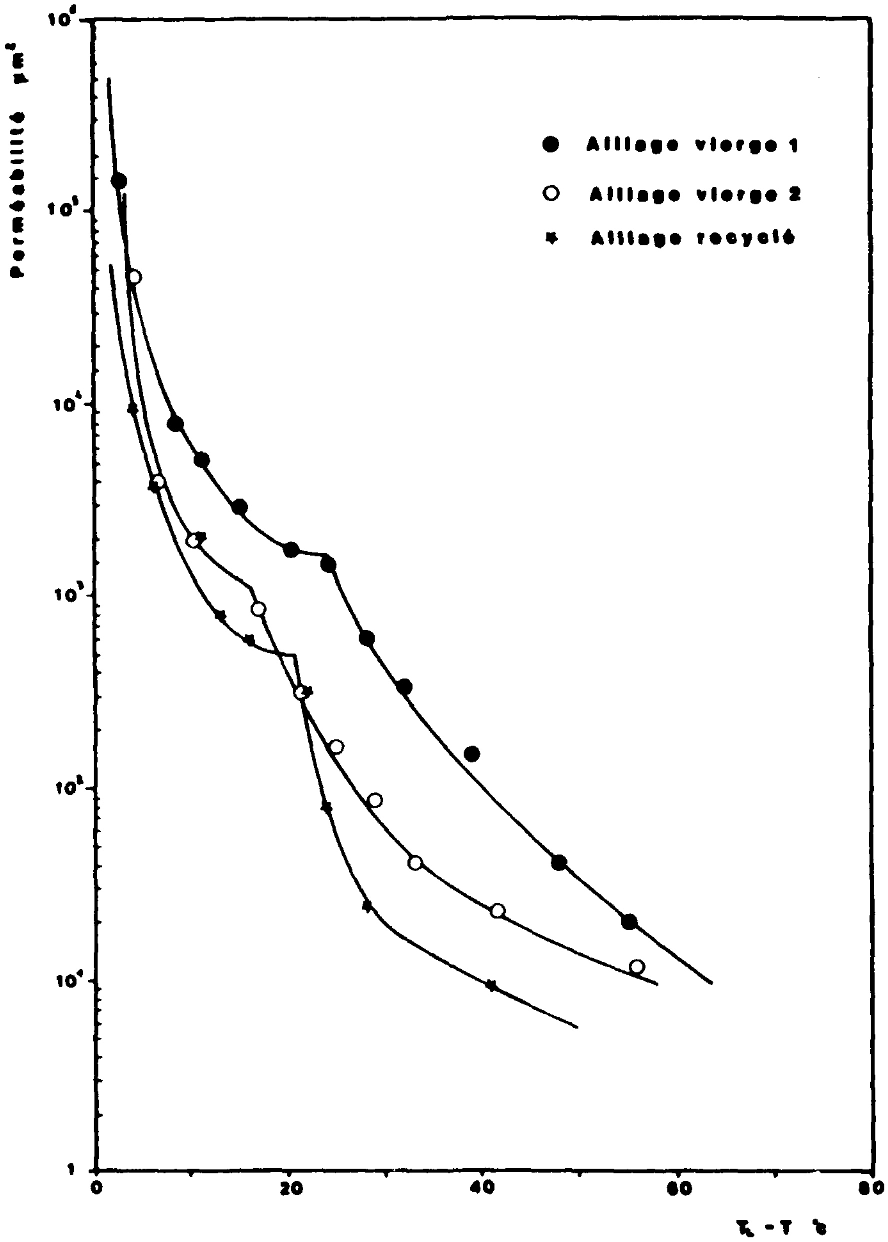


FIGURE 8 : Perméabilité spécifique du réseau dendritique en fonction de la température.

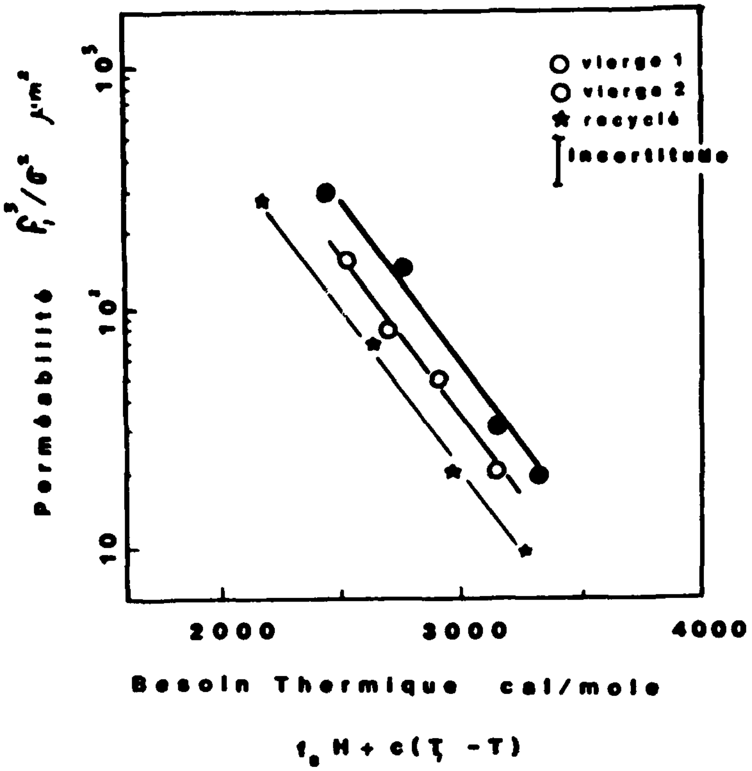


Figure 9 : Perméabilité relative en fin de solidification du réseau interdendritique liquide en fonction de la quantité de chaleur extraite de l'alliage (besoin thermique) depuis le début de la solidification.

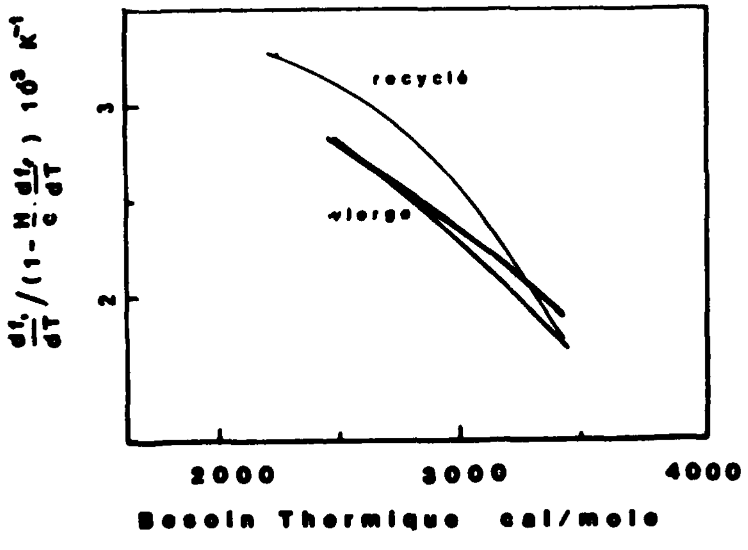


FIGURE 10 : Variation en fin de solidification du terme lié à la dérivée en fonction de la température de la fraction liquide, qui conditionne la vitesse de circulation du liquide.

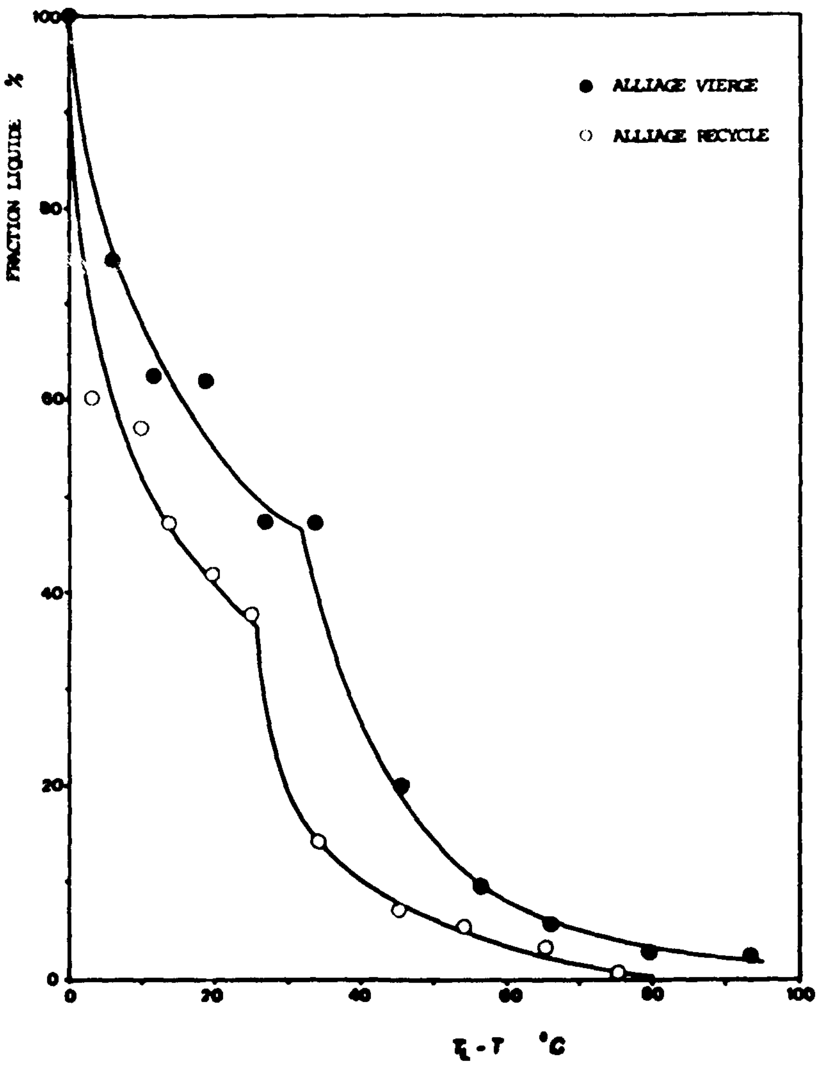


FIGURE 11 : Fraction liquide en fonction de la température
(deuxième série d'alliages IN 100)

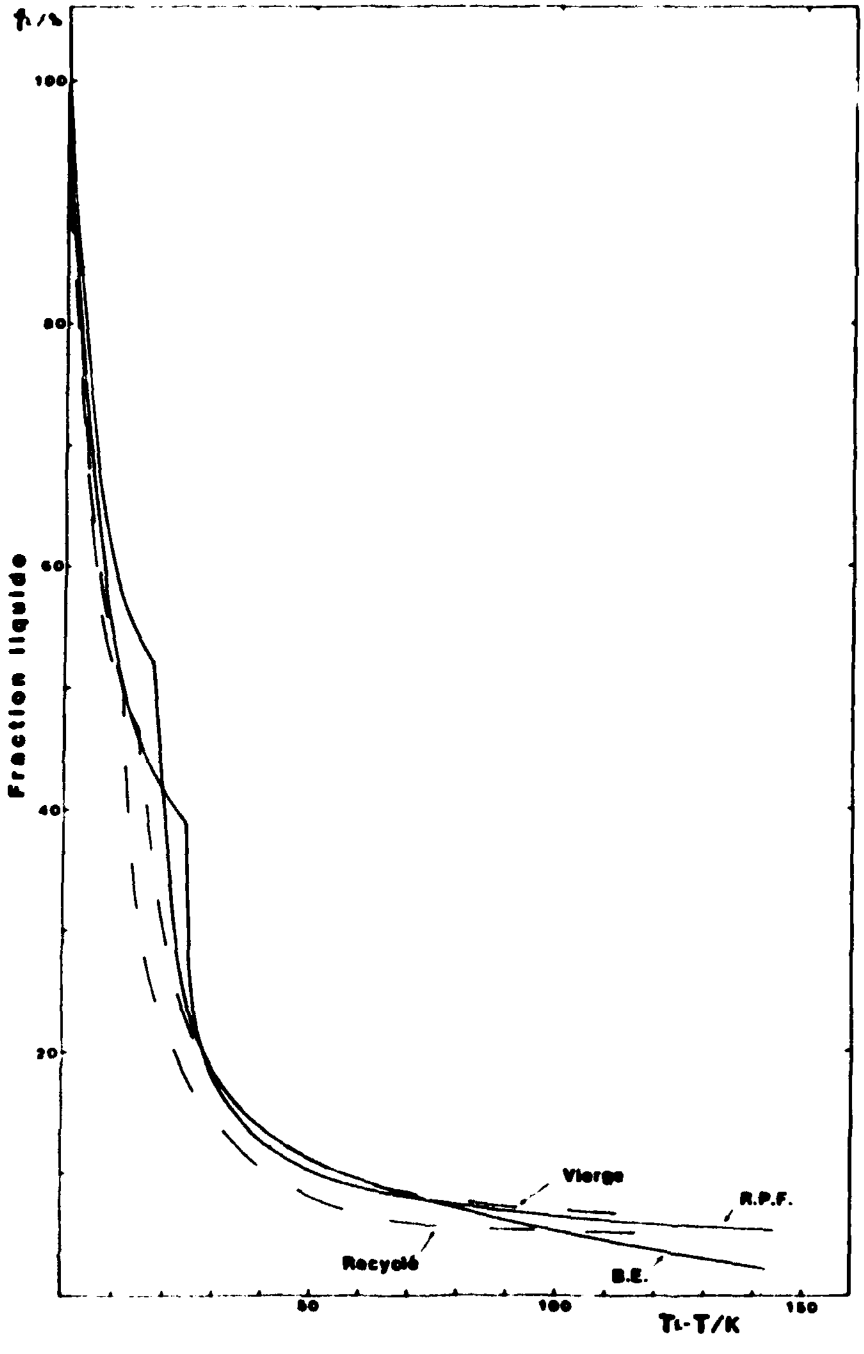


FIGURE 12 : Fraction liquide en fonction de la différence entre la température de liquidus et la température considérée. Alliage Mar M200 vierge, recyclé plusieurs fois R.P.F. et refondu B.E.

MISE EN OEUVRE DE SUPERALLIAGES DE REEMPLOI EN FONDERIE DE PRECISION

M. LAMBERIGTS, Chef Sce Adjoint, C.R.M., Rue E. Solvay, 11 - B 4000 LIEGE
J.M. DRAPIER, Chef de Secteur, F.N., Division Formétal, B 4400 HERSTAL

Le recyclage des chutes de fonderie ne se justifie pas uniquement par la crainte de difficultés d'approvisionnement en matières premières métalliques ou par le souci de préserver les réserves naturelles relativement limitées pour certaines d'entre elles : il s'impose au fondeur pour minimiser ses coûts. Le recyclage peut cependant conduire à une détérioration de la propreté métallurgique des superalliages de fonderie de précision et à une certaine contamination chimique pouvant être dommageable pour le comportement en service des pièces moulées. Il ne peut donc être introduit qu'après contrôle soigneux de toutes ses conséquences.

L'étude vise à évaluer l'influence du recyclage sur la composition (éléments en traces), le comportement à la solidification, la microstructure de coulée, et les propriétés mécaniques d'emploi de divers alliages de nickel tels l'IN 100, l'IN 738 et le Mar-M-002 ou de cobalt, par exemple le X 45 et le WI 52. Elle met un accent particulier sur le contenu inclusionnaire et sur la tendance à la microporosité. Dans ce dernier domaine, elle évalue l'incidence technique et économique d'un éventuel cycle de compression isostatique à chaud.

INTRODUCTION

Malgré de nombreux avantages actuellement bien connus, la fonderie à modèles perdus pour applications aéronautiques doit chercher les voies d'une meilleure économie des matières métalliques qu'elle utilise. Certaines études récentes (1,2) conduisent en effet à penser que les pièces en alliages de nickel ou de cobalt moulées de précision aux Etats-Unis au cours de l'année 1976 ne représentent que 39.6% du poids de métal effectivement consommé en fonderie. Compte tenu du rendement global de l'élaboration de ces alliages, la part vraiment utile des matières métalliques mises en oeuvre n'est au plus que de 31.8%.

Les tentatives de récupération de la plus grande part possible du solde se justifient autant par sa valeur intrinsèque que par les possibilités d'épuisement de certaines réserves naturelles ou le danger de difficultés d'approvisionnement que pourraient susciter des remous politiques dans les pays producteurs ou des mouvements spéculatifs sur les marchés de matières premières.

Une telle récupération sans déclassement implique que les chutes de fonderie ou d'aciérie à recycler respectent certains critères de qualité. Pour ce qui concerne la fonderie de précision, il ne peut s'agir que des parties les plus propres des masselottes et de certaines pièces rebutées pour non conformité dimensionnelle ou pour d'autres raisons n'affectant pas la qualité métallurgique de l'alliage. Ces chutes sélectionnées doivent être réexpédiées à l'aciériste qui les utilisera pour élaborer des coulées-mères partiellement ou totalement recyclées en les soumettant à des procédures permettant d'en garantir la propreté métallurgique(3).

Il est évident que les fonderies qui sont arrivées à dominer les problèmes liés au recyclage de leurs chutes, tant dans leurs aspects métallurgiques que dans ceux de l'organisation interne ou de la gestion, se présentent aux clients dans une position concurrentielle avantageuse. Les coûts liés à leurs approvisionnements en alliages peuvent en effet être considérablement réduits.

Le recyclage des superalliages pose cependant d'importants problèmes techniques. Il conduit en effet généralement à une augmentation de la teneur en gaz (azote et oxygène), en raison de certaines difficultés d'affinage à la refusion, et en fonction de la qualité des chutes de fonderie ou d'aciérie réintégrées à la charge. Le recyclage tend également à augmenter les teneurs en silicium et en zirconium, par suite d'une contamination des chutes de fonderie par les moules-carapaces. Il présente en outre un danger d'augmentation de la teneur de certains éléments en trace (Bi, Pb, Fe,...), par suite de l'éventuelle utilisation de poudres exothermiques. Enfin, il tend à augmenter le contenu inclusionnaire, malgré les nombreuses précautions prises en aciérie et en fonderie pour lutter contre ce défaut.

Le but de la présente communication est de faire état de l'expérience acquise à la Division Formétal de la Fabrique Nationale sur le recyclage de divers alliages de nickel ou de cobalt utilisés pour le développement ou la fabrication d'aubes de turbines à gaz aéronautiques ou industrielles. Elle aborde successivement l'examen des conséquences métallurgiques et pratiques du recyclage et la critique des remèdes susceptibles d'en supprimer ou d'en atténuer les effets néfastes.

CONSEQUENCES DU RECYCLAGE

a. Composition et comportement à la solidification

Il est généralement admis qu'une bonne part des contaminations chimiques dont les chutes de fonderie sont le siège se trouvent concentrées au voisinage immédiat de leur peau. C'est notamment le cas de l'indésirable enrichissement en azote qui risque d'être plus important lorsque les chutes sont constituées de pièces rebutées à grande surface spécifique plutôt que de masselottes ou de barreaux d'alimentation plus massifs. Une telle concentration superficielle est également constatée pour les éventuelles augmentations des teneurs en silicium et en zirconium pouvant dériver d'interactions entre le métal liquide et le moule-carapace de première utilisation.

D'autres contaminations provenant de l'utilisation de poudres exothermiques sont au contraire concentrées au niveau du cône de coulée et peuvent être éliminées par simple étêtage de celui-ci.

