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Technical Aspects of Critical Materials Use by the Steel Industry

Volume II A

Proceedings of a Public Workshop; "Trends in Critical Materials Requirements for Steels of the Future; Conservation and Substitution Technology for Chromium".

4-7 October 1982

Vanderbilt University
Nashville, TN

Public Workshop Sponsored by:
U.S. Department of Commerce, National Bureau of Standards
U.S. Department of the Interior, Bureau of Mines
U.S. Department of Defense, Army Research Office

June 1983

Center for Materials Science
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Chairman
Allen G. Gray
American Society for Metals
Adjunct Professor of Metallurgy
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U.S. Department of Commerce, Malcolm Baldrige, Secretary
National Bureau of Standards, Ernest Ambler, Director

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Critical Material Needs for Future Steels and the Challenge of the Chromium Situation

By

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Presented at

Public Workshop on

Trends in Critical Materials Requirements for
Steels of the Future
Conservation and Substitution Technology
for Chromium

Sponsored by

U.S. Department of Commerce/National Bureau of Standards
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at

Vanderbilt University
Nashville, Tennessee

October 4, 1982

It's not news to those of you who are participating in this workshop that the United States, as well as Europe and Japan, are heavily dependent on foreign sources for supplies of many key metals that are essential to the nation's defense and necessary for the operation of this country's vital industries. For example, the U.S. imports almost 100 percent of the strategic metals, chromium, cobalt, niobium, tantalum, manganese, and the platinum metals.

I should say at the beginning that one objective of this workshop is to focus on chromium, which must be rated at the top of the priority list of strategic materials. This country must address policy, research and development tactics to ward off a crisis with chromium. The technological search for substitutes, conservation measures, and displacement materials must be unrelenting, despite the frustration of some attempts to date. Likewise, it is prudent to have such technologies on the shelf, piloted, and ready as a contingency plan.

An equally important objective of the workshop is to focus on critical materials needs of the U.S. Steel Industry. The emphasis here is on future steels and to seek out the viewpoints of a panel of steel users on properties of steels needed to meet the challenges of future applications. Then, based on this information assess, to some degree, the potential technological trends in critical materials required for these steels. Steel mill production controls and recovery of strategic metals in processing have an impact on the costs of special alloy steels, and developments in these areas are being considered in the workshop program. I believe we will all agree that steel is a remarkably economical material, but in its basic form, it would not be very effective for many purposes. In some of its most simple uses, steel requires special properties such as mechanical stability, resistance to changes in temperature and chemical attack, as well as good manufacturing properties including formability, ductility, and tensile strength. Because of these requirements, in many instances alloying elements are needed to enhance steel properties through the control of microstructure. A number of these alloying elements are included in the list of critical and strategic metals.

As we all know, when a material is chosen for an application in design, the choice reflects a combination of effectiveness in the application considered with the cost of the material. However, trends indicate that in the future, increased emphasis will be placed on evaluating total costs in terms of performance, durability, and the life cycle of the material, and these trends may influence the requirements for critical alloys in a variety of ways.

In the area of the specialty steels, reliability and performance characteristics are being constantly upgraded, and alloy conservation is being achieved as well through the latest production tools including argon oxygen decarburization (AOD), vacuum induction melting (VIM), vacuum arc remelting (VAR), electro slag remelting (ESR), and the latest in this series of new processes, powder metallurgy (P/M). Powder metallurgy not only improves the performance characteristics of specialty steel products, but reduces critical raw material and energy input as well.

Certainly potential future changes in the cost and availability of energy and raw materials are of considerable concern in the specialty steel industry. Recognition of the potential seriousness of the critical materials problem may help avoid a future materials crisis through increased research and development in areas of substitute alloys, substitute raw material sources, increased recycling and longer product life cycles.

In the stainless steels, the adoption of the AOD process into tonnage production has enabled very low carbon contents to be achieved with a consequent improvement in corrosion resistance. The process is economically attractive, but in the austenitic steels more nickel may be required to balance the loss in austenite stability by the lower carbon content.

In the ferritic stainless steels, the ultra low carbon contents now available have resulted in the development of "super" ferritic steels with higher chromium contents and molybdenum to improve corrosion resistance.

Currently, the duplex ferrite-austenite stainless steels are gaining much favor as readily castable and weldable high strength stainless steels with good stress corrosion resistance and potentially better toughness than the ferritic grades. Although these steels can be produced in relatively inexpensive compositions, they do contain about 25% chromium (typical composition 25 Cr; 3.5 Mo; 6 Ni). The areas of application are significant in chemical processing equipment and tubing for oil and gas wells. These examples illustrate some trends in alloy requirements, particularly increased reliance on chromium, to produce specialty steels that are essential for many industries.

The whole issue of critical and strategic materials continues to be urgent. It is gaining more attention as the complexities of this country's materials vulnerability become known.

We should also note that never before have strategic materials and minerals received as much attention from the President, the Congress, and the many federal agencies with materials responsibilities. In April, President Reagan sent a message to the Congress which emphasized the importance of materials to the economy and security of the United States. This was in response to National Materials Policy legislation passed almost unanimously in the House in 1979 and the Senate in 1980. Without passing judgement on the President's report to Congress, we should note that this is the first administration in thirty years to issue a key statement on the importance of materials to the economy and to the nation's security.

The next few years will be particularly significant to the U.S. in the development of national materials policy. Substitutes, conservation, reclamation, and innovative new materials -- topics which we are considering in this workshop -- can all help reduce the country's materials dependency.

The case history information on the potential for substitution and conservation of chromium in many types of steels, along with the user's viewpoints on types of steels needed for the future, and the impact of processing innovations will be a valuable input to the Department of Commerce report on "Critical Materials Requirements of the U.S. Steel Industry". The information will also be useful in the compilation of technologies available and those that show promise for development as the basis for a substitution preparedness initiative for a chromium contingency plan.

Chromium continues to appear more critical than the other strategic metals. Unless we develop alternative materials technologies, a cutoff of oil supply and chromium supply would attack this country on two fronts.

Aside from the fact that without chromium we cannot make an efficient durable gas turbine engine, the metal has many important industrial applications: oil refineries, petro-chemicals, conventional and nuclear power plants, tanker trucks, industrial machinery, transportation, and all stainless steels.

The problem affects U.S. industry overall as much as potential defense needs. However, until recently there has been all too little awareness of our enormous dependence on foreign sources of critical nonfuel minerals.

The overall theme of the presentations in the workshop is that technology is among the most viable options for reducing this country's vulnerability to a cutoff of supply of chromium and other critical metals. Also, an important point of emphasis, is that now is the time to start to develop these technologies for substitution and conservation.

As a spokesman for "substitution preparedness" in Congressional testimony, the proposal was made that the United States should embark on an organized effort to foster and support research and development programs that will advance the practical application of substitution and conservation technology to reduce the impact of supply interruptions in critical metals, particularly chromium. Likewise, it's evident that a plan should be developed to document known substitution technologies and "stockpile" this information.

As R & D programs are developed to plug gaps and create new options for substituting for critical metals, this technological information would be added to the information stockpile.

Substitution programs should be an important part of strategic materials planning for individual manufacturing firms. The opportunities here will be explored in a workshop on "Materials Risk Management" being held later this month by the U.S. Department of Commerce. The objectives of a national initiative on substitution can be applied to company substitution R & D programs.

An important point is that the essential nature of chromium and other critical and strategic metals requires that all options to provide supplies or alternatives must be pursued. On the supply side, effective steps must be taken to strengthen the strategic stockpile and develop domestic resources. The development of alternatives requires that viable materials technology options derived from substitution, conservation, coating systems, and reclamation be available at reasonable cost.

Also, I should emphasize in this overview of objectives of the workshop that although technology for substitution and conservation are an important approach to meeting the challenges of chromium and other strategic metals, there is, of course, an underlying need to understand and develop advanced technological options which may displace the need for chromium or reduce the amount required in essential applications. These include processing technologies for high performance, netshapes, engineered ceramics, intermetallics and composite materials, and the application of existing and developing technology for metallurgical coating systems and surface modification techniques.

In fact, in developing the workshop program, I arrived at the feeling that an entire workshop could be devoted to opportunities for conservation utilizing surface modification technologies.

For example, hard facing as a method of effective corrosion control should receive increasing attention to impart essential surface properties with minimum use of chromium. Likewise, designing with available clad materials can economize on critical materials compared to use of solid alloy products.

The concept behind surface modification is that properties of the critical metal are utilized only where they are required. New techniques are available for surface alloying, as we will hear. High rate surface fusion provides rapid solidification rates which give valuable surface properties. Ion implantation with chromium provides the basis metal with greater corrosion resistance, and design goals can be achieved with implanted ions.

The future will see advances in composite and ceramic components to provide displacement technology and these options will be considered in the workshop.

As I said earlier, this is a "technology" workshop with the message that technology can provide answers (some say the best answers) for reducing this country's vulnerability to the potential of cutoff of supplies of critical metals. An important reality, however, is that it takes time and considerable investment to develop, quantify and establish designer confidence in a new material or even a modified alloy, and I feel sure that this point will be made during the workshop.

In spite of the currently abundant supply situation for all materials, risks remain for possible future supply disruptions. Materials such as chromium, cobalt, tantalum, manganese and others are vital to our national security and economic well-being. We are dependent upon foreign sources for their supply and are becoming increasingly dependent for their processing. Import dependence is not in itself the issue, as normal international commerce will continue to supply raw materials to us. Vulnerability to disrupted supply is the issue of concern. The vulnerability issue involves our preparedness to adapt to any potential supply disruption without serious consequences to our national security, industry and commerce.

The vulnerability issue must be viewed in terms beyond raw materials supply because it also involves the vitality of the processing and manufacturing sectors which convert these materials into the products we need. A cornerstone of reduced vulnerability is the National Defense Stockpile which can serve as a source of supply for vital operations during a disruption.

There is a need to improve our preparedness for possible future disruptions through greater knowledge about the technologies for production, substitution and conservation. Tapping marginal deposits, improved beneficiation methods, alternate materials, manufacturing with lower input of materials, and recycling are all tools to reduce vulnerability. While materials are readily available, as they are today, the motivation to pursue such technologies is limited. Incentive and support for these approaches warrents consideration.

Let me say that in behalf of the workshop sponsors, the U.S. Department of Commerce/National Bureau of Standards, the U.S. Department of the Interior/Bureau of Mines, and the U.S. Department of Defense/Army Research Office, we sincerely appreciate your participation in this important program to provide input for materials policy direction, for the report being prepared by the U.S. Department of Commerce, and for guidance on future directions for study and actions.

INDUSTRIAL LIFE WITHOUT CHROMIUM - TECHNOLOGICAL CHALLENGES

Keynote Address for Public Workshop on
"Trends in Critical Materials Requirements
for Steels of the Future
Conservation and Substitution Technology
for Chromium"

Vanderbilt University
Nashville, Tennessee
October 4-7, 1982

Arden L. Bement, Jr.
TRW INC.

INDUSTRIAL LIFE WITHOUT CHROMIUM - TECHNOLOGICAL CHALLENGES

Opening Statement

I am delighted to be invited by Dr. Allen Gray to participate in this workshop on the trends in chromium conservation and substitution in steel. Thanks to the foresight and leadership of both Dr. Allen Gray and Professor Robert Nash, Vanderbilt University has become known as the site for outstanding public workshops on the major technical, economic, and political issues surrounding non-fuel critical and strategic materials. I am greatly impressed with the creative thought that has gone into the content and structure of this workshop. I believe that by Thursday afternoon everyone here will have been highly stimulated and informed about the progress being made in this important field.

What is so Special About Chromium?

To begin with, I would like to ask you to reflect on the technological importance of chromium as an element. Just like Joseph's Coat, chromium has a wide variety of highly "colorful" properties. This attribute is also conveyed by its name, which is taken from the Greek word "chromos" meaning color and which was derived from chromium's many-colored compounds.

Chromium's high melting temperature makes it an important alloy addition for heat resistant steels and superalloys. It is both a ferrite promoter and austenite stabilizer which in combination with molybdenum, nickel, manganese and vanadium renders it an important alloying element for a broad spectrum of heat-resistant, corrosion-resistant, and speciality steels. Its ability to form a tight, adherent, passive oxide film makes it indespensible for alloys subjected to combinations of high temperatures and highly-corrosive environments. As a bright coating, chromium is a nearly-ideal reflector. As a black chrome coating, however, it is a nearly-ideal selective absorber, with a high absorptivity over the solar spectrum and low emissivity in the infrared. While chromium has not come into its own as a technically important metal due to its low ductility at ordinary temperatures, it is indispensible in providing technical importance to other metals. Consider, for example, how many applications of iron-base alloys would remain without the corrosion and oxidation resistance imparted by chromium. Try to imagine nickel-base alloy heating elements without the high heat and electrical resistance provided by chromium. Finally, how useful would cobalt-base alloys be without the hardness, oxidation, and hot-corrosion resistance imparted by chromium? Although some possibilities for chromium substitution in these alloy systems exist, chromium stands alone today as the clear technical and economic champion.

Moreover, because of chromium's multivalency states and special optical properties the oxides of chromium are favorites for paint pigments, green granules in asphault roofing, and camouflage paints. Finally, with increased steel production by the electric furnace process and the vacuum-oxygen and argon-oxygen decarburization processes the demand for chrome-bearing refractories has increased relative to that for the open hearth process, which is phasing out.

What Would the Future be Like With Reduced Chromium Availability?

Having quickly reviewed the special properties of chromium, we can now try to picture the tradeoffs we would have to make in chromium content against performance, lifetime and maintenance costs for the major engineered systems we now depend on and will be increasingly dependent upon in the future. A conservative estimate of the cost to the U.S. economy of corrosion, wear, fatigue and the inefficient use of energy is $200 billion annually.(1) Of this cost, the bill to the Department of Defense is about $8 billion. A reduction in the use of chromium in bridges, propulsion systems, heat engines, steam plants, petroleum production platforms and other such systems, would surely cause this cost to rise rapidly unless suitable substitute materials or protection methods were available and could be deployed.

A sustained chromium supply disruption can be expected to have serious economic consequences to the United States. If we examine the leading chromium-using industries, (SLIDE 1) we find that nearly half the total chromium consumed in the United States is by industries below the top thirteen users.(2) Therefore, we find that chromium consumption in the U.S. is generally unconcentrated. Of these chromium-using industries the top 32 accounted for 16.1 percent of the gross national product and 9.2 percent of the U.S. nonagricultural employment in 1979.(2) While it would be erroneous to infer that these numbers properly reflect the direct economic impact of a severe chromium supply disruption, they nevertheless indicate that the impact would be significant and widespread. By comparison, Helmit Schmidt, the former Chancellor of West Germany, has noted "that if West Germany's supply of chromium were cut off, 2.5 million of the nation's 60 million would be unemployed and the West Germany gross national product would drop 25%."(3) It is especially noteworthy that during World War II the Germans claimed that a cutoff of oil would have done less damage to their war effort than a cutoff of chrome. This is largely because it was possible for the Germans to produce fuel synthetically.

An examination of chromium used by defense-industries reveals a slightly different pattern, however (SLIDE 2).(2) We find that 15 percent of the total chromium used by defense industries in 1979 was used for the manufacture of aircraft engines and engine parts. Moreover, aerospace industries, as represented by the first three categories, consumed 35 percent of the total. While the aerospace industry might have to absorb a disproportionate amount of the price volatility resulting from a supply disruption, one should note that the amount of chromium used by aerospace industries and all defense industries in 1979 represented only 2.4 and 6.8 percent, respectively, of total U.S. consumption. These numbers can be compared to an average chromium recovery from prompt stainless-steel scrap in the U.S. of 9.0 percent of total demand.(4) One can also note that approximately 60 percent of the superalloy scrap generated during aircraft engine production, which represents about 5.5 pounds for every pound of fly weight, is recovered and reused.(4) Furthermore, the ratio of scrap weight to fly weight in engine production is decreasing with time with the greater use of near-net-shape forging and CAD/CAM technology. Likewise, the percentage of scrap recovery is increasing with improved scrap sorting and reclamation techniques.

A comparison of chromium usage by end-use categories (SLIDE 3) reveals that the transportation sector has the greatest market share at 20 percent followed by construction and machinery categories at 17 and 16 percent, respectively.(4) Future trends in overall chromium demand in the transportation sector are uncertain. The development of more efficient heat engines and the use of broader spectrum fuels could increase the demand for chromium in this sector. However, there are also trends which show chromium reductions in airframes and in auto and truck bodies through weight reductions, increased use of composite materials, and the growing prospects for the introduction of ceramics and intermetallic compounds in advanced heat engines. However, some 90 percent of chromium applications in the alloy materials used by the aerospace industry are irreplaceable at present technology levels without serious compromises in performance characteristics.

Both conventional and nonconventional energy technologies, which are included in the construction and machinery categories in Slide 3, are especially dependent on chromium availability. Chromium is today a critical requirement for both nuclear and fossil steam supply systems, central power gas turbines, turbogenerators, and petroleum production and refining operations. Chromium in the form of corrosion-resistant steels and hard-facing alloys is critical for well casings, bottom pumps, and fluid-end pumps which must withstand the agressive errosive and corrosive environments of deep, sour oil wells. Furthermore, high chromium steels and nickel-base alloys will be indispensable to the synthetic fuel plants and combined-cycle, energy-conversion power plants of the future.

The National Materials Advisory Board has estimated that an average of 19,500 tons per year of chromium will be needed by the energy industry over the next decade on a "business as usual" basis. An average of 33,700 tons per year will be required under accelerated development.(5) This usage represents 3.8 percent and 6.5 percent, respectively, of 1979's total U.S. chromium consumption. For comparision, the General Accounting Office and Lawrence Berkeley Laboratory have recently estimated chromium demands out to the year 2000.(6) Their estimates are as high as 20 percent of total U.S. demand for conventional technologies and 30 percent for alternate technologies, depending on the specific oil pricing scenario assumed. Nuclear power, synthetic fuels, and solar energy represent the high chromium demand sectors in these studies.

These trends indicate that future energy technologies could be heavily impacted by sustained descriptions in chromium supply or by preemptive, denial, or monopolistic trade practices.

What Have Been the Trends in Chromium Supply?

Before examining the specific issues for assuring a stable chromium supply in the future, we should first review the salient trends in chromium supply over the past two decades.

During the period 1956-60, the U.S. provided 5-10 percent of its chromium needs through domestic production subsidized under the Defense Production Act. With the termination of this Act in 1961 the U.S. became totally dependent upon imports for chromite ore. Today the U.S. imports chromite ore primarily from six countries (SLIDE 4) of which The Republic of South Africa supplies 44 percent and the Soviet Union and Albania together supply 30 percent.(2)

Prior to 1973 the U.S. produced most of the ferrochromium required for its steel industry and other metallurgical applications domestically. However, with the advent of OPEC and the dramatic increase in oil prices in 1973, substantial ferrochromium production shifted offshore. The major economic factors for this shift were lower transportation costs, lower differential energy costs for ore reduction, and the increased cost of domestic environmental regulations. Whereas, the U.S. produced nearly five times as much ferrochromium as it imported during the period 1970-72 it now imports 20 percent more than it produces. The U.S. government now finds it necessary to place a protective tariff on both low-carbon and high-carbon ferrochromium because of declining prices for imported ferrochromium in the face of increasing costs of domestic production.

Concurrent with the dramatic rise in energy costs in the early 1970's, the introduction of the argon-oxygen-decarburization process further encouraged major chromite producing countries to increase their ferrochromium production for export. This occurred because the AOD process permitted considerable interchangeability among various grades of ferrochromium. The Republic of

South Africa capitalized on this opportunity for an increasing metallurgical market for their low-grade ore by dramatically increasing productive capacity for high-carbon ferrochromium. As a result the combined South African and Zimbabwean ferrochromium share of the world market has increased from 15 percent in 1970 to about 37 percent in 1979.(4) Together these two African countries currently supply nearly 80 percent of total U.S. imported ferrochromium (SLIDE 5).(2) It is important to note that as more of the U.S. ferrochromium requirements are imported and as these imports become more concentrated in Southern Africa, the flexibility in chromite ore supply to the U.S. for metallurgical use, to include the contingent use of our own domestic sources, will become more and more restricted.

What is the Good News?

In spite of these disturbing trends there is good news in chromium availability for the future. World chromite production, which was estimated at 7 million short tons in 1980, has more than doubled over the past 20 years.(4) Substantial new finds of chromite reserves and projects to increase chromite mining capacity have been announced by Brazil, Greece, the Philippines, Sudan, USSR, Finland, India, Madagascar, Papua New Guinea, and Yugoslavia.(4) There is currently an estimated excess chromite production capacity worldwide, and this capacity is expected to increase at slightly over three percent per year over the next 20 years. An excess capacity is expected to overhang world demand for the foreseeable future. However, there is concern regarding the continued adequacy of world refractory chromite production.

Prospects are now good for a modest decentralization in world chromite supply over the next one or two decades. However, a recentralization of supply toward South Africa and Zimbabwe, where over 90 percent of the estimated world chromite reserves are located is expected after the turn of the century. Some also suspect that chromite reserves in the Soviet Union are actually uneconomic to produce at current world prices and that the Soviet Union will begin to retreat from being a net chromite exporter.

Even though domestic chromium availability is limited, the U.S. Bureau of Mines has recently evaluated 34 domestic deposits that contain chromite mineralization (SLIDE 6).(7) Results of this evaluation show that demonstrated resources of chromite contain about 4.6 million tons of chromite concentrates that could be used in the chemical and metallurgical industries. However, the price of concentrates from currently demonstrated deposits would be about double the current market price for metallurgical-grade chromite. At a price slightly greater than the current market price for chemical-grade chromite an estimated 1.6 million metric tons are potentially recoverable at the identified resource level. Finally, at a price about 33 percent above the current market price for metallurgical-grade chromite about 3.8 million metric tons are potentially recoverable. If these chromite resources were processed into ferrochromium as much as 21.1 metric tons of identified resources are potentially recoverable at the current price of low-carbon ferrochromium and 4 million metric tons are potentially recoverable at the current price of high-carbon ferrochromium.

These domestic chromium resources could provide an important economic ceiling on the price the U.S. will have to pay for imported ferrochromium in the future, but only if our domestic ferrochromium production capacity is protected and if these indicated resources are further developed for potential extraction and processing.

A major category of good news is the major efforts currently underway to reduce chromium consumption in the U.S. by a number of technical strategies (SLIDE 7) to include:

- Substitution and displacement
- Conservation through design and processing
- Reclamation and
- Life extension

There are a number of advanced materials which can displace critical materials (SLIDE 8) where high-temperature strength, erosion and corrosion resistance, and low maintenance costs are key design parameters. The substitution of many of these advanced materials for chromium-bearing alloys will be described in several papers at this conference. More specifically, the U.S. Bureau of Mines is exploring a series of iron-base alloys which have molybdenium, titanium, aluminium and silicon additions in place of chromium for applications requiring high temperature, oxidation resistant performance.(7) Candidate iron-base alloys containing various combinations of aluminum, molybdenum, tungsten, columbium, nickel and silicon are being actively explored by others. One such alloy containing manganese, silicon, and copper is being developed as a replacement for chromium-bearing spring steels.(4)

Rapid solidification technology looks particularly promising for improving surface hardness and corrosion resistance through compositional homogenization and microstructural refinement. An iron-aluminum alloy containing a finely-dispersed titanium diboride phase has already been commercially introduced for producing wire drawing dies. The Department of Defense is actively pursuing a variety of rapid solidification technologies to develop new families of alloys which will permit less use of chromium, cobalt, and other critical and strategic materials.

Near-net shape technologies (SLIDE 9) are already providing dramatic improvements in chromium conservation through reduced scrap generation and recycle. Examples of where dramatic savings in chromium use are already being realized are the use of hot-die, superplastic forgings to reduce grinding and machining losses in the manufacture of superalloy jet engine disks and the increasing use of powder metallurgy in the manufacture of high-alloy bearings, tools and dies.

Advanced surface modification technologies (SLIDE 10) are also displacing chromium in both coating and base alloy compositions. These new surface modification processes are not only reducing the strategic metal content in the coatings applied but are also greatly extending the life of the tool or part.

Many other examples can be given of technological trends which have the potential of leveling out or even reducing chromium demands. A few additional examples will suffice:

- The U.S. Bureau of Mines is developing processing technologies for recovering chromium from slags, furnace dusts, and other particulate wastes; for reducing chromium losses in electroplating operations through the recycle of waste chromic acid solutions; and for reducing the chromite additions to refractories by improving the magnesia grains used in these refractories.(7)

- The aircraft industry has increased the use of titanium and composites to replace corrosion-resistant steels in the interest of weight reduction for some applications.

- The automotive industry is replacing chromium used in exterior trim, wheel covers, seat belts, windshield wipers, suspension springs, iron castings, engine components, gears, bearings and other parts through selective material substitutions. There is the potential of reducing 3 pounds of chromium of the 5.5 pounds used in the average 1980 U.S. car.(4) Moreover, with the development of stratified-charge diesel engines the approximately two pounds of chromium currently used per car for catalytic converters could be eliminated.

Adding up all of the potential chromium savings from technology now in hand, the U.S. Commerce Department has estimated that approximately 150,000 short tons of chromium per year could be saved, which represents about 29 percent of current demand.(4) This would be equivalent to the chromium used in over one million F-100 jet engines or in over 150 thousand Boeing 767 aircraft on the basis of fly weight. As dramatic as these numbers appear they represent less than half the savings in chromium consumption that are projected as possible following 10 years of research and development. Therefore, research and development can be a very important factor in curbing our future import dependence on chromium, and can also help contain future chromium costs when leveraged with our current 26 percent world share in chromium demand.

What Then Are The Issues?

With all of this apparent good news, what are the key concerns or issues? These can be summarized as follows:

- The growing concentration of chromite and ferrochromium supply in just two countries, namely South Africa and Zimbabwe, should be a major concern to our long-term strategic interests. The potential for establishing a monopoly that could be many-fold more effective than OPEC will increase with time.

- The declining ability of the Soviet Union to supply its chromium needs from its own reserves is a concern with respect to the future political stability and independence of South Africa and Zimbabwe (SLIDE 11).(8) Although the current production of chromite ore in the USSR is currently a large fraction of South African production, the future chromite reserves in the USSR are very small relative to those for South Africa.

- The continued viablity of domestic ferrochromium production in the face of foreign competition is a key issue that impacts both our commercial and defense industrial base. It is important to establish appropriate policy tools to provide the assistance needed to protect this vital element to our national security.

- The composition of our strategic stockpile is not aligned to current technology or future national needs. Current stockpile goals for metallurgical and chemical grade chromite ores are about 15 times larger than those for high- and low-carbon ferrochromium. This high ratio is inappropriate considering the fact that we now import more than we produce domestically. The goals for ferrochromium need to be raised relative to chromite to reflect the decline in domestic ferrochromium capacity over the past decade. Also those lots of ferrochromium in the strategic stockpile which contain sulfur levels higher than current steelmaking practice would accept need to be rotated.

- Research and development into technical strategies for substitution preparedness and in finding ways to use chromium more effectively need to be given sustained federal support.

It is encouraging to note, however, at a time when there is little economic incentive to reduce chromium consumption that so much is being attempted, as reflected by the titles of the papers in this workshop. It seems clear to me in following the actions of the U.S. Congress, that the need for new process technologies and for alternative materials to prepare the U.S. for dealing with reduced supply availability of chromium and other critical and strategic materials is gaining in acceptance.

The contributions that you as technologists and public administrators can make in keeping the technical, economic and political issues surrounding strategic materials in both balance and perspective will be of enormous national value as the countries of the world continue to contend for available natural resources.

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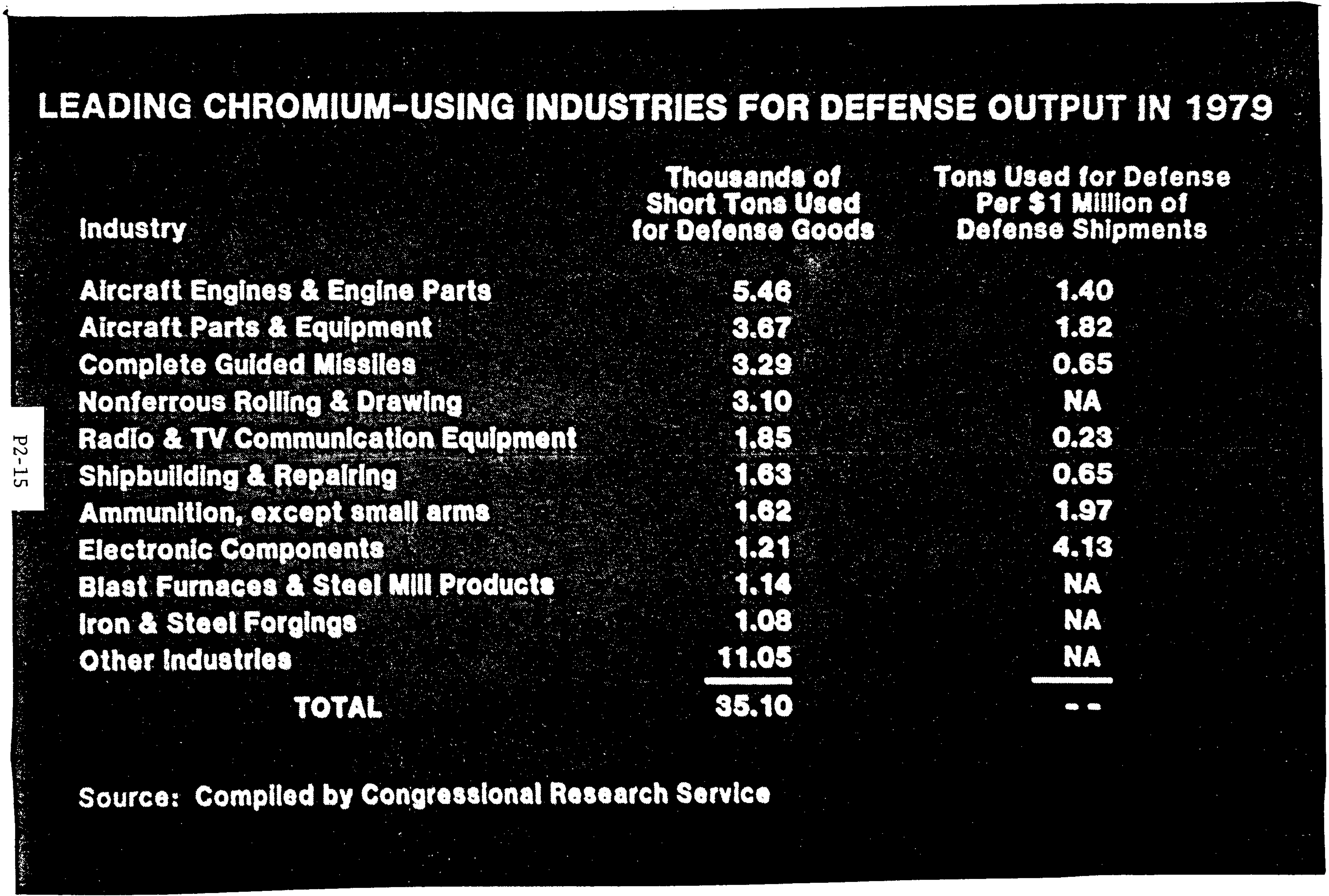
7. Bureau of Mines Research 1981, U.S. Department of the Interior, U.S. Government Printing Office, 1981-0-357-261/9964.
8. Alert Letter on the Availability of Raw Materials, Issue No. 1, McLean, Virginia, May 1981, p. 11.

LEADING CHROMIUM-USING INDUSTRIES FOR DEFENSE AND CIVILIAN PRODUCTION IN 1979

Industry	Thousands of Short Tons Used	Tons Used Per $1 Million of Industry Shipments
Nonferrous Rolling & Drawing	37.69	11.25
Metal Stampings	28.81	4.59
Blast Furnaces & Steel Mill Products	27.49	0.41
Motor Vehicle Parts & Accessories	24.10	0.61
Construction	23.00	0.20
Fabricated Platework	21.50	2.36
Crude Petroleum & Natural Gas	19.08	1.18
Iron & Steel Forgings	16.94	4.85
Pipes, Valves & Pipe Fittings	15.83	1.61
Hardware	14.52	2.33
Aircraft Engines & Engine Parts	13.91	1.43
Refrigeration & Heating Equipment	12.77	1.04
Fasteners & Screw Machine Products	11.19	1.63
Other Industries	249.05	NA
TOTAL	515.88	--

Source: Compiled by Congressional Research Service

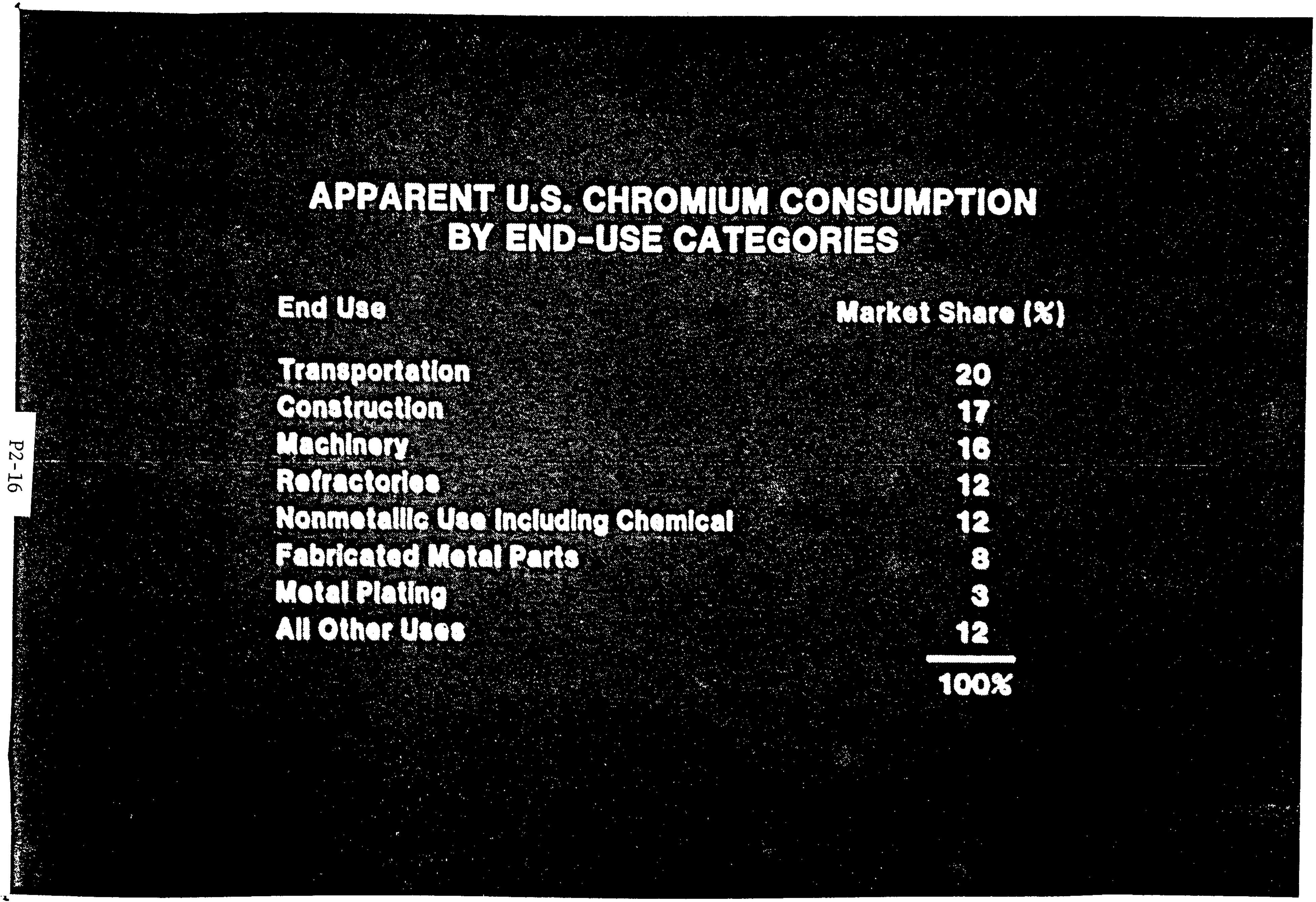
SLIDE 1



LEADING CHROMIUM-USING INDUSTRIES FOR DEFENSE OUTPUT IN 1979

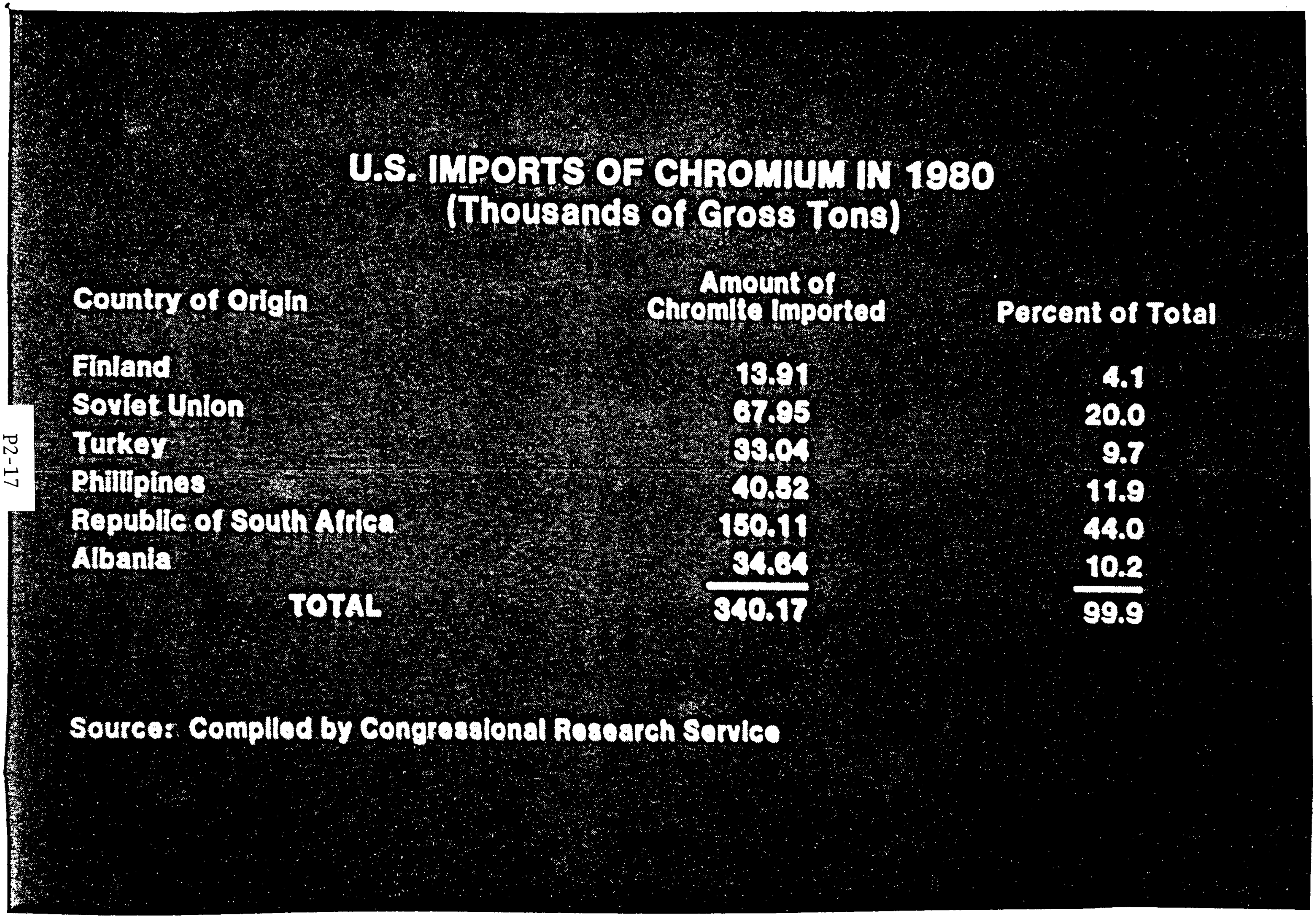
Industry	Thousands of Short Tons Used for Defense Goods	Tons Used for Defense Per $1 Million of Defense Shipments
Aircraft Engines & Engine Parts	5.46	1.40
Aircraft Parts & Equipment	3.67	1.82
Complete Guided Missiles	3.29	0.65
Nonferrous Rolling & Drawing	3.10	NA
Radio & TV Communication Equipment	1.85	0.23
Shipbuilding & Repairing	1.63	0.65
Ammunition, except small arms	1.62	1.97
Electronic Components	1.21	4.13
Blast Furnaces & Steel Mill Products	1.14	NA
Iron & Steel Forgings	1.08	NA
Other Industries	11.05	NA
TOTAL	35.10	- -

Source: Compiled by Congressional Research Service



APPARENT U.S. CHROMIUM CONSUMPTION BY END-USE CATEGORIES

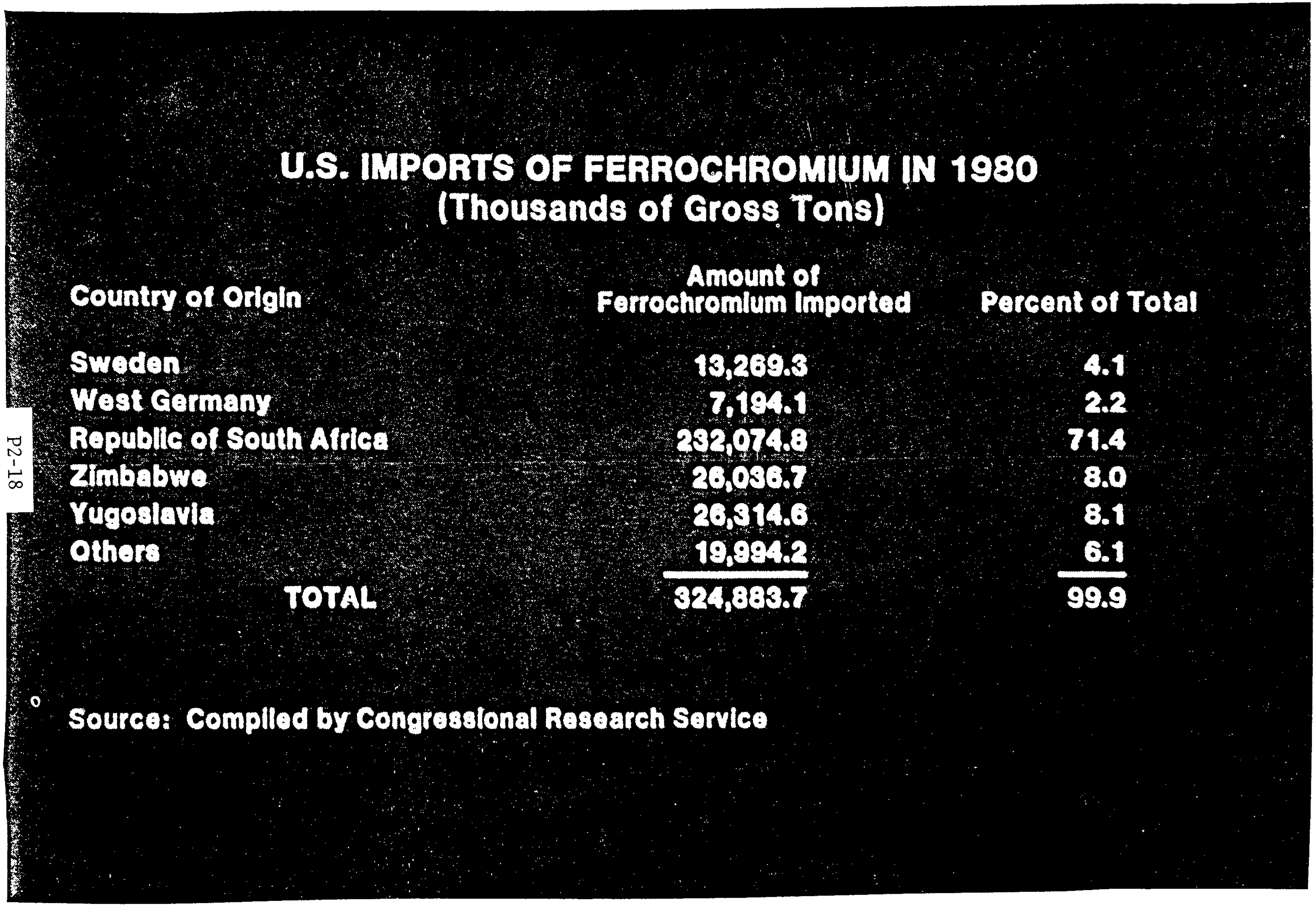
End Use	Market Share (%)
Transportation	20
Construction	17
Machinery	16
Refractories	12
Nonmetallic Use Including Chemical	12
Fabricated Metal Parts	8
Metal Plating	3
All Other Uses	12
	100%



U.S. IMPORTS OF CHROMIUM IN 1980
(Thousands of Gross Tons)

Country of Origin	Amount of Chromite Imported	Percent of Total
Finland	13.91	4.1
Soviet Union	67.95	20.0
Turkey	33.04	9.7
Phillipines	40.52	11.9
Republic of South Africa	150.11	44.0
Albania	34.64	10.2
TOTAL	340.17	99.9

Source: Compiled by Congressional Research Service

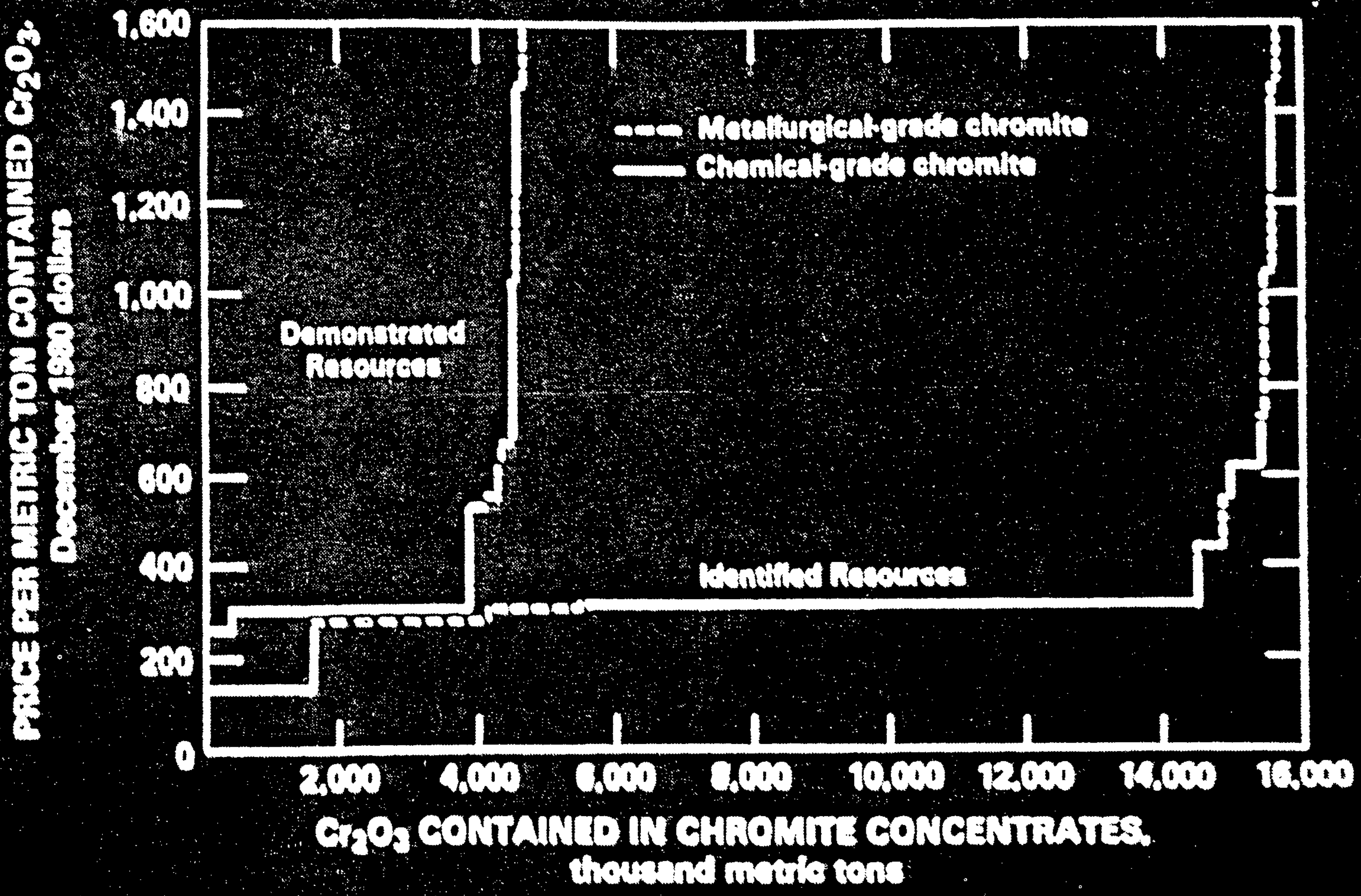


U.S. IMPORTS OF FERROCHROMIUM IN 1980
(Thousands of Gross Tons)

Country of Origin	Amount of Ferrochromium Imported	Percent of Total
Sweden	13,269.3	4.1
West Germany	7,194.1	2.2
Republic of South Africa	232,074.8	71.4
Zimbabwe	26,036.7	8.0
Yugoslavia	26,314.6	8.1
Others	19,994.2	6.1
TOTAL	324,883.7	99.9

Source: Compiled by Congressional Research Service

RECOVERABLE Cr_2O_3 FROM DOMESTIC RESOURCES AT 15 PERCENT RATE OF RETURN



Source: U.S. Bureau of Mines

TECHNICAL STRATEGIES

- Substitution and displacement
- Conservation through design and processing
- Reclamation
- Life extension

ADVANCED MATERIALS WHICH CAN DISPLACE CRITICAL MATERIALS

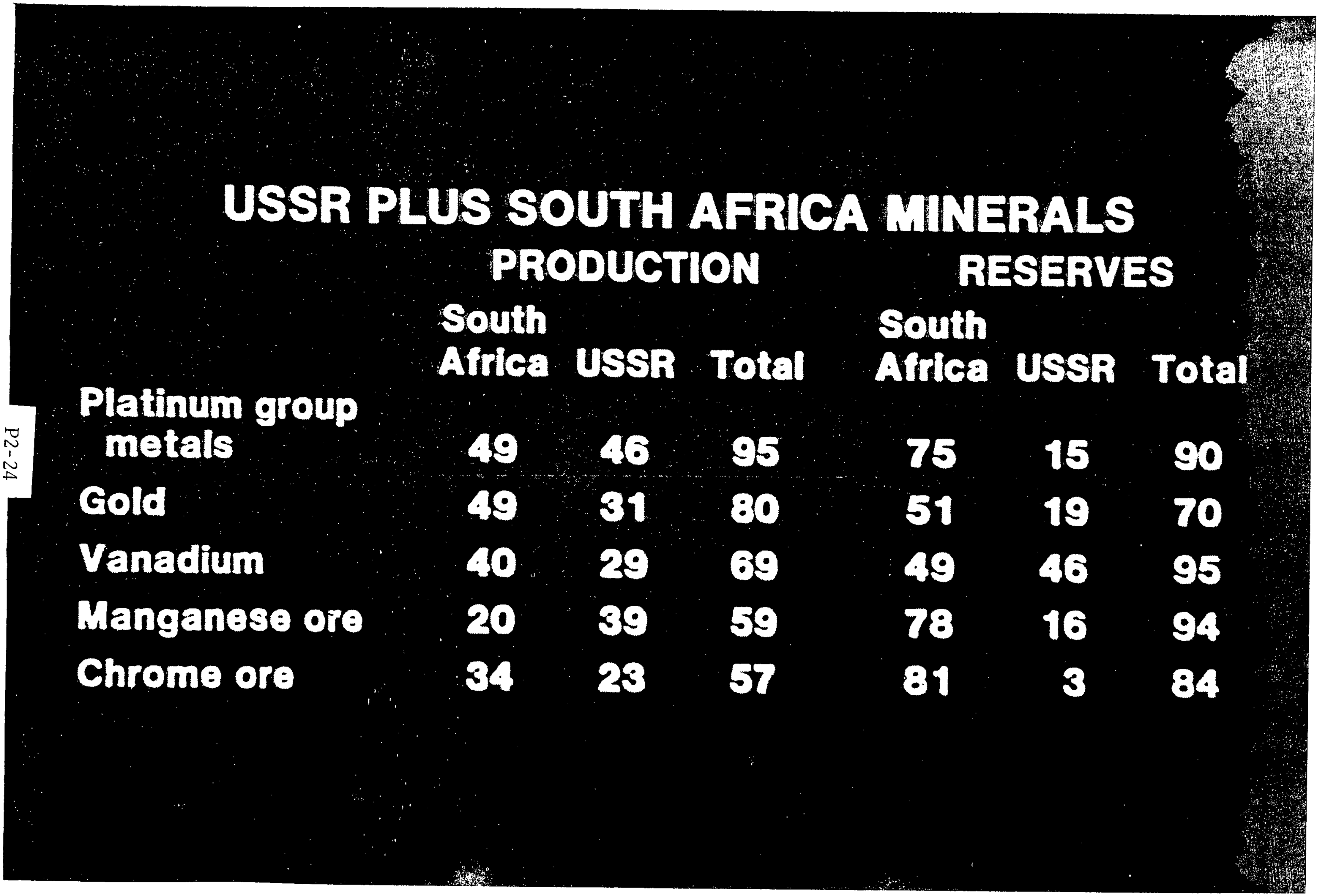
- Advanced composites
- Rapidly solidified metals
- Structural ceramics
- Intermetallic compounds
- Structural polymers
- Coated graphite
- Advanced glasses
- Advanced coatings

NEAR-NET SHAPE TECHNOLOGIES

- Investment and precision die casting
- Powder metallurgy
- Stepped extrusions and forgings
- Improved welding, joining and soldering techniques
- Superplastic forming

ADVANCED SURFACE MODIFICATION TECHNOLOGIES

- REACTIVE CHEMICAL VAPOR DEPOSITION
- ION IMPLANTATION
- ION NITRIDING (GLOW DISCHARGE)
- ION PLATING
- REACTION MAGNETRON SPUTTERING
- ARC COATING



USSR PLUS SOUTH AFRICA MINERALS

	PRODUCTION			RESERVES		
	South Africa	USSR	Total	South Africa	USSR	Total
Platinum group metals	49	46	95	75	15	90
Gold	49	31	80	51	19	70
Vanadium	40	29	69	49	46	95
Manganese ore	20	39	59	78	16	94
Chrome ore	34	23	57	81	3	84

SLIDE 11

KEYNOTE TALK

BY GORDON GEIGER *

AT

WORKSHOP/CONFERENCE ON CRITICAL MATERIALS ISSUES

VANDERBILT UNIVERSITY/US DEPARTMENT OF COMMERCE

OCTOBER 3-7, 1982

POTENTIAL FOR CRITICAL MATERIAL CONSERVATION IN THE INTEGRATED STEEL INDUSTRY

The topic for this Workshop is the potential for continuing output by the steel industry of metallurgical products in the event of a disruption in the supply of critical raw materials.

There are several questions that have to be addressed when attempting to establish the potential for critical material conservation:

1. What are "critical materials" for steel?
2. What raw materials are involved?
3. What are the factors that influence consumption of critical materials per ton of product?

Beyond these, the question of policy recommendations for present and future government actions and the strategy to be followed by government and industry in the event of a supply disruption need to be addressed, because technological solutions to the problems posed are not necessarily the best solutions.

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* Gordon Geiger is Vice President and Technical Director, Chase Manhattan Bank

I will attempt to give some answers to the questions posed, and then to raise some further questions for this Workshop to ponder.

I. What are the critical materials for steels?

In my opinion, they are the materials whose supply we believe could be curtailed or cut off, and whose use is absolutely necessary. Consider the various elements:

Manganese is 100% imported and used all steels.
Chromium is 100% imported and vital for stainless steels.
Molybdenum is domestically available in adequate quantities.
Nickel is domestically available or obtainable from Canada.
Tungsten is domestically available (at a price).
Niobium has been obtained domestically in the past and could be again (at a price).
Boron is domestically available.
Silicon is domestically available.
Vanadium is domestically available, to some degree
Aluminum is domestically available (at a price).
Titanium is domestically available.

It would appear that, of these, only manganese and chromium are really critical. This assumes, of course, that a period of short supply of other elements could be tolerated while some old processing plants or mines are restarted. It also assumes that several of the above elements are cut off simultaneously.

Reflecting on this latter point, the only way in which that could or would happen is as the result of major worldwide conflict or concerted action by Third World countries as a result of significant political events. In either case, the length of time involved in disruption is open to debate. Either event would probably result in intense diplomatic efforts arriving at a solution, or military action with unknown results. The majority of manganese and chromium come from South Arica, chromium from Zimbabwe, and manganese from Brazil and Gabon. Other supplies of chromium come from the USSR, Albania, Greece, Finland the Philippines, and Turkey. The potential for supply disruption clearly exists, yet it would probably require World War at sea to cut off supply entirely.

II. What raw materials are involved in manganese and chromium supply?

Manganese is obtainable from imported ferromanganese, from imported manganese-rich ores smelted in the U.S., from iron ore concentrates and pellets that are high in manganese, from low-grade domestic ores, from slag, from scrap, from fume and dust, and from deep sea nodules.

Chromium is obtainable from imported ferrochromium, from imported ores, from scrap, from slags, from fume and dust, and from low-grade domestic ores.

I have listed these in the order of increasing cost and difficulty of recovery. Presumably only a cutoff of supply lasting a long time would result in the necessary investment of capital to obtain either element from domestic ores, slags, wastes, or fume and dust. Several processes for separation and recovery of chromium, nickel, molybdenum and tungsten from complex waste materials exist, but have not been invested in because of the continued availability of virgin materials, making their economics marginal. Investment in mines and processing facilities takes a long time and they must be continually operated, once built, to keep them available in times of crisis, which may never come.

With regard to deep sea mining, in my opinion, mining of nodules for their elements is a 21st century project, if then, because of the capital cost/risk situation and the continued availability of land-based minerals.

III. What are the factors that influence consumption of critical materials per ton of product?

There are only two:

--Yield in processing raw materials to product.

--Specification in product.

IV. Potential for Conservation via Specifications

Specifications are usually the result of compromise between producer and consumer. They are both technical and economic in nature. They are often the result of historic patterns of raw material supply and technological limitations, e.g., sulfur was allowed to be as high or higher than 0.050% in many steel products when only acid steelmaking was prevalent. For many products, as basic steelmaking was introduced, consumers requested, and got maximum sulfur levels of 0.025%. However, AISI specifications for many steel products did not decrease in maximum sulfur.

Because of hot working problems, manganese had to be added to tie up the sulfur in less troublesome form. Therefore, the amount of manganese in the specifications was made to cover all allowable sulfur levels under the specifications.

While it is necessary to maintain the Mn/S ratio for hot working reasons, (10/1 is the usual ratio) the specifications for S itself are continually decreasing. Today, about 10% of flat-rolled steel calls for 0.010% S, and perhaps another 10% calls for 0.015% S. These levels, in turn, do not need as much Mn for hot working control, and so Mn levels of 0.20% are adequate, whereas Mn levels of +0.3% are more common when sulfur levels of 0.025% are encountered. The net result of the decrease of S specification levels will also be a decrease in Mn consumption, <u>provided</u> the opportunity is recognized and implemented.

The specifications for Mn are often very broad, e.g., 0.25 to 0.6%. There are reasons for including Mn beyond hot workability aspects which only benefit the producer, such as for strengthening weldability or hardenability. Yet specifications do not differentiate between these reasons. Since many decisions of materials specifications are made by persons that do not recognize these factors, a tremendous educational effort will be needed to educate purchasing agents and others that where they specify, e.g., AISI 1010 steel for a non-stressed part, they are going to get average Mn levels, e.g. 0.45%, (the Spec. is 0.3 to 0.6%) yet for property reasons they may not need any Mn, and all that a producer need put in is enough to counteract the effect of sulfur, e.g., 0.25% Mn may be enough. The total of manganese over-consumed each year because of purchasing/specification synergisms may be as much as 25% of consumption.

In recent years, AISI and SAE have moved to lower the Mn limits on 1005 and 1006 steels, to correspond to lower sulfur levels, but have done nothing on 1010 and higher steels. Much more needs to be done along these lines. Customers need to be able to specify only properties needed. Chemistry needed to meet those properties should be the responsibility of producers. This would also allow producers to make better use of residual elements in scrap. Scrap each year accounts for larger proportions of the steel made, and this will continue to grow. However, the elements in scrap must be better utilized.

There are quite a few relationships available now between chemistry and mechanical properties. It is entirely possible to use linear programming and other computational techniques to project the least expensive composition to achieve the desired mechanical properties, including the effects of residual elements. The necessary constraints to meet various applications can be incorporated. If the goal is to minimize the use of a particular element, its "price" can be made very high and the programs will automatically minimize its use.

Fig. 1 is an example of the differences in alloying cost needed to meet various levels of strength and/or chemistry for one steel. Fig. 2 shows that meeting minimum chemistry for various steels can result in mechanical properties both failing to meet and exceeding minimum strength requirements. Clearly, the relationship between chemistry and properties, in specifications, needs to be readdressed.

With regard to chromium, development of substitute alloys, to be discussed throughout the conference, is proceeding. However, a number of questions need to be raised in this regard.

- Is a product made with a lower-grade material going to be competitive on the world market? Many countries making stainless products do not compromise on alloy and will not be likely to do so unless actually cut off from supply. Therefore, for U.S. firms to use less than optimal materials, for the sake of conservation, will put them at a competitive disadvantage and they are not likely to do so, and should not be required to do so.
- Is development of such alloys going to increase the use of another critical material, for example, Mn? If so, does it make sense as a substitute?
- How much high-chromium steel is really needed in the event of a siege?
- Could any country, for long, afford not to export manganese or chromium to one of its largest customers? Certainly not Brazil or most African countries, probably including South Africa.

V. Opportunities for Conservation by Improved Yield

The most obvious opportunity for yield improvements that will conserve alloying elements is the installation of continuous casters. U.S capacity for continuous casting is only about 25% of its capacity for raw steel production. Most of the bar and rod production in the country is continuous cast today, but not the large structural and the flat products. Many companies are constructing or engineering new slab and bloom casters at the present time, but much remains to be done. The major obstacle is simple: money. Every steel company is having to conserve cash, and none have made much money in recent years, partly as a result of not having casters in the first place. The global competition has a much higher percentage of continuous casting, and at today's operating levels is producing essentially everything via this route. They have, in many cases, not earned the money to invest, but have received government assistance, either in the form of outright subsidies or subsidized financing, to carry out this modernization. U.S. industry is investing only $1B, this year, when $4B+ is needed for modernization. It is imperative that this investment be carried out as soon as possible.

Other opportunities for savings in the melt shop include:

- improved addition techniques, such as submerged injection technology and furnace additions using smaller particle size ferroalloys which allow more rapid melting and mixing of alloying elements out of contact with slag or air. Yields should be improvable by 20%.

- Use of bottom tapping systems in arc furnaces to minimize tapping stream oxidation.
- Improved systems for weighing heats in process, in order to minimize overcompensation for uncertainty in weights at the time of addition.
- Recycling of fume and dust. The manganese to iron ratio in fume is 100 times greater than in the metal bath from which it comes. Systems exist for compacting and recycling this material and it should be done.
- Recycling of BOF slag through blast furnaces or using it as EAF slag making material, to recover manganese.
- Improved melting practices for Cr containing heats. AOD processing has increased yields for Cr, but not to the extent it should have and further improvements in control are possible.
- Increased use of melt control by computer. Dynamic control systems available today for BOF control and used in every plant I have visited overseas and practically never here.need to be installed to minimize excess oxidation of metallic elements. The use of linear programming techniques to optimize alloy additions is increasing, but should be extended.

In the area of hot and cold working there are a number of technologies that need to be implemented. They include:

- Increased hot connection of slabs and blooms to reheating furnaces in order to minimize scale loss.
- Improved drafting sequences to minimize end crop losses on account of width changes near ends of plates and coils.

- Improved gauge control to minimize end losses on account of out of gauge material for considerable length into coils.
- Improved shape control on cold mills. This will require investment in new mills.
- Increased use of thermo mechanical processing for property enhancement. This requires investment in continuous annealing and quenching lines, controlled cooling lines on hot strip mills, and rebuilding or replacement of older mills to increase their stiffness.
- Improved segregation of scrap to allow better recovery of alloying elements.
- Improved in-process corrosion protection to minimize downgrading of material from prime to secondary.
- Improved corrosion protection at customers' manufacturing facilities. Significant losses of material occur at this stage.
- Improved coating systems to protect material in service. Most metallic systems do not fail for mechanical reasons, but do so because they have corroded away.

While decreases in crop losses due to continuous casting replacing ingot casting and slab rolling do not decrease requirements for raw melting stock, they do result in several percent less loss in slag, scale, and fume, because less of each of these unrecovered items is made per ton of products. Furthermore, in the case of low alloy steel (not stainless) the chromium and other alloy elements are not recycled for recovery because of a lack of scrap segregation and so the virgin alloy requirements are actually decreased by the full increased yield savings of 10% or more.

VI. Implementation

Some of the above opportunities for conservation can be implemented by technologists, but many of them will require capital investment, and all require management commitment. Unfortunately, the steel industry generally is presently in a serious financial situation and its future prospects are poor. If the dollar continues strong, as many believe it will, the competitiveness of the domestic industry vis-a-vis foreign competition will be poor, and its arguments for dumping will be invalid. On the other hand, subsidization of foreign industry has occurred, and has resulted in substantial modernization and restructuring for more efficient operation, making future competition tougher.

As a result, it is difficult for management to make the commitment to investment in modernization of facilities when the return on investment is not there. Thus, both the availability of capital and management commitment are questionable at this time. The question then becomes not conservation of critical materials, but conservation of the industry itself! The first question I pose for policy debate is, therefore:

1. Should the U.S. government give outright grants to steel companies to invest in continuous casters and other needed capital equipment?

- It may be the <u>only</u> way to quickly get U.S. industry into competitive conditions in flat products. The market mill segment is competitive in bar products, but the flat product producers are not.
- The U.S. is the only country that does not give outright or indirect financial support to its steel industry.
- Without an injection of capital for investment in this technology, U.S. industry will continue to be at a significant cost disadvantage when economic recovery occurs, and may never be able to earn enough to reinvest in it and become profitable.

<u>Other policy questions for discussion are</u>:

2. In the event of a supply disruption, how much of the consumption of <u>(element)</u> is <u>really</u> critical?
   - Is it critical from a military standpoint?
   - Is it inconvenient from a consumer standpoint?
   - Is there a reasonable substitute alloy?
3. How many elements can be cut off for long by exporting countries? (How well does an embargo work?!)
   - What proportion of their net exports does it represent? <u>Often a large part</u>.
   - Can they cut off supply to only one customer nation effectively? <u>Not very well</u>.
   - Are they self-sufficient themselves? <u>Usually not</u>.
4. Should specifications be reviewed with an aim of allowing more freedom to use residual elements to meet mechanical property requirements? <u>Yes</u>.

5. Can specifications for alloying elements, including manganese, be more specifically oriented towards their function, so that when not needed for specific properties, but only for processing reasons, they may be eliminated by suitable alterations in processing? Yes.

6. What price are we willing to pay for domestic supply?
   - Should or will the government subsidize development and operation of otherwise uneconomic domestic mines, smelters and refineries? It seems unlikely.
   - If not the government. who would do so?
   - How can the use of more expensive but less strategically critical alloy material be justified, or paid for, in times of non-crisis? It cannot.

7. How can better manufacturing techniques and rolling technologies be introduced, when the American engineering education system has practically ignored these subjects?
   - What can be done to improve the teaching of macro-mechanical processing in universities?
   - What can be done to improve the teaching of manufacturing?
   - What can be done to improve the teaching of engineering?

8. Since many critical materials are not necessarily the most expensive materials, their use is economic today. Chromium and manganese are the least expensive alloying

elements in steel. Without changing their cost, how does a plan to implement changes, in the event of a supply crisis, get designed and implemented?

- Is it done by artificially adjusting price?
- The plan will have to be organized and on the shelf to be of any use.

CONCLUSIONS

The major problem is not necessarily methods or technologies to save chromium or manganese, or to replace them. Technologies exist and substitute alloys exist. Implementation of the substitute alloys will often result in inferior products. Implementation of technology requires massive capital spending that the integrated steel industry cannot afford.

Therefore, the problem is really the preservation of the steel industry in some form and at some reasonable level of capacity. This will require injection of capital from sources outside the industry. Otherwise, there will be no competitive industry to use chromium or manganese and the critical materials problem will have disappeared.

4858D/jc

Potential Areas for Chromium Conservation in Stainless Steels

R. A. Lula, Consultant

During the past five to ten years the critical metallic materials have been the subject of numerous conferences, committee meetings or other kind of activities which can be categorized as public debate within the technical community. In many respects this has been a successful and fruitful endeavor: it certainly has awakened the public awareness, it has defined the problem and has yielded contingency planning to be used in case of sudden disruptions that might make it impossible to produce essential equipment for our national defense. It has also resulted in legislative action by the enactment of the National Materials and Minerals Policy, Research and Development Act of 1980. This public debate has yielded, however, only a modicum of positive action and commitments to implement the necessary steps to alleviate the short and long range critical materials problem.

My assignment at this workshop deals with chromium conservation in stainless steel, a narrow but vital portion of the critical materials debate. The most pertinent research on chromium conservation in government and industry will be reviewed and some possibilities of chromium conservation will be discussed.

The Role of Chromium in Stainless Steel

A pertinent discussion of chromium conservation in stainless steel has to be made in the context of the various functions provided by chromium when added to stainless steels.

The first function of chromium is to provide corrosion resistance. No other element is known to perform this function and none are expected to be discovered in the future. If chromium cannot be replaced it can, however, be reduced in certain applications for which some stainless steels might be overdesigned.

A reduction of the chromium content in ferritic and martensitic stainless steels does not appear appropriate. The situation is different with the austenitic stainless steels which are locked to 18 percent minimum chromium by tradition and the low cost of chromium. A reduction of chromium should be feasible since in many of the applications in which these steels are being used a lower content could be adequate.

The second function of chromium is to impart resistance to oxidation. Partial or even complete replacement by aluminum is considered feasible in certain applications especially in the absence of corrosive compounds such as H_2S.

The third function of chromium is to stabilize the austenite in austenitic stainless steels by depressing the M_s temperature. Since all the common elements used in steelmaking lower the M_s temperature, replacement of chromium is feasible.

Short and Long Range Materials Criticality

Among the many issues clarified by the public debate is the division of the materials criticality problem into short and long range. A sudden disruption of supply is, of course, short range while the possibility of gradual erosion of world resources is a long range possibility. For the long range criticality at least in regard to chromium in stainless steel, I am inclined to discount the need to advocate any R & D on chromium substitution or conservation at this time. The gradualism that characterizes the long range situation will permit to solve the chromium problem, in case it ever materializes, in concert with the economic and technological factors prevalent at that time. Indeed who can predict, for instance at this time, the impact of the surface modification technology and economics on the utilization of stainless steel, ten, twenty or thirty years from now?

For this reason this presentation will deal only with the sudden cessation or disruption of chromium supply as it might affect the national defense and military security as well as the national economic and industrial strength and well-being.

Review of Activities on Chromium Conservation

A review of the studies and the R & D on chromium conservation has to start with the report "Contingency Plans for Chromium Utilization" - MNAB-335, published in 1978. This is a comprehensive and detailed study made by a committee with broad representation from government industry and academia. The data, conclusions and recommendations of this report can easily form the basis for all subsequent work on chromium conservation.

The basic assumption adopted in this study is the worst possible supply situation, that of a total embargo of all foreign sources of chromium ore or ferrochromium. Among the conclusions and recommendations the following are worth citing:

- A drastic curtailment of chromium supply would have serious short and long-term effects.
- The location of chromium deposits are such that in 25 to 50 years the world will depend completely on South African and Zimbabwe deposits.
- No substitutes exist or are likely to be developed for chromium in high-strength steels, high temperature alloys and corrosion resistant alloys that are essential for jet engines, gas turbines, power plant equipment, petro-chemical and various other critical products.
- It is very unlikely that corrosion resistant iron or nickel-base alloys without chromium will be developed.

- The optimum response to the increasing vulnerability to a disruption of the chromium supply would involve a combination of four approaches: stockpiling, conservation, substitution and exploration for new deposits.

The U. S. Bureau of Mines has several projects dealing with chromium conservation and substitution in stainless steels. An Fe- 8 Al-6 Mo alloy (Table 1) is being investigated as a chromium-free substitute for high-chromium heat-resistant alloy. More research is needed to optimize the composition and mechanical properties of this alloy but it is important to note that it has already demonstrated that a chromium-free iron-base alloy can achieve high-temperature oxidation resistance in air superior to that of Type 304 stainless steel.

In another project funded by the Bureau of Mines and carried out at International Nickel Company's Research Center, the aim is to determine if other elements could replace part of the chromium in stainless steels in corrosive environments. Based on the conclusions of this work, it appears feasible to develop an austenitic stainless steel containing on the order of 9 percent chromium with addition of molybdenum and possibly copper and vanadium (Table 1) that would have corrosion resistance comparable to 18-8 grades of stainless steel in less severe environments but would be inadequate in most severe environments, for example, in boiling nitric acid. This steel, according to S. Floreen, could be used in decorative, aqueous and some industrial applications.

NASA - Lewis Research Center also has a program to determine the feasibility of substituting less critical elements for chromium in Type 304 stainless steel. After an extensive evaluation of various alloying elements an optimized composition was selected containing 12 percent Cr plus Si, Al, Ni addition as shown in Table 1. Based on anodic polarization tests, this alloy has corrosion resistance in aqueous environment superior to that of Type 304. The oxidation resistance in air of this alloy is also superior to that of Type 304, undoubtedly due to the presence of aluminum.

The Specialty Steel Industry whose well-being depends on the availability of raw materials at a reasonable cost has experienced in the past some crises which were weathered successfully. In mid-nineteen fifties, during the Korean war, the industry overcame a nickel shortage by promptly developing high manganese-nitrogen-bearing austenitic stainless steels with 1 percent max. nickel content. These steels did not survive when nickel became readily available but they were the precursor to the AISI 200 Series stainless steels in which half of the nickel content of the 300 Series is replaced by manganese and nitrogen. These steels have found a permanent niche in the family of austenitic stainless steels.

In 1974-75 we experienced a self-inflicted surge in the price of chromium as a result of the U. S. embargo of Rhodesia. This was followed shortly by the intense public debate on critical materials. The Specialty Steel Industry reacted to this by researching ways of saving chromium and other critical metallic elements. One example of this type of work done at Allegheny Ludlum Steel Corporation's Research Center will be described here.

