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

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## 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 $\beta$-phase (NiPtAl).

2) a basic coating of $\beta$-phase the outer part of which contains $PtAl_2$ precipitates

3) a coating consisting solely of $\beta$-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 care 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 established 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 $\beta$-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 reached 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 [illegible] 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 Aluminide 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 $\beta$-NiAl being converted to the less oxidation resistant $\gamma$'-phase ($Ni_3Al$).

This process occurs progressively with service exposure until $\gamma$' 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 $\beta$ -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 $\beta$-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 $\beta$ -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 imcompatible 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 $\gamma'$ stability resulting from an increase in the $\gamma'$-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, viz 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 substantially 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 $\sigma$-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 $\sigma$-phase were shown to extend from the coating/substrate interface for up to 100 microns into the substrate itself. Under certain conditions the $\sigma$-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 fatique 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 $\sigma$-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 $\sigma$ -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 aggressive 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 $927^{\circ}$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 $871^{\circ}$C and $1000^{\circ}$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 $1000^{\circ}$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 $500^{\circ}$C and $900^{\circ}$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 $\sigma$-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, including U700 and Wl-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

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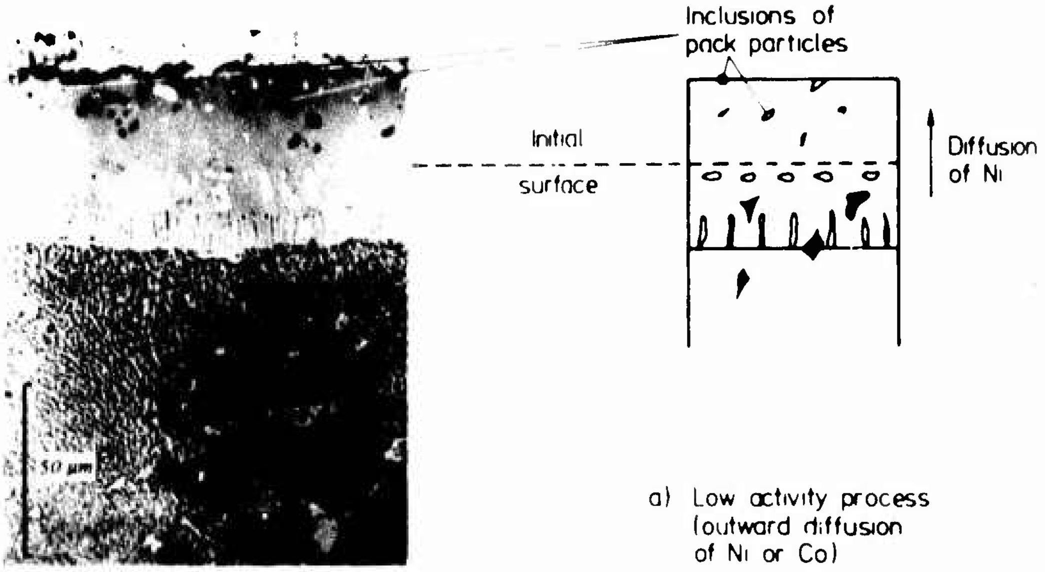
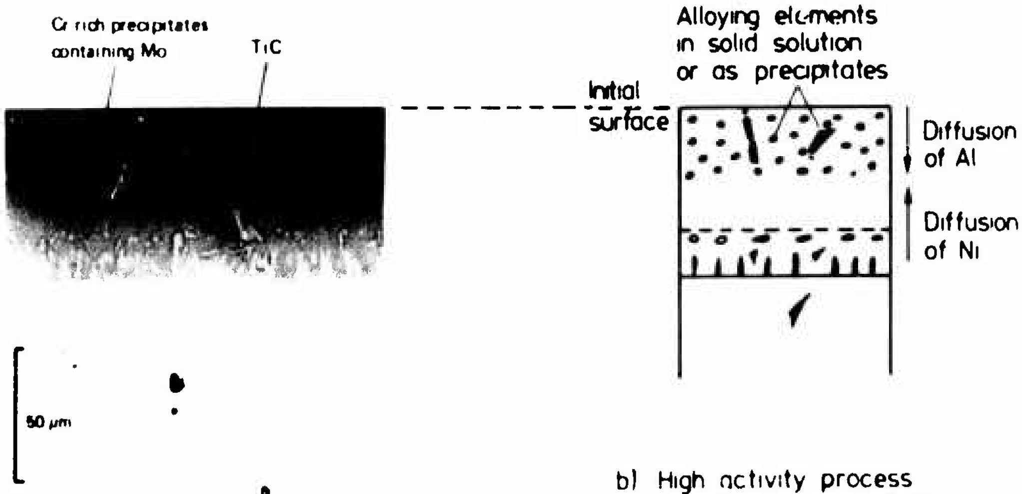
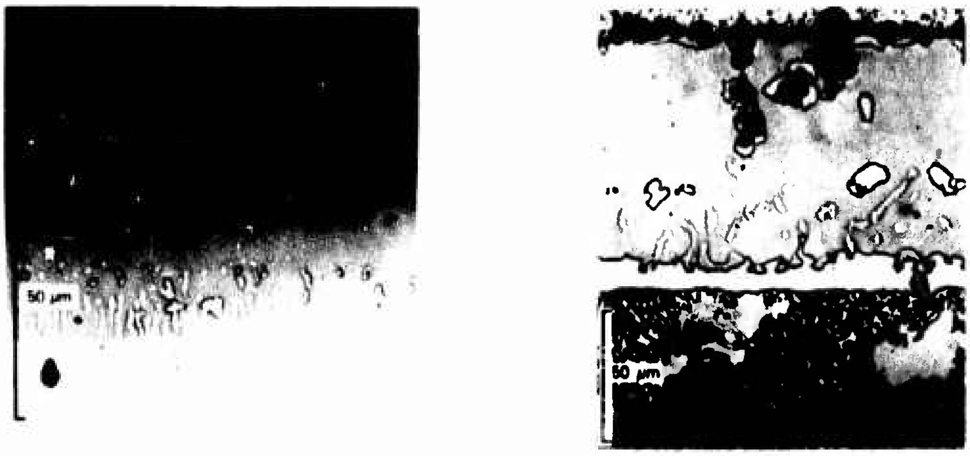


a) Low activity process (outward diffusion of Ni or Co)