La Figure 1 confronte à titre d'exemple les teneurs en azote et en fer de quelques coulées-mères d'IN 100, partiellement (50%) ou totalement recyclées, de diverses provenances à celles de coulées vierges comparables. Les distributions de ces teneurs sont assimilables à des lois normales pour les coulées-mères vierges, indiquant qu'elles proviennent d'un lot statistiquement homogène. Celles des coulées recyclées en sont suffisamment éloignées pour qu'on puisse conclure à la tendance globale à l'enrichissement introduite par le recyclage proprement dit. Cette tendance est relativement faible pour l'azote, puisque le seuil de signification du test de Kolmogorov-Smirnov utilisé pour la comparaison des deux populations est de 0.124 ; elle est par contre beaucoup plus nette dans le cas du fer (seuil de signification inférieur à 0.01).

L'existence de telles tendances à la contamination chimique doit être considérée dans son aspect statistique global et n'implique évidemment pas que toutes les coulées recyclées sont individuellement enrichies en azote et en fer par rapport à n'importe quelle coulée-mère vierge. Il existe des coulées recyclées particulières nettement meilleures à cet égard que la plupart des coulées vierges.

Ces tendances laissent cependant entrevoir la possibilité de modifications du comportement à la solidification pouvant affecter la microstructure finale des pièces coulées dont les conditions de fabrication devraient peut-être être modifiées pour en assurer la qualité métallurgique.

La Figure 2 compare à ce propos les moyennes des températures de transformation mesurées au refroidissement à 15°C/min depuis l'état liquide pour des groupes de coulées-mères vierges ou recyclées de divers alliages de nickel fréquemment utilisés en fonderie de précision pour applications aéronautiques (René 77, IN 100 et Mar-M-002). Compte tenu de la dispersion naturelle de telles mesures, les différences de comportement observées entre qualités de matières sont très faibles et souvent sans aucune signification statistique. L'observation la plus intéressante qu'il est possible de faire à partir de cette figure est que le recyclage n'entraine pas nécessairement l'élargissement de l'intervalle de solidification (différence de température entre le liquidus et la transformation eutectique), souvent considéré comme un moyen d'évaluation de la tendance naturelle des alliages à la microporosité.

b. Microstructure.

A conditions de coulée égales, le recyclage des superalliages de nickel peut induire une nette altération de la distribution des carbures observés sur pièces (4,5). Cette tendance, également mise en évidence pour le Mar-M-002, est illustrée aux Figures 3 et 4 dans le cas de l'IN 100. Elles comparent respectivement les distributions granulométrique et morphologique des carbures observés le long d'une coupe particulière d'aubes moulées dans des conditions figées au moyen de trois coulées-mères vierges et d'une coulée-mère recyclée à 50%.

Ces figures donnent en fait les enveloppes des courbes de distribution individuelles déterminées par métallographie quantitative sur plusieurs aubes pour chaque coulée-mère. Elles fournissent de ce fait une idée de la précision des mesures et partant, de la signification statistique des différences observées.

Il découle de leur examen que le recyclage favorise la coalescence des carbures, puisqu'il conduit à déporter vers les grandes valeurs les courbes de distribution de leurs tailles (S représente la section droite des carbures dans le plan de coupe métallographique) et de leurs facteurs de forme S/P^2 (définis par le rapport de la section droite au carré du périmètre; ce facteur est nul dans le cas de carbures idéalement effilés et vaut 0.0796 dans le cas de carbures parfaitement ronds).

Contrairement à ce qu'on pourrait penser, cette évolution de la distribution des carbures ne semble pas correspondre à une altération de leur composition moyenne (5). Les analyses chimiques quantitatives locales effectuées au moyen d'une microsonde équipant un microscope électronique à balayage montrent en effet que les teneurs des éléments constitutifs principaux des carbures forment des groupes homogènes indiscernables en fonction de la qualité de l'alliage IN 100 utilisé. (Figure 5).

Il faut cependant insister sur la délicatesse de telles mesures qui risquent toujours d'être influencées par des effets de matrice, même lorsqu'elles sont limitées aux plus gros des carbures observés : la teneur en nickel estimée peut en effet atteindre des valeurs très élevées (jusqu'à 8%).

Une autre caractéristique structurale risquant d'être affectée par le recyclage est le taux de microporosités présentes dans la structure. La Figure 6, relative à une aube rotorique de turbine aéronautique coulée en alliage IN 738 C, montre en effet que le recyclage risque globalement d'augmenter le taux de rebut pour ce genre de défaut.

Il faut cependant se garder de penser qu'il s'agit là d'une tendance inéluctable, dans la mesure où certaines coulées-mères entièrement recyclées peuvent présenter des comportements comparables ou même supérieurs à celui de la plupart des coulées-vierges. C'est ce que montre la Figure 7 qui classe des coulées-mères d'IN 100 vierges et recyclées à 50% ou 100% en fonction du taux de rebut pour microporosité dans le cas d'aubes particulières (6). Les deux qualités d'alliages n'y paraissent pas vraiment discernables l'une de l'autre, même si les meilleures caractéristiques de santé interne sont obtenues dans le cas des coulées-vierges.

Le recyclage n'entraine donc pas nécessairement une dégradation de la santé interne, mais doit plutôt être considéré comme un facteur d'aggravation possible de défauts en relation directe avec certaines caractéristiques du comportement à la solidification. Dans le cas de l'IN 100, il est par exemple établi que la tendance à la microretassure et la fraction volumique des carbures augmentent en même temps(5) : pour une aube particulière, cette fraction est d'environ 1.3% pour les meilleures coulées-mères et de 1.7% pour les plus mauvaises. La densité moyenne des carbures est également plus élevée pour les coulées-mères à forte tendance à la microretassure (environ 1200mm^{-2}) que pour les meilleures ou celles de qualité moyenne (environ 800 mm^{-2}).

Ce qui vient d'être dit pour le taux de microporosité peut pratiquement être répété en ce qui concerne le contenu inclusionnaire. La Figure 8, relative à une pièce structurale en alliage de cobalt WI 52, montre que le recyclage qui, dans ce cas, n'affecte pas la fraction volumique inclusionnaire, peut être la cause d'une augmentation de la taille des inclusions du type sulfure. Dans le cas des alliages contenant certains éléments très réactifs, le risque de présence d'inclusions d'oxydes augmente avec le recyclage. Cela est illustré à la Figure 9 montrant une inclusion d'oxyde de Hafnium présente dans une coulée-mère de Mar-M-002 recyclée à 50%. De telles inclusions peuvent provenir de la réduction par le Hafnium des réfractaires utilisés lors de l'élaboration ou de la refusion, voire de ceux qui constituent les moules-carapaces employés en fonderie. Leur grand inconvénient réside dans le fait que leur finesse et leur densité les rendent pratiquement indétectables par radiographie X.

On peut cependant se demander si de telles inclusions filiformes risquent vraiment d'être préjudiciables aux propriétés d'emploi.

c. Propriétés d'emploi

Les altérations de composition et de microstructure favorisées par le recyclage des superalliages utilisés en fonderie de précision pour applications aéronautiques peuvent laisser craindre une certaine dégradation des propriétés finales d'emploi. Les Figures 10 et 11 montrent cependant qu'une telle crainte n'est pas fondée dans le cas des propriétés de traction à température ambiante mesurées sur un grand nombre de coulées d'IN 738 C ou d'IN 100 à taux de recyclage variable entre 0 et 100%. A quelques exceptions près, par ailleurs indépendantes de la qualité d'alliage considérée, la plupart des coulées-mères satisfont en effet aux exigences des spécifications en vigueur, pour les applications visées. La Figure 12 pour laquelle chaque point expérimental caractérise une coulée-mère, montre que le recyclage ne peut être tenu pour responsable que d'une baisse quasi négligeable du niveau moyen des propriétés ou d'une très légère augmentation de leur variation de coulée-mère à coulée-mère.

La Figure 13 montre par ailleurs que les craintes de dégradation systématique des propriétés de fluage-rupture de l'IN 738C sont également injustifiées. Si certaines coulées-mères recyclées peuvent en effet paraître plus faibles à cet égard que les vierges, la plupart d'entre elles satisfont cependant aux exigences des spécifications. La Figure 14, construite sur le même schéma que la Figure 12, montre d'ailleurs que dans le cas d'éprouvettes d'IN 100, le danger de dégradation existe principalement pour la durée de vie en fluage-rupture à température modérée (760°C/585MPa).

REMEDES PROPOSES CONTRE LES DEFAUTS INTRODUITS PAR LE RECYCLAGE.

Ce qui précède indique que le risque de dégradation introduit par le recyclage concerne plus le taux de microporosités et le contenu inclusionnaire que les propriétés mécaniques d'emploi des pièces coulées. C'est donc sur ces caractéristiques de santé métallurgique que les efforts d'amélioration doivent principalement porter.

En ce qui concerne les microporosités, il y a tout d'abord lieu de contrôler strictement la composition chimique des coulées-mères partiellement recyclées au niveau de tous les éléments en faibles teneurs ou en traces qui peuvent exercer une certaine influence sur la solidification dendritique et la précipitation eutectique (Si, Zr, Hf, N_2,...). Cet objectif peut être approché par une sélection soignée et un conditionnement approprié des chutes de fonderie à recycler, de façon à éviter les contaminations par les réfractaires utilisés pour la refusion et la coulée ou par d'éventuelles poudres exothermiques.

Les observations rapportées plus haut sur les relations entre la précipitation des carbures et le taux de microporosités dans des aubes moulées de précision en alliage IN 100 suggèrent d'étendre dans certains cas ce contrôle de la composition chimique à tous les éléments carburigènes (C, Ti, Nb, Mo, Cr,...) pour minimiser la fraction et la densité des carbures. Il y aurait cependant lieu de confirmer et de préciser ces relations structure-santé métallurgique pour améliorer l'efficacité de telles actions correctrices.

De toutes facons, les procédures de fusion, d'affinage et de coulée en aciérie doivent être adaptées pour tenir compte des caractéristiques et des besoins particuliers des coulées recyclées. Dans ce domaine, une collaboration technique approfondie s'impose certainement entre les fondeurs et les élaborateurs d'alliages.

Dans le cas où les précautions précédentes ne permettent pas d'éviter que le recyclage induise une détérioration de la santé métallurgique des pièces coulées, il est toujours possible de soumettre ces dernières à une compression isostatique à chaud. Un tel traitement est effectivement bien connu pour son aptitude à résorber les microporosités et les microretassures de coulée (7,8).

Il faut cependant prendre soin de bien adapter les conditions de cycle aux caractéristiques métallurgiques particulières du métal traité, pour éviter d'y induire des perturbations structurales éventuellement irrécupérables. La température de palier est à cet égard le premier paramètre à ajuster. Il est généralement admis qu'elle doit être choisie entre le gamma prime solvus et le solidus, pour permettre la fermeture facile des pores sous l'action de la pression extérieure, sans provoquer la fusion commençante ou les distorsions des pièces traitées (9). La Figure 15 donne, à titre d'illustration, les moyennes de ces températures de transformation mesurées au chauffage à vitesse constante (15°C/min) pour diverses coulées-mères vierges ou recyclées des alliages René 77, IN 100 et Mar-M-002.

Il est cependant important de faire une nette distinction entre les alliages qui ne peuvent être utilisés qu'après un traitement thermique comportant une mise en solution et un vieillissement et les autres, utilisables directement. Pour ces derniers, la microstructure du produit sera donc celle qui découlera du cycle de compression isostatique à chaud et certaines précautions doivent être prises pour en préserver les caractéristiques essentielles.

L'homogénéité de la précipitation gamma prime implique tout d'abord de dissoudre entièrement cette phase au chauffage ou pendant le maintien isotherme. Dans les cas où la présence d'une faible fraction de particules primaires est souhaitée, la température de palier doit au contraire se situer légèrement en-deçà du gamma prime solvus. Compte tenu de ces remarques et des températures de transformation moyennes indiquées à la Figure 15, la compression isostatique à chaud de l'IN 100 s'effectue habituellement à 1220°C et celle du Mar-M-002, à 1230°C. Dans le cas du René 77, la fenêtre de traitement est particulièrement large et offre beaucoup de liberté.

Les caractéristiques de reprécipitation de la phase gamma prime dépendent de la vitesse du refroidissement imposé en fin de cycle : Les Figures 16 et 17 montrent l'ampleur de cette influence dans les cas de l'IN 100 et du Mar-M-002. Des observations analogues peuvent d'ailleurs être faites en ce qui concerne la précipitation des carbures : dans le cas de l'IN 100 par exemple, on a pu montrer que la précipitation intergranulaire de carbures préjudiciables à la tenue en fluage-rupture ne peut être évitée que si les vitesses de chauffage et de refroidissement sont suffisamment élevées (3). Dans la majorité des cas examinés jusqu'à présent par les auteurs, les cycles HIP dont les conditions sont ajustées pour préserver les caractéristiques de la distribution de la phase gamma prime et de la précipitation des carbures conduisent également à une amélioration des propriétés mécaniques d'emploi (3,7,8).

Il serait cependant audacieux de croire que la compression isostatique à chaud constitue une espèce de panacée permettant de résorber tous les défauts de santé interne. Dans le cas de l'alliage de cobalt X-45 par exemple, les importantes microretassures observées dans une zone particulière de pièces structurales coulées à partir de métal recyclé à 100% présentaient des bords durcis par une fine précipitation de carbures $M_{23}C_6$ (M = Cr et W)(Fig.18). Une étude approfondie de la séquence de fusion de l'alliage par analyse thermique différentielle et par examens métallographiques sur échantillons trempés à diverses températures a montré que ces carbures ne se dissolvent complètement qu'au-dessus de 1300°C. La fusion commencante de l'alliage, associée à la dissolution de carbures massifs M_6C devenant notable dès 1345°C, divers échantillons ont été soumis à un cycle HIP à 1310°C pour tenter d'en résorber la microretassure.

Les temps de maintien à haute température généralement imposés lors de la compression isostatique à chaud sont malheureusement insuffisants pour assurer la diffusion des éléments constitutifs de ces carbures qui ont dès lors reprécipité aux mêmes endroits au cours du refroidissement. Les lèvres des microretassures ne se sont donc pas suffisamment adoucies et ont par ailleurs vraisemblablement été soumises à des contraintes internes engendrées par les variations volumétriques associées à la dissolution, puis à la reprécipitation des carbures. C'est sans doute pour ces raisons que, dans ce cas particulier, la compression isostatique à chaud dégrade la santé interne plutôt que de l'améliorer (Fig.19). Finalement, ce problème n'a pu être résolu en fonderie que par une modification du montage des grappes et le recours à des procédures particulières permettant d'éviter à la fois les microretassures et la précipitation fine de carbures $M_{23}C_6$ qui leur est systématiquement associée.

Enfin, il ne faut pas perdre de vue que le traitement de compression isostatique à chaud grève le coût de production, dans la mesure où il constitue un traitement supplémentaire à ajouter à la séquence de fabrication. Dans les cas où il peut efficacement résorber les défauts de santé interne, et compte tenu du taux de rebut caractéristique de l'état moulé, il peut cependant être avantageux, tant techniquement qu'économiquement, de l'imposer de façon systématique (3)(Fig.20).

En ce qui concerne les inclusions, il n'y a guère que le choix judicieux des réfractaires, le filtrage de l'alliage en aciérie et en fonderie et la sévère sélection des chutes à recycler qui puissent minimiser leur probabilité de présence. Il faut cependant admettre que cette probabilité ne peut jamais être nulle, même dans le cas d'alliages entièrement vierges.

Les filtres utilisables sont constitués de mousse céramique ou présentent une structure en nid d'abeille (3). Leur efficacité dépend évidemment des tailles relatives des inclusions à arrêter et des chenaux de passage. La Figure 9 montre à ce propos le cas d'une inclusion d'oxyde de Hafnium très petite, mais cependant arrêtée par un filtre en nid d'abeille disposé dans le cône de coulée d'une grappe d'aubes en alliage Mar-M-002 recyclé à 50%. La probabilité d'arrêt dépend évidemment de l'hydraulique au niveau du filtre, la viscosité du métal étant fonction des conditions de coulée.

CONCLUSIONS

Le recyclage des superalliages de nickel ou de cobalt utilisés en fonderie de précision pour applications aéronautiques s'impose pour diminuer les coûts de fabrication, pour éviter le déclassement de matières métalliques à haute valeur intrinsèque, pour éviter d'éventuelles difficultés d'approvisionnement et pour préserver les réserves naturelles.

Il peut cependant augmenter le risque d'une dérive de la composition au niveau des éléments en faibles teneurs ou des éléments en traces et il peut renforcer la probabilité de rebut pour défauts de santé interne ou pour contenus inclusionnaires trop élevés. Il ne s'agit pourtant pas d'une tendance inéluctable à la détérioration de la qualité, dans la mesure où des précautions peuvent être prises pour rendre les coulées-mères recyclées aussi satisfaisantes que la plupart des coulées vierges.

Ces précautions concernent les pratiques de fonderie, la sélection et le conditionnement des chutes à recycler et les procédures d'élaboration en aciérie. Dans le cas où de telles précautions restent insuffisantes, les coulées-mères recyclées peuvent tout de même être avantageusement exploitées, à condition d'utiliser des filtres en fonderie ou de soumettre les pièces à une compression isostatique à chaud finale. Ce dernier traitement ne constitue cependant pas une panacée universelle et ses conditions de réalisation doivent être soigneusement ajustées aux particularités métallurgiques du problème posé.

REFERENCES

1. L.R. CURWICK, W.A. PETERSEN, J.J. DE BARBADILLO, "Superalloy scrap-generation and recycling". Superalloys 1980, Edited by J.K. Tien, S.T. Wlodek, H. Morrow III, M. Gell and G.E. Maurer, AMS, 1980.
2. J.J. DE BARBADILLO. "Nickel-base superalloys; physical metallurgy of recycling". Metallurgical Transactions A, Vol. 14A, March 1983, p. 329.
3. J.M. DRAPIER. "Precision casting of turbine blades and vanes". High temperature alloys for gas turbines 1982, Edited by R. Brunetaud, D. Coutsouradis, T.B. Gibbons, Y. Lindblom, D.B. Meadowcroft and R. Stickler; D. Reidel Publishing Cy, 1982.
4. M. LAMBERIGTS, J.M. THERET, J.M. DRAPIER. "Relations between chemistry, solidification behaviour, and microstructure in IN 100", ibidem.
5. J. LECOMTE-BEKCERS, M. LAMBERIGTS. "Optimized use of complex superalloys in precision casting". Project 3B2 annual report ; European Concerted Action on Materials for Gas Turbines COST-50/ round III, 15 February 1983.
6. M. LAMBERIGTS (CRM). "Etude métallurgique de l'alliage IN 100 moulé", janvier 1981, Rapport CRM ML/FNF/81/2.
7. M. LAMBERIGTS, E. DIDERRICH, D. COUTSOURADIS, E. de LAMOTTE and J.M. DRAPIER."Effect of HIP on the microstructure of as-cast IN 713 LC turbine blades". AIME Annual Meeting, Las Vegas, February 24-25, 1980.
8. M. LAMBERIGTS, E. DIDERRICH, D. COUTSOURADIS, E. de LAMOTTE, J.M. DRAPIER and E. DERIDDER. "HIp'ing various cast engine components in nickel base superalloys". Superalloys 1980, Edited by J.K. Tien, S.T. Wlodek, H. Morrow III, M. Gell and G.E. Maurer. AMS, 1980.
9. G.E. WASIELEWSKI and N.R. LINDBLAD. "Elimintation of casting defects using HIP". MCIC Report 72-10, September 1972, p. D 1.