More than 50 percent of all the chromium used in this country is for stainless steels. Of the total stainless steels, production Type 304 and other 18 Co-8 Ni represent over 75 percent. For this reason the main thrust on any chromium-saving effort should be aimed first at Type 304. The immense popularity of Type 304 is based not only on its resistance to corrosion but also on its outstanding versatility as illustrated by ease of fabrication and good mechanical properties. It is interesting to note that all austenitic stainless steels have at least 17-18 percent chromium content when it is well-known that passivity can be achieved with only 12 percent chromium. This has to be undoubtedly credited to the low and constant cost of chromium over the years. It is believed that with the exception of some chemical industry application, in most other uses an austenitic stainless steel with lower chromium content will have adequate corrosion resistance. Lowering the chromium in an austenitic stainless steel demands replacement by other elements since its role is not only to provide corrosion resistance but also to stabilize the austenite. Otherwise the austenite becomes unstable upon cooling or cold working.

With these considerations in mind, Allegheny Ludlum Steel Corporation has proceeded to devise a theoretical method to develop new austenitic steel compositions with an austenite stability, and hence general mechanical properties characteristics, equivalent to that of Type 304 stainless steel. The austenite stability, expressed as M_S or M_D temperatures, was the quantitative criterion for chromium replacement. Three empirical formulas shown in Table 1 were used to determine the M_S and M_D temperatures.

The average Type 304 composition used as model for stability is shown in Table 2, together with its calculated stability factors. The Mn and N_2 levels of the new compositions were calculated assuming Cr levels of 12, 14 and 16 percent. Austenite stability contours were calculated with all three stability formulas and were plotted on a Mn versus N_2 graph as shown in Figure 1. Examples of compositions selected from the three graphs in which the Mn and N_2 were averaged are shown in Table 3. This approach can be extended to 10, 8 or even lower chromium content and other elements can be brought into the picture.

This method fits well in the concept of stored information to be used in case an emergency arises. The practical value would be considerably enhanced if the theoretical work would be followed by an experimental phase in which several composition with chromium content from 6 to 16 percent will be made and evaluated.

The processing, mechanical properties, the corrosion and especially long-time exposure corrosion should be evaluated.

Table 1

Fe-Base Compositions of Cr-Savings Alloys

Sponsor	Objective	Composition C	Ni	Si	Cr	Mo	Al	Other
U.S. Bureau Mines	Oxidation resistance	.1	-	-	-	6.0	8.0	.8 Zr
U.S. Bureau Mines (INCO)	Corrosion resistance	.011	23.5	2.3	9.3	1.0	-	2.2 Cu, 1.9V
NASA	Corrosion and oxidation	.06	10.0	1.65	12.0	2.0	1.0	1.1 Mn

Table 2

Formulas for Austenite Stability

1. Eichelman and Hull

$$M_S = 75\ (14.6 - Cr) + 110\ (8.9 - Ni) + 60\ (1.33 - Mn) + 50\ (.47 - Si) + 3000\ [.068-(C\ \&\ N)]$$

2. Angell

$$M_D = 413-462\ (C + N) - 9.2\ (Si) - 8.1\ (Mn) - 13.7\ (Cr) - 9.5\ (Ni) - 18.5\ (Mo)$$

3. Monkman

$$M_S = 2160 - 66\ (Cr) - 102\ (Ni) - 2620\ (C + N)$$

Table 3

Average Type 304 Composition

C	Mn	Si	Cr	Ni	Mo	Cr	N_2
.07	1.70	.50	18.50	8.75	.20	.45	.05

1 - M_s = -461   2 - M_s = +.6   3 - M_s = -414

Table 4

Selected Compositions with Stability Equivalent to Type 304

C	Mn	Si	Cr	Ni	Mo	Cu	N_2
.07	4.75	.50	12.0	8.75	.20	.45	.15
.07	2.20	.50	14.0	8.75	.20	.45	.15
.07	5.30	.50	14.0	8.75	.20	.45	.075
.07	3.10	.50	16.0	8.75	.20	.45	.075

Conclusions

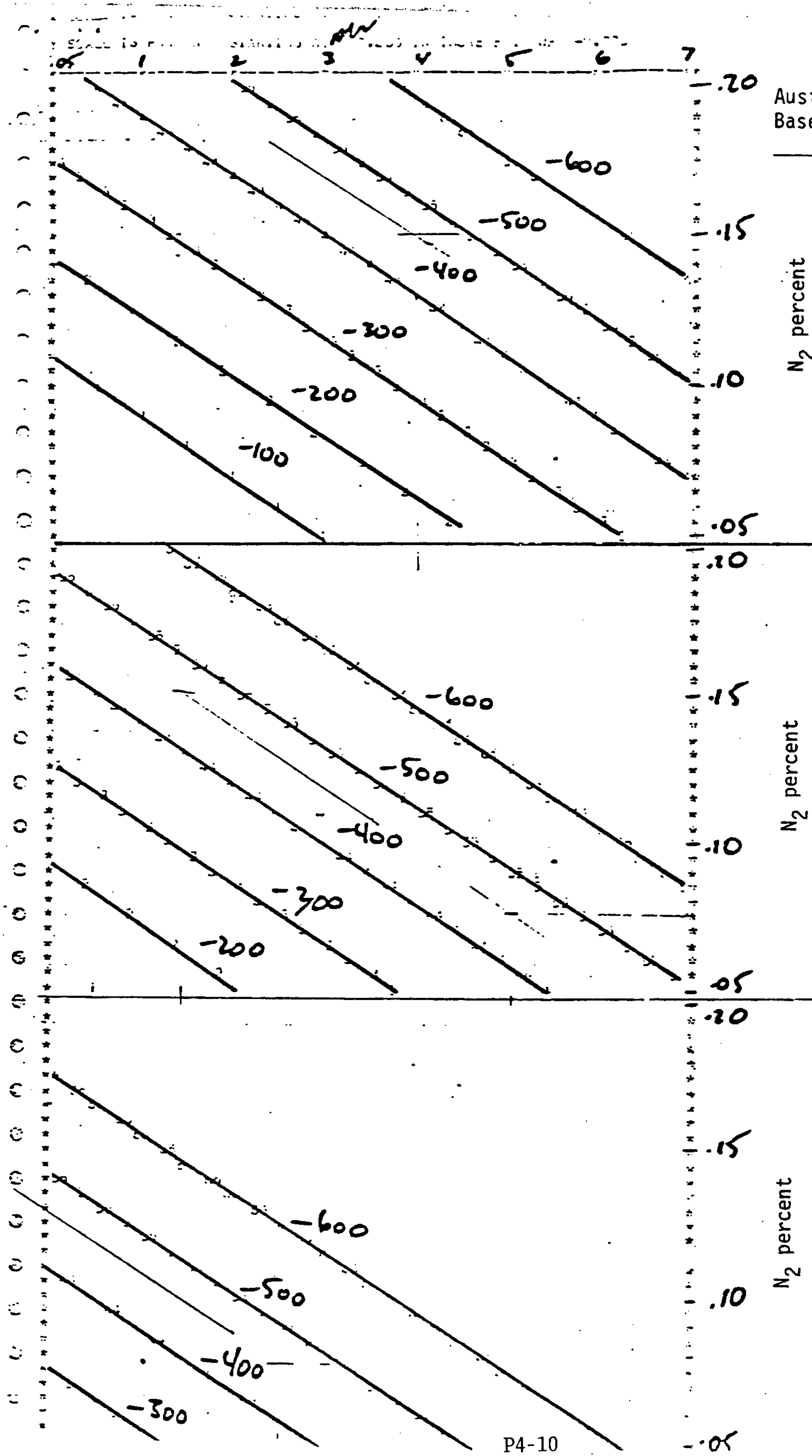
In closing I would like to reiterate that in this rapidly changing world we should leave the long range materials availability problems be solved gradually as they occur, probably in the form of cost escalations, by the technological and economic means prevalent at that respective time.

The short range problems such as would be a sudden cut-off of all chromium supply need extensive advanced preparation in the form of research and development to act as stored know-how ready to be implemented on a production scale at the onset of an emergency. This is now termed substitution preparedness. The work done so far has indicated promising possibilities of chromium saving. Considerably more research is, however, needed and this work should not be confined in the ivory tower of the laboratories but should be broadened to encompass processing, fabrication and evaluation of the materials or methods that have been developed. The traditional producing, fabricating and users industries should be brought into the picture in order to gain their eventual acceptance.

There is little justification for the industry to put their R & D monies in new materials or new methods designed for very specific and not very likely to occur circumstances and, hence, are not economically viable in present day conditions. For this reason, this should be funded by the government.

Figure 1

Austenite Stability Contours Based on Eichelman and Hull Formula



The Value of a Generic Technology Base: Substitution Based on Hardenability

It is a pleasure to be a part of this important and timely workshop. Being a keynoter I find is no small challenge as I have spent considerable time just considering what might be an appropriate contribution. Certainly to give you information on the importance of chromium as an alloy or statistics on how much we import is not necessary as these factors have already been well established. Chromium certainly has a very positive impact on our lifestyle. Its attractive properties as a metal and as an alloying agent are well known to engineers and metallurgists interested in the performance of machinery and appearance and performance of structures. There are very few elements that have as attractive cost/benefit ratio as chromium.

I finally settled on trying to use one aspect of the technology related to hardenability, chromium and substituteion to make a broader point for the position of technology in contemporary society.

"Substitution technology," as a descriptive phrase, has recently moved to the forefront. I'm not a critic of it, I enjoy it, but I would like to point out that substitution is a normal ongoing engineering activity and has been for many years. It would be difficult to pinpoint the origin of substitution technology. Its roots go into antiquity. Of industrial significance though mayby a century ago would be a place to start. About that time cast irons, wrought iron and crucible steel were the essential metallic materials of construction. Cast irons are still with us and their associated technology has been expanded greatly. Wrought iron and crucible steel were however rendered non-competitive by new developments. Substitution of Bessemer steel as a material of construction took place on a large scale in the 1870's. It is interesting to note though that it occurred was some 15 years after Bessemer read his famous paper to the British Association of Advancement of Science (1). William Leslie gives an interesting historical documentation concerning developments in the steel industry in the December 1971 issue of the Journal of Metals. In my comments I have drawn freely from his work.

There are no components on which materials are specified that the specified material isn't in jeapordy from a competitor material. Improvements in processing, performance and cost are perpetually in demand. Harry McQuaid once said in his own inimitable style that, "I was once told that the ideal design is one that is just good enough; that anything better than good enough was wasting someones money; and that anything not good enough means you wouldn't have a job very long." (2)

That is a very succinct and on target statement. It has two elements, one, components must perform and two, their costs must be optimized. The implications of this are, however, profound. This implies that we must have comprehensive technical knowledge concerning what the performance criteria are in terms of loads, their frequency and variations, the states of stress they induce, invironmental conditions, and so on. In addition, we must quantitatively understand properties of materials of construction in terms of fatique and fracture resistance and the influence of the myriad environments components are exposed to and thirdly, we must have comprehensive knowledge concerning producing the complex shapes required, including costs and sensitivity to capital equipment requirements. This is common knowledge to the insightful technologist. I just wanted to bring it into focus.

The simple challenge expressed by McQuaid and an understanding of the complex technical nature of our varied disciplines provides the starting point to map future strategies and emphasizes the necessity for expanded knowledge and interdisciplinary cooperation.

In the first portion of my remarks I'd like to dwell on substitution technology related to applications where hardenability is the major requirement. This discussion will provide background for the work on chromium substitution to be reported by C.J. Kieth on Wednesday. I think it will be of value to dwell a bit more in the past and briefly review some of the milestone events in the surrounding technology that provided us the tools that allow our current accomplishments.

Figure #1, embellished somewhat from its first appearance, (3) shows how our usage of individual alloying elements has changed through the years since the turn of the century. Technology during this early period was developing rapidly.

Alloying was in its infancy, although chromium was added to crucible steel as far back as 1865. A 0.60 chromium containing steel was used in a complex tubular structure in the construction of the Eads bridge at St. Louis in 1871 (4). In these steels chrome ore was added to the steel. The alloying was successful in the crucible process because of the highly reducing conditions associated with the process. The approach didn't work though with the open hearth process and it wasn't until ferro-alloys became available, around 1880-1890 that alloying was practiced on a large scale. Even so, alloying was done principally for solution strengthening. As for the most part only tool steel were heat treated in this period.

Nickel was the major alloying element in the 1900's. Chromium was used in combination with nickel and by itself but in very small tonnages. In contrast, by 1970, chromium was used by itself and in combination with nickel and molybdenum in very high tonnages. I would like to get two the concepts across using this chart. One being, these steels throughout this seventy, now 82 years, have been used principally in the production of machinery and structures. Steels of varying alloy types can be and have been replacements one for another over the years. The most notable substitution based on hardenability, occured in the early 40's during World War II when nickel was in short supply. The Ni-Cr-Mo system, i.e. the now popular 8600 series steels were developed. These were known early on as NE (National Emergency) Steels. The switch to these steels was made with fear and trepidation but with very little difficulity considering the level of technology existing at the time. Note also, that many of our changes are motivated by necessity.

For my second point on this graph, I'd like to use the horizontal axis as a technological time line about hardenability developments and thus help define the current state of the art. Building complex efficient machinery would be a cumbersome task indeed if it were not for technical advancements in materials. Heat treatment of steel can be listed as one of the very important contributors to our current advanced lifestyles. An understanding of hardenability concepts is essential to providing an appreciation for this contribution.

Hardenability is defined as the capacity of a steel to transform partially or completely from austenite to some percentage of martensite at a given depth when cooled under some given condition. Another definition, from the ASM handbook, is the property that determines the depth and distribution of hardness induced by quenching. These two definitions are different in that in the first the criteria is microstructure, whereas in the latter the criteria is hardness. The first is preferred, however, it is sufficient for our purpose to recognize that hardenability is the capacity of a steel which allows it to develop strengthening in components by heat treatment and the higher the hardenability the larger the component which can be adequately strengthed. Hardenability is dependent on nucleation and growth of non-martensitic products, the austenite grain size which affects nucleation sites, and the effect of alloying elements on nucleation and growth.

Technology surrounding this phenomenon was slow in developing. A great deal was known about advanced stress calculations as far back as the mid 1800's, however, the factors involved in the development and control of strengths weren't understood until much later. Around the turn of the century, as indicated earlier, only tool steels were regularly receiving heat treatment. Most early tests where depth hardening was observed had to do with testing for toughness. Bars were heated to a "good cherry red", quenched in water, then broken to examine the fracture texture. A rough surface would indicate brittleness, a fine texture surface would indicate toughness. The texture was generally controlled by grain size. During the course of this test, however, effects were observed in terms of depth of hardening. However, it wasn't until about 1926 that any standardization of hardenability testing began to occur. The test, which evolved from the grain size work, was known as the P-F test sponsored by Shephard (5). It was in this same period that McQuaid and Ehn (6) developed the grain size measuring method which is a standard today. Not much happened after that related to measurement of hardenability for almost a decade. However, during this period Bain (7) began to shed important knowledge about phase transformations and developed the TTT diagram. Our understanding of microstructural development and control through heat treatment was advancing rapidly. Shortly after this several hardenability tests were developed. The "end-quench" test by Jominy has turned out to be the most significant, and what a contribution it has turned out to be. Data from this test are the basis for the description of standard H steels. Heat treatable steels are purchased to these standards world-wide. It even, in many respects, overcomes language barriers. But most importantly, the data can be used to effect rational metallurgical design of heat treated components. The test was first developed to measure carburized hardenability, but quickly was extended to measuring hardenability of a whole broad class of heat treatable steels. Publications (8) related to this development are dated in the 1938-39 period. There was a flury of work related to hardenability during this period and many important contributions were made. It does not match my intent, however, to dwell in detail. The next important generic type development followed soon after. Now that hardenability was accurately quantifiable and knowledge of transformation kinetics was becoming more sophisticated, it was logical that hardenability prediction based on chemistry and cooling conditions should follow. Grossman (9) lead off in this technological area followed by many others such as Kramer et al (10) Crafts and Lamont (11) and others, to provide a means of calculating hardenability based on the contribution of individual alloys. Again there was much work from many sources. The technical meetings of that day were exciting. Technical papers were given in detail, not 15 minute summaries, and prepared discussions provided the public challenge necessary to affect quality of the work. To hasten along though, other important work took place related to <u>using</u> hardenability data in metallurgical design. Boeghold (12), Grossman (13), Carney (14) and others made significant contributions during the period 1940-54 and in 1957 Jatzak and Girardi (15) published their classical work on multiplying factors for high carbon and the case carburizing steels. From that time, things were somewhat dormant until the start of the 70's when the computer was utilized in computing hardenability using the regression analysis approach. Just (16), Kirkaldy (17), ourselves (18) and others had been working in this area during this period. CCT diagrams became common place and improved multiplying factors were developed by de Retana and Doane (19). Our work on cost optimization through computer aided design was also started in this period. My colleagues, Walter, Sponzilli and Keith (20) were very instrumental in this work.

Well, this has been quite a dissertation on the history of alloying and hardenability. Recognition of this technological area is very important however. Close to ten million tons of alloy heat treatable steels are produced in the U.S. annually. There are about 90 different standard alloy systems. Since 1952, 70 systems have been deleted and there are about 42 systems known as SAE EX steels awaiting their turn to become standard steels. Some, of course, won't make the tonnage requirements to qualify for the standard category. Figure (2) is a typical hardenability band and should be kept in mind as we discuss additional substitution concepts. The dark area defines the limits for EX-6 and/or 8620 H steel. These limits are based on experience. Comments related to calculation of H-bands appear later in this paper.

In that respect, I would like to give a brief on the CHAT system. CHAT is an acronym for Computer Harmonized Application Tailored. This system is being utilized to develop chrome-free steels to replace the 8600 and 4100 steels as a contingency plan. This work, sponsored by Bureau of Mines, will be reported on fully by C.J. Keith on Wednesday. The CHAT system has been used extensively at International Harvester to develop cost optimized replacement and alternate steels for over a decade. The CHAT process is comprised of two parts. They may be done independently or in combination. When done together, the AT part of CHAT, i.e. Application Tailoring is done first. I'll not go into detail but it is the engineering work that is necessary to quantify hardenability requirements in terms of D_I for a given application. D_{IB} (base chemistry hardenability) is required for through hardening application. Both D_{IB} and D_{IC} (case hardenability) is required for carburized applications such as gears and shafts.

Once hardenability requirements are quantified the CH, i.e. computer harmonizing is done. The job of the computer is to provide a least cost chemistry combination which will meet the hardenability requirements. To show the principles involved refer to figure (3) thru (7). Figure (3) is a photo of the end-quench test in progress. Figure (4) is a plot of hardness vs. distance from the quenched end. Although not completely accurate D_I can be thought of as a single number which describes the fall off rate of the hardness vs. distance curve. This figure also indicates the ability to use multiplying factors to calculate D_I. Figure (5) indicates the relation between D_I and a series of hardenability curves. Deeper hardening steels have higher D_I's. This curve also shows the major role of carbon on initial hardness. Carbon content is the limiting factor in developing maximum hardness in the fast cooled area where 100% martensite is formed. It also makes a significant contribution to hardenability. Figure (6) and (7) show the key to the CH system. The contribution of each alloying element, i.e. multiplying factor divided by cost, is known as hardenability efficiency. The computer is programmed to use this type of data to build chemistry combinations which will simultaneously meet D_{IB} and D_{IC} requirements at minimum cost. Incremental hardenability efficiency, Δ log (mf) divided by Δ log (cost), also plays an important role. I have rushed through this rapidly but I believe with sufficient detail to provide the gist. One quick demonstration will suffice to show how it works. Figure (8) shows a carburized rear axle hypoid pinion. This application was targeted to develop an alternate steel to replace the 3.5% nickel steel being used because of cost considerations. An extensive review of the design, its field performance history and some innovative experimental stress analysis work during the AT portion of the program resulted in the understanding that a strength gradient (expressed as hardness) as shown in Figure (9) would provide adequate performance. Cooling conditions were defined in terms of Jominy equivalent conditions (Jec's) and the case and core D_I's derived, Figure (10). This information along with limits on carbon were the basis for Computer Harmonizing (CH). The least cost computer designed analysis is shown in Table I. Sample heats were made and tested to verify the accuracy of the computations (refer to Figure (11). Parts were produced and subjected to engineering and manufacturing tests. A program such as this never goes without a hitch, but after some innovative work by some of the people at the factory the bottom line was major savings, as summarized in Table II.

When one is involved with substitution on the basis of hardenability the question invariably comes up as to the influence of individual alloys per se on performance. There are some areas where we feel very comfortable in this respect. In many instances we can safely subscribe to the notion that performance is related to carbon level, microstructure and residual stress, all other things such as presence of non-metallics and grain size being equal. We are, of course addressing a multitude of applications when considering heat treated components. Springs, shafts, gears, wheel spindles and fasteners are but a few of many. Carbon levels vary significantly from very low to very high carbons so it would be difficult to cover the subject adequately but it should be discussed with the warning that there are exceptions to the rules. Fatigue and toughness are two of the prime performance criteria. Figure (12) from Garwood et al,(21) demonstrates some principles about fatigue that have become pretty well accepted. There is a linear relationship between hardness and fatigue strength for martensites up to 40 HRC fairly independent of alloy content in these medium carbon steels. Above that hardness the relation deviates from linearity, seemingly dependent on carbon content. Carbon, however, is in an intermediate role here, because of its affect on temperability. Because response to tempering is dependent on carbon and alloy levels, it was necessary for samples of the different grades shown to be tempered at different temperatures to achieve the same hardness; consequently, a variety of residual-stress conditions resulted. The tempering temperatures were necessarily sufficiently high to obtain 40 HRC; the residual stresses were reduced to a very low level, making all samples similar in that respect at 40 HRC and below. Above that hardness, however, tempering temperatures were such that residual stresses from heat treating were of sufficient magnitude to affect fatigue strength. It can be surmised, on considering the samples used in the study, that the groups having higher resistance to tempering (groups tempered at the highest temperatures) had better performance. This leads to the conclusion that, in general, the specimens initially contained detrimental residual stresses, which were relieved in differing amounts by tempering. This is consistent with the theory of development of residual stress in heat treatment, which considers specimen size, hardenability and carbon level. In principle, the level of residual stress in through-hardened as-quenched steel is usually tensile for small sections such as used in this study and decreases with increasing section size and/or decreasing hardenability to compressive values. The sequence of transformation from surface to center and the temperature gradients govern the outcome.

Very low carbon steel and very high carbon steels are more sensitive to alloying variations. Case carburized applications should be considered carefully, however, there is considerable evidence that in lower alloy steels, alloying effects per se are not significant. In high alloy steels complications arise which sould be considered separately. That is not the intent of this writing.

Effects of alloy per se on toughness have not been studied extensively. Figures (13 and 14) summarizes the work of Vishnevsky and Steigerwald did on medium carbon martensites. Most alloys, including chromium, causes a shift to higher transition temperatures. Nickel lowers the transition temperature. Diesburg (23) using a simulated gear specimen has recently started building a technical base in this area for carburized steels. Much more needs to be accomplished.

Substitution through hardenability is not a panacea, however, competent technologists should be able to discern trouble spots and accomplish much using the technological principles just described.

Some discussion on the value of this technology is, I believe, appropriate, before I try to make my point regarding technology in general. The, what now appears to be a simple test, the end-quench test - how valuable was this technological development? Look what it does for commerce. Steels are bought and sold based on the response to the test. Standards are developed. Plant inspectors use the test to see if the material they purchased meets the specified "end-quench" hardenability. As I've just demonstrated parts are provided with optimum metallurgical design on the basis of it. This influences both size and cost. This discussion could be longer but I believe it's time to ask "what was the ROI on Jominy's work? A silly question perhaps, but it must be astronomical. And this is my point, generic technology base-building GTBB type effort is so essential, yet it is difficult for it to be supported because of the way industry is currently structured. Few executives would overlook an opportunity to support high technology efforts to develop new products where the promised ROI was lucrative or even reasonable. Many communities vie for high technology research companies on the hope that their developments will create employment opportunities. Support for GTBB type effort in industry though can be found only in isolated spots and frequently even that is being bootlegged. Most GTBB effort is being conducted in a university setting. In recent years universities have been criticized, and partly justifiable, for not being coupled to the needs of industry. Their GTBB work was not on target. Our competitors abroad seem to have a more effective link between industry and academia. Industrialists, not understanding the importance of generic technology base-building research, were not willing to support it in their own laboratories nor at the universities. Certainly there are exceptions and some of them have made fantastic contributions. Well, things are changing but much to slowly. We must see the big picture. What is the role of GTBB? How do we promote entrepreneuring with the technology base to develop superior products? How should GTBB be financed? How can we effect cooperation among our various technological resources, how can we inhance the understanding of executives and legislators as to what industrial technology is about, that it is more than patents, and, the impact that technological activities have in our society? How can we assure a growing supply of technical professionals for industry. How can we assure that industry will use them? An article appeared in our local newspaper not long ago entitled "Don't Wait on the Invisible Hand to Save Us." It was partially politically motivated and hence in its entirety not proper for this presentation, however, it described the Japanese situation, their constancy of purpose (ala Demming), willingness to sacrifice and emphasis on technology as has been done in many other publications. It pondered on the woes of industries such as, automotive, steel, electronics, garments, etc. and asked - why? It implied that our faith was in some unstable, vague force. Well, certainly nothing will be accomplished by an invisible hand. The strong implication then is that we, the technologists who have and are earning our livelihood in the technical arena, are probably the minority who can develop an appreciation of the situation and thus are saddled with the responsibility to be more active in setting policy, educating, and just simply effectively asserting our understanding.

Certainly this has been a very superficial coverage of an important question (What can be done to improve our lot?) The root causes go very deep. If you haven't read about the recent convocation of educators, scientists, legislators, etc., organized by the National Academy of Science, you should. It's reviewed in the May 24 issue of Chemical and Engineering News. It focuses on the problems of our educational systems. High school science problems gained the spotlight. International comparisons were made and we come off second best on a regular basis. Why? Are our technical people held in high enough esteem? Are they paid in proportion to their real contribution? And so on.

I have used the very old but important technology, substitution technology to make a couple of important points. One, of course, being that it can be used to help conserve chromium. Another that it can be used as an ongoing means of operating at optimum costs, but most important that it demonstrates the value of generic technology base building efforts.

In closing, with regard to the situation with chromium here are a couple of excerpts from a document produced by the National Materials Advisory Board entitled Contingency Plans for Chromium Utilization (23). "The CHAT procedure could be used to maintain steel production efficiency in the face of potential chromium shortages by permitting increased flexibility in alloy substitution based on available elements and by broadening the standard chemical analysis range limits (while maintaining hardenability within the required range) to new range limits established by CHAT analysis."

"To provide a basis for minimum chromium use in the tonnage alloy steels without sacrificing properties, a system such as

International Harvester's CHAT should be advanced on a national basis and incorporated into design handbooks and specifications. This system requires considerable data to be developed on the effect of carbide formers other than chromium -- tungsten, vanadium, titanium, and columbium -- upon properties such as hardenability, resistance to intergranular cracking, and resistance to hydrogen environments."

These insightful statements properly assess the situation in that they not only recognize value but point out that additional technology base-building efforts are required even in this technology, one which we consider mature.

Entrepreneurship is well understood by the business world. It should be an acceptable term for the technological world even applicable to TBB. Not the slick Madison avenue concept of entreprenuership but the activities of substance where interdiscipline and intradiscipline knowledge is coupled to advance the state of the art and subsequently to enhance performance, productivity and cost. Technological entreprenuership should be understood by the technical community and all importantly the business community. An understanding of the way technology is developed, how it is used, and its ultimate impact on society should be second nature to our business leaders. It's so important. Education about it should start at a very early age for most citizens. Not just those events that are newsworthy and are rewarded by Nobel Prizes but everyday bread and butter technology should be given its appropriate position in our lives and the lives of our children.

It would be hard to imagine a more dismal state of affairs for our industry. The statistics related to sale of foreign cars are overwhelming. For a decade the economy has suffered set back after set back. Re nown economists are in disagreement as to the cause. A combination of rising oil prices, slumping productivity, soaring labor costs, declining capitol investments, and stiff, even sometimes unfair, competition from abroad have shook the very foundations of great corporations that were once considered as institutional.

The economic news continues to be pessimistic, sagging profits, unemployment and increased deficit spending by government are difficult to digest even when interest rates appear to be on the way down. Corporate performance is from bad to mediocre in practically every industry. Please don't get the impression that I think GTBB is the cure for our nations ills, but I do think there is enough historical and contemporary evidence to allow the conclusion that it is a factor. We need to develop a more comprehensive technology base in every technological arena and we need to train engineers to entreprenuer with it for the betterment of our economy and society. I've heard it said that the U.S. is fated to become a country of nothing but rock groups, video games, junk food restaurants, marginal movies and immature TV programming. We need to reasses our values and effectively promote activities of substance.

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Part II	Metal Progress	February 1973
Part III	Metal Progress	April 1973
Part IV	Metal Progress	June 1973
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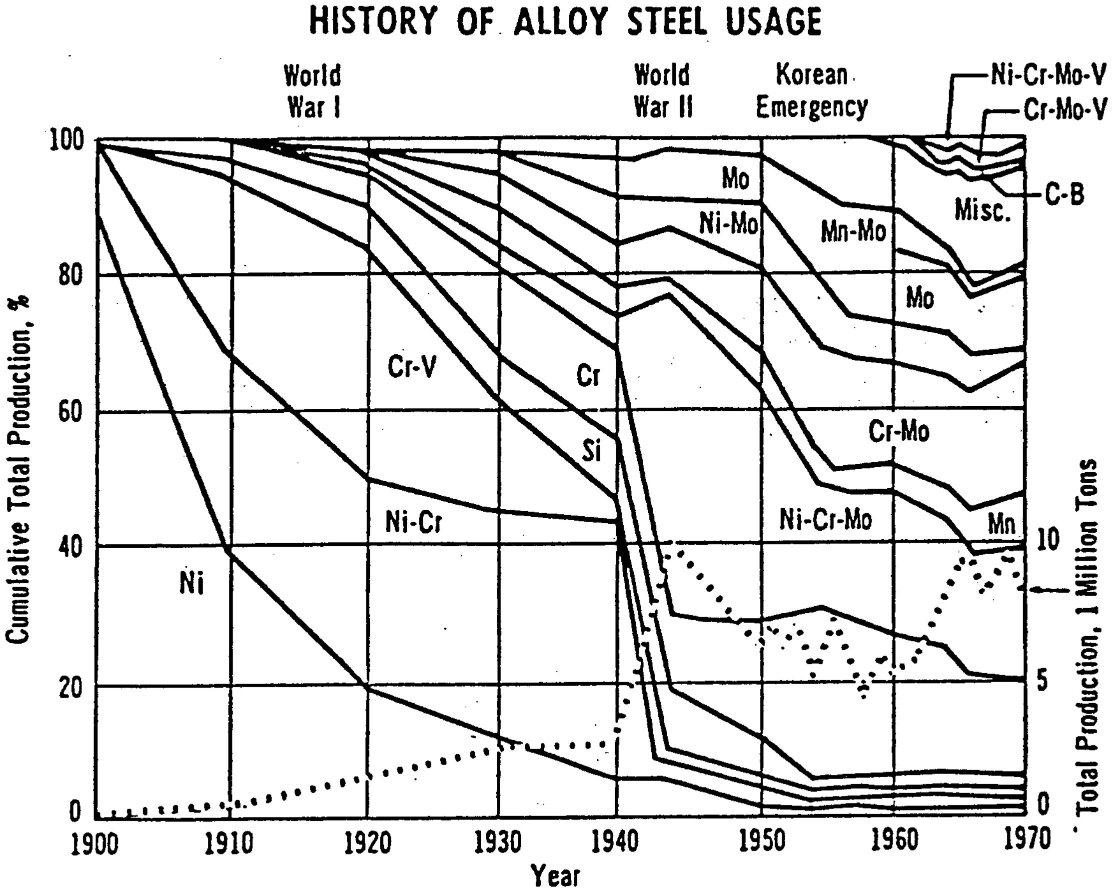
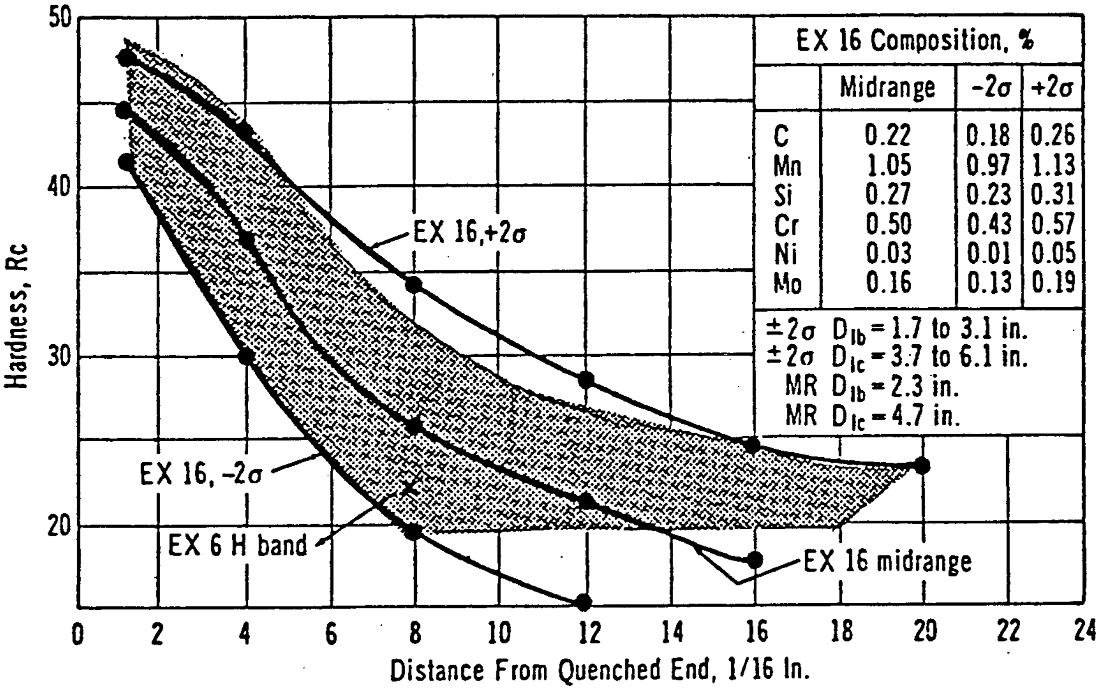


Figure 1 - Through the years since 1900, the pattern of alloy steel usuage has changed greatly. The dotted line indicates alloy steel production (24).



EX 16 Composition, %

	Midrange	-2σ	+2σ
C	0.22	0.18	0.26
Mn	1.05	0.97	1.13
Si	0.27	0.23	0.31
Cr	0.50	0.43	0.57
Ni	0.03	0.01	0.05
Mo	0.16	0.13	0.19

±2σ D_{Ib} = 1.7 to 3.1 in.
±2σ D_{Ic} = 3.7 to 6.1 in.
MR D_{Ib} = 2.3 in.
MR D_{Ic} = 4.7 in.

Figure 2 - Calculated +/- 2 o chemistry band vs. EX 6 band.

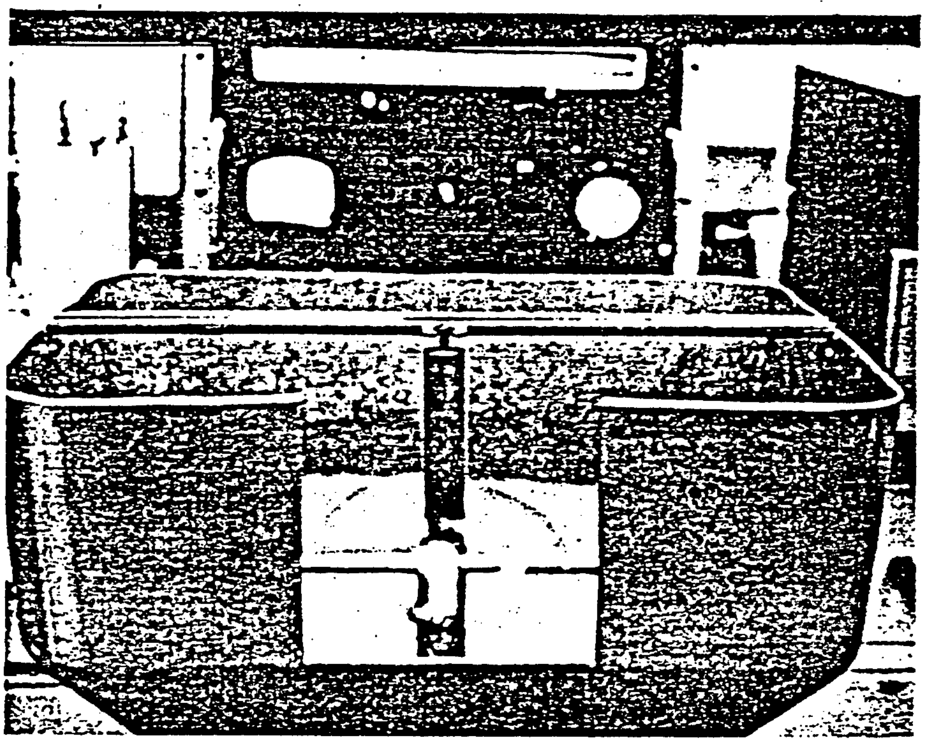


Figure 3 - End quench test in progress.

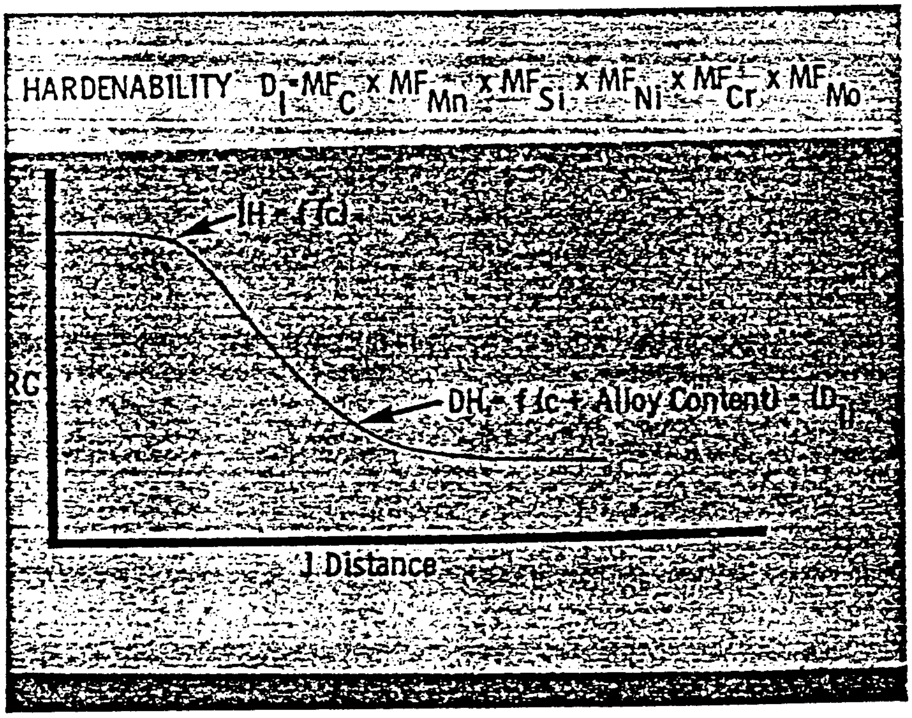


Figure 4 - Hardness vs. Jominy Distance Curve. Initial Hardness (IH) is shown to be a function of carbon and Distance Hardness (DH) a function of carbon plus alloy. Role of multiplying factors (MF on D_I is also shown.

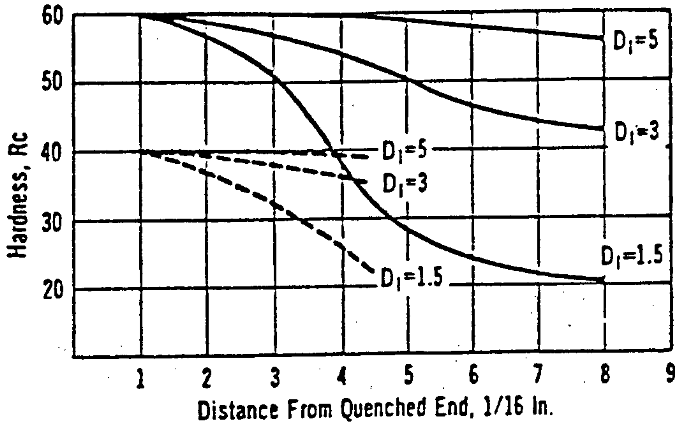


FIG. 5 — Determined by end-quench tests, these curves show hardenabilities of six different steels, three with 0.12% C (dotted lines) and three with 0.48% C. Increasing D_I indicates greater quantities of alloying elements other than carbon.

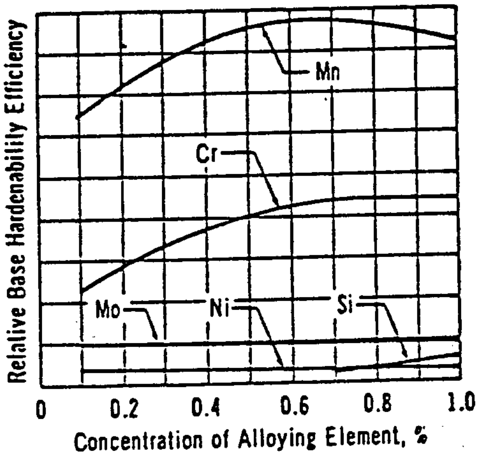


FIG. 6 — Given equal amounts of alloy, manganese has the greatest relative base hardenability followed by chromium, molybdenum, silicon, and nickel.

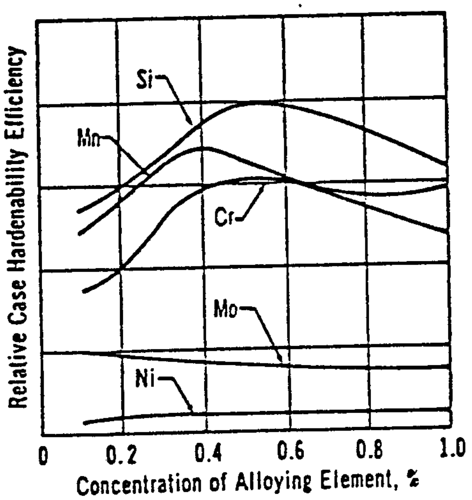


FIG. 7 — In carburized cases, the relative case hardenability efficiency is greatest for silicon, followed by manganese, chromium, molybdenum, and nickel. Compare with Fig. 6.

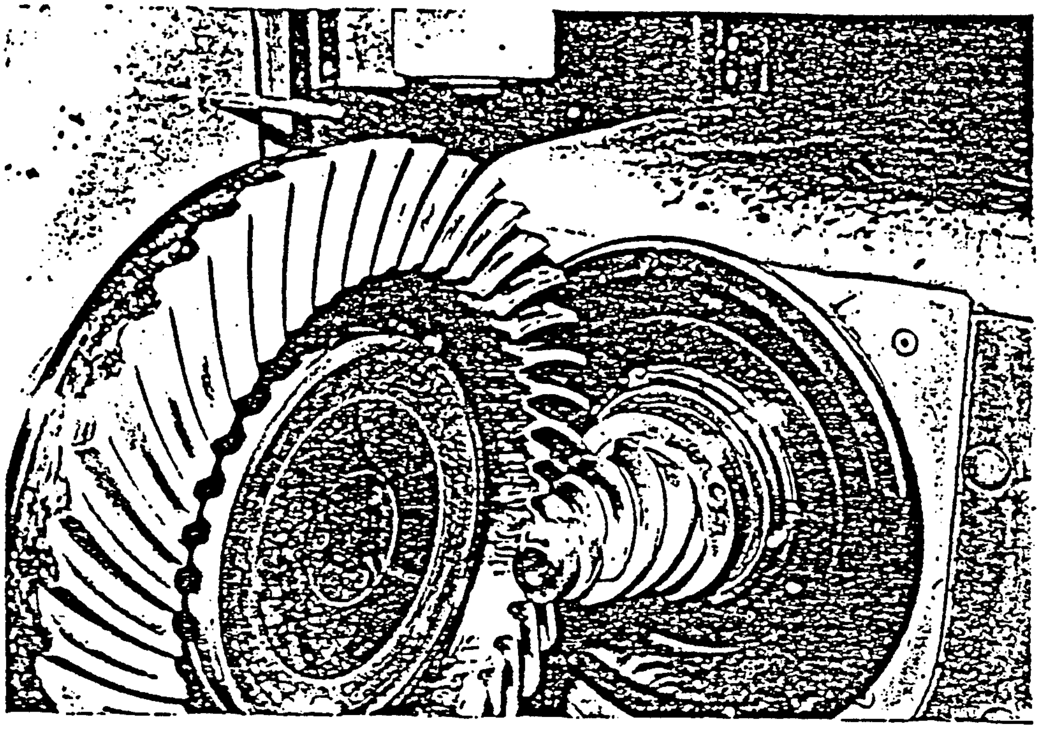


Figure 8 - Hypoid pinion selected for CHAT analysis. Figure shows the contract pattern developed between the pinion and ring gear under light loading.

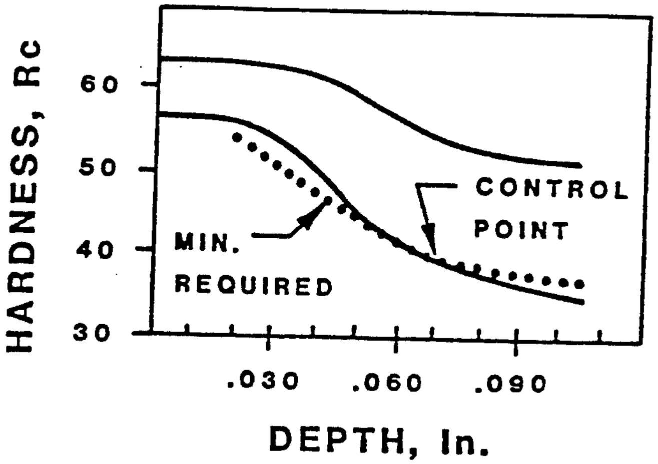
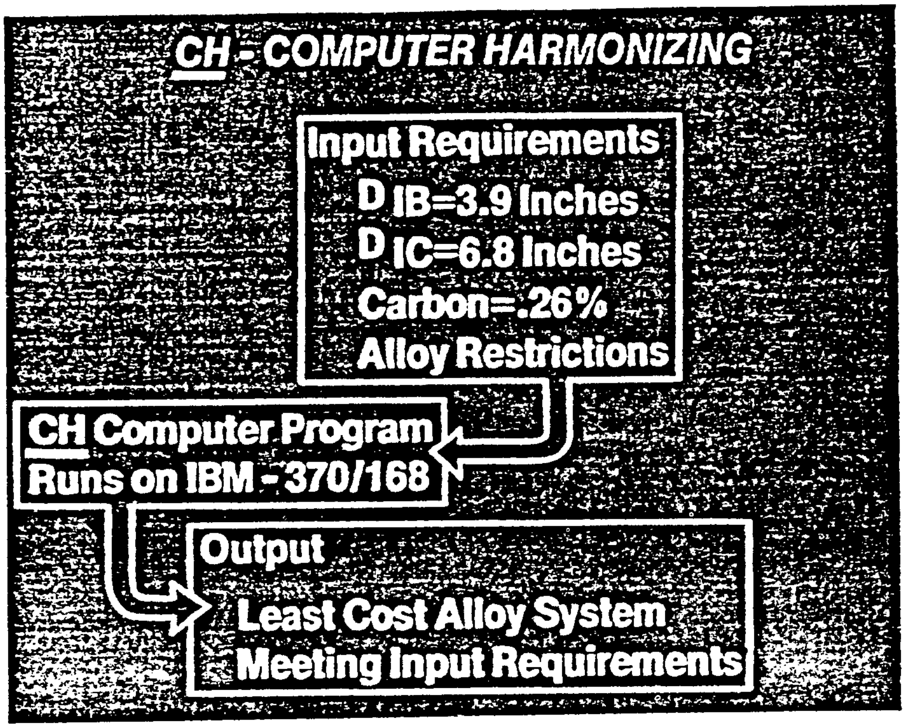


Figure 9 - Comparison of the minimum and maximum calculated hardness gradients with design requirements.



CH - COMPUTER HARMONIZING

Input Requirements

D_{IB}=3.9 Inches

D_{IC}=6.8 Inches

Carbon=.26%

Alloy Restrictions

CH Computer Program

Runs on IBM - 370/168

Output

Least Cost Alloy System

Meeting Input Requirements

Figure 10 - Flow diagram for CH portion of CHAT System.

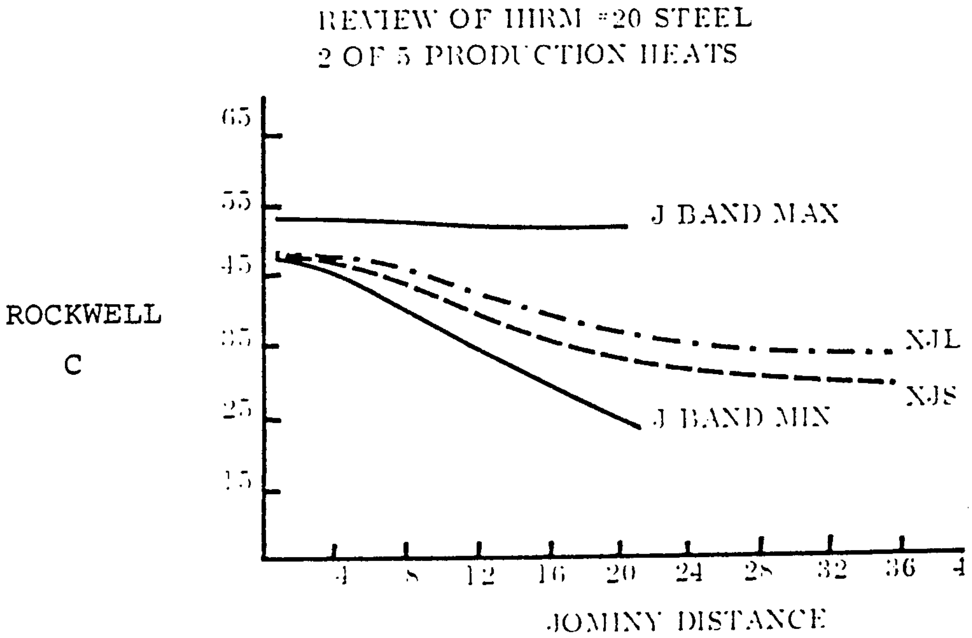


Figure 11 - Calculated H band and actual experimental heat results.

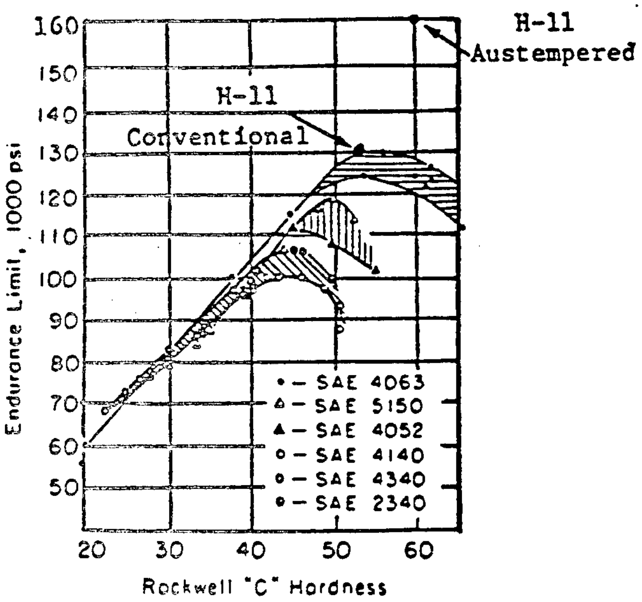


Figure 12 - Relation of hardness and fatigue strength for several steels.

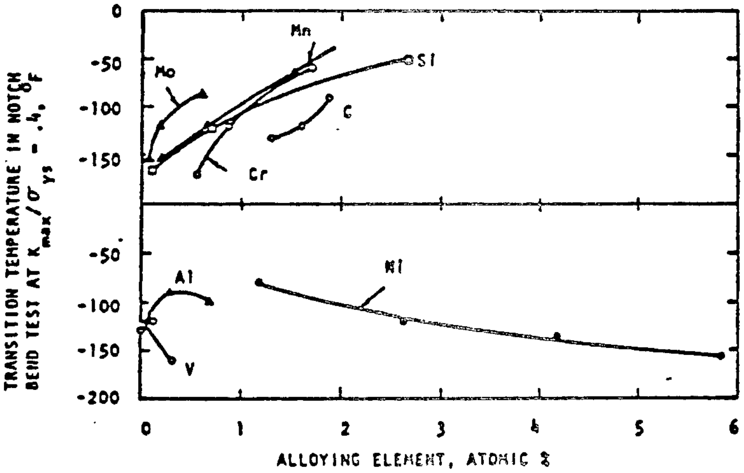


Figure 13 - Effect of chromium on notch-bend fracture toughness.

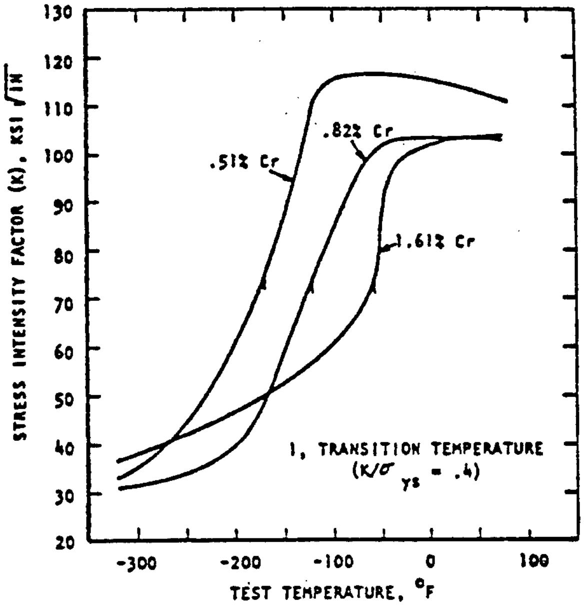


Figure 14 - Effect of alloying elements on the notch-bend fracture-mode transition temperature.

TRENDS AND NEEDS FOR FUTURE STEELS IN BUILDINGS AND BRIDGES
AMERICAN INSTITUTE OF STEEL CONSTRUCTION

by Lewis Brunner

Today I report to you not as an expert in metallurgy or steel making, and certainly not as a scientist or scientific researcher, but as a long-time observer of the commercial scene and the competitive factors at work in the construction marketplace. As an observer of this industry and the changes that have taken place--as well as the changes that have not taken place--during the past thirty years, I hope to be of assistance in helping this conference develop answers to the question of future needs for critical minerals. As I understand it, my personal assignment is to report to you on the subject of steel for buildings and bridges, and during the next few minutes I'll confine my remarks to those major areas of the construction industry, more specifically to the structural materials that become an integral part of the supporting frame, and let others deal with the machinery and equipment used to make, fabricate and erect the finished members, so when you get right down to it, we are talking about a rather narrow band of steel grades, despite the fact that the size and shape of the products vary widely and the work performed on the base material can be simple or complex and the total tonnage rather substantial.

At the American Institute of Steel Construction, we have for years kept records about the size and nature of the fabricated structural steel market.

Over the past decade it has varied from 3.5 million tons per year to almost 6 million tons, depending upon the economic conditions of the country and the nature of the construction market. However, for the most part we generally agree that the normal market is just under 5 million tons per year. Less than one-fifth is used for the support structure for bridges, almost all of that being carbon and low alloy plates, while the four-fifths is used for a wide variety of non-residential building frames. The building market is satisfied primarily with structural shapes, nearly all of which are wide flange plus some plates. For statistical purposes we subdivide this area into 11 building types, such as industrial buildings, utilities, commerical, office, parking, assembly, residential, medical, public, bridges and transportation. To give you some idea of magnitude: in 1981 the building market used 1.4 million tons for the frames of industrial building, while offices and commercial buildings consumed 2.25 million tons. Again, most were wide-flanged shapes in the full range from 8 inches to 36 inches deep. Most of these two segments of the construction business--bridges and buildings--are satisfied by three grades of construction steels--the common carbon grade, ASTM A36, which is considered acceptable for riveted, bolted or welded construction, ASTM A572 and ASTM A588, both considered to be High Strength Low Alloy or HSLA steels. We estimate that more than 60 percent of the material used is the garden variety A36 carbon shapes and plates, a pattern that has held steady for the past few years but a marked reduction from a few decades ago when carbon grades accounted for practically the total requirement.

Now what will the future bring and what are the factors that may influence the mix or create a need for new and different steel grades, and what is the likelihood that they will be used in great quantities?

I think the best way to answer that question is to pull out some recent history and look closely at what has gone before and why.

Through the first half of this century the construction industry was satisfied exclusively by carbon steel grades A7 and A9, manufactured by the open hearth process, which performed satisfactorily for riveted and bolted construction. These two specifications combined in 1939 into the new A7. That specification permitted a wide range of chemical composition with limits only on phosphorous and sulfur. With the advent of new and improved welding technology, the need for a better structural grade became apparent and out of that need came the present carbon grade A36. Not only did the new specification place limits on carbon content, there were requirements for manganese and silicon for heavy sections and the yield strength was increased from 33,000 psi to 36,000. It is interesting to note that this new higher strength product, introduced in the late 1950's, carried a premium of $1 per ton, which was not expected to deter the complete switch to the new and better material. However, it was not until that premium was dropped that A7 disappeared from the construction market. This is an indication of the price sensitivity of construction materials.

The development and acceptance of High Strength Low Alloy steel for structural applications is a more recent story and one that developed rapidly in the 1960's and 70's as welding became a more economical and popular way of joining members, coupled with a strong attempt by the producing mills to reduce the overall weight of structures as a way of opposing the inroads of competitive materials.

HSLA steels are a group of steels intended for general structural or miscellaneous applications and that have specified minimum yield points above about 40,000 pounds per square inch. These steels typically contain small amounts of alloying elements to achieve their strength in the hot-rolled or normalized conditions. Those listed by the American Society for Testing and Materials (ASTM) and Society of Automotive Engineers (SAE) specifications for HSLA steels have minimum yield points ranging from 42,000 to 80,000 pounds per square inch within certain thickness limitations. These steels are also available as sheet, strip and bars, as well as shapes, and were generally introduced as proprietary grades. A complete listing of HSLA steels available in 1969 from producers in the United States and Canada would include almost 250 brands or variations thereof. The material is made in thicknesses up to 8 inches.

Although a steel containing chromium was specified for certain members of the Eads Bridge, erected at St. Louis between 1867 and 1874, the most widely used steel for construction used before 1900 was mild carbon steel having a tensile strength of about 60,000 pounds per square inch.

In 1901, the design engineers of the Queensboro Bridge that was to span the East River in New York City requested a stronger steel so that the number and size of supporting members could be reduced. Carnegie

Steel Company, now part of the United States Steel Corporation, supplied 3.25 percent nickel steel for this application. This steel also was used in the stiffening trusses of the Manhattan Bridge in 1906. Although it was satisfactory for riveted structures from the standpoint of strength, this material was relatively expensive and economical only for structures in which reduction in weight or size of members was a necessity. Another steel, offering higher strength than mild carbon steel and containing about 1.00 percent silicon and 0.25 percent carbon, was used for the hull plates in the S. S. Mauretania in 1907. Although this latter steel was less expensive than the nickel steel mentioned above, its use was ultimately discontinued because of many difficulties encountered in its application.

Another steel, stronger than mild carbon steel, that contained only a nominal amount of silicon and depended for its strength on its high carbon content (usually over 0.3 percent), was first used in 1915 in a bridge spanning the Ohio River at Metropolis, Illinois. This grade, under the designation of "structural silicon steel", was one of the most widely used materials for riveted structures.

In 1927, the American Bridge Company used a 1.60 percent manganese steel for the lower chord members of the Kill van Kull Bridge connecting Staten Island with the mainland at Bayonne, New Jersey.

Similiar developments had taken place in other countries. Engineers in Great Britain, attempting through weight reduction to effect economies in ocean freights and handling charges, had used carbon steels containing generous amounts of silicon and manganese.

The earliest present-day HSLA steels was "COR-TEN" brand, which was introduced by the United States Steel in 1933. This steel has been improved continuously to meet the increasingly severe demands of fabricators --an experience common with most new steels. Since COR-TEN steel was introduced, many other steel-producing companies have developed their own grades, so that--as mentioned previously--there are at present a considerable number of HSLA steels on the market, all of which now fall under the designation ASTM A588. It was required by the steelmakers, fabricators and designers that to be of interest as construction materials, HSLA steels must have characteristics and properties that result in economies to the user when the steels are applied properly. They should be considerably stronger, and in many instances tougher, than structural carbon steel. Also, they must have sufficient ductility, formability and weldability to be fabricated successfully by customary shop methods. In addition, improved resistance to corrosion could be an attractive and valuable characteristic in both building and bridge construction.

The late 50's and early 60's seemed ripe for new design innovations and HSLA steels seemed to fit the bill. Weight reduction as a way of reducing construction cost and increase sophistication in design resulted in more efficient use of materials with members stress to their maximum allowables and improved welding made it possible to manufacture hybrid elements such as plate girders, using a combination of steels more efficiently resulting in increasing the strength to weight utilization.

Functional architecture was in vogue. The desire for true expression of the structural elements both inside and on the facade of buildings was popularized by the creations of Mies van der Rohe whose "less is more" philosophy adopted by others was satisfied by unpainted weathered steels. Althought this fashion has faded in buildings, the maintenance-free aspects of the steel for bridges makes it an onging attractive market for the material. It was also the period when the major producing mills recognized the technological advancement of structural concrete and the dilution of markets that were heretofore exclusively steel. The two major mills--Bethlehem and U.S. Steel--both responded with a broad range of steels marketed under the familiar proprietary names of V steels, Cor-Ten, MannTen, TriTen, Mariar, ExTens TI, etc. This group of high strength low alloys were known as the Family of Steels, with yield strength from 42,000 psi to 100,000. Extensive promotional campaigns were waged by both mills and large amounts of technical data were distributed to potential users.

At the same time, the process of establishing new ASTM standards was underway and by the mid and late sixties these new construction steels were covered by the ASTM Standards mentioned.

Although moved and pushed by the mills because of enhanced corrosion resistance, the modified A242 enjoyed a brief increase in popularity for buildings. This interest generated a desire for thicker weathering materials with higher yeild strength and, as a result, the A588 specification was born. This gave the industry a high strength weather resistant material in the full range of structural shapes, sizes and heavy plates. In order to acheive these characteristics, it was necessary to add quantities of vanadium and chromium. In studying the specification it is noted that there are ten grades, A through K, each one of them with a slightly different chemical composition, each produced by a different mill with different melting and finishing practices. All grades contain amounts of manganese, silicon and nickel. Most contain chromium and/or vanadium. At the same time, users were demanding steels with higher strengths where corrosion was not a consideration. Having gotten used to the advantages of 50,000 yield material they looked to ways of designing frames at lower costs. These factors, along with the desire on the part of the mills to reduce frame costs through weight reduction led to the development of the ASTM A572 series of structural steels. The specification includes Grades 42 - 50 - 60 and 65 with yield strenghts ranging from 42,000 psi to 65,000.

Here the higher strength was achieved through the addiion of vanadium or columbium and improved mill practices. Since that time, popularity of the weathering steel concept for buildings has subsided somewhat, and certain questions regarding the performance under extreme atmospheric conditions in bridges has dimmed the popularity of A588. However, the desirability of structural grades with strength greater than A36 continues to grow and is satisfied in large degree by A572 Grade 50. Furthermore, the pricing of that product makes it the least expensive structural material on a strength to weight basis, assuming the full strength of the material can be utilized. If we look at the economics of the various steel grades more closely, we see the current published price of A36 wide flange shapes is $478 per ton, plus certain extras depending upon size section and quantity, which applies to all grades. The price of A572 Grade 50--which is the most popular HSLA structural grade--is $536 per ton and $619 for A588. The selection of one grade over the other therefore has become a function of economics and designers are becoming more sophisticated in determining the cost per unit of strength for individual or groups of members. This, therefore, accounts for the mix of carbon and HSLA steels in most building frames.

This also accounts for the fact that most of the structural shapes produced in this country for building and bridge construction is A36, with about 11 percent A572 Grade 50 and 4 percent is A588.

Now the question is, what does the future hold for higher strength steels or new steels?

As we see it, the answer lies primarily in the competitive marketplace. Generally speaking, the amount of steel used in structures is limited by competitive pressures from other materials, primarily reinforced concrete. There was a time when most medium and high rise buildings and all long span bridges were built with steel. During the past twenty years, concrete's market share has steadily risen and at the present time there are very few conditions where concrete cannot satisfy the structural needs of the designer. We see 80 story buildings and bridges with over 1,000 foot spans being designed and built in concrete at very competitive prices and many times at prices below alternate steel designs. The pressure, therefore, in the building and bridge business, is for lower cost structural material and the addition of expensive alloying elements to increase the yield strengths generally run contrary to the demands of the competitive marketplace. Furthermore, from an engineering point of view, many times deflection, drift and mass are characteristics that may outweigh the need for increased unit strength in a particular design. This would indicate a sizeable market for a lower yield, weldable carbon steel at a lower price to satisfy these engineering problems and at the same time meet the challenge of competitive materials. Recently, AISC surveyed 3875 engineers to determine the attitude of these people regarding the need for a newer high strength steel - 738, or 19 percent, responses were received. 50 percent of those who responded felt that materials currently available were adequate to take care of the present and future demands.

From the recent experience cited here regarding the acceptance of HSLA steels and the apparent attitude of designers, it would make it appear that the materials presently available are satisfactory to carry out industry into the future. Since progress is difficult when you stand still, this attitude may seem to indicate a sudden lack of foresight on the part of our industry for the first time, because in the past we have always worked toward stronger, better, lighter, more workable materials. In addition, it is hard to believe that we have reached a point of perfection in materials. This is certainly not the case, but we may be close to the limit on ratio of yield strength to section size. There is no doubt that there is need for improvement in quality, toughness, and workability of structural steel grades. Material problems on major bridges and the introduction of such programs as AASHTO fracture control plan highlight the need for improved quality. Whether critical materials or changes in mill practices are the answer, I don't know--but the solution of that problem outweighs the need for higher yield strengths.

Our short and medium forecast is for improvement in the growth of the construction industry and we are optimistic about our ability to improve steel's share of the market. As I mentioned before, we peg the normal structural steel market at just under 5 million tons. In 1981, it was 5.2 million tons, somewhat less in 1982 and will probably fall to 4.6 million tons in 1984, because heavy construction is usually one of the last industries out of a recession.

With an upturn from that point, we expect the market to reach 5.7 million tons by 1987 with growth continuing. As you can see, these are modest improvements over the current levels and the figures are based on our industry maintaining its present share of the construction market.

Naturally, we are hopeful that we will be able to improve and thereby move the demand above the 6 million ton per year mark. This expansion, regardless of size, will probably have a product mix very similar to today's. Thus very little change in the future demand for critical materials is foreseen. We hope that this information will be helpful to this seminar in determining what we in the steel fabricating business may need from the critical materials supply.

The Materials Use and Research Outlook in the Railroad Industry

Dr. W. J. Harris, Jr.*

October 4, 1982

The railroad industry must provide four main kinds of service that shippers need. There are heavy haul customers, those concerned with moving large masses of grain or coal or ore. There are speciality shippers, those shipping containers and piggyback cargoes. The chemical industry is concerned with shipping quantities of high valued commodities, some of which are particularly hazardous materials. The automobile industry required rapid movement of parts and secure movement of cars. In order to respond to those needs, of course, we would prefer to have more business than we have today as does almost every other manufacturing or service business. Customarily, the railroad industry buys on the order of 1 million tons of rail per year for replacement rail or for line adjustments and corrections. But rail lasts for a very long time. We have some rail still in service in branch lines or in yards manufactured more than 40 years ago, that is operating satisfactorily and effectively. But the mainline rail now in service is facing a set of more and more demanding operating requirements. Rail is essentially a eutectoid steel, .70-.85% carbon and 1% manganese. Only in a few instances is it alloyed. When the wear characteristics require its replacement in less than about 4 or 5 years, alloyed or heat treated rail

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is often used. Only under those circumstances is the industry in position to justify the additional cost of heat treatment or alloying.

Some relatively fundamental work supported by AAR at Carnegie-Mellon some years ago made it clear that alloying and heat treatment lead to very fine-grained pearlite [1]. Heat treatment can involve only the head or quenching of the entire rail.

But there are a number of other approaches to extend rail life. A special set of tests at the Transportation Test Center at Pueblo, Colorado, a government owned facility that the AAR took over for management purposes last Friday, suggests that lubrication is effective in reducing wear. However, it is difficult to get a lubricant on the rail and therefore, lubrication is not an ideal solution at the present time. In South Africa, rail wear has been reduced by the introduction of what is called a steerable truck, that is a truck whose axles do not remain parallel through a curve, so that there is less flanging pressure of the wheel on the rail [2]. In our tests in this country with our operations, we have observed somewhat less reduction in wear. Most railroads are not able to justify that technical solution. Should a cheaper technical solution to rail wear be found, the railroads will surely be satisfied to use plain carbon steel for rail.

The second technical difficulty that we are confronting with rail has to do with fatigue. In order to match the barge lines and to try to stay even with the trucks, both of them exceedingly effective competitive modes of transportation, we strove for economies of scale by going from 50 to 70 ton cars, and then to cars that carried 100 tons of lading. Those cars weigh of the order of 63,000 pounds light, and therefore, loaded, 263,000 pounds. The wheel size was adjusted in an attempt to keep the effective pressure on the rail about the same. However, on those parts of the system now carrying large numbers of unit trains of 100-ton cars, we are finding that the fatigue life, instead of being on the order of 800-900 million gross tons, is now down to 500-600 million gross tons. To put that number in perspective, a reasonably heavy duty railroad line operates about 40 million gross tons per year, but some of the western coal lines are carrying 100 million gross tons per year. On a 100 million gross ton line, rail will last for 8 to 10 years or on 500 million gross tons, from 5 to 6 years. This is a very large difference considering the cost of rail and the cost of re-installation of the rail. That fatigue problem we have determined in studies with AISI is not related to the alloy content or to the microstructure, but rather to manufacturing technology and to a large extent, to micro porosity and non-metallic inclusions [3].

Under those circumstances, we have tried to change our rail specifications. The steel industry, with its limited capital resources, is making a valiant effort to put in new production capabilities to satisfy our needs. The U.S. railroads, very reluctantly went overseas, especially to Japan, but also to Italy and the Continent, where newer mills with better melt shops and with continuous casting practices were found to deliver a product more free to micro porosity and non-metallic inclusions and, therefore, with longer fatigue life.

Freight cars are an extremely variable source of demand for materials. The railroads of the United States own about 1,600,000 cars. Because of the shortage of business, about 250,000 of those cars are currently not in use. Because of an ICC decision a few years ago, everyone was encouraged to invest in freight cars. From an average production of about 60-70,000 per year, with a fairly stable supply industry, the demand burgeoned to 125,000 cars per year. That demand led the railroad supply industry to expand all of its capability. Now we are in a depression as far as freight traffic is concerned. Very few cars are being ordered. As a result, we have total disaster in the supply industry today. The demand of cars has dropped to 7,000 to 10,000 cars per year.

The car technical problem is not a terribly serious one. As a result of fatigue problems, we have introduced a new set of fatigue guidelines so as to require better design practices for the essentially plain carbon steels used in cars. There is some advantage toward reducing the weight of cars. An aluminium car carrying the same capacity as the current steel car weighs roughly 20,000 pounds less. Aluminium is more difficult to maintain and therefore it has not been a favored material. We require a much more elaborate braking system with a light car, because when you combine a light and a loaded car in a train, and apply the same air reduction in the braking system, you will have differing braking response. But these issues do not lead to a demand for alloy steels in cars. The principle competition in the future may be aluminium or on the other hand, fiberglass. We do have one or two examples of glass fiber wound covered hopper cars in experimental service to evaluate the unique characteristics of fiberglass and its reduced weight.

Tank cars carrying hazardous chemicals and other chemicals are an important part of the fleet, but we are not building many tank cars today because the market is essentially stable. There have been a fascinating series of technical issues in the redesign of tank cars for their safety behavior. We have had high temperature failures, and in a few cases over the past 17 years, brittle fracture. The number of brittle fracture incidents are low enough that I do not think we will have to change tank car materials; indeed, I do not know how to make a car at acceptable costs that achieve the toughness necessary to resist failure if there is a sufficient impact at -40°F operation.

The violent rupture of tank cars was not a brittle fracture problem, but rather one of overheating of the material. As the liquid product vented, an unvented area was presented to the engulfing flame. The steel overheated. In about 8 minutes, the steel got to 1200 degrees. At that point, under the internal pressure, it blew a bubble and a tensile crack developed. When the crack got to be 7 feet long, fracture mechanics took over and we had a rapidly running crack.

That problem we have dealt with by reducing the frequency of tank head punctures and by putting thermal insulation on the car. That is not a problem we can solve by changing the composition of the materials.

The railroad industry is the largest commercial user of heavy castings in the United States. These castings have been improved in quality by improvements in casting technology, but we are competing all over the world with casting technologies and we have the problem of trying to keep the cost on a cents per pound basis instead of a dollar or tens of dollars per pound basis as some other industries can. We have not found it necessary to go to alloyed materials. We have perhaps 0.20 to 0.30% chrome, a little Mo and a little vanadium, but those can be introduced by the proper selection of scrap. Accordingly, we are not expecting to have any particular requirements for alloy materials in castings for the future [4].

As a result of a number of research programs in the past, we can control trains more effectively. The stress on the castings are lower. We have fewer failures than in the past.

As far as wheels are concerned, we have studied the deficiencies of designs that gave us premature failures. We have made very real progress in the design of the wheel to allow the wheel to have the proper interaction between the thermal loads introduced by braking and the mechanical loads introduced by the weight of the car on the wheel. Our wheel failures are down very significantly, but because of some current rules and regulations we are having to take a great many wheels out of service that are perfectly satisfactory. Here, the barrier is not one of metallurgical technology, but one of non-destructive technology. We do not have an adequate means of inspecting the 13 million wheels in service in an effective way to find only those 3/4 inch cracks that are really critical. And we do not have a good means of inspecting in service, especially on a moving train, the state of stress on the wheel, which would be the determining factor. Wheels are manufactured with residual compressive stresses in their rims. If the rim goes into tension, you have the potential of early failure, but the inspection technology is not in hand.

The opportunities, then, for the railroad industry to benefit extensively from improvements in metallurgy and from the use of highly alloyed materials are not very great. We are hoping that the railroad industry, however, will be able to stay a vigorous user of the products of the steel industry and we, therefore, think that railroads will be an important contributor to the demand for steel. We would like to have the steel industry to be a healthier industry so we can ship their products more effectively.