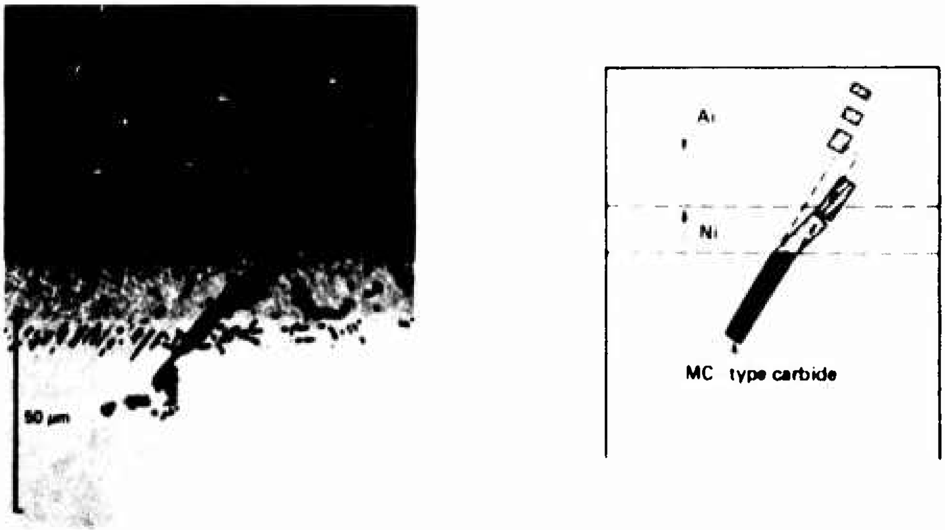
b) High activity process (inward diffusion of Al)

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.

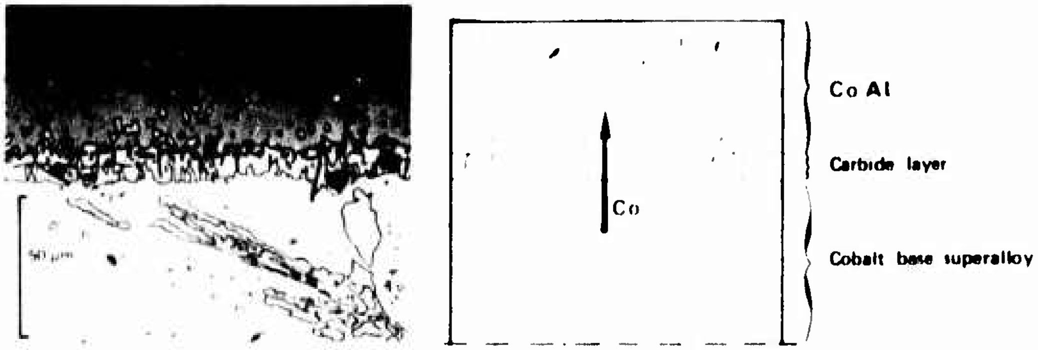
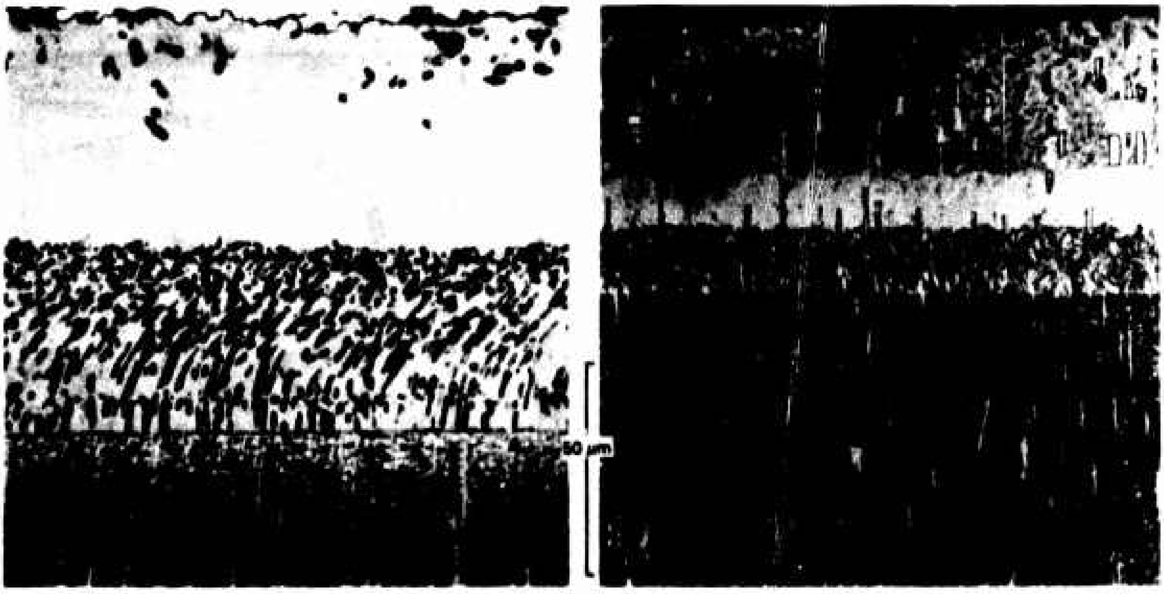


Fig 3 – Low activity aluminide coating on Co base superalloy X 40.