REMERCIEMENTS

La plupart des travaux rapportés ci-desus ont été effectués sous les auspices de l'IRSIA (Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture). Certains résultats dérivent de collaborations entre CRM, FN-Formétal et SNECMA ou d'une participation à l'action concertée COST-50 pour l'étude des matériaux pour turbines à gaz.

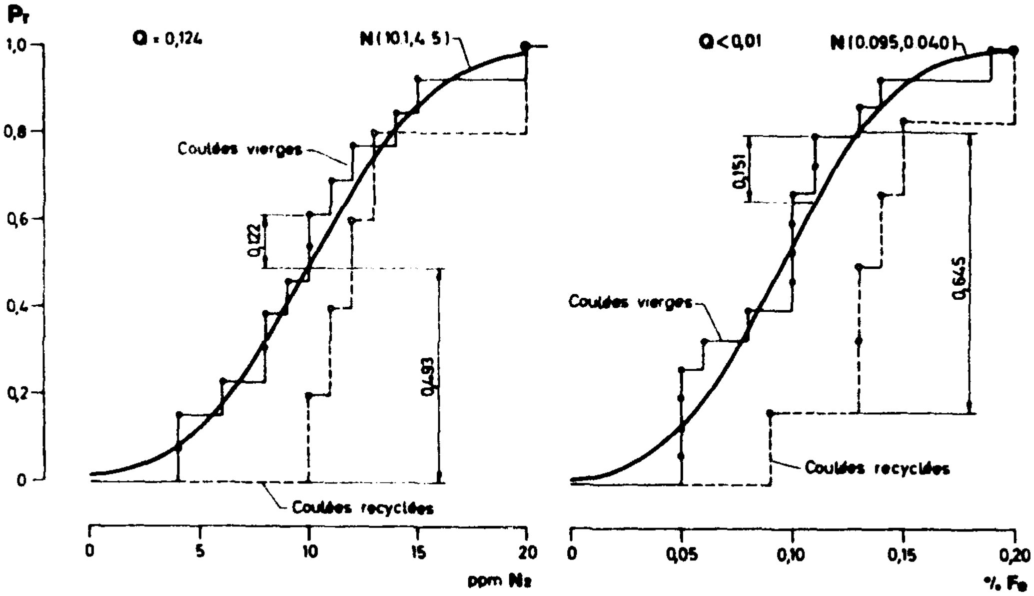


Fig.1. IN 100 : comparaison entre coulées-mères vierges et recyclées. Composition

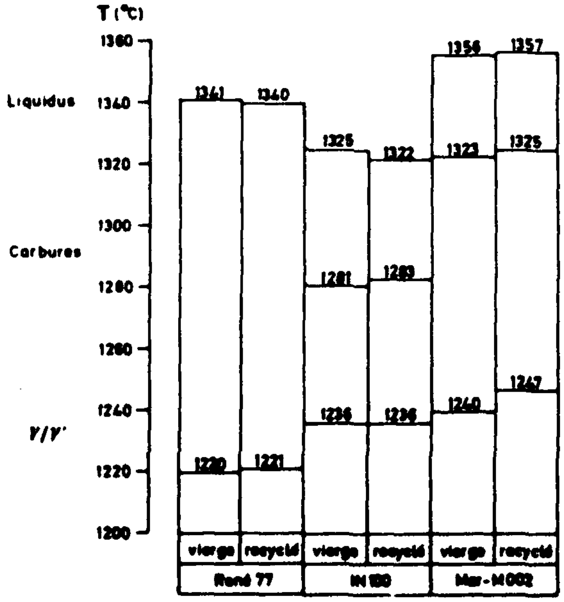


Fig.2. Influence du recyclage sur la séquence de solidification (refroidissement à 15°C/mn.)

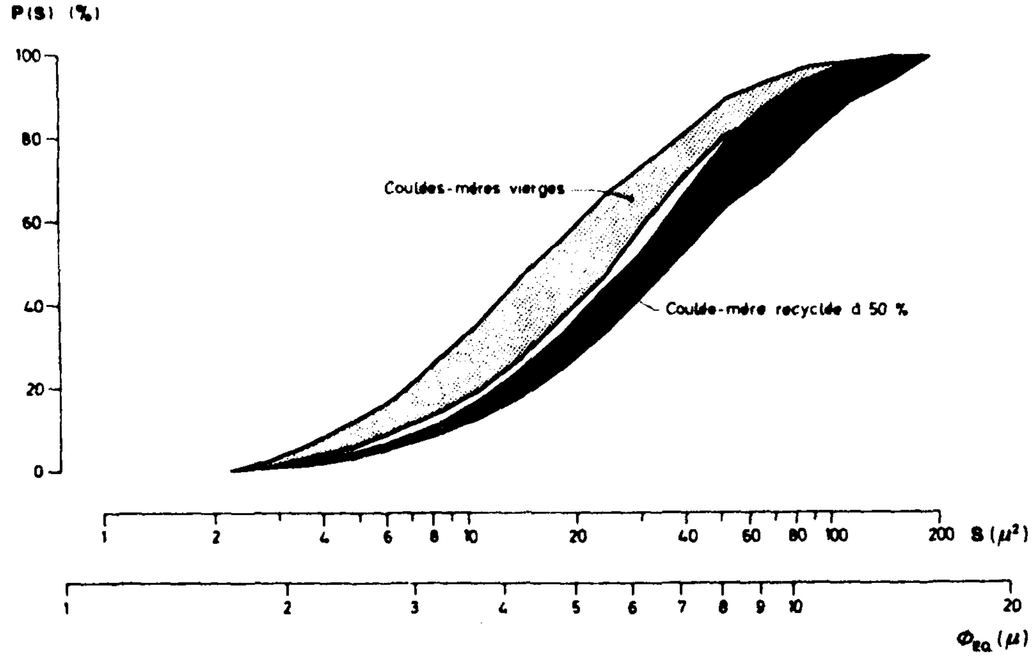


Fig.3. Distribution granulométrique des carbures observés sur aubes coulées par FN-Formétal

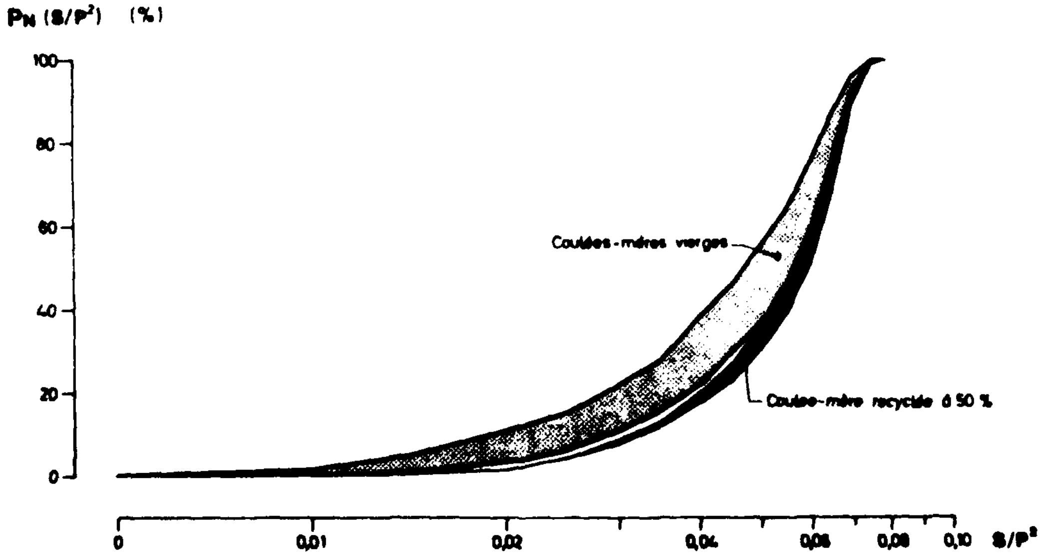
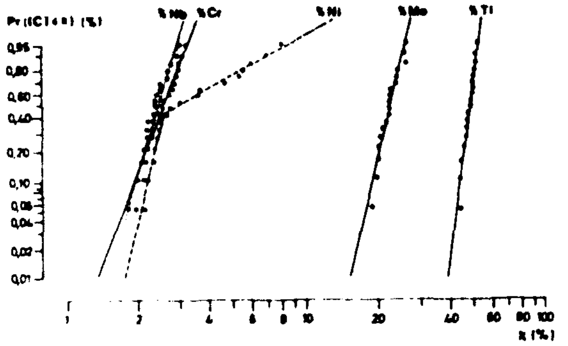
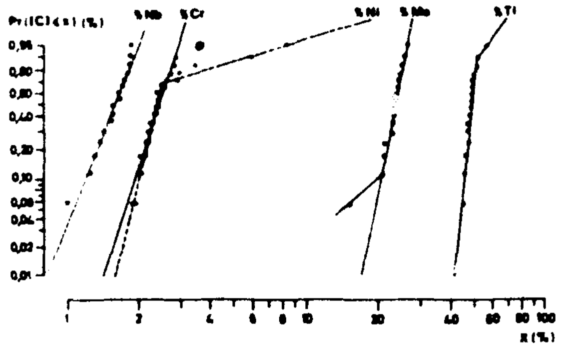


Fig.4. Distribution morphologique des carbures observés sur aubes coulées par FN-Formétal



a) Coulée-mère vierge



b) Coulée-mère recyclée à 100 %

Fig.5. Distribution de compositions chimiques des carbures observés sur éprouvettes tronconiques

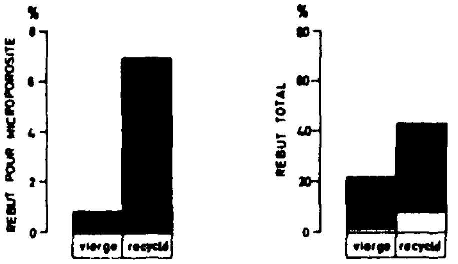


Fig.6. Influence du recyclage sur le taux de rebut pour microporosité et pour tous défauts métallurgiques confondus dans le cas d'une aube particulière

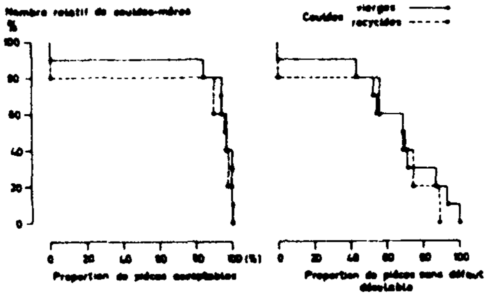


Fig.7. IN 100 : influence du recyclage sur la tendance à la microporosité.

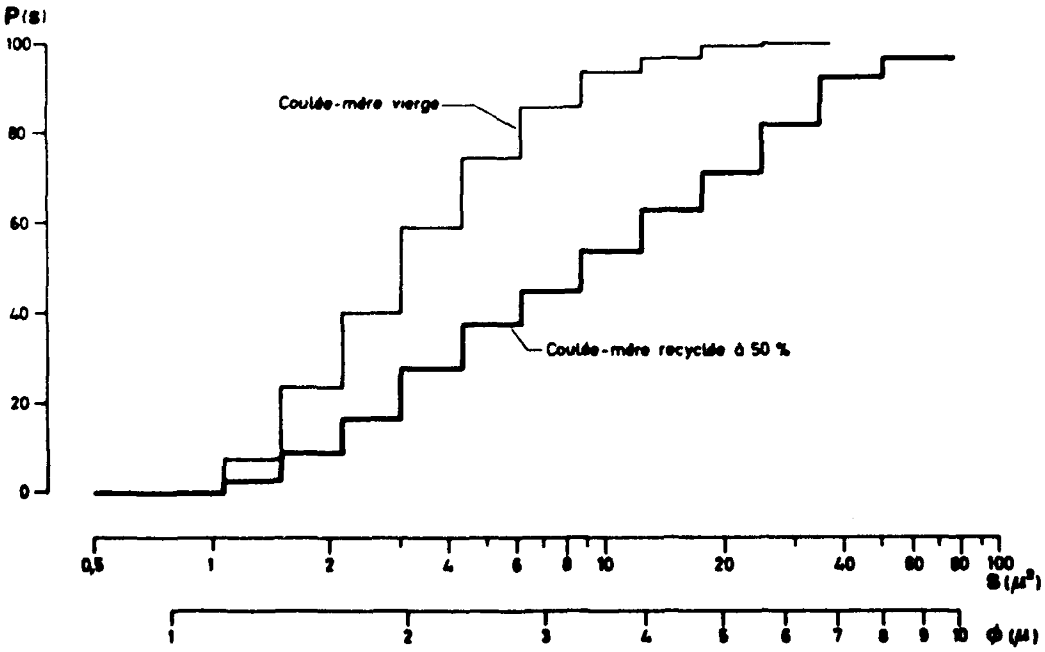
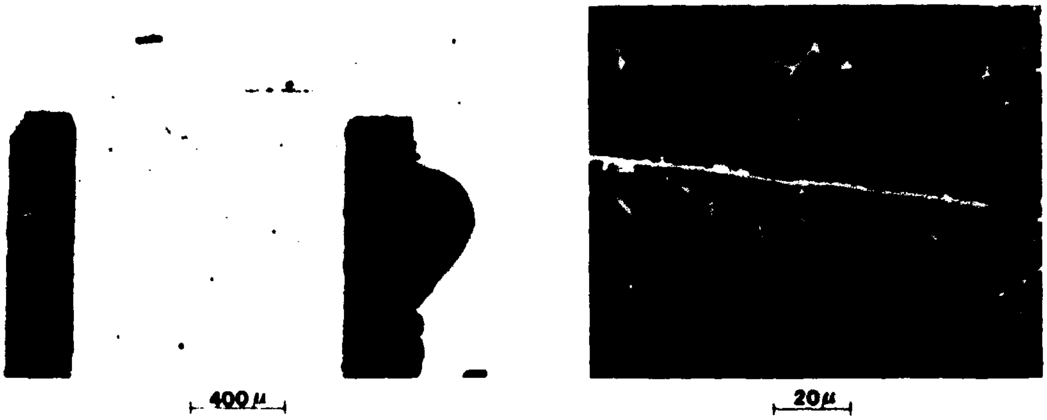


Fig.8. Distributions granulométriques des inclusions du type "sulfure" présentes dans une pièce structurale en alliage WI 52



Localisation de l'inclusion à l'entrée du filtre

Image en constraste de composition

Fig.9. Inclusion d'oxyde de hafnium recueillie au-dessus d'un filtre "nid d'abeille" disposé dans le cône de coulée d'une grappe d'aubes moulées en alliage Mar-M-002 recyclé à 50%

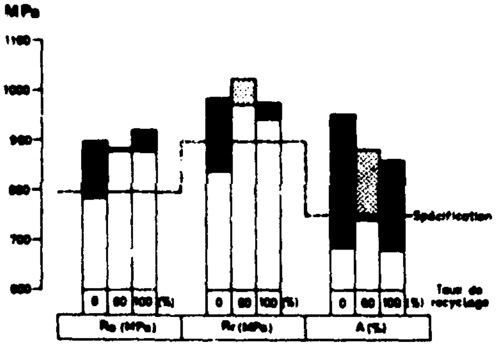


Fig.10. IN 738 C : influence du taux de recyclage sur les propriétés mécaniques de traction de quelques coulées-mères (éprouvettes coulées en grappes et soumises au traitement thermique complet : 1121°C/2h/air + 843°C/24h/air)

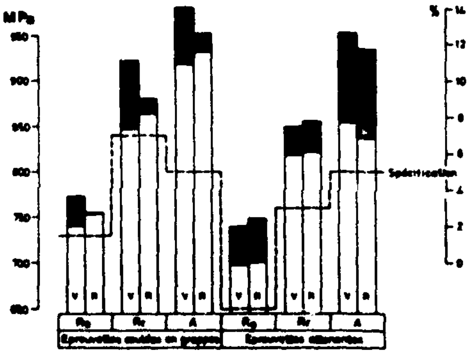


Fig.11. IN 100 : influence du recyclage sur les propriétés de traction moyennes

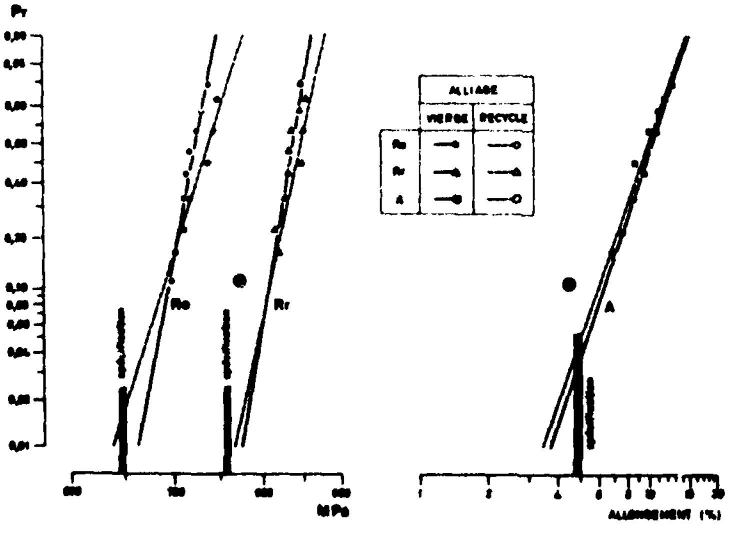


Fig.12. IN 100 : influence du recyclage sur les propriétés de traction d'éprouvettes attenant à des grappes d'aubes

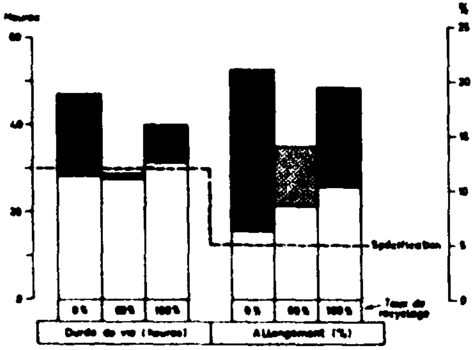


Fig.13. IN 738 C : influence du recyclage sur la tenue au fluage-rupture à 982°C/152 MPa de quelques coulées-mères (éprouvettes coulées en grappes et soumises au traitement thermique complet : 1121°C/2h/air + 843°C/24h/air)

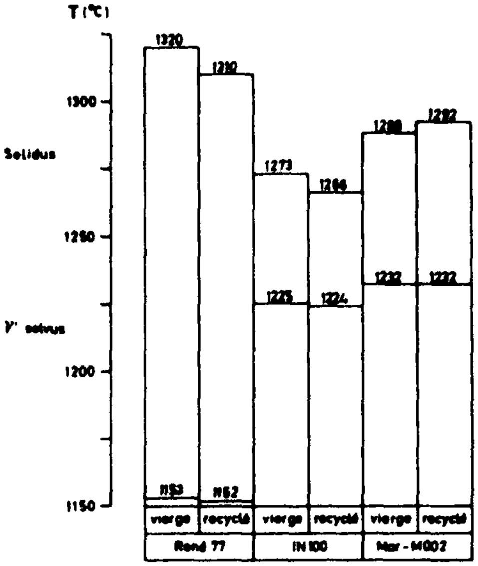


Fig.15. Influence du recyclage sur la séquence de fusion (chauffage à 15°C/mn.)