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[4] D. H. Stone and W. S. Pellini, "Fracture Properties of AAR Cast Steels," R&D and Railroading: 1977, Pueblo, Federal Railroad Administration, (March, 1978), pp. 191-202.

TRENDS AND NEEDS FOR FUTURE AUTOMOTIVE STEELS

I have been asked to review the current trends in automotive steel usage and to describe the kinds of alloys we will be asking the steel producers to supply in the coming decade. Specifically, what properties will we need in steels for our future vehicles, and how much will we need of each grade or type of steel?

The truest answer I can give to these questions is "I don't know," but I can make some educated guesses based on recent history.

Let us begin by reviewing the total material makeup of automobiles over the past 25 years (Fig. 1). The data represents an average of many car models and should provide a fairly representative picture of the overall materials distribution, although individual models may vary appreciably from the average. It is obvious that the average ferrous content of the car is declining, from about 85% of the total car weight in 1960 to about 70% in 1985. Part of the decline represents substitution of cast aluminum for cast iron in engine components–primarily intake manifolds and cylinder heads. I expect this trend to continue and to extend to engine blocks as well. Most of the remaining loss is in steel, largely replacement of steel stampings by polymers. We probably haven't seen the end of this trend either, although I don't expect the steel fraction to go below 50% in the coming decade. As a point of reference, the 1979 Chevrolet Corvette, which has a fiberglass reinforced polymer body, is 51% steel by weight.

Some ferrous content may shift from one form to another. For example, I anticipate sintered iron powder to replace some forged steel components. Over the years, many steel forgings have also been replaced by cast ductile iron. These include crankshafts, steering knuckles and, more recently, a rear axle ring and pinion gear. Whether or not this trend will continue depends on the relative economics and structural efficiencies of the two approaches, plus possible competition by other materials like forged aluminum. Stainless steel stampings are invading some traditional cast iron applications such as exhaust manifolds.

The steel exhaust manifold would add to the stainless steel share, currently about 1.5% of the total. Current stainless usage is split about equally between decorative items like trim and wheel covers and the catalytic converter structure.

Since a part of the workshop is also concerned with chromium, I'll digress for a moment to consider that topic as it relates to the automotive industry, since the stainless steel applications just cited account for most of our chromium demand.

Figure 2 shows the chromium usage, in terms of pounds of contained chromium metal, for the several automotive material categories. The basis here is a 1975 full size vehicle; source of the data is the NMAB 1978 report on chromium utilization (NMAB-335). Since vehicle weight has been reduced considerably since then, the ordinate is no longer accurate. However, the general breakdown proportions still apply.

As I indicated, by far the major automotive chromium demand is in stainless steels, and the bulk of this is in the converter and the wheel covers. The latter are primarily decorative and are not critical to the function of the vehicle. I personally expect this application to decline in favor of the decorative stamped or cast "Rally" wheel which does not employ a cover. In the case of the converter steel, the 11% minimum chromium content is needed to provide the required oxidation resistance. We have made good progress, however, in replacing part of the chromium with silicon or aluminum in experimental steels without sacrificing properties and are hopeful that these lower chromium alloys will enable us to significantly reduce the automotive chromium demand.

Having considered the overall materials picture, let's now concentrate on the steel portion.

Figure 3 shows an estimate of the division, over the past 6 years, among bar, tube and forgings, and sheet and strip, with the latter subdivided further into carbon, high strength and coated products.

In the bar and forging category, I anticipate a growing interst in substitution of low carbon boron steels for medium carbon alloy grades. The motivation is primarily economic, in terms of lower alloy cost and in improved cold heading properties of the low carbon steel. Beyond this, however, is the potential for reducing our dependence on potentially critical alloying elements like chromium.

Turning our attention to the sheet and strip category, the most obvious trend is toward a higher proportion of precoated product, both galvanized and the organic zinc-rich coatings. This reflects industry commitment to improved corrosion durability of the automobile. Protective coatings are particularly important to the application of high strength steel sheet. The corrosion resistance of these alloys is no different than that of carbon steel. Since the high strength steels are used to reduce gage, and thereby weight, they are stressed to a higher level than the carbon steel they replace and are thus more sensitive to the effects of gage reduction by corrosion.

Also evident, but to a much lesser degree, is increased use of high strength steels, commonly referred to as high strength low alloy steels or HSLA. General practice in the U.S. is to group all steels having a minimum yield strength specification in excess of about 40 ksi in this HSLA class. Conventional low carbon sheet generally averages about 30-35 ksi yield, and may reach 40 ksi occasionally. The real difference is that carbon steel specifications are generally limited to gage, width, surface quality and, often, a "must make the part," provision without any specified mechanical properties, whereas high strength grades involve an additional specification, minimum strength. I'll get back to this later.

The motivation for using HSLA is weight reduction. Providing the part is not deflection or stiffness limited, use of a higher strength steel allows a reduction in thickness to carry the same load. Most current HSLA applications in the automobile are in the 45-55 ksi yield strength range, with a lesser but significant application in the 80 ksi and higher levels.

This class of steel has been available for over thirty years, but with use limited to construction, heavy truck and bus frames and the like. The major deterrent to automotive application, particularly of the 60-80 ksi levels, has been formability. Complex automotive stampings couldn't be made without high scrap due to inadequate ductility. The development of GM 980X by Dr. Rashid of our laboratory, in the early 1970's, promised to mitigate this problem. This material, the first commercial "dual phase" steel, has a 50 ksi initial yield strength and elongation approaching the lower end of the carbon steel range, but work hardens during forming to provide an 80 ksi yield material in the finished part. It is currently used for several GM automotive parts. This development led one steel producer to project, in 1977, a major growth in automotive applications of dual phase steel (Fig. 4). This growth has not materialized, for several reasons.

One is basically psychological. If a part is changed from carbon steel sheet to aluminum sheet, the materials are obviously different and the stamping plant accepts the fact that dies and forming sequences may have to be modified to make the part. When the change is from carbon steel to HSLA, changes are not considered necessary, and the resulting high scrap is taken as proof that HSLA is a "bad steel." The fact is that HSLA does behave differently in forming than carbon steel, but stamping plants can learn to handle it successfully, with no higher scrap than is common with carbon steel. We know this, because we have done it on several parts now in full production. However, the bad reports tend to get more visibility than the good reports, inhibiting designers from specifying HSLA.

The other major complaint is that HSLA tends to exhibit wide variations in properties. The implication, that carbon steels do not vary in properties, is not correct. As shown in Figure 5, summarizing yield strength data from 50 carbon steel heats, and 47 heats of an HSLA grade, both show a variation of ± 20% of the average strength. The difference is that stamping operations have evolved over the years to accommodate the spread in carbon steels and, furthermore, the greater ductility of carbon steel reduces the sensitivity of the operation to property variations.

As our production experience grows, I anticipate an acceleration in HSLA applications, particularly in the more formable dual phase grades.

An important prerequisite to this growth is that the variability in properties of high strength steels be reduced, by closer control of casting, rolling and annealing operations in the mill.

This matter of property uniformity is becoming increasingly critical as automotive design moves to maximize the efficiency of the structure.

Whereas mechanical properties of carbon steel are normally not specified, meaning that the design is conservative enough to accept the lowest strength end of the range, parts using HSLA steels depend on a specified minimum strength. Furthermore, the realization is growing that the important property is not the strength of the sheet as it comes into the plant; it's the strength of the steel in the formed part. GM 980X, as mentioned, work hardens from about 50 ksi to 80 ksi as a result of the forming strain, so uniformity of work hardening is also important. Also, since forming becomes more difficult as strength increases, the spread in strength must be closely controlled to avoid excessive forming scrap because of coils being too strong. Thus, the acceptable "window" becomes narrower as steel strength is increased.

As I noted at the beginning, I was asked to respond to two questions: What properties will be needed in future automotive steels,? and, How much of each grade will be used? Regarding properties, I offer the following: The critical need is for more uniform and closely controlled properties of strength and ductility, including response to strain and age hardening. As we achieve improvements in this area, the application of advanced high strength steels will continue to grow.

Summarizing the probable trends in automotive steel grades, in addition to increased application of HSLA grades, I see more extensive application of precoated sheet, replacement of cast iron exhaust manifolds by stainless steel sheet, lower chromium stainless grades for such applications, and increasing substitution of boron grades for conventional medium carbon alloy grades in heat treated parts.

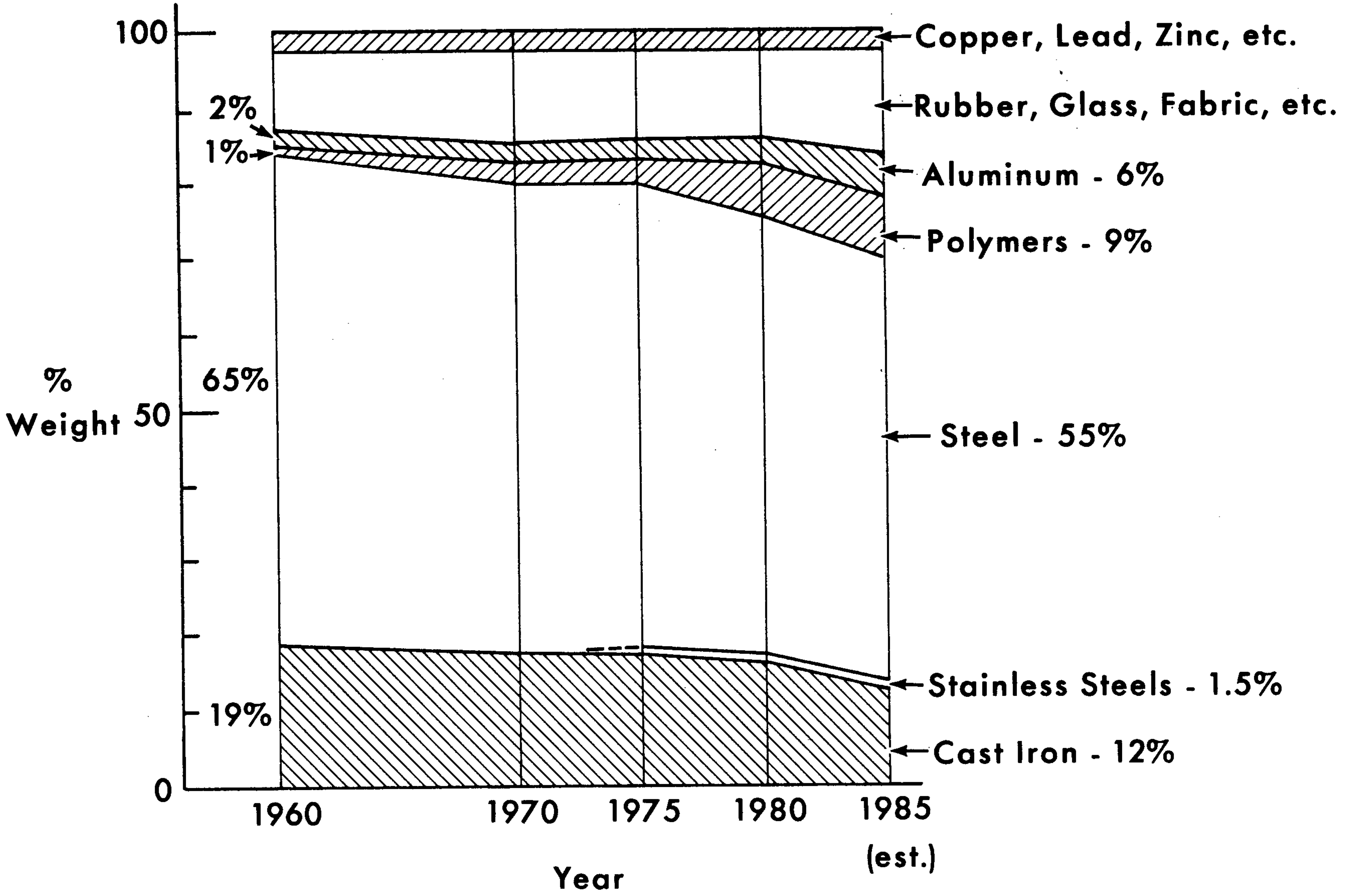


Figure 1. - Materials Make-Up of the Automobile.

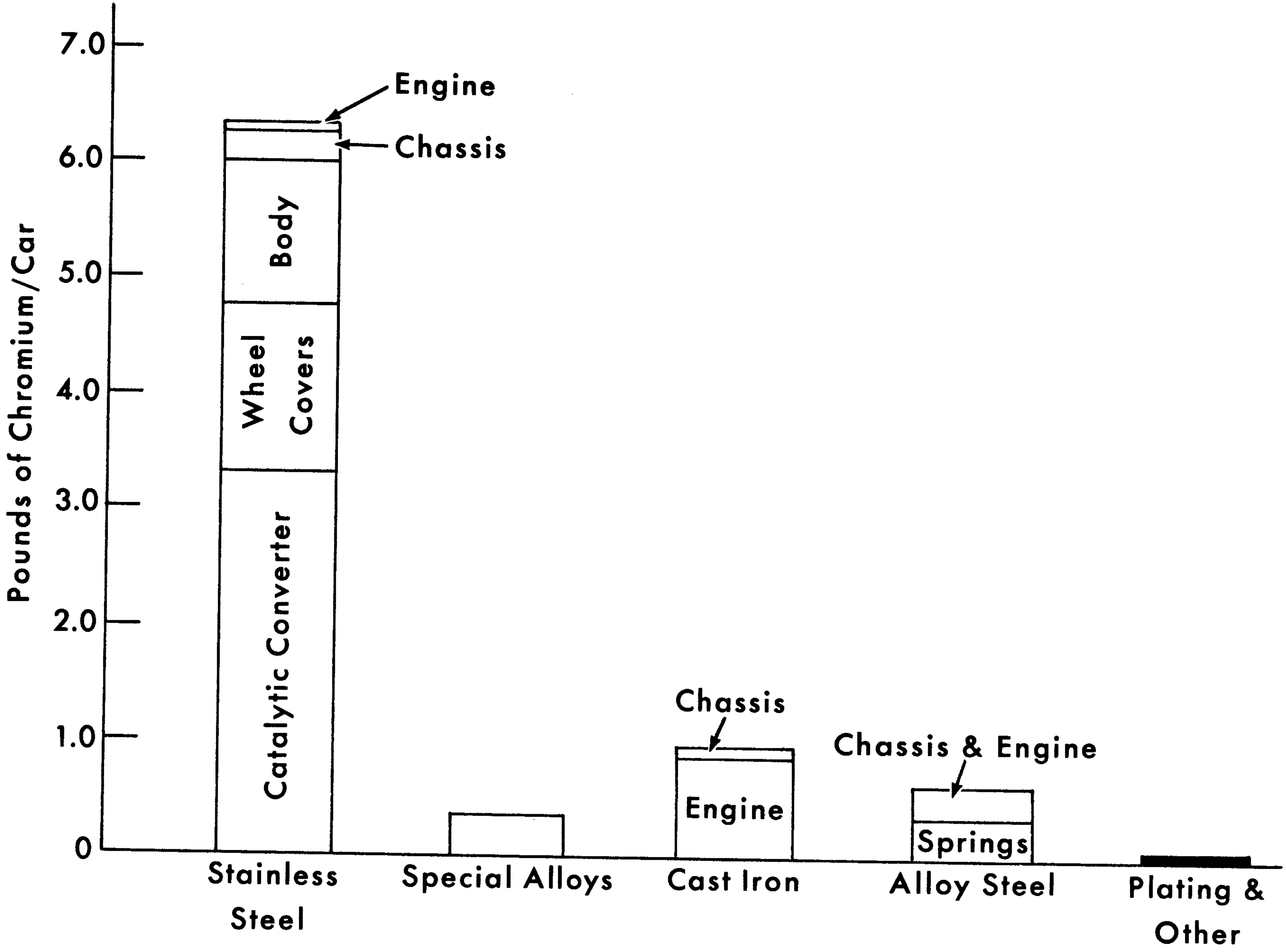


Figure 2. - Chromium Used in 1975 Full Size Car (8.3lbs. total).

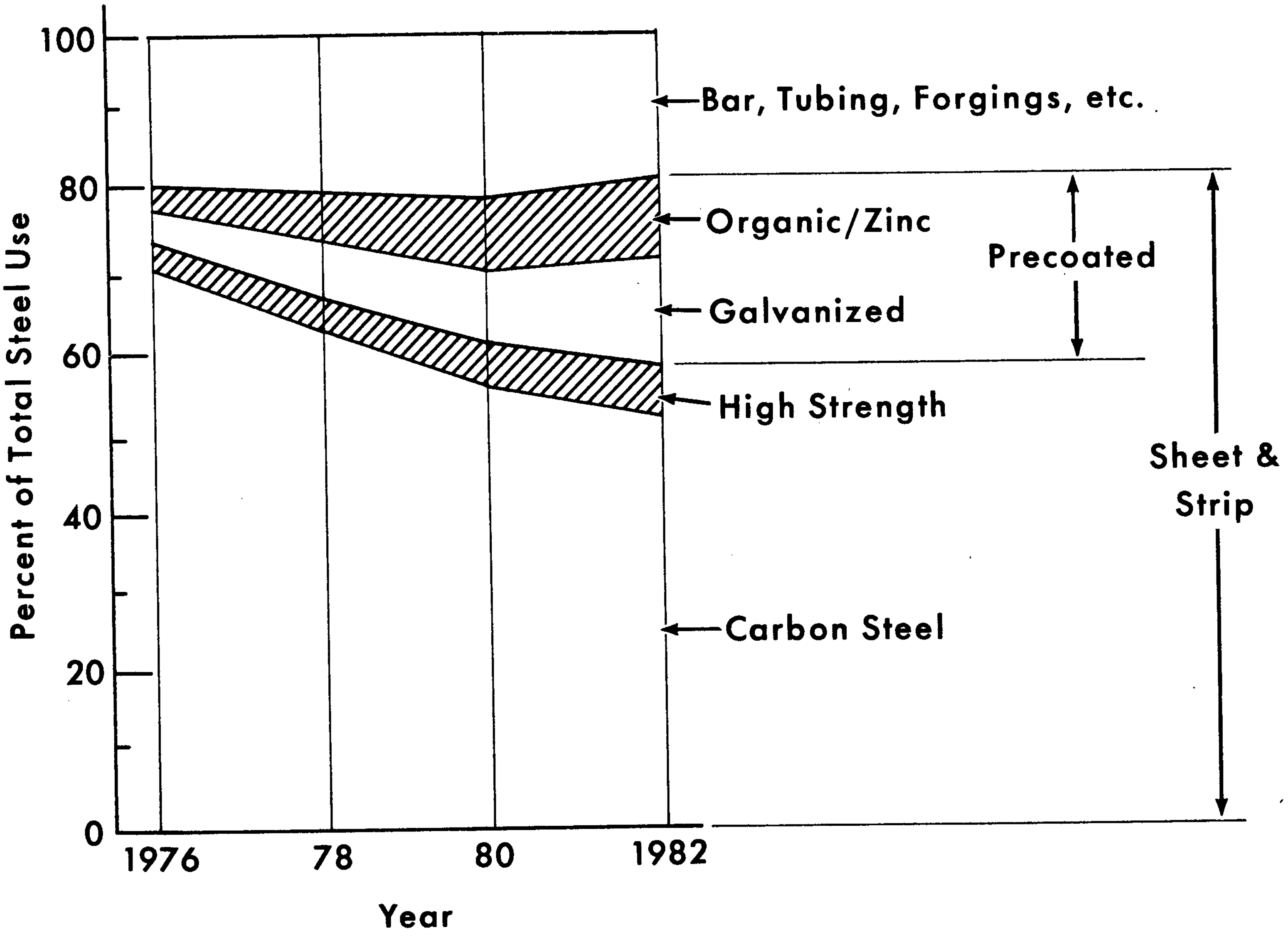


Figure 3. - Steel Product Distribution in Automobile.

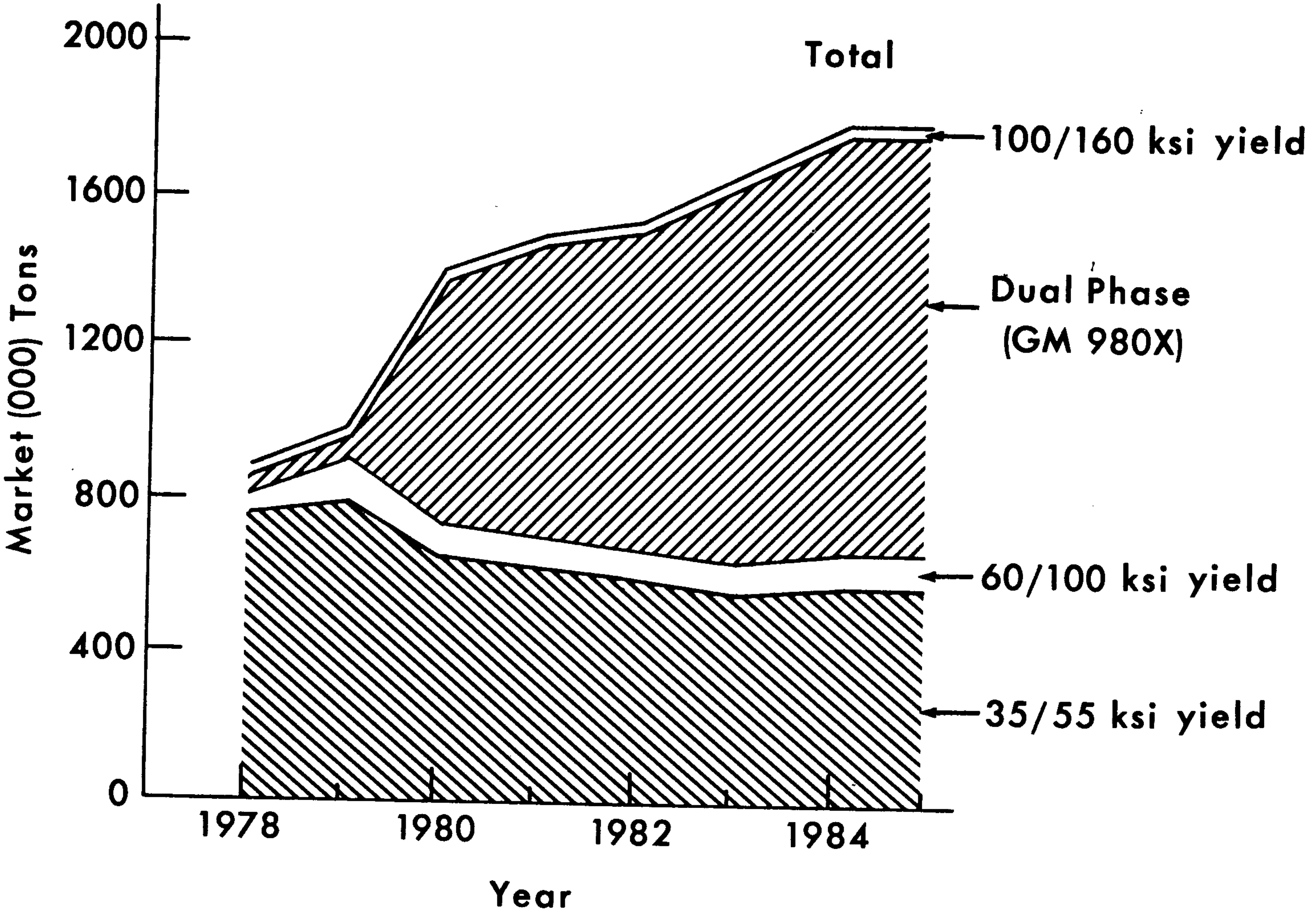


Figure 4. - Steel Producer Forecast of High Strength Steel Sheet Market (1977).

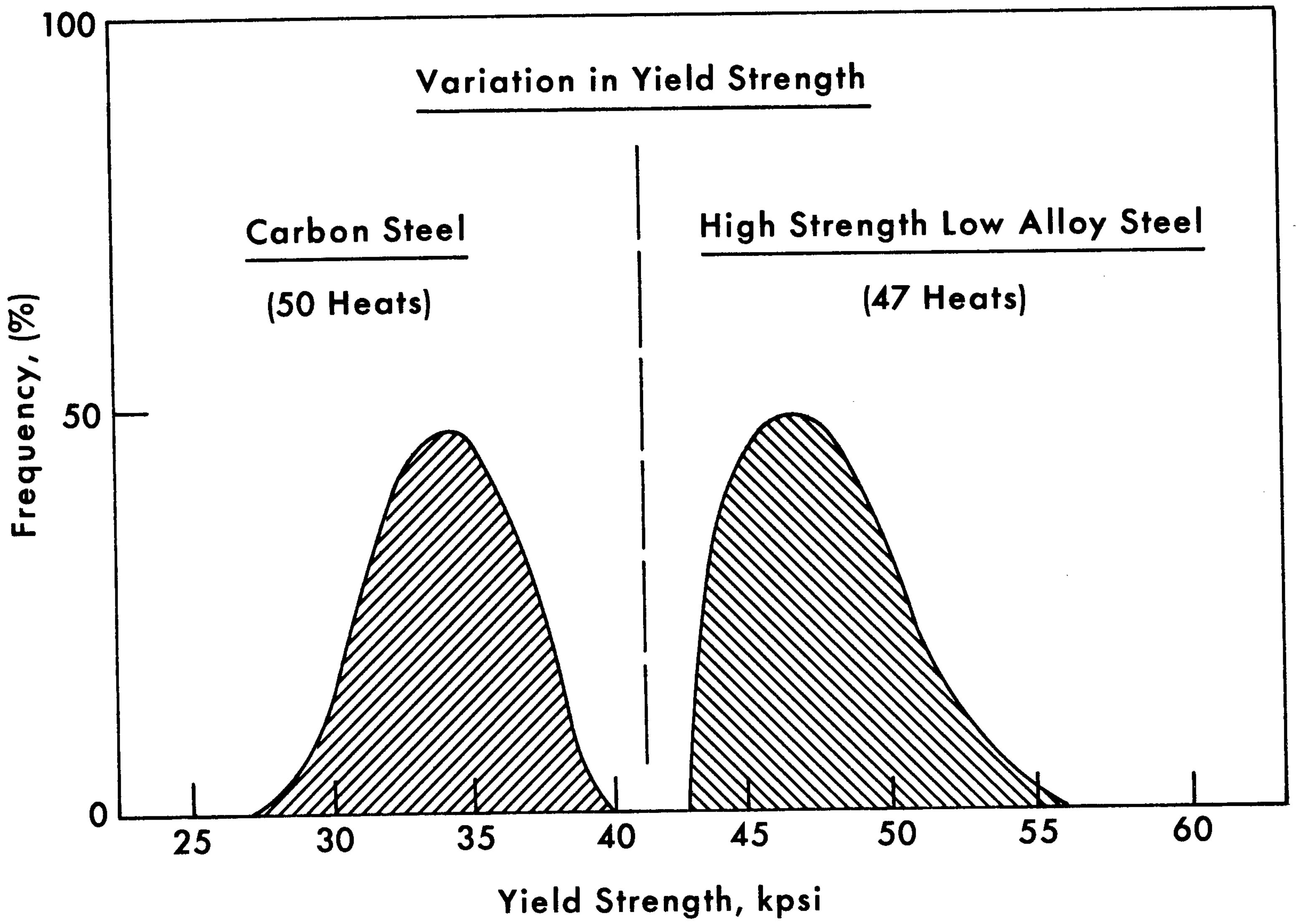


Figure 5.

Source: ASM Metals Handbook
Vol. 1, 8th Ed., pp 82, 89.

Introduction:

Good morning Ladies and Gentlemen. I'd like to explain at the outset that Caterpillar's views on steels needed for the future are not based solely upon what we would like to have. Our views are based on a knowledge of some of the improvements in steelmaking that have come about in the past 10 - 15 years that make improved steels possible. They are based upon a knowledge of what is available around the world, some of our own development work, and finally, belief that an understanding of theory and practice, along with some well directed development work, can lead to products not yet available anywhere.

I'd like to tell you first what we need generally, and then become more specific. In our industry we need higher strength hot rolled steel, and more formable steels; steel that is tougher in the through thickness direction at high hardness levels. We need low cost forging grade steels that harden $\leq$ Rc 34 in heavy sections while air cooling from forging to eliminate the need for heat treatment and/or alloy steel. We need steels with chemical analysis and hardenability bands more restricted than what is offered today. We need lower cost nitriding grades of steel. We need steels with fewer laminations and forging grades with better surface quality to avoid scrap to the forge shop.

Microalloyed Forging Materials

I mentioned that we need low cost, forging grades that harden to ≤ Rc 34 in air from the forging temperature. I was referring to a class of steel called "microalloyed forging materials". (1)

(2) I would like to begin with a definition. Microalloyed forging materials are medium carbon, or carbon-manganese steels that are alloyed with small amounts of vanadium or columbium to provide hot worked mechanical properties that are equivalent to those found in hardened and tempered carbon, carbon-manganese, alloy or boron steels.

(3) This means that microalloyed steels can be considered for any application where the body hardness is less than Rc 34 and the carbon level of the present material is in the .35 - .55 weight % range. The microalloyed replacement materials will typically be alloyed with vanadium and sulfur. In some cases material cost savings can be realized.

(4) Historically, microalloying has been used domestically for flat products. We believe that this same technology can be extended into hot rolled bars, thick walled seamless tubing, and forging quality bars.

(5) These materials were developed in West Germany to make forgings more competitive with castings in automotive crankshaft applications. They have also been used in connecting rods and automotive suspension parts like stabilizer bars and wheel spindles. Another application has been universal joint yokes. I should mention here that all of the domestic experience has been in captive, automotive forge shops. This experience is not available to Caterpillar. Therefore, to learn more about the properties and behavior of microalloyed forging materials we have had to look to foreign forging suppliers.

(6) Now I would like to review what we believe are conditions that must be met before microalloyed forging materials can be implemented at Caterpillar. First, we must develop dependable and capable sources of supply. Second, we need predictable hot-finished properties. This is particularly true for forgings. We must have adequate shearability and machinability. To obtain good cold shearing of forging bars, the steel suppliers may have to slow cool the material. Satisfactory response to surface treatments is also important. These treatments range from nitriding and induction hardening to shot peening. Finally, we need proven cost savings potential. Costs should be reduced by changing to lower cost materials, by eliminating some heat treating or straightening operations and by improving machinability.

(7) Development of Higher Hardness, Higher Toughness Steels

Steels are needed that have inherent toughness at high hardness levels. I'm referring to medium carbon, low alloy steels used in structural components: Steels such as the SAE 4100 and 8600 series. In many structural components, high hardness is essential to endure high contact stress, and to combat wear. Adequate toughness is required to withstand occasional overloads and prevent early hour catastrophic failures. When it is required to straighten parts after hardening, sufficient toughness is required to resist cracking. In high strength welded structures, adequate toughness is needed to prevent delayed cracking under the influence of residual stresses. At high hardness levels steels tend to be notch sensitive - to both geometrical and metallurgical notches. However, fatigue resistance, and fracture toughness, is required to sustain the damage encountered in service while enduring flaws and discontinuities that are inherent or inadvertently brought about during manufacturing. For satisfactory performance during both manufacturing and field performance, it is, therefore, imperative that high hardness steels have sufficient toughness.

(8) Let us look briefly at the intrinsic factors that can affect toughness. The chemical analysis, primarily the carbon level, influences the level of toughness that can be obtained. Hardness has a profound effect on toughness. Optimum combination of strength and toughness can only be obtained when the microstructure is fully martensitic. The presence of non-metallics, oxides, and sulfides

and their amount, size and distribution all have an impact. The various embrittling factors, such as temper embrittlement, temper martensite embrittlement, hydrogen embrittlement (that are related to either mill practice or heat treat practice) can lower the level of toughness that may otherwise be obtained.

(9) When the microstructure is fully martensitic and no embrittling conditions are present, and testing is done in plain strain conditions, our observation is that longitudinal fracture toughness is strictly a function of BHN and % C. The transverse toughness, on the other hand, may be as low as 50% or even as high as 100% of longitudinal toughness. With inclusion shape control and lower sulfur levels that are feasible today through ladle metallurgy techniques, transverse toughness can be as high as longitudinal toughness. Note that the evaluation defining the maximum level of toughness that can be obtained does not contain terms for nickel, chrome, molybdenum or any other alloying element, because the alloying elements at nominal levels do not really have toughening or embrittling effects. They are, however, effective in producing fully martensitic microstructures necessary for high levels of toughness. In order to develop steels having high hardness and high toughness, it is imperative that there be a simple, but accurate method for measuring toughness. Fracture mechanics tests quantify fracture toughness as a material property that can be used in design to derive allowable stress, flaw-size relationships. While charpy impact test results have very little meaning when working with high hardness steels, the well established ASTM E399 LEFM test is very

rarely used on a routine basis. The test is too expensive and laborious to conduct and is rarely used by other than the aircraft and aerospace industries, and by the steel and aluminum suppliers to these industries. For people in the earthmoving and automotive industries, the test has remained one of only academic interest. In the past two years, however, we have identified an economical, affordable, and practical method of fracture roughness testing.

(10) While the LEFM method requires that the specimen be fatigue pre-cracked prior to tensile testing, the short rod specimen generates its own crack that grows in steady state during the test. The chevron slotted notch geometry in the short rod specimen provides adequate constraint and minimizes the specimen size requirements for obtaining plain strain conditions. An inch diameter specimen is equivalent to 2 1/2" thick compact tension LEFM specimen. While an expensive, strain controlled servo-hydraulic machine is necessary for conducting LEFM tests, the short rod test can be done on any tensile machine, or by using a commercially available piece of test equipment called the Fractometer.

(11) Here is evidence of the correlation experiments we ran between the ASTM E399N and the SR test. The SR specimens were prepared from the broken halves of the ASTM E399 CT specimens. Testing was conducted over a hardness range of Rc 35 - 59. As you can see, there was excellent correlation.

(12) For those of you not familiar with a short rod specimen, it is esentially a cylindrical sample with a length to diameter ratio of 1.5. An inch diameter specimen is 1.5" long. On one end it has a V-shaped grip slot. Two narrow side slots are cut on the sides to produce a V-shaped region in the center that is constrained to plain strained conditions. The specimen is loaded by wedge opening the V-shaped grip slot. During the test, a crack starts from the tip of the V and grows in a stable and steady state. The energy to fracture a unit area of the material as the crack grows in a steady state is the measure of the toughness of the material. This specimen may be rectangular or circular in cross section and is called a short bar or short rod specimen, respectively.

(13) This slide shows an inch diameter short rod, 1" thick, short bar 3/4" diameter short rod and 3/4" short bar. The short rod or bar specimen can be as small as 1/2" or 1/4". With the smaller sizes, however, it is difficult to get valid results when one is testing very tough materials. The small size of this short rod or bar specimen enables one to characterize the directionality or the anisotropy of toughness in a rolled or forged section. One can prepare specimens with different fracture planes to quality longitudinal, long transverse and short transverse properties.

(14) The SR specimen can be used to characterize the toughness of the material as it exists in the critical location of fully processed components. You would machine a short rod or bar specimen from

the desired location and test to establish the component toughness. On the other hand, by preparing a short rod or bar sample from the forged mill sample and heat treating to hardness levels that are seen in the part and testing it, we would be able to establish the material toughness or the fully martensitic toughness. By comparing the two toughness values, one can establish the quality of heat treating, and the adequacy of hardenability for the section size.

(15) In summary, you will note that the short rod test is a powerful method for characterizing steel toughness and it has a lot of potential. The SAE aerospace group has issued a document recommending this as an alternative to ASTM E399 tests. An ASTM E24 subcommittee is going through a Round Robin test program to establish a correlation between the short rod and ASTM E399 test. A symposium is scheduled for April, 1983, to discuss the results. The work we have done here at Caterpillar show that the short rod method is equivalent to the current ASTM method, and we believe it will eventually be accepted by the rest of the community. The real point I wish to make is that the steel industry needs to develop fracture toughness testing as a process control at the mill. It should serve as in-house quality control of the steels they are making. And finally, this kind of testing capability can be used for the design and selection of alloys.

(16) <u>Improved Nitriding</u>

Nitriding is one of the many heat treatments used to enhance engineering properties of steel beyond that which can be obtained through simple quenching and tempering. It has the advantage of being able to provide high surface hardness and residual compressive stress for improved fatigue resistance with very low distortion. On the other hand, it has the disadvantage of costing significantly more than it cost to either quench and temper a part, or to carburize and harden. Most of the high cost of nitriding is directly related to the long times required to nitride. And therefore, new steels which will shorten existing nitriding cycles could offer a significant economical advantage. Additionally, developments leading to improved nitrided properties would allow the use of nitriding on parts currently requiring carburizing, hardening, and grinding. Nitriding consists of exposing a part to atomic N at temperature so that it can diffuse into the surface and form alloy nitrides. A thin layer of iron nitride forms first. This layer, commonly known as a "white layer", is necessary for adequate diffusion to occur. The white layer basically provides the source of nitrogen that diffuses into the steel to form alloy nitrides. They are commonly formed of Cr, Mo, Al, and V. A typical hardened, nitrided case will provide a surface hardness of Rc 65 with Rc 45 at .3 mm, and the surface residual compressive stress of approximately 50- 60,000 psi. Steels are normally quenched and tempered before nitriding, so the core will consist of a quenched and tempered martensitic microstructure. I am aware of recent developments in the areas of salt bath nitriding, and ion-nitriding to reduce the cost of this process, but what is needed additionally are steels that inherently nitride faster.

(17) This slide shows the composition of the current, most commonly used nitriding steel, 41L40, and two improved nitriding steels that are now being evaluated. One is a 41LV30 which can reduce the gas nitride cycle by 20- 45%, depending on the required nitride case depth. And the last one is a 41LV30 steel modified with the addition of Al. This grade is expected to offer not only further reductions in cycle time, but also increased engineering properties over the more conventional nitriding steels. One can see from this work that further material development is needed to achieve the optimum cost benefit for nitriding grades.

Restricted Hardenability

Our major objectives, as heat treaters, are to heat treat steels as efficiently and economically as possible, while maintaining the best possible product quality and performance for the customer. We believe that Caterpillar's heat treat processes have historically been one of the key factors in providing our customers with a dependable, rugged, superior piece of earthmoving equipment. In order to meet our goal for efficient heat treating, we attempt to utilize every bit of hardenability we pay for. With current composition and hardenability ranges, however, it is difficult to produce optimum results from both high and low side heats.

(18) This brings me to the subject of this part of the talk - Restricted Hardenability. Here is a slide that represents what we mean by restricted hardenability. Our current specifications are shown as the broad, dark blue range, whereas, the light blue range represents

the restricted hardenability that we feel we need. Let me explain with some examples, some of the benefits we expect to obtain with a restricted spread in hardenability. We expect to gain both processing and functional advantages. Restricted hardenability will allow us to process parts from heat to heat with fewer adjustments in the heat treat set-up. This provides an obvious improvement in productivity. Also, with restricted hardenability, the designer is able to design his product to a narrower spread in hardness. This will result in a direct benefit to the customer, particularly in wear components.

I will present three examples of heat treated product where a restricted spread in hardenability can result in both processing and functional benefits. The three examples are: 1) track links, 2) coarse pitched, high strength gears, and 3) extreme service track shoes.

(19) Track Link

My first example is a track link forged from a modified SAE 15B36 steel currently used in our largest track type tractors. The track link serves as a link in the track chain. It obviously must withstand high fatigue loads as the chain drives the tractor. It must also withstand high wear, particularly on the track roller and idler contact face as sand and gravel abrade the surface. This is not an unusual application for a large track type tractor. The current specification for the SAE 15B36 steel is shown here. The

(20) current Carbon and Manganese ranges, as well as the hardenability bands, are shown in this slide. The Jominy hardenability requirement specifies a minimum and maximum hardness at J1 and 2 other points. To produce the required engineering properties, the link is first direct hardened to the machinable hardness range. The wear surface is then given a severe water quench to provide high hardness and high wear resistance. Experience has shown that high

(21) hardenability heats are very suspectible to quench cracks such as the one shown here. This requires that the heat treat set-up be adjusted.

(22) Similarly, low side heats also require set-up changes of a different sort. This slide shows both high-and-low extremes of the presently specified steel. In some instances, changes in hardenability from the beginning to the end of the heat can require similar set-up adjustments as I have already explained. This is seen occasionally in Boron steels where Boron effectiveness may vary from the front to the back of a heat.

As you can see from the previous two slides, we as heat treaters have an interesting balancing act to perform. We know that statistically speaking, we are going to continue to make frequent heat treat set-up adjustments for the current hardenability band.

(23) The steel grade has already been modified to the point where quench cracking has virtually been eliminated, but with the standard 5 point

Carbon spread, and 30 point Mn spread, and a minimum hardness of Rc 43 at J6, we feel there are still too many heat treat set-up adjustments required. A step in the right direction would be to reduce the minimum Mn spread to only 20 points, from 1.10- 1.30% and allow the minimum at J6 to be raised from Rc 43 to Rc 45 while still maintaining the maximum of Rc 48 at J10. This would allow us to fine tune the heat treat process further. The proposed specification would reduce the set-up adjustments needed in heat treat. And, if the composition and hardenability bands could be narrowed even further, track link processing problems could be reduced while the value to the customer could be increased. The current Carbon level of .32- .37%, with product analysis tolerance of .02% on each side, results in a potential range of .30- .39% C. This can result in a quenched surface hardness that varies between Rc 51 - 56. The difference between 51 and 56 Rc can yield a significant variation in wear life. Thus, if the Carbon and Manganese ranges could be tightened up, our heat treat set-up could be modified to tolerate a slightly higher Carbon content. The resulting increase in hardness can provide a customer with even greater value. With a Carbon range close to an absolute spread of .35- .40% for instance, the hardness would vary only between Rc 54 - 56. The increase in the minimum hardness from Rc 51 - 54, will give a measurable increase in wear life and thus more customer value. This is an obvious benefit to the customer. The undercarriage replacement parts market is one of the most competitive in our industry. An improvement such as this, directly resulting from more controlled composition and hardenability, can only result in greater customer satisfaction.

(24) Restricted hardenability can also provide benefits in heat treating gears. Here is an example of a coarse pitch gear manufactured from SAE 4122 modified alloy steel. These large gears are found in the final drives of the large crawler tractors. The gears are carburized and hardened.

(25) The composition in range and hardenability bands are standard for an alloy steel. Jominy specifications are shown as X on this hardenability plot. The highlighted area is a composite of a hardenability data of all the heats received at Caterpillar between 1981 and 1982. Notice the at J4 we can expect a hardness of Rc 37-47, and at J6 there can be a 13 point variation from Rc 27 - 40. In gearing this kind of variation means one thing, dimensional change. The wide hardenability range means, of course, that there is a wide variation in the amount of core material transformed to martensite during hardening. This results in varying dimensional change from machining to the finished heat treated size. Size change is expected, of course, but it is important that it be consistent.

These final drives are about 31" in diameter. A pitch diameter can vary by ten thousandths of an inch, and possibly even more, even with die press quenching due to hardenability alone. This uses up a substantial portion of our allowed tolerance. And again, changing hardenability from the first part of the heat to the last further aggravates the situation and can require adjustment to the heat treat set-up.

(26) Here is a study of broached internal splines on the gear shown here. The study shows the size change of the spline through carburizing and hardening varies directly with hardenability. The gears were taken from four different heats of SAE 4122 steel and carburized at the same time. They were all carburized together on a press using die tooling to control spline size. An ideal diameter variation of 2 1/4" to 3 1/2" resulted in .004" size change difference. This again used up a significant portion of the pitch diameter tolerance on the spline. Caterpillar uses several basic specifications to classify SAE 4100 series carburizing steels. As tooth thickness increases, higher hardenability steel is specified. With the current hardenability ranges, each specification extensively overlaps the others.

(27) This slide shows the Jominy specification overlap of two SAE 4118 steels, for which we have separate specifications. These two specifications could easily be combined into one, shown as the overlapping area with more resulting control of hardenability. The elimination of two specifications through closer control of hardenability may seem somewhat trivial, but when you consider the

possible reduction in material inventories at forge shops; the reduced paperwork required to support two additional specifications; and the reduced size variation, you can see that it all adds up. Controlled core hardness is needed to achieve optimum gear properties. This can only be achieved through closer control of hardenability.

Ladle refining techniques will probably be required to produce this restricted hardenability. We do have steel specified to have reduced hardenability on order with some suppliers. Moving back to
(28) Undercarriage - a final example is an extreme service track shoe rolled from a modified SAE 41B25 steel. These too are used on the large track-type tractors. They are one of the most highly stressed, shock loaded, high wear components on our product. This is the steel specification for these extreme service shoes. The
(29) highlighted area represents all of the supplier data for a year. Alloy composition ranges are standard, and the hardenability specification is very loose, with only three points specified. The track shoe is hardened by water quenching and tempering to a very high level. The processing considerations for track shoes are the same as those described for links and gears. The dimensional consideration for track shoes is bolt hole spacing. The bolt holes are punched before heat treating. Therefore, the spacing can vary with hardenability. It needs to be consistent, and thus has to be consistent, and thus has to e controlled by adjusting the heat treat

set-up. Restricted hardenability and chemical composition will again result in better process control with it's attendant increase in productivity, as well as providing greater value to the customer. I have given only three examples of where current hardenability and composition ranges affect the heat treater. Caterpillar's objectives are to produce tractors of superior quality and reliability while maintaining a favorable cost/price/value relationship in order to be competitive worldwide. In order to do this, we believe that Product Analysis Tolerances on all steels should be eliminated. Further, we believe that the Carbon range should be restricted to an absolute five point range.

Machinability

(30) Caterpillar machines a variety of steels in various conditions by a multitude of different machining methods. With every combination of these three variables, there are occasional machinability problems for one reason or another. However, the three areas of greatest concern are high speed steel machining of carburizing and nitriding steels, turning with carbide tools, and the future of leaded steels.

(31) Today, high speed steel (HSS) tools are mainly restricted to gear cutting operations such as hobbing, shaping, and Gleason cutting.

(32) Here we have a Gleason cutter used to form the gear teeth on bevel gears and pinions. Gear shaping tools are expensive and, even without catastrophic failures, can only be resharpened a limited number of times.

Gear Forgings are machined in two conditions; as-forged, and as-annealed. As-forged hardness normally varies from 4.0- 4.8 mm
(33) Brinell Rc 1 - 20 with microstructures ranging from acicular, as shown here, to equiaxed ferrite and pearlite typical of an annealed
(34) structure.

Turning operations are performed on the entire cross section of wrought steels, with microstructures ranging from annealed to quenched and tempered. Turning inserts most commonly used are TiN, TiC, and AL_2O_3 coated carbides, with and without chip breakers. Additionally, many of the turning operatons at Caterpillar Tractor Co. are done without coolant. In both gear cutting operatons with HSS and in turning with carbide tools, cases where tool life is reduced by 50- 90% on certain "schedules" (batches of parts from a given heat of steel) are not uncommon. Occasionally defects such as alloy segregation, which result in microscopic hard spots or forging defects are the cause of the reduced tool life, but in the majority of cases no obvious explanations can be found. We at Caterpillar Tractor Co. probably machine at higher rates of metal removal than most of the rest of the industries involved in machining the type parts discussed here, and therefore probably "detect" more subtle differences in steels from heat to heat. From our experience, the distribution and make-up of inclusions in steel seems to be one of these differences. In these regards, not only is development needed in the area of inclusion modification, perhaps along the lines of shape control combined with higher sulfur contents, but also in understanding what effect the inclusions in the forging quality steels used today have on tool life. It needs to be realized that over the past 20 years great strides have been made in the rate and accuracy of metal removal. To take full advantage of these developments, equal strides must be made in steel technology as related to machinability.

(35) Caterpillar Tractor Co. uses leaded steels mainly in nitrided parts which are machined in the quenched and tempered condition. Since we are machining in this condition, lead is necessary to maintain acceptable production rates. We all know lead presents several environmental problems, especially when vaporized during any melting process. These problems confront primary lead producers, producers of leaded steels, and those who attempt to remelt leaded steel chips. Although Caterpillar Tractor Co. does not produce primary lead, we do rely on leaded steels for increased machinability, and we do remelt machine chips at our foundries, hence we have two problems. First, will leaded steels continue to be available, and economical? Secondly, we must currently segregate leaded and non-leaded chips in all our machining facilities. In those facilities where chip segregation is not feasible, we have had to change from leaded to non-leaded steels with an attendant loss in machinability.

Lead, of course, promotes machinability by providing lubrication at the too - workpiece interface. As a microconstituent in steel,
(36) it appears as the dark area on this manganese sulfide inclusion shown at 1000X. Several replacements for lead have been considered; for instance, selenium, tellurium, and special calcium treatments. Selenium and tellurium, however, suffer from the same environmental drawbacks as lead, and calcium treatments are designed to improve carbide tool life, not HSS tool life. Our most promising work has been with Bismuth (Bi). Bi has no current or anticipated vapor toxicity limits; it is added to steel in the same manner as lead; and other than being gold in color, it appears in the microstructure the same as the lead we sae in the previous slide.
(37) Furthermore, our machinability tests and trial production lots have shown Bi to perform as well as lead. Unfortunately, bismuth containing chips can cause casting chill when used for remelt scrap and no practical "antidote" for this effect currently exists. Our work to date has been solely on the hypothesis that "someday" lead may not be available to promote economical machinability promoter due to environmental restrictions. Essentially, we feel that as a company we need to be ready for any situation which may develop concerning leaded steels.

Continuously Cast Steel

I mentioned at the outset that we need plate steel with fewer laminations and forging grades with better surface quality in order to avoid scrap and the forge shop; and I believe I also mentioned that we would like to have these things at lower cost. There is a way to achieve all of these things, and that is through continuously cast steel. In the past decade there has been a dramatic increase in foreign competition in the steel user's market. In this market, the major competition has been due to the increased usage of continuously cast steel by Japan and Western Europe. Domestically, continuous casting has been in commercial existence for over 20 years, but only recently has it begun to assume a dominant position in our steelmaking industry.

(38) This slide shows the growth of continuous casting in the United States in recent years. Seven years ago, in 1975, on 9% of domestic steel output was continuously cast. By 1981 it had risen to 21.6%, and it is predicted that by the end of the decade 45% of all American made steel will be continuously cast. This change occurred rather rapidly. The United States is still significantly behind Japan and Europe. In 1981, they produced 70.7% and 45.1%, respectively, of their total steel output by this process. To the steelmaker, continuous casting offers many cost advantages compared with traditional ingot practice. Listed below are a few of these:

(39) 1). Because continuous cast steels are essentially a semi-finished product, the need for blooming mill is eliminated.

2). And, because the amount of required cropping is reduced, the yield is increased from approximately 70% to 90%.

3). Energy consumption is reduced. This is primarily due to the elimination of the blooming operation and the corresponding soaking operation prior to it. While these cost advantages are primarily related to the producers of continuous cast steel, it can obviously benefit users in the form of cost savings passed on.

While continuous casting will undoubtedly help to restore cost competitiveness to the domestic steel industry, it is of extreme importance that both users and producers understand the engineering properties of this product so that it can be used with confidence as an equivalent replacement for ingot cast steel. With ingot cast steel the only major difference between one mill's product and another are such items are cleanlines, surface finish, level of residual elements, etc. Because of the large amount of reduction imparted by the rolling process, a user need not concern himself about matters such as reduction ratios and their impact on fatigue resistance, or on internal defects, shearability of the billet, or the availability of Boron and leaded steels. On the other hand, when purchasing continuously cast steel, the user must be concerned about all of these things. In addition, there are substantial differences to be found among the various mills and casters. In fact, different strands from the same caster and from the same heat of steel can vary greatly with respect to items such as cleanliness, level of internal defects, surface finish, and boron effectiveness. Our experience with continuous cast steel, however, reveals certain

(40) merits of the product. 1) Better homogeneity due to the rapid soldification rate, 2) with proper deoxidation, ladle treatment, and protection of the molten stream while casting, continuous casting provides beneficial inclusion morphology and improved inclusion distribution. 3) Continuous cast steel offers improved surface quality, fewer seams and other defects. And, 4) because a steel receives less reduction in area, parts made from continuously cast steel will have more isotropic properties than its ingot cast counterpart. Of course, along with these merits, there are a few limitations. Some of these are:

(41)

1) Continuous cast size steel billets cannot be cold sheared unless they have been reduced at least 2 to 1.
2) Some reduction of as-cast material is necessary to heal internal defects, such as internal looseness and mid-radius cracks.
3) The availability of Boron and leaded continuously cast steels is limited. (A recent development by Foote Mineral Company has now started to make Boron steel available).
4) Tests have shown that even with a reduction ratio of 20 to 1, hardened and tempered steels have a lower torsional fatigue resistance than ingot cast steel, having a reduction ration of 190 to 1.

5) And finally, section size availability of continuous cast steel is limited. Only a handful of the larger mills can produce the wide variety of sizes most users would require on a production basis.

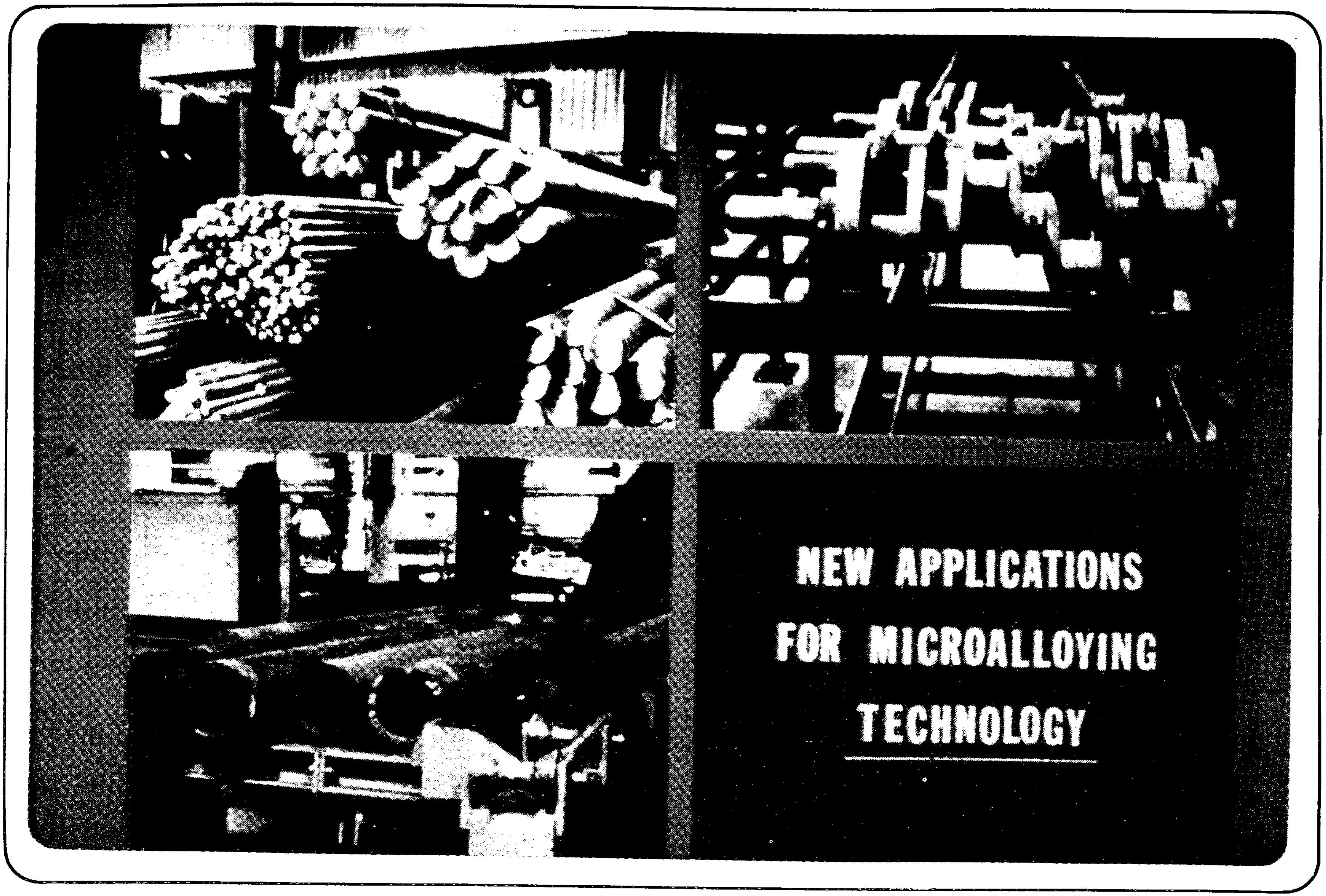
In summary, due to the economic advantages inherent to continuous cast steel, there is little doubt that it will dominate future steel production, both domestically and around the world. Because of its current liimitations, however, it cannot presently be interchanged with ingot cast steel for all applications. Steel producers need to continue to make technological improvements to the process, such as the adaption of ladle metallurgy, improved shrouding and electromagnetic mold stirring. Users, on the other hand, need to learn to optimize the design of their components to accommodate continuously cast steel.

MICROALLOYED FORGING MATERIALS

MICROALLOYED FORGING MATERIALS ARE MEDIUM CARBON, OR CARBON-MANGANESE STEELS THAT ARE ALLOYED WITH SMALL AMOUNTS OF VANADIUM OR COLUMBIUM TO PROVIDE HOT WORKED MECHANICAL PROPERTIES THAT ARE EQUIVALENT TO THOSE FOUND IN HARDENED AND TEMPERED CARBON, CARBON-MANGANESE, ALLOY OR BORON STEELS.

DEVELOPMENT TRENDS FOR STEELS WITH 0.35 TO 0.55% CARBON

HARDENED AND TEMPERED UP TO RC 34 (3.4MM BR.)		MICROALLOYED WITH CONTROLLED COOLING
10XX 15XX 41XX 15BXX 41BXX	→	10XX + V (+S) 15XX + V (+S)



NEW APPLICATIONS
FOR MICROALLOYING
TECHNOLOGY

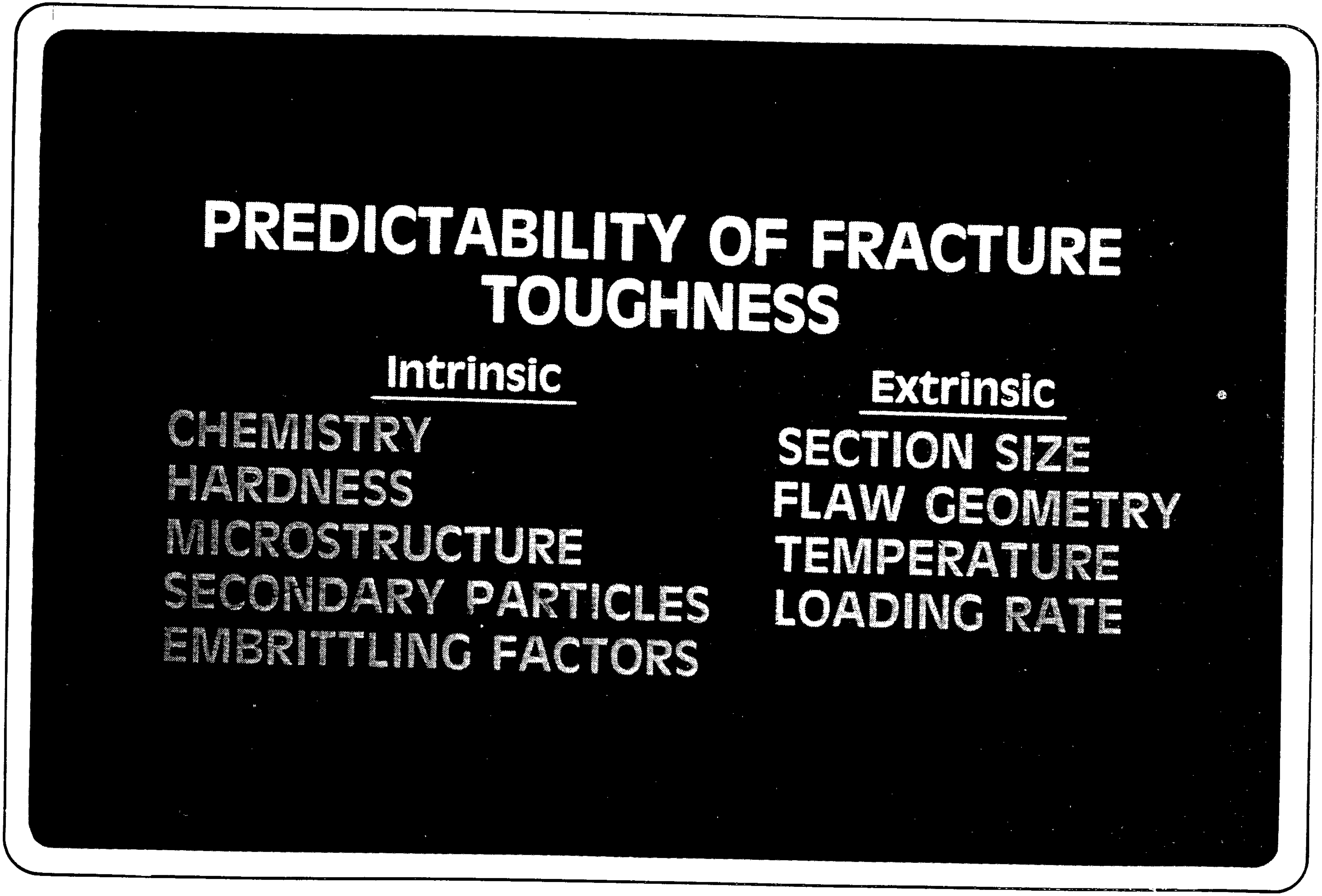
INTERNATIONAL ACCEPTANCE OF MICROALLOYED STEELS FOR FORGINGS

CRANKSHAFTS - GERMANY, ENGLAND, JAPAN
CONNECTING RODS - GERMANY, ENGLAND, JAPAN, U.S.A.
AUTOMOTIVE SUSPENSION PARTS - GERMANY, JAPAN, U.S.A.
U-JOINT YOKES - U.S.A.

CONDITIONS FOR IMPLEMENTATION AT CATERPILLAR

- DEPENDABLE AND CAPABLE SOURCES OF SUPPLY
- PREDICTABLE HOT FINISHED PROPERTIES
- ADEQUATE SHEARABILITY AND MACHINABILITY
- SATISFACTORY RESPONSE TO SURFACE TREATMENTS
- PROVEN COST SAVINGS POTENTIAL

QUANTIFYING
TOUGHNESS AS A MATERIAL PROPERTY



PREDICTABILITY OF FRACTURE TOUGHNESS

Intrinsic

- CHEMISTRY
- HARDNESS
- MICROSTRUCTURE
- SECONDARY PARTICLES
- EMBRITTLING FACTORS

Extrinsic

- SECTION SIZE
- FLAW GEOMETRY
- TEMPERATURE
- LOADING RATE

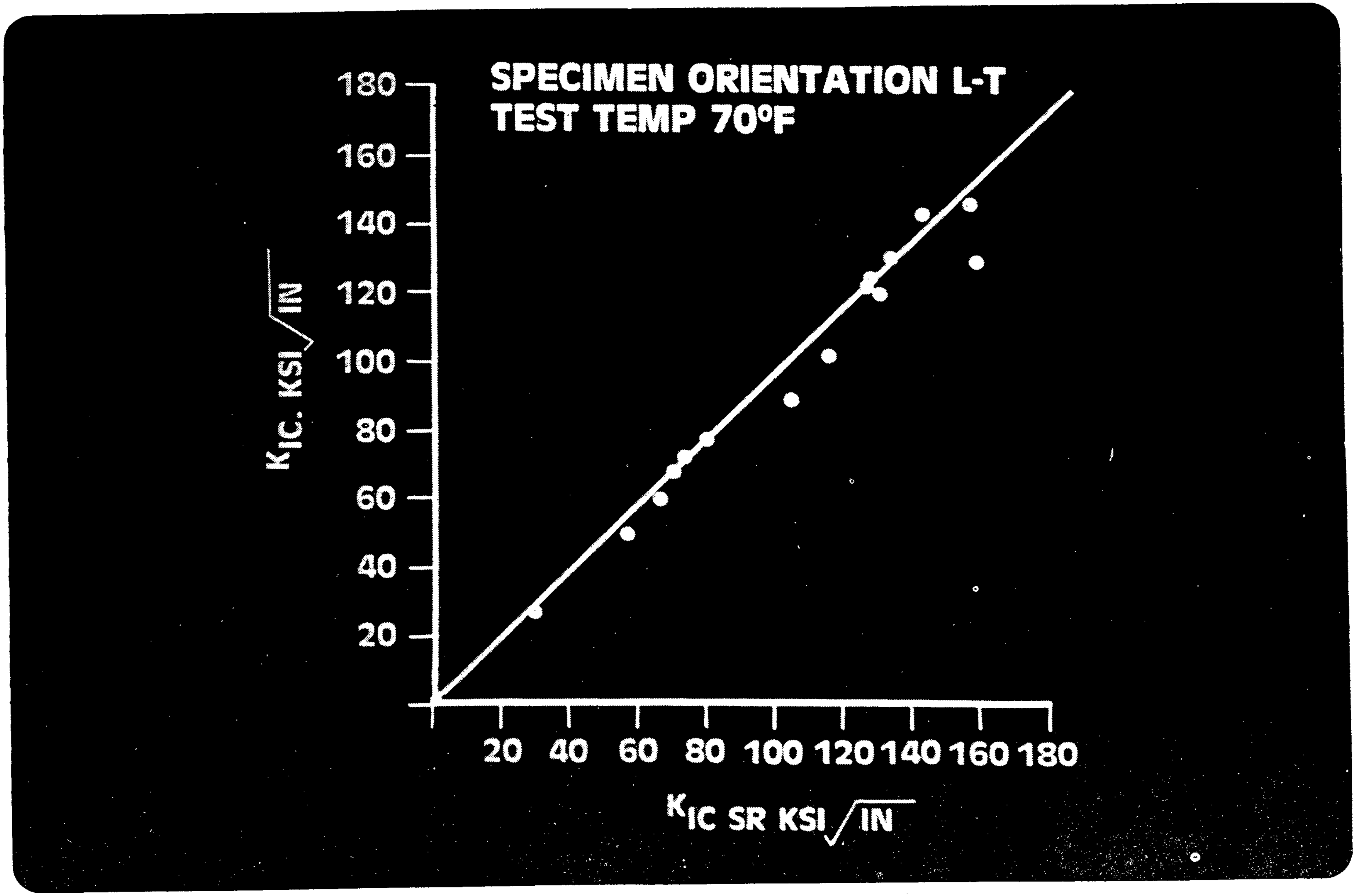
CONDITIONS:

A. FULLY MARTENSITIC
B. NO EMBRITTLEMENT
C. PLANE STRAIN

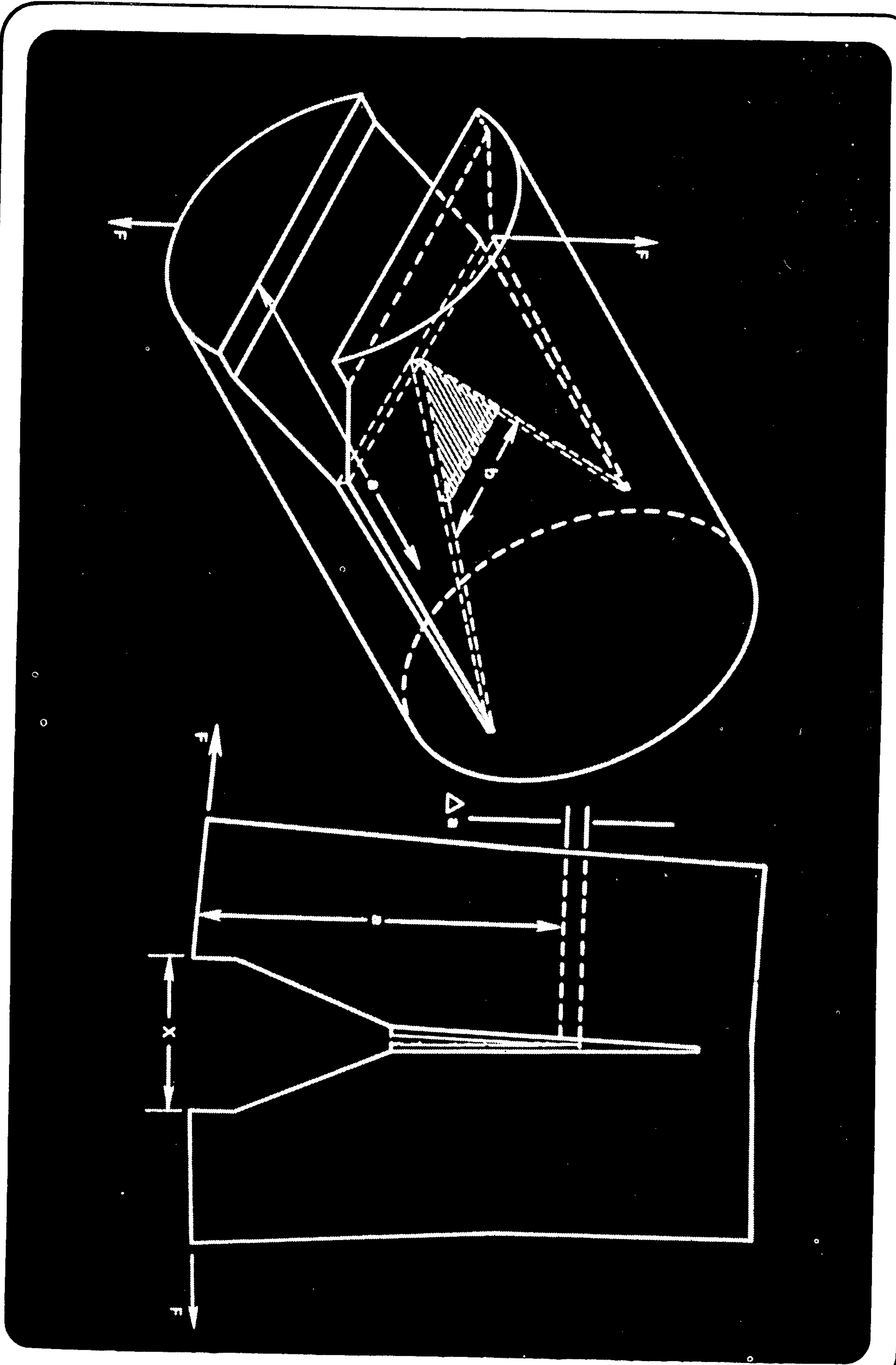
$$K_{IC} = \frac{85100}{BHN} - 45 - 150\ (\%\ \text{CARBON})$$

FRACTURE MECHANICS TESTS COMPARED

ASTM E399	Short-Rod
	Chevron-Notched Specimen
FATIGUE PRE-CRACK	STEADY STATE
2.5"	1"
$600 / SPECIMEN	$100 / SPECIMEN
$100,000-MTS	$20,000-FRACTOMETER



SPECIMEN ORIENTATION L-T
TEST TEMP 70°F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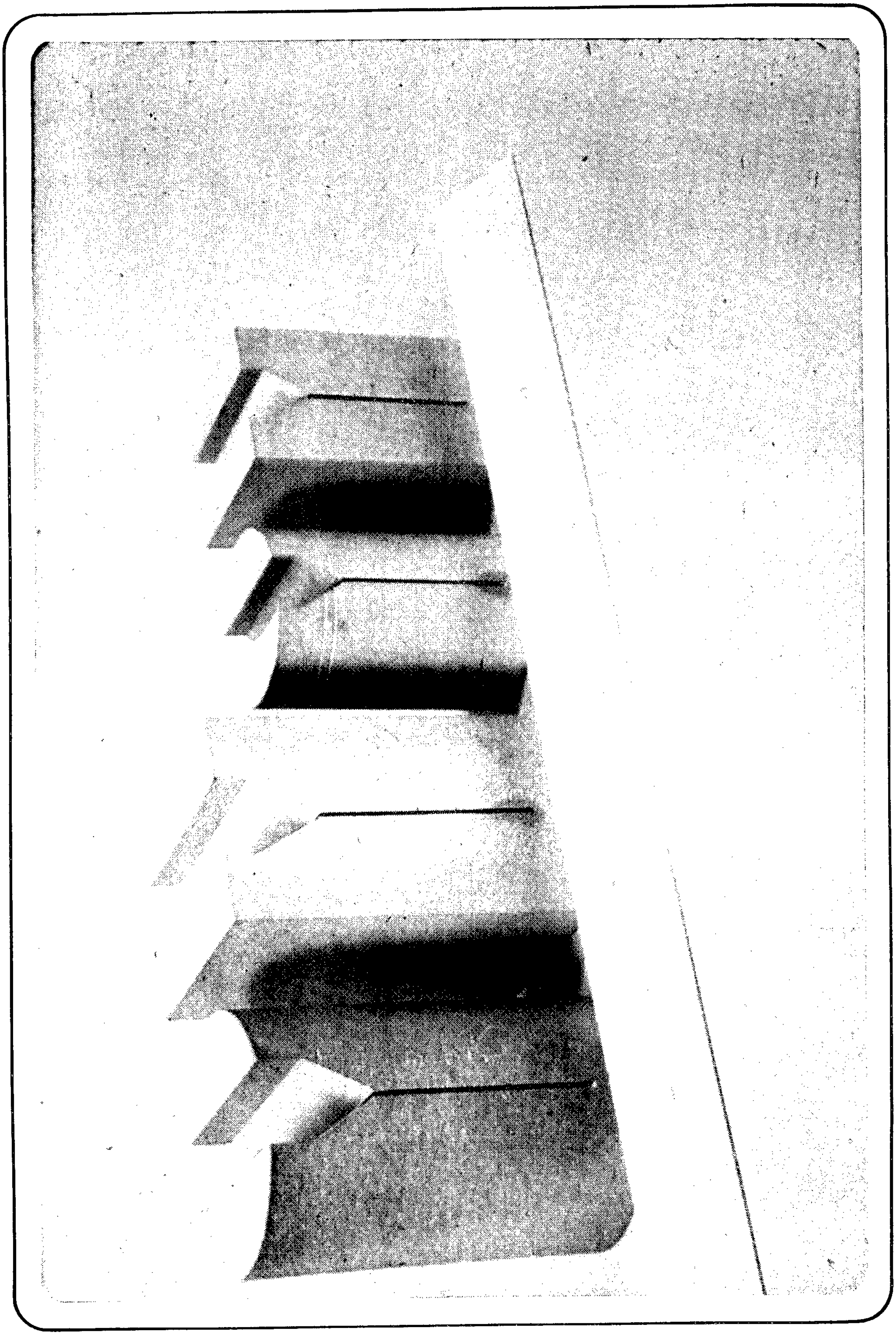
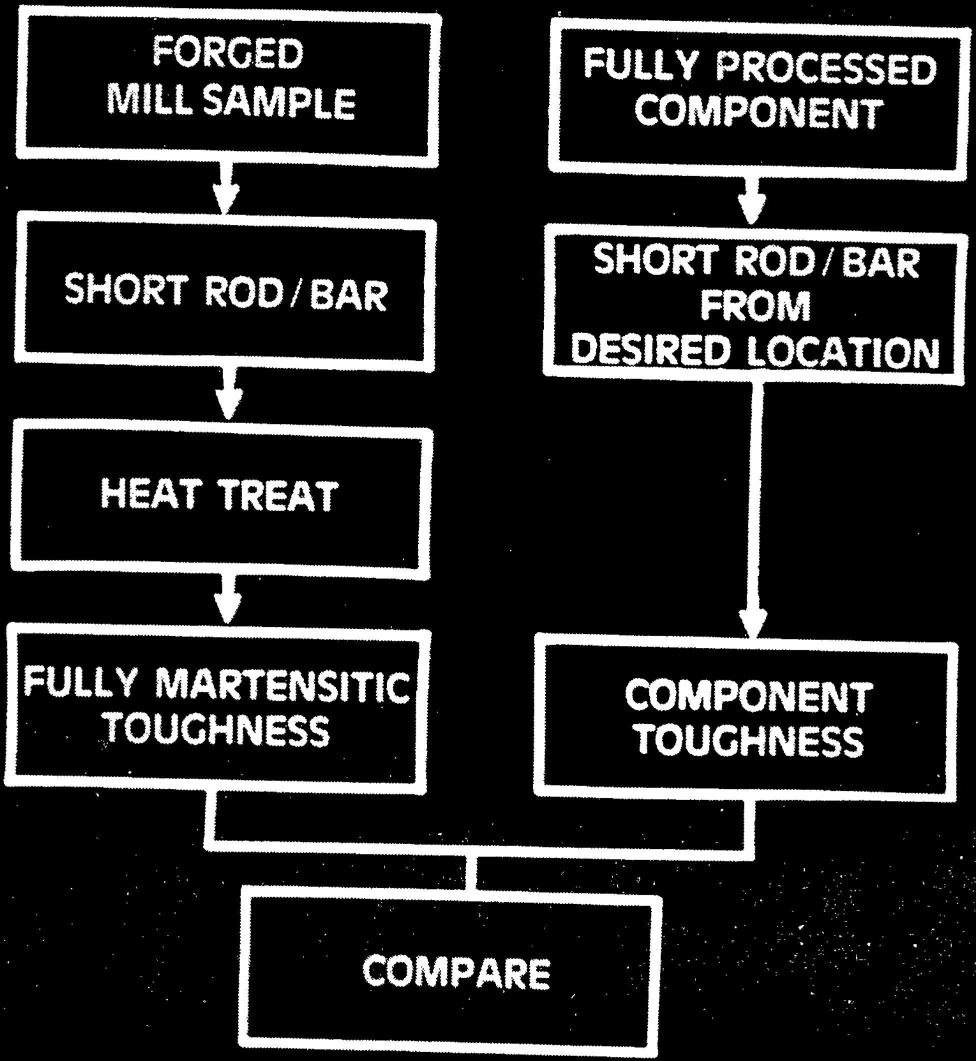