Low activity aluminizing treatment

High activity aluminizing treatment

Fig. 4 – NiAl-type coatings on COTAC 744 ($\gamma/\gamma'$ – NbC eutectic).

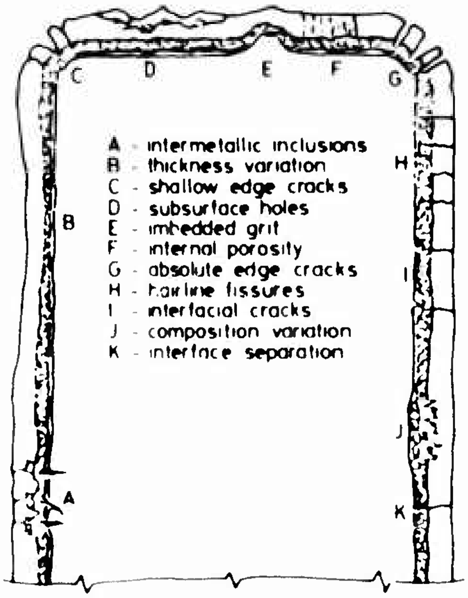


**Fig. 5 – Representative random defects in coatings (from ref. 25).**

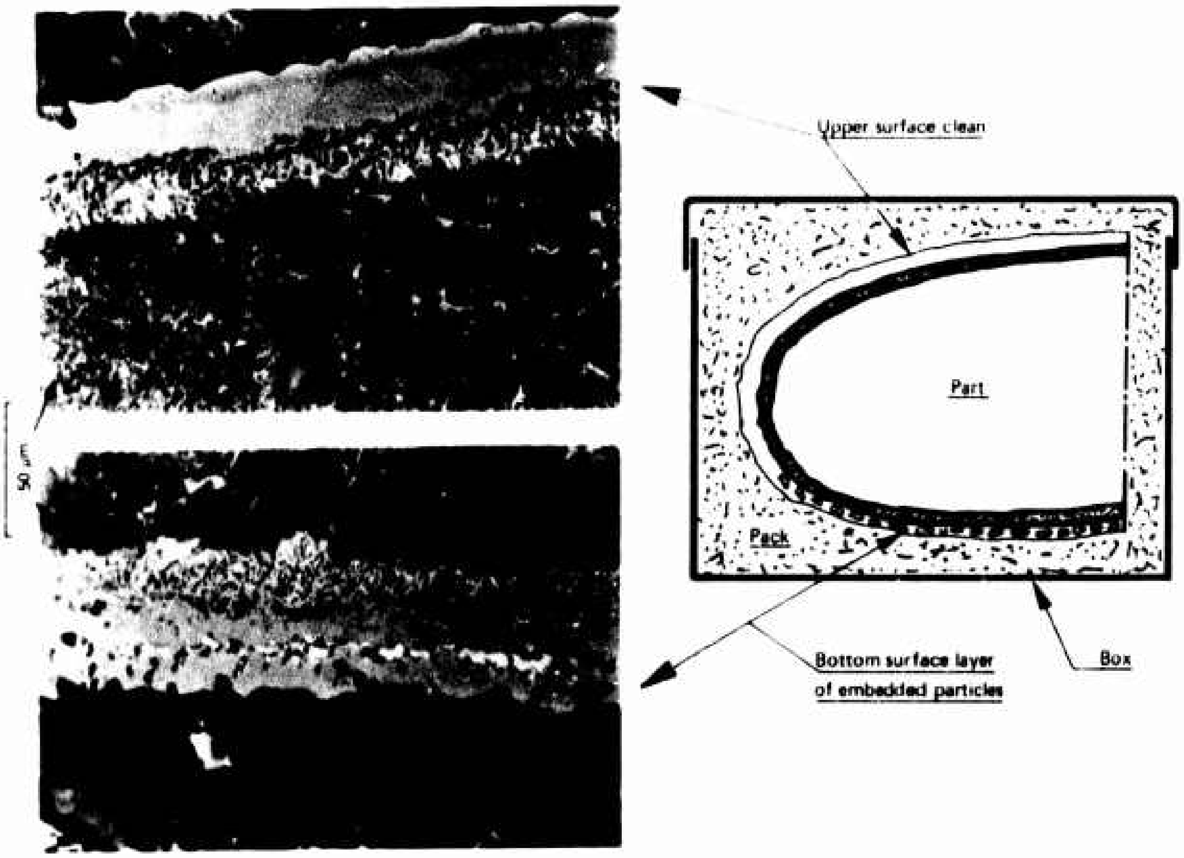


**Fig. 6 – Variation of coating structure caused by positioning of the part in the cementation pack ; HI-15 on IN 738 LC.**