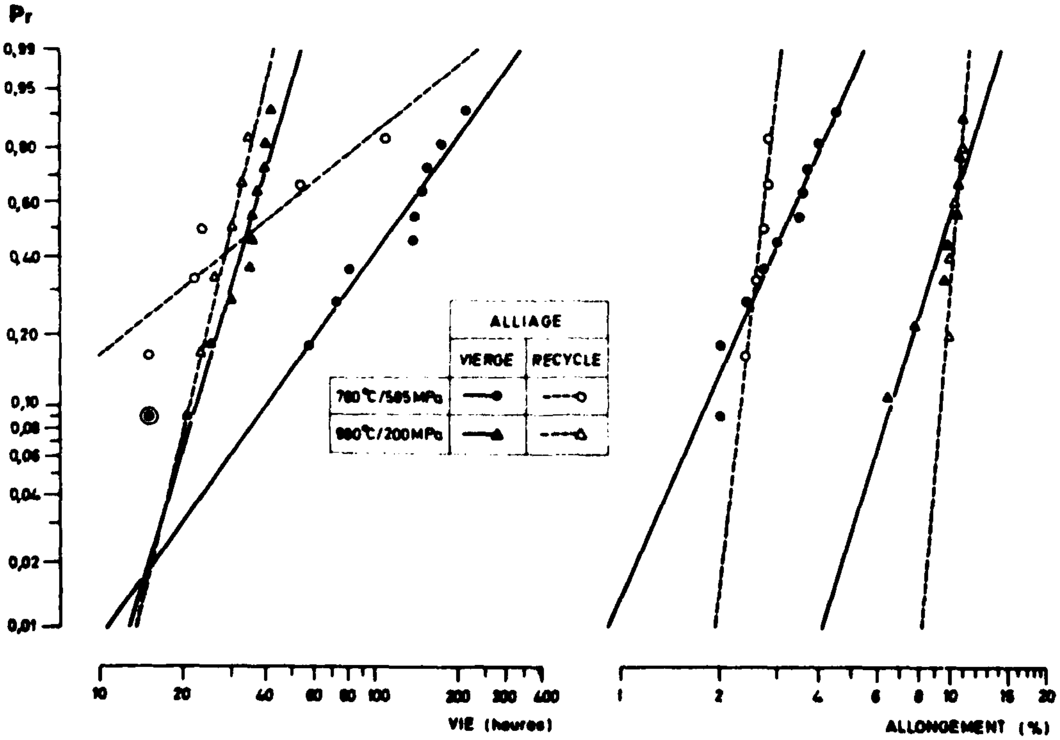


Fig.14. IN 100 : influence du recyclage sur les propriétés de fluage-rupture d'éprouvettes attenantes

Cycle 0063 (V_R = 2°C/min) Cycle 0066 (V_R = 16°C/min)

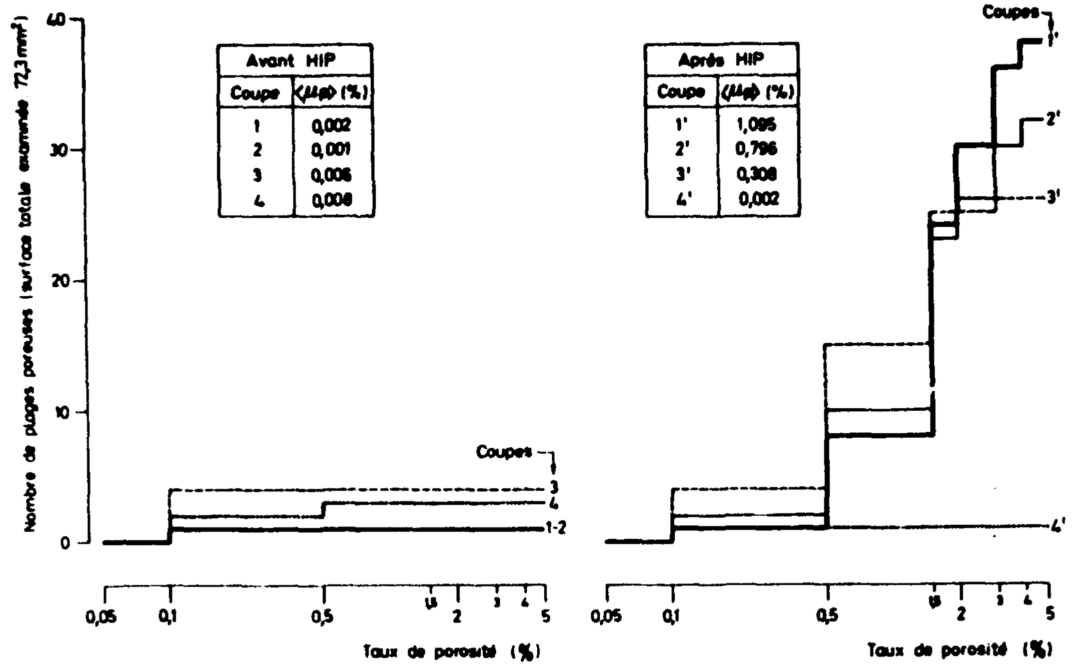
Fig.16. Influence de la vitesse de refroidissement après HIP sur la finesse de la distribution à coeur de la phase γ' des éprouvettes tronconiques en IN 100

Cycle 0067 (V_R = 2°C/min) Cycle 0071 (V_R = 16°C/min)

Fig.17. Influence de la vitesse de refroidissement après HIP sur la finesse de distribution à coeur de la phase γ' d'éprouvettes tronconiques en Mar-M-002

Zone 1 (point chaud coeur)

Fig.18. Relation entre microretassures et carbures. Matière recyclée à 100%



Avant HIP	
Coupe	$\langle\mu\phi\rangle$ (%)
1	0,002
2	0,001
3	0,006
4	0,008

Aprés HIP	
Coupe	$\langle\mu\phi\rangle$ (%)
1'	1,095
2'	0,796
3'	0,308
4'	0,002

Fig.19. Influence d'un cycle HIP à 1315°C sur la porosité d'une pièce en X-45.

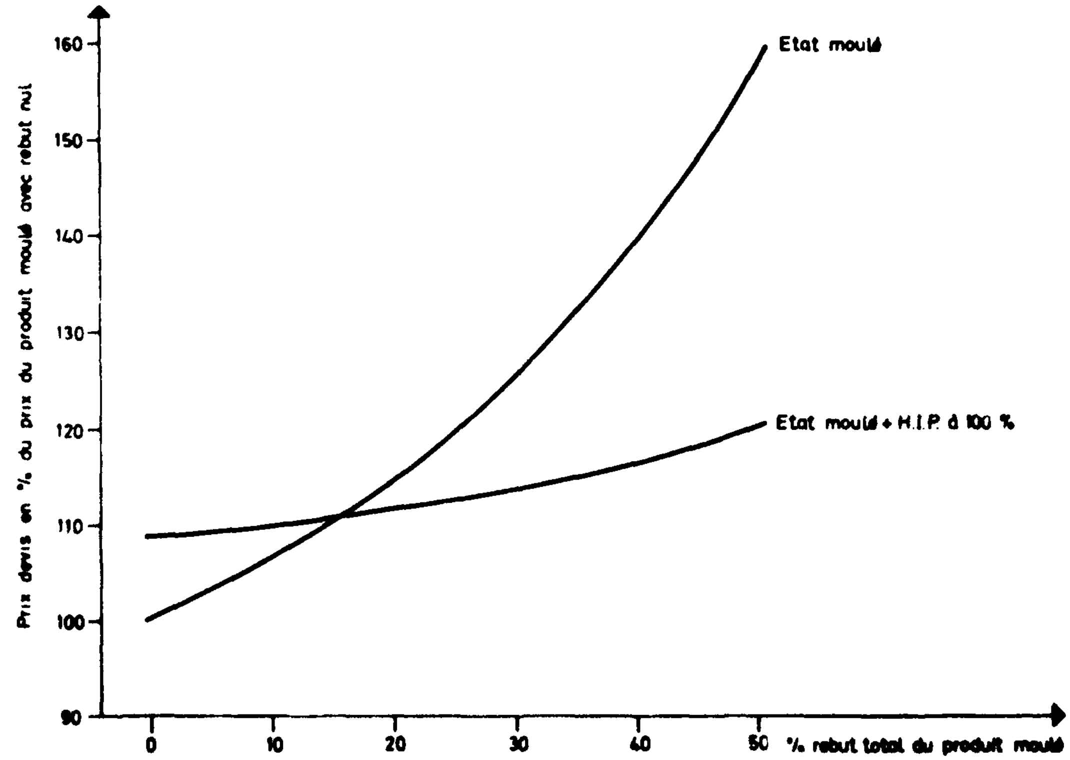


Fig.20. Influence du % rebut-fonderie et du traitement HIP sur le prix devis.

TRACE ELEMENTS AND RESIDUAL ELEMENTS IN SUPERALLOYS

by Richard T. Holt
Structures and Materials Laboratory
National Aeronautical Establishment
National Research Council
Ottawa, Ontario, Canada
K1A 0R6

AD-P004 228

SUMMARY

This paper is a sequel to an earlier review (1) entitled "Impurities and Trace Elements in Nickel Base Superalloys" and covers work performed in this field from 1976 to present.

Improvements in refinement technology are discussed. This includes evaluation of refractory materials to ensure minimal accumulation of inclusions. The following section on detrimental (or tramp) elements covers: (i) residual gases and porosity, (ii) non-metallic inclusions (with particular emphasis on fatigue crack formation in inclusions which can lead to premature failure) and (iii) residual elements such as sulfur, phosphorus and other tramp elements (primarily those in AMS 2280) which segregate to grain boundaries. Since this segregation can lead to intergranular fracture, these elements have been the subject of several studies by Auger Electron Spectroscopy (AES).

There is also a section on beneficial elements which are added in small amounts to counteract the effect of the tramp elements. Some of those beneficial elements in small residual amounts may also help with grain size control.

Finally, some recent work on the processing of scrap is discussed, with particular reference to minimizing the inclusion and trace element content of the alloys.

1. INTRODUCTION

The theme of this meeting "Materials Substitution and Recycling" is an important subject and its discussion is timely for it has received much attention lately, particularly in the USA, which is of course one of the main consumers of specialty metals. According to the publication "Aviation Week and Space Technology" (December 21, 1981 p.11, January 17, 1983 p.16, February 7, 1983 p.15 and May 2, 1983 p.16) concern over dependence on foreign sources for strategic materials was one reason why Congress agreed to the adoption of the specialty metals provision for the Defence Department Appropriations Bill. This provision, which was supported by the specialty steel industry in the US, but not by Defence Department Officials, severely restricted the importation of defence items containing foreign-produced specialty metals. More recently (AWST July 18, 1983 p.15), Congress has agreed to changes in the Bill which will allow the importation of certain strategic materials. The concerns raised by this Bill are a good example of the very high level of importance which governments are placing on self-sufficiency. The metallurgist is therefore responsible for developing, and then fine-tuning, alloys which can meet all specifications for the required properties, while ensuring as far as possible, that the ingredients are readily available at a reasonable cost.

Nickel base superalloys are used for two primary functions:- (i) high strength/high corrosion resistance at ambient temperatures and (ii) high strength with creep and oxidation resistance at high temperatures. A good example of materials substitution for a particular application is the alloy designated Hastelloy 'D', developed by Cabot Corporation. Hastelloy 'D' (Ni-9Si-3Cu) has good resistance to corrosion in an environment such as H_2SO_4 and can therefore replace Inconel 600 (Ni-16Cr-8Fe) for many industrial applications, thereby saving a large amount of chromium.

For optimum high temperature properties for a given alloy one can control the heat treatments and mechanical processing to obtain the required grain size and microstructure. Also, it is usual to specify vacuum melting and vacuum refining and to add small quantities of materials as refining aids to help remove undesireable "tramp" elements and help with grain size control.

A review of the effects of both beneficial and minor alloying elements, and the effects and control of detrimental trace elements in nickel-base superalloys was published in 1976 (1). Since then, a number of published conference proceedings have devoted at least one session to this topic. This paper is essentially a sequel to the earlier review, and will contain citations to many papers presented at conferences or in the literature, but will not discuss papers already referenced in the previous review.

This paper will use the same general classifications as the previous one covering refining aids, detrimental and beneficial elements. There may be some overlap in the treatment since the role of beneficial elements is often to remove or to counter the effect of tramp elements. Although the word superalloys has been used in the title, most of the work over the past 7 or 8 years has again concentrated on nickel base alloys. The compositions of the alloys discussed in this paper are given in Table 1.

2. REFINING PROCEDURES

Most of the nickel-base superalloys in common use rely on precipitation hardening by γ'. This is an intermetallic phase of the stoichiometric composition $Ni_3(Al,Ti)$ and hence aluminium, titanium or both aluminium and titanium must be added to the melt. Since these elements are highly reactive, their stabilization is very difficult to control, especially in the presence of oxygen. One of the main reasons why most γ' strengthened superalloys used for high strength, high temperature applications are vacuum melted is to reduce the oxide inclusion content.

The first melting stage of high quality superalloy production is usually by vacuum induction melting (VIM) where the charge is melted in an induction furnace lined with carbon or some other refractory such as magnesia or alumina. During this process, the oxygen and nitrogen contents of the melt decrease with time; the oxygen is removed during the carbon 'boil', which also purges the nitrogen (1). These gases along with sulfur also react with Al, Ti or other reactive elements which may be added for refining purposes such as Hf, B or Zr. The resulting oxides, nitrides and sulfides pass into the slag. At the same time, it is well known (1) that certain tramp elements are stabilized during VIM. After casting, the resulting ingot is clean but has a large and non-uniform grain size. Therefore subsequent grain refinement for improved mechanical properties is required, and this occurs after one of several forms of remelting, depending on whether the material will be used in cast, wrought or powder form.

TABLE I

CHEMICAL COMPOSITIONS OF ALLOYS DISCUSSED IN THIS PAPER

	Condition*	Ni	Al	Co	Cr	Fe	Hf	Mo	Nb	Ta	Ti	V	W	Zr
Inconel 600	W	Bal			17	8								
IN-100	C	Bal	5.5	15	10			3			4.7	1.0		
MERL-76	P	Bal	5.1	18	12		0.6	3.2	1.5		4.2			0.08
Astroloy	C	Bal	4.4	15	15			5.25		3.5				
Hastelloy-X	W	Bal			22	19		9						
NSC-1	W	Bal			18								15	
B-1900	C	Bal	6	10	8			6		4.3	1			
IN-738	C	Bal	3.4	8.6	15.5	0.2		1.75	0.9	1.9	3.2		2.65	0.1
Hastelloy C-276	W	Bal	0.2	1.1	16.5	5.3		16					3.8	0.01
Hastelloy-C4	W	Bal		2	16	3		15.5				0.2		
Nimonic 105	W	Bal	4.7	19.7	15			5			1.3			0.1
MAR-M002	C	Bal	5.7	10	9		1.6			2.5	1.5		10	0.06
MAR-M509	C	10.4	0.14	Bal	23.4					3.7	0.17			
MAR-M200	C	Bal	5	10	9				1.8		2		12.5	0.05
PE 16	C	Bal	1.3		16.5	34.7		3.3			1.3			
INCO 901**	C	Bal	0.2		12.5	34		6			3			
Haynes 718	W	Bal	0.6		18	19		3	Nb + Ta = 5.2		1			

* C = Cast P = Powder W = Wrought

** U-901, Udimet 901 and Unitemp 901 are also of similar composition.

For cast products, vacuum remelting furnaces are usually small induction furnaces which allow precision parts to be cast under vacuum. For wrought products, vacuum arc remelting (VAR) is commonly employed to convert the VIM ingot into a similar bar of finer grain size. The VIM ingot forms one electrode which gradually melts back when an arc is struck. The resulting liquid forms a pool which cools quickly for a fine grain size.

One of the newer refining procedures (2) is vacuum arc double electrode remelting (VADER) in which the product is uniformly finer grained because the cooling rate is much higher than for other types of refining.

It is probable that in a uniformly fine-grained structure the impurities would be uniformly distributed and would be unlikely to concentrate into pools from which potential hazardous cracks could emanate. It is clear, however, that since the electrode material is melted in vacuum and drops of this liquid fall onto the surface of the refined ingot, there is no time for the removal of any unwanted elements. Therefore, control of beneficial and tramp elements must take place in the initial vacuum induction melting (VIM) process.

Another new process being developed in the USSR is vacuum plasma arc remelting (VPAR) (3). For this process, it is claimed that evaporation losses of alloying elements is low, but that the removal of impurities is high. In comparison to other refining methods, reductions of bismuth (by 90%), lead (by 90%), antimony (by 70%), oxygen (by 50%) and nitrogen (by 75%) have been reported.

3. DETRIMENTAL ELEMENTS

These may be in the form of residual gases, residual non-metals, or residual metals and metalloids.

(a) Residual gases and porosity

Casting defects due to shrinkage and porosity have always caused problems for premature crack initiation. Consequently, over the past few years, hot isostatic pressing (HIP'ing) of castings has been more widespread (4,5) and companies such as Howmet and Industrial Materials Technology Incorporated offer a comprehensive service including the HIP'ing of any aerospace component and including advice on various appropriate HIP treatments etc. Typical improvements for a nickel-base alloy B-1900 before and after HIP'ing are as follows (5): 760°C/650 MPa rupture life increases from 52 to 100 hours and elongation increases from 6% to 7.5%. It has also been shown (5) that the low cycle fatigue life of cast hafnium-modified IN-792 can be improved by a factor of eight times after HIP'ing. Fatigue life is improved because porosity obviously weakens the structure by providing paths of least resistance to advancing fatigue cracks.

There has recently been a great improvement in casting technology of superalloys to the extent that net shape integral castings of turbine wheels consisting of disc and blade assemblies are possible. After many experiments involving a high reject rate, it has been determined by Harris et al (6) that a low oxygen and nitrogen content of the remelt bar is essential. A limit for each element of 15 ppm has been established to reduce (i) the formation of oxide inclusions, and (ii) microporosity (which was found to be controlled mainly by the nitrogen content). The same authors have indicated that O and N levels in the melting stock consistently below 10 ppm are possible and that this further improves the castability of IN-100.

In the consideration of defects which arise from high gas contents, particularly oxygen and nitrogen, it is important to relate the size of the resulting defect to the damage that can be caused by it. A defect may grow in size during service particularly when high stress can induce crack propogation. Design concepts based on fracture toughness testing should indicate the maximum size to which a defect may be allowed to grow during the life cycle of the component such that a critical size (ie. a defect leading to failure) is not attained.

Microporosity and inclusions resulting from an initially high N and O content are examples of defects which can grow under creep-type conditions at high temperature. Interstitial solute atoms such as H, O, C etc. can migrate under the influence of stress at high temperature and accumulate at cavities in the grain boundaries (7). The improved properties ascribed to the addition of B and Zr (to be described later) are probably largely a result of the ability of these elements to restrict the grain boundary diffusion of impurities and thereby increase the resistance to creep cavitation.