CHARACTERIZING FRACTURE TOUGHNESS



FORGED MILL SAMPLE

SHORT ROD / BAR

HEAT TREAT

FULLY MARTENSITIC TOUGHNESS

FULLY PROCESSED COMPONENT

SHORT ROD / BAR FROM DESIRED LOCATION

COMPONENT TOUGHNESS

COMPARE

SHORT-ROD TESTING

A. PROCESS CONTROL AT THE MILL
B. IN-HOUSE QUALITY CONTROL
C. DESIGN & SELECTION OF ALLOYS

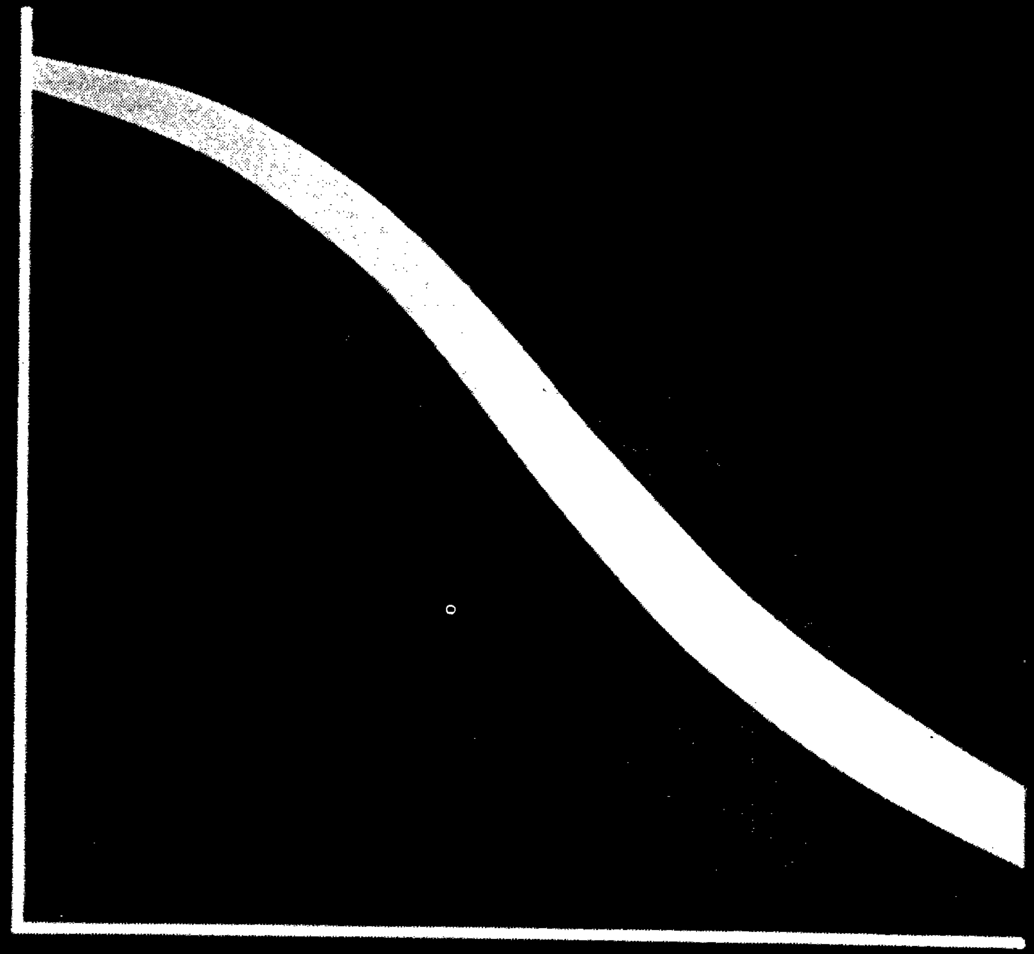
IMPROVED NITRIDING

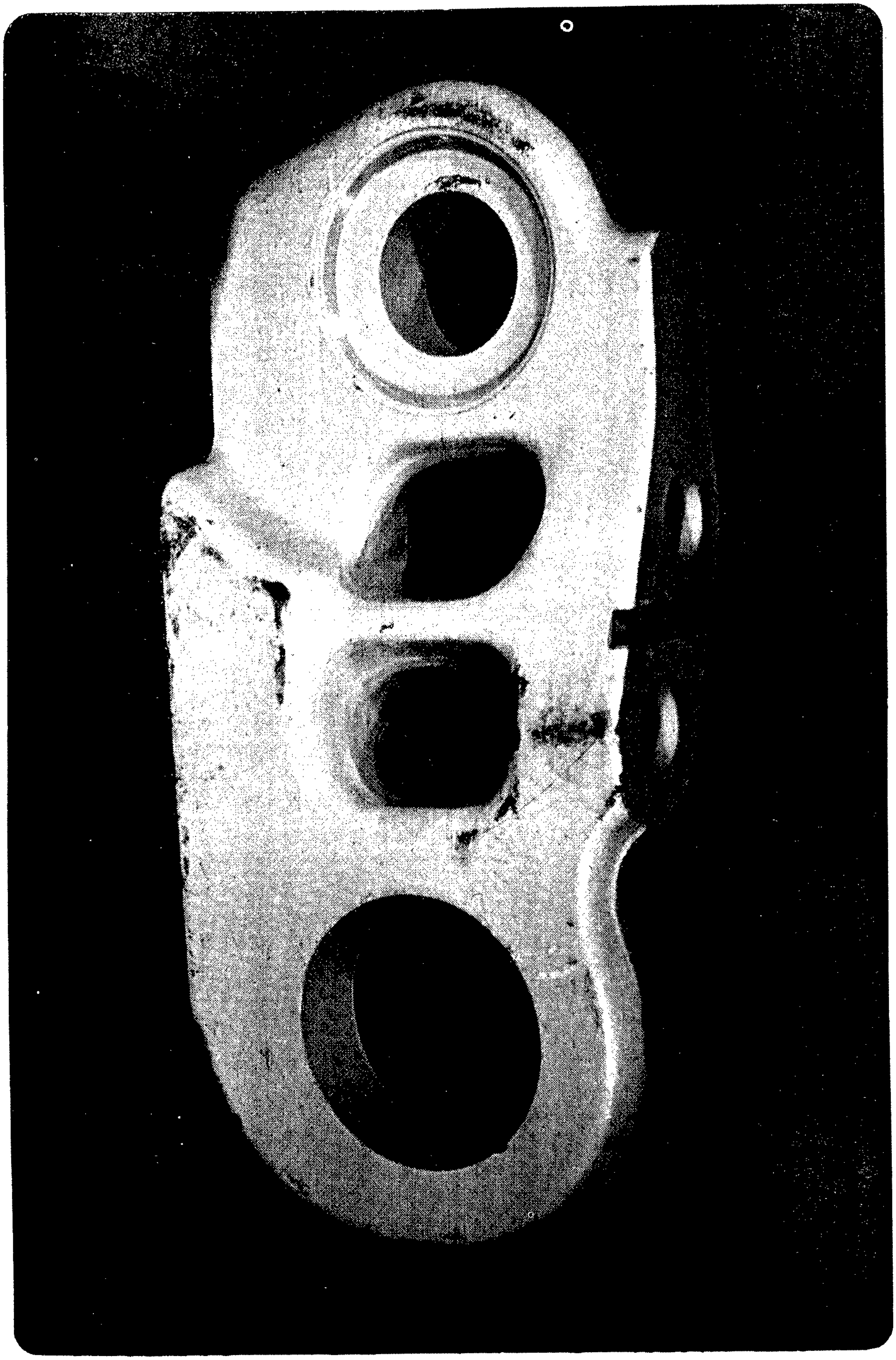
- HEAT TREAT
- MATERIALS

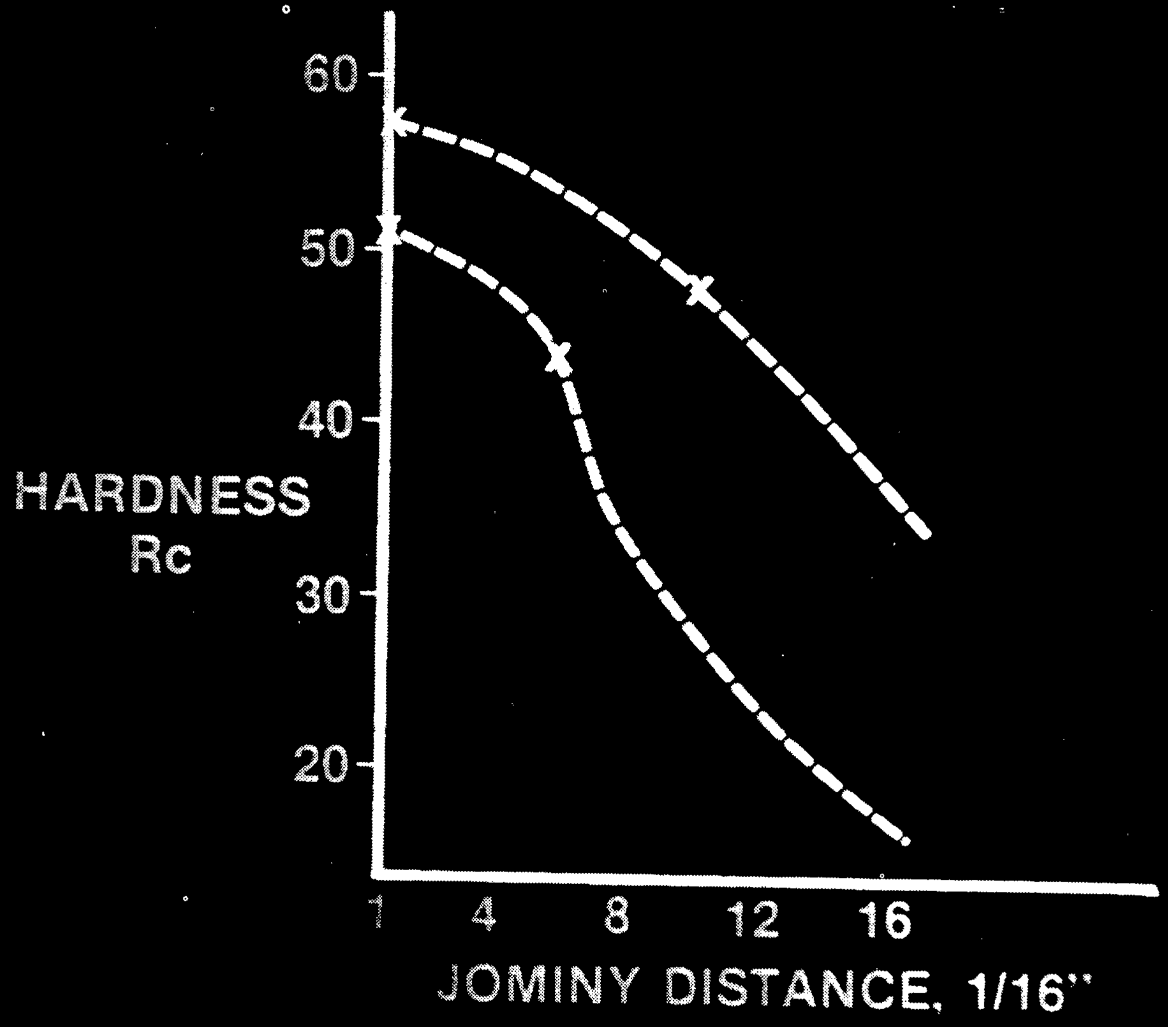
NITRIDING STEELS

Nominal Composition (%)	41L40	41LV30	41LV30®
C	.40	.32	.32
Mn	.90	.90	1.15
Cr	1.05	1.05	1.05
Mo	.20	.20	—
V	—	.07	.07
Al	—	—	.15

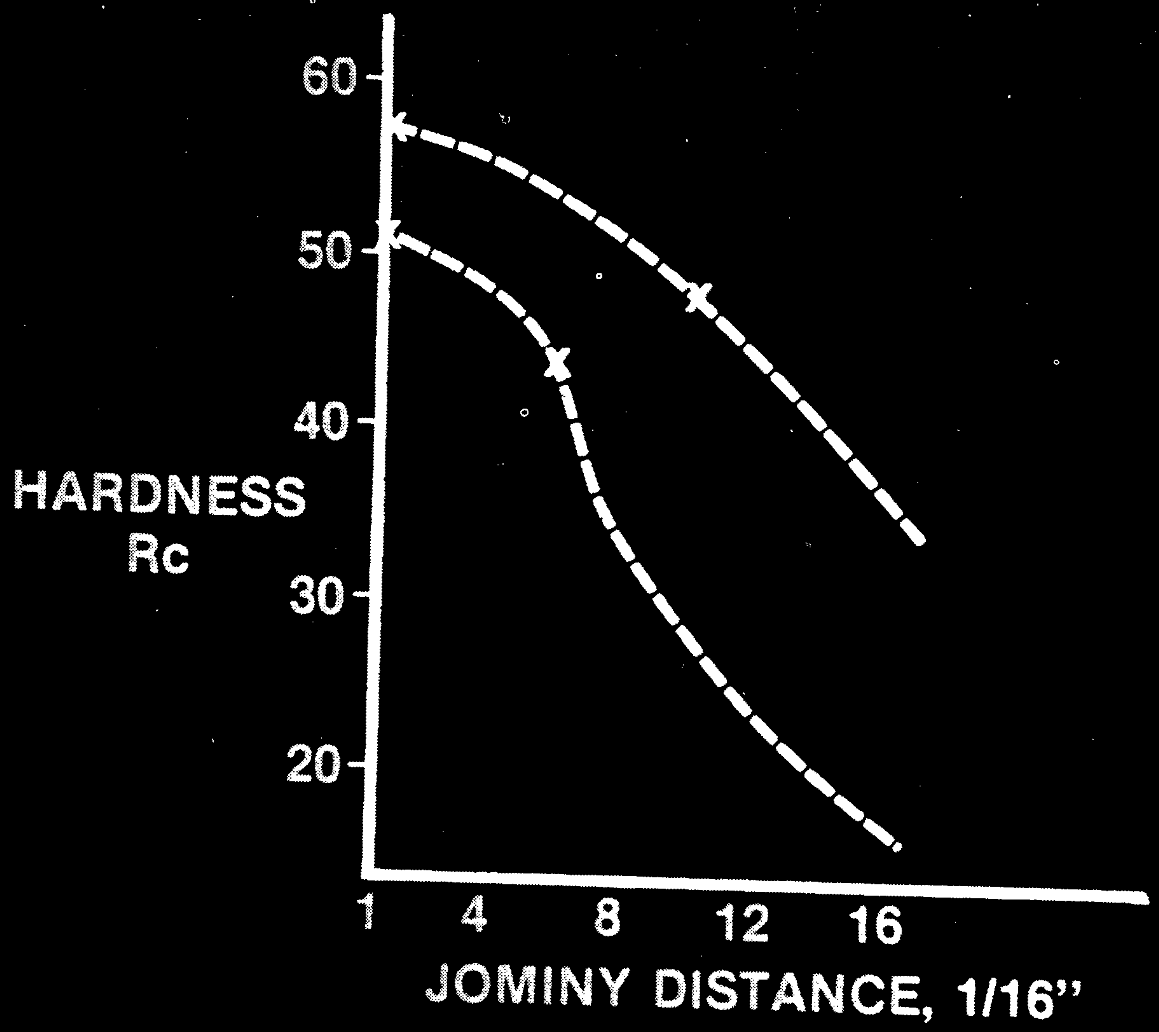
RESTRICTED HARDENABILITY





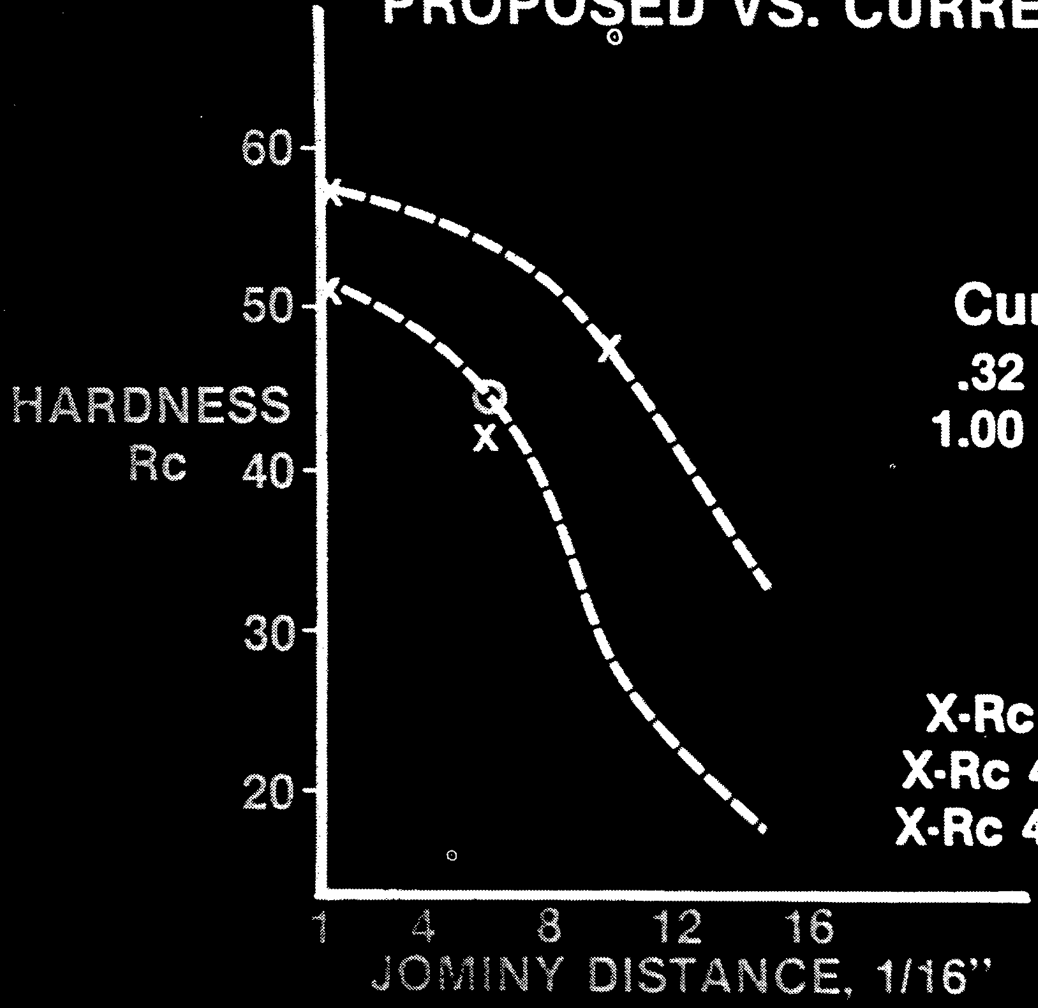


C .32 - .37
Mn 1.00 - 1.30

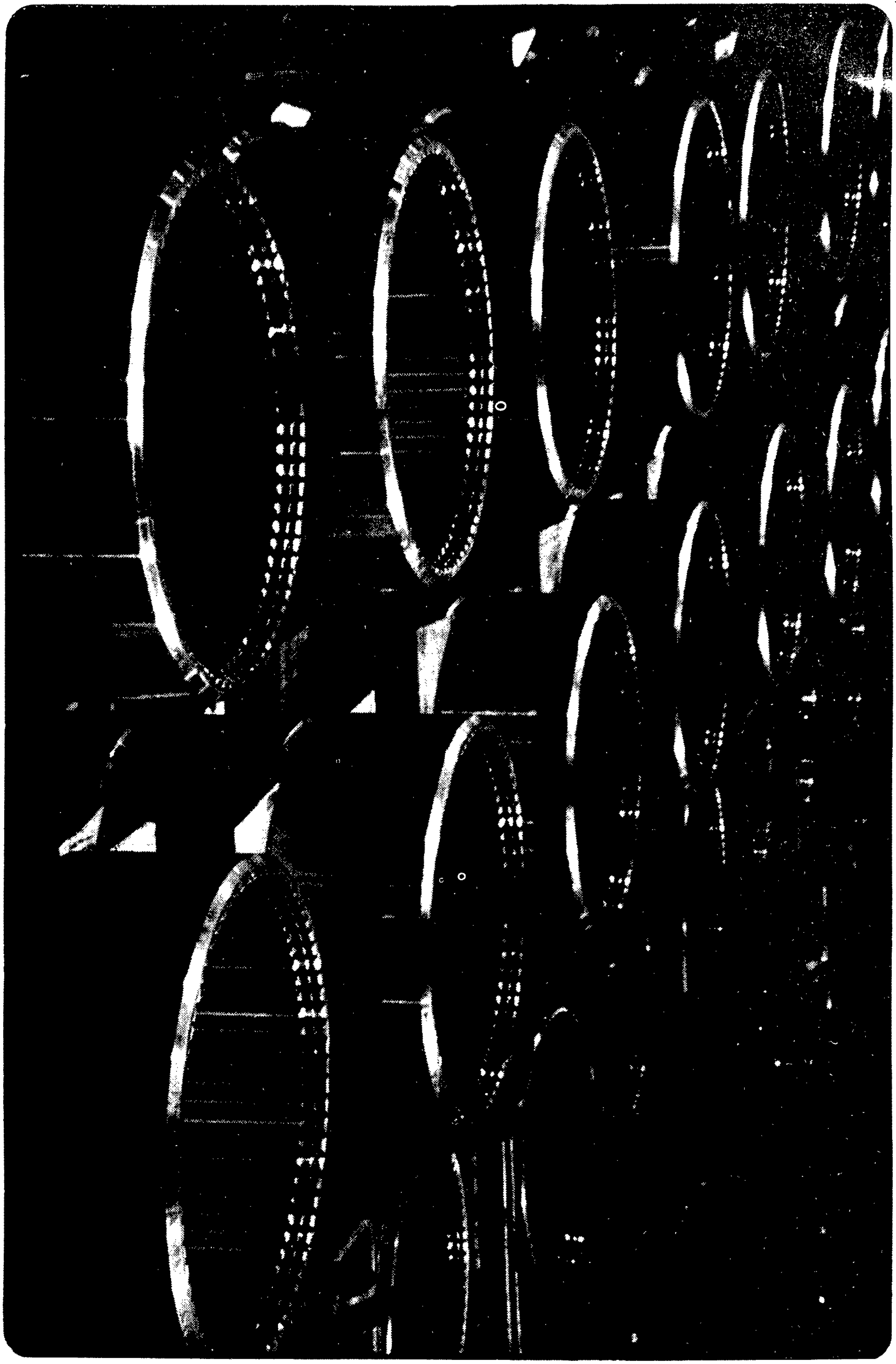


C .32 - .37
Mn 1.00 - 1.30

PROPOSED VS. CURRENT SPECIFICATION

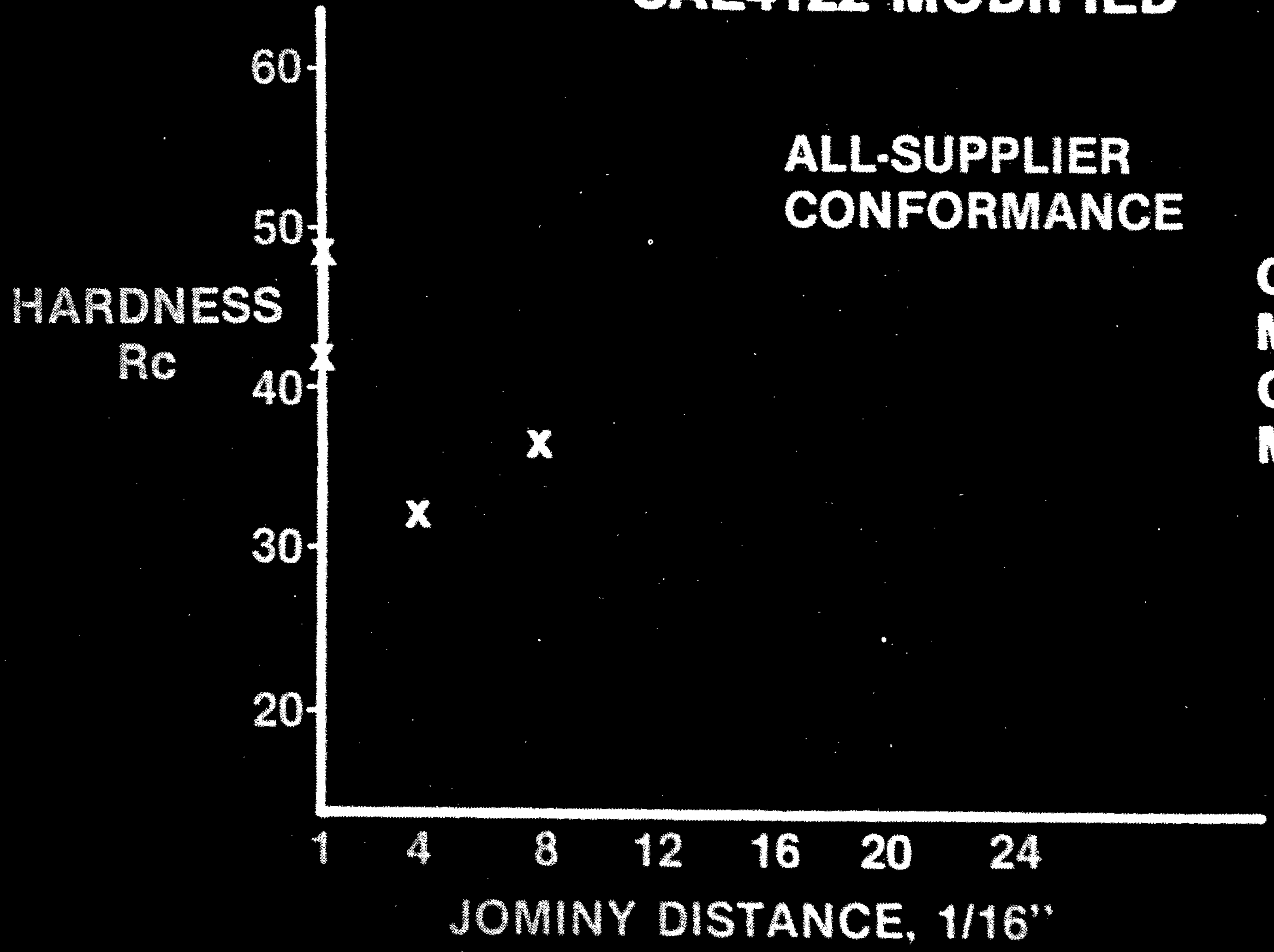


Current		Proposed
.32 - .37	C	.32 - .37
1.00 - 1.30	Mn	1.10 - 1.30
X-Rc 51-58	J1	Rc 51-58-X
X-Rc 43 MIN	J6	Rc 45 MIN-O
X-Rc 48 MAX	J10	Rc 48 MAX- x



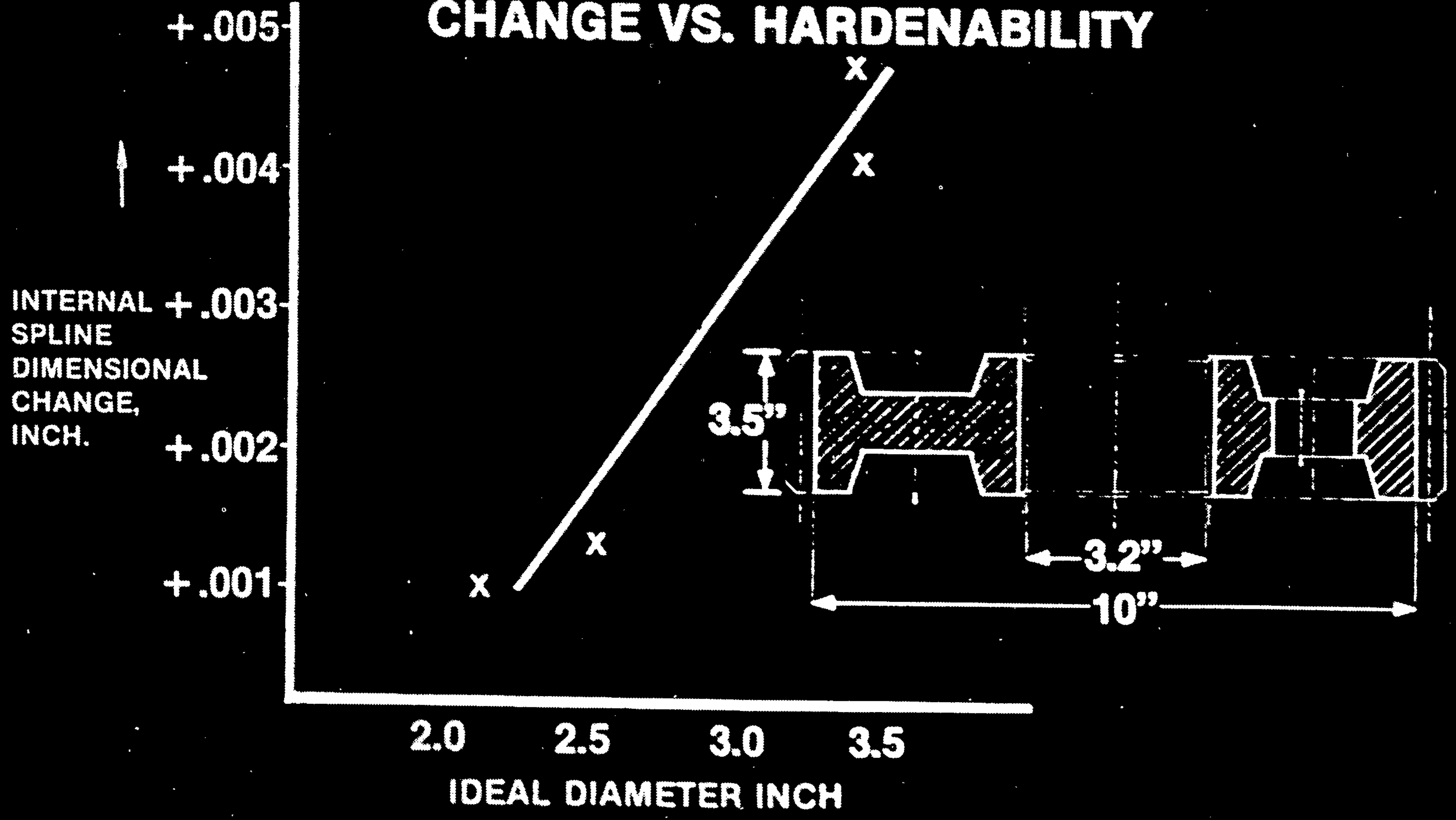
SAE4122 MODIFIED

ALL-SUPPLIER
CONFORMANCE

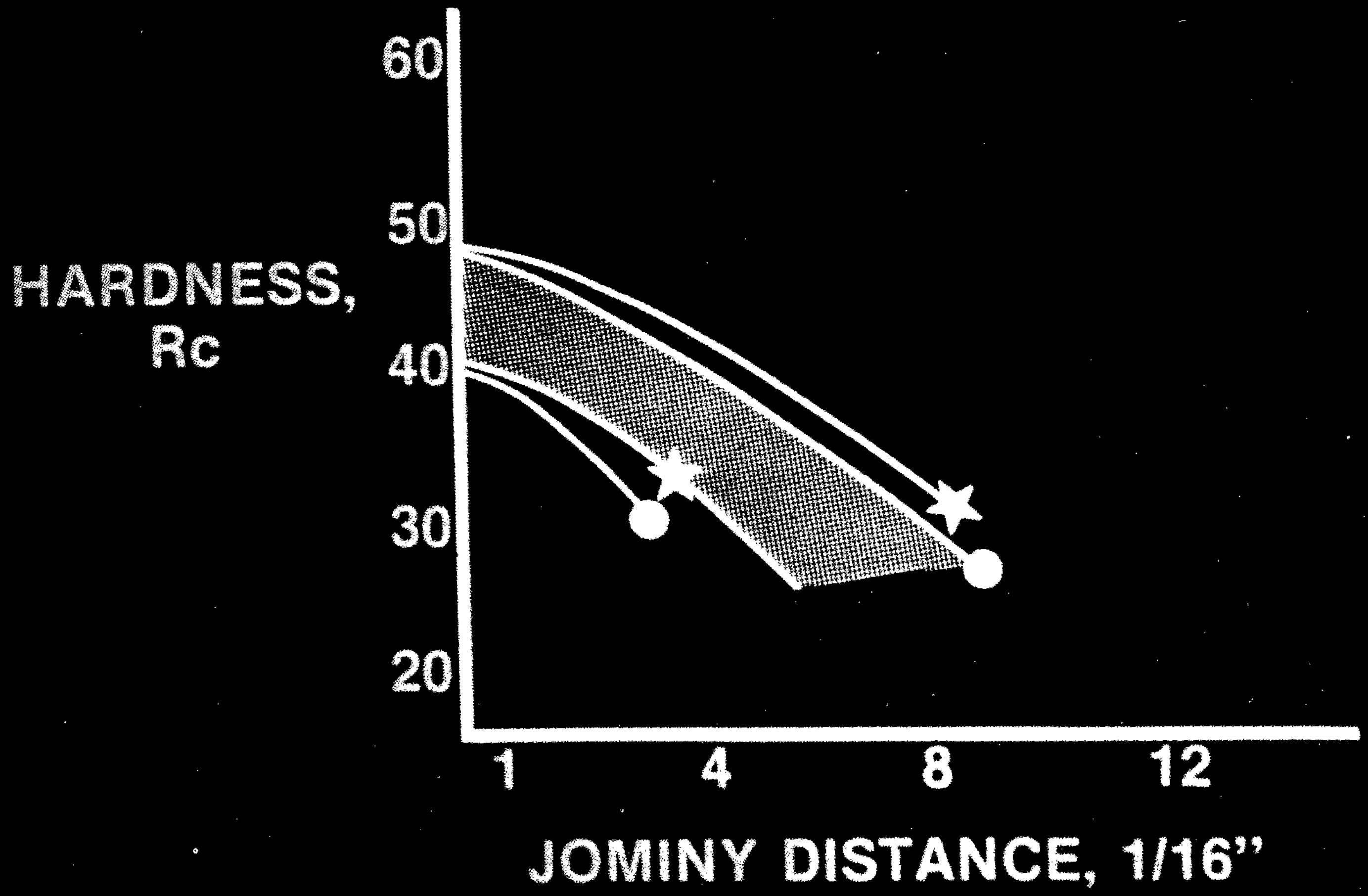


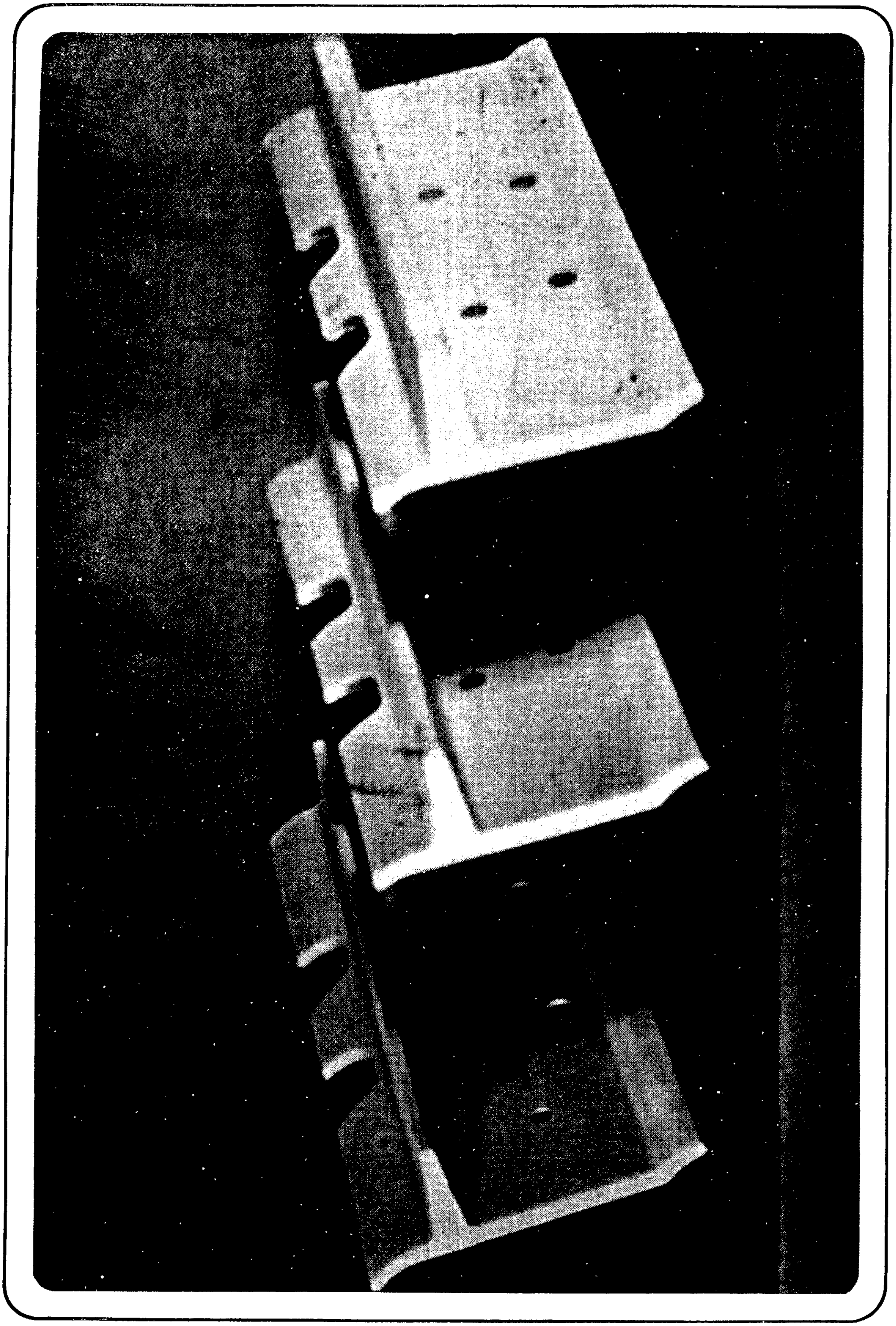
C .19 - .25
Mn .75 - 1.00
Cr .70 - .90
Mo .25 - .35

INTERNAL SPLINE DIAMETER CHANGE VS. HARDENABILITY



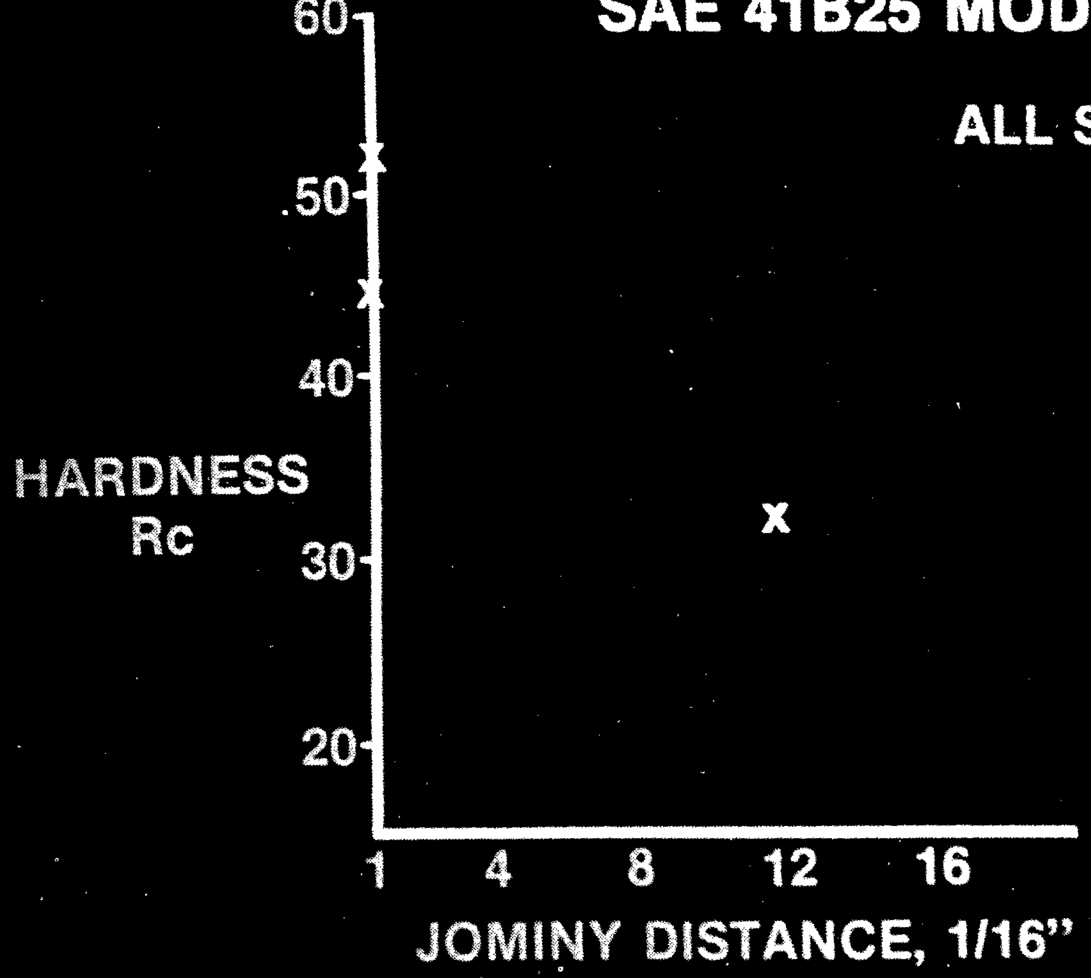
OVERLAPPING HARDENABILITY SPECIFICATIONS





SAE 41B25 MOD

ALL SUPPLIER COMPOSITE

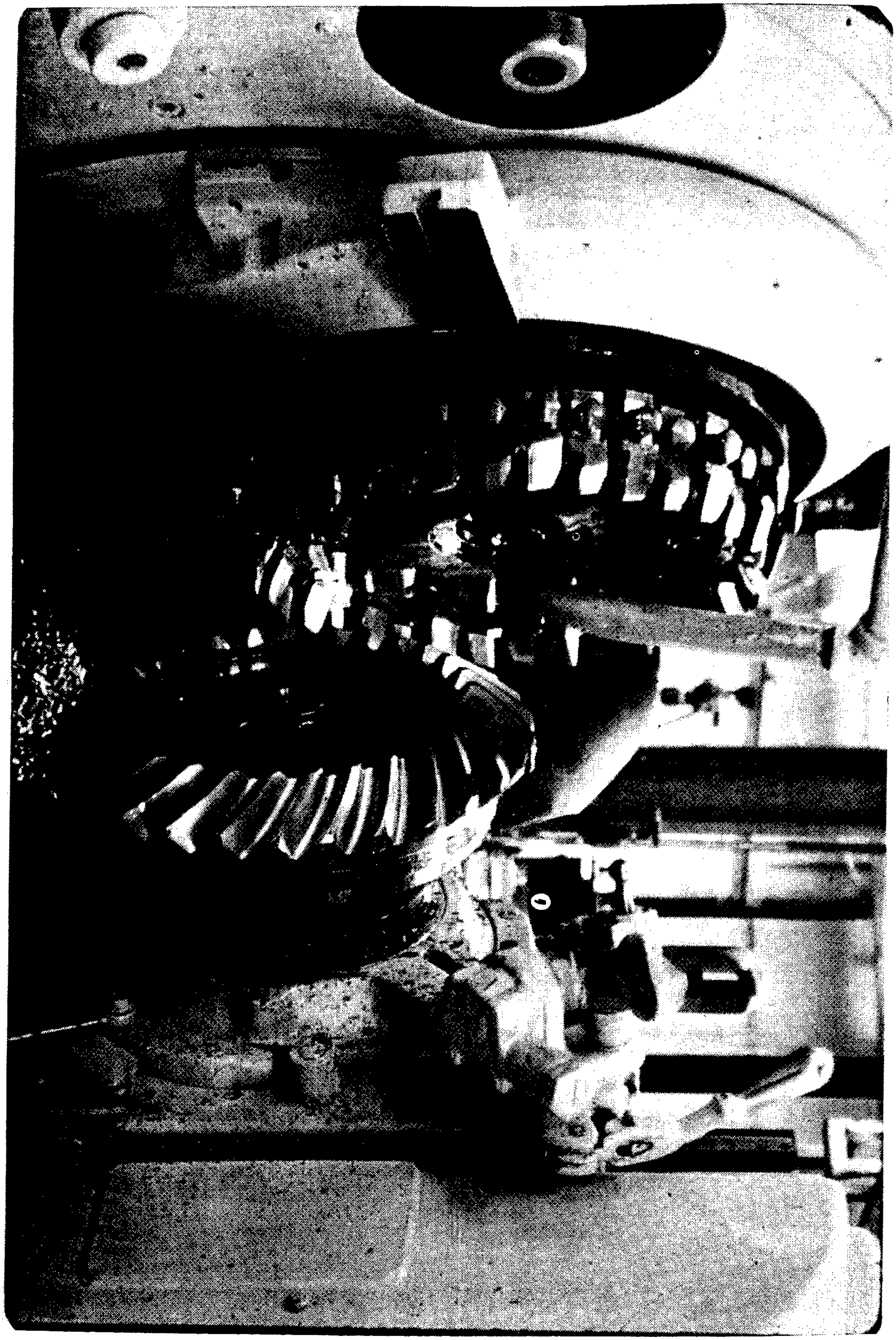


C .23 - .28
Mn 1.00 - 1.30
Cr .45 - .65
Mo .05 - .10

MACHINABILITY

✓ MACHINING OPERATIONS

- TURNING - COATED CARBIDE
- GEAR CUTTING - HSS
  - HOB
  - SHAPE
  - GLEASON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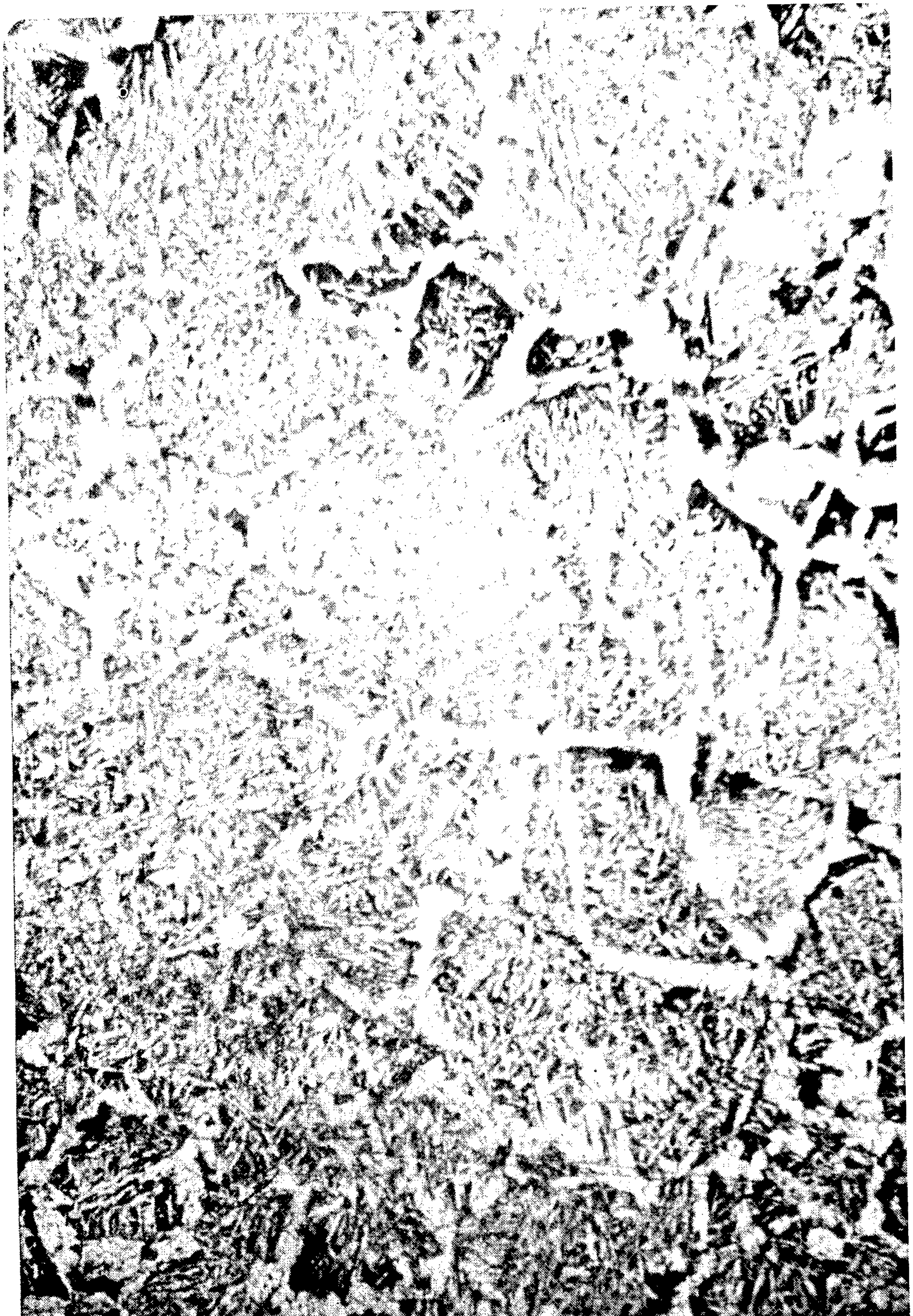
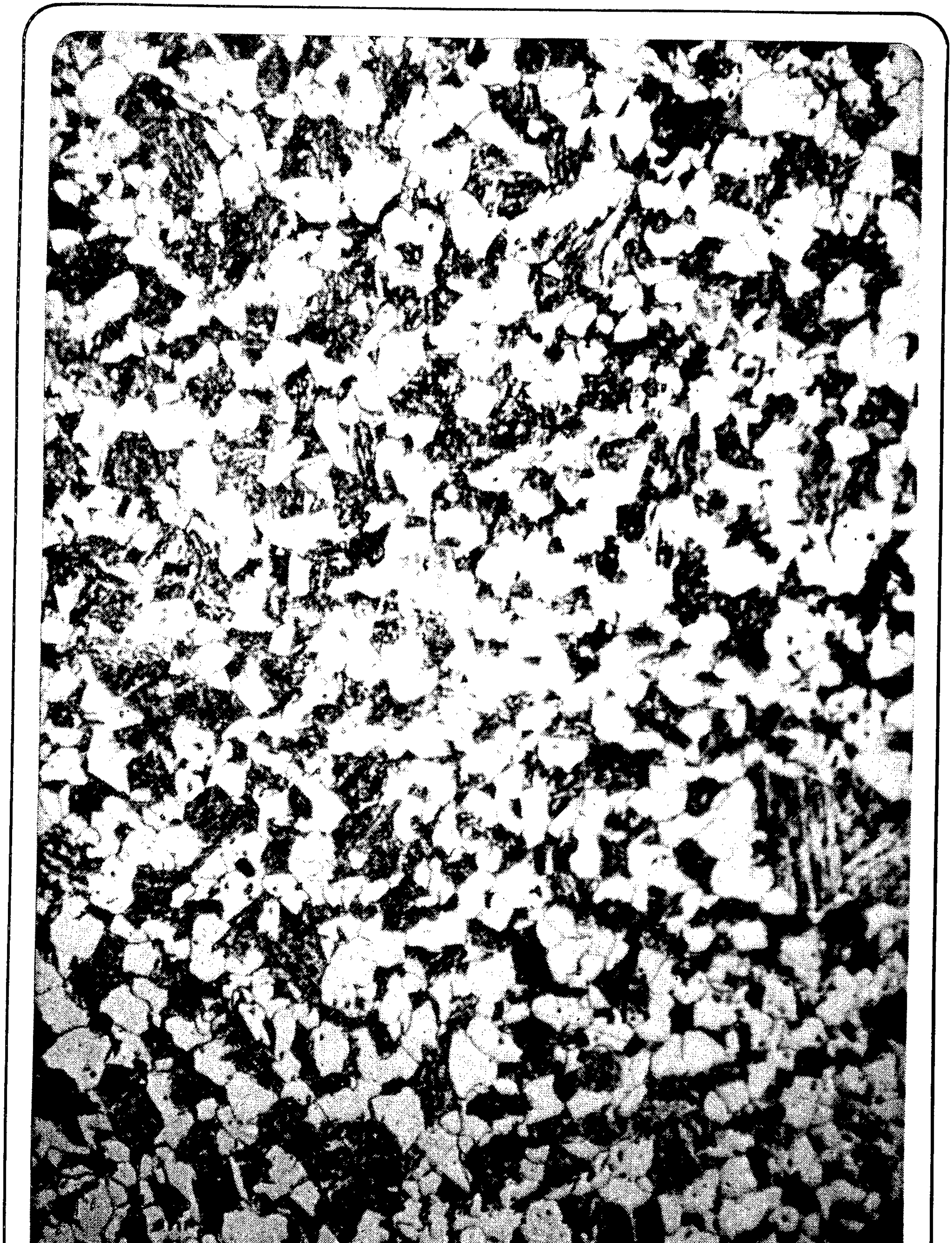
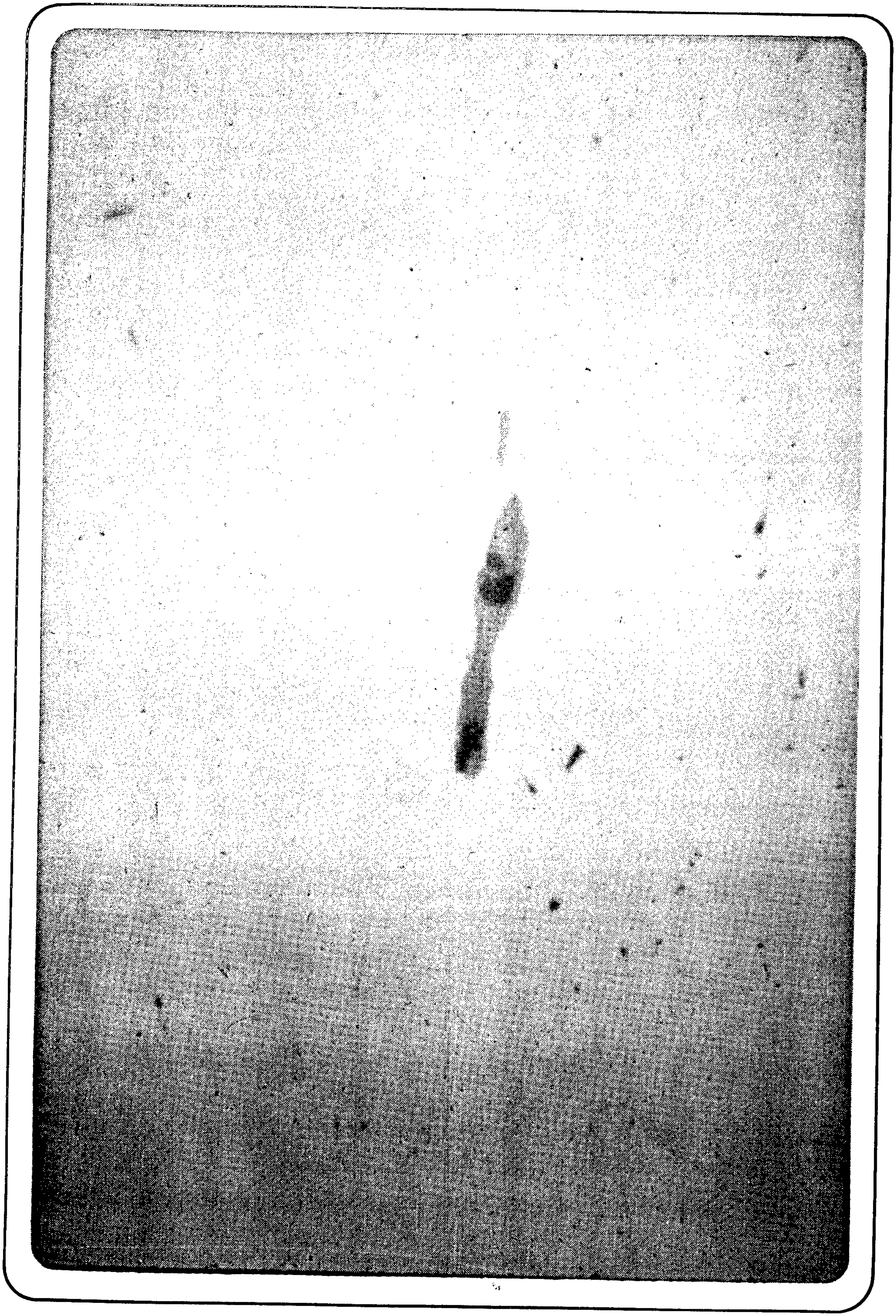
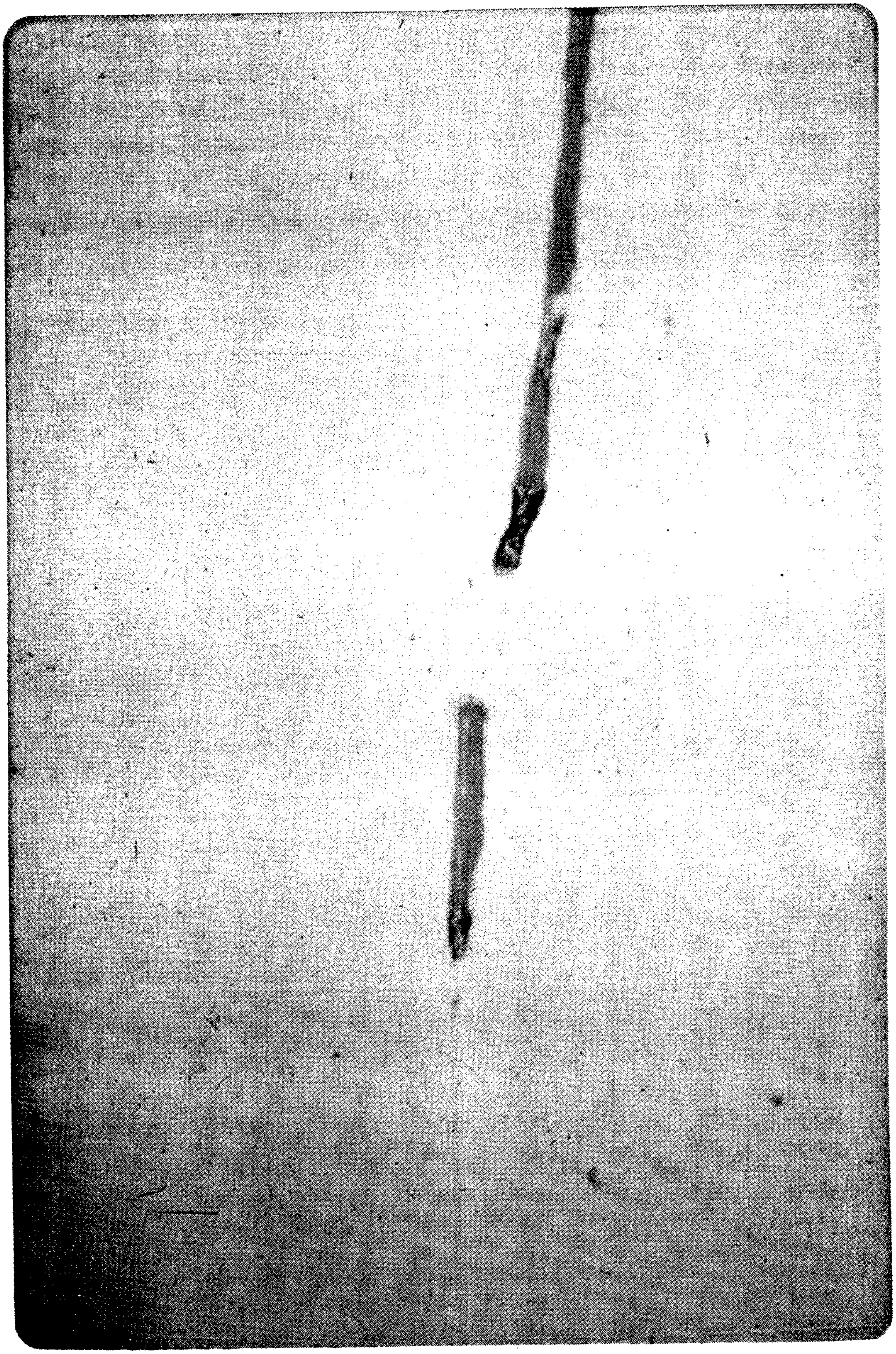




LEADED STEELS





CONTINUOUSLY CAST STEEL OUTPUT
(Domestic)

1981:
JAPAN—70.7%
EUROPE—45.1%

SOURCE: A.I.S.I.

COST ADVANTAGES
OF
CONTINUOUSLY CAST STEEL

— ELIMINATE NEED FOR BLOOMING MILL

— INCREASED YIELD

— REDUCED ENERGY CONSUMPTION

MERITS OF
CONTINUOUSLY CAST STEEL

- BETTER CHEMICAL HOMOGENEITY
- BENEFICIAL INCLUSION MORPHOLOGY & IMPROVED DISTRIBUTION
- IMPROVED SURFACE QUALITY
- PROPERTIES ARE MORE ISOTROPIC

LIMITATIONS OF CONTINUOUSLY CAST STEEL

- CANNOT COLD SHEAR AS CAST MATERIAL
- REDUCTION IS NECESSARY TO HEAL INTERNAL DEFECTS
- LIMITED AVAILABILITY OF BORON & LEADED STEELS
- LOWER TORSIONAL FATIGUE RESISTANCE
- SECTION SIZE AVAILABILITY

SESSION II

USERS' VIEWS ON STEELS NEEDED FOR THE FUTURE

Chemical Equipment

By
Edward A. Kachik
Materials Technology Institute

I am replacing James D. Anderson of the DuPont Company who was originally listed as the presenter in this session. Mr. Anderson regrets not being able to attend; the following brief comments are based upon his intended remarks.

We want to emphasize the uniqueness of the stainless steels and their uses in the chemical process industries. We will always need corrosion-resistant alloys but more importantly alloys that combine corrosion resistance with some other characteristic, among which wear-resistance and high temperature strength are good examples.

I want to emphasize that current applications of specialty materials like the stainless steels resulted only after much evaluation and study on the part of CPI materials engineers, based on the continuing need for selecting the best materials from an economic viewpoint. The materials work well in the chemical process environments and make for continuity in production, a much-needed mode of operation.

Chromium is a unique metal: it confers corrosion resistance when alloyed with iron in amounts greater than about 12%. These alloys, generally termed stainless, provide a wide range of physical and mechanical properties in combination with needed corrosion resistance. As such, the chromium-containing stainless steels have no really satisfactory substitute when used in chemical processing plants. I will give two illustrations of stainless steel usage for which we believe it will be almost impossible to substitute another material, at least from those now known to us. It is applications like these that identify the chemical process needs for new alloys.

The first is for cutting edges used in the production of films and film-like materials. Films like cellophane, Mylar^R, polyethylene and Saran^R come off the processing line as large rolls whose widths range upwards of four feet. For delivery to the customer, widths as small as one to two inches are needed. These are obtained by passing the wide film across slitting knives imbedded in a platen. This is a critical operation: the cut edges of the film must be of high quality, and the keenness of the cutting edge has to be retained for at least several hours or production and customer acceptance suffers. Stainless steel cutlery is mandatory for this service. High-speed steel or carbon steel cutlery, the usual materials for long life cutting edges simply will not work, because a small amount of residual chemical in the film rapidly corrodes and dulls the knives.

A second example is in the polymer spinning operation that converts molten polymer into filaments. The polymer is extruded through a spinneret which contains an extremely large number of very small holes. The operation occurs at an elevated temperature and requires corrosion resistance to the polymer and oxidation resistance so as to preserve the orifice contours of the orifices in the spinneret. Oxidation of the spinneret surface or corrosion of the spinneret holes will adversely affect the operability of the spinneret and destroy the production of clean, continuous filaments.

Stainless steels are unique to the above two uses. Materials other than the stainless steels now used have been tried but have been found wanting in one or more respects. If we are faced with a chromium shortage, and if the stainless steels could not be supplied for applications like these, production of chemical products would suffer.

The possibility of a chromium shortage has connotations much like those we encountered when cobalt supplies were deemed critical several years ago. In one application I know of, Stellite 6^R is needed for a critical wear-resisting part on a polymer processing line. It is the <u>only</u> material found in years of evaluation and testing that combines the appropriate wear resistance and other properties needed for this particular application. In the face of the expected cobalt critical supply situation, the plant undertook a number of programs to develop a substitute. Coatings, welded overlays, recovery of cobalt from worn parts, as well as other materials, were all considered as approaches; none was satisfactory. The situation was deemed so serious that shut-down of the plant was a possibility if Stellite 6^R were no longer available.

Fortunately, cobalt became available in time and no crisis resulted.

The incident dramatically illustrated how important a relatively small item can be, and reinforces our belief that a chromium shortage that limits or eliminates the availability of specialty materials could be equally serious.

In closing, I can only reiterate what the speakers representing other industries have said before me, about their needs. The chemical process industries must have materials that combine corrosion resistance, oxidation resistance, and high temperature strength, along with suitable mechanical and physical properties. Chromium as a metallic element is a vital contributor to materials that provide these combinations of properties. Coupled with the availability of these materials as plate, tubing, piping, pumps, valves and the like, and their ability to be fabricated into vessels and process lines, these materials constitute a resource that the chemical process industries would find almost impossible to do without.

10/27/82

Electric Utility View of the Use of Critical Metals in Steel

R.I. Jaffee, Senior Technical Advisor
Electric Power Research Institute
Palo Alto, California

The selection of steels for the generation of electricity in the United States is dominated by the large size of utility plants and the capital intensiveness of the industry. In general, the lowest alloy content is used that will do the job. This means that the utility industry already is practicing conservation with regard to chromium and other critical alloying elements.

The utility industry is a minor consumer of critical metals. A study of the usage of critical metals was conducted recently for EPRI by A. Servi and S.D. Beggs of Charles River Associates, Boston, Massachusetts.(1) They found the total usage of six potentially critical metals in fossil plants, nuclear plants, and combined cycle plants to be as shown in Table 1(1). As of 1980 there was approximately 600 GWe of installed capacity to generate electricity in the United States, comprised of 9percent nuclear, 41 percent coal, 36 percent oil and gas, 11 percent hydro, and 3 percent storage and other(2). It is estimated that the capacity to generate electricity will increase to about 1000 GWe by year 2000, an average increase of about 20 GWe per year. It must be noted that in the past 10 years the increase in US generating capacity was much less than this. However, there will have to be a substantial increase by year 2000 in order to avoid a major shortfall.

Charles River Associates (1) estimated the average 20 GWe net annual expansion plus retrofitting and maintenance in electrical generating capacity to be 9 GWe nuclear, 11 GWe coal steam, and 2 GWe coal gas combined cycle. Using this estimate, and the critical metal utilization estimate in Table 1, the average annual consumption of critical metals by the electrical utilities for new and retrofitted plants shown in Table 2 was calculated. Taking the cost for 20 GWe increase in capacity, the approximate $135 million contribution by critical metals to capital costs is only $6 per KW. The capital cost for steam plants is roughly $1000 per KW for fossil plants and $1250 per KW for nuclear plants. Thus, critical materials comprise less than 1% of the cost. Should there be an interruption in the supply of critical metals, the most likely result would be an increase in price of metals. Even a three-fold increase in the cost of critical metals would have a negligible effect ($<2\%$) on the capital cost of the power plants.

Another way to view the critical metals problem from the utility viewpoint is to see what percentage of national consumption they utilize, as shown in Table 2. Utilities generally use less than 5 percent of total consumption. In the case of titanium and zirconium utilities utilized about 8 percent of the primary metal production of 27,000 tons of titanium mill products in 1980 and almost all of the 6,000 tons of zirconium metal in 1968.

If anything, utility use of chromium and other critical metals will increase in the future. The current mainstay coal-steam generating plants, subcritical 2400 psi, 1000 F single reheat, will be changing to supercritical plants with higher steam temperatures and pressures. Supercritical plants will employ more highly alloyed steels in the steam generator and high pressure turbine than subcritical plants. The saving in fuel for such plants may be as high as 10 percent. The use of critical metals in fossil plants is dominated by low temperature heat exchangers, not high temperature components. It is felt that the small increase in critical metal usage would be more than offset by the major saving in fossil fuel consumption.

Because of the importance of the generation of electricity to the nation's economy and the small extent of its consumption of critical metals, there will be no effort made to develop substitutes for chromium and other alloying elements used in high temperature alloys. The major changes foreseen in utility needs for steels in the future will be a greater emphasis on quality. The so-called clean steels will replace conventional steels. Such steels will have sulfur contents of 0.002 percent S and phosphorus contents of 0.005 percent P or less. They can be made from scrap by melting in electric furnaces and desulfurized using ladle furnaces after dephosphorizing in the electric furnace. Clean steels also may be made from pig iron, utilizing torpedo car desulfurization, basic oxygen furnace conversion, and ladle furnace deoxidation. In all cases hydrogen can be controlled to less than 1 ppm by vacuum treatment in the ladle furnace and vacuum casting. Silicon deoxidation will be superseded pretty much by vacuum carbon deoxidation. The use of manganese to tie up sulfur as MnS will become much less important with the low sulfur contents of modern clean steels. Thus, the use of manganese will be evaluated on the basis of its effectiveness as an alloying element, rather than a mandatory element essential to tie up the sulfur as an innocuous inclusion. Modern utility steels will minimize silicon and manganese usage because they cosegregate with P and Sn and promote austenitic grain boundary segregation with consequent detrimental effects on susceptibility to temper brittleness and intergranular stress corrosion cracking.

Summary

The electric power industry is a small user of critical metals, and has been practicing conservation of critical metals for many years. The cost of critical metals comprises only a negligible component of overall power plant capital costs, and the industry could pay for probable increases in critical metal costs without significantly affecting the cost of power plants. Because of an anticipated trend to supercritical plants to save fossil fuel costs, it is expected that the utilization of chromium and other critical elements will increase modestly in the future. The future needs of the utility industry will be for the same types of steels utilized at present, but processed with more emphasis on quality than in the past as a result of the advances made in steel making technology.

References

1. Charles River Associates, EPRI Contract TPS 82-621, 1982.
2. EPRI Report No. P-2156-SR, "1982-1986 Overview and Strategy," 1981, pp. 70.
3. Bureau of Mines Bulletin 650, "Mineral Facts and Problems," 1970 edition.

Table 1

Quantities of Potentially Critical Elements in Electric Power Generating Plants. (Short Tons/GWe)

Type of Plant	Cr	Ni	Mo	Co	Ti*	Zr
Nuclear	200	75	25	1	150	40
Coal-Steam	200	150	30	1	30	--
Coal-Gas Combined Cycle	75	100	20	20	--	--

*Assumes half of the nuclear plants and 10 percent of the fossil plants will use titanium condensers.

Table 2

NET ANNUAL AVERAGE CONSUMPTION OF MATERIALS FOR U.S. POWER GENERATNG PLANTS BETWEEN THE YEARS 1980 AND 2000

(Short Tons per Year, Unless Otherwise Indicated)

	Element					
	Chromium	Nickel	Molybdenum	Cobalt	Titanium	Zirconium
Gross Consumption for New Plants	6,305	4,880	1,045	30	1,850	365
Gross Consumption for Retrofitting	4,280	3,840	340	--	660	575-2,410
Total Gross Consumption	10,585	8,720	1,385	30	2,510	940-2,775
(Supply Recycled)	(2,035)	(1,620)	(100)	(25)	--	--
Net Consumption	8,550	7,100	1,285	5	2,510	940-2,775
Value at Long-Run Equilibrium Prices (Millions of 1982 Dollars per Year)	12.8	71.0	15.4	0.1	22.6	9.4-27.8
U.S. Total Consumption	500,000	180,000	33,000	6,600	30,000*	(not available)
Gross Consumption for Power Generation, As a Percentage of U.S. Total	2.1	4.8	4.2	0.5	8.4	(most)

*U.S. consumption of titanium in the metal form only.

Sources: Charles River Associates, 1982. Estimates of total U.S. consumption were rounded from data for the early 1980s in U.S. Bureau of Mines Mineral Commodity Summaries. (See Tables A-7, A-11, A-12, and A-13.)