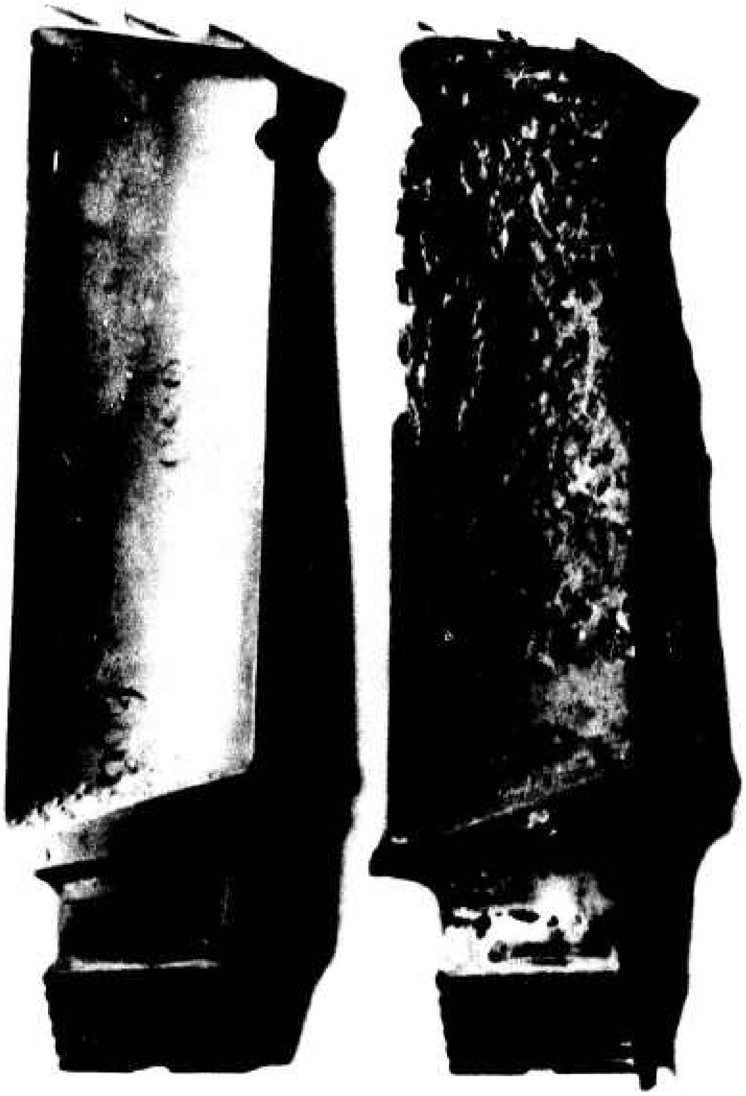


Fig. 7 – Industrial gas turbine blades from a desert location in the Middle East. Pack aluminised IN 738 blade after 12,000 hours service (left) and pack aluminised Nimonic alloy 115 blade after 2000 hours service (right) (from ref. 68).

Fig. 8 — (a) Uncoated and (b) aluminised Dart turbine blades after "inter-island" operation (from ref. 69).

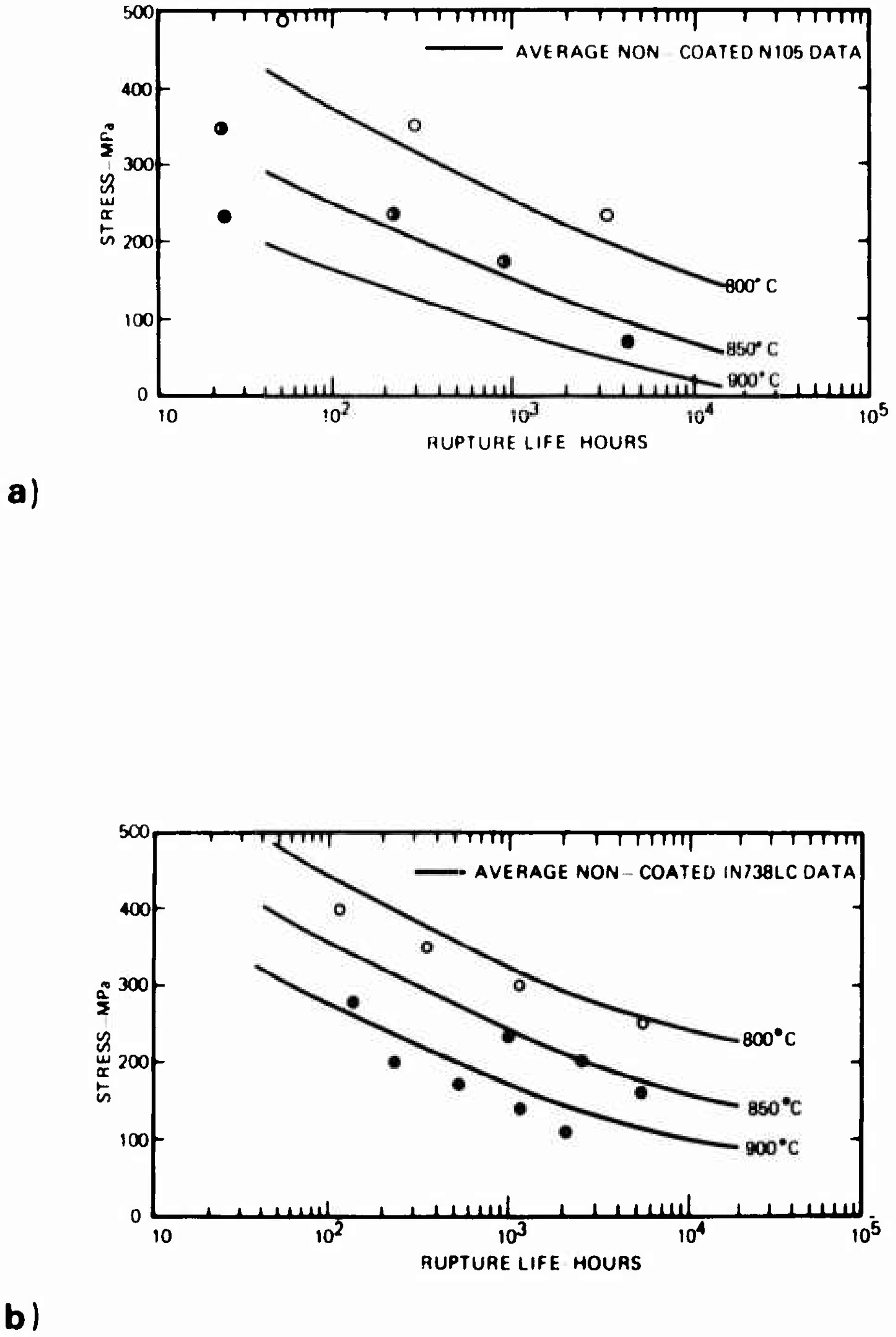


Fig. 9 – Effect of CVD Si-coatings on creep rupture life : no detrimental effect being observed on Nimonic 105, (a) ; while same coating leads to reduction of $t_r$ for IN 738 LC, (b). (after ref. 70).