The two main sources of inclusions are: (i) oxides etc. formed during melting and (ii) furnace and crucible refractory materials. Inclusions (and porosity) are a primary source of fatigue crack initiation, particularly in high temperature aerospace components fabricated from powders (8,9). Eylon and Uyzak (8) used a precision sectioning technique to investigate the fatigue crack origins of two powder nickel base superalloys. They found that in all cases where the fatigue crack initiation site was based on a subsurface location, the fatigue crack origin was at a pore or non-metallic inclusion such as MgO. These materials were produced by argon atomization and during this process it is possible to pick-up significant oxygen, typically 40 to 200 ppm.

In order to understand the exact role of ceramic inclusions in nickel-base alloys, a modified IN-100 powder alloy designated MERL 76 was seeded with two types of oxides, Al_2O_3 and MgO, both of which are used as refractories in the powder-making process. The specimens were then compacted and fatigue tested and, as a result of this work, Law and Blackburn (9) were able to show that crack nucleation in the base metal was invariably preceded by cracking either in these large (up to 1 mm diameter) inclusions or at the inclusion/matrix interface. This damage occurred at low stress (340 MPa) and after very few cycles. Since cracking occurred with equal ease in both Al_2O_3 and MgO inclusions, it could be concluded that each are equally damaging to the structure.

The subsequent cracking through the matrix was monitored for various inclusion sizes, stress levels and test temperatures. The effect of inclusion size is shown in fig. 1 where it can be seen that crack rate is almost independent of size until the crack reaches a length of about 0.1 mm at which point prior inclusion size plays a role in the crack growth rate; the larger the inclusion the greater the crack growth rate. Similarly, crack growth rates increased with increasing stress and decreasing temperature of testing, but were not affected by inclusion shape. It was concluded that the inclusions behaved like notches rather than cracks in the structure.

Also working with a powder alloy (Astroloy), Track and Betz (10, 11) have shown that stress-controlled low cycle fatigue (LCF) lives at room temperature are not affected by the introduction of small (≤ 20 µm diameter) inclusions. In fact inclusions up to 100 µm had little effect on the LCF lives. However, in stress-controlled experiments, at high stress and elevated temperature (600°C) defects with diameters as low as 40 µm considerably shortened the life.

Hence, although oxide inclusions cannot be avoided completely, it is certainly advisable to limit the size if possible. Two recent investigations on MERL 76 (12, 13) have concluded that the crucible refractory material is of prime importance in limiting inclusions. Unfortunately, the conclusions in each case were somewhat contradictory, although the reasons for this may have been due to the order in which ingredients such as reactive metals like Hf were added to the melt.

Brown et al (12) have developed a procedure for the extraction of oxide inclusions and on the basis of this technique have concluded that, for VIM material, magnesia (MgO) crucibles gave the lowest oxide content in the melt followed by Al_2O_3 followed by Zr_2O_3. VAR had little or no effect on the oxide level, but ESR resulted in significantly lower oxide levels.

On the other hand, Sutton and Johnson (13) in melting the same material found that Al_2O_3 crucibles gave the lowest oxide content followed by spinel ($MgAl_2O_4$) followed by MgO. MERL 76 contains about 0.8% Hf, and in each study the dominant oxide was found to be HfO_2.

Residual Non-Metals

As was true in 1976, sulfur continues to be one of the elements of major concern to superalloy users.

Several investigations have used Auger Electron Spectroscopy (AES) during recent years to study the segregation of sulfur to free surfaces and grain boundaries. For example, it is shown in fig. 2 (14) that in Inconel 600 with a sulfur content of 0.002% by weight, the distribution of sulfur (i) after furnace cooling and (ii) after water quenching from 1100°C is markedly different. This was demonstrated by taking small pieces from each of these samples and annealing them at different temperatures in an Auger unit. In the furnace cooled specimen the sulfur was already distributed in the grain boundaries and was able to migrate to the free surface at temperatures between 500°C and 800°C whereas in the quenched sample, the sulfur was locked in to the matrix and unable to diffuse to the surface. Assuming the free surface of a sample is similar to a grain boundary or region of porosity in that it offers a low energy site for migrating atoms, then it is not surprising that sulfur is found in higher concentrations at fracture surfaces than in the bulk material. Kny, Stolz and Stickler (15) studied the alloy IN-738 and found that in the normal heat treated condition (1120°C 2h, cool to RT, 843°C 24h) the bulk S level, measured chemically to be about 0.003 wt % was in the order of 0.008% ± 0.003% when measured by AES. In a fracture surface this level increased to about 0.03%. When the same material was aged at 788°C for 10,000 hours - i.e. simulating a use condition - the bulk level of S was below the level of detectability, while the average sulfur level in the surface was 0.12%.

Some areas had a sulfur concentration as high as 0.33% which is about 100 times the original bulk concentration. A similar result has been obtained by Yamaguchi et al (16) where AES analysis confirmed that in Inconel 600, for those samples with a high sulfur content (30 ppm and up), the grain boundary zone (2nm wide) was enriched with sulfur. Fig. 3 shows the relative sulfur content in the fracture surface (i.e. at sputtering time = 0) for a number of samples, some of which were treated with Ca or Mg and did not exhibit high grain boundary sulfur levels. For untreated samples the sulfur content decreased with increasing sputtering time. This correlated with their ductility experiments which showed that when the S (or Ca or Mg) content was high, the ductility was dramatically reduced in the temperature range 950 -1150°C.

From all this evidence, it is clear that sulfur is a very harmful element, and its migration to grain boundaries under long term high temperature service can have serious consequences. Recently, Messmer and Briant (17) have described a model based on quantum mechanical cluster calculations showing that the degree to which embrittlement is caused by impurity atoms is related to the chemical bonding between those atoms and the base metal. Hence, strongly embrittling elements such as sulfur are strongly electronegative with respect to the host metal (nickel) and draw charge from the metal atom onto themselves, (i.e. heteropolar). Some metal-metal bonds are thus destroyed. Those impurity atoms such as boron which improve the ductility are called cohesive enhancers, because in this case the bonding between impurity and host metal is homopolar (i.e. the charges involved are equally shared between the impurity atom and host atoms) and metal-metal bonds are not destroyed. Since it is these metal-metal bonds which hold the grain boundary together, the latter case obviously describes a non-embrittling situation, and the bonding between a cohesive enhancer and the host metal may in fact strengthen the grain boundary. One can estimate that other electropositive elements such as Mg, Ca or Ti would behave like B, while electronegative elements such as oxygen would behave like sulfur.

The authors do not speculate on what happens to chemical bonding when both S and B atoms are present in the grain boundary. There is some experimental evidence however (18) which indicates that the two opposing effects would tend to cancel each other out, so that the presence of boron in a grain boundary would reduce the tendency of S to weaken the grain boundary bonding. Apparently, boron-doped nickel does not change the sulfur content of the fracture surface but does improve the ductility. Recently, Mulford (19) has also shown that the deleterious effect of sulfur in Ni and Ni binary alloys (where nickel was alloyed with Cr, Mo, Al, Cr, W, or Hf) was countered to some extent by the formation of sulfides which then limits the amount of sulfur available for grain boundary segregation.

Other work (20) on pure nickel supports the evidence that sulfur strongly segregates to grain boundaries, (again measured in an AES) and also is the segregant primarily responsible for hydrogen embrittlement (which was introduced by testing in H_2SO_4 at cathodic potential). Both the presence of sulfur or the application of a strongly cathodic potential were effective in changing the fracture from transgranular to intergranular with the accompanying sharp loss in ductility.

The sulfur segregation effects in pure nickel and simple binary alloys are probably representative of the effects of sulfur in the highly complex nickel base superalloys. Certainly the presence of sulfur renders an alloy such as IN-738 susceptible to intergranular cracking because of its tendency to segregate without forming sulfide inclusions.

Mulford (19) showed that the rate of sulfur segregation was strongly influenced by annealing temperature in Ni and Ni-Cu alloys. Equilibrium levels are achieved after 400 hours at 560°C, or less than one hour at 700°C. However, in Ni-Mo, Ni-Al, Ni-Cr and Ni-Hf binaries the sulfide solubility level decreases, primarily due to the increased tendency to form sulfides. In the case of the Ni -0.5% Hf alloy the sulfide forming tendency was very high so that the amount of free sulfur was very low.

Another element which has traditionally been classified with sulfur as highly deleterious is phosphorus. It is somewhat surprising that although their atomic radii are very similar (20) phosphorus has a coefficient of diffusion in nickel about 2 orders of magnitude greater than that of sulfur (14). Consequently, many investigations have shown that phosphorus also segregates to grain boundaries (14)(20)(21), but recent evidence indicates that phosphorus segregation is not responsible for brittle intergranular fracture. Bruemmer et al (20) show that, in general, phosphorus has a slight embrittlement effect on pure nickel which in the presence of sulfur translates into a beneficial effect since phosphorus reduces the strong embrittling effect of that element.

In Inconel 600, Was et al (21) have performed some very nice experiments using a Scanning Auger Microprobe to show that annealing treatments at 700°C caused severe chromium depletion and enhanced phosphorus concentration at the grain boundaries. However, it was the former that was the most likely cause of the observed intergranular corrosion (because the intergranular corrosion rate varied with thermal treatment whereas the grain boundary concentration of phosphorus did not).

Incidently, it is shown that when the grain boundary chromium level falls to 9% (from the nominal level of 15 or 16%) then the structure is highly susceptible to intergranular attack. Much of the chromium is removed through the formation of the chromium carbide Cr_7C_3.

This is one of the reasons that the carbon content has to be closely controlled in nickel-based alloys, particularly in those alloys which must retain their good corrosion resistance after welding without further heat treatment. For example, in the Hastelloy alloys C-276 and C-4 (which are used in severe corrosive environments) the carbon levels must not exceed 0.02 and 0.015% respectively. Venal and Klein (22) found that for electroslag remelted alloys, a high proportion of the carbon in the ingot originated from a high level of carbon in the slag. They showed that by adding NiO to the molten slag (70% CaF_2, 15% CaO and 15% Al_2O_3) before it was placed in the ESR crucible, the carbon content of the slag was significantly reduced, which in turn lead to lower carbon contents in the resulting Hastelloy ingots.

Residual Metals and Metalloids

The unwelcome elements which have received the most attention in the literature for their deleterious behaviour in nickel alloys are lead, bismuth, selenium, tellurium, thallium, silver, antimony and arsenic. The AMS 2280 standard recognizes that these elements, which are not normally analysed for most applications, can seriously affect the mechanical properties of highly stressed rotating parts such as turbine blades. Hence the following limits (ppm by weight) have been set in AMS 2280:

Pb 5ppm, Bi 0.5ppm, Se 3ppm, Te 0.5ppm, Tl 5ppm

A number of other elements have been included each of which should not exceed 50 ppm and the total amount of trace elements should not exceed 400 ppm.

In addition SAE have published an Aerospace Recommended Practice (ARP 1313) which describes the methods which may be used to analyse for these trace elements.

In the earlier review (1), the role of some of these elements on the high temperature mechanical properties of nickel-base alloys was described. In general, it had been found that bismuth was the most harmful element at ppm levels and that lead, tellurium, thallium and selenium in decreasing order adversely affected creep and hot workability properties. Impurities such as As, Sb and Sn were far less damaging. More recently some of these earlier results have been confirmed for Nimonic 105 by Thomas and Gibbons (23, 24). Fig. 4 is a normalized plot of the effect of various impurities (i.e. as compared to the base metal) on the stress rupture life and ductility at 815°C. For plain samples (σ = 556 MPa), Te Pb and Se were the most harmful in that order. For Sn, the life-to-rupture decreased slightly at 12 ppm Sn (more so in notched samples) and thereafter actually increased with further additions of Sn. The effect of Te was also interesting since there did not appear to be a decrease in life-to-rupture as the Te content was increased from 1 ppm to 5 ppm, but dropped sharply when the Te content increased to 7 ppm. In all cases, notched samples (σ = 350 MPa) were more sensitive to the effect of impurities than plain samples, and this was particularly noticeable for Tl and Sn.

It was thought that the effect of Sn may be sensitive to temperature variations, but it was demonstrated that changes in Sn at 750°C and at 900°C had no effect on life-to-rupture or reduction in area. It was also shown for Pb and Te (the most damaging elements) that grain boundary cavitation increased drastically with increasing impurity and increasing deformation as compared to the cavitation recorded under the same conditions for the base alloy.

It was proposed that segregation of the impurity to grain boundaries (thereby reducing the surface energy γ_s) could result in the increased cavitation because the size of a stable cavity is given by $r = 2\gamma_s/\sigma$, where σ is the applied stress. However, it is interesting to note that the increase in cavitation (by a factor of 10) was not directly proportional to the rupture life, which decreased by 25%.

A *more detailed examination (24) of the effect of Pb on the creep properties of a cast nickel-base alloy* MAR-M002 resulted in the conclusions that small concentrations of lead (approx. 2ppm) could seriously impair the rupture life and ductility of MAR-M002 and that this alloy was more sensitive to small concentrations of impurity than was the wrought Nimonic 105. Using Auger Electron Spectroscopy the authors showed that lead was present as a monolayer on the stress rupture surface. This supports the earlier postulation that impurity segregation to cavities results in an increased amount of cavitation.

Kleemann et al (25) have investigated how creep rupture properties of a high-strength cobalt-base alloy can be affected by trace elements. The alloy was identified by its chemical composition and appears to be the casting alloy MAR-M509, to which 90 ppm bismuth and 35 ppm selenium were respectively added to two heats. The authors had intended to add 100 ppm of each element, but at least for Se, seemed to have inadvertantly discovered a refining process.

TABLE 2

THE EFFECT OF SELENIUM AND BISMUTH ADDITIONS ON THE STRESS RUPTURE LIFE AND DUCTILITY OF A CAST COBALT BASE ALLOY MAR-M509. KLEEMANN ET AL (25)

Test Temperature (°C)	Stress (MPa)	Property	Control	Control Plus 35 ppm Selenium	Control plus 90 ppm Bismuth
982	110	Rupture Life (h)	107	78 (27)	76 (29)
		Reduction of Area (%)	14	25	9 (34)
	70	Rupture Life (h)	3042	1746 (42)	904 (70)
		Reduction of Area (%)	2	2.5	3.1
899	186	Rupture Life (h)	76	24 (68)	31 (59)
		Reduction of Area (%)	20	27	4.8 (76)
	124	Rupture Life (h)	1753	1596 (9)	1141 (35)
		Reduction of Area (%)	14	15	5.5 (60)

NOTE: Numbers in brackets are the percentage reductions in property values in comparison to the control casting.

The results have been redrafted as in Table 2 to show the percentage reduction in properties due to the impurities, and it can be seen from Table 2 that the authors' conclusion that "at the lower test temperature the results show the absence of appreciable effects on rupture strength due to impurities" is not strictly true. In fact, at the lower temperature and higher stress, impurities had their most damaging effect on rupture life, percentage-wise. In general 90 ppm of Bi were more damaging than 35 ppm of Se.

In comparison to results on nickel-base alloys where a few ppm of Bi can have a disastrous result, it appears that cobalt-based alloys may be much more tolerant to impurities; this relatively large amount of Bi did not, for example have a large effect on ductility at 980°C. It is also interesting to note that Se actually improved the ductility under all conditions of temperature and stress, which is different to the result quoted earlier for Ni-based alloys (23).

Metallic and other impurities in nickel base alloys have been studied by AES by Walsh and Anderson (26). *Grain boundary fracture surfaces* contained significant levels (in decreasing order) *of S, Bi, Te and Pb when the bulk levels* of these elements was as low as 40, 4.4, 6.8 and 10 ppm respectively. The elements Tl, Se, Sn, Sb and As were not found at the grain boundaries. The same alloys (B-1900 and MAR-M200) with Hf additions contained a much lower S content in the boundary. Te and Pb levels were independent of Hf content. In general, the elements which segregate to the grain boundaries are those which have the worst effect on high temperature mechanical properties as already described both in the current paper and the former review (1).

Control of Ag, Bi, Pb, Se, Te and Tl, introduced to levels of 50 ppm during vacuum induction melting, have *been discussed by Schwer et al (27) in a follow-up report* to that referenced in (1). This subsequent report is equally vague in terms of numerical data, but the conclusion remains that Tl is almost completely removed, Pb and Bi substantially removed, Te and Ag partially removed, and Se is almost unaffected by VIM. It was also concluded that time was the most important variable followed by melting temperature and operating pressure.

In contrast, Burton (28) has shown that in U-700, it is possible to reduce the Se content from about 120 ppm to *15 ppm by volatilization during VIM. In other tests, it was shown that selenium* can be further reduced from 3 ppm to 0.3 ppm by the addition of calcium (in the form of CaO or Ca Ni) to the melt. At the same time S, Pb and Zn were also lowered by this calcium treatment, while Sb, Sn, Ge and Ga were unaffected.

BENEFICIAL ELEMENTS

We have seen in the previous paragraphs that Hf and Ca continue to be used to control the level of sulfur and other elements (26,28). Several other elements such as Mg, B, Zr and the rare earths are used either in a similar way, or to control the microstructure, but in each case the level of additions must be carefully controlled.

Both Ca and Mg are effective deoxidisers during the melting of nickel base alloys, and these elements are also used to control sulfur (29), but at the same time both these elements can cause severe hot shortness when present in excess. *One of the main problems is that these elements, particularly Ca, form brittle grain boundry phases, which are* visible when the solute concentration is only 0.05%. Mg is not so critical because the Ni-Mg phases are soluble at the soaking temperatures, and so the structure can tolerate a higher level of Mg before cracking is observed during forging.

Other common additions to nickel base superalloys are boron and zirconium both of which can markedly improve creep and fatigue behaviour of nickel-base superalloys. Floreen and Davidson (30) have recently studied the effects of small amounts of B ($\leqslant$ 0.006%) and Zr ($\leqslant$ 0.05%) on a Nimonic alloy PE16. Under creep conditions (650°C/380 MPa), the doped samples had a rupture life of about 1550 hours whereas for undoped samples it was about 900 hours (with a much higher creep rate). By interrupting the creep tests it was shown that surface and grain boundary cracking was far less prevalent in samples containing B and Zr, although the creep and fatigue crack growth rates did not seem to be affected by B and Zr. Also, B and Zr were more effective in air tests than in an inert atmosphere, indicating they do indeed counteract the deleterious effect of oxygen, but neither B nor Zr affected the microstructure.

On the other hand, Antony and Radavich (31) studying the effects of B and Zr on MAR-M002 have shown that stress rupture properties can deteriorate markedly with higher Zr content, as shown in Table 3. This was due in part to the increase in microporosity (which in turn may be related to the decrease in solvus temperature) with increasing Zr. It was also found that increasing boron decreased the amount of microporosity and increased the stress-rupture properties. In fact, it was concluded in this report that the use of Zr should be eliminated from cast nickel base alloys used for integral turbine wheels where microporosity could be a critical factor.