The Use of Chromium in Steels for Aerospace

By: R.F. Simenz

The Dept. of Commerce conducted a comprehensive study of the "Critical Material Requirements of the U.S. Aerospace Industry", under the National Materials & Minerals Policy Research and Development Act of 1980. The study covered cobalt, chromium, titanium and tantalum and two advanced technologies; rapid solidification and composites. The approach used covered a baseline year of 1980 and a family of projections of aerospace growth in the years 1985, 1990 and 2000, with lower and upper bound cases where upper bound mix contains more military, space and missiles. Replacement, conservation and recycling (RCR) with high and low cases of RCR were also taken into consideration which helps establish a range of minimum and maximum cases.

A baseline case listing of aerospace product requirements for chromium compiled in the NBS study is given in Figure 1 for the years 1980, 1985, 1990 and 2000. These data were then factored for the scenarios discussed above and are compared in bar graph form in Figure 2. An interesting conclusion reached is that R&D with improved RCR is very effective in reducing the risk of shortage of chromium in the long run even under worst case scenario.

Figure 3 shows that engines account for approximately 75% of total chromium usage in aerospace. The chromium used in engines is primarily present in heat resistant alloy compositions. Most of the remaining requirement for chromium (25%) consists of steels and stainless steels for general aerospace applications. This latter application will be addressed in detail in this paper.

As shown in Figure 4 a wide variety of steel alloy compositions are used in a typical large transport aircraft. The applications range from ultra high strength low alloy steels used extensively in landing gear parts and structural fittings to stainless steels used in tubing and ducting. On a weight basis the first category predominates the applications for steel in aircraft, the largest usage being landing gear which represent 75% of the steel used. Low alloy steel has been the accepted service proven material for landing gear for over 20 years. Basically high strength steel is used because it usually provides the lightest weight component. A ship's set of landing gear for a large aircraft may contain over two hundred different part numbers of steel. Typically approximately 80 to 85% of these steel parts will be used at an ultimate tensile strength level of 260 ksi or greater.

Steel parts offer high strength and stiffness which allows a designer more flexibility in configuring a landing gear that will occupy minimum space. This is an important consideration since the volume available in an aircraft for gear stowage is always at a premium, Figure 5. Desired properties for an improved alloy to replace materials in use today are given in Figure 6. Basically we are interested in a steel with at least 260 ksi ultimate tensile strength with improved fracture toughness and stress corrosion resistance compared to current steel alloys. Producibility and cost aspects of advanced technology steels should also compare favorably with those of currently used alloys if they are to be considered. For the past 15 to 20 years there has been little change in the alloy compositions of low alloy high strength steel used in aircraft. One reason for the status quo is that new steel compositions have not been able to meet the stated goals for an improved high strength steel. Some improvement in toughness and stress corrosion resistance has been obtained in developmental steel compositions but the increments of improvement have not been sufficient to warrant the cost of scaling up and generating material characterization data, fabrication practices and design allowables.

There is a favorable trend in the usage of precipitation hardening stainless steels with regard to lower amounts of chromium used on airframes. The use of precipitation hardening bar, forging and casting alloy 17-4PH with 17% chromium, is being decreased in deference to 15% Cr 15-5PH and 13% Cr PH13-8Mo alloys. A catalyst for this trend is the reduced amount of ferrite structure in the lower chromium alloys making them less prone for spurious indications during magnetic particle inspection. Additionally the vacuum melted PH13-8Mo has improved mechanical properties without a compromise in corrosion and toughness characteristics.

Opposite to this trend in reducing the percentage of chromium used in structural precipitation stainless steels is a trend to use increased quantities of these alloys. The service performance of some low alloy steel parts has been unacceptable due to corrosion and stress corrosion behavior. This has caused these parts, such as pins, fasteners, and fittings with from 1 to 5% chromium, to be replaced with a precipitation hardening stainless steel with from 13 to 17% chromium.

Another trend affecting the use of chromium by aerospace is the use of the higher chromium containing 21-6-9 alloy rather than 321 stainless steel for hydraulic tubing. This is due to the superior cold worked mechanical characteristics of the 21% Cr alloy which results in significant weight savings over the 18% Cr 321 grade. Titanium is also used for hydraulic lines but titanium's substantially higher cost, more difficult fabrication requirements and sensitivity to phosphate ester hydraulic fluids have limited its use. A schematic of the hydraulic systems in the L-1011 is depicted in Figure 7 and a view of the hydraulic service center is shown in Figure 8.

Cost reduction has been an effective driver which has resulted in material conservation practice even though that wasn't the original intent. For example large landing gear forgings as shown in Figure 9 have a large buy to fly weight ratio. In recent years trepanning has been used effectively to recover stock which is then used for additional parts. This process is depicted in Figure 10 which also depicts a large machine facility used for this specialized task. Increased use of this approach can be expected in the future. In addition net and near net shape forgings are receiving more attention. This technology offers some conservation in raw material usage.

It is worth noting that the interest in near net shape is not limited to steels. The trend in aircraft is to make increased use of "precision forged" aluminum and titanium, Figure 11. This is relevant to this work shop because of the use of steels for the dies and tools. Lockheed has been a leader in the use of forgings, both conventional and precision. In the L-1011 over 2,500 different forgings are used. We estimate that roughly 14,000,000 pounds of steel were required to produce the required tooling for this quantity of forgings. Analysis of future requirements for chrome bearing steels should consider these substantial and growing needs for aerospace projects, Figure 12.

The severe shortages of titanium during the 1979 time frame caused considerable disruption to aircraft manufacturing activities. Numerous efforts were made to alleviate the shortages through substitution of other materials. In most cases this was found to be unfeasible on existing designs. The lesson learned is equally applicable to steel usage for aerospace; that is short range substitution is seldom practical or feasible in current production applications. However, alternate materials and design approaches can be considered for new projects.

High strength steel is expected to receive competition from titanium, and composite materials as well as hybrid design concepts. Examples of competitive concepts for landing gears and other components are shown in Figures 13 through 15. Nevertheless, steel usage in aircraft is predicted to remain relatively constant as indicated in Figures 16, 17 and 18.

In summary the needs for chromium for the aerospace industry clearly are most critical for high temperature alloys for engine applications. The consumption of chromium in alloys for aircraft excluding engines is a minor part of U.S. consumption, apparently less than 3%. Furthermore, the Department of Commerce concluded these needs could be met through priority usage. The percent usage of steel is predicted to be relatively constant through the 1990's, although titanium, organic and metal matrix composites will offer competition. Innovative alloying concepts that provide the strength and stiffness and relatively low cost of steel but with improved durability and damage tolerance will be welcomed as will improved specialty grades of high strength stainless steels. We are watching RST efforts with great interest, but progress seems to be slow in the application of RST to steel for aerospace structural applications.

FIGURE 1

AEROSPACE INDUSTRY REQUIREMENTS FOR CHROMIUM

(QUANTITY IN SHORT TONS)

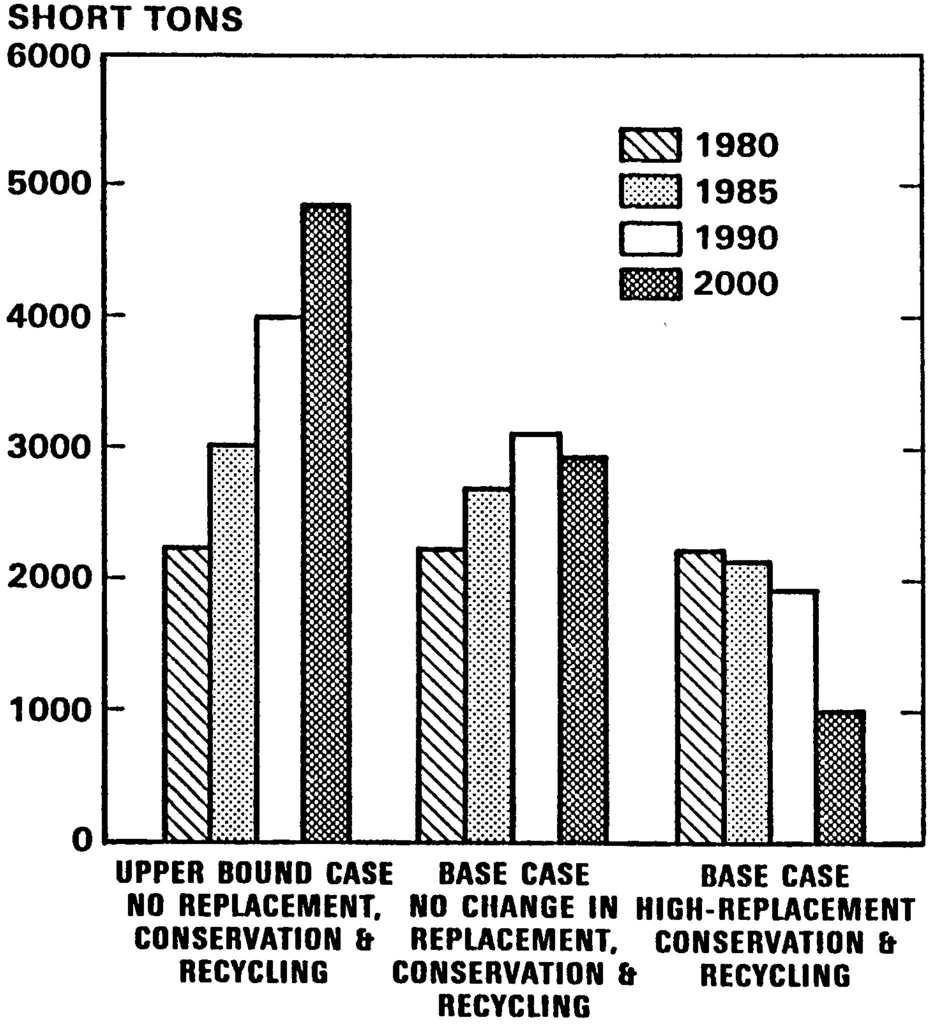
	1980	1985	1990	2000
MILITARY A/C, FXD. WING	127	157	187	178
MILITARY HELICOPTER	23	30	38	38
CIVILIAN HELICOPTER	38	68	76	83
CIVILIAN TRANSPORT	110	129	139	129
GENERAL AVIATION	83	96	96	96
ENGINES, MILITARY, CIVILIAN/SPARES	1683	2024	2342	2170
SPACE AND MISSILE	109	132	159	183
AIRCRAFT PARTS	45	57	63	61

SOURCE: CRITICAL MATERIALS REQUIREMENTS OF THE U.S. AEROSPACE INDUSTRY, U.S. DEPT. OF COMMERCE, OCT. 1981

FIGURE 2

TOTAL AEROSPACE INDUSTRY MATERIALS REQUIREMENTS 1980-2000

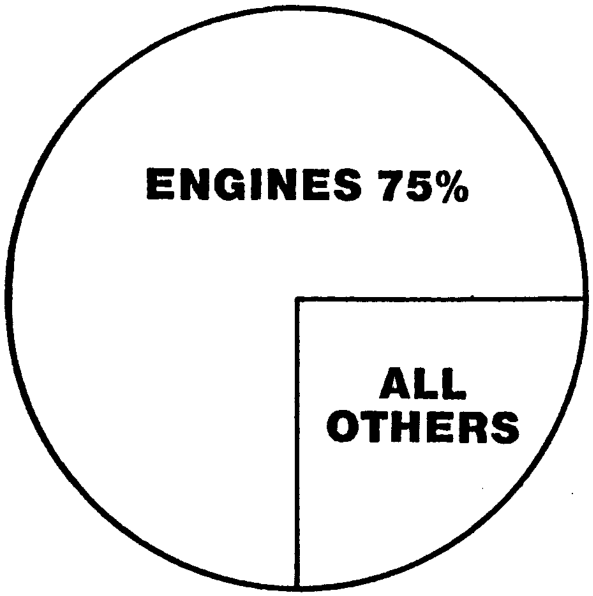
(QUANTITY IN SHORT TONS)
FOR CHROMIUM
(SELECTED DEMAND
SCENARIOS)



SOURCE: BUREAU OF INDUSTRIAL
ECONOMICS, U.S. DEPARTMENT
OF COMMERCE

FIGURE 3

AEROSPACE REQUIREMENTS FOR CHROMIUM



- ESTIMATED AEROSPACE USAGE > 1% < 6% OF U.S. TOTAL CONSUMPTION
- 90% OF AEROSPACE USAGE IS IRREPLACEABLE AT PRESENT TECHNOLOGY LEVELS
- AT LEAST 80% OF VACUUM MELT STEEL ALLOYS CONTAINING Cr IS FOR AEROSPACE

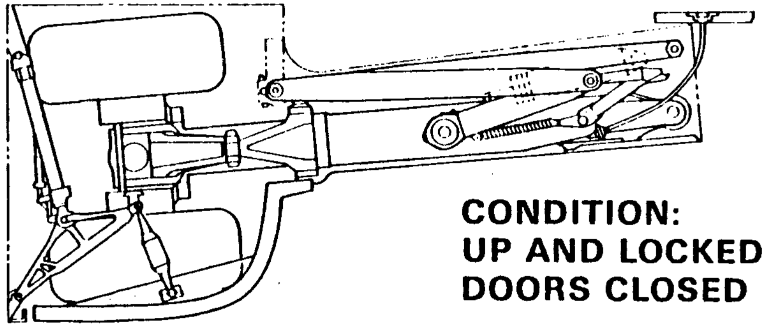
SOURCE: U.S. DEPT. OF COMMERCE STUDY, CRITICAL MATERIALS REQUIREMENTS OF THE U.S. AEROSPACE INDUSTRY, OCT. 1981

STEELS TYPICALLY USED IN AIRFRAME CONSTRUCTION

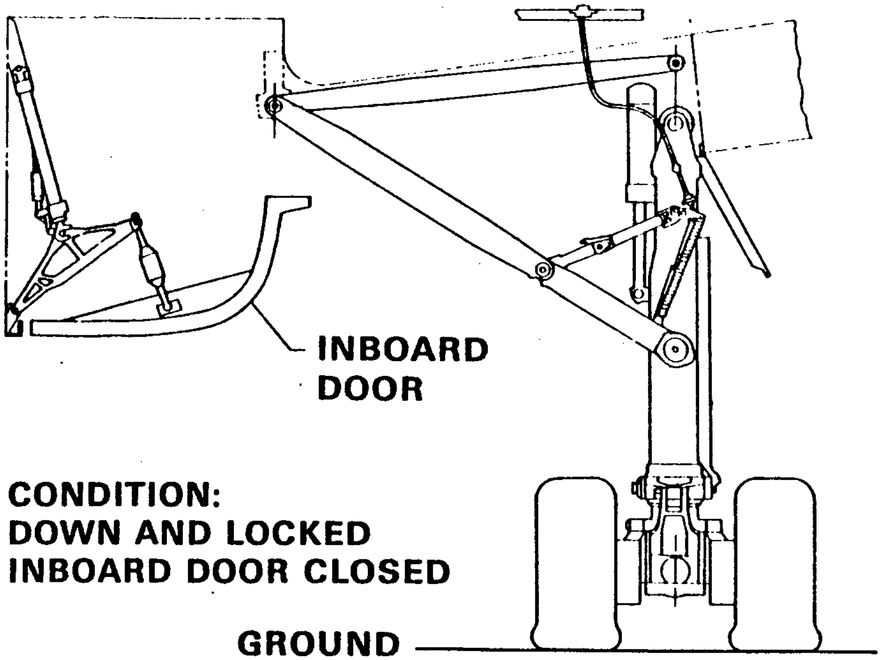
ALLOY STEELS	PRODUCT FORMS	APPLICATIONS
4130, 4140	BAR, FORGINGS, TUBING	FITTINGS, FASTENERS, WELDMENTS
4340, 300M, D6AC, 9Ni-4Co	BAR, FORGINGS	FITTINGS, LANDING GEAR STRUCTURE
H-11	BAR	FASTENERS
52100	BAR	BEARINGS
1085, 6150, 9254	WIRE	SPRINGS, CONTROL CABLE
STAINLESS STEELS		
17-4PH, 15-5PH	BAR, CASTINGS,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

FIGURE 5

CONFINED STOWAGE AREA OF LANDING GEAR



CONDITION:
UP AND LOCKED
DOORS CLOSED



CONDITION:
DOWN AND LOCKED
INBOARD DOOR CLOSED

FIGURE 6

MATERIAL REQUIREMENTS FOR LANDING GEAR STEEL

- HIGH STRENGTH COMBINED WITH MAXIMUM DAMAGE TOLERANCE AND DURABILITY
- CORROSION AND STRESS CORROSION RESISTANCE
- TOUGHNESS
- FATIGUE RESISTANCE
- THROUGH HARDENING
- LOW MATERIAL COST, LOW FABRICATION COST

GOALS

F_{tu} = 270Ksi [illegible] MIN.
K_{Ic} = 80 Ksi $\sqrt{in.}$ MIN.
K_{Iscc} = 20 Ksi $\sqrt{in.}$ MIN.

FIGURE 7

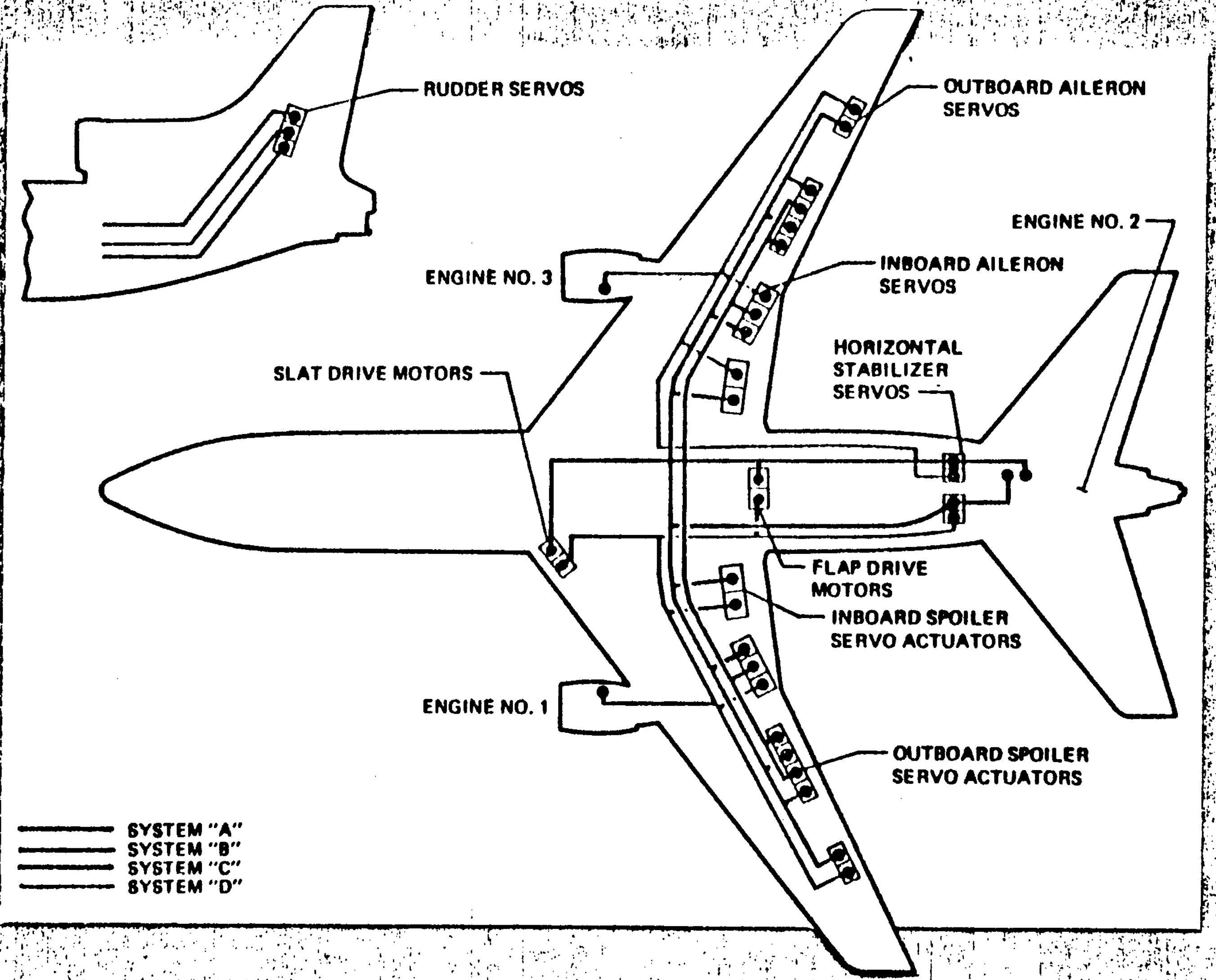

RUDDER SERVOS
OUTBOARD AILERON SERVOS
ENGINE NO. 2
ENGINE NO. 3
INBOARD AILERON SERVOS
HORIZONTAL STABILIZER SERVOS
SLAT DRIVE MOTORS
FLAP DRIVE MOTORS
INBOARD SPOILER SERVO ACTUATORS
ENGINE NO. 1
OUTBOARD SPOILER SERVO ACTUATORS
SYSTEM "A"
SYSTEM "B"
SYSTEM "C"
SYSTEM "D"

FIGURE 8

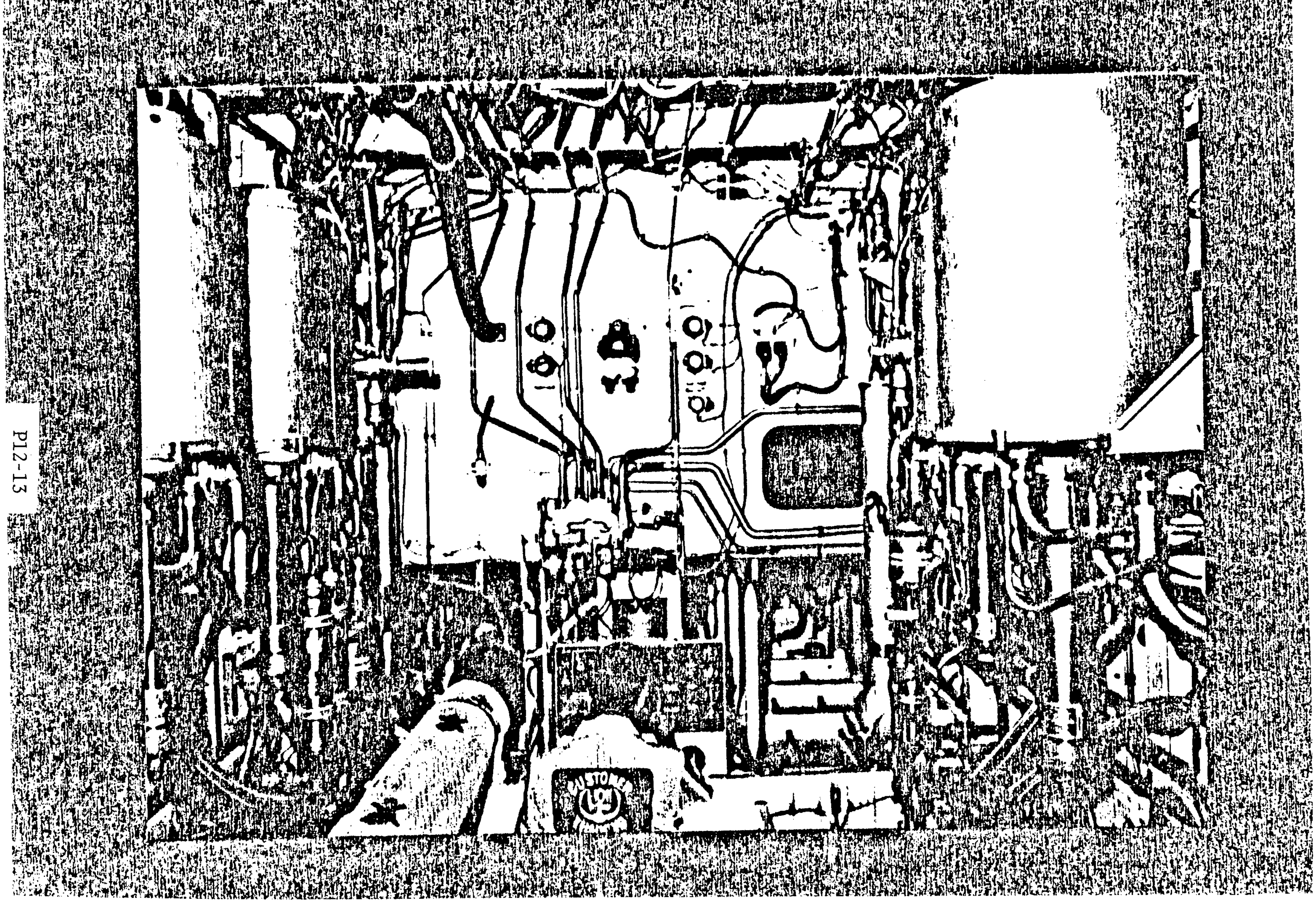


FIGURE 4

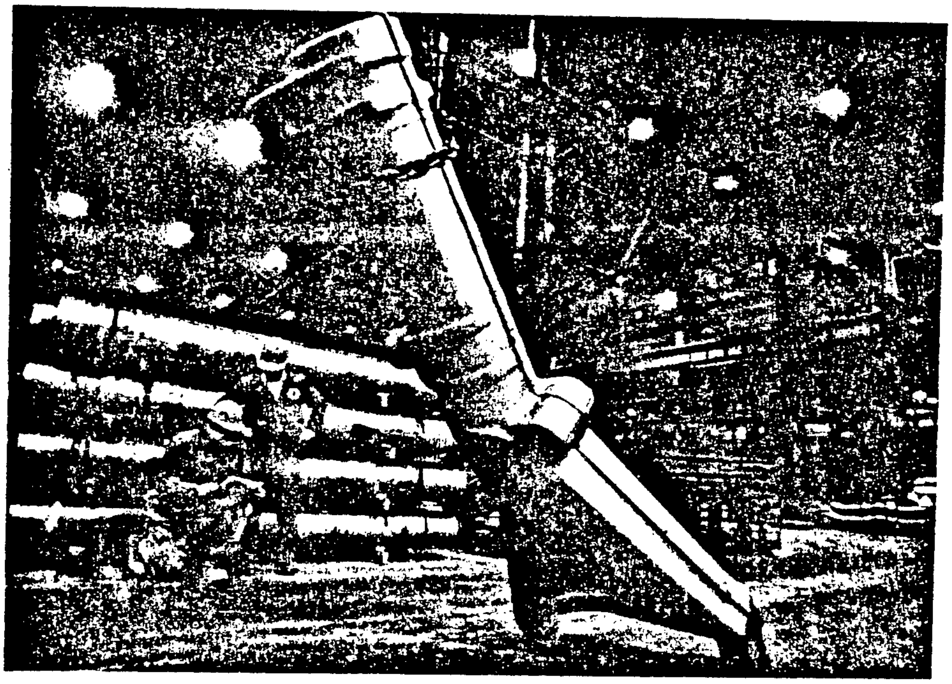
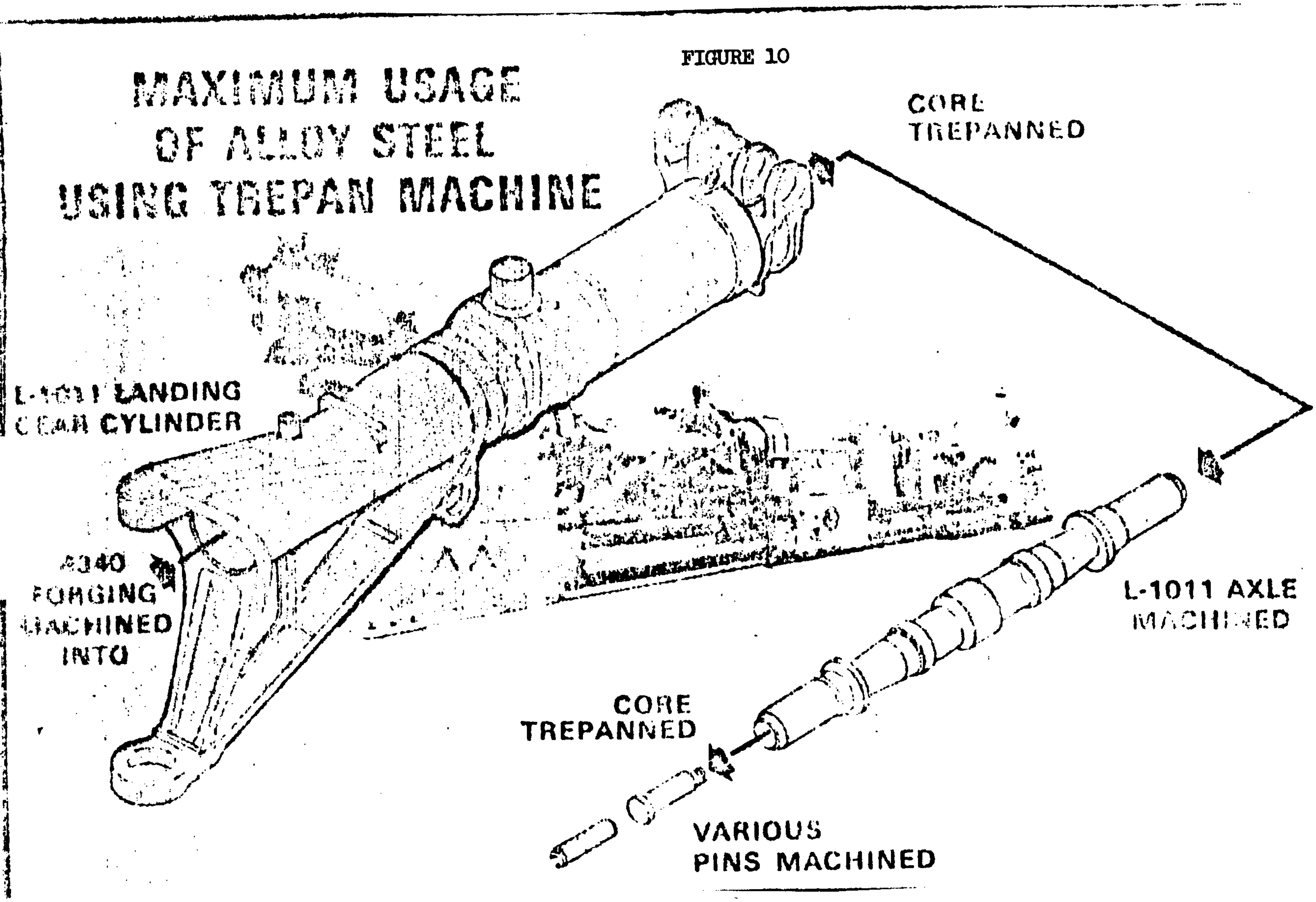


Figure 9 - L-1011 Main Landing Gear Cylinder Forging

FIGURE 10



MAXIMUM USAGE OF ALLOY STEEL USING TREPAN MACHINE

FIGURE 11

PM ALUMINUM FORGINGS OFFER THE FOLLOWING POTENTIAL BENEFITS

- LARGER CONVENTIONAL FORGINGS ON A GIVEN PRESS SIZE AND NEW CONFIGURATION POSSIBILITIES
- GREATER USE OF PRECISION FORGINGS

CURRENT L-1011 USAGE	**POTENTIAL IN NEW DESIGN**
1,000 PRECISION FORGINGS MAX. PLAN VIEW AREA – 200 SQ. IN.	UP TO 400 SQ. IN. PLAN VIEW AREA PERMITS 800 MORE PRECISION FORGINGS THAN CURRENTLY USED • AVOIDS 20,000 LBS OF MACHINED CHIPS PER L-1011 SIZE A/C AND SAVES ≈ $200,000 PER A/C

FIGURE 12

STEELS USED FOR TOOLING IN AIRFRAME MANUFACTURE

FORGING DIES

ALLOY	
6G	1.0% Cr
6F2	1.0% Cr
H-12	5.0% Cr HOT WORKING ⇒ Press X 2.0% Cr

FABRICATION TOOLING

ALLOY	
S-1	1.50% Cr
O-1	.50% Cr
D-2	12.0% Cr

ESTIMATED REQUIREMENT FOR FORGING DIES FOR A LARGE TRANSPORT ≈ 14,000,000 POUNDS

FIGURE 13

MLG SHOCK STRUT SIDE BRACE

HYBRID DESIGN

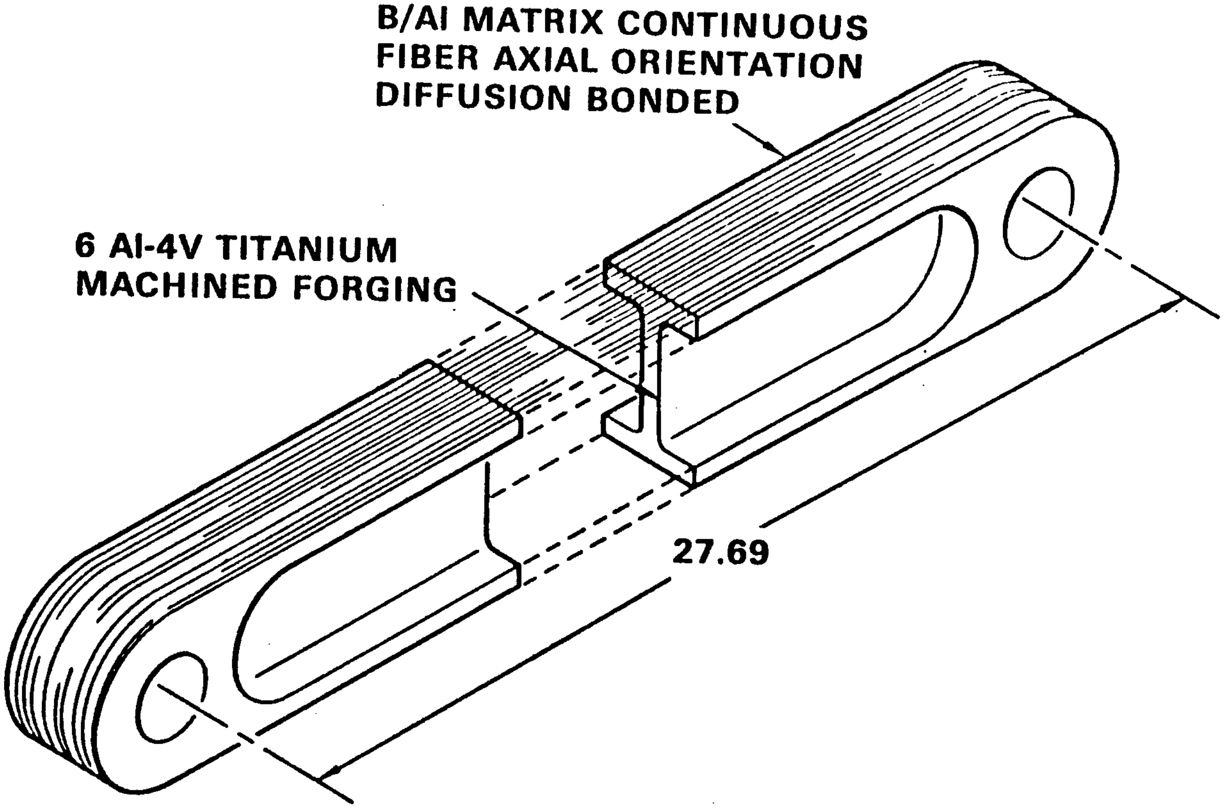


FIGURE 14

ALTERNATE DESIGN APPROACHES

CYLINDER

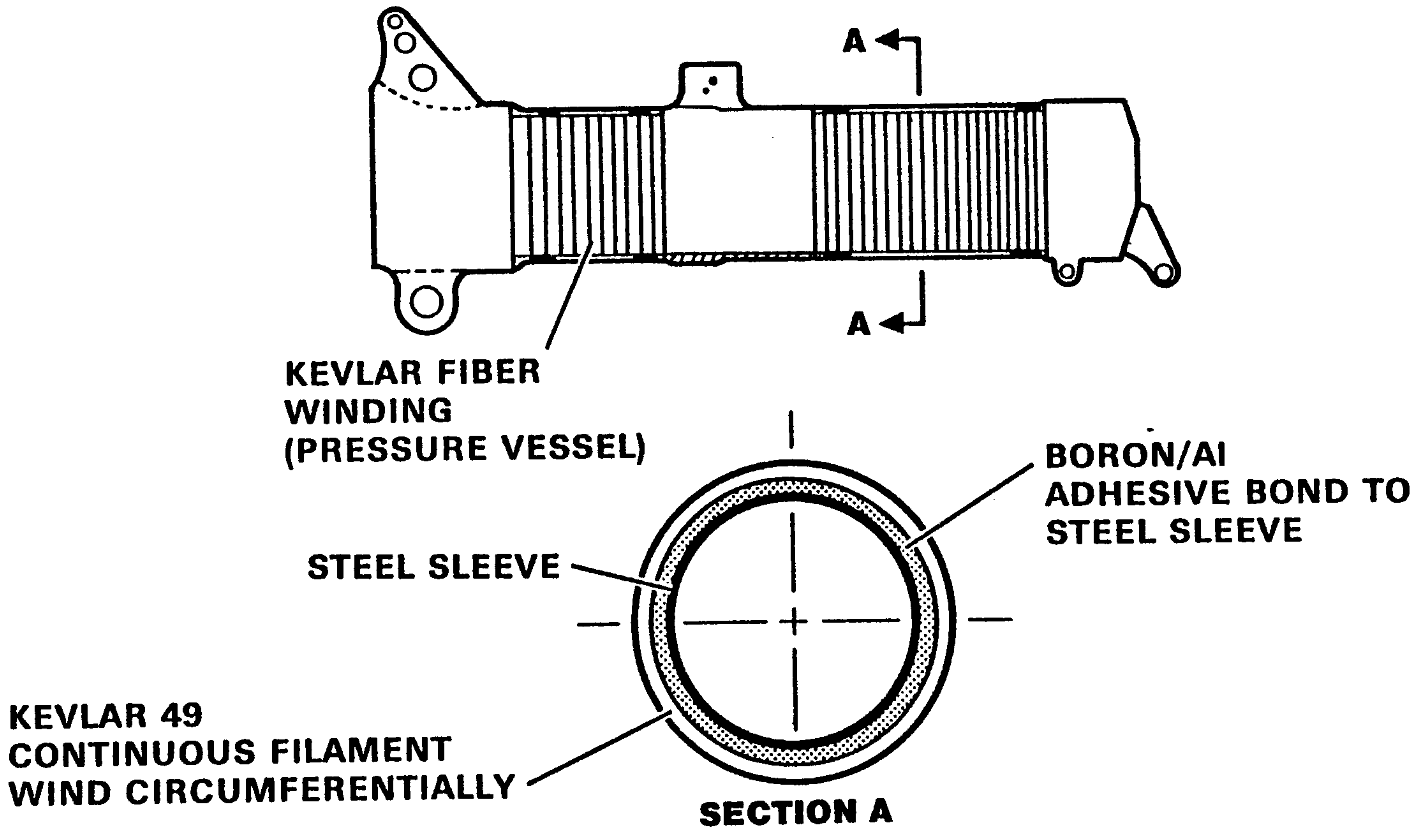


FIGURE 15

ALTERNATE DESIGN APPROACHES

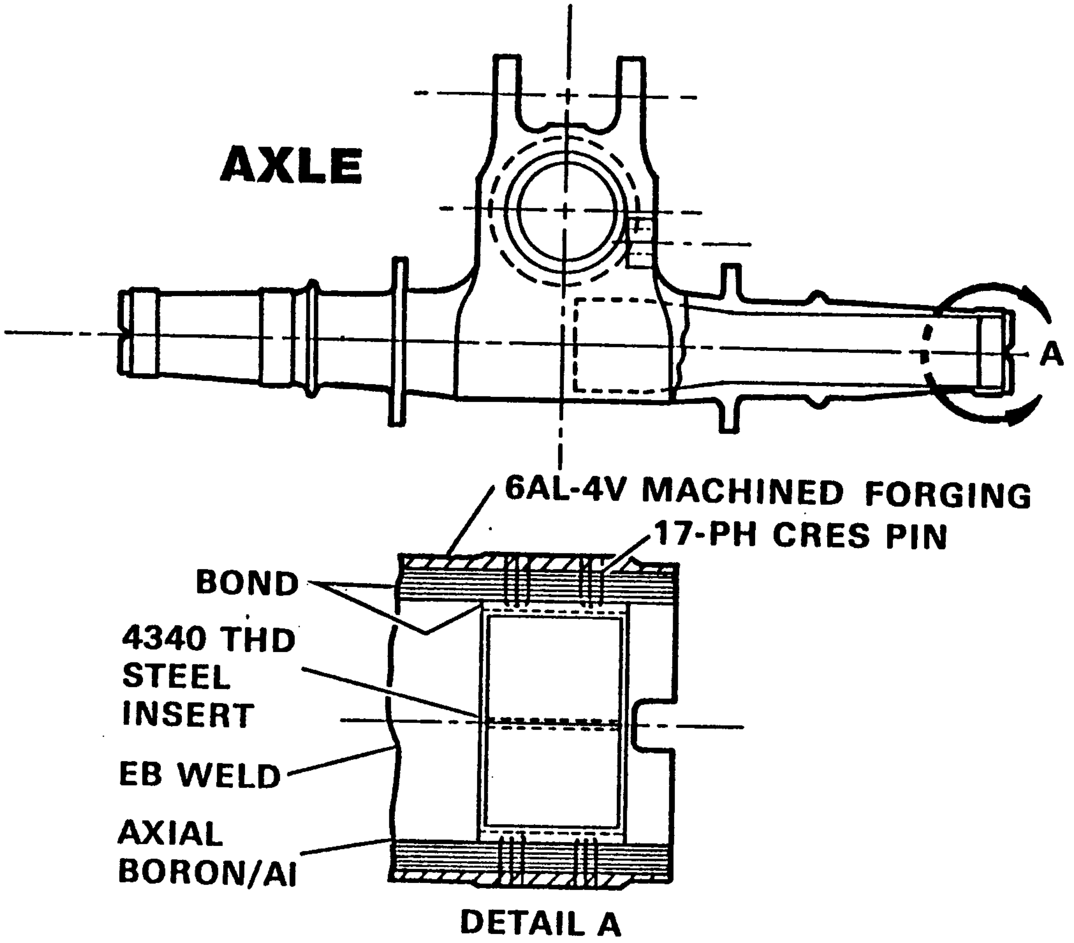
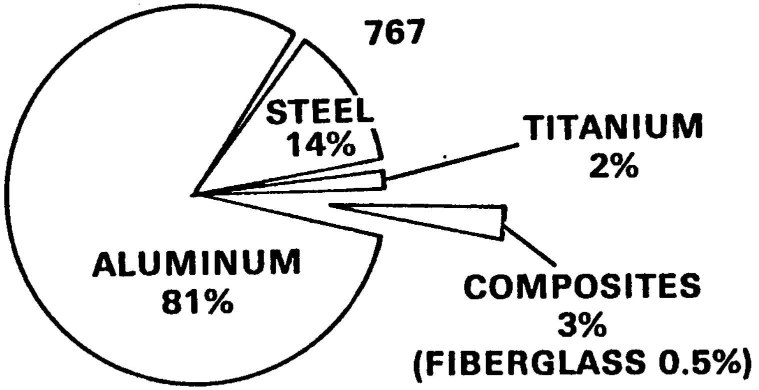
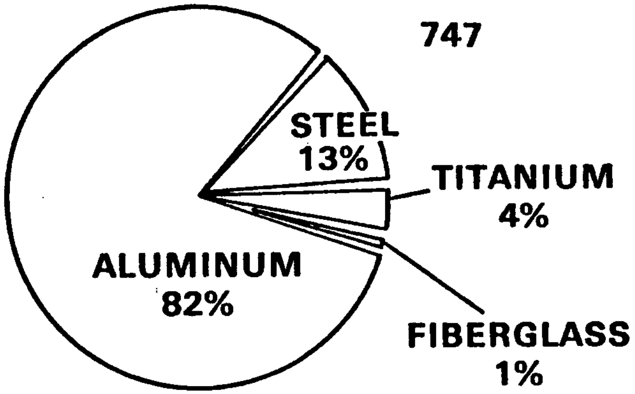
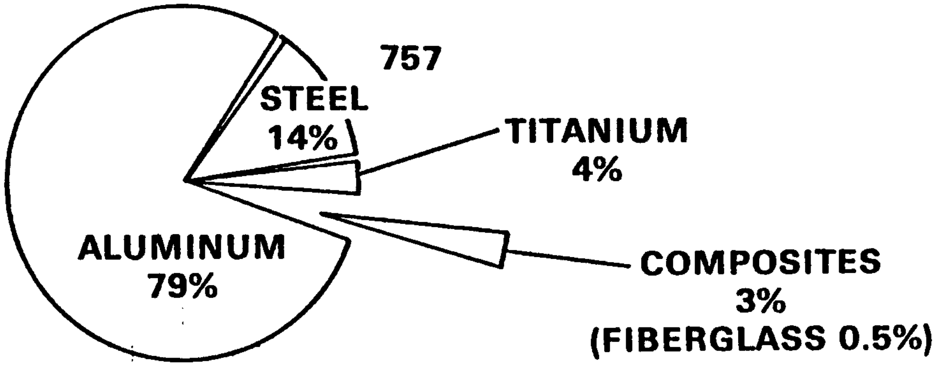


FIGURE 16

STRUCTURAL MATERIALS USAGE



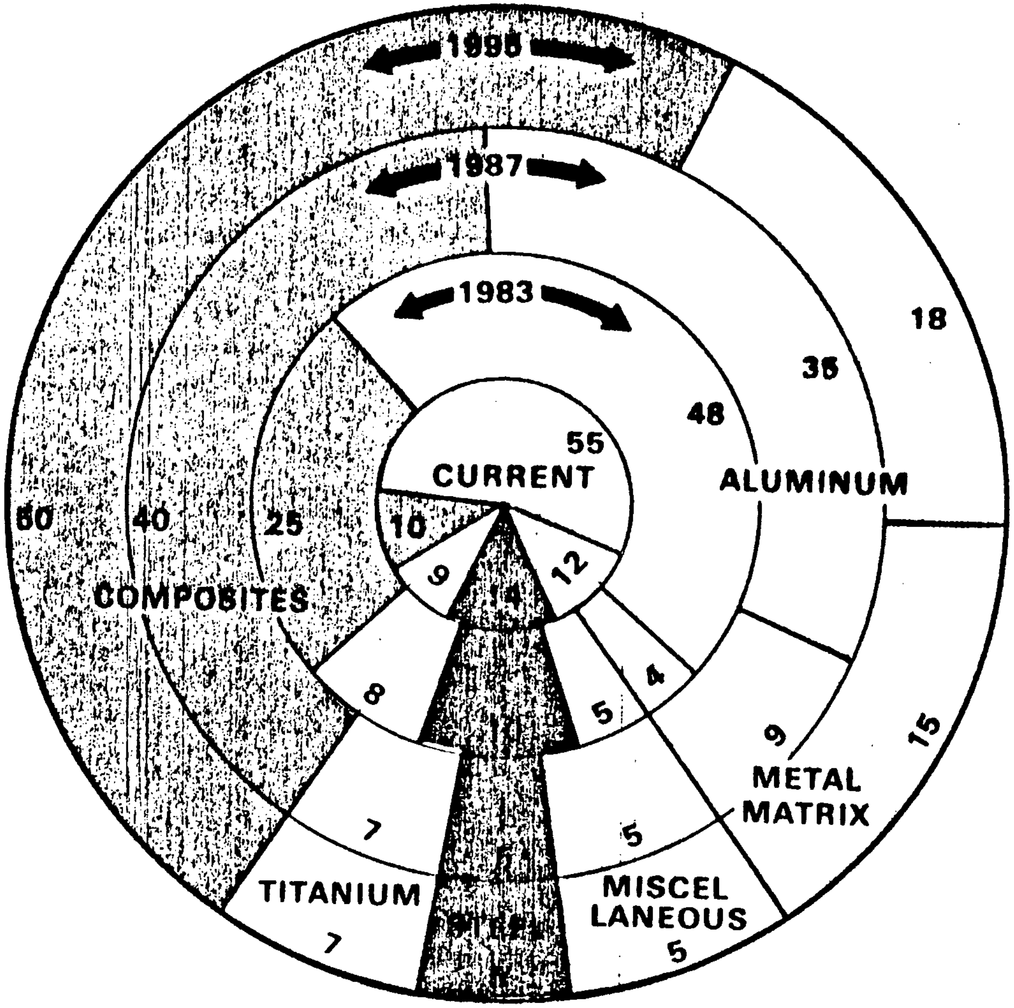




SOURCE: U.S. DEPT. OF COMMERCE STUDY, CRITICAL MATERIALS REQUIREMENTS OF THE U.S. AEROSPACE INDUSTRY, OCT. 1981

FIGURE 17

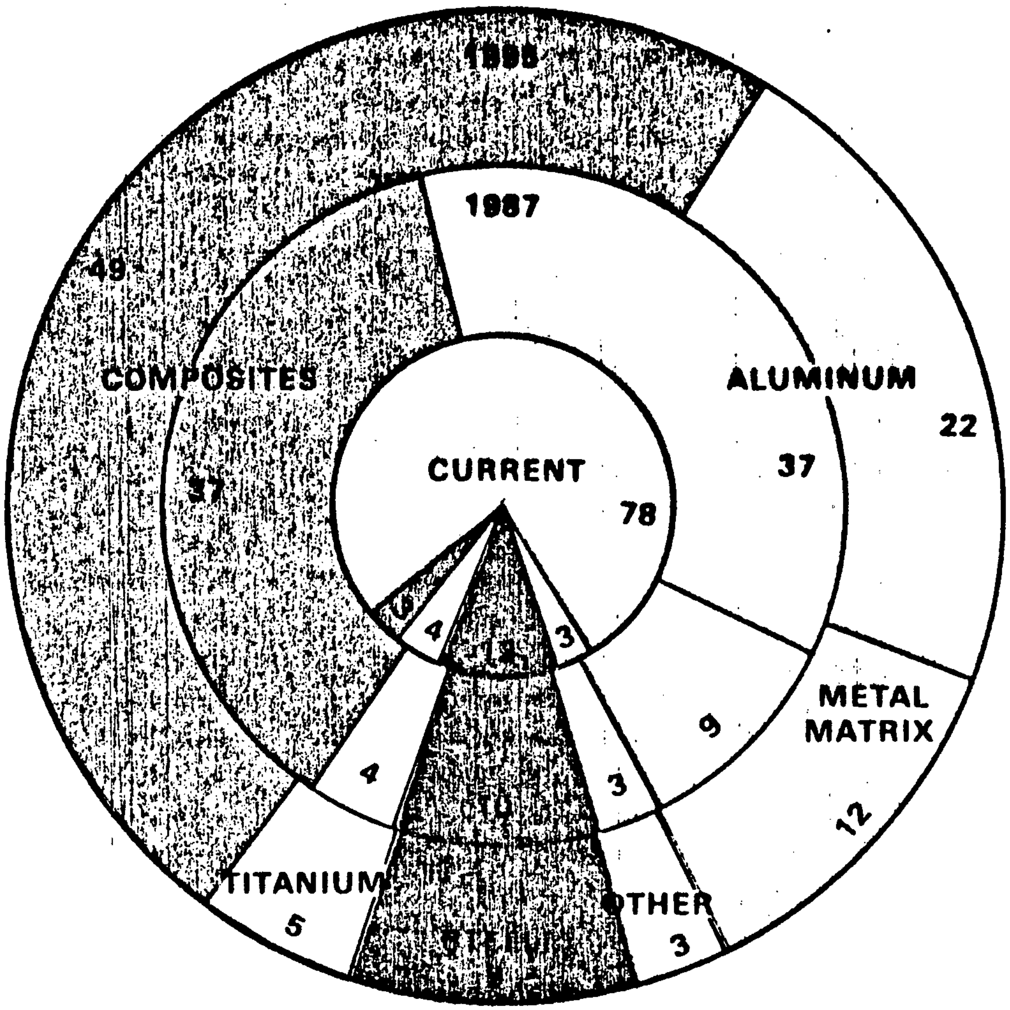
PERCENT MATERIAL DISTRIBUTION



CONVENTIONAL FIGHTER

FIGURE 18

PERCENT MATERIAL DISTRIBUTION



TRANSPORT AIRCRAFT

USERS' VIEW - OIL COUNTRY USAGE TRENDS IN CRITICAL MATERIALS FOR STEELS OF THE FUTURE - CHROMIUM

Prepared by

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Introduction

Metals in which chromium is present to enhance mechanical properties or corrosion resistance have experienced accelerated usage in recent years in oil and gas production. This trend can be discerned for low alloy steels, the traditional martensitic and austenitic stainless steels, and the moderate to high nickel-based alloys. In many instances, these chromium-bearing metals compete economically with alternate metals or with other operating schemes wherein the benefits of chromium are not crucial. In some instances, chromium is critical to the timely development of our hydrocarbon resources.

Two arenas of exploration and production have provided the impetus for this accelerated usage:

1. Deep geological zones where the hydrocarbon reservoirs are contaminated with acid (H_2S and CO_2) gases and brine, and
2. Enhanced oil recovery projects using CO_2 as a miscible solvent to promote additional production from reservoirs (often long-standing) of low or declining response.

Prepared for Workshop on "Trends in Critical Materials Requirements for Steels of the Future - Conservation and Substitution Technology for Chromium", Vanderbilt University, October 4, 1982

Deep Horizons

The interest in deep geological zones as a source of potential gas supply has increased dramatically during the past decade. In the United States in 1981, 1,066 wells were drilled below 15,000 feet (5,000 m)[1]. The deepest well of the year was 28,700 feet (8,700 m). Figure 1 illustrates the growing activity in deep drilling. Approximately 600 of these 1,066 wells successfully located hydrocarbons.

Much of the challenge associated with producing from deep reservoirs arises from the high pressures (varying from 0.45 to 1.0 psi /ft of depth), high temperatures (400 to 600°F/200 to 315°C), and often hostile environments containing CO_2, H_2S, S, and brine. High pressures imply high strength metals to resist the tensile, collapse, and burst loads. Hostile environments demand effective corrosion control generally either by inhibition or use of corrosion resistant alloys. Plastic coatings may serve a palliative role when not limited by high temperatures or aggressive fluids.

CO_2 Floods

Numerous existing oil fields in the U.S. exhibit only low fractions (1/5 to 1/2) of recovery of the original oil in place. Enhanced oil recovery (EOR) projects increase the ultimate recovery, although still at fractions of the original reservoir content. Water flooding to maintain production is common. Further enhancement by tertiary techniques such as surfactant floods, thermal floods, and miscible CO_2 floods is increasing. [2] For the latter, several sources of CO_2 are used including offgas of combustion processes and production from naturally occurring reservoirs. [3,4] CO_2-based EOR projects provide significant corrosion related problems.[5] Plastic coatings and linings, inhibition, dehydration, and corrosion resistant metals are means of corrosion control. Historically, corrosion resistant metals are used when the alternate schemes prove unreliable. For example, plastic coatings fully adequate for downhole tubular protection in a given environment may not have sufficient ductility to be useful in surface flowlines where cracking and disbonding during installation are ever-present dangers. Candidate alloys under these conditions have been the austenitic stainless steels (AISI 316) and the duplex stainless steels (near to ASTM A669).

Chromium-Bearing Metals and Their Application

Low Alloy Steels

The benefit of chromium in low alloy steels for the oil and gas production industry arises from its influence on hardenability, specifically, from the desire to have a uniform strength (hardness) and martensitic microstructure through relatively heavy (1.5 to 2.0 inches/37-50 mm) walls. The utilization of high strength in steels for highly pressured, deep wells containing H_2S is constrained by the threat of sulfide stress corrosion cracking. A recent review of Shell's wellhead and tubular requirements has shown a significant shift of these needs from largely conventional equipment to the present situation which requires more than 50 percent to be capable of handling sour gas conditions. The H_2S contents range from a few parts per million to nearly 85 percent of the gas phase.

Industry standards to handle safely and effectively these sour fluids are available; i.e., NACE* MR-01-75 (1981 Revision) and API* 5AC. When considering downhole tubulars and when the pressures require higher strengths than available in hot rolled carbon steels, heat treated low alloy steels are used. Traditionally, manganese-molybdenum steels (< 2.0 Mn, ~ 0.2 Mo) with moderate carbon content were available; but over the last decade, increasing use was made of chromium-molybdenum steels (modified AISI 4130) because of the perceived dangers of manganese segregation and localized hard spots.[6,7,8,9]

Other metallurgical considerations have been advanced in support of Cr-Mo over Mn-Mo steels including a fine dispersion of well tempered carbide produced at higher tempering temperatures, and a less detrimental interaction of trace elements/solute element on the hydrogen embrittlement proclivity.[10] The percentage of Cr-Mo steels devoted to high strength oil country tubular goods is small--on the order of 1 percent, but these steels enjoy a reputation of outstanding performance and their use is expected to grow. Inhibition for weight loss control must be practiced.

Wellheads consist of numerous valves, crosses, tees, chokes, and hangers and for the most part experience the same demands as downhole tubulars. Low alloy steels for wellheads on critical, sour wells evolved to the Cr-Mo series based largely on the success of the downhole tubulars. Section sizes are much greater, often 6 to 12 inches/150 to 300 mm; and it

---

* NACE - National Association of Corrosion Engineers, Houston, Texas.
API - American Petroleum Institute, Dallas, Texas.

is obvious that a substantially martensitic microstructure is not obtained even after liquid quenching. Laboratory evaluations of the steels as valve bodies vis-a-vis tubulars show the latter to be superior in sulfide stress cracking resistance. Counteracting this behavior is the practice of limiting wellhead components to lower strengths and generally lower operating stresses. Again the steel has performed well. The composition/hardenability/sulfide stress cracking relationships have certainly not been optimized. Chromium may not be essential, but currently higher Cr-Mo steels (2-1/4 Cr-1 Mo) are being advocated. Limited work has been done on this problem and is an area of active study.[11]

12 Cr Martensitic Stainless (AISI 410 Type) and 9 Cr-1 Mo Stainless Steels

NACE Standard MR-01-75 (1981) permits these alloys in sour service. Significant quantities have been used in wellhead and downhole equipment for some time; and in the last few years, sizable tonnage as downhole tubing of 410 has been produced and installed in wells with high CO_2 and trace (< 50 ppm) H_2S.[12] Performance has been satisfactory. Nevertheless, this family of alloys is viewed with caution for several reasons. Pitting corrosion can be severe in areas of high velocity or turbulence in high CO_2-containing streams, and this behavior can be aggravated when low concentrations of H_2S (ca. > 100 ppm) are additionally present. Furthermore, a bank of disturbing laboratory data suggests the risk of sulfide stress cracking in sour brines is distinctly greater for the 410 alloy than low alloy steels of comparable strength.[13,14] This potential risk is not borne out by field experience, however.[15]

Finally, poor inherent notch toughness and restricted weldability characterize the standard martensitic stainless steels. Variations in chemistry in which approximately 4 percent nickel is added overcome the latter objections, but these alloys (ASTM A487-CA6NM type, ASTM A182-F6NM) in turn have increased chloride stress cracking propensity. All in all, a better stainless of moderate chromium levels is desirable.

Corrosion Resistant Metals

Austenitic stainless alloys depend heavily on chromium to effect protection with Cr contents typically in the range 16 to 27 weight percent (Table 1). There is no known substitute alloying element.

Certain of these stainless alloys--herein designated "Superalloy"--began to receive intense attention about a decade ago as a possible means for alleviating a severe weight loss corrosion problem encountered in production tubing of low alloy steels in highly pressured sour gas wells producing from the Smackover formation in Mississippi.[16] Some characteristics of these wells were depths of 20,000 to 22,250 feet/ 6,100 to 6,800 m; bottom hole pressures from 1200 to 1500 atmospheres; bottom hole temperature near 375°F/190°C; 30 to 45% H_2S, 3 to 8% CO_2, 50 to 70% methane; no hydrocarbon condensate; and 6 to 8 barrels of water/million cubic feet of gas. Concurrent with the development of superalloy tubulars, a successful inhibition procedure was also developed and applied.[17] But the qualification and definition of constraints for these alloys--strengthened by cold work to high yields (nearly 200 ksi/1400 MPa)--have served as guidelines for their successful application such as downhole liners and retrievable tools. Subsequent investigations have focused on the qualification of less expensive stainless alloys--herein denoted as CRA--for use in more widespread gas wells producing acid gas contents varying over the range 0 to 100 percent CO_2 but limited to 0 to 1 percent H_2S.

The gas production industry has shown favorable acceptance of these alloys. During the period 1975 to 1980, approximately 2000 tons of austenitic stainless alloys--CRA and Superalloy--were produced as oil country tubular goods (OCTG); and during 1981-82, approximately 5000 tons[18]. Further evidence of the activity is indicated by the rise in number of oil companies using or inquirying of the alloys from 2 in 1975 to approximately 15 in 1982. It is too early to predict future growth.

Although the difficult period of first acceptance of austenitic stainless alloys for OCTG has been overcome, a certain reserve will continue. Technical problems exist. Corrosion and stress cracking--both anodic and cathodic (hydrogen)--are possible in these alloys.[19,20] Qualification and approval for use is specific to the alloy/environment combination under consideration, and this involves extensive testing which could inhibit potential substitutions because of time constraints. Long lead times for approval have been the rule. Typically 4 or 5 years pass between the initial definition of application and the metal selection. This lag should decrease as our knowledge matures. Research is under way at oil companies, metal suppliers, and equipment manufacturers as well as industry cooperative programs such as the Battelle[21] investigations and the NACE T-1F-21 task group.

In order for stainless alloys to be a viable alternative system, many components of the gas well must be considered. These include not only the tubulars; but also downhole accessory equipment such as packer bodies, landing nipples, subsurface safety valves; portions of the christmas tree including valves, hangers, tees, and crosses; and in some instances, also the surface facilities such as flowlines, separators, and vessels. Again, the choices are specific to the project, but this listing is provided to emphasize that not only are tubular manufacturers involved but also many equipment specialists. As such, numerous fabrication options must be evaluated. In wellheads, for example, solid stainless alloy bodies compete with overlay techniques such as welding and hot isostatic pressing (HIP).

* * * * * *

In summary, chromium is both convenient and crucial. The trend is toward greater utilization in the oil patch.

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Table I. Representative Chromium Bearing Metals* Used in Oil and Gas Production

GROUP	ALLOY	APPROXIMATE COMPOSITION, WT %					
		Cr	Mo	Ni	Fe	Mn	C
Low Alloy Steel							
	Mod. AISI 4130	1.0	0.5	--	97	0.5	0.3
	--	2.3	1.0	--	96	0.5	0.2
Martensitic Stainless Steels							
	AISI 410	12	--	--	87	1	0.1
	CA6NM	12	0.2	4	83	0.8	0.05
Austenitic Stainless Steels							
	AISI 316	17	2.5	13	65	2	0.05
Austenitic Stainless Alloys							
Duplex		22	3	5	68	2	0.03
CRA							
	Sanicro 28	27	3.5	31	37	1	0.02
	Incoloy 825	22	3	42	30	--	0.03
Superalloy							
	Hastelloy G-3	22	7	50	20	--	0.01
	Hastelloy C-276	16	16	65	--	--	0.01
	Inconel 625	22	9	60	5	(3 Nb)	0.05
	Inconel 718	19	3	50	20	(5 Nb)	0.05
	MP35N	20	10	35	--	(35 Co)	0.01

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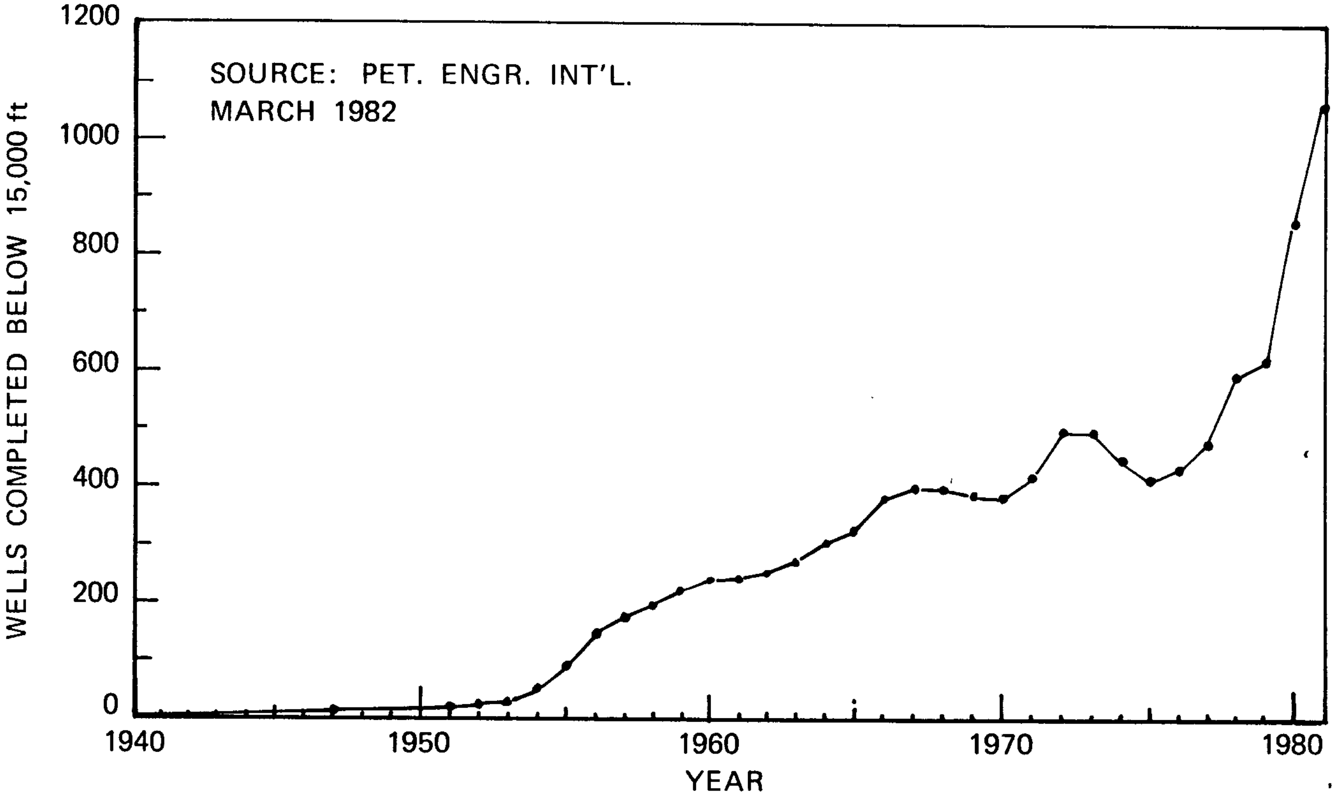
* Meant only to illustrate range of chromium and other major alloying elements. This list is not all-inclusive, nor precise.

Sanicro - TM Sandvik AB
Inconel and Incoloy - TM Huntington Alloys
Hastelloy - TM Cabot Corporation
MP35N - TM Standard Pressed Steel



SOURCE: PET. ENGR. INT'L.
MARCH 1982

Figure 1. U.S. Deep Drilling Activity

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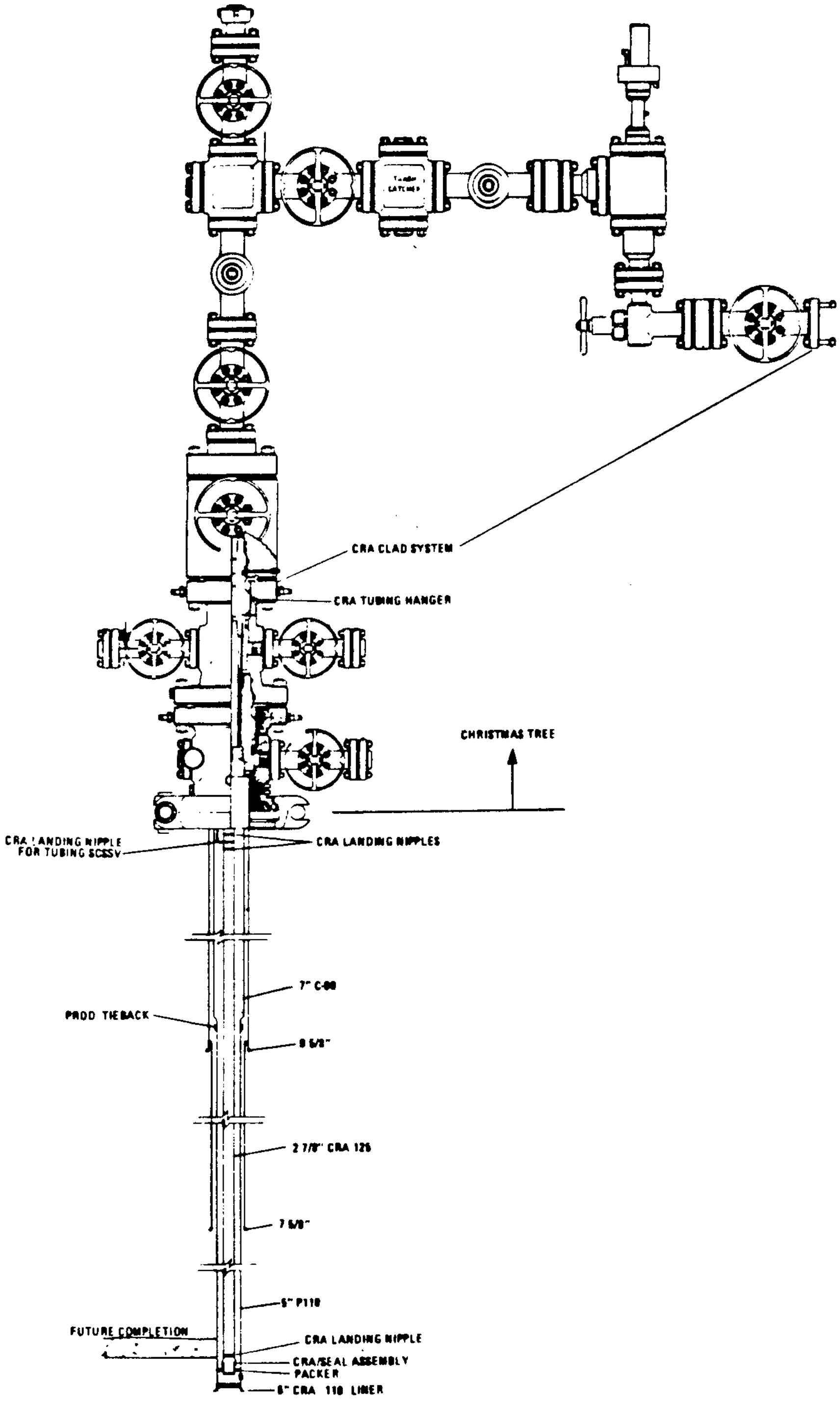

TYPICAL CRA COMPLETION

Figure 2. Typical CRA Completion

STAINLESS AND SPECIALTY STEELS
AOD, VOD, VIM, VAR, ESR, P/M

Let me begin this presentation by defining the major role the stainless and specialty steel industry plays in the consumption of chromium and therefore, the possibilities of conservation of chromium. Approximately 66%(1) of all of the domestic chromium is used directly as an alloying element in steels and other alloys.(Figure 1) A breakdown by type of alloy(2) showing the consumption of chromium indicates that stainless steels are far and away the major use at 72%.(Figure 2) Alloy steels are the second major category at 14%, followed by superalloys at 7%. Part of the reason for stainless steel's dominance in consumption becomes clear when we look at the average chromium content of these groups.(Figure 3) Stainless steels have an average chromium content of 16.4%. A further breakdown of stainless steels show that the austenitic stainlesses such as Type 304 contain an average of 18%, followed by the ferritic stainless steels at 15%, and the martensitic stainless steels at 12%. The super ferritic stainless steels, which are gaining increased attention, require a much higher percentage of chromium, in excess of 25%. Increased utilization of these super ferritics would result in increased consumption of chromium.

At the outset I feel it is important to discuss what is meant by conservation and to expand this topic to include increased utilization of types of chromium which previously could not be used. Obviously there is DIRECT CONSERVATION, where the initial amount of chromium needed has been reduced, either by reduction in the amount of chromium lost during processing, such as to a slag, or by alloy design. Somewhat less apparent is what I will call SECONDARY CONSERVATION. In a broad sense this might also be called yield improvement, where the impact on chromium conservation is not direct but rather allows a smaller amount of starting material to produce a given end quantity. This is a significant point for at first glance one might think that yield losses are simply recycled with no loss of chromium. However, less starting material required reduces the amount of material exposed to processes where irrecoverable chromium losses occur such as melting or in some cases, grinding. This area of conservation would include such items as better chemistry control, thus minimizing the need to remake a heat, improved workability, improved quality, etc.

I'll now describe the major melting processes used in the stainless and specialty steel industry and their impact on chromium conservation. There are a significant number of different major melting processes. This is a direct consequence of the variety of alloys produced and the diverse end use requirements.

First I'll deal with the primary melting processes. All complex metallic alloy systems must first be rendered liquid in order to: 1) intimately mix alloying elements in a predetermined ratio, 2) effectively recycle scrap, 3) facilitate refining, and 4) produce the desired shape for mill product starting form. In the stainless and specialty steel industry, the two major methods of achieving this are electric arc melting and vacuum induction melting. Air induction melting is used to a very limited extent and will not be discussed here.

Electric Arc Melting - In the electric arc furnace, a charge of solid scrap, alloys and ferro alloys is melted in air within a refractory lined shell by heat from an electric arc generated between graphite electrodes and the charge. Oxygen is blown into the bath to lower the carbon content. Fluxes are added for refining purposes and the impurities are removed as gases or liquid slag. The molten metal is continuously cast into ingots for processing to mill products or cast into electrodes for remelting to obtain further refinement and/or improved ingot structure. The melting characteristics of the electric arc furnace include efficient and economic operation, which when combined with the unit's versatility and tolerance for a broad range of charged materials, including heavy scrap, result in a low cost operation. This practice's major contribution to chromium conservation is its ability to utilize a wide variety of chrome containing scrap.

Vacuum Induction Melting (VIM) - Most advanced high temperature alloys are melted in the vacuum induction furnace, which provides optimum capabilities for close chemistry control and removal of detrimental elements including gases. To reduce the refining time, the use of high quality charge materials, including scrap, is usually preferred. The absence of an oxidizing atmosphere assures that the reactive elements will be retained in the melt, resulting in very close chemistry control. Of particular importance is the vacuum furnace's capability of evaporating many detrimental trace elements due to their high vapor pressure. The elimination of many of these elements has resulted in a marked improvement in the workability and rupture ductility of superalloys. Melting under vacuum eliminates the need for a slag cover which in an electric furnace is a cause of irrecoverable chromium loss. The close chemistry control achievable in the VIM results in very few off analysis heats and contributes to chromium conservation by minimizing remaking of heats.