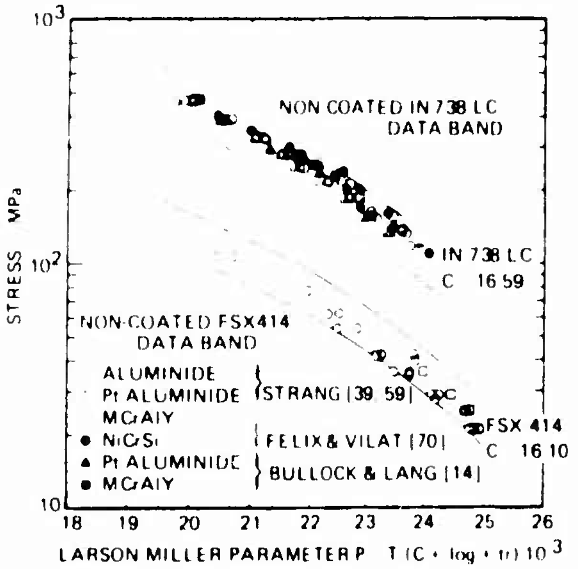


**Fig. 10 – Rupture properties of coated and non-coated IN 738 LC and FSX4 14. (Quality heat treatment had been applied after coating process).**

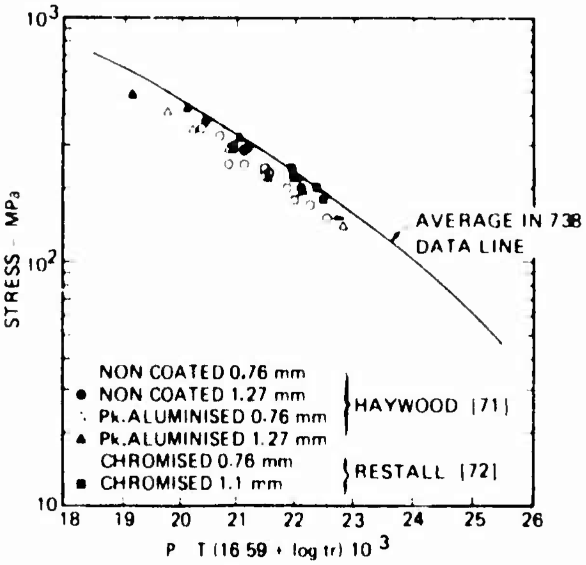


**Fig. 11 – Rupture properties of thin section IN 738 C in the coated and non-coated condition.**

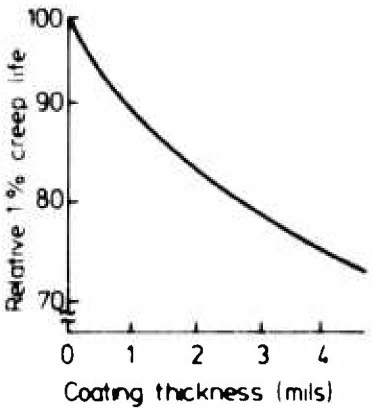


**Fig. 12 – Effect of coating weight (thickness) on blade creep life (from ref. 3).**

**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.**

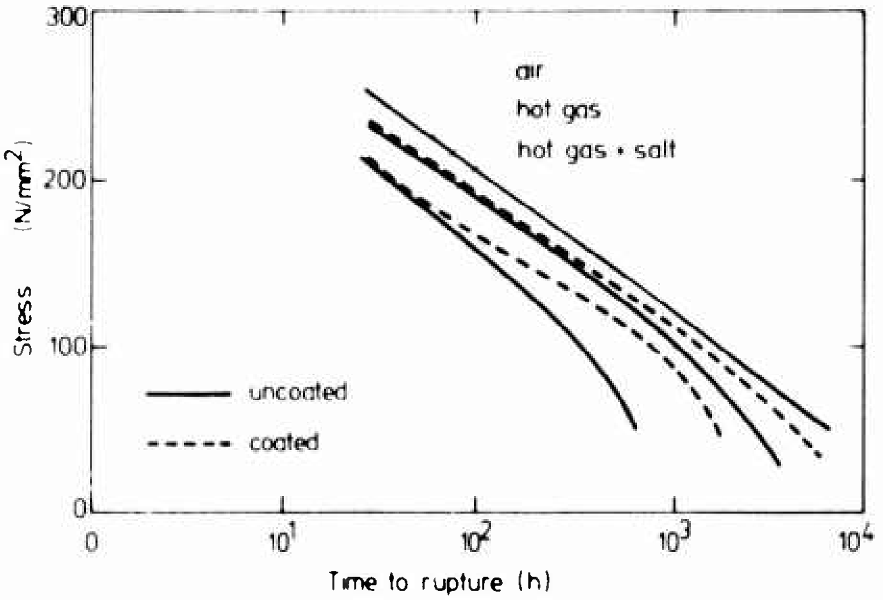


Fig. 14 – Influence of hot gas corrosion on creep rupture life of uncoated and coated turbine blade alloy : IN 100 (950° C) (after ref. 45).