TABLE 3

EFFECT OF Zr AND B ON MICROPOROSITY AND STRESS RUPTURE PROPERTIES OF MAR-M002. ANTONY AND RADAVICH (31)

Doping Levels (%)		Microporosity (%)	Stress Rupture Life (hrs)	
B	Zr		760°C/588 MPa	928°C/294 MPa
0.012	-	0.20	105	36
0.012	0.07	0.36	50	54
0.012	0.15	0.50	30	49
-	0.07	0.44	1	14
0.012	0.07	0.36	50	54
0.025	0.07	-	128	46

Boron tends to form M_3B_2 borides rich in chromium dispersed along the grain boundaries, often replacing MC carbides (31). Zirconium affects the morphology of carbides and may also increase the γ' precipitate size. It is quite clear that in complicated superalloys each element may interact in several ways to enhance and detract from overall properties. For example, adding boron frees titanium (which normally is taken up by MC carbide formation) and this allows more Ti to form a $\gamma - \gamma'$ grain boundary eutectic (32). The net result can be an increase in both strength and ductility.

Rare earth metals (REM) usually cerium or lanthanum are added in very small amounts to superalloy melts, solely to control S and O. It has been found that larger cerium additions (to Inco 901) did not refine the grain size (33) but did cause the formation of brittle Ni and Ce-rich phases in the grain boundary.

Fig. 5 (34) shows how Ce affects the removal of oxygen from a melt of Udimet 901, from about 14 ppm to 4 ppm after only 10 minutes. The further time of holding is required to reduce the residual Ce level to about 0.02 to 0.03 wt%. It was found that the optimum residual cerium content to prevent hot shortness during subsequent working was within the range 0.02 to 0.05 wt%, or 200 to 500 ppm.

Mischmetal, an REM mixture (54%Ce, 24%La, 15%Nd, 5%Pr, 2% other REM) has frequently been used in nickel-base alloys. For example, fig. 6 shows the desulfurization of two VIM heats of Haynes alloy 718 (35) by different Mischmetal additions. It is usual to experience a greater desulfurization or deoxidation with larger REM additions, but this usually leaves a high REM residual.

Bailey et al (36), using REM treatments on Unitemp 901, showed that when the initial sulfur level is lower (20 ppm), the final sulfur level is also much lower (1 to 5 ppm). Their results for oxygen removal agree with those of Li et al (34). The oxygen content went from 35 ppm to between 5 and 10 ppm following a La addition of 400 ppm to the melt. The La residual was about 25-30 ppm which was very close to the expected (calculated) value of 40 ppm based on physical and thermodynamic data. These authors showed also that creep properties at 650°C/586 MPa were superior in the La treated version as compared to a standard Unitemp 901, but noted that there is a danger of reducing high temperature properties when the REM residual is high.

In fact the danger is very real, as has recently been shown by Cosandey et al (37), whose results for high temperature (1093°C) tensile tests on Udimet 901 are presented in Table 4.

It can be seen that a Ce residual of 30 to 90ppm increases strength but higher residuals lower the strength to values below that of the untreated alloy. Cosandey et al also showed that the 649°C/638MPa creep ductility was increased by 30-90 ppm residual Ce, but the rupture times for these tests were lower than those for untreated samples. This therefore emphasises the need to effectively control the REM residuals. Ce has a low solubility in nickel and therefore the grain boundary concentration is much higher than the bulk concentration. At low Ce levels the Ce reacts with O and S to form Ce_2O_3, Ce_2O_3S and Ce_2S_3, and this improves the ductility, but at higher concentrations the brittle Ni_5Ce phase forms in the grain boundaries and the ductility is then reduced.

TABLE 4

ULTIMATE TENSILE STRENGTH (UTS), ELONGATION (EL), AND REDUCTION IN AREA (RA) AS A FUNCTION OF Ce ADDITION AND RESIDUAL Ce CONTENT FOR HIGH TEMPERATURE TENSILE TESTS OF AS-CAST U-901

Cosandey et al (37)

Ce Addition		Ce Residue (ppm)	UTS (MPa)	EL (Pct)	RA (Pct)
(Wt Pct)	(ppm)				
0	0	0	202.7	49.4	75.1
0.02	82	30	210.3	58.6	82.2
0.04	164	63	207.5	41.0	74.1
0.06	246	90	215.1	34.9	30.3
0.08	328	139	153.1	4.1	2.0
0.12	492	238	92.4	1.3	0
0.24	985	484	77.9	1.2	0

EFFECT OF TRACE ELEMENTS ON RECYCLING

In line with the theme of this conference it is appropriate to discuss the possible build-up of inclusions and detrimental trace elements through the use of scrap material during the initial melting stage.

Woulds (38) has described an elegant method of recycling nickel-base alloys which consists of a two part process. The material is first air melted in an arc furnace and oxygen is introduced through a lance to remove reactive elements prior to casting. The cast ingots are then vacuum refined either from the as-cast condition, or by mixing with virgin material to make up a required alloy composition and during this treatment the required Hf, Ti Al etc., can be added. Even after the oxygen treatment, the yield of the most valuable materials - Ni, Co, Cr, Mo, Ta, W etc. -is very high indeed, about 99% of the charge. Furthermore, it has been shown that trace element pickup during processing is negligible and that the oxygen content after vacuum refining is about 3ppm. During VIM, many of the deleterious trace elements such as Te, Pb and Bi are removed by volatilization but the extent of the removal is limited by the charge content. Hence, if possible the content of these elements in the charge should be known prior to melting. The above-mentioned (38) scrap was in the form of blades and vanes and the sulfur level of the charge was 0.001%. However, if a charge were to contain heavily corroded blades, the higher level sulfur in the scrap would undoubtedly be oxidized during the oxygen lancing.

In order for the system described by Woulds to work, the source of scrap must be reliable, and one of the main problems in recycling is that there is a danger of mixing the alloys and possibly mixing grades of alloys. These problems have recently been discussed in detail by deBarbadillo (39), including a review of the refining processes and sources of inclusions. Problems associated with inclusions have already been dealt with in this review, but it is important to realise that even with the use of high quality magnesia refractories, the probability of picking up exogenous inclusions derived from the crucible will increase with time of contact.

One of the most successful methods for remelting of superalloy scrap has been described by deBarbadillo (39) and is a two stage process: (i) melting in a electric arc furnace and (ii) argon-oxygen decarburization (AOD) in a crucible. During the melting, which should be as rapid as possible, the melt may be purged with oxygen but most of the refining is done after transfer to the AOD crucible. Through tuyeres in the base, oxygen and argon are blown. This purges out N_2 and H_2 gases, oxidises the reactive elements such as Al, Ti, Zr, etc. and allows volatilization of some of the high vapour pressure tramp elements such as Pb, Bi, Te and possibly Se. Sulfur is also removed by oxidation and volatilization. This material could then be cast into small ingots as a charge for subsequent vacuum arc remelting but, in general, most scrap (and many virgin melts) will be air melted.

At the 1977 Vacuum Metallurgy Conference, Cremisio et al (40) discussed superalloy scrap processing and the role of trace elements. They focussed on problems arising from analysis and at the same conference the same author, in conjunction with a group of distinguished superalloy metallurgists (41), presented the results of an ASME-ASTM gas turbine panel task force on trace elements. This program was called "Tracealloy" in which 24 laboratories analysed three heats of a nickel base superalloy which had been doped with different quantities of tramp elements, namely Bi, Pb, Se, Te and Tl. Upon completion of this program the remaining material was sent to the National Bureau of Standards (NBS) in Washington D.C.. In September 1980 NBS issued a Certificate of Analysis for the three materials known as Tracealloy A, B and C. These materials, which are respectively Standard Reference Materials (SRM) 897, 898 and 899, can be purchased from NBS for $163 per 35 g sample. Table 5 shows:

a) the amounts of trace elements added to each heat
b) the arithmetic mean and standard deviation for each element as determined by the participating laboratories and
c) the NBS certified values for SRM's 897, 898 and 899.

TABLE 5

RESULTS FROM THE TRACEALLOY PROGRAMME (41) AND SUBSEQUENT NBS CERTIFIED VALUES FOR TRACEALLOYS A, B AND C

(all values are ppm by weight)

Alloy	Element	Amount Added	Participating Lab. Results		NBS Standard Reference	
			Arithmetic Mean	Standard Deviation	Value	Estimated Uncertainty
A	Bi	0.5	0.582	0.294	(0.53)	-
	Pb	10	10.7	1.93	11.7	0.8
	Se	5	8.81	1.89	9.1	0.1
	Te	1.0	1.03	0.368	1.05	0.07
	Tl	1.0	0.563	0.249	0.51	0.03
B	Bi	1.0	1.18	0.523	(1.1)	-
	Pb	2	2.36	0.948	2.5	0.6
	Se	1.0	1.82	0.673	2.00	0.02
	Te	0.5	0.68	0.521	0.54	0.02
	Tl	5	2.79	1.24	2.75	0.02
C	Bi	0.2	0.314	0.247	(0.26)	-
	Pb	5	4.18	1.28	3.9	0.1
	Se	10	9.16	1.71	9.5	0.1
	Te	5	4.99	1.40	5.9	0.6
	Tl	0.5	0.542	0.565	0.252	0.003

NOTE: NBS have not certified the bismuth contents

There are several important points regarding these results:

i) the certified values for lead given in Table 5 are the latest available from NBS and are about 20% lower than the values issued on the NBS Certificates of Analysis between September 1980 and August 1983. Apparently the errors were due to incorrect calculations following peak-height measurements, but the admission by NBS that even they are capable of errors only goes to emphasize the care with which superalloy producers must perform their analyses. It is fortunate that the incorrectly certified values were too high rather than too low.

ii) NBS used "definitive" methods based on isotope dilution spark source mass spectrometry for Se and Te, and isotope dilution mass spectrometry for Pb and Tl. Since Bi has only 1 isotope, this method cannot be used for Bi, and so NBS do not have a "definitive" method for Bi, and therefore do not list Bi in the certification. The bracketed values for Bi are non-certified values as quoted by NBS, and are the arithmetic mean of the acceptable values provided by the ASME-ASTM panel.

iii) Most of the 24 laboratories participating in the Tracealloy programme used atomic absorption techniques, and none used the sophisticated techniques that NBS used. Also, it is almost certain that none of the laboratories would perform the large number of trials that NBS would perform. Nevertheless, it is interesting to note that the arithmetic means given in Table 5 are in good agreement with the values certified by NBS.

iv) However, the large deviations calculated from the results of the participating laboratories indicate that the chances of obtaining a poor result are quite high. The equipment should be frequently calibrated against one of the NBS reference materials.

v) It appears that one or more of the constituents of Tracealloys A and B were contaminated with Se since the analysed values exceed the amount deliberately added to the melt.

vi) It is interesting to note that Bi, Pb, Se and Te were not "lost" during the course of melting. About half the Tl appears to have been lost, probably by volatilization. Compare this to the results of Schwer et al (27) - one might also expect that some of the Pb and Bi would have volatilized too!

vii) There are several methods that can be used for quantitative chemical analysis of nickel base superalloys and most require that the sample be dissolved in acids. Since this can be difficult, there is a danger that some constituents may be lost. Even with the latest equipment, most analysts need a lot of experience before they can routinely and confidently report on ppm levels of trace elements.

SUMMARY AND CONCLUSIONS

A review paper inevitably includes a large number of conclusions which have been reached by a large number of workers representing a wide variety of interests. It is possible to go through the work on trace elements conducted over the past eight years and verify many of the statements made in the earlier review (1). At the same time advances in the field of Auger Electron Spectroscopy have lead to a more complete understanding of why some of these elements are a problem.

A summary of the state-of-the-art is as follows:

1. The elements which are most frequently associated with a deterioration in high temperature properties of nickel base alloys are sulfur, lead, bismuth, tellurium and selenium.
2. These elements can all be removed to a large extent during scrap processing, for example by the AOD process (39) or during VIM by volatilization.
3. Ca, Mg and REM additions to the melt can all help with the removal of tramp elements, but care must be taken to keep the residual of the additions to a low level otherwise the properties of the alloy can be adversely affected. Bailey et al (36) describe a calculation for REM additions to limit the residual content.
4. Boron and zirconium are used successfully to remove tramp elements, but since Zr can increase the amount of microporosity (which can adversely affect mechanical properties), it is not recommended as an addition to castings for high stress/high temperature applications.
5. Even though the bulk level of impurities may be low, most of these elements can segregate and concentrate in grain boundaries. This causes a loss of ductility and leads to intergranular fracture.
6. Bismuth and selenium do not appear to be so harmful in cobalt-base alloys as they are in nickel-base alloys.
7. Particularly for elements such as Cu, Fe and Sn which are difficult to remove during AOD processing, care must be taken to analyse any scrap which is to be used for recycling.
8. Accurate analysis to ppm levels is difficult even for those laboratories which must routinely perform such tasks.

REFERENCES

1. R.T. Holt and W. Wallace, "Impurities and Trace Elements in nickel-base superalloys", Int. Metall. Revs, 21, March 1976, p. 1-24.
2. William J. Boesch, John K. Tien and Timothy E. Howson, "Progress in Vacuum Melting: From VIM to VADER", Metal Prog., October 1982 p. 49-56.
3. A.V. Nikolaev, "A study of Nickel-base alloy refining during Vacuum Plasma Arc Remelting", Fiz. Khim, Obrab Mater, 1981 (2) 46-50, (In Russian).
4. Peter E. Price, "Hot Isostatic Pressing in the Aerospace Industry", Metal Prog., February 1982, p. 46.
5. Hugh D. Hanes and John M. McFadden, "HIP'ing of castings - an update", Metal Prog., April 1983, p. 23.
6. K. Harris, R.E. Schwer, G.W. Brown, and D.C. Valentine, "The Influence of nitrogen and oxygen on the castbility of IN-100", Vacuum Metallurgy, Science Press, Princeton, N.J., 1977, 389-422.
7. M.H. Yoo and H. Trinkaus, "Crack and Cavity Nucleation at Interfaces During Creep", Metall Trans A, 14A, April 1983, 547-561.
8. D. Eylon and J.M. Hyzak, "Investigation of Fatigue Origins in Superalloy Powder Compacts", Metall. Trans. A, 9A, 1978, 127-129.
9. C.C. Law and M.J. Backburn, "The Effects of Ceramic Inclusions on Fatigue Properties of a Powder Metallurgical Nickel Base Superalloy", Modern Dev. in Powder Met., Vol. 14, 1981, 93-114.
10. W. Track and W. Betz, "Effects of Defects on Fatigue Properties of P/M disk alloys", Modern Dev. in Powder Met., Vol. 14, 1981, 15-25.
11. W. Betz and W. Track, "Living with defects in PM Superalloy Materials", Powder Metallurgy Superalloys, Vol. 2, 1980, 19-1 to 19-27.
12. E.E. Brown, J.E. Stulga, L. Jennings and R.W. Salkeld, "The Influence of VIM Crucible Composition, Vacuum Arc Remelting and Electroslag Remelting on the Non-Metallic Inclusion Content of MERL 76", Proceedings of the 4th International Symposium on Superalloys,American Society for Metals, Metals Park, Ohio, September 1980, p. 159-168.
13. W.H. Sutton and W.A. Johnson, "Reactions Between Al_2O_3/MgO Crucible Materials and a Vacuum-Melted Hf-Bearing Superalloy", ibid, p. 311-320.
14. H.E. Chaung, Z. Szklarska-Smialowska and R.W. Staehle, "The Effect of Heat Treatment on Surface Segregation in Inconel 600", Scripta Metall., 13, 1979, p. 753-756.
15. E. Kny, W. Stolz and R. Stickler, "Phase Boundary Segregation in the Multiphase-Multicomponent alloy IN-738 studied by AES and SEM", J. Vac. Sci. T., 17(5), 1980, 1208-1212.

16. S. Yamaguchi, H. Kobayashi, T. Matsumiya, and S. Hayami, "Effect of Minor Elements on Hot Workability of Nickel Base Superalloys", Metal Tech., 6, May 1979, p. 170-175.

17. R.P. Messmer and C.L. Briant, "The Role of Chemical bonding in Grain Boundary Embrittlement", Acta Metall., 30, 1982, p. 457-467.

18. R.A. Mulford, "The Simultaneous Grain Boundary Segregation of Phosporus and Boron with Sulfur in Nickel", Submitted to Metall. Trans. A.

19. R.A. Mulford, "Grain Boundary Segregation in Ni and Binary Ni Alloys Doped with Sulfur", Metall. Trans. A., 14A, 1983, p. 865-870.

20. S.M. Bruemmer, R.H. Jones, M.T. Thomas and D.R. Baer, "Influence of Sulfur, Phosphorus and Antimony Segregation on the Intergranular Hydrogen Embrittlement of Nickel", Metall. Trans. A., 14A, 1983, p. 223-232.

21. G.S. Was, H.H. Tischner and R.M. Latanision, "The Influence of Thermal Treatment on the Chemistry and Structure of Grain Boundaries in Inconel 600", Metall. Trans. A., 12A, 1981, p. 1397-1408.

22. W.V. Venal and H.J. Klein, "Control of Carbon Pick-Up in ESR Melting of Nickel Base Superalloys", 1977 Vacuum Melting Conference, Pittsburgh, June 20-21, 1977, Published by Science Press, Princeton, p. 205-219.

23. G.B. Thomas and T.B. Gibbons, "Influence of Trace Elements on Creep and Stress Rupture Properties of Nimonic 105", Metall. Tech., 6, 1979, p. 95-101.

24. G.B. Thomas and T.B. Gibbons, "The Effect of Small Amounts of Lead on the Creep Performance of a Cast Ni-Cr Base Alloy", Superalloys 1980, Amer. Soc. Metals, Metals Park, Ohio, 1980, p. 699-708.

25. W. Kleemann, C.G. Beck and F.B. Mercer, "The Effect of Two Trace Elements on Creep Rupture Properties and Microstructure in a Vacuum Melted Co Base Superalloy", Superalloys-Metallurgy and Manufacture, AIME, New York, 1976, p. 119-126.

26. J.M. Walsh and N.P. Anderson, "Characterization of Nickel Base Superalloy Fracture Surfaces by Auger Electron Spectroscopy", ibid., p. 127-136.

27. R.E. Schwer, M.J. Gray and S.F. Morykwas, "Trace Element Refining of Nickel Base Superalloys", Vacuum Metallurgy Conference, 1975.

28. C.J. Burton, "Selenium Control in Vacuum Induction Melting", Vacuum Metallurgy, Science Press, Princeton, N.J., 1977, p. 77-89.

29. John J. deBarbadillo, "Effect of Uncombined Calcium and Magnesium on the Malleability of Nickel Alloys", Superalloys-Metallurgy and Manufacture, AIME, New York, 1976, p. 95-107.

30. S. Floreen and J.M. Davidson, "The Effects of B and Zr on the Creep and Fatigue Crack Growth Behaviour of a Ni-Base Superalloy", Metall. Trans. A., 14A, 1983, p. 895-901.

31. K.C. Antony and J.F. Radavich, "Solute Effects of Boron and Zirconium on Microporosity", Superalloys -Metallurgy and Manufacture, AIME, New York, 1976, p. 137-146.

32. H.D. Maxwell, J.F. Baldwin and J.F. Radavich, "A New Concept in Superalloy Ductility", Metall Met Form, October 1975, p. 332-339.

33. D.M. Anliker and J.B. Newkirk, "The Effects of Cerium on the Microstructure of INCO 901 Superalloy", Metall. Trans. A, 7A, 1976, p. 1711-1718.