SECONDARY STEEL MAKING PROCESSES (DECARBURIZATION) - After the material has been melted in the electric furnance, it can then be cast or transferred into another vessel for additional processing. With respect to conservation of chromium, it is these secondary steelmaking processes that have resulted in the greatest impact. As was shown earlier, the largest consumption of chromium is utilized as an alloying element in stainless steels. Secondary steelmaking processes have their major impact in the production of stainless steel. These processes include: argon-oxygen-decarburization (AOD), vacuum-oxygen-decarburization (VOD), and a method developed by Creusot-Loire and Uddeholm (CLU). The CLU process uses steam and oxygen for decarburization and has been commercially operating since 1973. Its acceptance has been relatively limited and, therefore, I shall not discuss it further. Conversely, the AOD process developed by Union Carbide appeared commercially in 1969 and, because of its wide spread acceptance, has had the greatest impact on the conservation and utilization of chromium. As of 1981 it was licensed to 61(3) licensees throughout the world. The VOD method is currently employed by 16 plants located in Japan and Europe with no domestic facilities.

AOD AND VOD - In either of these methods, the electric arc furnace is relegated to a melting machine, substantially reducing the cycle time of this unit. The high carbon steel is transferred from the electric furnace to an auxiliary vessel or ladle. Argon and oxygen are blown into the bath for decarburization either at atmospheric pressure in the AOD system or under a vacuum in the VOD system.

The major difference between the conventional electric arc furnace practice for making stainless steel and either of these two processes is the reduction of the partial pressure of carbon monoxide rather than raising the bath temperature. In the electric arc furnace, in order to increase the activity of carbon to react with the oxygen in the presence of 10 to 15% chromium, it was necessary to increase the temperature to as much as 3500°F. At this temperature, as much as 30% of the chromium is also oxidized and transferred into the slag. While part of this is recovered, about 12% is irreversibly lost. In either of the two duplexing methods, argon and oxygen are blown into the bath, decreasing the partial pressure of carbon monoxide and thereby reducing the carbon concentration at constant temperature. In both of these methods, the irreversible chromium losses are reduced to approximately 5%, resulting in a direct conservation of chromium. At Universal-Cyclops, we have chosen the AOD method, and I will deal with that in the following example, although I feel the principles can be directly applied to the VOD process. Under the old electric furnace practice, oxygen was used to blow out the carbon to a relatively high equilibrium temperature.(Figure 4) Then, major additions of low carbon ferro chrome are needed to achieve the desired chromium level. In the AOD, carbon level is reduced at a significantly lower equilibrium temperature and only minor additions of low carbon ferro chrome are needed to obtain the desired end chemistry. The impact of these processes on the consumption of low carbon ferro chrome has been dramatic and has allowed increased use of lower cost charge chrome.(Figure 5)

REMELTING - Particularly in the superalloy area, but to a limited extent in stainless steels, various remelting processes are used. Generally speaking, these have little direct effect on the conservation of chromium, but do exert positive benefits with respect to yield and workability. The yield improvement is a result of the solidified structure having no pipe cavity from solidification and little if any hot top, which must be discarded. The increased workability is a result of the finer grain structure achieved through higher cooling rates and a more homogeneous product. The two major remelting processes are Vacuum Arc Remelting (VAR) and Electro Slag Remelting (ESR). Although two other processes are available, electron beam remelting and plasma arc remelting, their acceptance to date has been extremely limited and I will not discuss these.

Vacuum Arc Remelting (VAR) - In the vacuum arc remelting system, as-cast electric furnace or vacuum induction melted electrodes are progressively remelted and solidified in a water cooled copper mold, under vacuum, by an electric arc generated between the electrode and the molten metal above the solidfying ingot. Some refining occurs such as removal of impurities in the gaseous form and there is no contamination from air, slag or crucible.

Electro Slag Remelting (ESR) - As with VAR, ESR employes as-cast electric furnace or VIM melted electrodes. These are progressively remelted and solidified in a water cooled copper mold under a blanket of molten flux. Melting is due to heat generated by the resistance of the molten flux to electric current passing between the electrode and the solidifying ingot. Refining occurs as molten metal passes through the flux and impurities are removed as gas or by reaction with the flux to form slag. The ESR process is routinely used to directly produce slabs which need no additional hot working prior to processing to plate or sheet. This results in significant yield improvements.

Electron Beam, Cold Hearth Refining - In the area of superalloys, another remelting process has loomed on the horizon for many years and has yet to gain commerical acceptance - Electron Beam, Cold Hearth Refining. Briefly, first melted VIM ingots are introduced to the electron beam in a high vacuum chamber. The first metal to be melted is solidified as it contacts the water cooled copper hearth to form a skull of the same alloy which is to be further refined. From this point on, the molten metal flows only over its own non-contaminating alloy skull.

Unfortunately, there is an evaporation loss of about 5%(4) of the chromium content, and with respect to this particular conference, should the electron beam melting process gain in commercial acceptance, it would have an adverse effect on chromium conservation.

In summary, (Figure 6) the major development in chromium conservation and utilization has been in secondary steelmaking, either by AOD, the predominant method, or VOD. These two methods have not only increased the utilization of higher carbon forms of chromium, but have resulted in an actual conservation of chromium on the order of 7%. I think it is also important here to reemphasize the secondary benefits in many of these processes, such as the improved chemistry control out of the AOD, VOD, or VIM furnace and the improved workability and yield improvements that results from many of these practices.

As this subject was manufacturing processes, not just melting processes, let me briefly touch on some manufacturing processes in the stainless and specialty area (5), which I feel have significant impact on chromium conservation. (Figure 7) Again, in many respects, these improvements are secondary.

Improvements either on existing facilities or new mills which are being built, such as computerized control, improve the DIMENSIONAL CONTROL of the product resulting in yield improvement. Anything that improves the SURFACE QUALITY can also have a dramatic impact on the yield. There are products in the specialty steel industry that are ground at three different stages in their processing, resulting in an approximate 5% yield loss at each grinding operation. This grinding is necessary to assure the desired surface quality and remove any defects that result either from the melting operation or prior processing. CONTINUOUS CASTING, primarily of stainless steels rather than superalloys, has resulted in yield improvements approaching 10% and in many cases, superior surface quality. EXTRUSION can also result in significant direct yield improvement and for applications such as hollows for tubing, or aircraft gas turbine shafts, represents better material utilization. CLADDING with stainless steel provides an increased opportunity for reducing the consumption of stainless steels. ISOTHERMAL HOT WORKING provides major impact on the hot workability of many alloys, particularly superalloys. The increased utilization of GFM MACHINES can have a tremendous impact on yield as the intent is to form the material into desired shape rather than to grind or mill. These are radial forging machines which have been developed with advanced manchine controls, automated part handling, heating and quick tool changing, which provides great flexibility and permits application of these machines to a variety of materials.

The final area of manufacturing processes, which I want to touch on, is POWDER metallurgy. I'll divide this topic into two areas: NEAR NET SHAPES, which provides much better material utilization resulting in actual material conservation, and RAPID SOLIDIFICATION TECHNOLOGY, which opens new doors in alloy design and improves the hot workability of some alloys, which were practically impossible to work in the cast state, such as Rene' 95 and IN100.

Powder metallurgy represents a major portion of our research activity at Universal-Cyclops. Raw powder can be produced by one of three methods. At Universal-Cyclops we employ gas atomization and consolidate the powder using a patented process involving glass molds. The fact that these glass molds can be made into many different shapes and sizes has a direct bearing on our near net shape technology. Hollow molds and their resulting product are the focus of much interest. Let me share with you a case history which demonstrates the use of near net shape technology.

We are currently involved with an aircraft gas turbine manufacturer in producing a near net shape for high hub disk application. This part is a conical shape. The material cost here is approximately $20 per pound. Were we to produce this material from a conventional cylindrical starting stock, the starting stock would weigh approximately 50 pounds. Through the use of powder technology, we can produce a near net shape conical starting stock which weighs approximately 20 pounds. There of course is a price to pay and that price is mold cost. It is significantly more expensive to produce the conical shape glass mold needed, and mold cost increased from 3 to 15%. However, in this superalloys, the payoff is there with the total cost savings in the order of 55%, and the material savings including that of 18% rich chromium material is 60%. (Figure 8)

With respect to alloy design, Frank Richmond, who was originally to have spoken here, endorses the theory of alternating process and alloy development. (Figure 9) Historically, the efforts of alloy designers to develop improved specialty steel products have been periodically retarded by limitations of the existing state-of-the-art of melting and casting processes. An example of this was the limit on titanium and aluminum additions to nickel base alloys imposed by the difficulty of melting such alloys in the electric arc furnaces of the early 50's. Vacuum induction melting eliminated that barrier and alloy designers quickly took advantage of the VIM process to design improved high temperature alloys. The next process barrier was related to the limits on total alloy levels imposed by VIM ingot segregation. Vacuum arc remelting (VAR) and later electroslag remelting (ESR) raised this limit, kicking off another alloy development wave. Further expansion of the alloy designer's horizon awaited the recent development of powder metallurgy. This process not only provides the maximum flexibility with respect to alloy level and complexity, but offers significant improvement in the structure related properties and provides significant savings in energy and raw materials. We at Universal-Cyclops feel that the powder metallurgy technology provides opportunities for alloy conservation at the same property levels, improved property levels for given alloys level, and further improvement of properties heretofore not obtainable via additional alloy development. As this conference deals specifically with conservation of chromium, let me site a case history which shows the potential of chromium conservation via powder technology, where improved properties are obtained at the same alloying level.

Yurek(6) of MIT recently published the results of his work on the oxidation behavior of fine grained, rapidly solidified 18-8 stainless steel. The chemistries of the materials involved in this study are shown in Figure 10. The cyclic oxidation behavior of the fine grained rapidly solidified 303 stainless steel was determined in pure oxygen at 900C. This rapidly solidified alloy exhibited superior resistance to oxidation compared with that of a similar composition wrought 304 stainless steel.

In fact, its oxidation resistance was as good as that of a wrought 310 stainless steel, even though that alloy contained significantly larger quanitities of chrome and nickel.

In reviewing other conferences held recently dealing with the conservation of strategic or critical alloys, it has been pointed out that there are no known substitutes for chromium, and this to date remains true. However, I think these two case histories point out two specific areas in the relatively new field of powder metallurgy which provide opportunity for the conservation of chromium, in addition to the ongoing improvements in melting and process technology. The primary problem with chromium conservation is the economic driving force. Stainless steels with their 18% chromium content and 72% of domestic consumption sell in the area of $1 to $2 per pound, whereas superalloys in many cases cost ten times that amount. From a chromium conservation stand point, a disproportionate amount of conservation effort is directed in the superalloy area because of economic considerations. On the positive side, it is reassuring to know that although these technologies are not now currently being widely applied to stainless steels, should we find ourselves faced with a shortage of chromium, the potential avenues of conservation available to us, are increasing.

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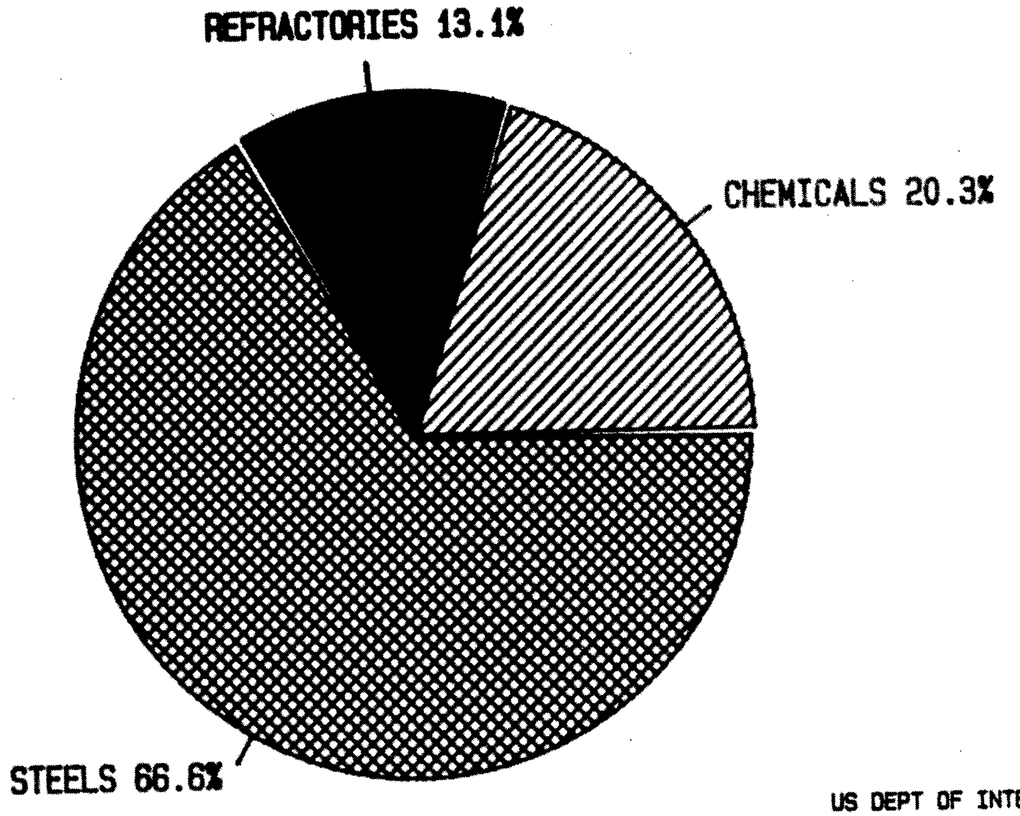
U.S. END USES OF CHROMIUM

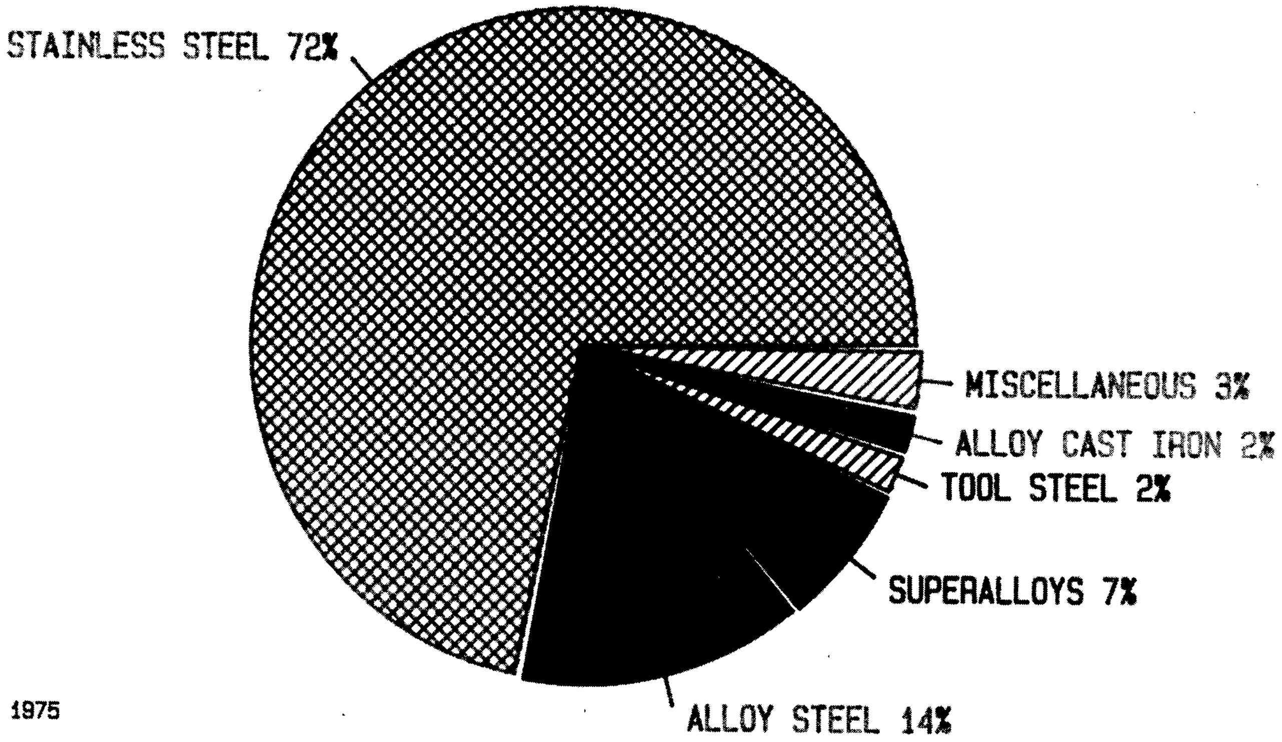
1980



US DEPT OF INTERIOR 1981

FIGURE 1

USE OF METALLURGICAL CHROMIUM



AISI 1975

FIGURE 2

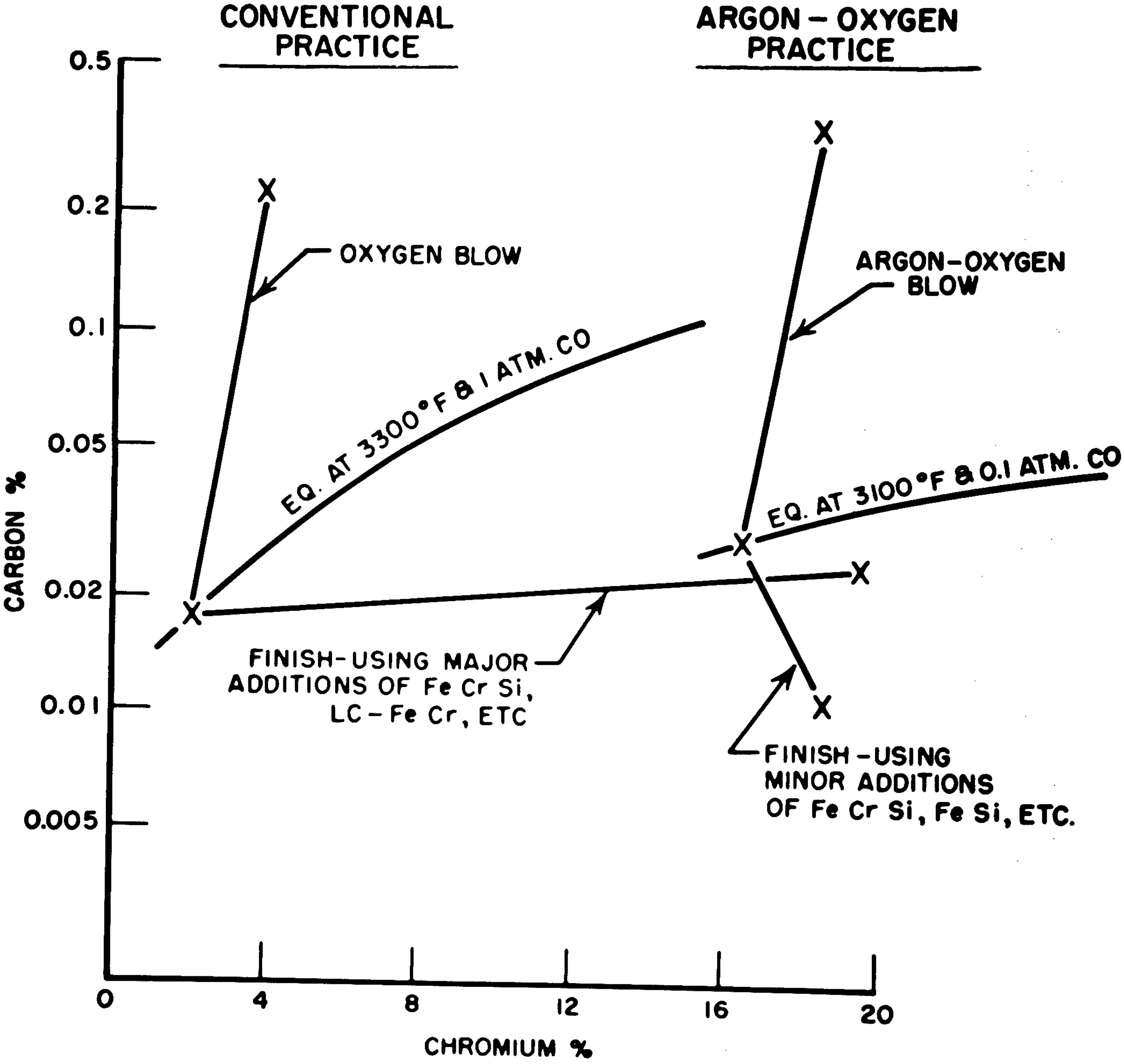
AVERAGE CHROMIUM CONTENT OF MAJOR ALLOY GROUPS

MATERIAL GROUP	AVERAGE CHROMIUM CONTENT (PERCENT)
STAINLESS STEELS	16.4
ALLOY STEELS	1.0
SUPERALLOYS	18.0
TOOL STEELS	6.0
ALLOY CAST IRONS	<1.0

AISI 1975

FIGURE 3

FIGURE 3

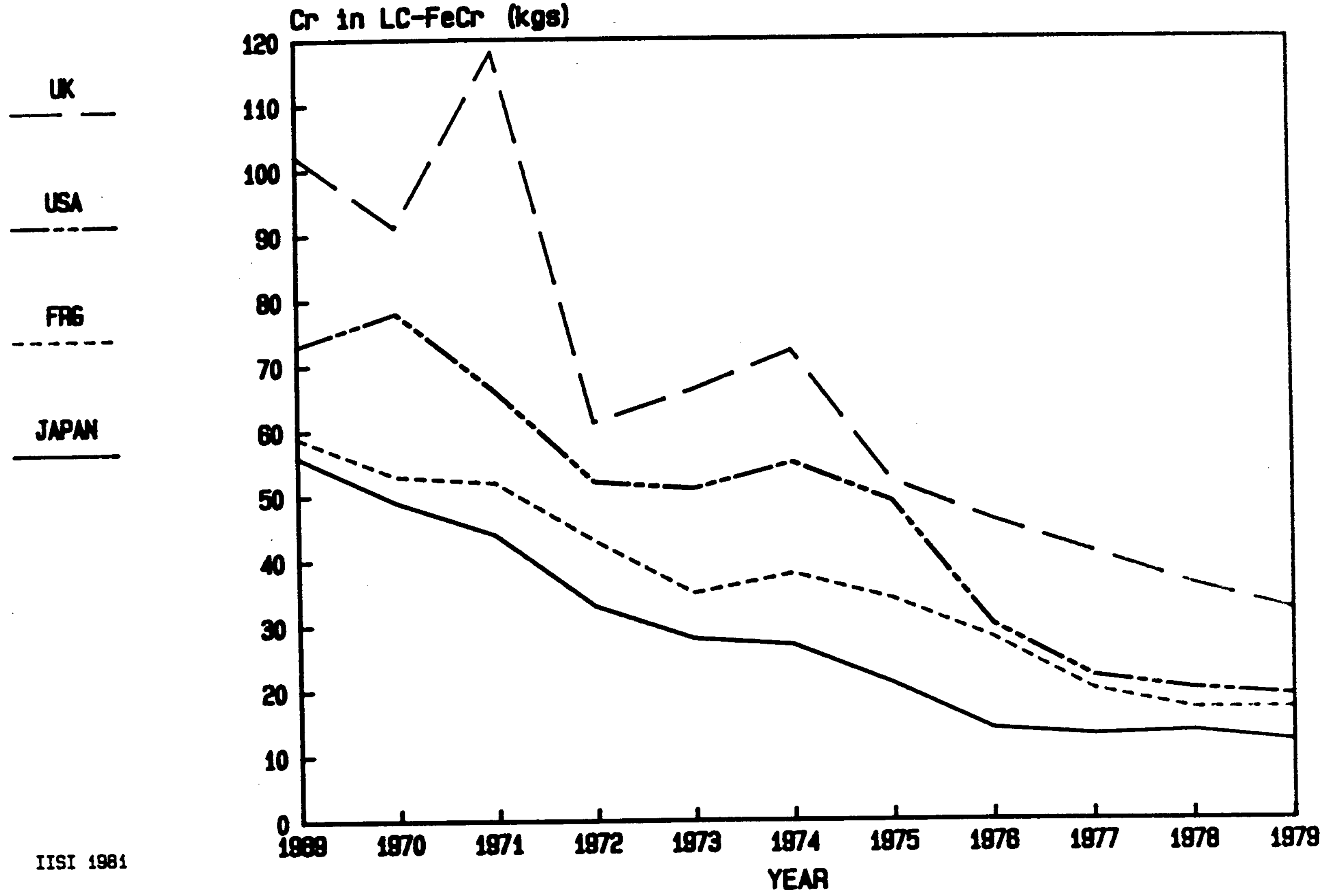


COMPOSITION CHANGES IN REFINING 304-L

FIGURE 4

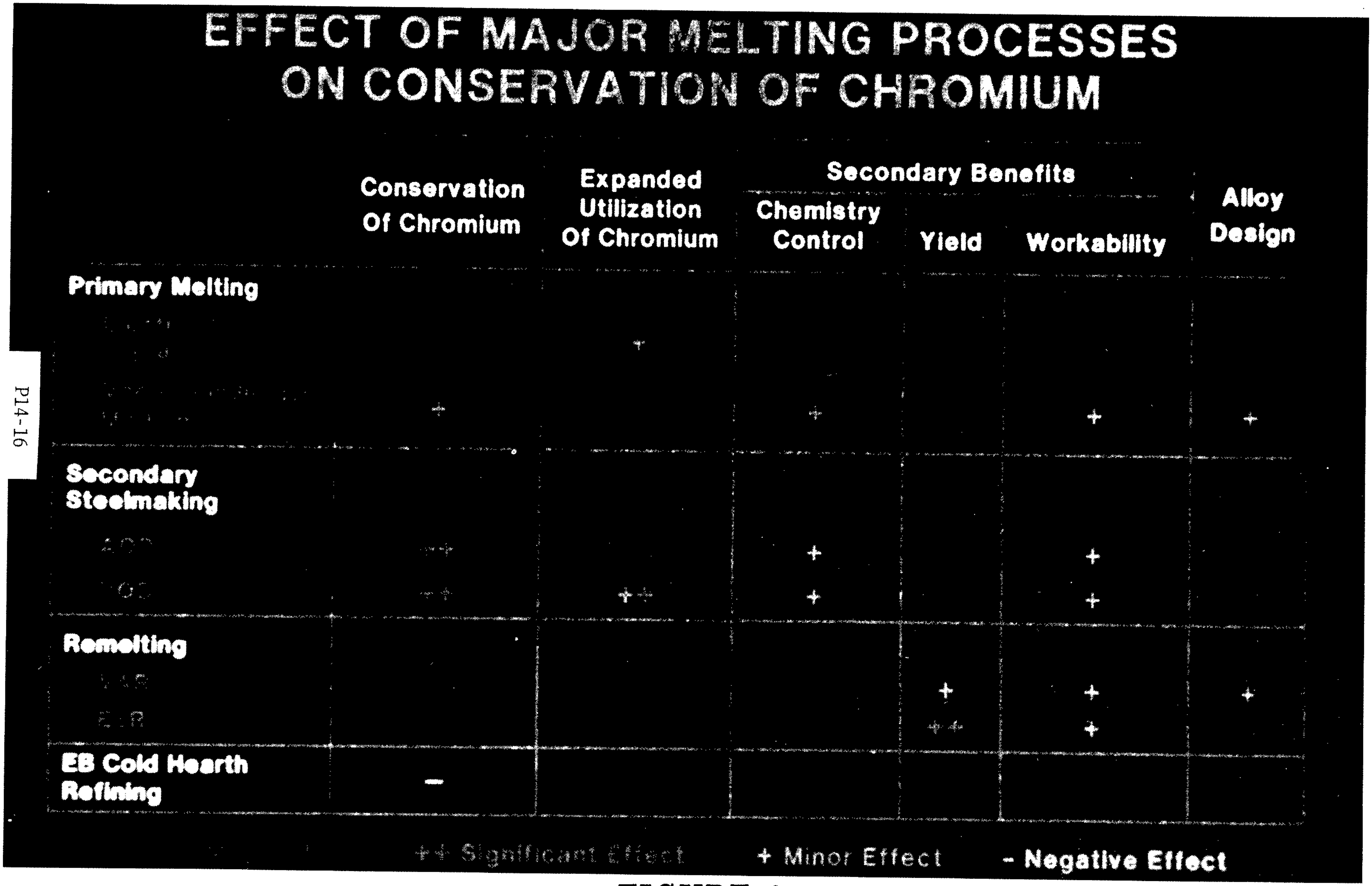
CONSUMPTION OF LC-FeCr IN SS

KILOGRAMS of Cr per TON of SS



IISI 1981

FIGURE 5

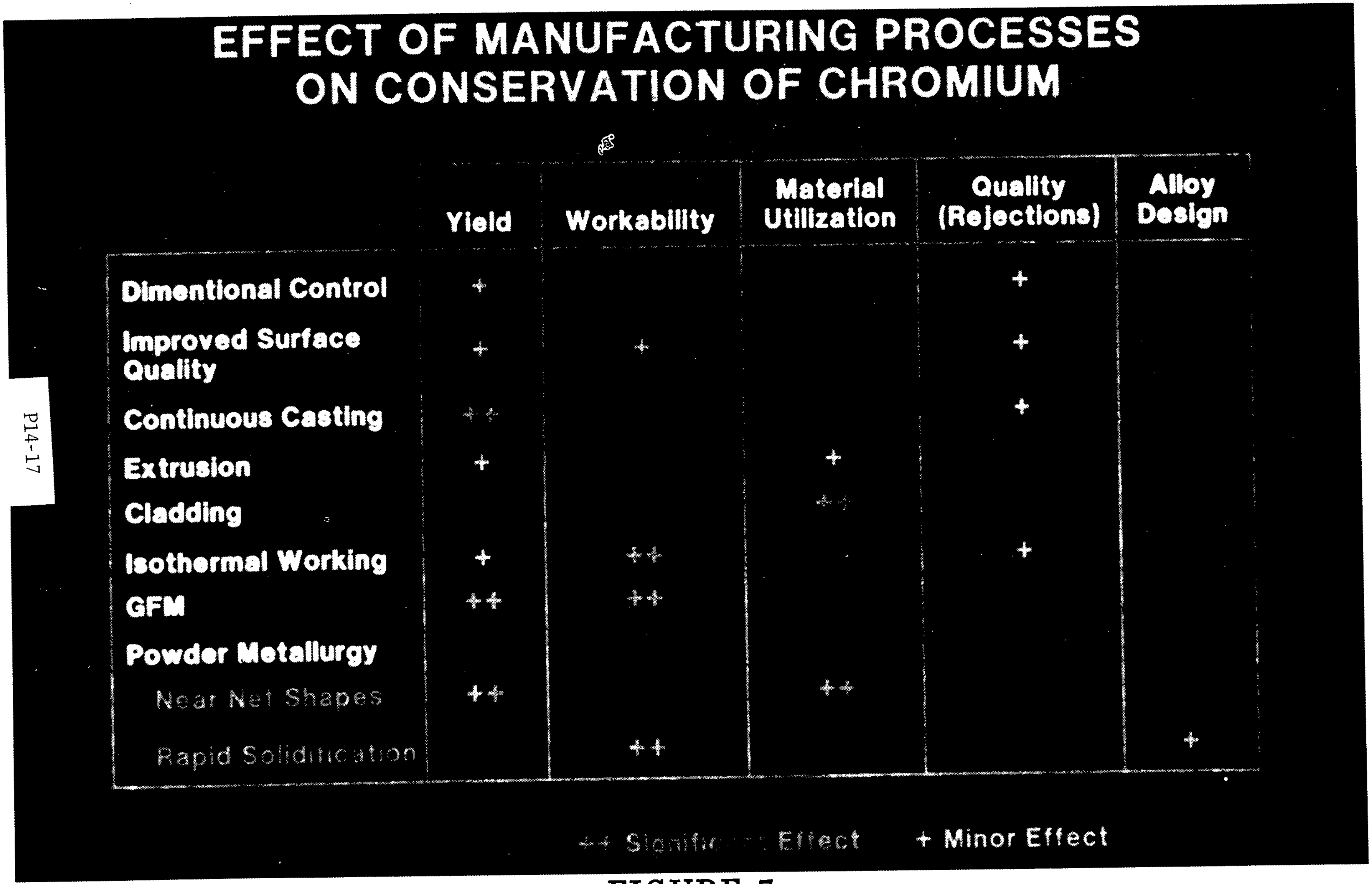


EFFECT OF MAJOR MELTING PROCESSES ON CONSERVATION OF CHROMIUM

	Conservation Of Chromium	Expanded Utilization Of Chromium	Secondary Benefits			Alloy Design
			Chemistry Control	Yield	Workability	
Primary Melting						
[illegible]		+				
[illegible]	+		+		+	+
Secondary Steelmaking						
AOD	++		+		+	
VOD	++	++	+		+	
Remelting						
VAR				+	+	+
ESR				++	+	
EB Cold Hearth Refining	−					

++ Significant Effect
+ Minor Effect
- Negative Effect

FIGURE 6



EFFECT OF MANUFACTURING PROCESSES ON CONSERVATION OF CHROMIUM

	Yield	Workability	Material Utilization	Quality (Rejections)	Alloy Design
Dimentional Control	+			+	
Improved Surface Quality	+	+		+	
Continuous Casting	++			+	
Extrusion	+		+		
Cladding			++		
Isothermal Working	+	++		+	
GFM	++	++			
Powder Metallurgy					
Near Net Shapes	++		++		
Rapid Solidification		++			+

++ Significant Effect + Minor Effect

FIGURE 7

NEAR NET SHAPE CASE HISTORY
HIGH HUB DISK FOR AIRCRAFT GAS TURBINE

MATERIAL COST approx. $20/lb

CONVENTIONAL CYLINDRICAL STARTING STOCK approx. 50 lbs

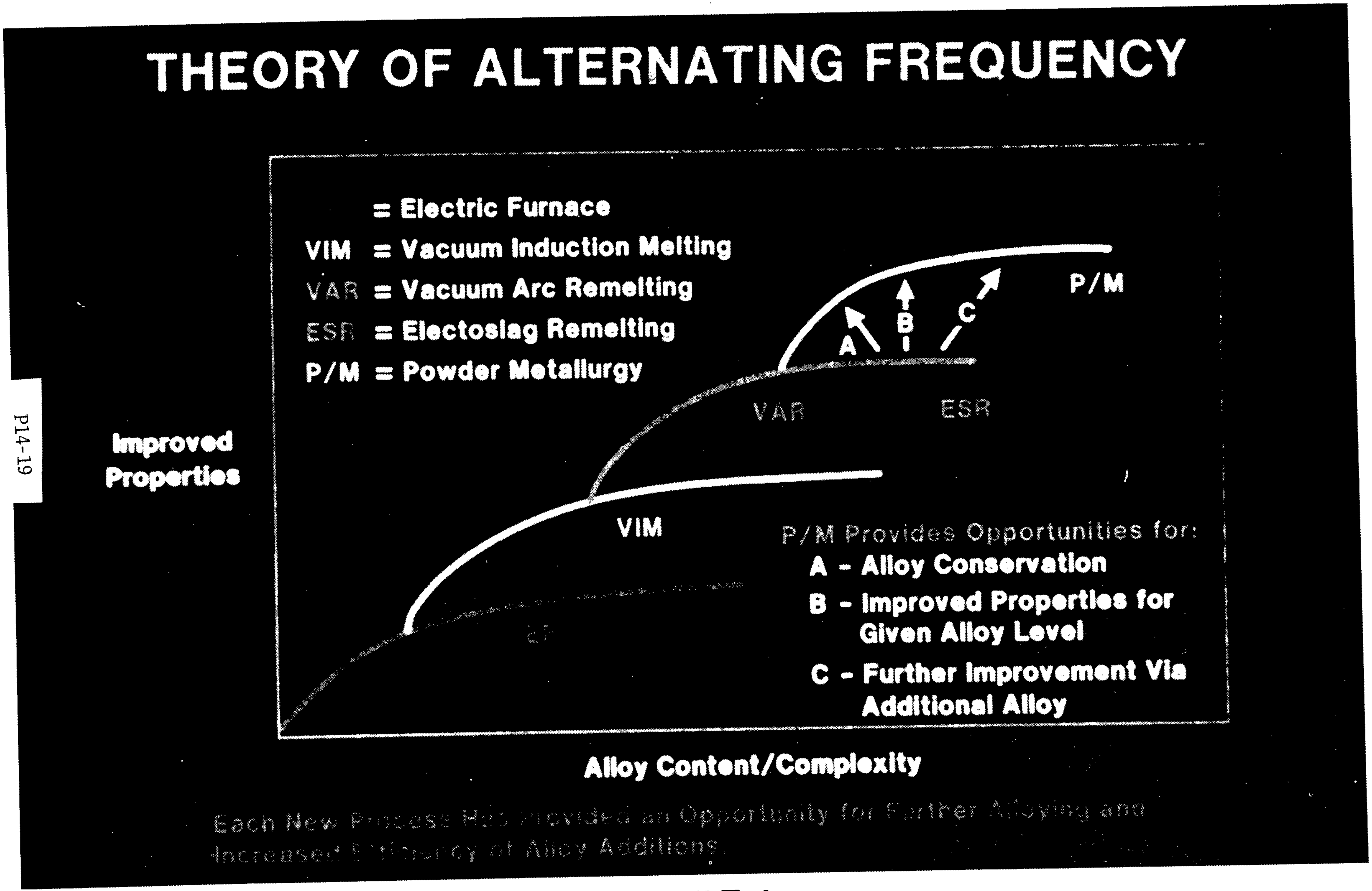
NEAR NET SHAPE CONICAL STARTING STOCK approx. 20 lbs

MOLD COST INCREASE (PER lb) 3% TO 15%

COST SAVINGS OF 55%

MATERIAL SAVINGS OF 60%

FIGURE 8



THEORY OF ALTERNATING FREQUENCY

= Electric Furnace
VIM = Vacuum Induction Melting
VAR = Vacuum Arc Remelting
ESR = Electoslag Remelting
P/M = Powder Metallurgy

P/M Provides Opportunities for:
A - Alloy Conservation
B - Improved Properties for Given Alloy Level
C - Further Improvement Via Additional Alloy

Each New Process Has Provided an Opportunity for Further Alloying and Increased Efficiency of Alloy Additions.

FIGURE 9

COMPOSITIONS OF STAINLESS STEELS EMPLOYED IN RS INVESTIGATIONS

STEEL	C	Mn	Ni	Cr	Mo
304W	0.04	1.62	8.78	18.28	0.32
303RS	0.059	1.60	8.68	17.31	0.37
310W	0.06	1.64	19.90	25.00	0.18

G. YUREK, MET TRANS A, MAR 1982

FIGURE 10

The term "Mini Mill" has been around since the mid 60's and originally referred to small, electric furnace, strand casting operations, producing a single product. Typically re-bar.

Through the 1960's, ecconomies of scale dominated the thinking of steel company executives world wide. The ideal operation was thought to be a 10 million ton per year integrated operation, with ocean access.

The repeated energy crises of the 70's reversed many of the arguments in favor of the multi million ton mill. Freight became an increasingly significant cost of operations within continental markets such as North American or Europe. Consequently the last decade has seen a rapid increase, in the number of mini mills, and in their product maturity. The very name mini mill has tended to be replaced by the term "market mill".

A typical market mill of the mid 1980's can be defined as follows: Small in size, capacity 200,000 to one million tons, normally constructed on a green field site.

Restricted product range. Typically small structural sections, special quality carbon and alloy steel rounds, and re-inforcing bars. Within its selected product groups, the market mill concentrates on popular high volume items to minimise mill size changes.

Consumes local raw materials, usually 100% steel scrap, in ultra high powered electric arc furnaces.

Supplies a local market area in which it becomes the low cost producer.

It has a low capital cost per unit of output. As low as one tenth that of an integrated operation for green field construction.

It uses 100% strand casting to minimise capital, energy and labor costs and maximise material yield. A comparison of yield for the ingot and strand casting process rout is shown in Table I. The net difference is 18.2% in liquid to billet yield. In the case of chromium steel, this equates directly to a chromium savings of 18.2%.

TABLE I

YIELD COMPARISON

Killed Steel Special Quality

	Ingot Practice %	Strand Casting %
Scrap - Liquid	89	87
Liquid - Ingot	96	-
Soaking Pit Scale	97	-
Blooming Mill Crops	90	-
Hot Scarfing	95	-
Billet Optimisation	98	-
Liquid - Billet	-	98
Billet Inspection	96	95
Total Scrap-Billet	66.7	81.0 (14.3%)
Liquid-Billet	74.9	93.1 (18.2%)

The market mill has high labor productivity with man hours per ton of finished product as low as 1.8. This compares to a national average of about 7.5.

It is often non-union, with no time clocks, and provides opportunities for the participation of all employees in the decision making process. It may provide staff status and profit sharing for all employees. It avoids the "us and they" syndrome.

It has a flat management structure and is normally managed directly from the plant, thus avoiding the burocratic restrictions of a head office.

Finally, resulting from many of the above characteristics it has a fast response time to changing situations.

The performance levels described in the above definition are impressive by national and international standards, but are by no means the ultimate achievable.

This workshop is convened to consider developments in the conservation of critical materials.

To the market mill operator, any expense is a critical material, whether it be chromium, energy or labor.

Almost 75% of the variable cost of producing a steel billet in a market mill is accounted for by the five items shown in Table 2.

TABLE 2

VARIABLE COSTS PER TON OF BILLET

Labor	6.7 %
Energy	20.4 %
Electrodes	14.5 %
Refractories	16.3 %
Alloys	14.6 %
	72.5 %

Energy is the most significant item. The energy efficiency of an electric arc furnace is less than 65%. The energy that is utilised, is then normally dissipated as the hot billets are allowed to cool before re-heating and rolling. Scrap pre-heating techniques using are furnace off take gasses, and direct charging of hot billets to re-heat furnaces or induction heating lines are being introduced.

Electrode consumption is under attack by the introduction of water cooled electrodes or by electrode coating. The successful development of the plasma arc furnace would eliminate completely the expense of consumable electrodes.

Refractory consumption is falling as water cooled roofs and side walls become standard equipment, thus permitting power levels and operating rates to be increased.

In spite of the inflation in hourly labor costs, the unit cost of labor is steadily falling as productivity increases.

The strand casting process itself is entering a revolutionary new state as the traditional vertical designs, (Figs. 1 & 2) are faced with two alternatives.

First the horizontal type machine (Fig. 3), which has the ability to cast a much smaller section. Ths leads to capital cost savings in the machine itself, and also in the finishing mill where for small rolled products the number of mill stands can be reduced.

One of the steelmakers cherished dreams is the concept of continuous steelmaking. Such a process would begin with a continuous feed of raw material to the steelmaking unit and proceed un-interupted to

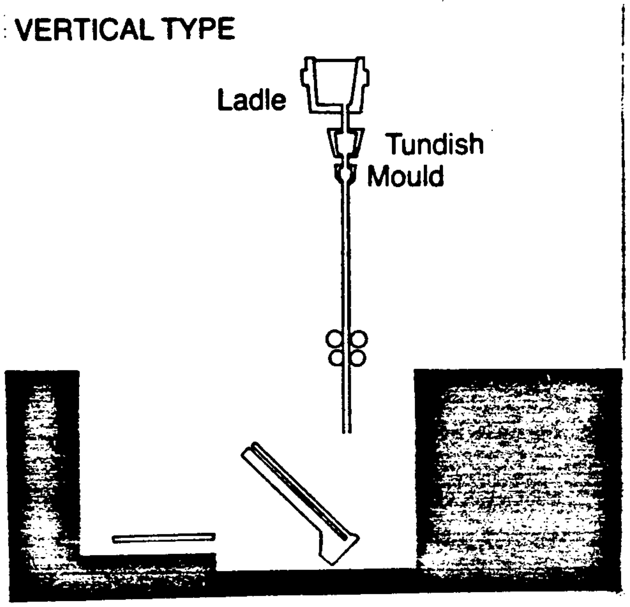


FIG. 1

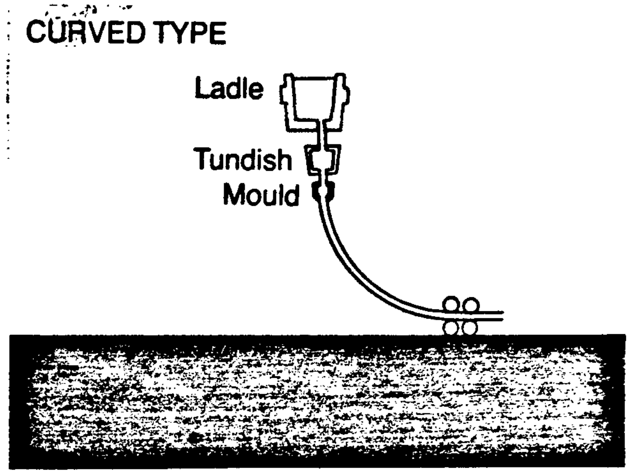


FIG. 2

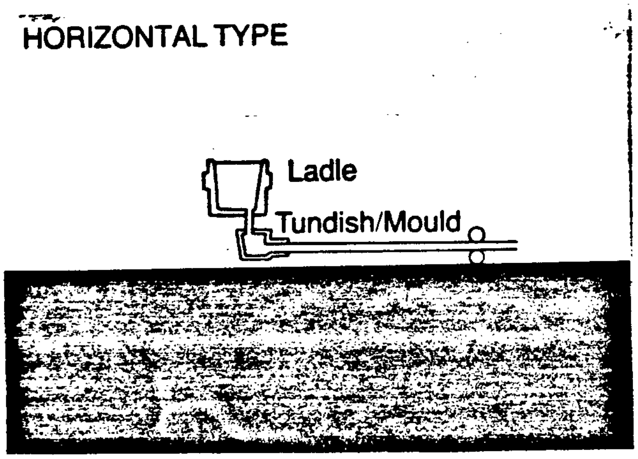


FIG. 3

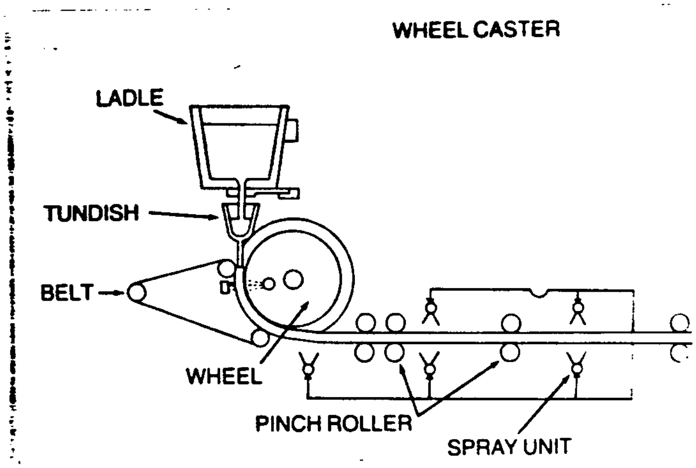


FIG. 4

Of all the chromium consumed in steelmaking, about 70% is accounted for in the stainless grades. Most of the remainder is consumed in constructional alloy steels, which are within the product scope of the market mills.

The AISI issued statistics for carbon and alloy bar products by grade for 1981. Significant points of the survey are:

Total consumption, carbon and alloy.	8,062,170 tons
Total alloy steels	3,073,135 tons
41XX Series	1,330,380 tons
86/87XX Series	472,748 tons
51XX Series	296,860 tons

The three grade series listed above account for 68.4% of all constructional alloy steels.

Of the 41XX series the most popular are 4140 and 4130 at 0.80 to 1.10% Cr. These are the most common heat treated engineering steels. Applications include fittings, valves, bolts, shafts, and teeth, etc.

The 86XX and 87XX series are Ni, Cr, Mo grades, the most common is 8620 used in the carburised condition for gears. Chromium content 0.4 - 0.6%.

Of the 51XX series, 5160 is the most popular. Chromium content 0.7 to 0.9%. This grade not used almsot exclusively in the hot wound coil spring and leaf spring industries.

Much has been written about the metallurgy of chromium in steel. The main reasons for its use are corrosion resistance, wear resistance, to retard softening at elevated temperatures, and finally as a cheap hardenability agent.

In the constructional alloy steels produced by market mills, only the hardenability factor is of metallurgical significance. The other major factor in the market place is "Tradition". Certain grades of chromium bearing steels are available and have long been used, often in-appropriately.

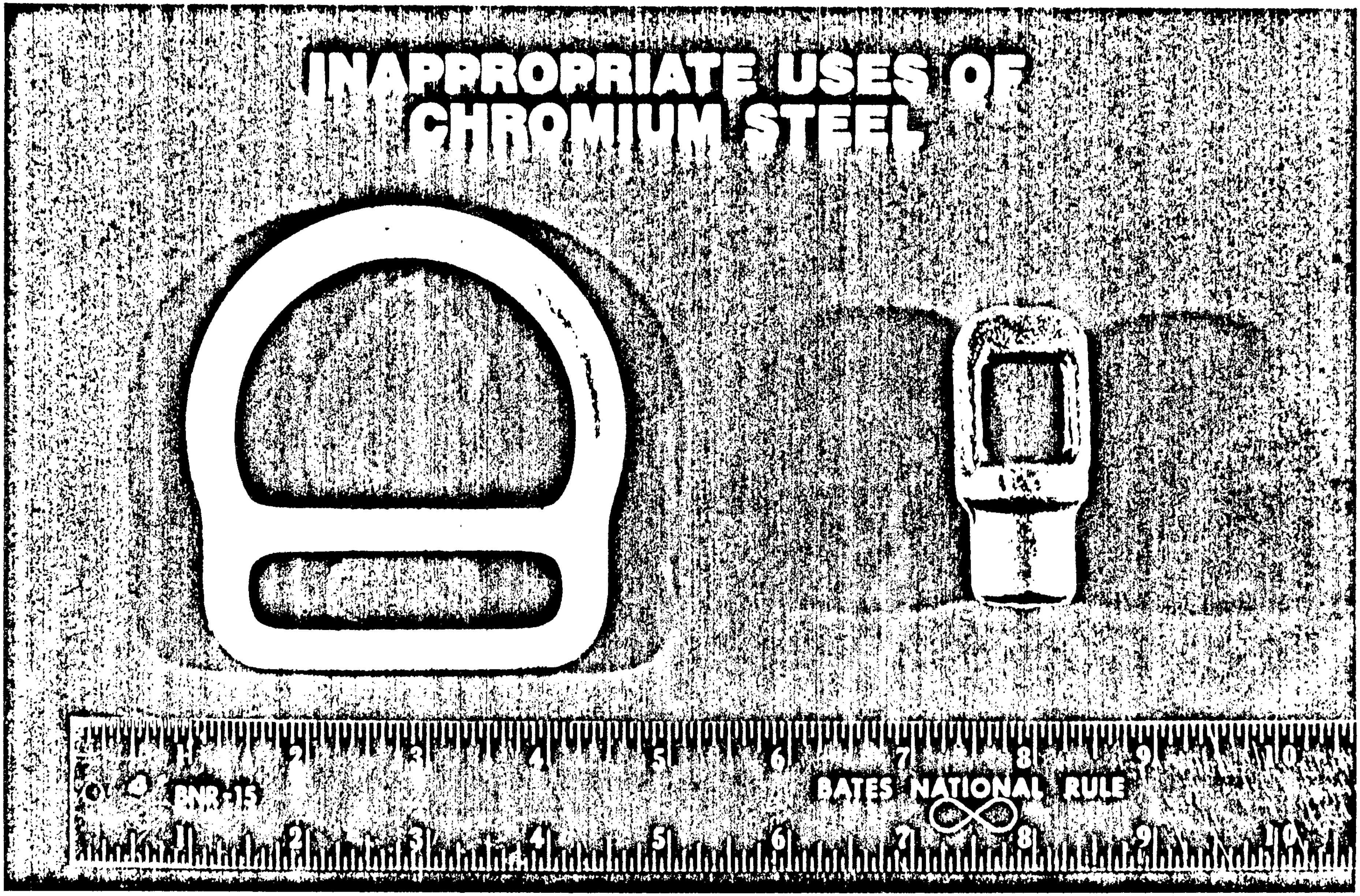
Cost effectiveness as a hardenability agent, has been the key to the tremendous use of chromium bearing low ally steels. Some alloy cost figures for example are: Ferro Manganese, 79% Mn, 26 cents/lb.
Ferro Chromium, 68% Cr, 51 cents/lbs.
Molybdenum Oxide, $6.75 per lb. of Mo contained.

The respective Grossman hardenability multiplying factors for these elements are .426, .318, .398 all at 0.5%. Manganese is about twice as cost effective as chromium but at present prices both are very cheap compared to molybdenum or other alternatives.

So much for the reasons for chromium utilisation in low alloy steel at present.

Faced with a major escalation in the price of chromium, the market mill would categorise its customers applications into two groups, by asking the question:

Is the hardenability contribution of chromium necessary for this application? In many cases the answer would be no. Two such examples



INAPPROPRIATE USES OF CHROMIUM STEEL

are shown in Fig. 5. These components are a bomb hanger and a safety belt fitting produced from 4130 and 4140 respectively. Both are safety critical items, both are over designed from a hardenability point of view. At some time in the past a design engineer thought, "This is a safety item, we should use an alloy steel, what is readily available?" Answer, chrome - molly 41XX series. A much higher volume example is in sucker rod steel used in artifical lift oil wells. Tens of thousands of tons of steel grade 4142 are used each year in the normalised condition for this application. The hardenability influence of chromium is totally wasted, but the steel performs well in the field. Such an application would respond very rapidly to price escalation.

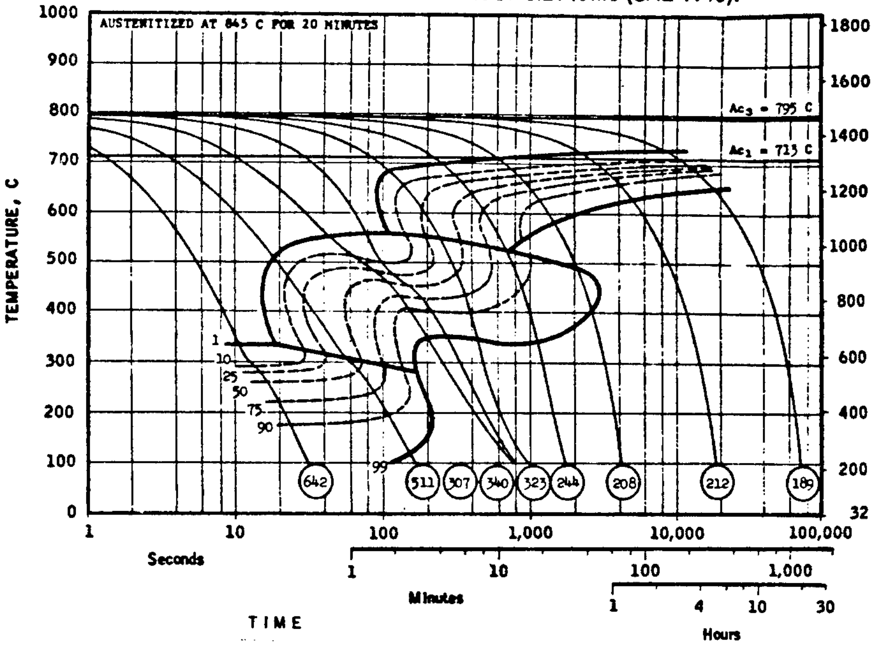
If it was decided that the hardenability effect of chromium was necessary, then replacements would be sought.

Manganese is the obvious contender in terms of both price and effectiveness. In the last resort it is very available as deep sea nodules.

Climax Molybdenum have performed extensive evaluations of the transformation characteristics of low alloy steels. Fig. 6 shows two continuous cooling transformation diagrams which are very similar.

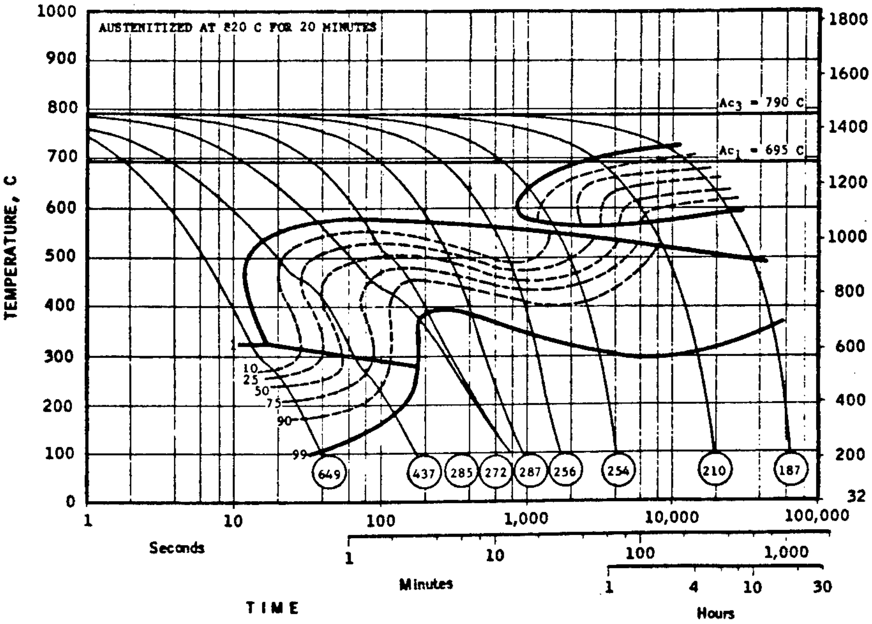
The steel compositions considered, differ only in the replacement of all the chromium by manganese, with an additional slight increase in silicon and molybdenum.

0.39% C-0.26% Si-0.82% Mn-1.00% Cr-0.21% Mo (SAE 4140).



Cr/Mo Steel

0.40% C-0.37% Si-1.47% Mn-0.26% Mo.



Mn/Mo Steel

FIG. 6

Calculation of D.I (Ideal Diameter which quenches to 50% martensite at the core of cylindrical bar) for these steels using the Caterpillar system gives the following results.

Cr Mo Steel (4140)	4.795"
Mn Mo Steel	3.040"

In order to equalise the D.I values, it would be necessary to increase the manganese content of the Mn Mo grade to 1.8%. Its D.I would then be 4.723" and for the same hardenability it would be cheaper to produce.

A similar excercise could be performed for 5160 and 8620. In the case of 5160 for spring applications, the single criteria is a fully martensitic structure throughout the section after quenching. This could be readily achieved by manganese substitution. Grade 8620 contains chromium to promote carburising as well as to impart hardenability. However in many cases the 86XX series is being replaced by the 40XX series which contains no chromium.

Boron has been used to replace more expensive alloying elements in many applications. The market mills in general, are not enthusiastic about boron steel because of problems encountered in the strand casting process. Again, commercial necessity would be an effective motivator in overcoming these problems. At the present time, new complex alloy additivies are being developed for boron steels. These show promise in facilitating the strand casting of a consistent product.

Another approach to reduction in alloy consumption would be to ask the question "Why fine grain?" Virtually all engineering steels are ordered "fine grain" in the U.S. The steelmaker adds elements such as Al Nb or V to refine the austenitic grain. This practice dramatically reduces hardenability. More alloys such as chromium or molybdenum are then added to replace the lost hardenability.

An austenitic grain size reduction of from 3 to 8 requries one of the following increases in alloy element content in compensation.

Carbon	0.25%
Chromium	0.24%
Molybdenum	0.18%
Nickel	1.44%

Grain size as measured by the McQuaid - Ehn test is a measure of a steels grain coarsening tendancy at 1700°F. Since engineering steels are normally quenched from well below this temperature, the test has little relevance. However tradition has it that steel shall be ordered fine grain with no understanding of the cost involved.

One final option which would be persued by market mills would be to make more use of residual elements. Most market mills operate with 100% scrap as raw material. Residual elements, Cu Ni, Cr and Mo are not removed in the steelmaking process. They are present to a greater or lesser degree depending on the scrap source. These elements all contribute to the hardenability of the rolled product and, generally speaking, the cheaper scrap grades have the highest residual content. There is therefore a saving in both scrap and alloy cost if these elements are utilised to their maximum advantage.

In order to capitalize on these constituents of the scrap mix, a trend toward H band specification and away from narrow chemistry ranges should be encouraged. Such a trend already exists, it should be persued by intensive user education.

The conclusion of this author is that in terms of market mill bar products, there are no insurmountable technical problems in the replacement of chromium.

Buyer acceptance is another matter all together. The inertia, of tradition and lack of understanding is enormous.

A conference such as this can have a major impact on the tradition and education problem.

Specifically what needs to be done, is for the AISI and other steel specifying institutions to consolidate the work that has been done on chromium substitution.

This consolidation should appear as an alternative and equivalent series of steels within the AISI steel grade system.

When the axe falls on chromium availability, the steelmaker will then have an immediate course of action open to him in his bid to educate his customer and overcome tradiiton.

Future Raw-Material Requirements for Steel Plant Refractories

by

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Although the total consumption of refractories is declining, a dependable supply of uniform, high-quality refractory materials is necessary for the long-range production of all grades of steel, just as refractories are critical for other metal industries, glass, and cement manufacture. An examination of trends in refractory usage in the steel industry indicates continuing and significant shifts in the refractory requirements because of changing processes, increasing equipment size, increased severity of process steps, increased steel-quality requirements, and more severe environmental restrictions. In the future, there will be increased requirements for refractories made from high-alumina or alumina (bauxite derived) raw materials, as well as those which include silicon carbide, natural graphite, zircon, and zirconia as components. The uses of alternate refractory materials in selected areas are discussed along with recycling and conservation possibilities for selected materials.

Introduction

The steel industry now consumes approximately 50 to 55 percent of the refractories produced, as compared with approximately 65 to 70 percent in the 1960's and 1970's. Although actual consumption figures vary considerably, reduction from ranges of 60 to 70 pounds of refractories per ton of steel to 30 to 40 pounds per ton have been reported. These quantities do not include slag-control additives such as calcined dolomites, which also influence lining life. Of course, the largest single factor in the total future refractory consumption will be in the worldwide production rate for steel for which predictions vary widely.

Recent changes in steel processing to more modern/efficient manufacturing techniques, new environmental restrictions, more stringent product demands, and the development of alternate containment technqies without refractories, have all had significant impact on refractory usage. Also, the developments of improved refractories have contributed greatly to improved service life and have resulted in trends toward lower refractory consumptions. In general, however, all these trends have been associated with the use of more sophisticated and expensive materials, based on the use of highly technical synthetic raw materials, rather than the use of more common refractory materials. As a result, the steel industry is more dependent on the long-term availability and cost of such materials than ever before.

This paper will briefly review the current and projected changes in refractory practices, resulting from changes in steel processing, and thereby identify what are believed to be the more critical raw-material areas. Following this review, some comments will be made on the particular critical materials, and suggestions to possible substitute materials will be made.

Changes in Refractory Usage in the Steel Industry

For convenience in this discussion, the areas of refractory usage will be grouped into four categories as shown in Table I, coke and ironmaking, steelmaking, secondary steelmaking, and casting and finishing. Subgroups within these categories identify trends in particular application areas. The trends discussed are summarized in Table I.

A. Coke and Ironmaking

The primary changes in this area have involved the use of fewer, larger, and more productive blast furnaces, higher temperature and more sophisticated stoves, cast-house systems to permit nearly continuous tapping, and more hot-metal treatment, such as removal of sulfur or phosphorous by injection of appropriate reagents. The larger and/or more productive blast furnaces operate under more severe conditions than the older furnaces and require longer and more dependable life. As a result, more expensive refractories using high-alumina, silicon carbide, silicon carbide carbon, and special carbon refractories are being increasingly used, replacing the naturally occurring fireclay materials. Also, more emphasis is being placed on furnace cooling by using large well-cooled cast-iron blocks (staves) in the entire furnace, Figure 1, or an increased number of copper insert plates, Figure 2. These systems necessarily require refractory materials with resistance to abrasion, erosion, alkali attack, thermal-shock, and carbon-monoxide attack, but also must have high thermal conductivity for effective cooling. Campaign lives up to 10 years can be achieved with proper furnace cooling, combined with upgraded burden materials and sophisticated changing techniques, and process control.

Requirements for more energy-efficient and higher temperature stoves have required the use of more creep-resistant silica and/or high-alumina refractories, Figure 3. Although the raw materials for silica refractories are readily available domestically, the high-alumina materials are normally made from imported high-alumina sources (bauxite, andalusite). The life of such stoves is very long, using combustion controls, gas-cleaning, and avoiding contamination of the stoves with furnace gases.

The cast-house systems to meet new production rates and environmental standards must have significantly longer refractory lives than before, as maintenance frequency has changed from several times a day to weekly or monthly. Figure 4 shows a modern cast-hours system with multiple troughs and runners. The better refractory materials for longer life use high-alumina, alumina, silicon carbide, and graphite materials rather than domestic carbonaceous clays. The hot-metal injection treatments, Figure 5 also require refractories made more from high-alumina or basic materials (periclase or dolomite).

On an overall basis, the total refractory consumptions in the coke and ironmaking areas are not substantially changed, but the emphasis on more complex refractories is obvious. (An increase in consumption in metal-handling facilities is probably offset by longer lives, using improved cooling in the furnace proper and by longer life in stoves.)

B. Steelmaking

Overall refractory consumption in steelmaking has declined significantly with the replacement of open-hearth furnaces by oxygen steelmaking (BOP, Q-BOP, LBE, etc.) and the long service life being achieved in oxygen-steelmaking furnaces. This long life is the result of both better refractories and the use of alternate methods of lining protection such as slag-composition control by dolomite additions and lining maintenance by hot-gunning, Figure 6. These factors, along with improved process control without furnace reblows and turndown, have given lives of as much as 10,000 heats with 2000 to 4000 heats being achieved routinely. It is also fortunate that the oxygen-steelmaking refractories used are based only on periclase (MgO) with carbon from pitch or amorphous ~~surces~~ Sources. This has greatly reduced steel requirements for chrome ore in refractories. Some refractories now used are made with imported natural graphite additions, but such refractories are not absolutely necessary for long life.

The trend in electric-furnace refractory consumption is also downward, as water-cooled sidewall panels and roofs have replaced refractory materials, Figure 7. These panels have lowered overall cost and permit more rapid application of electrical power. The remaining refractories in the electric-furnace bottom and slag lines will be based largely on periclase with carbon or graphite.

The AOD furnaces for producing stainless steels use refractories made from periclase-chrome or dolomite. Consumption in the AOD is down with improved materials and blowing practices. It also appears that dolomite could totally replace periclase-chrome in the AOD in the event of chrome shortage.

High-purity, high-quality periclase and dolomite are readily available domestically. Approximately 90 percent of the periclase used is made synthetically from brine or seawater, Figure 8. Synthetic periclase appears to represent an excellent long-term dependable raw-material source, as the magnesium salts and dolomite used in reaction to free the magnesium are readily available. Like more high-quality refractory materials, periclase is very energy-intensive and the cost can be expected to increase with rising energy costs. Excellent progress has been made, however, in the use of unfired refractories made from periclase to avoid the energy required in brick shapes.

Synthetic periclase is not too readily available in other parts of the world, and more use is made of refractories made from fired dolomite. This use is accelerated by the appreciably higher cost of periclase compared with dolomite, particularly in Europe. Large raw dolomite deposits of excellent quality exist in the United States, but expansion of a fired dolomite supply would require facility investments. It should be pointed out that the United States does use significant quantities of dolomite as the slag additive to retard BOP wear, and as an essential step in the manufacture of periclase (Figure 8). Note that as much MgO is recovered from dolomite as from the seawater of brine.

C. Secondary Steelmaking

Increased quality demands of steel are requiring significant changes in the refractories used in ladles and increased use of degassers and related processes. Continuous casting requires more ladle holding time and imparts more rigid requirements for refractories. Ladle processing for either continuous or ingot casting may range from simple argon stirring to remove impurities and homogenize the steel to special alloying and injection treatments, Figure 9. Flow control on ladles in which steel is preheated prior to casting now uses external rather than internal systems, Figure 10 and 11. Refractories in ladles and flow-control systems also must not contaminate steel by undesirable reactions such as reduction of silica, which provides oxygen forming undesirable Al_2O_3 inclusions, Figure 12.

As a result of these changes, ladles are increasingly lined with high alumina or basic (dolomite, periclase chrome, periclase carbon) rather than fireclay or fireclay-graphite materials. This represents a major shift in overall refractory consumption. The external flow-control systems also require more complex refractories made from alumina, periclase, or alumina graphite.

Degassers are conventionally lined with periclase chrome and alumina refractories, Figures 13 and 14. Increased degasser use will increase the consumption of these refractories, but this is partly offset by improved materials, design, and operating parameters.

D. Casting, Shaping, and Finishing

Conventional ingot casting uses only fireclay and silica as hot top and coatings, Figure 15. Continuous casting uses substantial quantities of refractories in the tundish, tundish flow-control device, and the shroud tubes for oxidation between the ladle and tundish, and tundish and water-cooled mold, Figure 16. Tundish linings are changing from the long-life-style tundish, using high-alumina products, to consumable liners made from periclase. This change was done to provide a clean contamination-free surface on the tundish on any start-up. The tundish flow-control devices require either alumina-carbon rods or external systems using high-alumina , alumina, or alumina-graphite materials, Figure 17 and 18. Shroud tubes are made from either fused silica or alumina graphite in a multiple of sizes and shapes with special features such as argon injection, Figure 19. The continuous-casting area requires many new refractories and a substantial number of them are based on imported bauxite or alumina from treated bauxite. Although not in substantial tonnages, many flow-control devices and certain critical wear areas of shroud tubes may use zirconia or zircon as an essential component.

Steel shaping and finishing furnaces (reheating and annealing furnaces, soaking pits) are still an essential part of steel production, but with an overall declining market because of fewer soaking pits on continuously cast steel. There have been several innovations in the steel shaping and finishing areas to reduce energy consumption including the use of improved insulations to cover the water-cooled supports in reheating furnaces, Figure 20. Alumina-silica fiber modules, blankets, and other fiber forms are also being used in both new construction and over old construction to reduce energy consumption. Fortunately, the raw materials required for normal fiber manufacture are readily available.

Overall Review of Material Requirements

From the foregoing brief discussion, it is apparent that changing refractory-use patterns in the steel industry will call for refractories containing increased amounts of alumina, high-alumina, silicon carbide, and graphitic raw materials with lesser increases for zircon and zirconia for refractories. Other materials such as silica, fireclay, carbon, periclase, and dolomite will show a more steady or somewhat decreased consumption. Chrome-ore usage appears significantly less critical today than only a few years ago, based on significantly reduced projected usage.

Two recent conferences have detailed world supply of raw materials for refractories, and it is not our primary purpose to detail raw material availability.[1,2)*] Some comments on the above conference material will, however, be included in the following sections.

Alumina and High Al_2O_3 Raw Materials

High-alumina and tabular, fused or calcined alumina materials derived essentially from bauxite present a significant projected increase in consumption. In high-alumina materials, we include materials such as various bauxite grades (60 to 88% Al_2O_3), andalusite, and kyanite. Recent reviews indicate that the bauxite usage increases do not represent significant problems in world supply because of expanded world availabilities. Approximately 10 percent of the bauxites will be used in refractories with the primary usage in metal manufacture. Despite these assurances of world bauxite supply, the domestic steel and refractory industry should continue their efforts to use the maximum amounts of domestic bauxite-type materials and kyanites and to take advantage of the unique properties of andalusite.

Several possible substitute materials for alumina and high-alumina refractories are already being investigated by the steel

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*See References.

industry. Periclase or dolomite materials have been used or proposed in many applications replacing these materials including the following:

1) In blast-furnace stove upper checkers where the thermal properties and density of the periclase are an added advantage.
2) In torpedo ladles or mixers where basic refractories can be used if properly insulated and slag chemistry adjustments made.
3) In steel ladles where basic refractories can be used with adequate preheating and rapid cycling to avoid thermal shock.
4) In tundish linings where consumable boards or monolithic coatings are quite successful.
5) In steel-handling devices where periclase might be used to replace alumina in alumina-graphite compositions.

Considerable reductions in alumina and high-alumina usage can be made using the basic materials, and this should be a goal of all connected with steel industry refractory developments. This would assure long-term dependence on raw materials available domestically with a virtually unlimited future supply.

If bauxite raw-material shortages occur on a long-term basis, the extensive research done to develop methods of extracting alumina from materials such as clay may have to be reexamined.3) This is not a matter of long-term research, but of updating known techniques.

Silicon Carbide

While the raw materials for making silicon carbide (carbon, sand) are readily available, long-range planning will be necessary to provide new plants with the energy-environmental standards required. The steel industry must use such products judiciously. Proper cooling design in blast furnaces can greatly decrease the demand for high-quality refractory products. This is illustrated by Figure 21, which shows the appearance of closely packed plate coolers, which can give good lives even with fireclay refractories.

Many of the silicon-carbide-bearing refractories can be recycled after use. For example, blast-furnace trough refractories could be recycled and made into lower quality runner materials. As in all recycling, however, economic conditions will dictate the extent to which recycling will be used. New practices, in which only parts of linings are periodically replaced in high-maintenance areas by vibration or by wet materials, are also being developed to reduce consumption and costs.

Graphite

Natural graphite is being used extensively as 2 to 20 percent of oxide refractories to impart special features to the refractories, such as high conductivity, thermal-shock resistance, and nonwettability by slag or metal. Care must be taken to avoid overdependence on such materials, and to develop alternate methods of obtaining the same property advantages as with graphite additions. The next route to follow appears to be isolation of the scarce premium graphite grades to only more critical applications.

The grades of graphite required in applications, such as trough materials, are not as restrictive as in stopper rods. The most scarce grades are apparently required in pouring tubes, slide-gate plates, and magnesia-carbon brick. As in all refractory applications, cost will ultimately dictate which of the areas really require the premium product grades. New developments are undoubtedly required and will depend on a better understanding of the true technical merits of graphite-type materials. Fundamental studies in the MgO-C and Al_2O_3 systems are needed to more fully develop this class of materials.

Zircon and Zirconia

Other countries, such as Japan, are making increased use of zircon-bearing refractories in steel ladle linings because of reported economic advantages over high-alumina or basic products. The domestic steel industry should only utilize such products in cases where technical advantages are clear because the world market price could be significantly altered by any substantial increased usage. Small zirconia parts will continue to be utilized in the continuous-casting area where their resistance to steel erosion is outstanding. New domestic sources of zircon and zirconia will be established if price/availability relationships are favorable. Recycling should be used whenever possible for zirconia materials.

Other Materials

Organic binders (pitches, synthetic polymeric binders) play an important role in refractories. Additional development work is required to better understand the relationship between the pyrolysis, graphitization, and high-temperature effects of such materials with refractory oxides. Other binder materials (cements, phosphates, borates, silicates) are generally available domestically and do not present long-term availability problems. However, changes in binder usage may occur with new application or environmental requirements, and continued attention to these products is required.

Summary

The domestic steel industry is very dependent on the long-term availability of consistent high-quality refractories and must compete worldwide for such materials. As the steel industry is constantly examining refractory costs, however, a system of checks and balances occur in which substitute refractories are continually developed to replace those containing raw materials, which are escalating in price. The domestic refractory and steel industry should continue their efforts to develop and use materials based largely on readily available domestic raw materials. Considerable progress has also been made in improving refractory life and lowering consumption by improved refractories and installation techniques, altering process conditions to provide conditions more favorable to refractory life such as less thermal cycling, using alternate containment techniques such as water cooling, and by slag and process control. Recycling of certain refractory grades containing materials such as silicon carbide, premium graphites, alumina, and zirconia should be increasingly practiced. Continued Research is required to develop the optimum use of more expensive additive and binder materials.