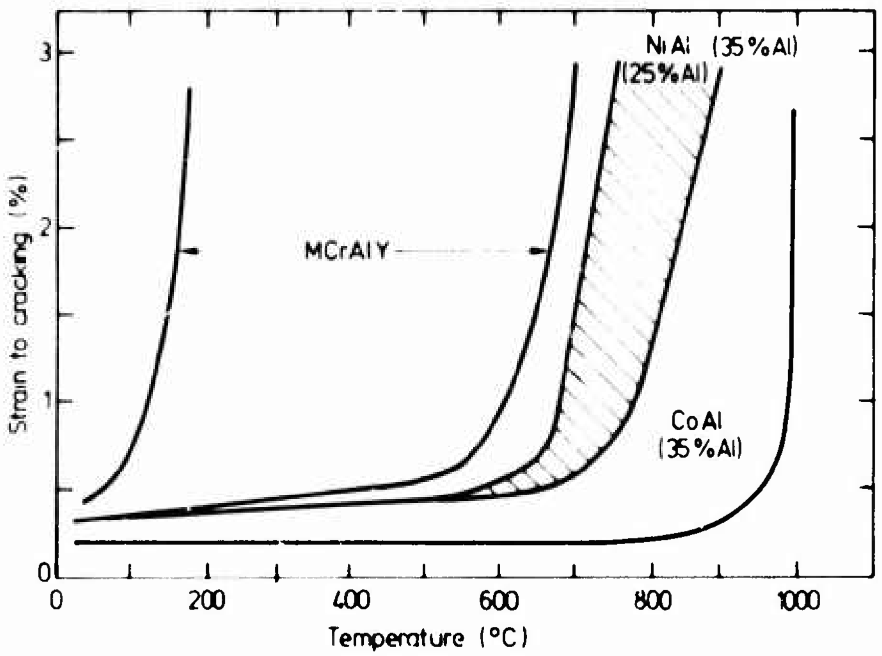
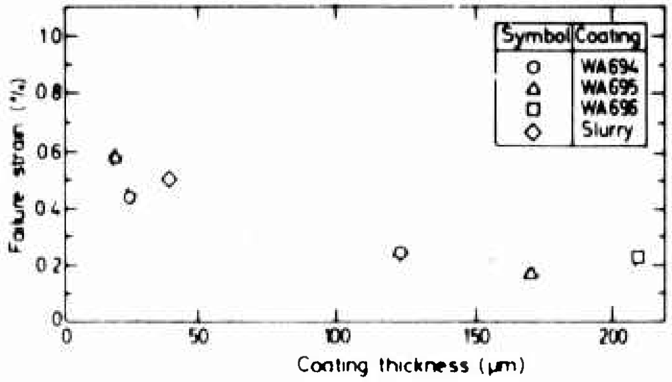
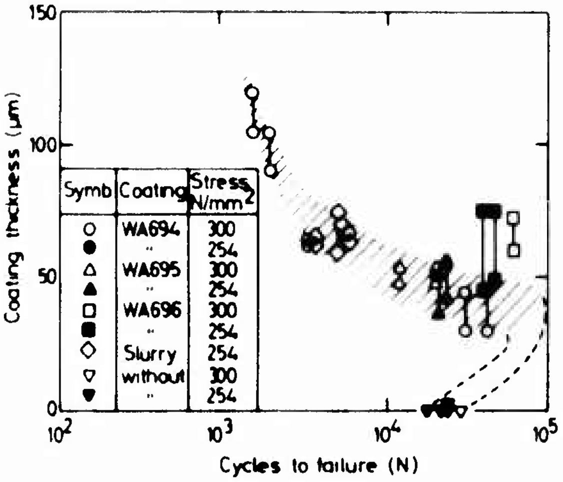


Fig. 15 – Relative brittle-ductile behavior of diffusion aluminide and MCrAlY coatings (after ref. 3 and 8).



a) Ductility of coating versus thickness



b) LCF strength of nickel alloy IN 100 : stress cycles at fracture versus coating thickness at 950° C in hot gas atmosphere

Fig. 16 – (from ref. 47).

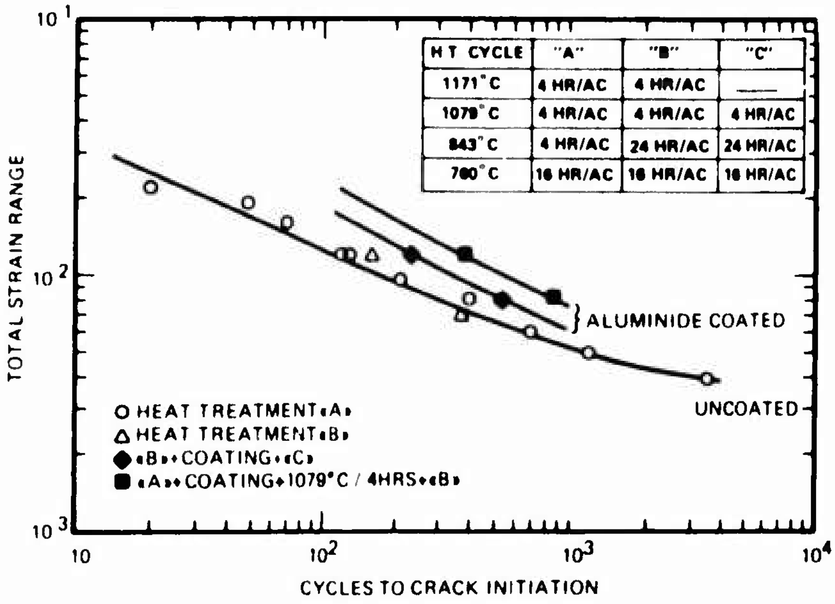


Fig. 17 – Low cycle fatigue properties of coated and non-coated U700 at 927°C (from ref. 41).