34. D. Li, F. Cosandey, G.E. Maurer, R. Foote and J.K. Tien, "Understanding the role of Cerium During VIM Refining of Nickel-Chromium and Nickel-Iron Alloys", Metall. Trans. B, 13B, 1982, p. 603-611

35. M.F. Rothman, "Desulfurization of a Nickel Base Superalloy During Vacuum Induction Melting by Means of Rare Earth Additions", Vacuum Metallurgy, Science Press, Princeton, N.J., 1977, p. 49-76.

36. R.E. Bailey, R.R. Shiring and R.J. Anderson, "Effects of a Rare Earth Addition on Unitemp 901", Superalloys - Metallurgy and Manufacture, AIME, New York, 1976, p. 109-118.

37. F. Cosandey, D. Li, F. Sczerzenie and J.K Tien, "The Effect of Cerium on High Temperature Tensile and Creep Behaviour of a Superalloy", Metall. Trans. A, 14A, 1983, p. 611-621.

38. Michael J. Woulds, "Recycling of Engine Serviced Superalloys", Superalloys 1980, Published by The American Society for Metals, Metals Park, Ohio, 1980, p. 31-41.

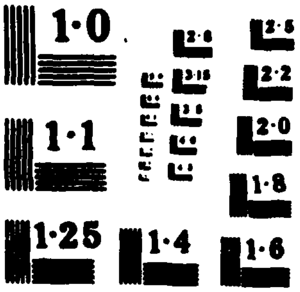
39. J.J. deBarbadillo, "Nickel Base Superalloys; Physical Metallurgy of Recycling", Metall. Trans. A, 14A, 1983, p. 329-341.

40. R.S. Cremisio and L.M. Wasserman, "Superalloy Scrap Processing and Trace Element Considerations", Vacuum Metallurgy, Science Press, Princeton, N.J., 1977, p. 353-388.

AD A148 598 MATERIALS SUBSTITUTION AND RECYCLING PROCEEDINGS OF THE MEETING OF THE ST..(U) ADVISORY GROUP FOR AEROSPACE RESEARCH AND DEVELOPMENT NEUILLY.. APR 84 AGARD CP-356 4/4

UNCLASSIFIED F/G 15/5 NL

END
DATE
FILMED
1 85


1·0
2·8
2·5
3·2
2·2
3·6
2·0
4·0
1·1
1·8
1·25
1·4
1·6

41. R.S. Cremisio, L.W. Lherbier, C.S. Freer, E.W. Ross and C.H. Lund, "Tracealloy - A Superalloy Standard", ibid, p. 333-352.

ACKNOWLEDGEMENTS

The author is grateful to all those persons who have unselfishly discussed their work and thereby contributed to the commentary in this review. Due recognition is also given to all the authors of the papers that have been cited; their considerable efforts have truly raised our knowledge of this subject over the past eight years.

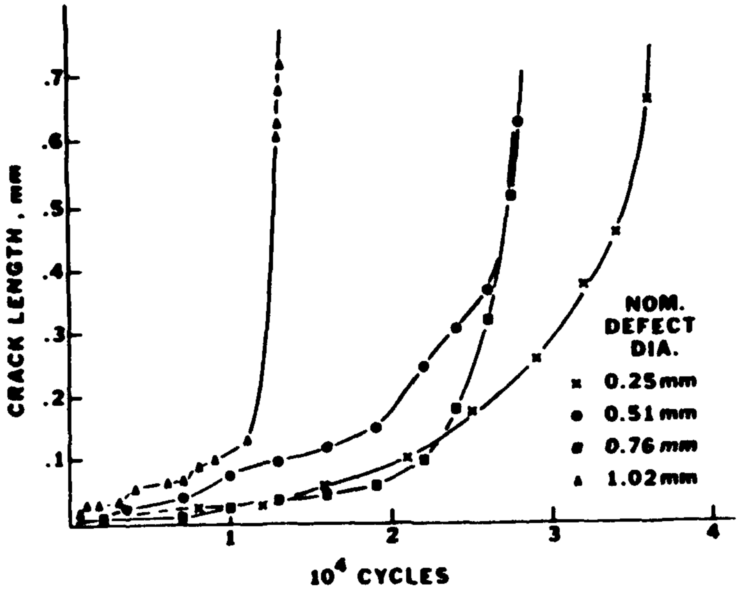


Fig. 1 Propagation rates of fatigue cracks in MERL 76 at 1068 MPa, 20°C. Cracks originated at alumina inclusions of various sizes. From Law and Blackburn (9).

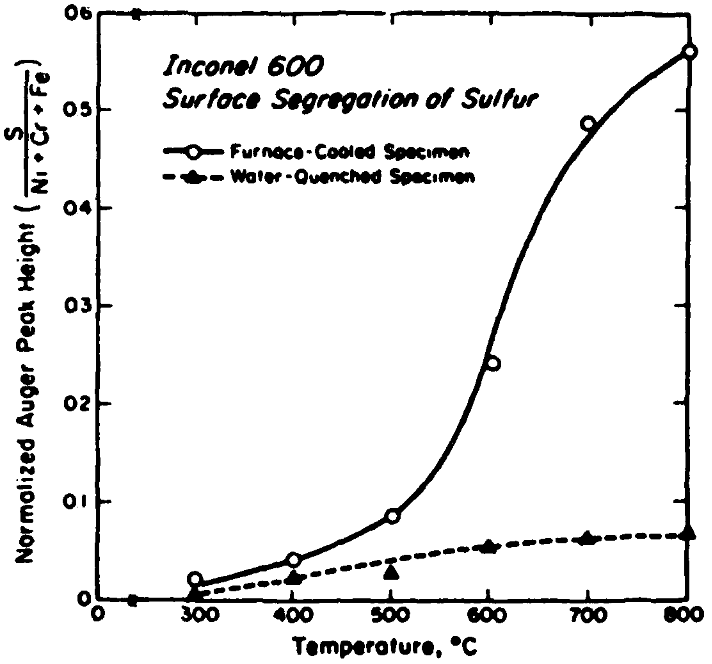


Fig. 2 Effect of annealing temperatures on the normalised Auger sulfur peaks for furnace cooled and water quenched Inconel 600 specimens. From Chaung et al (14).

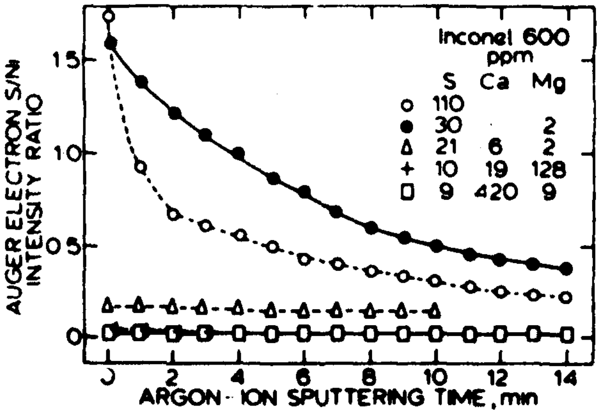


Fig. 3 Variation of S/Ni intensity ratio as a function of distance from intergranular fracture surface for Inconel 600 alloys with various residuals. From Yamaguchi et al (16).

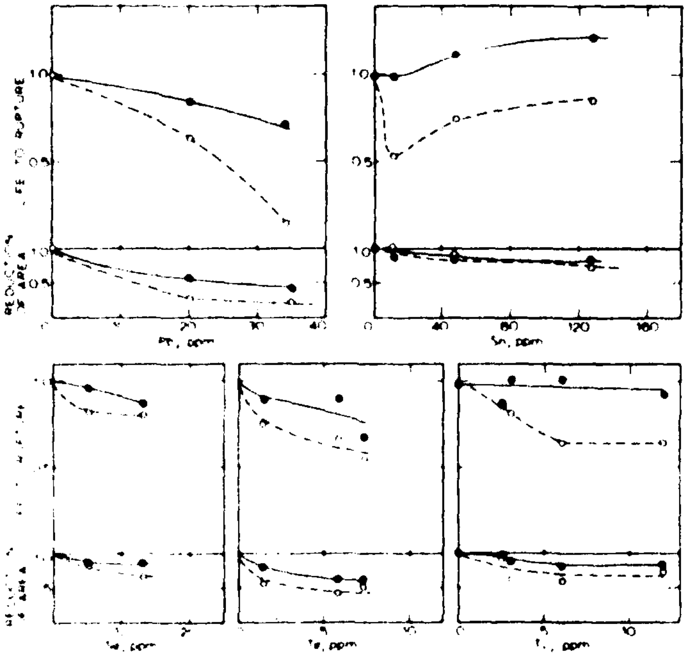


Fig. 4 Normalised stress-rupture properties of Nimonic 105 as a function of impurity content: ● = 815°C, 556 MPa plain specimens, O = 815°C, 350 MPa notched specimens. From Thomas and Gibbons (23).

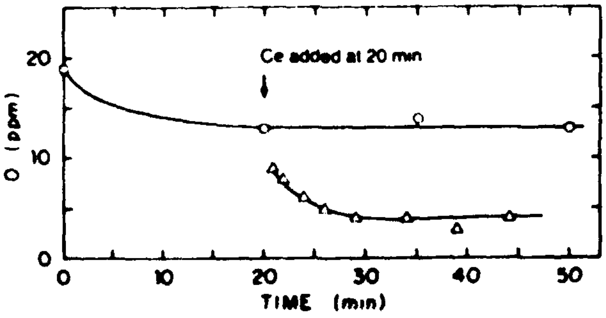


Fig. 5 Oxygen content in U-901 alloy melt without Ce (O) and with 0.16 wt pct Ce addition (Δ). From Li et al (34).

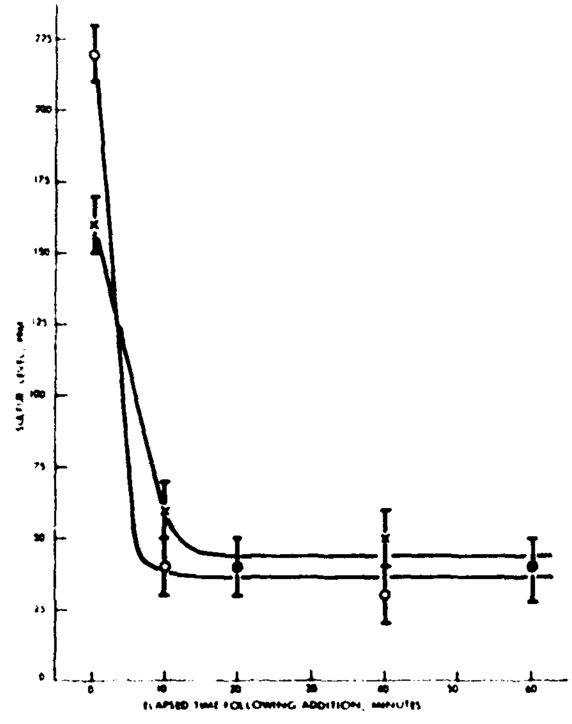


Fig. 6 **Rate of desulfurization in 454 kg heats of Haynes alloy 718;**
x = 1550 ppm Mischmetal addition,
O = 2000 ppm Mischmetal addition.
From Rothman (35).

RECYCLING CONFORM DESIGN

Prof. Dr.-Ing. Walter Jorden
Universität Paderborn, FB 10, Pohlweg 47/49, D-4790 Paderborn

SUMMARY

The flow of materials in a real recycling system can be demonstrated in a simplified manner by a recycling model system. The analysis of this system results in additional new goals and guide lines for design. The guide lines are interpreted by examples showing how a product can be designed in a recycling conform manner, i. e. each product should be prepared in an optimal way for the eventual reuse of the whole product and, after the end of product life, for regaining the residue materials. The guide lines point out to the future, but can be realised in part even today without additional cost.

1. DESIGNER AND RECYCLING SYSTEM

We need machines and apparatus' for solving problems; by producing and using machines we create new problems. Therefore we are responsible for controlling the technical development today, if we want to see a change in our course tomorrow - like a big ship.

Machines and apparatus' are created by the designer. He decides not only on their cost, but also on their quality in the use and the consequences for the environment. By the increasing amount of information and demand to be taken into consideration the designer is more and more overtaxed. Therefore the science of design must help him by information and guide lines suitable for practical purposes /1/.

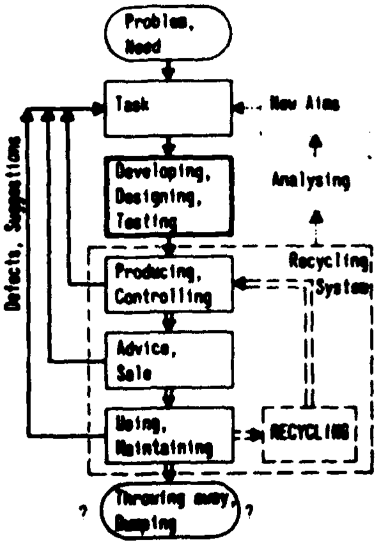


Fig. 1: Development and life phases of a product; recycling and information circles

Often the designer feels only like a link in a linear information chain going from the cause (task) over a procedure (design) to the result (product), Fig. 1. Really the result feeds back to the cause, so we have a closed loop. Mostly these feed-backs are caused by defects or by suggestions coming from production, sale or use. So the product is improved and by and by optimised for low price and sufficient fulfilment of its function.

But this "optimisation" is not optimal as seen from a higher view of economics. We are forced to preserve our material ressources as well as our energy ressources and our environment. Besides economising and substitution of materials, recycling must be the third measure (Fig. 1, dotted lines). This recycling loop is a material circle. The information circle including the designer is closed by analysing the recycling system and gaining new aims and tasks for designing (pointed lines). The consideration and realisation of them is "recycling conform design". It means that a product is designed in a manner that it is prepared in an optimal way for

- the eventual reuse of the whole product or parts of it and
- the regaining of the materials after the end of the product life.

2. REALISATION OF THE RECYCLING CONFORM DESIGN

The designer solves problems by technical means. Therefore we find the five steps of the problem solving in the design process too, Fig. 2. The same procedure is useful for developing the recycling conform design, Fig. 3.

At first we must realise the problem itself. Then we have to formulate the task, as done in /1/. The third step is developing ideas for solutions /2, 3, 4, 5/. In the fourth step we should introduce these ideas into practice, and test them. It is most important to wake up the consciousness of the problem in all men participating in our technical system,

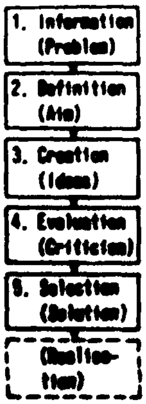


Fig. 2 (on the left): General problem solving process

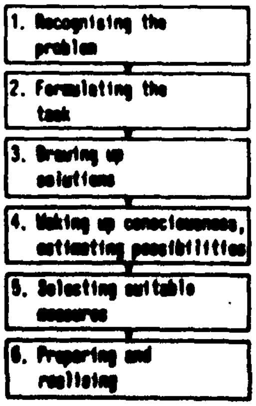


Fig. 3 (on the right): Measures for realising the recycling conform design, according to Fig. 2

especially on the management level. There is a series of possibilities for realising the recycling conform design without any or with little cost; we must find and pick them out in the fifth step. After that we can prepare and carry out measures.

Looking to the design process we find two points where the demand for "recycling conform" is of a special importance:

- In the planing phase the demand for "recycling conform" must be part of the task respectively the list of demands; otherwise the product will never show this feature.
- During the elaboration phase the designer must be supportet by guide lines and examples.

3. RECYCLING MODEL SYSTEM

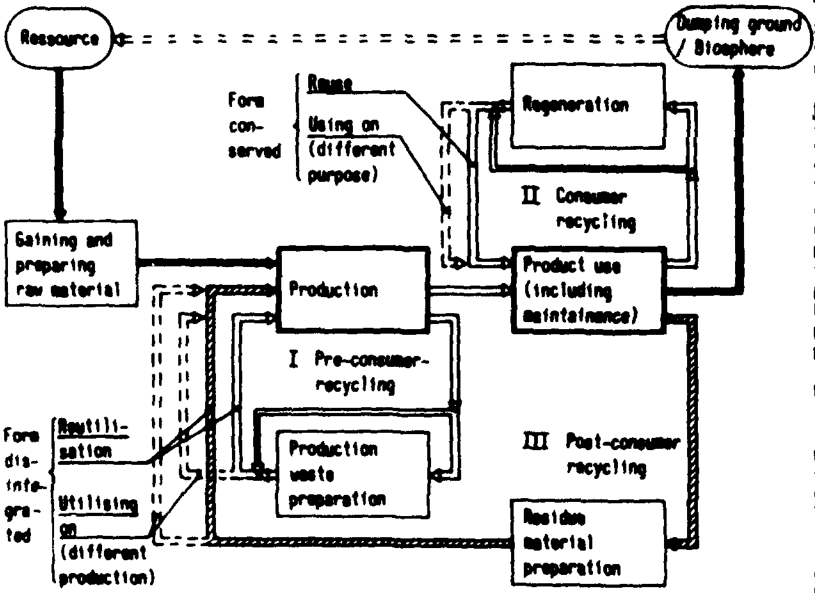


Fig. 4: Simplified recycling model system

The flow of materials in real recycling systems can be demonstrated in a simplified manner by a recycling model system, Fig. 4. *From* the ressources of the earth, raw materials are gained which flow into the production. The primary recycling circle ("pre-consumer recycling") consists of production waste. The material comes back to a production of the same kind with or – as far as possible – without preparing.

Now the product is used (double arrows). The main target is to prevent the product ending on the dumping ground or burdening the biosphere. Therefore we should try to prolong the product life. Measures as maintenance and repair do not belong to recycling, but to normal product use. There is, however, no exact border between these regions. *"Recycling during product use"* or "consumer recycling" means that a product, instead of leaving the stage of use, is regenerated by specific processes and given back to the same use (e. g. reconditioned car engines or mold tires).

This is called "reuse". The product does not lose its form or its function; it remains on a high value level; opposite to disintegration or reduction to small pieces which would imply a heavy loss of value. Therefore the reuse is the preferred way of recycling. Often the product may be "used on" for a different purpose, if it is no longer suitable for its original purpose (e. g. using tires as buffers in a port); that also means a certain loss of value.

When reusing or "using on" is no longer possible respectively economical, the product must be disintegrated or reduced to small pieces for regaining the materials. This "post-consumer recycling" may lead to a production of the same kind as before (reutilisation", e. g. steel scrap remelted to steel), or to a different production ("utilising on", e. g. producing grounds for sports facilitis from worn tires).

All procedures in these cycles imply losses of materials (and energy); we have to try to minimise these losses in an optimal way, respectively, in the borderline case, to remove them.

4. GUIDE LINES FOR RECYCLING CONFORM DESIGN

Guide lines for the recycling conform design can be developed from the processes in the recycling systems. Guide lines are *not* inflexible rules, but recommendations. The normal task of every designer is to find compromises between different demands; recycling gives a new category of design demands and criterions for optimisation. *We will consider* the main guide lines according to the three recycling circles.

4.1 Pre-consumer Recycling

Regaining the material of production waste is the most frequent kind of recycling, especially for these reasons:

- The materials are known.
- They can be collected in a simple, clean and separate way.
- The ways of transportation are simple and short.
- The profit can be calculated.