Reference

1. Proceedings of the "Raw Materials for Refractories Conference," sponsored by the U. S. Department of Interior, Bureau of Mines, University of Alabama, February 8-9, 1982. Co-sponsors included the American Ceramic Society.
2. Symposium, "Minerals in the Refractory Industry," Industrial Minerals Meeting, September 12-14, 1982, Pittsburgh, Pennsylvania.
3. F. A. Peters, R. C. Kirby, and D. B. Highie, "Methods of Producing Alumina from Clay," Journal of Metals, October 1967.

Table I

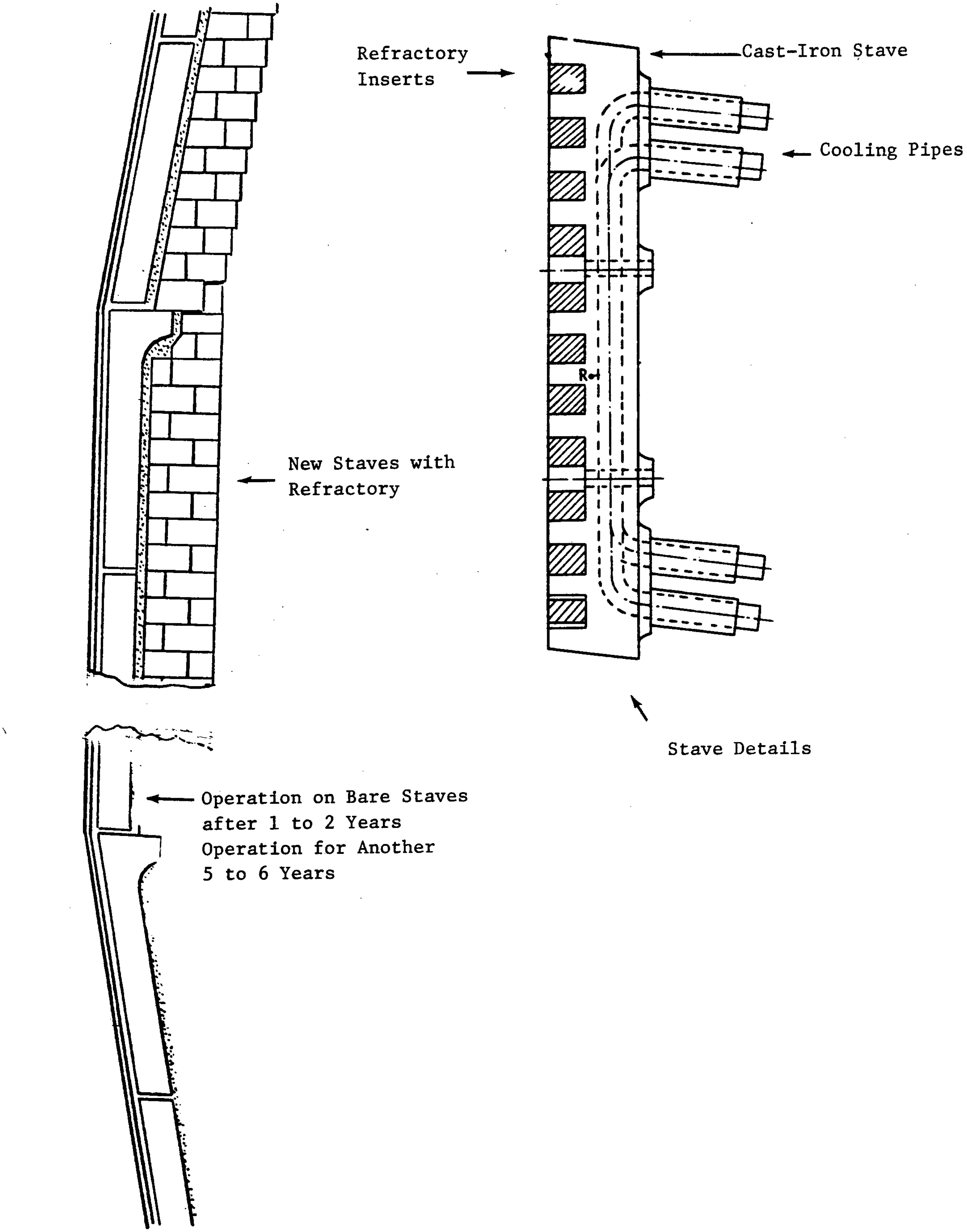
Current and Projected Use of Refractories in The Steel Industry

Item	Coke and Ironmaking				Steelmaking				Secondary Steelmaking			Casting, Shaping, and Finishing		
	Coke Oven	Blast Furnace	Stoves	Iron-Handling	BOP	Electric	AOD	Open Hearth	Ladles	Degassers	Steel Handling	Continuous Casting	Ingot Casting	Shaping and Finishing
Conventional Refractory	silica, fireclay	fireclay, high-alumina, alumina-carbon	fireclay high-alumina, silica	fireclay, high-alumina, carbons	periclase-carbon	periclase-chrome, periclase, high-alumina	periclase-chrome, dolomite	periclase-chrome, dolomite	fireclay, high-alumina	periclase-chrome, alumina	fireclay, clay-graphite, alumina, fused silica	high-alumina, fireclay silica, periclase-chrome	fireclay, silica	fireclay, high-alumi silica, periclase
Future Refractory	same	high-alumina SiC, carbon, fireclay	high-alumina silica, fireclay	high-alumina, SiC, graphite	periclase-carbon periclase-graphite	periclase-graphite, periclase-chrome	dolomite, periclase-chrome	strong downward, most shops replaced by BOP	high-alumina, dolomite, periclase-graphite	periclase-chrome, alumina	alumina, periclase, alumina graphite, fused-silica	periclase in monolithic form, high-alumina, alumina-graphite, zirconia	fireclay, silica	same
Consumption Trend, General	constant	constant, but material requirement more critical with fewer furnaces	constant	upward with more metal treatments and environmental requirements	downward because of better life	downward with use of water-cooled panels and better refractories	lower with longer life	none	upward with more ladle processing	upward with more degasser use	upward with more productive systems	strong upward with more continuous casting	downward with less ingot casting	downward with less soaking pits
Consumption Trend, Overall	About the same with less in furnaces/stoves and more in iron handling.				Strong downward with BOP replacing open hearth, use of water-cooled panels.				Upward with more ladle-degasser processing.			Upward with more complex materials required for casting		
Increased Raw Material Usages	none, but possible shortage production capacity	SiC, alumina	high-alumina	high-alumina, alumina, SiC, graphite	graphite	graphite	-	-	high-alumina	chrome ore alumina	alumina, graphite	alumina, graphite, zirconia	-	-
Possible Substitute Materials	-	extended use of stave or dense plate coolers	periclase,** silica alternate high-alumina sources	periclase,** dolomite**	periclase-carbon dolomite	periclase or periclase-carbon, more water-cooled panels	dolomite		periclase or dolomite	dolomite, periclase	periclase-graphite**	periclase-graphite**		

*Refractory Type	Raw Material Source
Silica	Domestic quartzites.
Fireclay	Domestic clays, raw or calcined.
High Alumina	Imported or domestic-fired bauxites, andalusite.
Alumina	Synthetic tabular, fused, or calcined alumina from imported bauxite.
SiC	Synthetic from silica and coke, domestic.
Carbon	Domestic petroleum or metallurgical cokes, calcined anthracite, amorphous carbons.
Graphite	Imported natural graphite.
Periclase	Largely synthetic from domestic brine or seawater and domestic dolomite.
Chrome Ore	Imported natural chrome ores.
Dolomite	Fired domestic raw dolomite.
Fused Silica	Synthetic from domestic sands or quartzite.
Zircon	Domestic or imported sands.
Zirconia	Synthetic from zircon sands - domestic or imported.

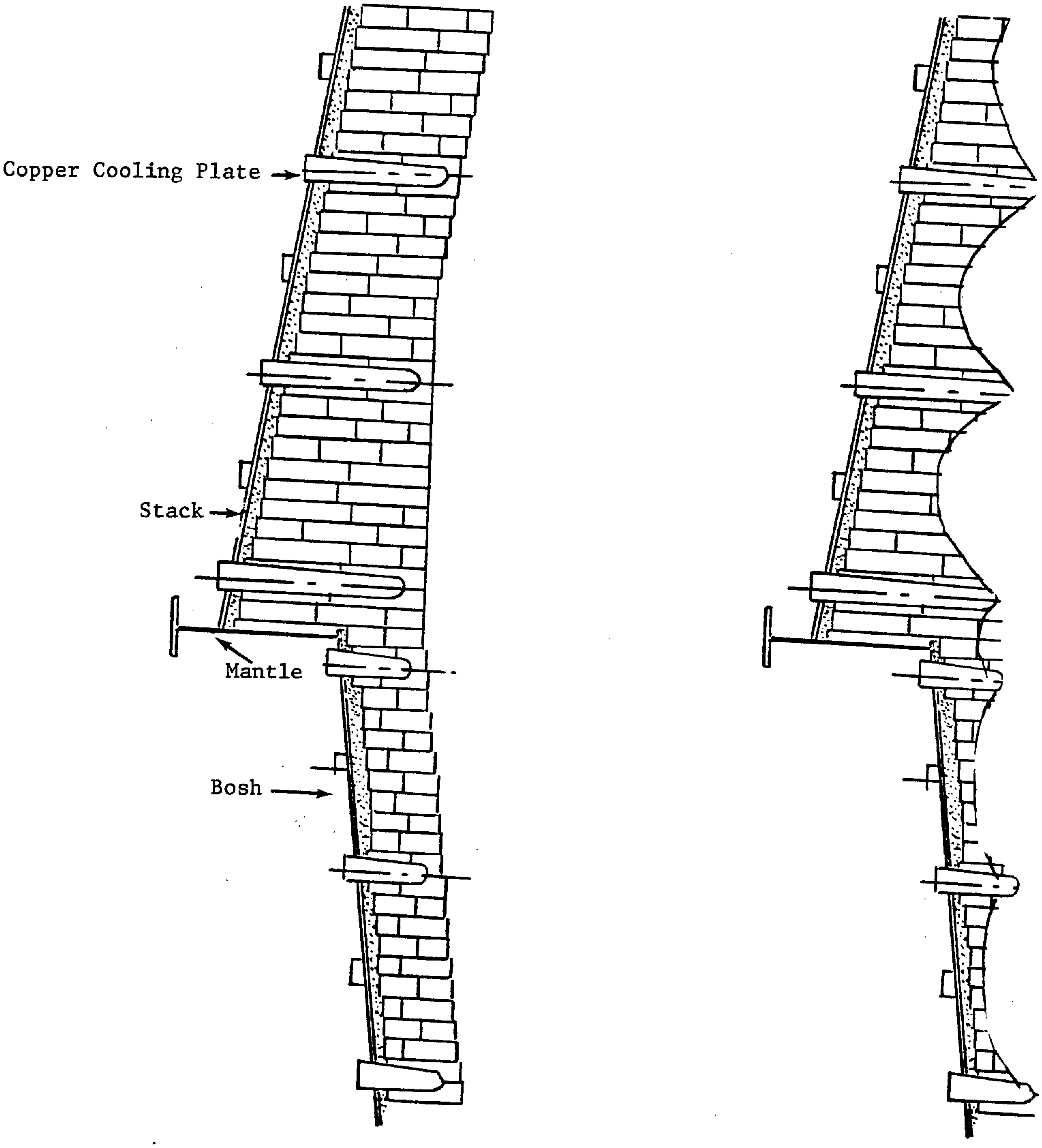
**Relatively new application for materials.

U. S. STEEL CORPORATION, RESEARCH, MONROEVILLE, PENNSYLVANIA



Stave Cooling in Blast-Furnace Stack

Figure 1

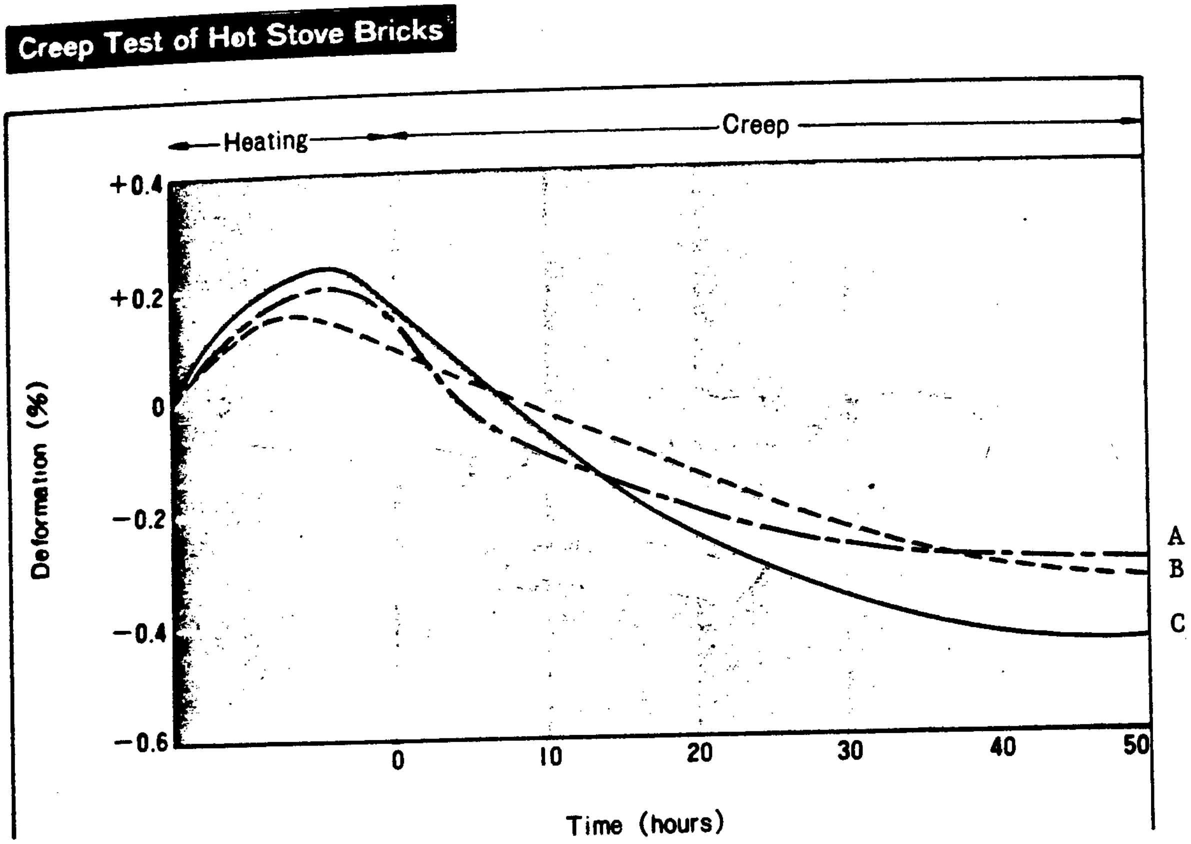


Original Lining

Used Lining

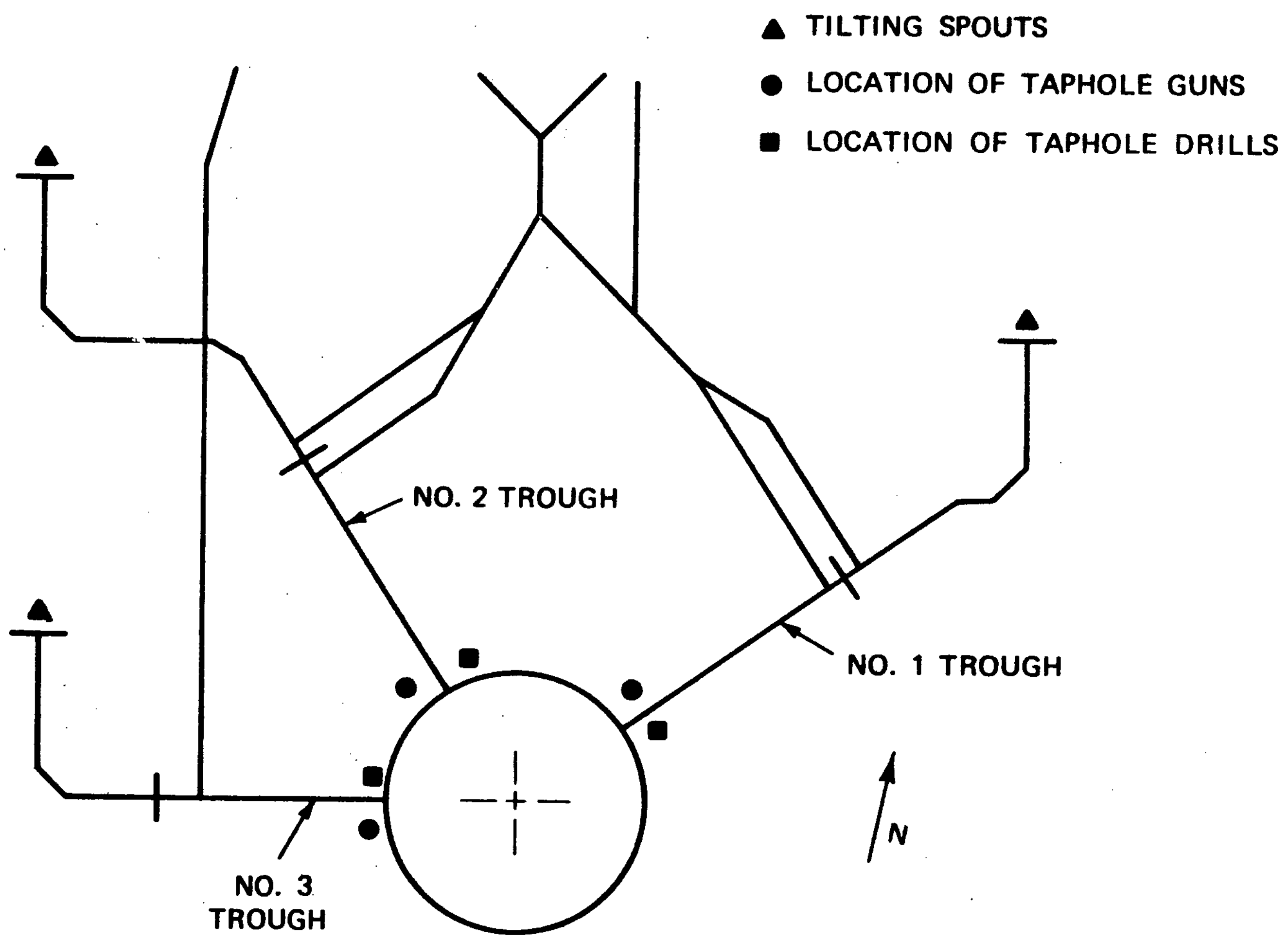
Plate-Cooled Blast-Furnace Lining

Figure 2



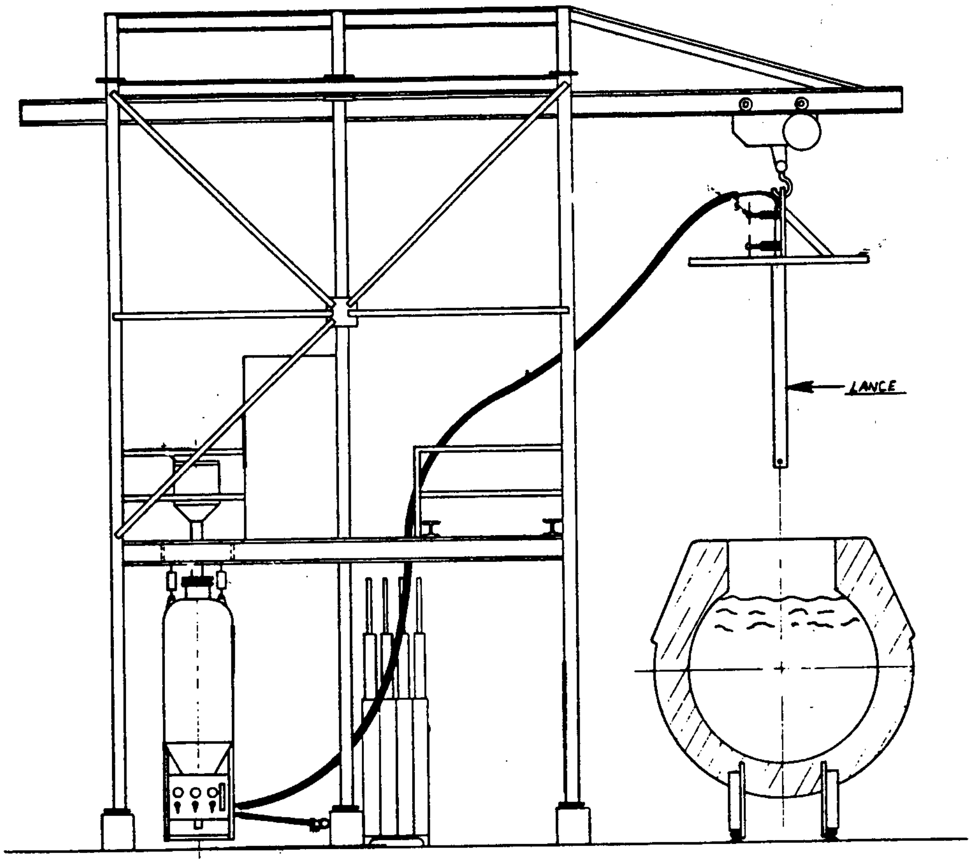
Creep Test of Hot Stove Brick

Figure 3



Layout of A Casthouse with Multiple Tapholes

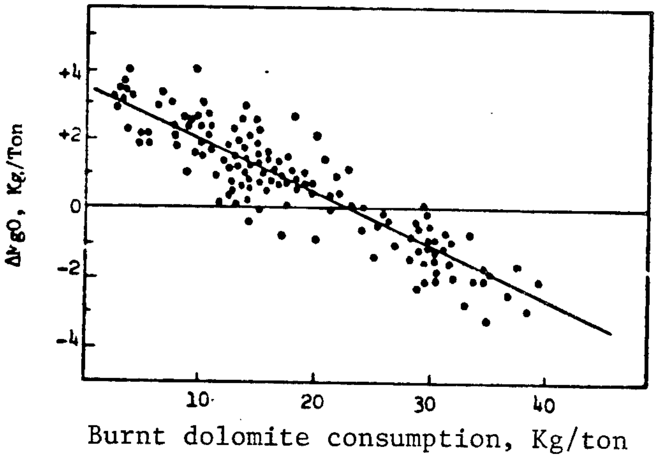
Figure 4



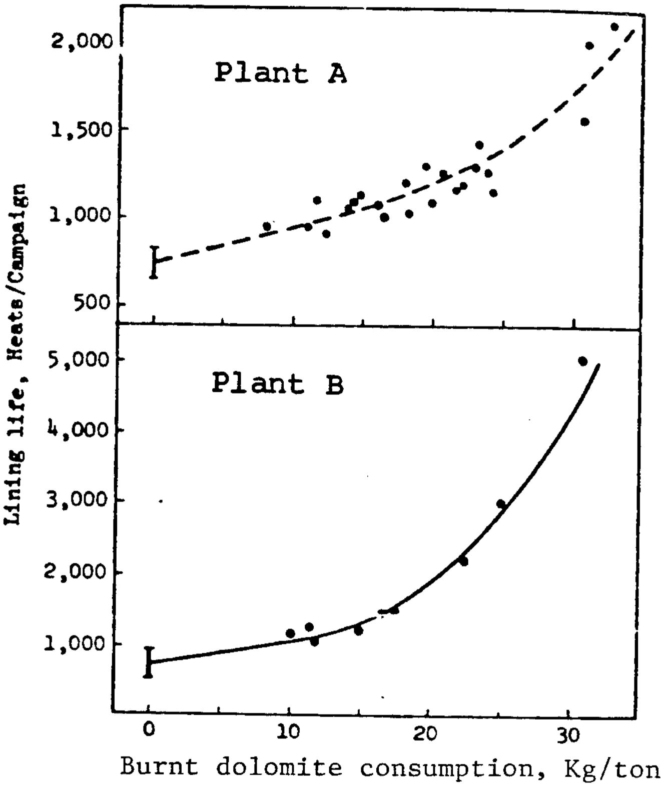
Torpedo Ladle

Injection Setup for Hot Metal Desulfurization
by Carbide or Lime Injection

Figure 5

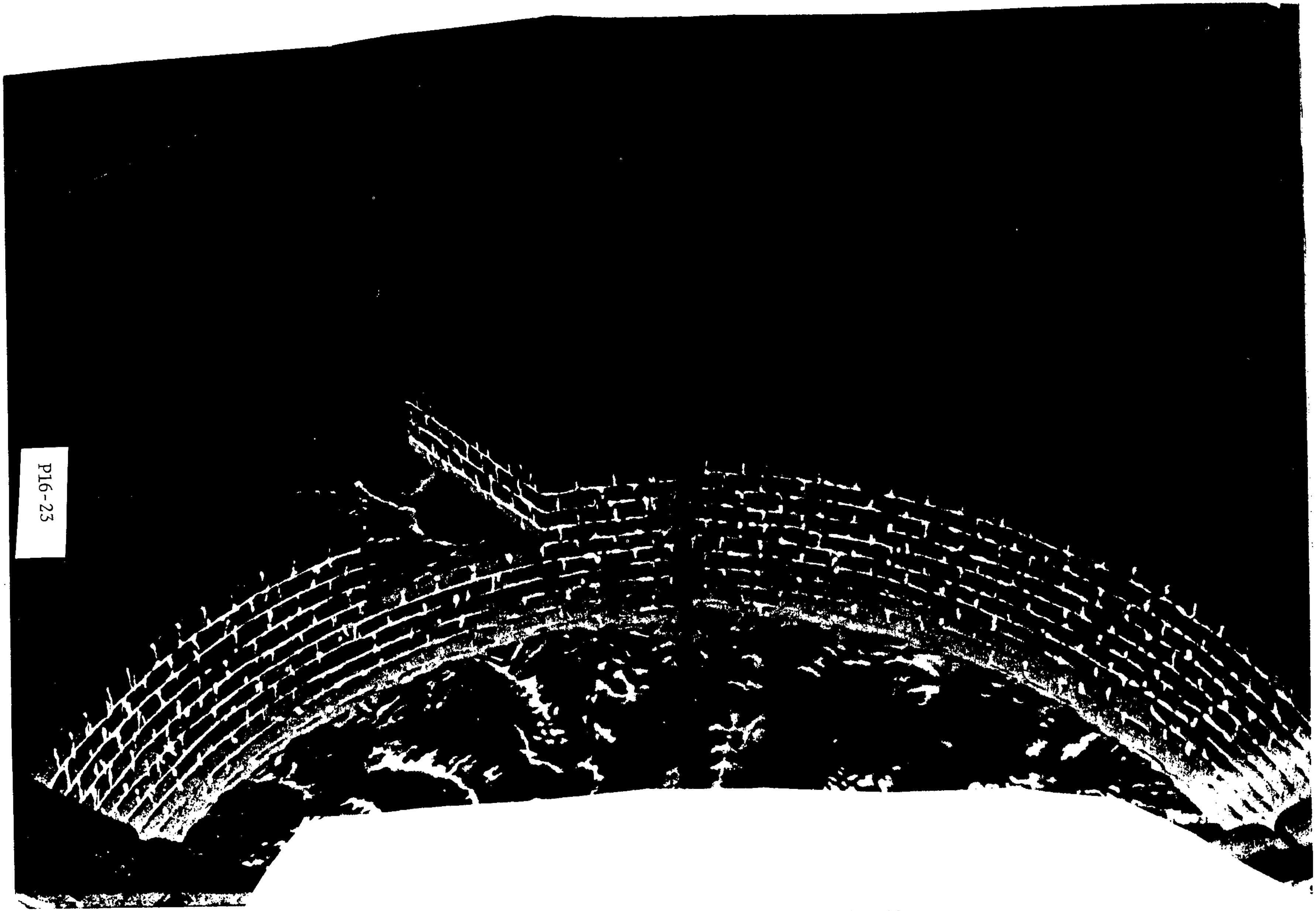


A —Relationship between burnt dolomite consumption and ΔMgO



B —Effect of dolomite consumption on lining life

Figure 6



Water-Cooled Panels in Electric-Furnace Sidewall

Figure 7

MAGNESIA PRODUCTION PROCESSES
SEAWATER OR BRINE

Dolomite $(Ca,Mg)CO_3 \xrightarrow{heat} CaO + MgO + CO_2\uparrow$

Limestone $CaCO_3 \longrightarrow CaO + CO_2\uparrow$

$$CaO+MgO+H_2O \text{ —— } Ca(OH)_2 + Mg(OH)_2\downarrow$$

$$Ca(OH)_2+Mg{+}{+} \longrightarrow Mg(OH)_2 + Ca{+}{+}$$

$$Mg(OH)_2 \xrightarrow{heat} MgO+H_2O$$

Dolomite: 2.29 tons produces 1 ton MgO, theoretically approximately 2.5 tons in practice.

Limestone: 2.48 tons produces 1 ton MgO, theoretically approximately 2.7 tons in practice.

SYNTHETIC MAGNESIA FROM SEAWATER

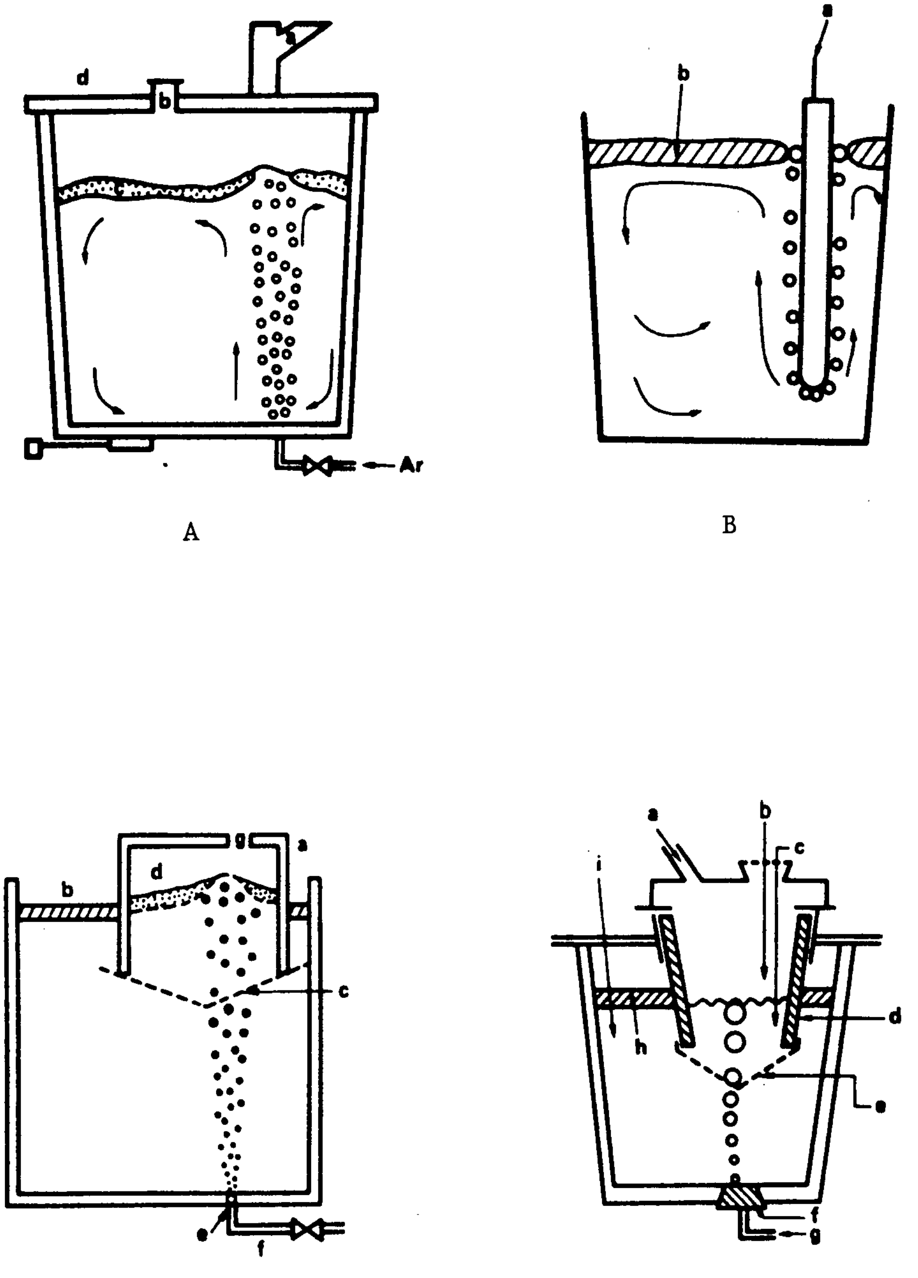
1 Ton seawater + dolime produces 8.6 lbs. MgO

1 Ton seawater + lime produces 4.3 lbs. MgO

1 cubic mile seawater could produce 1.09×10^7 tons MgO

All oceans contain 3.3×10^{15} tons MgO equivalent

Figure 8



A

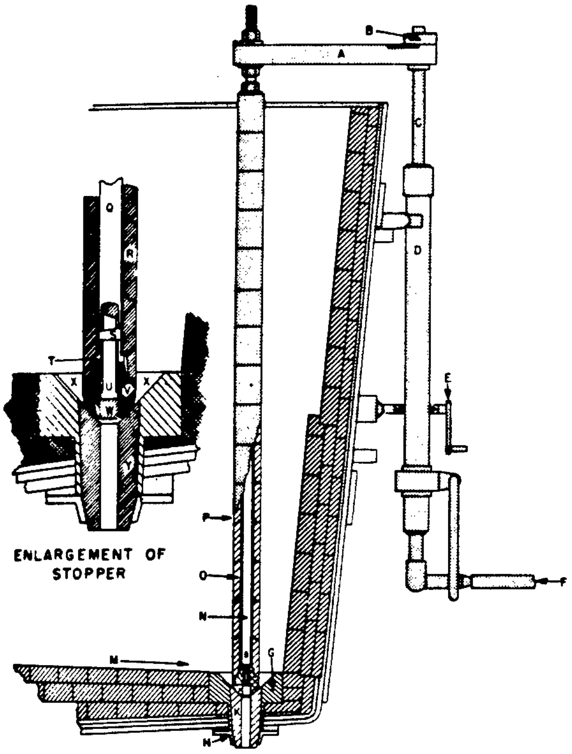
B

C

D

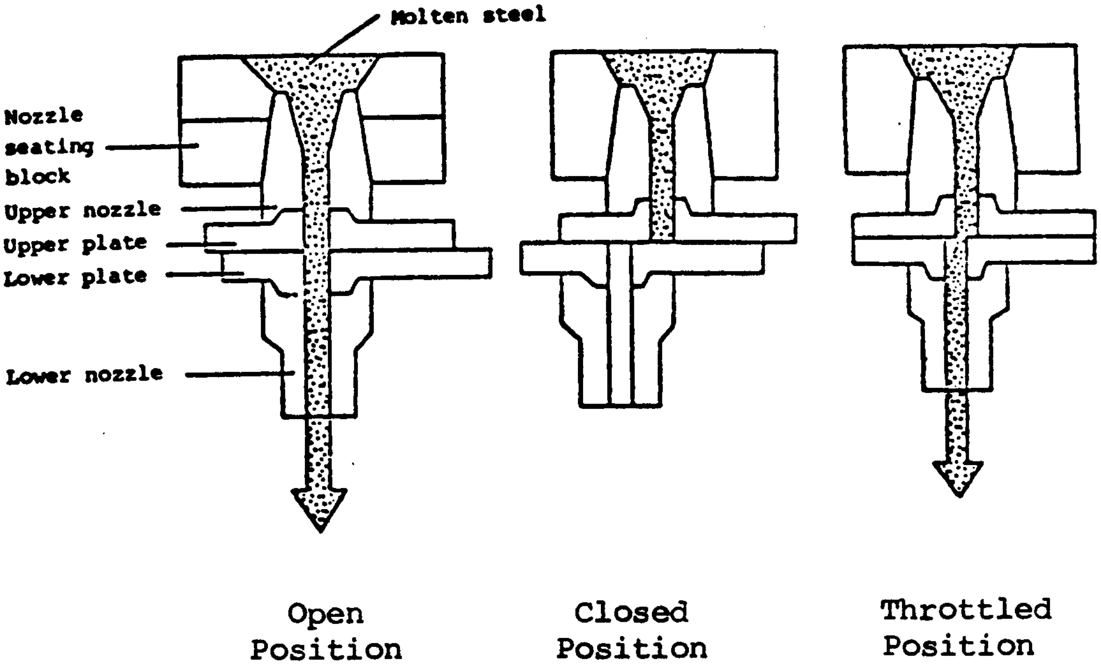
Some ladle processing methods such as argon stirring through bottom plugs (A) or rods (B) with synthetic slags (C) or alloy additions (D).

Figure 9



Stopper rod, well, and nozzle assembly
for a steel ladle, indicating materials
of construction and method of installation.

Figure 10



Different Positions of the Refractory Components in a Ladle Slide Gate

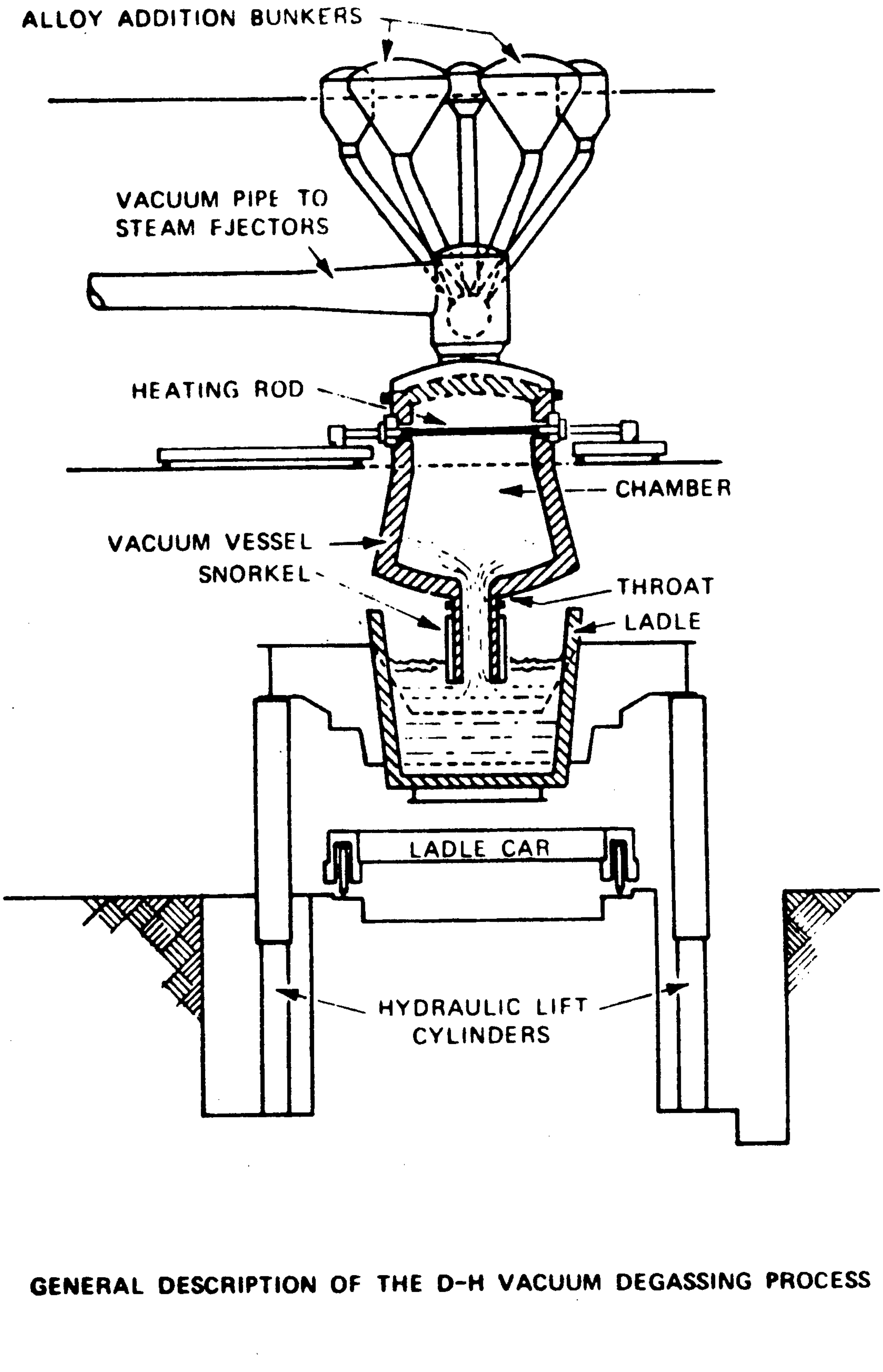
Figure 11

$$\underset{\text{Refractory}}{SiO_2} + \underset{\text{Steel}}{Al} \longrightarrow \underset{\text{Inclusion}}{Al_2O_3} + Si$$

$$\underset{\text{Refractory}}{Fe_2O_3} + \underset{\text{Steel}}{Al} \longrightarrow \underset{\text{Inclusion}}{Al_2O_3} + Fe$$

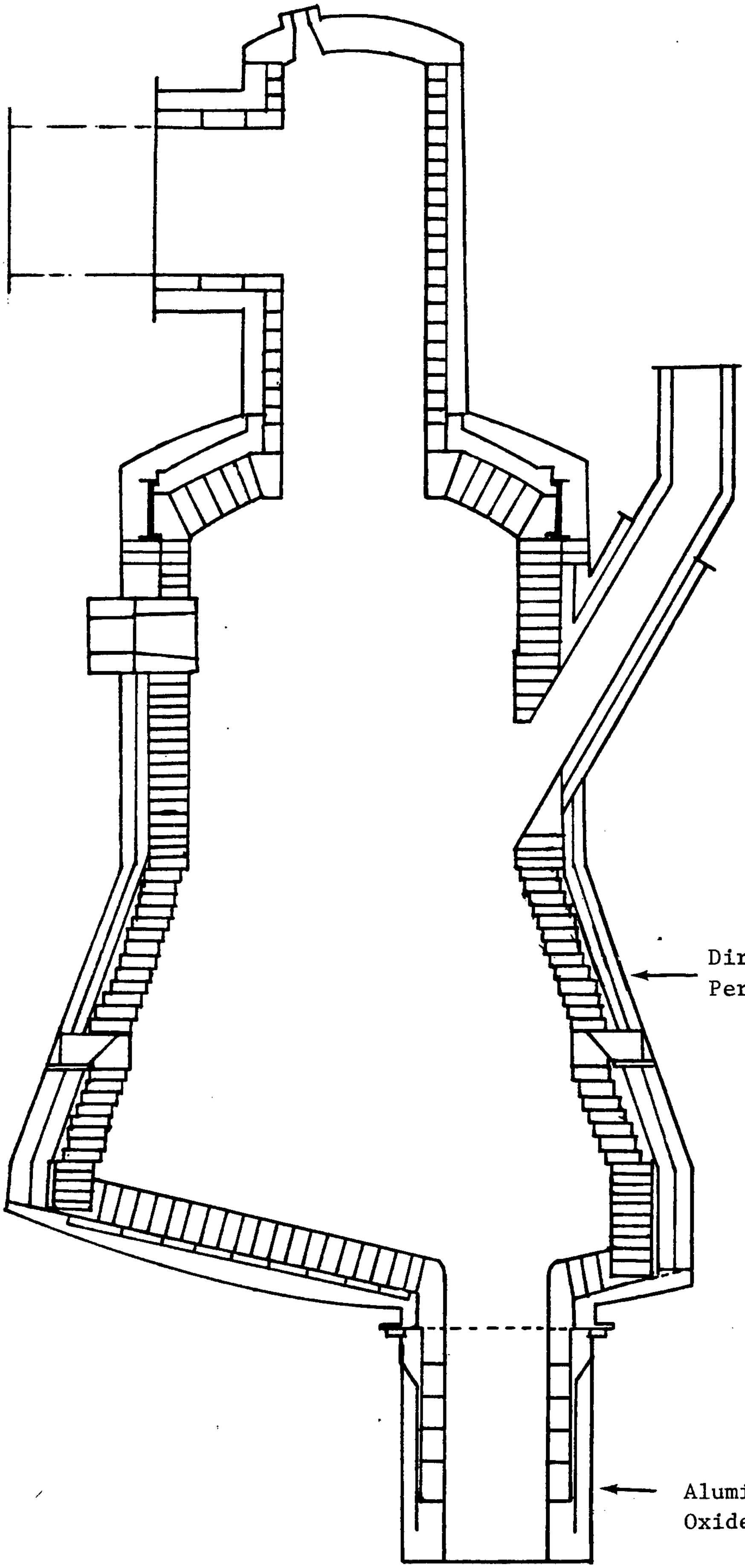
Reactions with refractory which can provide source of oxygen for alumina inclusions.

Figure 12



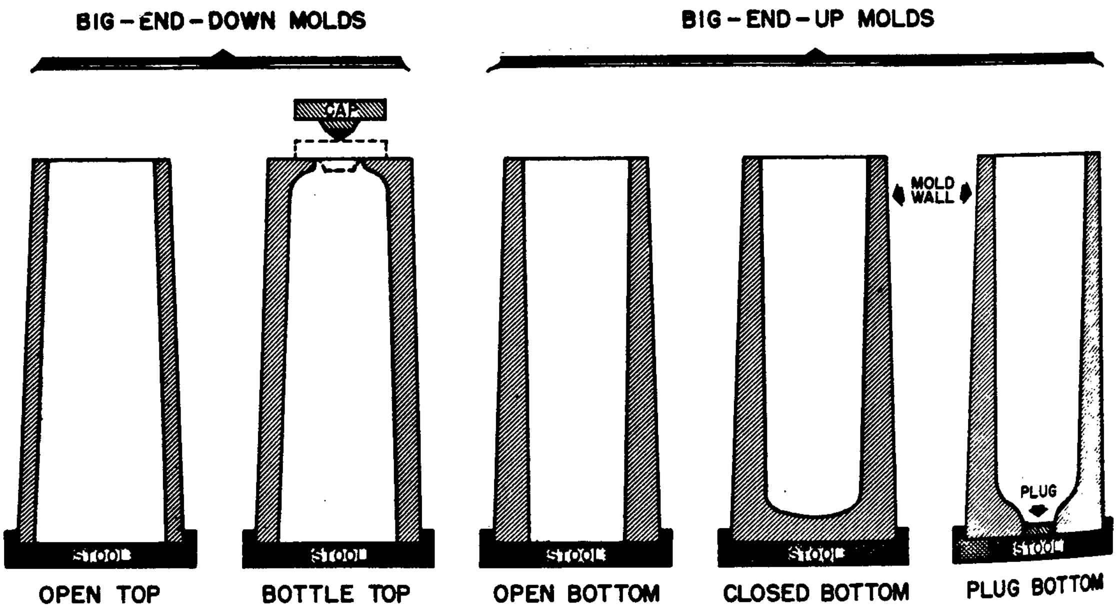
GENERAL DESCRIPTION OF THE D-H VACUUM DEGASSING PROCESS

Figure 13



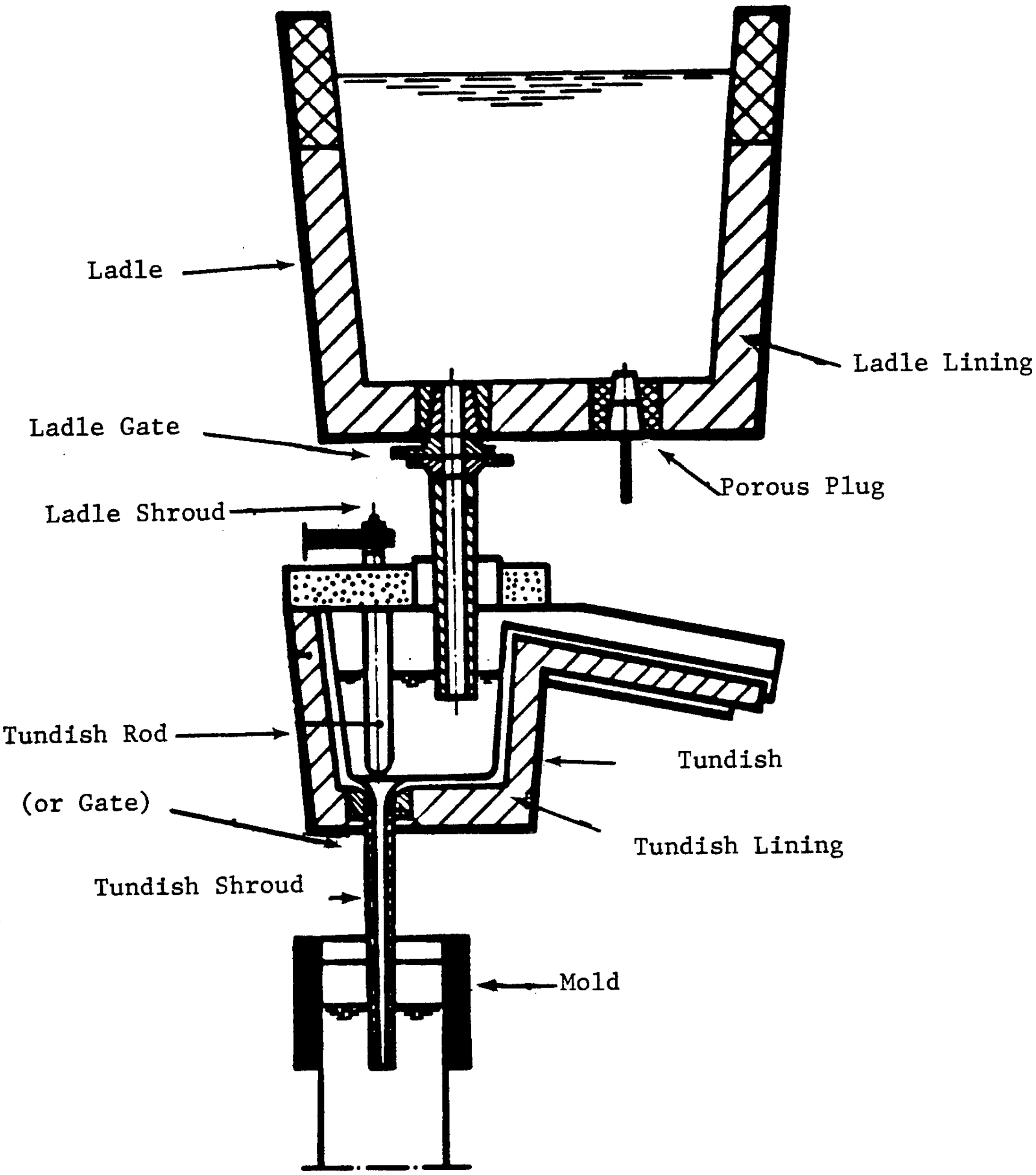
Details of Refractory Construction in Degasser

Figure 14



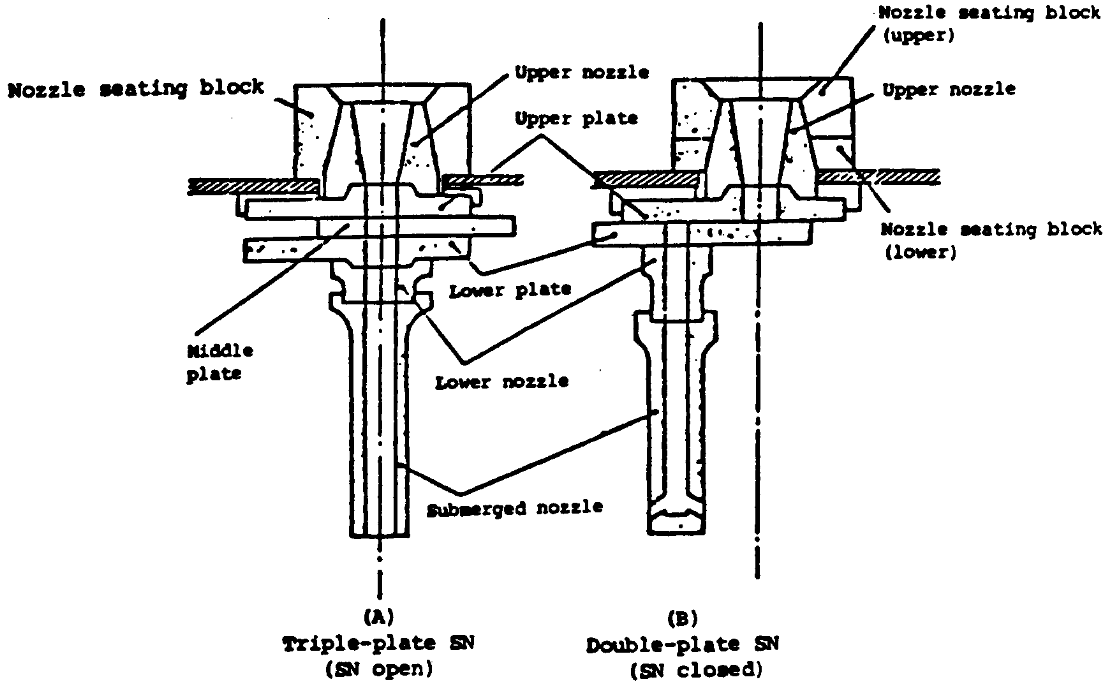
Sections of various types of cast iron-ingot molds. Refractories sometimes used as mold coatings, stool inserts, or hot tops.

Figure 15



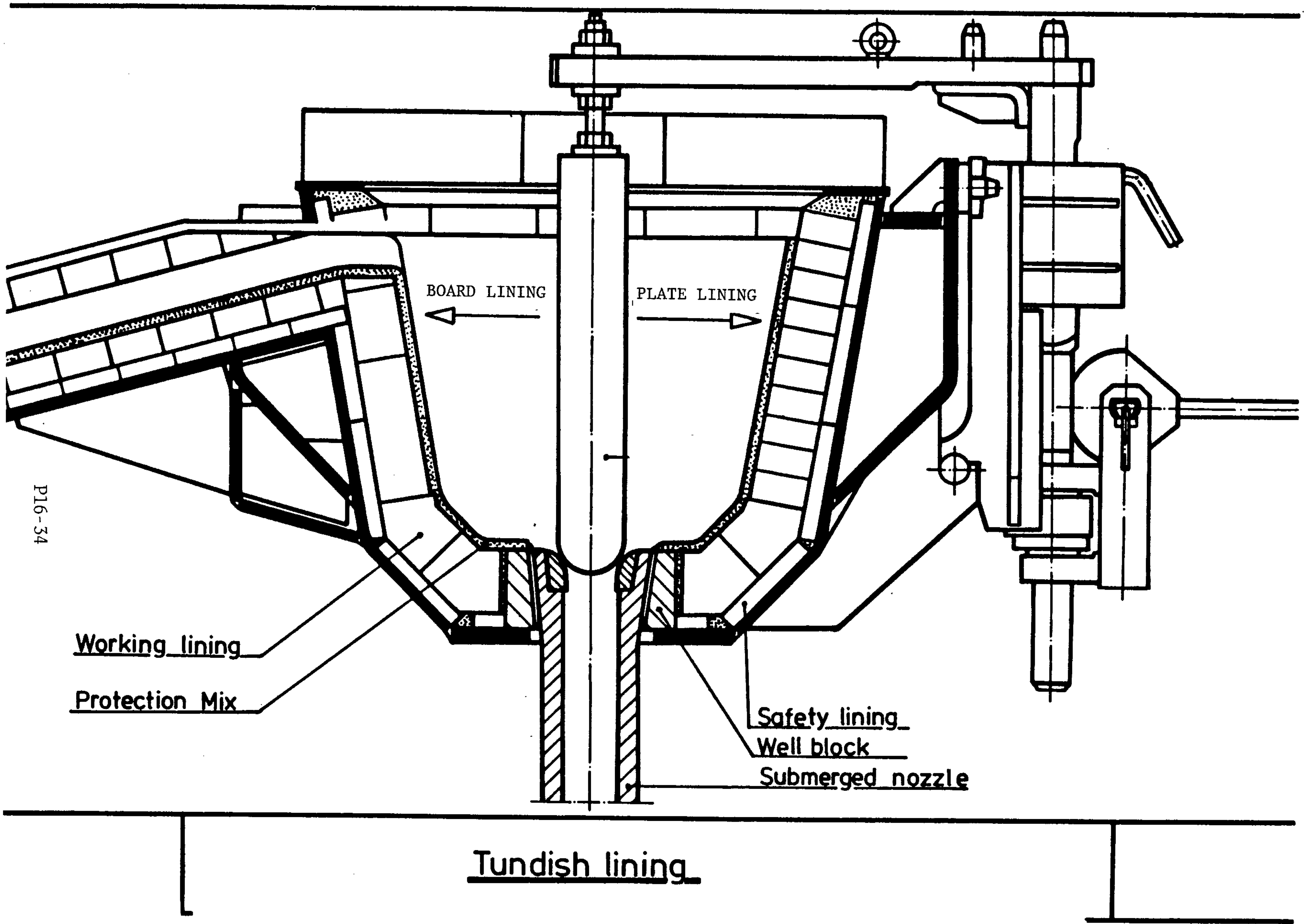
Molten Steel Flow-Control Portion of A
Continuous-Casting System

Figure 16



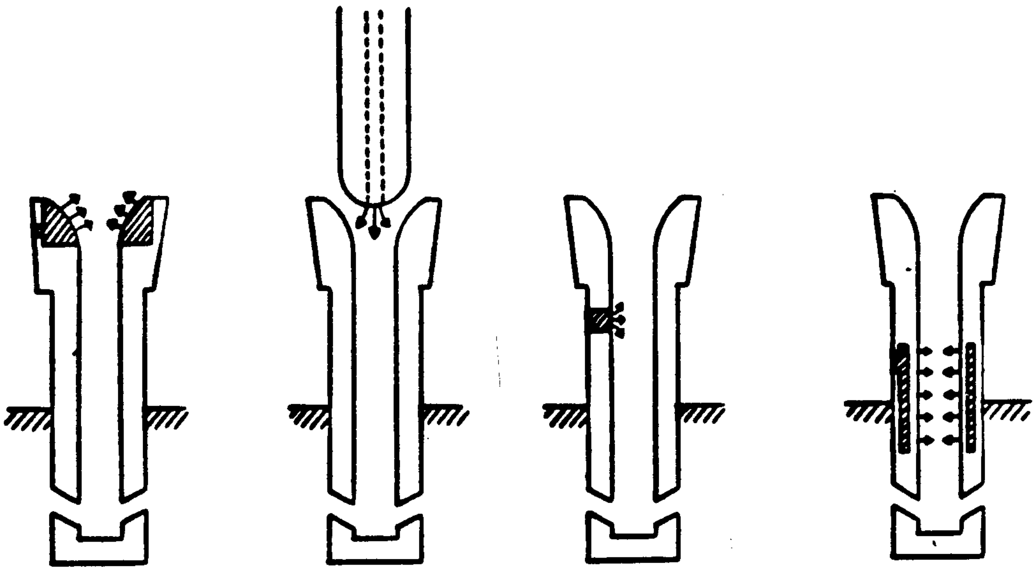
Tundish Sliding Nozzle Construction

Figure 17



Tundish with Stopper-Rod Control

Figure 18



(a) Porous Ring Method

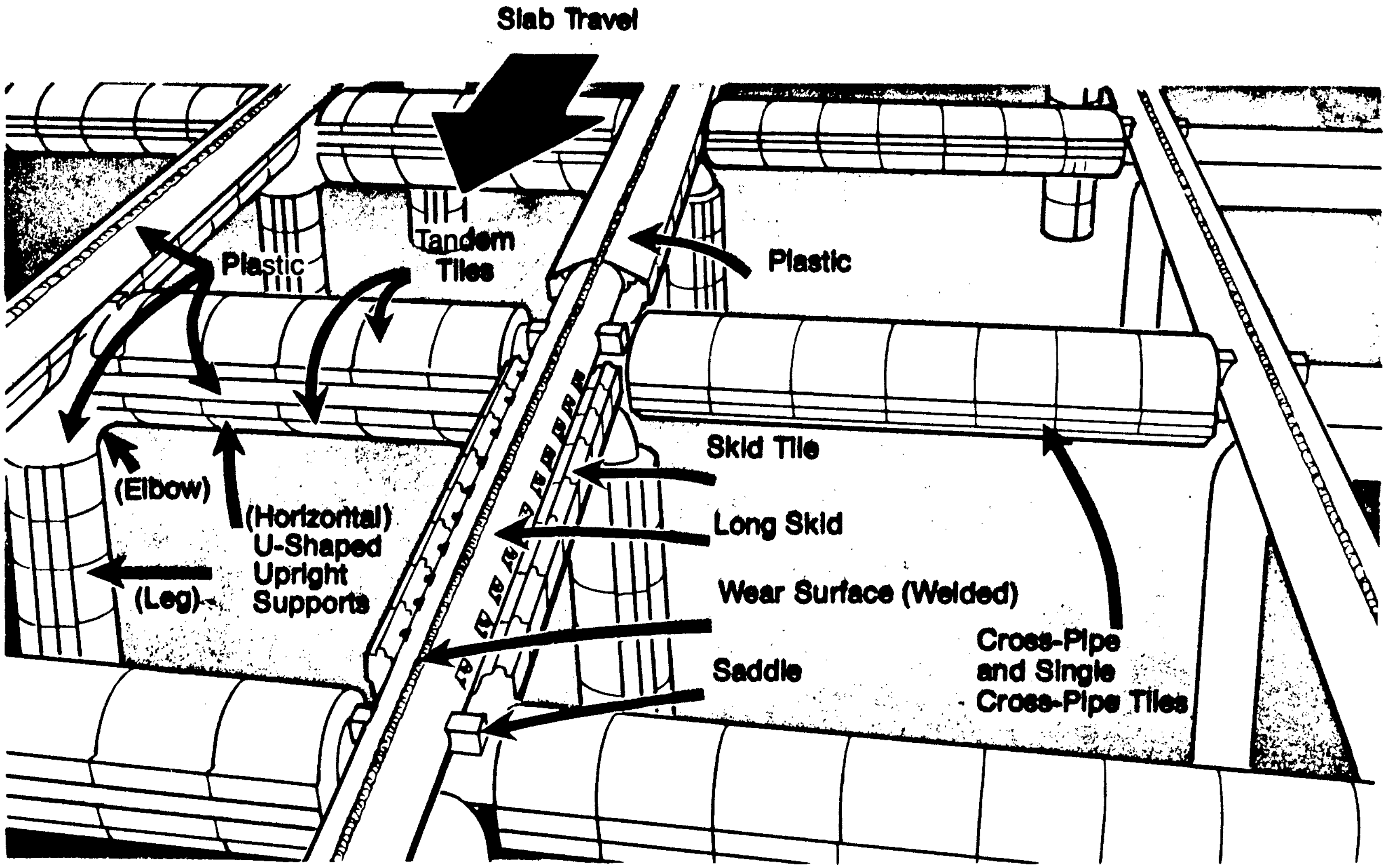
(b) Stopper Method

(c) Micro Pore Method

(d) Slit Method

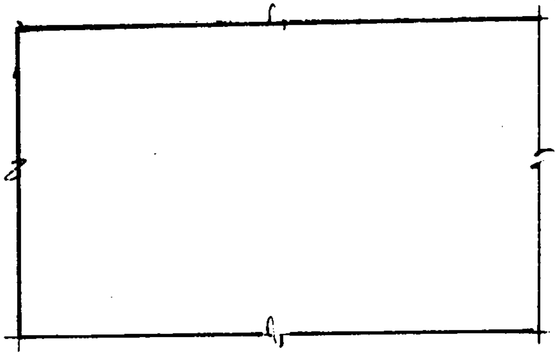
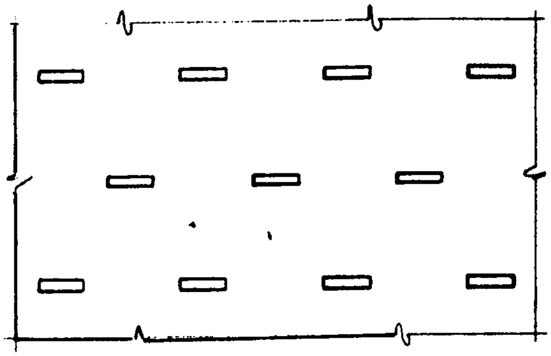
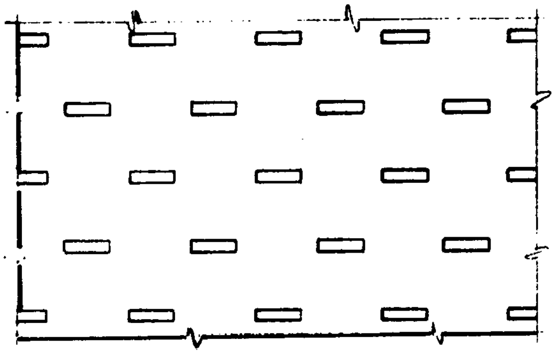
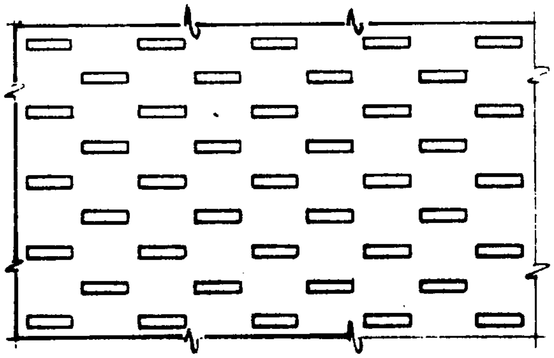
Inert Gas Bubbing Methods Used to Decrease
Alumina Clogging Problems

Figure 19



Identification of Major Components of Skid-Pipe System

Figure 20

	DESCRIPTION	NUMBER OF COOLERS PER ROW	VERTICAL SPACING OF ROWS INCHES
	ZERO (0)	0	–
	SPARSE (S)	28	36
	MEDIUM (M)	32	24
	DENSE (D)	36	12

Location of Cooling Plates Showing Large Number of Plates

Figure 21

-- 102 MILLION POUNDS; WATER USE IS REDUCED 40 PERCENT -- 6.7 MILLION GALLONS; AND MINING WASTES ARE REDUCED 97 PERCENT -- 2.8 MILLION TONS.

AND THAT'S NOT ALL. THERE IS A 74 PERCENT ENERGY SAVING. EACH ONE MILLION TONS OF SCRAP IRON USED INSTEAD OF IRON ORE TO MAKE NEW PRODUCTS SAVES OVER THREE MILLION BARRELS OF CRUDE OIL. IN 1980, THE U. S. WAS IMPORTING CRUDE OIL AT THE RATE OF SIX MILLION BARRELS A WEEK.

ENERGY IS EXPENSIVE, AND THERE IS EVERY REASON TO ANTICIPATE THAT IT WILL BECOME MORE EXPENSIVE. THIS RISING COST FACTOR HAS LED TO INCREASED EMPHASIS ON ENERGY CONSERVATION THROUGHOUT THE METALWORKING INDUSTRIES. TO BE COMPETITIVE, NOT ONLY WITH OTHER STEEL PRODUCERS, BUT WITH SUBSTITUTE MATERIALS AS WELL, EVERY COMPANY LOOKS TO CUT COSTS.

THERE IS LITTLE DOUBT THAT ELECTRIC FURNACE MILLS EQUIPPED WITH CONTINUOUS CASTERS ARE SOME OF THE MOST EFFICIENT STEEL PRODUCERS IN THE COUNTRY -- INDEED, IN THE WORLD. THE SAVING OF TIME, LABOR, AND ENERGY, COUPLED WITH HIGHER YIELDS AND IMPROVED PRODUCTIVITY, MAKE THE SCRAP BASED MILLS THAT CONTINUOUSLY CAST THEIR PRODUCTS ESPECIALLY COMPETITIVE.

NUMEROUS INDIVIDUALS WITHIN THE STEEL INDUSTRY AS WELL AS INDUSTRY WATCHERS HAVE ASSERTED THAT CONTINUOUS CASTING WILL RESULT IN GREATER DEMAND FOR SCRAP. HOWEVER, REALITY

REQUIRES A CLOSER LOOK AT THE ASSERTION. SINCE CONTINOUS CASTING IMPROVES PRODUCT YIELD, IF THE FINISHED TONNAGE DEMAND REMAINS THE SAME, THE ONLY ADJUSTMENT IS EITHER IN THE SIZE OF FURNACE HEAT OR THE NUMBER OF FURNACE HEATS. NO MORE SCRAP WILL BE NEEDED TO MAKE THE SAME VOLUME OF STEEL. YET, EVEN WITHOUT AN INCREASE IN SCRAP DEMAND DUE TO CONTINUOUS CASTING IN ELECTRIC FURNACES, THE GROWING SHARE OF STEEL PRODUCTS MADE IN SUCH FURNACES BODES WELL FOR THE SCRAP PROCESSOR.

TWENTY-FIVE YEARS AGO, ELECTRIC FURNACES ACCOUNTED FOR ONLY 7.1 PERCENT OF TOTAL U. S. STEEL OUTPUT. THAT SHARE ROSE TO 27.7 PERCENT LAST YEAR. THROUGH AUGUST OF THIS YEAR, ELECTRICS HAVE POURED 28.9 PERCENT OF THE STEEL PRODUCED IN THIS COUNTRY. IT'S GROWING, AND THE TREND IS EXPECTED TO CONTINUE.

THE AMERICAN IRON AND STEEL INSTITUTE SAID IN ITS PUBLICATION, STEEL AT THE CROSSROADS, "BY THE END OF THE 1980'S. . . .ELECTRIC FURNACE PRODUCTION IS EXPECTED TO ACCOUNT FOR OVER 30 PERCENT OF RAW STEEL PRODUCTION (VERSUS 24 PERCENT IN 1978). . ." OVER 30 PERCENT OF THE MARKET IS A LARGE NUMBER.

ON ANOTHER PAGE IN THAT SAME DOCUMENT, AISI SHOWS 1988 STEEL PRODUCTION OF 51 MILLION TONS FROM ELECTRIC FURNACES, 51 MILLION TONS, UP SHARPLY FROM THE 1978 LEVEL OF 33 MILLION TONS OR AN 18 MILLION TON INCREASE IN ONLY THAT

SEGMENT OF THE STEEL INDUSTRY IN 10 YEARS.

AND THIS GROWTH WILL OCCUR FROM BOTH NEW ELECTRICS AS WELL AS BY BETTER USE OF THE FURNACES ALREADY IN EXISTENCE. FOR EXAMPLE, ONE ELECTRIC FURNACE OPERATION IN WEST GERMANY HAS REDUCED THE TAP-ON-TAP TIME FROM 140 MINUTES PER HEAT TO 75 MINUTES PER HEAT. THIS ACTION VIRTUALLY DOUBLES THE CAPACITY OF THE <u>EXISTING</u> INVESTMENT -- TWICE AS MUCH OUTPUT IN THE SAME FURNACE -- TWICE AS MUCH SCRAP IS USED.

THE SITUATION WITH BASIC OXYGEN FURNACES EQUIPPED WITH CONTINUOUS CASTERS PRESENTS A COMPETITIVE MARKET OPORTUNITY FOR SCRAP. SINCE THE IMPROVED YIELD IN THE BOF WILL MEAN A REDUCTION IN HOME SCRAP PRODUCTION, THERE WILL BE A NEW DEPENDENCE ON ADDITIONAL IRON UNIS -- IRON UNITS, NOT NECESSARILY SCRAP IRON. BOFS WILL NO LONGER BE SELF-SUFFICIENT IN HOME SCRAP. TO SUPPLEMENT THEIR HOME SCRAP CHARGE, BOF OPERATORS WILL HAVE THREE ALTERNATIVES -- DIRECT REDUCED IRON, IRON ORE, OR SCRAP: OR A FOURTH POSSIBILITY, SOME COMBINATION OF THE THREE.

IF SCRAP PROCESSORS WERE MAKING THE DECISION AS TO WHICH FORM THE IRON UNITS SHOULD BE, THE RESULT WOULD BE OBVIOUS -- USE MORE SCRAP. UNFORTUNATELY, WE WON'T BE MAKING THAT DECISION, BUT I CAN ASSURE YOU WE WILL BE MAKING EVERY EFFORT TO INFLUENCE THE INCREASED UTILIZATION OF SCRAP IN THE BASIC OXYGEN FURNACE. WITH MORE THAN 60 PERCENT OF THE STEEL OUTPUT EMANATING FROM BOFS, THE SCRAP INDUSTRY

WANTS TO BE INVOLVED AS A SUPPLIER.

IN ADDITION TO CONTINUOUS CASTING, TECHNOLOGIES ARE BEING DEVELOPED THAT WOULD INCREASE THE PERCENTAGE OF SCRAP CHARGED IN THE BOF.

MANY OF YOU KNOW, FAR BETTER THAN I, OF THE NEWER TECHNOLOGY TO USE BOTH TOP BLOWING AND BOTTOM STIRRING IN THE BOF WITH ONE PURPOSE BEING TO INCREASE MARKEDLY THE RATIO OF SCRAP TO THE TOTAL CHARGE. MORE SCRAP IN THE BOF -- THE FUTURE MARKET IS THERE AND GROWING.

AND HOW HIGH CAN THE SCRAP CHARGE RISE? MAYBE 40 PERCENT, MAYBE 45 PERCENT, MAYBE EVEN 50 PERCENT SCRAP CHARGES IN THE BOF. IN WEST GERMANY TODAY, THERE IS A BOF OPERATING AT A 100 PERCENT SCRAP IRON CHARGE. NOT 33 PERCENT, NOT 50 PERCENT, BUT A 100 PERCENT SCRAP IRON CHARGE AND MAKING QUALITY STEEL.

NOT ONLY IS THE SCRAP AVAILABLE TO MEET THESE POTENTIAL INCREASES, BUT THE INDUSTRY HAS INVESTED HEAVILY IN THE PROCESSING CAPACITY TO PREPARE THOSE IRON UNITS FOR MELTING. ON A SINGLE SHIFT BASIS, THE SCRAP INDUSTRY HAS THE CAPABILITY TO PROCESS ABOUT 70 MILLION TONS OF MATERIAL ANNUALLY. AS A REFERENCE POINT, TOTAL SCRAP DEMAND IN 1981 WAS 48 MILLION TONS; THE RECORD DEMAND WAS 60 MILLION TONS IN 1974. IF A SECOND SHIFT IS ADDED TO THE ONE SHIFT TOTAL OF 70 MILLION TONS, THE ANNUAL PROCESSING CAPACITY RISES TO MORE THAN 130 MILLION TONS.

YOU MAY BE WONDERING TO YOURSELF, WHY SUCH OVERCAPACITY? IT'S A VALID QUESTION AND DESERVES AN ANSWER.