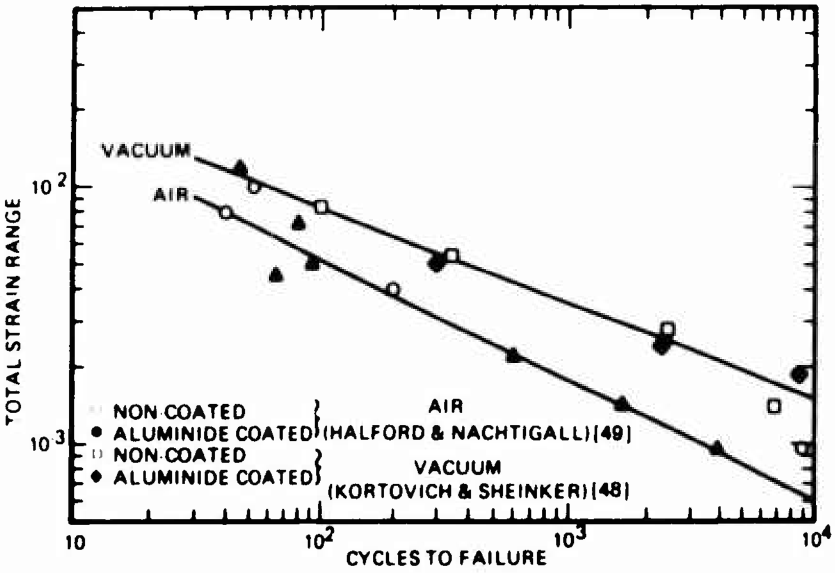


Fig. 18 – Low cycle fatigue properties of coated and non-coated René 80 at 1000°C.

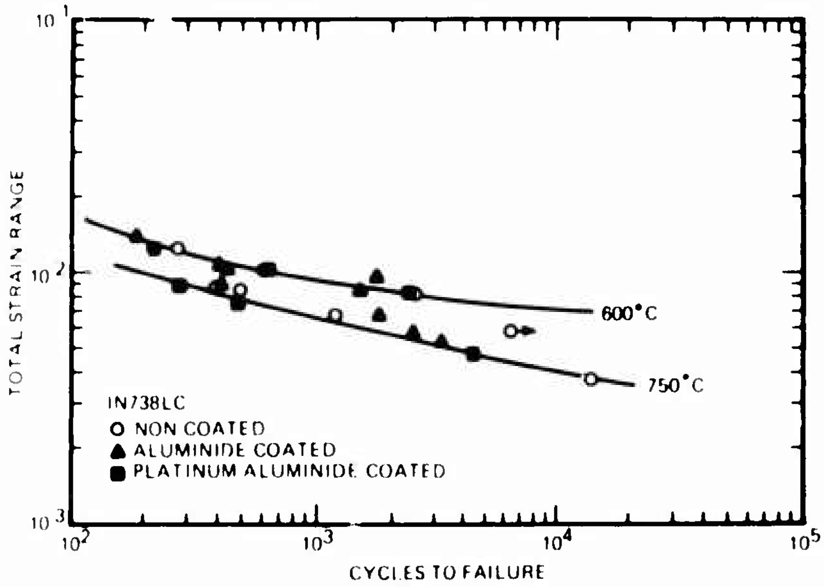
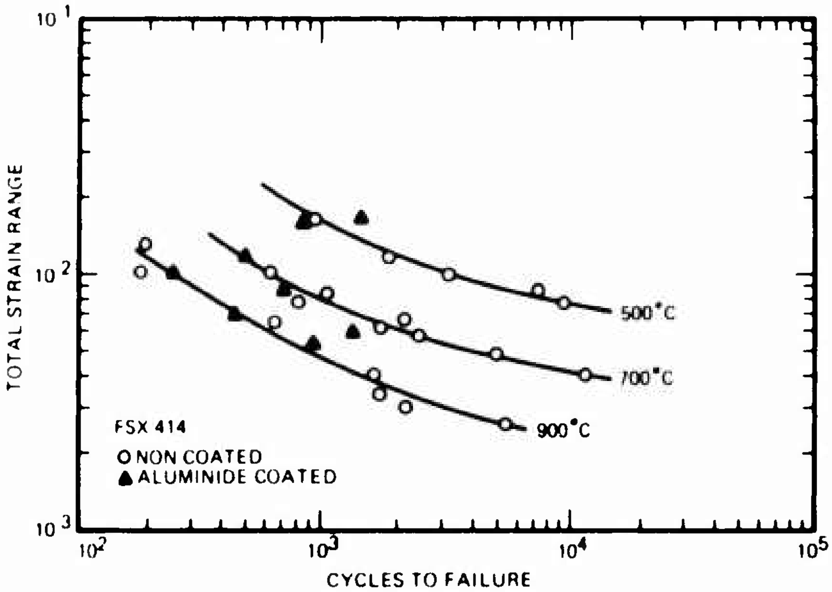


Fig. 19 – Low cycle fatigue properties of coated and non coated IN 738 LC.