The designer often has only an indirect influence upon these processes because they belong to the responsibility of the production. Therefore the following guide lines require a close cooperation between design and production - which will be helpful in every case.

<u>Basic rule I</u>: Such production processes should be used which do not cause waste, at least as little waste as possible.

The waste in cutting processes can be minimised by optimal positions of the shape on a sheet metal plate and by using-on cut off parts for smaller pieces.

<u>Recyclability</u>: Not avoidable production waste should be suitable for recycling, and that with as little cost and value loss as possible.

4.2 Recycling during use (consumer recycling)

The guide lines of this group are on the border between recycling and maintenance. A strict separation is neither possible nor efficient, because both of them intend to keep a product as long as possible in the using stage, i.e. on high value level. The repair or maintenance of a larger product, like an aeroplane, often means that singular units are replaced and recycled.

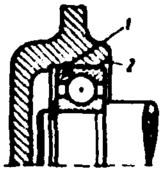
But there is a clear difference between an individual "repair" of a product after a defect and a "product regeneration" in an industry-like manner /4/. Examples of reconditioned engines, typewriters, machine tools show that it is possible to achieve recycling by plants or workshops in an economical way. Their products are as good as new ones or still better, if each of them is tested individually in contrast to new series of products which are only tested at random.

The next guide lines follow the range of procedures in a regeneration workshop:

<u>Basic rule II</u>: Every product should be suitable for a reuse with as little expense as possible; therefore regeneration or reconditionining should be as easy as possible.

This rule should be obvious, but we see only too often how it is violated by too short-sighted economical considerations. A positive example is the standard glass bottle for beverages. The aluminium screw cap does not only save the contents and the environs and seal the bottle, but also enables the bottle to be closed again and protects the empty bottle against dirt as well as the bottle thread against damage. The latter functions only concern the recycling of the bottle.

<u>Dis- and reassembly</u>: Every product consisting of several parts should be dis- and reassembled without damage as simply, clearly, and safely as possible.

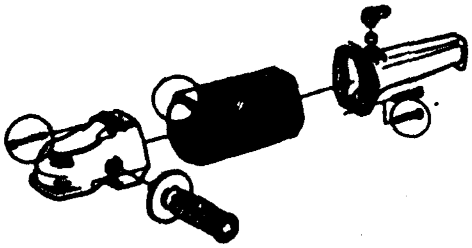


<u>Fig. 5</u>: Jointing between ball bearing and housing by snap washer 1, easily to be assembled by chamfer 2, but not to be disassembled /1/

The snap jointing between the ball bearing and the housing, <u>Fig. 5</u>, is a negative example for an easy assembly without being able to be disassembled. In every case disassembly should be possible without any special tools; all parts concerned should be well accessible.

<u>Connections</u>: Detachable connections must fulfil their function over the whole product life including recycling, i.e. they must neither be stuck by corrosion nor lose their function by repeated detachment.

Especially bolts are susceptible to corrosion; therefore there should not be any slit between screw head and contact surface (e. g. no open spring washer). The housing of the grinder, <u>Fig. 6</u>, could not be recycled because a thread hole had been torn out. Better solutions would be through-holes with longer bolts, or thread inserts. On the other hand in the aircraft industry we must take the weight into consideration.



<u>Fig. 6</u>: Not recycling conform design of the plastic housing for a grinder /4/ (thread hole torn out)

<u>Cleaning</u>: Parts should be able to be cleaned completely without damage.

Cavities and corners should be well accessible, letterings durable enough against solvents.

<u>Differentiation</u>: Parts with the same function should be either absolutely equal or clearly different.

That facilitates storage problems as well as the identification of parts after disassembly.

The next group of guide lines will help to reduce the number of necessary new parts in the regeneration process.

Wear: Wear should be eleminated, at least minimised. Unavoidable wear is to be limited to special, easily interchangeable elements.

Such elements are well known in brakes or clutches. Important are the whereabouts of the worn material, because it is lost for recycling and mostly scattered in the environment. Machining allowances and adjustment aids for regeneration are to be taken into consideration. The decision about sliding or rolling friction should depend on the life expectency (the rolling principal is not always the better one). The tribological knowledge should be transposed into practice in a more consequent way.

Corrosion: Every product should be designed in such a way that corrosion will not find a working surface.

E. g. gaps or slits are to be avoided, or stuffed, or designed large enough not to retain dirt and moisture. Water or condensate must not accumulate in cavities; they should be closed or have large enough drain holes.

Protective layers: Layers against corrosion and other destroying influences should be dimensioned for the whole product life; if not possible, they should be renewable as easily and completely as possible.

That concerns all kind of protective layers, also on joints, bolts, and other small parts. But we should note that each layer represents a compound material, and we have to weigh the enlargement of the product life against the perhaps negative consequences in an eventual recycling process.

Standardisation: Elements, assembly groups, or products with the same function should be standardised in structure, joining dimensions and materials.

This rule will facilitate the identification and the exchangement of parts as well as the identification of the material in the eventual recycling process. Each kind of misconceived individualism can only be injurious. Positive examples are anti-friction bearings.

4.3 Post-consumer recycling

Eventually each product will not be able to be regenerated; then it will be disintegrated for the reutilisation of the materials. Taking into consideration these processes brings new demands to the design of products.

Basic rule III: Every product (in addition to the consideration of all design demands) should be designed in such a way that it is prepard for a process to regain the materials after the end of use.

The main problems are to identify the materials and to sort them into compatible groupes /3/. E. g. it is possible to add scrap of unalloyed to high-alloy steel scrap, but not conversely. This problem becomes most difficult if aluminium alloys are considered, which are of high importance in the aircraft industry. Aluminium scrap from wrought alloy of high value can only be reutilised for inferior casting alloy if the composition of alloys is not exactly known or if the scrap is contaminated by different alloys.

From this point of view we find the following guide lines; their realisation still requires some preparatory work.

Identification: A clearly visible and durable identification symbol should state the material (respectively the compatible material group) and the possibilities of recycling.

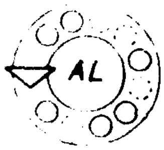


Fig. 7: Proposal of a symbol stating material and recycling possibilities, e. g. for aluminium /2/ (○ = raised; ◌ = deepened)

Such symbols already were used in a simple form during the last war for marking non-iron materials, e. g. for tubes. Fig. 7 shows a proposal for coding more than 640 000 different combinations. In this field intensive work should be done, being an important assumption for an economical recycling especially of aluminium and high-alloy materials.

One-material products: At first it should be aspired to that a product consists of only one recyclabl material, at least that all materials of the product belong to the same compatible material group.

An example is a ball bearing with a steel cage.

Non-disturbing materials: If an one-material product cannot be realised, then it is aspired to that the product consists only of materials which do not disturb in the recycling process, i.e. of an recyclable main material and as few as possible other materials which can be removed in the recycling process.

E. g. the plastic cage of a ball bearing is lost if the bearing is melted, but it does not contaminate the steel melt.

Compatible groups: If a compatible or a non-disturbing material combination cannot be achieved within the whole product, then it should be possible to separate the product as easily and clearly as possible into groups or assembly units each of them consisting of compatible or non-disturbing materials.

Disturbing materials should be avoided, at least their proportion should be kept under the admissible limit. E. g. in a steel melt the main disturbing materials are copper (admissible ≤ 0,15 %) and tin (≤ 0,02 %). A roller bearing with a brass cage would exceed the copper limit by far.

Seperation: Groups to be separated in the recycling process should be clearly marked and positioned in the outer areas of a product for easy access and detachment. Their number should be minimised.

This rule applies to units with disturbing materials (e. g. electric motors with a high copper proportion) as well as with scarce or high value material (e. g. cobald). Fig. 8 shows how a new design deteriorates the identification and the separation of an electric motor in a sewing-machine.

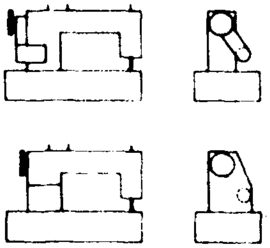


Fig. 8: Not recycling conform new design of a sewing machine /2/ (electric motor integrated in and hidden by the housing)

Combined materials: If combined or compound materials consisting of not separable and not compatible materials are to be used, the advantages (longer life etc.) should be carefully weighed against the disadvantages in the recycling process. One-material, compatible or separable principals should be prefered.

E. g. zinc is one of the best steel protective layers against corrosion, but in the melting process it is aggressive to the melting furnace. If a beverage tin consists of aluminium with a tin plate cover, neither of these materials can be recycled economically, whereas a "tin" only of aluminium is not more expensive, but conforms to recycling. Similar reflections should be made if aluminium parts are connected by steel rivets.

5. ECONOMY AND RECYCLING

There is the assumption that the recycling conform design would make the products more expensive, and therefore would decrease the industry against the competition of other countries. This meaning is not only shortsighted concerning the ressource situation, but also in a general sense not correct, for the following reasons:

- Several measures can be realised without any additional cost, if the designer is aware of the problem.
- Recycling conform products often are also maintenance conform; as the personnel costs are arising, this is throughout an argument for publicity.
- The change from "repair" to "regeneration" will result in new places of employment in regeneration centres or similar and help the plant to reduce the expensive repair departments.
- Regenerated recycling products can be of the same value as new products, but considerably cheaper.
- Secondary materials often need only a fraction of the energy necessary for primary materials. There is an economic optimum at a certain quota of recycling; therefore the recycling quota can have a positive influence on the raw material prices.

Experience shows that even today it is possible to achieve an economical recycling of residue materials with one-material products (e. g. glass) or with simple separation of materials (e. g. lead accumulators), an important condition for that being favourable transportation facilities. The recycling conform design will and can help here as well as in maintaining products in the state of use. The guide lines have not been developed for a special kind of products, therefore they can be transfered to aircraft products also. Recycling must not be done radically; but in a reasonable and selective way it should be part of measures for preserving our ressources and the economical basis of our life.

REFERENCES

/1/ Jorden, W.; Weege, R.D.: Recycling beginnt in der Konstruktion. Konstruktion 31 (1979) 10, P. 381-387.

/2/ Weege, R.D.: Recyclinggerechtes Konstruieren. Düsseldorf: VDI 1981.

/3/ Meyer, H.: Recyclingorientierte Produktgestaltung. Fortschritt-Berichte VDI-Z. Reihe 1 Nr. 98, Düsseldorf: VDI 1983.

/4/ Warnecke, H.J.; Steinhilper, R.: Instandhaltung, Aufarbeitung, Aufbereitung: Recyclingverfahren und Produktgestaltung. VDI-Z 124 (1982) 20, P. 751-758.

/5/ Jorden, W.: Recyclinggerechtes Konstruieren als vordringliche Aufgabe zum Einsparen von Rohstoffen. Maschinenmarkt 89 (1983) 61, P. 1406-1409.

REPORT DOCUMENTATION PAGE

1. Recipient's Reference	2. Originator's Reference	3. Further Reference	4. Security Classification of Document
	AGARD-CP-356	ISBN 92-835-0352-X	UNCLASSIFIED

5. Originator

Advisory Group for Aerospace Research and Development
North Atlantic Treaty Organization
7 rue Ancelle, 92200 Neuilly sur Seine, France

6. Title

MATERIALS SUBSTITUTION AND RECYCLING

7. Presented at

the 57th Meeting of the Structures and Materials Panel in Vimeiro, Portugal, 9 14 October 1983.

8. Author(s)/Editor(s)	9. Date
Various	April 1984

10. Author's/Editor's Address	11. Pages
Various	306

12. Distribution Statement

This document is distributed in accordance with AGARD policies and regulations, which are outlined on the Outside Back Covers of all AGARD publications.

13. Keywords/Descriptors

Heat resistant alloys
Substitutes
Materials recovery
Turbines
Jet engines

14. Abstract

The rarity of several metals such as cobalt, chromium, tantalum and niobium, which are used in high temperature materials for jet turbines induces a need for stockpiling, conservation, substitution and recycling.

This meeting was focused on the last two aspects, with special reference to superalloys with low critical element contents and substitutes to superalloys on one side, the identification of the sensitive impurities, the problems related to the increase of their concentration, and the possible ways to solve them on the other.

AGARD Conference Proceedings No.356
Advisory Group for Aerospace Research and Development, NATO
MATERIALS SUBSTITUTION AND RECYCLING
Published April 1984
306 pages

The rarity of several metals such as cobalt, chromium, tantalum and niobium, which are used in high temperature materials for jet turbine induces a need for stockpiling, conservation, substitution and recycling

This meeting was focused on the last two aspects, with special reference to superalloys with low critical element contents and substitutes to superalloys on one side, the identification of the sensitive impurities, the problems

P.T.O

AGARD-CP-356

Heat resistant alloys
Substitutes
Materials recovery
Turbines
Jet engines

AGARD Conference Proceedings No.356
Advisory Group for Aerospace Research and Development, NATO
MATERIALS SUBSTITUTION AND RECYCLING
Published April 1984
306 pages

The rarity of several metals such as cobalt, chromium, tantalum and niobium, which are used in high temperature materials for jet turbine induces a need for stockpiling, conservation, substitution and recycling

This meeting was focused on the last two aspects, with special reference to superalloys with low critical element contents and substitutes to superalloys on one side, the identification of the sensitive impurities, the problems

P.T.O

AGARD-CP-356

Heat resistant alloys
Substitutes
Materials recovery
Turbines
Jet engines

AGARD Conference Proceedings No.356
Advisory Group for Aerospace Research and Development, NATO
MATERIALS SUBSTITUTION AND RECYCLING
Published April 1984
306 pages

The rarity of several metals such as cobalt, chromium, tantalum and niobium, which are used in high temperature materials for jet turbine induces a need for stockpiling, conservation, substitution and recycling

This meeting was focused on the last two aspects, with special reference to superalloys with low critical element contents and substitutes to superalloys on one side, the identification of the sensitive impurities, the problems

P.T.O

AGARD-CP-356

Heat resistant alloys
Substitutes
Materials recovery
Turbines
Jet engines

AGARD Conference Proceedings No.356
Advisory Group for Aerospace Research and Development, NATO
MATERIALS SUBSTITUTION AND RECYCLING
Published April 1984
306 pages

The rarity of several metals such as cobalt, chromium, tantalum and niobium, which are used in high temperature materials for jet turbine induces a need for stockpiling, conservation, substitution and recycling

This meeting was focused on the last two aspects, with special reference to superalloys with low critical element contents and substitutes to superalloys on one side, the identification of the sensitive impurities, the problems

P.T.O

AGARD-CP-356

Heat resistant alloys
Substitutes
Materials recovery
Turbines
Jet engines

related to the increase of their concentration, and the possible ways to solve them on the other

Papers presented at the 57th Meeting of the Structures and Materials Panel in Vimeiro, Portugal, 9 14 October 1983.

ISBN 92-835-0352-X

---

related to the increase of their concentration, and the possible ways to solve them on the other

Papers presented at the 57th Meeting of the Structures and Materials Panel in Vimeiro, Portugal, 9 14 October 1983

ISBN 92-835-0352-X

---

related to the increase of their concentration, and the possible ways to solve them on the other

Papers presented at the 57th Meeting of the Structures and Materials Panel in Vimeiro, Portugal, 9 14 October 1983

ISBN 92-835-0352-X

---

related to the increase of their concentration, and the possible ways to solve them on the other

Papers presented at the 57th Meeting of the Structures and Materials Panel in Vimeiro, Portugal, 9 14 October 1983

ISBN 92-835-0352-X

[redacted]

AGARD
NATO + OTAN
7 RUE ANCELLE · 92200 NEUILLY-SUR-SEINE
FRANCE
Telephone 745.08.10 · Telex 610176

DISTRIBUTION OF UNCLASSIFIED AGARD PUBLICATIONS

AGARD does NOT hold stocks of AGARD publications at the above address for general distribution. Initial distribution of AGARD publications is made to AGARD Member Nations through the following National Distribution Centres. Further copies are sometimes available from these Centres, but if not may be purchased in Microfiche or Photocopy form from the Purchase Agencies listed below.

NATIONAL DISTRIBUTION CENTRES

BELGIUM
Coordonnateur AGARD – VSL
Etat-Major de la Force Aérienne
Quartier Reine Elisabeth
Rue d'Evere, 1140 Bruxelles

CANADA
Defence Science Information Services
Department of National Defence
Ottawa, Ontario K1A 0K2

DENMARK
Danish Defence Research Board
Østerbrogades Kaserne
Copenhagen Ø

FRANCE
O.N.E.R.A. (Direction)
29 Avenue de la Division Leclerc
92320 Châtillon sous Bagneux

GERMANY
Fachinformationszentrum Energie,
Physik, Mathematik GmbH
Kernforschungszentrum
D-7514 Eggenstein-Leopoldshafen 2

GREECE
Hellenic Air Force General Staff
Research and Development Directorate
Holargos, Athens

ICELAND
Director of Aviation
c/o Flugrad
Reykjavik

ITALY
Aeronautica Militare
Ufficio del Delegato Nazionale all'AGARD
3 Piazzale Adenauer
Roma/EUR

LUXEMBOURG
See Belgium

NETHERLANDS
Netherlands Delegation to AGARD
National Aerospace Laboratory, NLR
P.O. Box 126
2600 A.C. Delft

NORWAY
Norwegian Defence Research Establishment
Main Library
P.O. Box 25
N-2007 Kjeller

PORTUGAL
Direcção do Serviço de Material
da Forca Aerea
Rua da Escola Politecnica 42
Lisboa
Attn: AGARD National Delegate

TURKEY
Department of Research and Development (ARGE)
Ministry of National Defence, Ankara

UNITED KINGDOM
Defence Research Information Centre
Station Square House
St. Mary Cray
Orpington, Kent BR5 3RE

UNITED STATES
National Aeronautics and Space Administration (NASA)
Langley Field, Virginia 23365
Attn: Report Distribution and Storage Unit

THE UNITED STATES NATIONAL DISTRIBUTION CENTRE (NASA) DOES NOT HOLD STOCKS OF AGARD PUBLICATIONS, AND APPLICATIONS FOR COPIES SHOULD BE MADE DIRECT TO THE NATIONAL TECHNICAL INFORMATION SERVICE (NTIS) AT THE ADDRESS BELOW.

PURCHASE AGENCIES

Microfiche or Photocopy
National Technical
Information Service (NTIS)
5285 Port Royal Road
Springfield
Virginia 22161, USA

Microfiche
ESA/Information Retrieval Service
European Space Agency
10, rue Mario Nikis
75015 Paris, France

Microfiche or Photocopy
British Library Lending
Division
Boston Spa, Wetherby
West Yorkshire LS23 7BQ
England

Requests for microfiche or photocopies of AGARD documents should include the AGARD serial number, title, author or editor, and publication date. Requests to NTIS should include the NASA accession report number. Full bibliographical references and abstracts of AGARD publications are given in the following journals:

Scientific and Technical Aerospace Reports (STAR)
published by NASA Scientific and Technical
Information Branch
NASA Headquarters (NIT-40)
Washington D.C. 20546, USA

Government Reports Announcements (GRA)
published by the National Technical
Information Services, Springfield
Virginia 22161, USA

Printed by Specialised Printing Services Limited
40 Chigwell Lane, Loughton, Essex IG10 3TZ

ISBN 92-835-0352-X

DATE
FILMED
-8