Fig. 20 – Low cycle fatigue properties of coated and non coated FSX414



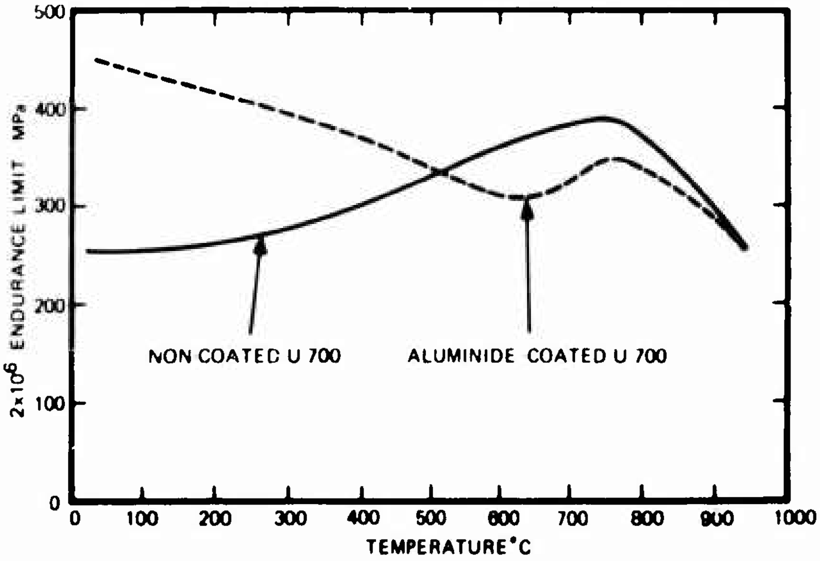


Fig. 21 – High cycle fatigue properties of coated and non-coated U 700 (from ref. 56).

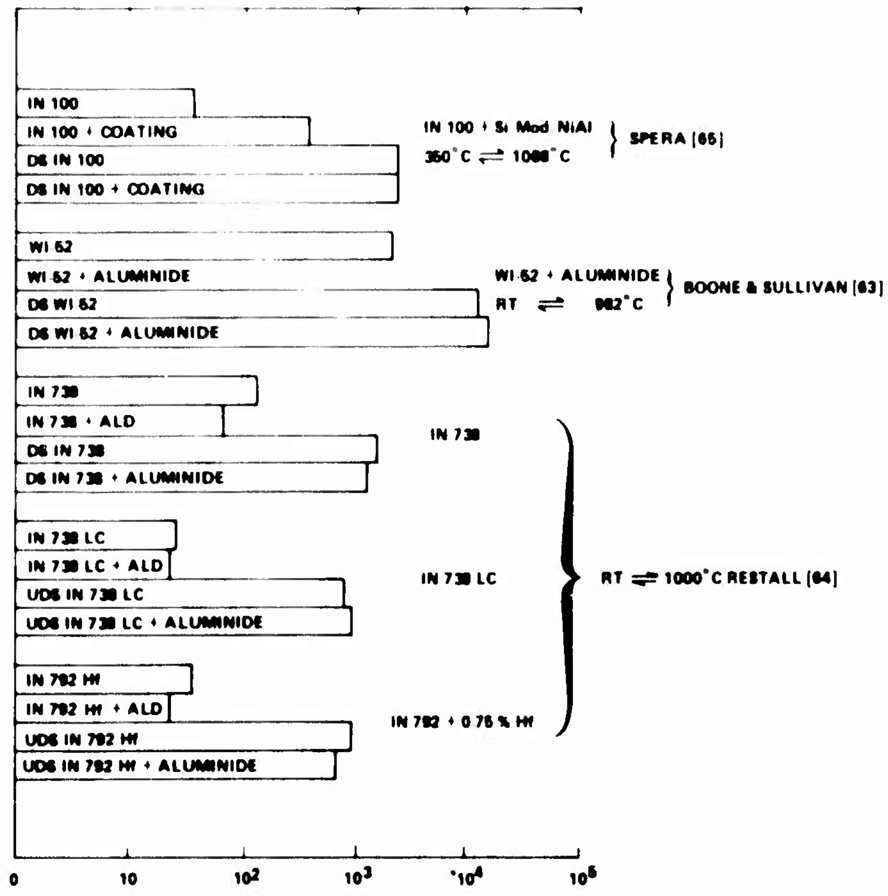


Fig. 22 – Thermal fatigue properties of polycrystalline and UDS superalloys in the coated and non-coated condition.

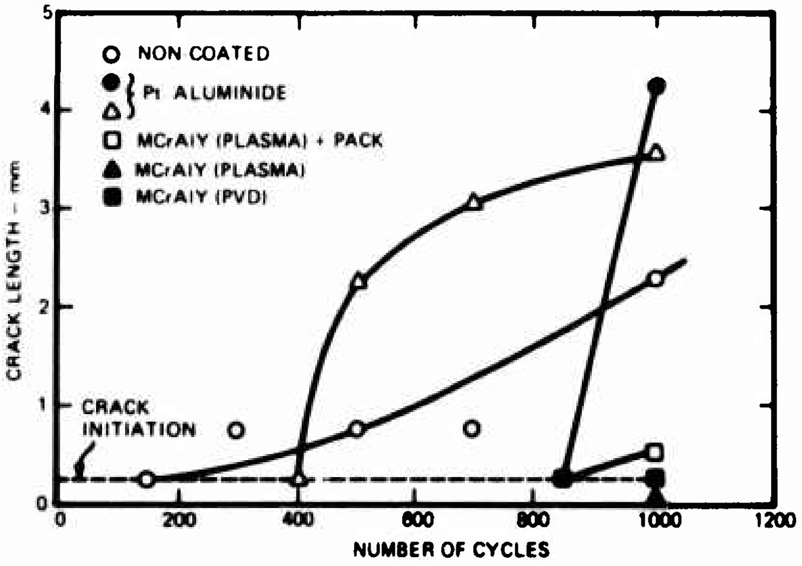


Fig. 23 – Effect of coating on thermal fatigue crack growth in U 710 (from ref. 67).