OVER THE YEARS, THE SCRAP INDUSTRY HAS EVOLVED FROM LABOR INTENSIVE TO CAPITAL INTENSIVE. SCRAP PROCESSORS HAVE BECOME VOLUME ORIENTED OUT OF NECESSITY. HIGH PRODUCTION EQUIPMENT WAS REQUIRED TO MEET THE GROWING NEED FOR SCRAP AT A LOW COST. FOR INDIVIDUAL PROCESSORS, THIS PRESENTED A DIFFICULT BUSINESS DECISION. WHEN A BALING PRESS OR HYDRAULIC SHEAR NEEDED REPLACING, IT WAS NOT POSSIBLE TO REPLACE THAT MACHINE WITHOUT BUYING A LARGER VOLUME MACHINE; THE SMALLER SIZE MACHINE WAS NO LONGER AVAILABLE. IT WAS AND IS GET BIGGER OR GET OUT OF THE BUSINESS. THAT BECAME THE BUSINESS DECISION. THE RESULT HAS BEEN AN EVER INCREASING CAPABILITY TO PREPARE SCRAP AS WELL AS AN EXTREMELY COMPETITIVE INDUSTRY.

ALTHOUGH ON A SMALLER SCALE, THE SITUATION IS NOT UNLIKE THE STEEL INDUSTRY. THERE IS NO INVESTMENT IN A NEW MILL TO PRODUCE 10,000 TONS OF STEEL A YEAR, SIMILARLY, THERE IS NO INVESTMENT IN A SHREDDER TO PRODUCE 5000 TONS OF SHREDDED SCRAP A YEAR. THERE ARE ECONOMIES OF SCALE THAT DICTATE MINIMUM OUTPUT AND THOSE ECONOMIES HAVE ENTRENCHED THEMSELVES IN THE SCRAP INDUSTRY.

WE HAVE A VAST RESERVOIR OF OBSOLETE SCRAP AND THE CAPABILITY TO PREPARE THAT SCRAP TO MEET THE NEEDS OF ALL CONSUMERS. THERE IS AN INTERMEDIATE STEP, HOWEVER, THAT CAN

HAVE A DRAMATIC IMPACT ON THIS ENTIRE PROCESS -- THE COLLECTION MECHANISM.

ALL OF THE ECONOMIC KNOWLEDGE AND PRINCIPLES YOU HAVE EVER LEARNED ARE BACKWARDS WHEN APPLIED TO THE SCRAP INDUSTRY. SINCE IT IS A DEMAND-DERIVED COMMODITY, THE MARKET IS ESTABLISHED BY THE NEEDS OF SCRAP CONSUMERS -- IT STARTS -- NOT ENDS -- WITH THE STEEL MILLS AND FOUNDRIES. IT IS THE LEVEL OF CONSUMER DEMAND THAT DETERMINES THE PROCESSORS' BUYING PRICE FOR OBSOLETE SCRAP FROM COLLECTORS. WHEN THE PRICE OFFERED IS SUFFICIENT IN THE COLLECTOR'S MIND THAT HE CAN MAKE A PROFIT BY BRINGING IN SCRAP, THE MATERIAL WILL FLOW. CONVERSELY, WHEN THE PRICE IS SUCH THAT THE COLLECTOR FEELS HE CANNOT MAKE A PROFIT, THE FLOW DRIES UP AND SCRAP SITS. OBVIOUSLY, IN A SEVERELY DEPRESSED MARKET, AS WE ARE NOW EXPERIENCING, MANY PROCESSORS SIMPLY ARE NOT BUYING ANY SCRAP FROM COLLECTORS.

A MAJOR PROBLEM WITH THIS SYSTEM COMES WHEN THERE IS RAPID INCREASE IN THE DEMAND FOR SCRAP FOLLOWING A PERIOD OF SLACK DEMAND. THE PROBLEM CENTERS ON THE REACTIVATION OF THE COLLECTION SYSTEM, WHICH IS HIGHLY INFORMAL AT BEST. THESE PRIVATE ENTREPRENEURS MUST BE ENTICED TO AGAIN LOAD UP THEIR TRUCKS WITH SCRAP AND BRING IT TO THE PROCESSOR. GENERALLY SPEAKING, THE MORE DEVASTATING THE DOWN MARKET, THE LONGER IT TAKES TO GEAR UP THE COLLECTION SYSTEM, AND THE MORE INTENSE THE PRICE REACTION NEEDED TO GET THE

COLLECTORS TO RETURN.

IT IS THIS KEY FUNCTION WITHIN THE OVERALL SCRAP CYCLE THAT DETERMINES THE SHARP MOVEMENTS -- UP AND DOWN --IN THE PRICE OF SCRAP.

THERE ARE THOSE WHO RAISE THE QUESTION OF SCRAP QUALITY. WHAT ABOUT IT?

IN A RECENT U. S. BUREAU OF MINES CONTRACT WITH THE BATTELLE COLUMBUS LABORATORIES, TO STUDY AN ALLEGED PROBLEM WITH SCRAP QUALITY IN THE FOUNDRY INDUSTRY, BATTELLE SAID, "NO SUBSTANTIAL BODY OF EVIDENCE HAS BEEN FOUND TO SUPPORT THE THESIS THAT THE QUALITY OF FOUNDRY FERROUS SCRAP IN GENERAL HAS DETERIORATED OVER THE PAST DECADE OR TWO, OR IS EXPECTED TO DECLINE SUBSTANTIALLY OVER THE NEXT DECADE."

BATTELLE ALSO MADE THE FOLLOWING POINT: "THE SEARCH FOR ACTUAL CASE HISTORIES DOCUMENTING ADVERSE EFFECTS OF TRAMP (ELEMENTS) ON PRODUCTION IN THESE FOUNDRIES WAS VIRTUALLY FRUITLESS. THIS REFERS TO TRAMPS ARISING FROM PURCHASED SCRAP. SOME CASE HISTORIES WERE CITED, BUT ALMOST ALL OF THESE DEALT WITH TRAMPS INTRODUCED THROUGH CHANNELS OTHER THAN PURCHASED SCRAP.

THERE IS A PERCEPTION THAT SINCE ALLOYS ARE BEING ADDED TO IRON AND STEEL, THE RESULTANT SCRAP IS CONTAMINATED WITH HARMFUL RESIDUALS. THE STATEMENT IS ONLY A PERCEPTION BECAUSE, AS HAS BEEN REPEATEDLY FOUND BY OBJECTIVE ANALYSTS,

THERE IS NO FACTUAL BASIS FOR THE CHARGE.

CAN YOU IMAGINE WHAT A CONTRIBUTION IT WOULD BE TO THIS COUNTRY IF EVERY TON OF IRON AND STEEL MADE WAS EVENTUALLY RECYCLED -- IF WE WERE ABLE TO COMPLETELY CLOSE THE SCRAP CYCLE. IF THE STEEL IN THE PRODUCT WAS GOOD ENOUGH TO BE MADE, IT IS SURELY GOOD ENOUGH TO BE RECYCLED.

IMPOSSIBLE YOU SAY -- IT WILL NEVER HAPPEN. YOU ARE RIGHT, IT WON'T. THERE ARE PRACTICAL AND ECONOMIC RESTRAINTS THAT COULD NEVER BE OVERCOME.

I CAN ASSURE YOU, HOWEVER, THAT WE COULD DO FAR MORE THAN WE ARE NOW DOING AND IT CAN BE DONE WELL WITHIN THOSE PRACTICAL AND ECONOMIC RESTRAINTS. THE OPPORTUNITY TO RECOVER MORE SCRAP EQUATES TO HUNDREDS OF MILLIONS OF TONS OF MATERIAL THAT COULD BE USED. DOING SO WOULD CONSERVE FINANCIAL, ENVIRONMENAL, ENERGY AND MINERAL RESOURCES -- IT WOULD CONSERVE ENERGY, NATURAL RESOURCES, CLEAN AIR AND CLEAN WATER.

IT COULD BE DONE WITH THE STEEL AND SCRAP INDUSTRIES WORKING TOGETHER. AND, IN KEEPING WITH THE TOPIC, IT IS CRITICAL THAT IT BE DONE NOW.

AN OVERVIEW OF THE POTENTIAL FOR CHROMIUM CONSERVATION IN STAINLESS STEELS FOR CORROSION APPLICATIONS

by

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INTRODUCTION

The United States is doing a remarkable job of conserving chromium in stainless steels right now. If business does not improve, the question of conservation may be moot. No domestic stainless producers will be left.

More optimistically, we intend to survive and be prepared to deal with a real chromium shortage should it occur.

The market is efficient. The present mix of stainless steel products provides cost effective solutions to the wide variety of corrosion problems encountered in a modern industrial economy. If the supply of chromium from Southern Africa were to be embargoed or its price drastically increased, the cost effective solutions to corrosion problems would change. These changes would be in design and fabrication as well as in materials and processing. Substantially higher prices for chromium also would promote development of alternative sources such as Greece, Turkey, Albania, the USSR, Greenland, and domestic. Furthermore, significantly higher prices would encourage the development of processes capable of extracting chromium from the scrap stockpile.

Several specific strategies short of completely replacing stainless with other materials for reducing chromium usage are described below.

LEANER CHROMIUM ALLOYS

The present corrosion resistance of Type 304 stainless steel exceeds the requirements of many applications. Lower chromium alloys would serve just as well. Part of the chromium in this alloy is required to balance the composition such that the austenitic structure is maintained. It is possible to reduce the chromium content and rebalance the alloy with other elements to achieve the same effect. Presently, there is no economic incentive to do this because chromium is cheaper than the nickel or manganese which would replace it. Further, this approach would require the user to make a much more rigorous assessment of the corrosion resistance required in a particular application. The basic research in this area has been done and the concepts can be applied when, and if, the price of chromium requires it.

HIGH STRENGTH DUPLEX STAINLESS STEELS

These alloys, which are just now being commercialized, exhibit significantly higher strength than either austenitic or ferritic stainless steels. They contain the same or more chromium than the traditional stainless steels but because of their higher strength the section size of products fabricated with them may be reduced by 50% or more. Thus a net savings in chromium use could be achieved by their widespread application. The economic incentive exists to make such substitution now in some applications such as oil field surface piping and offshore equipment.

SUPERFERRITIC STAINLESS STEELS

This emerging group of stainless steels is characterized by having very high chromium contents ranging up to 30%, and it may seem strange to suggest them as a mechanism for saving chromium. However, the corrosion resistance of these materials is far superior to the traditional austenitic stainless steels and their intelligent application would result in an overall long term lower net chromium consumption. Because of their outstanding corrosion resistance, components fabricated from superferritic stainless steels would not require replacement as often as those made from lesser alloys. In cases where section size or thickness is determined by corrosion rates rather than mechanical strength, superferritics provide an opportunity to reduce section size. Superferritic stainless steels are available today and have been proved in a wide variety of severely corrosive applications.

CLAD AND COMPOSITE MATERIALS

A brief laundry list would include weld overlay, chromeplating, chromizing, roll bonding, and explosive bonding. All of these processes are well known to industry and they are used when they embody the most effective solution to a particular problem.

A more recent entrant into the field of composite materials for corrosion resistance is laser or electron beam surface treatment to enhance the corrosion resistance of chromium lean alloys. By melting and rapidly solidifying a very thin layer on the surface of such an alloy an amorphous layer can be created in which 5% chromium can do the work of twelve or more. There are some obvious limitations to this approach. The amorphous layer is metastable and exposure to moderately high temperatures in the range 300 to 400°C may cause it to revert to the crystalline state and lose its enhanced corrosion resistance. Another problem is that any break in the amorphous layer which exposed the substrate would most likely behave as a chemical drill in a corrosive environment. This is in contrast to the behavior of conventional stainless steels in which the passive layer generally is self healing if it is breached by mechanical damage.

CONCLUSIONS

If the United States were cut off from the chromium sources in Southern Africa, there would be a temporary and possibly severe dislocation of the economy but no disaster should occur. Chromium still would be available at a higher price, and that price would be likely to fall somewhat as alternative sources were developed. Adjustments would be made and a new set of cost effective solutions to corrosion problems involving less chromium than at present would emerge. The technology to implement these solutions either exists or is under development and will be applied when the cost of chromium justifies such implementation.

SUMMARY OF STUDIES OF THE METAL PROPERTIES COUNCIL, INC. ON CHROMIUM CONSERVATION IN STAINLESS STEELS FOR CORROSION APPLICATIONS

Adolph O. Schaefer
Executive Director
Metal Properties Council

To summarize the studies of The Metal Properties Council on Chromium Conservation in Stainless Steels for Corrosion Applications which is the assigned subject for these remarks, it in necessary to describe the present activities of the Task Group on Critical Materials of the Council, and its present objectives. MPC is organized to respond quickly to expressed needs. In the present instance this particular field of activity rests in a Task Group set up by and reporting to the Technical Advisory Committee of the Council.

I find myself on this program, surrounded by participants in MPC, as well as in its Task Group. Dr. Allen Gray, chairman, has long been a member of the Technical Advisory Committee of MPC as has Bob Jaffee, one of your speakers. Three members of the MPC Board of Directors are listed on the program. These are Bill Dennis, Frank Richmond, and Horace Lander. Arden Bement has made important contributions to MPC in the past.

Focusing on the subject of this particular session, Ray Lula is the Chairman of the MPC Task Group on Critical Materials. The leader of the chromium program of MPC is today's chairman, Dr. Houze, and Joseph Stephe is a member of the Group. I will be followed by Jim Heger, who is the Task Group consultant on chromium.

The primary interest of MPC is "properties". This is accepted in its broadest possible sense. If we are forced to define it we would say our attention is directed toward those properties the engineer wishes to know in designing, building, or using a structure. Corrosion resistance is a property, just as ultimate tensile strength, hardness, etc., are properties. MPC is interested in properties as affected by environment, and hence, our work on stress corrosion.

The Metal Properties Council is involved in the so-called critical or strategic materials, particularly in the availability of information on the properties of the substitution materials we might be forced to use. We are therefore, looking into whatever substitution of other elements might be necessary in an emergency, and attempting to anticipate situations which might arise. It can be said that our primary interest is in the possibilities of substitution for critical alloys in today's materials, and the properties of those alloys in which such substitutions might be made.

We contemplate, at this time, studies on the effects of substitution for chromium. Dr. Houze heads this activity in MPC, and Dr. Heger is the Task Group consultant.

In passing, we mention that similar attention is being given to manganese, but plans are not so far advanced in this case. It is possible that other strategic alloying elements may be considered in the future.

Other activities to date of the MPC Task Group on Critical Materials include a proposed plan for assigning priorities to critical materials which will soon be published. Consideration is also being given to the subject of stockpiling.

The Task Group on Critical Materials of The Metal Properties Council now consists of 36 members, representing some 26 companies and organizations.

After due consideration of those available, The Metal Properties Council decided to utilize the good services of Mr. James J. Heger, formerly of the Research Laboratories of the United States Steel Corporation to act as a consultant to the Task Group, and to pursue the outlined course of study which it is hoped will reveal the most promising alloy combinations which have been developed in efforts in all parts of the world to accomplish savings in chromium by lowering the chromium content with minimum sacrifice of other useful properties, including corrosion resistance, strength, ductility, weldability, etc.

The search will cover literature, patents, and people. The people are those active in making as well as in using stainless steel, in particular. It may lead to a testing program as well as recommendations to others who might take appropriate action. This would include government agencies. It is thought that materials substituting other elements for chromium, were wholly or partially developed in those countries deprived of chromium during World War II. Some of these development were never put into practice because the overall situation was relieved when the war ended. Jim Heger, following me, will enlarge on this program.

The Metal Properties Council, Inc. has other programs in which consideration is being given to economies in the use of chromium. Mention is made of the program on materials for pressure vessels for the containment of hydrogen. As the temperature and pressure rise at which chemical processes take place, and the presence of hydrogen increases the difficulties of finding suitable materials, the tendency has been to increase chromium contents of the steels used. As the old standards 2 1/4 chrome 1 moly proves inadequate, advantages are found in 3, 5, and 9 percent chromium steels. Obviously, all of these represent conservation of chromium as compared to a shift to the old reliable 12 percent chromium grades.

The Metal Properties Council, Inc. has for nine or ten years been engaged in a major testing program with respect to materials for utilization in plants for the gasification of coal. Only the very high nickel-chromium, sometimes with molybdenum, cobalt, etc. materials have been found at all desirable in the "internals" of such equipment. A very significant area of interest, however, lies in the quench stage properties of the process train. It is encouraging that it appears possible that much of the structure may be made of carbon steel, and that stainless steel can be restricted to only certain portions of the structure.

Subcommittee 8 of the Technical Advisory Committee is directed to the study of materials for corrosion resistance. It is in this group that a test program on corrosion resistance area will be treated.

Finally, before Jim Heger undertakes to enlarge on his work on the chromium conservation program of The Metal Properties Council, a word should be spoken about the necessity of extensive and time-consuming test programs to qualify materials (in this case stainless steels) for applications under any code, in particular the ASME Boiler and Pressure Vessel Code. This includes consideration of the added requirements for materials used in nuclear reactors subject to the rulings of the Nuclear Regulatory Commission. In my opinion, we have never had a universal expression of the extent of testing necessary to qualify a new material for use under the "Code." The trend seems to be increasing this. Consideration must be given to source, manufacturing process, heats, product form and size, heat treatment and processing factors. Welding must be considered. Stress-rupture testing, for one example, is time-consuming. Parametric analysis may satisfy questions of extrapolation, but there remain questions which can only be answered by some long-time tests. The purpose of these remarks is to indicate that desirability of trying to reach decisions on the substitutional alloys we may have to rely on, so that a start can be made in the necessary testing programs to establish the engineering properties of the materials.

So we await the results of the program being carried on my the next speaker as an important indicator of where we should be heading in our studies for the future and in reducing our dependence in critical materials, in this case, chromium.

CHROMIUM CONSERVATION IN STAINLESS STEEL
STATUS OF MPC ACTIVITY

James J. Heger
Consultant
Metals Properties Council

If an international group of metallurgical engineers were requested to construct a list of alloy systems that had outstanding properties over a wide variety of environmental conditions, the stainless steels, particularly the austenitic stainless steels, would be given a very high rank. Consider, for example the type 304 stainless steel and its low carbon and titanium or columbium modifications. This system is used under cryogenic conditions because of its excellent toughness, under ambient conditions because of its excellent corrosion resistance and formability, and under elevated temperature conditions because of its excellent strength and oxidation resistance. Morevoer, it is producible in mass quantities, and it is weldable. The assignment facing those of us concerned over critical materials is to find a substitute for this alloy system and this substitute must contain little or no chromium.

In the stainless alloy system, chromium is the element that makes a major contribution to the excellent corrosion and oxidation resistance. Also, because of its so-called hardenability effect, chromium retains, or stabilizes austenite at room temperature in the chromium-nickel stainless steels. It can be added to steel without undue difficulty and it can be recovered from scrap at reasonably high yields. Most important, under present market conditions, its cost is such as to permit the stainless alloy system to enjoy a wide usage in the automotive and consumer-goods areas not to mention the power generation, petroleum, chemical and aircraft areas.

The MPC Group on chromium conservation, under the leadership of Dr. Houze, fully recognizing the size and complexity of its assignment, logically has recommended a comprehensive review and analysis of previous activities on the development of low- and non-chromium stainless steels. In a carefully prepared work statement, the Task Group suggests that the review comprehend all of the work done from 1930 to the present and include technical literature, patent literature as well as personal contacts with industries and individuals who have been active in this field. A partial list of those to be contacted include:

Colt Industries
CARTECH
Republic Steel
U.S. Steel
Armco
Universal Cyclops
Allegheny Ludlum
International Nickel
Climax Molybdenum
Union Carbide
General Electric
Combustion Engineering
Westinghouse
Chrysler
General Motors
Ford
NASA
Bureau of Mines
Thyssen Edelstahlwerke
Krupp
Max Plank Instutute
IRSID
British Steel

With respect to the analysis of the information obtained from the reviews and contacts, the Task Group's work statement suggests several important items for consideration, including:

1. The substitute material must be capable of being melted and processed in large quantities to desired product forms.

2. The mechanical properties, physical properties and corrosion characteristics of the substitute materials must be equal to those of the stainless steel being replaced.

3. The fabricating characteristics of the substitute materials must be adequate. These characteristics include forming, joining and machining.

Not mentioned, but equally important, is that the substitute materials must be capable of being profitably marketed at price levels that are competitive.

Currently, a number of the aforementioned contacts have been made and literature has been received. The results are summarized under two categories: (1) Elevated Temperature Application, requiring oxidation resistance. Common denominators to both applications are producibility and formability which includes weldability.

Elevated Temperature Applications

1. A modified 9% Cr-1% Mo steel appears to be a promising replacement for the type 304 stainless steel in power generations at temperatures up to about 1200° F. This development is close to being a reality.

2. Chromium-nickel austenitic steels having chromium contents of about 14% instead of the nominal 18% minimum appear to have adequate strength and oxidation resistance for service up to about 1400° F.

3. Sheet product of an aluminum coated 6% al steel has been successfully used in the duct work of automotive gas turbine engines. The materials that was replaced contained over 18% chromium.

4. Modified 6% Cr steels appear to be promising replacements for the 12% Cr, type 409 stainless steel in automotive emission control system.

Ambient Temperature Applications

1. Laboratory quantities of non-chromium and low chromium austenitic

steels based upon high carbon manganese and aluminum have been made. Compared with the 18-8, type 304 stainless steel, the corrosion resistance of these new steels is marginal.

2. A number of non-chromium and low-chromium, iron-aluminum and iron-aluminum-silicon steels have been made in laboratory quanitities. Although the corrosion resistance of these steels is very good, their producibility and formability characteristics are much inferior to those of the stainless steels.

The information developed to date suggests that, for some limited elevated temperature applications, a few low chromium substitutes for the stainless steel system are possible. For the large usage areas, the development and acceptance of substitutes is of such a large scope that it negates, in both a technical and economic sense, the efforts of individual companies and government agencies. A coordinated and cooperative program that must include producers, fabricators, consumers (among which is the general public who uses such items as kitchen sinks, flat-ware, utensils and refrigerator trays), and government agencies is required. The Metal Properties Council is prepared to participate in such a program.

The American Sterilizer Company, AMSCO, manufactures capital equipment for the health care industry. AMSCO's market demands equipment which is reliable with minimal maintenance, easily cleaned with strong cleaners or disinfectants, and resistant to prolonged exposure to steam and/or hot water. To meet these demands, AMSCO depends on corrosion resistant engineering materials typically processed in the United States from ores or semi-finished raw materials produced in other nations. This dependency led AMSCO Research and Development to create a materials forecasting capability within the Materials Engineering Group both to plan for potential material shortages and to monitor potentially useful new materials. From the materials forecast, Materials Engineering selected chromium, in the form of stainless steel, as the material with the highest potential for an unpredictable, sudden supply disruption and initiated a substitution planning program.

The Materials Engineering chromium substitution planning program has three distinctive features. First, substitution planning has been integrated with on-going materials development. Second, planning is based on a scenario of a shortage situation. Finally, substitution needs have been classified in terms of performance needs of product components.

Materials Dependency

From a materials perspective, AMSCO's products are similar to petro-chemical refining in terms of the use of nickel alloys and stainless steels. In a typical year, nickel-based alloys and austenitic stainless steels account for about 20% of the weight of all purchased metals. Nickel-clad steel plate represents 15% of purchased metallics. Carbon steel is about 45%. The balance is aluminum and copper alloys. AMSCO operates both a captive foundry and a weld fabrication shop with welders certified to the ASME Boiler Code for stainless steel, nickel alloys and steel welding.

The use of stainless in health care equipment, such as surgical tables and surgical casework, is well organized. However, the extensive use of nickel frequently surprises engineers outside the health care field. Experience has proven that nickel and its alloys are required to provide reliable, long service life when exposed to the chloride levels in water and the steams typical of health care establishments. Unlike stainless, nickel and its alloys are virtually immune both to chloride-induced stress corrosion cracking, a potentially catastrophic failure mode, and to chloride pitting, a condition requiring high maintenance for preventive cleaning or repair. Sterilizers are constructed from nickel-clad steel and stills and other water-handling equipment use nickel alloy components.

MATERIALS AVAILABILITY

As part of the materials forecast, the shortage potential for materials necessary to AMSCO's product lines were examined. In terms of world resources, the conclusion of the National Commission on Materials Policy, in 1973, that use predictions, compared to resources, "do not indicate shortages of supply". (1) Indeed, the current worldwide economic downturn has made forecasters even more optimistic that adequate ores exist to satisfy all industrial needs for the balance of the century.

However, the engineering materials AMSCO purchases are typically refined in the United States from minerals or semi-finished feedstock imported from foreign sources. Thus, materials availability is very much dependent on geo-political, economic, and industrial factors. The OPEC oil embargo clearly illustrated the political factor in supply. Fortunately, minerals appear far less susceptible to producer cartels. (2) On the other hand, several minerals are sited almost exclusively in politically unstable southern Africa.

Generally, mineral-rich nations depend heavily on mineral exports so the current economic downturn is exacting a severe toll on their economies. These nations must continue to export, inspite of falling prices, to raise hard currency for fuel and food imports. Mines in developed countries, facing both higher labor costs and environmental protection expenses,are closing. Thus, minerals dependency on less developed countries increases. Further, investment in upgrading U.S. mining is less attractive under current conditions, a trend which makes the labor cost differential difficult to overcome.

A similar problem confronts the U.S. materials processing industry. A generation of low profitability and governmental neglect has seriously impaired materials processing capabilities. Other nations, in contrast, have subsidized both their minerals refining and their materials processing capabilities. This encouragement is partially responsible for the flood of imported semi-finished and finished materails. Now, when evaluating materials availability, the technological and industrial capabilities of remaining U.S. firms must be carefully considered.

CHROMIUM AVAILABILITY

The Materials Engineering study identified chromium, in the form of stainless steel, as the material most likely to face supply disruption. While chromite ore resources are plentiful, the bulk of these resources, and of active mining, is in South Africa and Zimbabwe. The socio-economic problems besetting these nations are, unfortunately, likely to continue for some time. Political upheaval can, at any time, disrupt supply. Since a chromium shortage is not solely dependent on marketplace changes in supply or in demand, substitution planning is necessary even during the current abundance of chromium.

Further, the U.S. stainless steel industry is in trouble. The productive capacity for making ferro-chrome, stainless'principal ingredient, has been severely diminished by subsidized foreign competition. Further, South Africa has embarked on a program to enhance its own ferr-chrome production and stainless steelmaking capacity. In the U.S., stainless producers have suffered with the rest of the steel industry. By the end of this decade, U.S. stainless steelmakers may be facing very serious foreign challenges.

The political factor in chromium availability also, unfortunately, applies to the U.S. government. The Federation of Materials Societies, and others, have been calling for a national policy on materials for years. To date, the strategic stockpile of selected materials has been the only tangible response. Unfortunately, the stockpile was not tied to any fixed policy of assisting industry during shortages.

Finally, Congress has recently become more attentive to the materials issue. The current Administration has also begun to address this issue, including a start to true management of the stockpile. But, if past is prologue, the rate of action will be slow. In short, AMSCO had to plan a chromium substitution strategy without counting on a near-term national materials policy.

CHROMIUM SHORTAGE SCENARIO

Materials Engineering constructed a "most likely" scenario for a sudden chromium shortage. Useful material for scenario construction was drawn from 3 principal sources. The National Research Council created a scenario in a study to develop national strategies in case of a chromium shortage. (3). The Federal Government's behavior in previous mineral/material shortages can be found in the industrial and technical press. Finally, statements by current Administration representatives indicated the probable direction of near-term response to a chromium shortage.

This scenario has several salient features. First, although numerous substitutes for chromium/stainless steel can be found, the first several years of the shortage will be quite difficult for industry. While considerable laboratory data exists, far less test data or life history of potential chromium/stainless steel substitutes exists. Therefore, the transition to new materials will be difficult. Second, the Federal Government will most likely protect industries deemed vital to national security from the shortage. Rationing releases from the stockpile, and priority ratings will probably favor security/defense related contractors at the expense of essentially civilian products.

Third, "rollover" shortages will develop as the demand for obvious replacements quickly grows. For example, nickel alloys can be used, at a cost penalty, to replace stainless steel in many applications. This could lead to a temporary shortage in nickel which is normally produced at only a fraction the level of chromium production.

Finally, the role of regulatory agencies and standard setting bodies has been paid little attention in the literature. Many products covered by regulation or industrial standards have materials of construction specified or registered. The process of securing approval by these agencies is painfully slow in normal times. During the early part of a chromium shortage, rapid switching to alternatives may be delayed until these agencies develop a rapid response mode.

AMSCO CHROMIUM SUBSTITUTION PLANNING

The shortage scenario indicates a two stage plan was necessary. In the early stage of a chromium/stainless shortage, AMSCO could apply its existing experience with nickel alloys. For example, AMSCO already possesses the design expertise and manufacturing practices to substitute Monel, a copper-nickel alloy, for many components fabricated from austenitic stainless steel, currently cheaper and more available. Thus, the worst effects of the initial shock of a chromium/stainless shortage could be averted.

However, if the shortage became protracted, the scenario predicted serious problems in the broad-brush substitution of nickel alloys for stainless. As many other industries adapted to using nickel alloys, the sudden demand increase could create a "roll-over" shortage in nickel. Since nickel is crucial to aerospace, defense, energy-generation, and petro-chemicals, the Federal Government would begin rationing or allocating nickel supplies to these industries. Thus a chromium shortage could soon become a nickel shortage as well. Further, since nickel is also a component of austenitic stainless steel, the types necessary to AMSCO, the stainless shortage would continue.

A prolonged chromium shortage could, therefore, seriously disrupt stainless and nickel alloy supplies for some time. Therefore, other materials, generally outside AMSCO's existing technical experience, would have to be considered. Materials Engineering initiated investigations into alternatives. This preliminary survey quickly concluded that the scope and cost of rapidly developing substitution plans for every stainless part was prohibitive.

Then, Materials Engineering decided to fuse substitution planning with the materials forecast to develop a bank of both knowledge and new materials to facilitate potential substitutions. This approach reduces the cost of substitution planning by essentially piggy-backing it into normal development. Further, on-going development of new materials and processes will be serving the dual roles of laying the foundation to move the firm's technology ahead while creating opportunities to quickly bring into use those materials/processes offering immediate advantages. Additionally, the potential of increasing dependence on foreign stainless steel infers on-going substitution planning.

To further refine the substitution problem, Materials Engineering developed a classification system for stainless steel applications based on analysis of stainless' successful performance in health care applications. Clearly, corrosion resistance was the principal reason. However, for health care applications, corrosion must be interpreted quite broadly. The general corrosion resistance of austenitic stainless provides resistance both to attack and staining from the powerful disinfectants, biocides, and cleaners used in health care facilities. Stainless does not encourage bacterial growth. Further, the smooth, virtually pore-free surface of polished rolled stainless products do not provide sites for bacterial growth. The analysis identified a surprisingly limited number of health care environments in which stainless was the only suitable common engineering material.

Stainless steels provide adequate strength and good formability. Thus, load carrying products with good corrosion resistance, can be readily manufactured. Further, while stainless has problems in longtime continuous exposure to steam and chloride, stainless products easily withstand repeated steam sterilization cycles at 300°F and/or washing operation at 180°F.

Finally, the glistening appearance of polished stainless has gained wide acceptance in health care. Therefore, stainless products can have a market appeal not found in potential alternate materials.

These factors were then reduced to three substitution categories:

1. Appearance
2. General corrosion resistance combined with structural integrity under load.
3. Specific severe service requirements.

Then potential substitutions were hypothesized using published technical data as well as the considerable data in the N.R.C. study. This investigation was broad spectrum, attempting to turn up as many alternatives and substitutes as possible from simple materials substitutions to arcane new technologies.

Next, the alternatives and substitutes were evaluated in two ways. First, the short term feasibility was considered by asking both "could we switch to these within a week to a month?" and "at what cost?" Next, the apparently less feasible alternatives were compared to the long-term plans set forth in the materials forecast. This comparison enabled Materials Engineering to establish long range programs to develop alternatives both by seeking funding for materials research and by adapting the materials portion of planned product development programs to pursue stainless substitutes.

The combination of short term and long range planning resolves several of the stumbling blocks to effective substitution programs. Substitution programs are like life insurance premiums -- you pay for protection that you really don't want to use. Justifying such a program in traditional economic terms is difficult. An additional deterrent to private industry support of substitution planning is the government's failure to formulate a national materials policy. However, if substitution planning is made intrinsic to the firm's development activities, then it is not only easily justified but can actually uncover cases where immediate substitutions can provide an immediate return in cost savings or product improvement.

ALTERNATES FOR STAINLESS STEELS IN THE CHEMICAL PROCESS INDUSTRIES

Edward A. Kachik*

The chromium-containing stainless steels are about as close to being an indispensible commodity as one can get in the spectrum of corrosion-resistant materials of construction used by the Chemical Process Industries. I believe that without the stainless steels and related alloys, much of the progress in chemical manufacture, the resultant new products, and the growth of this industry could not have occurred.

I believe we must also accept as fact, that the current usage of stainless steel in chemical processing applications has been dictated as much by economics as it was the ability of these alloys to resist the corrosive conditions or provide the physical and mechanical properties needed. In some instances, stainless steels are the only acceptable corrosion-resistant materials: they cost less, or require less maintenance, or reduce the frequency of failure. To quote from Professor Nash's remarks, performance vs. cost is paramount. This preamble simply means that alternates

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for already entrenched applications of stainless steel are going to be difficult to find and will result in increased operating costs to the user. The materials will cost more, have a shorter life, be more difficult to install, require more maintenance attention or have some other disadvantage. In any case, we will have to accept the probability that higher costs will result, even if corrosion-resistance is acceptable.

The following discussion of alternates is based primarily on what is available from existing technology. New developments that have not reached commercialization will, in general, not be included.

1. STAINLESS-CLAD - CARBON STEELS

These materials are already extensively used throughout the industry for distillation columns and similar large vessels. The first cost of clad steel is lower than solid stainless, but usage is limited to configurations that can be made from sheet and plate. Specialized welding techniques must be used and the carbon steel edges must be protected from contact with the process fluid that demands the use of stainless. Quality of this material is usually excellent and failure from holes, defects or "holidays", in the stainless is rare.

Additional usage of this type of material is certainly possible for smaller vessels where clad steel is not now considered economically attractive. Valves, pump bodies, and similar components are probably amenable to more extensive use of weld overlay, but at some cost penalty. Piping provides a much more difficult technical problem; stainless lining by various pressure bonding methods is a possibility, but it's sure to be expensive and subsequent installation in the chemical plant will pose many problems.

2. LOWER CHROMIUM CONTENT STEELS

There is always the possibility that some applications of stainless steels in the chemical industry have been "over-designed" by using a high chromium stainless steel where a lower chromium one would suffice. However, I don't believe that there is much of this, and the opportunity to conserve chromium is slight unless we accept the cost penalty of a shorter life.

3. OTHER METALS AND ALLOYS

The high Ni alloys immediately come to mind, but they are already being used extensively where they provide advantage. It should be possible to use some low-Cr high-Ni alloys that have not been employed up to now because they are more costly, or have characteristics that make them more difficult to weld or form, than the stainless steels.

High silicon irons were used effectively in a wide variety of acid and chemical environments approximately forty to fifty years ago. Their inherent brittleness and the extreme care required for their manufacture, fabrication, installation, and use, caused them to be supplanted by the stainless steels. From the corrosion resistance standpoint, these are effective alternates. Dr. Asphahani will discuss these later in this session.

Titanium and titanium-base alloys have unique properties that have suited them to many chemical plant applications. They have been widely used within the overall capabilities of the forms available and limitations imposed by their higher price. They continue to find new applications as the cost drops and availability increases. Only a few years ago, Ti delivery dates were almost intolerably extended, a condition which doesn't exist today. Titanium is an excellent material for sea water exposure and does not show the stress corrosion cracking behavior of austenitic stainless steels in chloride environments. It is not an acceptable alternate for a number of acid environments. (There is another paper on titanium later today).

Tantalum is an excellent material from the corrosion-resistance standpoint. Its high cost and limited availability have been deterrents to its wider usage; Ta-clad materials are another possibility. A new Ta Co (60-40) alloy promises to be lower in cost and to be less dense than tantalum itself. (Not so long ago, cobalt supplies were critical).

Zirconium is another possibility but limited in production; the high-cost precious metals -- notably Pt, (gold is "out of sight"), have much potential from the corrosion standpoint, but cost and availability will litigate against a significant increase in usage.

Aluminum alloys have found their place in chemical plants and are uniquely useful in some environments. However, their relatively low strength, particularly at elevated temperatures, is a disadvantage. Except for applications that are now considered as marginal, additional usage is not likely.

Lead was used extensively at one time for sulfuric acid service, and has some unique properties for other service. However, low strength usually limits it to use as a lining. Much of the art of lead-burning and working that once existed in chemical plants has been phased out and doesn't exist anymore. Safety of workers is another concern.

4. OTHER MATERIALS AND APPROACHES

Metallic Coatings: Chromium electroplates, chromium-rich diffusion coatings, nickel plate (electrolytic and electroless), zinc galvanizing, and cadmium plating are metal coatings that have corrosion-resistant properties. All such coatings are subject to limitations that relate to their thinness as a corrosion barrier.

Chromium Electroplates: Relatively thick crack-free chromium electro-deposits can be produced and are useful; the biggest limitation is in the size and shape of the component or vessel that can be plated. Widespread application is not possible.

Chromium-rich coatings produced by diffusion are available and have been shown to be more widely applicable than electroplates. Distinct limitations exist in the size and shape of items that can be chromized and the high temperature required for processing is also a deterrent. In addition, since the chromium content diminishes with depth toward the basis material, corrosion has a tendency to increase as the coating is corroded away.

Electroless and electrolytic nickel deposits have already found a rightful place in chemical plant usage. They are limited to those applications where nickel is a preferred material because nickel will not always replace stainless steel in a corrosive environment. The general plating deposition limitations apply, although the electroless process is more amenable to use on process equipment in place.

Zinc and cadmium coatings have their application, but the likelihood that they can be used more extensively than they are now as an alternate for stainless steels is remote.

Elastomeric Linings: Linings of rubber-like or other plastic materials are extensively used in the industry already. Lined vessels, lined pipes and lined valves combine the corrosion resistance of the lining material with the structural capabilities of the backup or basis material. Extensive lining composition variations are available, and additional usage can be expected in the event that the use of stainless steels must be decreased. However, linings have already found a rightful economic place in plant installations and again as a replacement or alternate, in uses where stainless is preferred material, a cost penalty will have to be accepted. Also, linings are not without their problems. Extreme care in joining must be taken, equipment must be designed to accommodate the lining procedures, and detection and repair of voids or leaks in the lining require continued attention.

Organic coatings are available, notably as phenolics and urethanes, but have limited applicability.

Non-Metals: Fiberglas Reinforced Plastics (FRP) and plastics in general have achieved substantial penetration as materials of construction throughout the industry. The unreinforced plastics come in many compositions (polyethylene, Teflon^R, polyurethane, rubbers, epoxy, etc), have excellent resistance to many chemical corrodents, and are readily fabricated into plant equipment. The addition of reinforcement in the form of glass mat or glass filament in filament-wound construction effectively provides the strength needed and extends the applicability of these materials, particularly when used with epoxy and similar resins. Plastics are widely used instead of stainless steels already, in a wide variety of acids, alkalis, and solvent-type environments. Plastics are limited to low temperatures, and except for a few plastics of limited fabricability, unreinforced plastics lack the strength of metallic materials. Their usage is limited accordingly.

With reinforced plastics, quality control at the manufacturing level has been a continuing concern. MTI has recognized this problem and has carried out work in cooperation with the Society of the Plastics Industry (SPI) to provide information on the design, properties, and quality control of FRP. This information is now being used by the ASME to establish pertinent standards. When completed, this standarization work should go a long way toward improving the consistency and reliability of FRP as a quality material of construction for chemical plant service. A joint MTI/SPI report has been published by the SPI on the work done to date.

Also, installation in the plant requires specialized care and handling. MTI has published a manual for guiding users in the handling of FRP and plastic components during plant installation, maintenance and repair.

Glass: Glass has excellent resistance to most acids and, in fact, to most chemicals, alkalis being a notable exception. Installation systems have been devised and are marketed that compensate for the brittleness and fragility of glass as a material of construction. Mostly, however, glass finds its place in plant construction as a coating or lining material and is subject to the same limitations as are other coatings. Glass linings are easily damaged in the plant by dropped tools, for example. Defects and discontinuities caused by defect or damage render the basis material accessible to the corrodent, with possible failure as a result.

Ceramics: Some newer materials resulting from research on high purity oxides, carbides and silicides have found a useful niche in chemical industry operations. These are usually expensive; are limited as to the size and shape available, and installation can be complex.

Brickwork: Acid-proof brick has been used extensively for special applications but installations are cumbersome, membranes are usually required, and quality control of the installation is a concern. It's an expensive route.

Carbon or Graphite: This material is extremely expensive and is primarily useful for applications where strength is a primary consideration. It must be classed as a highly specialized material with an extremely limited range of utility.

Anodic and Cathodic Protection: These methods depend upon the application of electrochemical principles to protect the alloy or metal against corrosion by the environment. Cathodic protection is much used for buried pipe lines, and anodic protection has been successfully employed in sulphuric acid coolers. Extension of the technology will not be easy, but it does have promise for permitting the use of other metals or alloys to replace high chromium stainless alloys.

Process Chemistry: No discussion of alternatives would be complete without considering the process chemistry aspects. Inhibitors are well known as an effective method for preventing corrosion. Instances are known where a carbon steel is acceptable in an inhibited stream that would require a stainless steel for the same stream without the inhibitor. Much research has already been done, and, under the pressure of a chromium shortage, more could be. The inhibitor, obviously, has to be innocuous as far as the final product is concerned and must have no effect on the process chemistry. The research involved is expensive and success is by no means assured.

Minor changes in the process stream or elimination of contaminants can also change the materials of construction requirements. Eliminating water from a non-aqueous hydrocarbon process stream, and elimination of ammonia and mercury from equipment containing brass or bonze, are illustrations of stratagems that permit use of less exotic materials of construction.

RECAPITULATION

Review of these possibilities leads me to suggest that increased use of plastics is the most viable route to alternates for the stainless steels, particularly in those instances where elevated temperature service is not a factor. A continuing critical look at the problems with plastics as materials of construction, and at the limitations these problems impose, with a view to overcoming these problems, is a fruitful area for research.

In retrospect, I feel that the CPI have already taken a good look at alternates to the stainless steels and has a number of possibilities available. The picture for economical solutions is discouraging. As I stated at the beginning, suitable alternates have already achieved their acceptance, or penetration, in those cases where the economics are favorable or some other consideration such as plant safety is involved.

Whatever is used as an alternate, the cost picture is sure to change and in the wrong direction. Substantial reduction in the use of stainless steels in the CPI is not going to be achieved without increasing chemical production costs. Increased maintenance attention will be required, shorter equipment life may result, additional down-time from unexpected failures may occur, first or installed cost may be higher.

Finally, most of us have had at least one experience where the availability of materials of construction, at a suitable cost, even with a full spectrum to select from, was vital to the successful introduction of a new product. Without one important member of that spectrum available, viz. the stainless steels, it's possible that a new chemical product of value to the consumer may not reach the marketplace.

Although this discussion may paint a rather pessimistic picture, I don't mean to imply that the CPI will not be cooperative in the event that a chromium shortage develops. The industry will accept the challenge and, through its materials engineers, work with the alloy and materials producers to develop and install suitable alternates.

EDWARD A. KACHIK

BIOGRAPHICAL

Edward A. Kachik graduated from the Pennsylvania State University in 1942 with a B.S. in Metallurgy, and then joined the Engineering Department of the Du Pont Company. With Du Pont, he held a succession of supervisory and management positions in research, development, testing, and consultation within the broad fields of materials engineering and mechanical engineering. He was manager of the Engineering Department's Mechanical Engineering Consultants Section of Du Pont when he retired in 1979.

Since 1979, he has been the Technical Director for the Materials Technology Institute of the Chemical Process Industries, Inc. MTI is a not-for-profit organization, based in Columbus, Ohio, with a membership now numbering 38 chemical, petroleum, and materials producer companies. MTI identifies, develops, and sponsors projects that will provide solutions to materials engineering problems common to MTI members, in particular, and CPI organizations in general.

He is a member of ASM and NACE.

ABSTRACT

There are several ways to conserve the use of chromium in equipment used in the chemical process industry. Among them are the following:

1. Substitute other elements such as molybdenum, silicon, and aluminum as partial replacements for chromium in stainless steels. These alloys are still in the development stage at the present time.
2. Use alternative materials such as titanium, nickel-copper alloys, fiber-reinforced plastics, carbon steel, or cast iron instead of stainless steels.
3. Coat the exposed surfaces of readily available materials such as carbon steel with protective materials by cladding, plating, weld overlaying, metallizing, or by applying one of a variety of non-metallic materials.
4. Replace low-strength stainless steels with stronger alloys to allow use of smaller section size or lighter gage for equivalent strength.
5. Up-grade to more corrosion-resistant stainless alloys to minimize frequent replacement of chromium-containing equipment.

None of these approaches can be used across-the-board in all of the areas where stainless alloys are presently being used in the chemical industry. Each should have at least some areas of application, however, and all of them together could lessen considerably the chromium-dependency of that industry.

INTRODUCTION

There is no doubt about the strategic importance of chromium to this nation and the problems that would arise if we were unable to obtain this element.

One of the major uses of this element is in the production of stainless steels - a large family of iron-base alloys that contain 11% or more of chromium, often along with a number of other elements. These alloys are used for several reasons, primarily corrosion resistance, high-temperature oxidation resistance, and strength at elevated temperatures.

In the chemical processing industry, like many others, there is a real need to have at hand, in case of such an emergency, a new family of alloys with corrosion resistance as good as the stainless steels, but wherein the chromium content has been greatly reduced or eliminated entirely. Whatever element or elements that might be used to replace chromium must be readily available either within the United States or from stable, friendly countries. Additionally, it is desirable that these materials be relatively inexpensive and easily handled.

There are several ways to conserve the use of chromium in equipment used in the chemical process industry. They are described in the following sections of this report.

SUBSTITUTIONAL ALLOYS

A number of experimental alloys have been suggested wherein molybdenum, silicon, and aluminum are added in various combinations as partial or complete replacements for chromium in iron-base alloys, where good corrosion resistance is the desired property(1-5). Some of these materials also contain increased levels of manganese and nickel in order to maintain the austenitic structure of the AISI 300 series of alloys.

Substitutional Alloys (cont'd.)

The chemical process industry in general needs materials that are at least as corrosion resistant as Type 304 stainless - the workhorse of the industry. At the present time, it does not appear that it will be possible to achieve this level of corrosion resistance in iron-base alloys without at least some chromium present. In fact, based on the work that has been published to date(3), probably a minimum of 12% chromium, along with additions of molybdenum, silicon and aluminum, is necessary in order to maintain the level of corrosion resistance of Type 304 stainless.

While this approach certainly does not solve the chromium problem entirely, alloys of this type conceivably could enable us to save one-third of the chromium normally used to produce Type 304 stainless. Since 40% of the chromium used in this country for the production of alloy steels and superalloys goes to make this one alloy alone(5), the savings of this element could be substantial.

Most likely a variety of substitutional corrosion resistant alloys will have to be developed, each tailored to a specific need, much like the various stainless steels of today. Along with corrosion resistance, various other factors such as producibility and ease of fabrication (forming, bending, machining, welding, etc.) must be taken into consideration. These substitutional alloys are still in the development stage.

ALTERNATIVE MATERIALS

There are several other ways of conserving the use of chromium in the chemical process industry.

One is by substituting entirely different corrosion resistant materials such as titanium, nickel-copper alloys, or non-metallics such as fiber-reinforced plastics. Or, in some cases, the components could be downgraded to carbon steel, cast iron, or the like, and replaced periodically.

PROTECTIVE COATINGS

Another method of conserving chromium is to fabricate equipment out of readily available materials such as carbon steel and coat the exposed surfaces by cladding, plating, weld overlaying, metallizing, or with a variety of non-metallic materials. This approach, like the alternative material approach, can only be used in certain applications, but it is feasible, and could save appreciable amounts of chromium in an emergency.

USE OF STRONGER MATERIALS

A fourth way of conserving chromium is by using higher-strength stainless steels to replace weaker alloys. Even though the stronger alloys may contain as much chromium as the ones they are replacing, a savings in this element can be effected in a number of applications by allowing the use of a smaller section size or lighter gage for equivalent strength.

Use of Stronger Materials (cont'd.)

For example, many shafts that are used in pumps, blowers, mixers, etc. are made of Type 304, which has a typical 0.2% offset yield strength of 35 ksi. If the corrosion resistance of Type 304 is adequate for the job at hand, these shafts can be replaced with smaller diameter ones made of a precipitation hardening grade of stainless such as S17400 (17-4 PH)*** The 0.2% yield strength of this widely available alloy ranges from 85 to 185 ksi, depending on heat treatment. It contains slightly less chromium than Type 304 (16% chromium for S17400 vs. 18.5% for Type 304), so this element can be conserved two ways - by reduction in alloy content and smaller section size.

Where conditions are more corrosive and shafts of Type 316 or Type 317 (typical 0.2% yield strengths of 35 ksi) are now being used, replacements could be made with smaller ones made from S20910 (NITRONIC 50)**. This alloy has a typical 0.2% yield strength of 60 ksi in the annealed condition. Shafting of this alloy in sizes up to two inches in diameter also can be obtained with a minimum 0.2% yield strength of 105 ksi. This is three times the yield strength of Types 316 and 317, so a substantial savings in size and hence critical material could be effected by using the stronger material, even though it contains somewhat more chromium than the standard AISI grades (about 21% chromium for S20910 vs. about 18.5% chromium for Types 316 and 317).

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*The various alloys mentioned in this paper are for illustrative purposes only. It is not intended to limit the possible replacement alloys to those specifically named.

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Use of Stronger Materials (cont'd.)

Reactors, pressure vessels and piping - if now made from Type 304 or 304L stainless steel and performing adequately - could be replaced with one of the newer nitrogen-strengthened austenitic stainless steels. Two examples of these are S30451 (Type 304N) and S24000 (NITRONIC 33)**. These alloys have typical 0.2% yield strengths of 45 ksi and 60 ksi, respectively, in the annealed condition, compared to about 30-35 ksi for annealed Types 304 and 304L. Substitution of these stronger alloys could save chromium through the use of lighter gages for equivalent load capacity.

If the corrosive conditions are more severe, requiring the use of Type 316 or 316L (typical 0.2% yield strength of 30 to 35 ksi), again one of the newer nitrogen-strengthened austenitic stainless steels may be used. Several examples of these alloys are S20910 (NITRONIC 50)**and S21600 (Type 216). The 0.2% yield strength of these alloys in the annealed condition typically is 60 ksi - about twice that of Types 316 and 316L.

The attached plot shows the maximum ASME allowable tensile stresses as a function of temperature for several of these nitrogen-strengthened stainless steels versus AISI Types 304, 316, and 347. The appreciably higher working stresses allowed for these newer alloys could enable lighter gages to be used in construction, thereby saving critical chromium and other raw materials.

USE OF MORE CORROSION RESISTANT MATERIALS

A fifth approach to conserve chromium is through the use of more corrosion resistant stainless alloys to replace inferior ones. This may seem contradictory at first, since greater corrosion resistance often is achieved through the use of increased amounts of chromium (along with other elements such as nickel, copper, and molybdenum). However, if the equipment has to be replaced less often - or perhaps not at all - then a net savings in chromium can be realized, since not all of the scrapped equipment finds its way back into the steelmaking furnace.

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Use of More Corrosion Resistant Materials (cont'd.)

An obvious example of this concept is to replace Type 304 with Type 316, or Type 316 with perhaps Type 317 or S20910 if the equipment has failed from pitting, crevice corrosion, or general attack. It may be necessary to up-grade Types 316 and 317 to the very highly alloyed stainless steels or even nickel-base alloys if corrosion is severe. Although much more expensive than Types 316 and 317, these materials are far more resistant than the standard stainless steels to all forms of corrosive attack, including stress-corrosion cracking.

The new super-ferritic alloys, such as S44700 (29 Cr-4 Mo) and S44800 (29 Cr-4 Mo-2 Ni) are quite resistant to pitting as well as stress-corrosion cracking. Although much higher in chromium content than the standard stainless steels, their use in applications such as heat exchangers could effect a real savings in chromium through decreased frequency of replacement - or perhaps no replacement at all.

The attached chart summarizes some of the available choices for higher strength, better corrosion resistance, or both. The alloys shown are given as examples only. Their ranking with regard to corrosion resistance is only approximate, since some of these materials may be superior to others in certain media, and inferior in different ones.

SUMMARY

There are several ways to conserve the use of chromium in equipment used in the chemical process industry. Among them are the following:

Summary (cont'd.)

1. Substitute other elements such as molybdenum, silicon, and aluminum as partial replacements for chromium in stainless steels. These alloys are in the development stage at the present time.
2. Use alternative materials such as titanium, nickel-copper alloys, fiber-reinforced plastics, carbon steel, or cast iron instead of stainless steels.
3. Coat the exposed surfaces of readily available materials such as carbon steel with protective materials by cladding, plating, weld overlaying, metallizing, or by applying one of a variety of non-metallic materials.
4. Replacement of low-strength stainless steels with stronger alloys to allow use of smaller section size or lighter gage for equivalent strength.
5. Up-grading to more corrosion resistant stainless alloys to minimize frequent replacement of chromium-containing equipment.

None of these approaches can be used across-the-board in all of the areas where stainless alloys are presently being used in the chemical industry. Each should have at least some areas of application, however, and all of them together could lessen considerably the chromium-dependency of that industry.

INCREASED CORROSION RESISTANCE

Type 304 → Type 316 → S 21600(Type 216) → Alloy 20 Type
Or Or
S 20910(NITRONIC 50) 904 L Type

Type 430 → S 44400 → S 44625,S 44626 →
(18Cr-2Mo) (26Cr-1Mo)

S 44700,S 44800
(29Cr-4Mo)
(29Cr-4Mo-2Ni)

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SUBSTITUTIONAL ALLOYS

18.5% Cr - 9% Ni (Type 304)

Add Mo, Si, Al
To Replace Cr

Add Ni, Mn, N
To Stabilize Austenite

ALTERNATIVE STRUCTURAL MATERIALS

- Titanium
- Nickel-Copper Alloys
- Cast Irons
- Carbon Steel
- Fiber-Reinforced Plastics

PROTECTIVE COATINGS

- Cladding
- Weld Overlay
- Plating
- Metallizing
- Non-Metallic Coatings

INCREASED STRENGTH - BARS

Types 304 or 304 L ⟶ S 17400 (17-4PH)

30 to 35 ksi. Y.S. 85 to 185 ksi. Y.S.

Types 316 or 316 L ⟶ S 20910 (NITRONIC 50)

30 to 35 ksi. Y.S. 60 to 125 ksi. Y.S.

INCREASED STRENGTH - FLAT ROLLED PRODUCTS

Types 304 or 304 L ⟶ S 30451 (304 N) -
30 to 35 ksi. Y.S. 45 ksi. Y.S.

Or

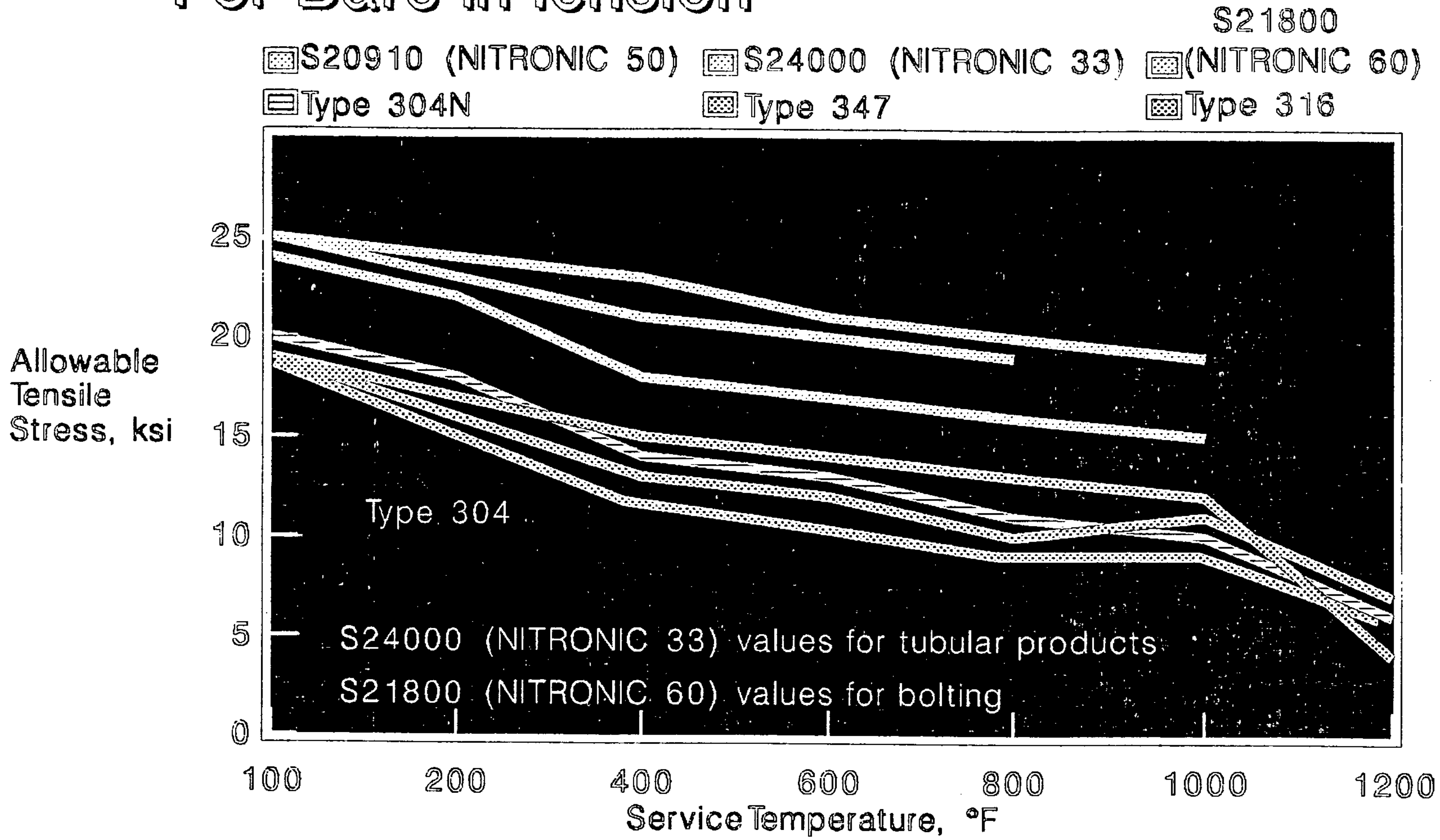
S 24000 (NITRONIC 33) -
60 ksi. Y.S.

Types 316 or 316 L ⟶ S 21600 (Type 216) -
30 to 35 ksi. Y.S. 60 ksi.

Or

S 20910 (NITRONIC 50) -
60 ksi.

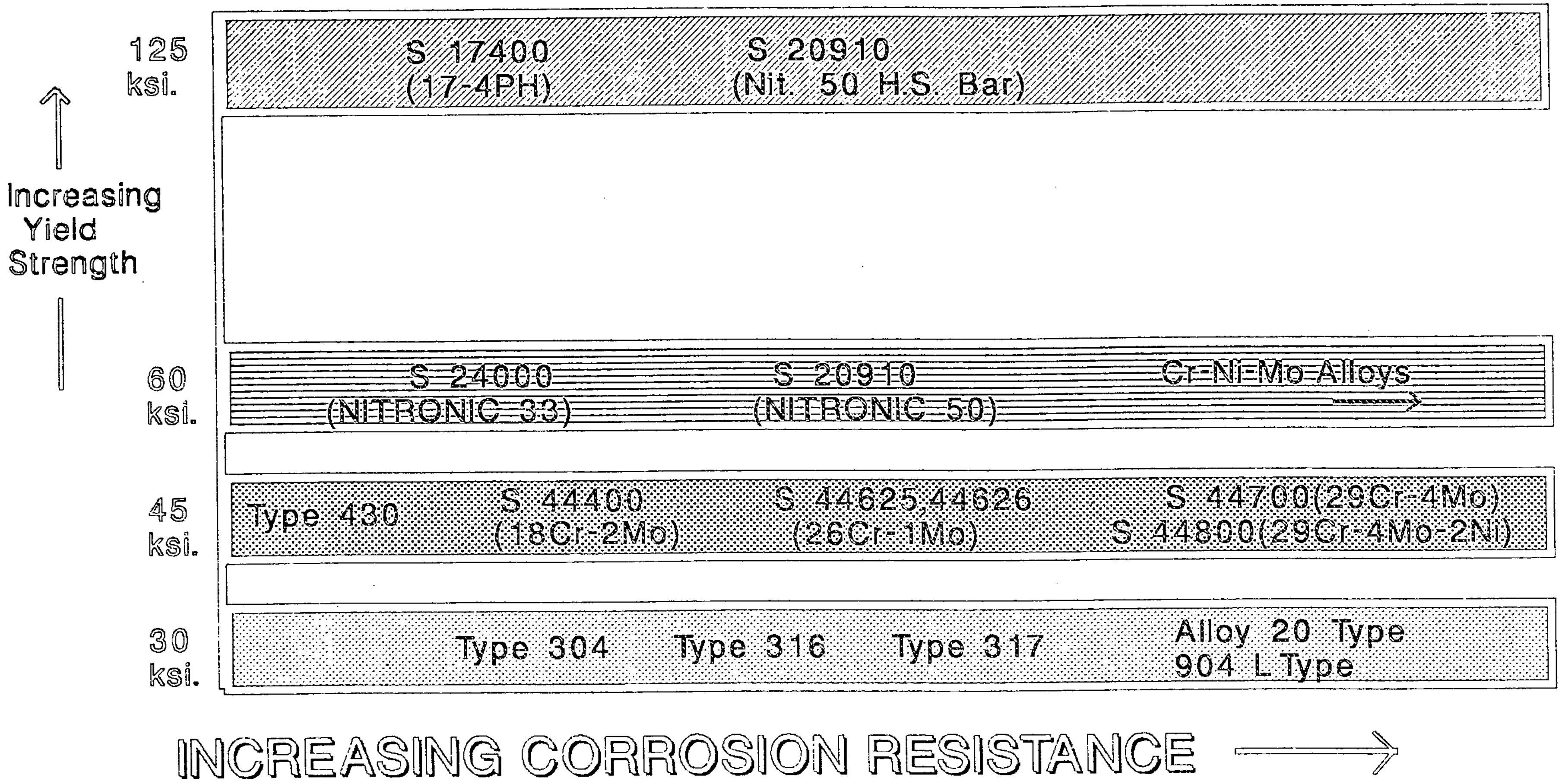
Maximum ASME Allowable Stresses For Bars In Tension



S24000 (NITRONIC 33) values for tubular products

S21800 (NITRONIC 60) values for bolting

STRENGTH vs. CORROSION RESISTANCE



APPROACHES TO CHROMIUM CONSERVATION IN MATERIALS FOR THE CHEMICAL PROCESS INDUSTRIES

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I. INTRODUCTION

Of all metals, chromium is presumed to be the "most critical" (1). No metal is more essential to the economy than chromium, and while the US is the world's biggest end-user of chromium, it has no indigenous production of this metal (2). These two aspects of being essential to the nation's economy (and defense) and not being domestically produced, qualify chromium as a definite strategic metal (3). Furthermore, the lack of adequate"chromium-substitution" research along with the "wrong forms" of stockpiling (insufficient characterization and nonconformance to current specifications) render the chromium situation critical (4,5).

Hence, there is a large incentive to use materials containing little or no chromium. However, the fact remains that at the present time chromium is the most cost effective alloying element for corrosion-, heat-, and wear-resistance (6). Also, no single substitute is presently identified as the "universal" replacement for chromium in many essential alloys, even though several new alloy systems (e.g., manganese-aluminum and iron-aluminum) appear to be viable candidates to displace some chromium-bearing alloys (7). The widespread applications of chromium are directly related to its very special properties, thus imposing many constraints on existing and potential substitutes (8).

A quick examination of the consumption of chromium in its various end uses (Table 1) clearly identifies the metallurgical sector as the area having great opportunities for potential conservation of chromium presently consumed in the U.S. It is evident that about 75% of metallurgical chromium consumption is for stainless/heat-resisting steels and high performance alloys. Since these alloys are widely used in the chemical industry (required resistance to sulfuric acid, phosphoric acid, hydrochloric acid and other chemicals) and the petroleum industry (required resistance to hydrogen sulfide and other sulfur compounds), any major chromium substitution effort will not be adequate without the successful reduction of metallurgical chromium consumption in these industries.

It is the purpose of this communication to provide information about the role of chromium in corrosion resistant materials, to examine viable technologies for chromium conservation, and to focus on the role of silicon as an effective chromium substitute in corrosion resistant alloys of interest to the chemical process industries.

II. ROLE OF CHROMIUM - AQUEOUS CORROSION

Chromium offers excellent resistance to oxidizing corrosive media (e.g., nitric acid, chromic acid) due to its outstanding, stable passivity (9).

Chromium is unstable in reducing media or in solutions containing active chloride ions (e.g., dilute sulfuric acid, hydrochloric acid). As a metal, chromium is hard and brittle, due to its very high affinity to oxygen, nitrogen and carbon. When alloyed with most metals, chromium easily confers its unique properties to the alloy. This behavior can be detected in iron where the Fe-Cr alloys with higher chromium contents corrode at a higher rate in reducing sulfuric acid solution (Figure 1). However, in oxidizing sulfuric acid, these alloys with more than 12% Cr exhibit, like chromium, a passive behavior with corresponding low corrosion rates (10). An improvement in corrosion resistance to oxidizing media is also observed for nickel and cobalt when alloyed with chromium. The passivation of iron, nickel, and cobalt is enhanced with chromium addition, e.g., the critical current density for passivation decreases as chromium is added to pure cobalt (11), and a Co-15% Cr alloy exhibits an electrochemical behavior resembling that of chromium (Figure 2).

When considering the ability of chromium to promote passivity and its relatively low cost and abundance, one is not surprised to observe more research efforts devoted to the increased usage of chromium rather than to the search for a chromium substitute (12). This is a logical step for countries with very rich chromium deposits (e.g., USSR) and therefore, with "unlimited prospective" for development of high chromium, corrosion-resistant alloys (9). Yet even within countries having virtually no domestic sources of chromium, several high chromium containing alloys (11, 13, 14) have been designed/developed to improve the resistance to corrosion (e.g., uniform corrosion, localized corrosion, stress corrosion cracking - Table 2)

While chromium, in general, is accepted as an effective alloying eleme imparting corrosion resistance, its beneficial effects have limitations, especially from the standpoint of corrosive species and mode of corrosive attack. In designing alloys for better resistance to phosphoric acid, higher chromium contents are a necessary feature, but they are still not sufficient to avoid higher corrosion rates in acid solutions containing chloride ions (Table 3). Molybdenum is an essential element needed to enhance resistance to such chloride-containing media. Another example is shown in Figure 3, which illustrates the need for additional alloying elements (e.g., molybdenum and nitrogen) and the proper microstructure (duplex, austenite-ferrite structure) to provide adequate resistance to localized corrosive attack. Finally, increasing the chromium content of alloys may not be the answer for improving resistance to stress corrosion cracking. Higher chromium austenitic alloys do not provide improved resistance to chloride-sulfide stress-corrosion cracking in simulated deep sour gas environments. Rather, nickel (and molybdenum) appear to be the essential elements in minimizing the susceptibility to stress cracking (Table 4).

III. VIABLE TECHNOLOGIES FOR CHROMIUM CONSERVATION

The fact that chromium is a critical metal and the US would be vulnerable to a chromium shortage makes it necessary to define chromium conservation options. For metallurgical chromium, the realistic options can be grouped in three categories: resource recovery, reduced consumption, and substitution (Table 5).

Technically, several thousand tons of chromium can be reclaimed annually from process wastes, but very little of this waste is presently recovered. For practical, economic reasons, chromium does not lend itself to waste reclamation. As for industrial scrap, it is estimated that 73,000 tons of chromium in scrap metal is lost annually, because it is not collected, downgraded for use in lower quality materials, or is exported (15). The opportunity apparently exists, with present technologies, to recover and reuse chromium waste and scrap if the price is right.

From the standpoint of reducing chromium consumption, many possibilities can be offered. Improved and more efficient techniques/equipment can be adopted to increase yields and minimize chromium losses during various processing steps (melting, refining, atomizing, consolidating). Also, usage of high performance alloys in applications where less resistant, chromium-containing materials are frequently wasted and replaced is an additional contribution to reduce the annual chromium consumption (e.g., a vessel made of Ni-16Cr-16%Mo high performance alloy can last a full "20-year market life" of a chemical product, while vessels made of "20-Cr" stainless steels are wasted on a yearly basis).

Such chromium conservation through usage of high performance alloys can be pushed further by relying on "surface protection." Less chromium will be needed to provide adequate corrosion resistance to chemical process streams through clever designs implementing the usage of low grade steels which have been surfaced with high performance alloys. Many "surface protection" systems are presently available and are being used (lining/cladding, weld overlaying/hardfacing, thermal spray, surface impregnation), with additional systems for surface alloying being explored (selected surface melting, laser alloying, ion implantation). In contrast to chromium resource recovery, several "surface protection" systems are presently adopted in various process industries due to favorable economic reasons. Lining, cladding, weld overlaying, and thermal spraying are being used not only to preserve the base metals (and reduce chromium consumption) but mostly to improve service performance and avoid the high and rapidly escalating costs of maintenance and downtime. Table 6/Figure 4 list examples of "surface protection" systems presently used in corrosive services due to favorable economics and not because of concerns for chromium conservation. Improvement of these present systems and innovations in surface alloying are underway in many organizations, with a promising, potential reduction of chromium consumption for applications in the chemical process industries.

As to options for chromium substitution in chemical processing, their feasibility depends on the severity of the environment and the mode of corrosive attack. Several materials are presently available and can be used to replace some of the chromium-containing alloys in specific applications (Ni-Cu alloys, Ni-Mo alloys, Ti, Zr, Pb, Al). However, few of these alternate materials possess the appropriate mechanical properties and the versatility of the chromium containing alloys. Also, most of the alternates are presently more expensive than several stainless steels. As to potential chromiuum substitutes, several metals (e.g., nickel, molybdenum, cobalt), when alloyed to steel, impart only a limited corrosion resistance. Also, these substitutes are more expensive to use and do not provide the same corrosion resistance that alloying with chromium does (16).

One practical approach to avoid sacrificing the established performance of stainless steels is the partial substitution of chromium. Generations of ferritic and austenitic stainless steels have been developed with aluminum, molybdenum, and/or silicon partially substituting for chromium (17,18). The chromium content is reduced from 18 percent to 12 percent by adding 2% Mo + 2% Al, or 3-4% Si. The limited laboratory corrosion tests show the performance of these alloys compare favorably with that of the baseline 18% Cr stainless steel. Also, another testing program suggests that stainless steels containing ~9% Cr with additions of Ni, Mo, Cu and/or V have corrosion properties comparable to those of 18% Cr alloys, in less severe environments (19).

For applications in very severe corrosive environments, most assume that there are no substitutes for chromium, whether partial or total. In this regard, there is an interesting option for chromium substitution in corrosion applications that has escaped the attention of many parties involved in developing solutions to future chromium problems. This option is the use of alloys with high silicon contents.

IV. SILICON AS AN EFFECTIVE CHROMIUM SUBSTITUTE

Silicon as an alloying element imparts corrosion resistance to many metals (e.g., iron, nickel and cobalt). A small addition of silicon (≈1-4% Si) enhances the oxidation resistance of many materials, while alloying with larger amounts of silicon (≈9-18% Si) has been known to provide excellent resistance to aqueous corrosion in many aggressive acid media. High-silicon iron alloys (introduced in 1912) and high-silicon nickel alloys (introduced in

1929) are among the most universally resistant materials as they withstand almost all severe acid conditons (20). Similarly, cobalt-silicon alloys (patented in 1924) have been known to resist the very aggressive corrosive conditons of anodes in acidified electrowinning baths (21). This corrosion resistance of silicon alloys is typified by the low corrosion rates of an Fe-14% Si alloy in all concentrations of sulfuric acid (Figure 5). Zirconium, Ni-29Mo alloy, and Ni-chromium alloys do not exhibit such a resistance to all concentrations of sulfuric acid as the high-silicon iron alloy does (22).

In general, the initial corrosion rates of silicon alloys tend to be much higher than the final rates (Table 7). It is presumed that these alloys acquire their improved corrosion behavior through the gradual buildup of a protective silica (SiO_2) surface film. It is thought that the corrosion resistance of the silicon alloys to a wide variety of aggressive corrosive media is the result of the silica film formation. Such film presumably renders these alloys resistant to oxidizing and reducing conditions (23). As the silicon content rises, the corrosion rate decreases (Figure 6). However, no significant benefit is derived by increasing the silicon content beyond 14-15 percent in iron-base alloys. At this concentration of ≈14.5% Si, a typical electrochemical passive behavior (Figure 7) is observed in both sulfuric acid hydrochloric acid solutions (24). While the exact role of silicon is not fully researched, it is rationalized that acid resistance is achieved due to the "no marked base-forming properties" of this metaloid (25).

The universal corrosion resistance of silicon alloys has been known for quite sometime. These alloys have been shown to perform well in many aqueous chemical media (Table 8), with the exception of hydrofluoric acid (26). Furthermore, in aggressive sulfuric acid environments, the corrosion resistance of the high-silicon alloys surpasses that of high-chromium stainless steels (Table 9), as well as those of high-performance alloys and tantalum. Also, it is of interest to note the better cavitation-erosion resistance of silicon alloys (Figure 8) when compared to some chromium-containing stainless steels. These corrosion and wear properties of high-silicon alloys have been fully recognized and successfully utilized in the past. Various components of Ni-9Si-3Cu alloy (e.g., vessel, piping, agitator, propeller, valve) are reported to have performed well in chemical (cellulose products, chromic acid, dye intermediates), petrochemical (ethyl alcohols, alkylation spent acid), and pulp and paper industries (Table 10).

Despite the excellent corrosion resistance of the high-silicon alloys, the trend has been toward an extensive and wider use of the chromium-containing stainless steels. The reason for this is the obvious brittleness, limited mechanical properties, impractical fabricability, and poor weldability of the silicon alloys. While the silicon-nickel alloys are less brittle than the silicon-iron and silicon-cobalt alloys, the fact remains that all high-silicon alloys are available and used only as castings. It is evident that, as a chromium substitution option, there is a need to pursue development efforts aimed at improving the mechanical properties and fabricability of the silicon alloys in order to capitalize on their excellent corrosion resistance. Wrought, hot- and cold-workable silicon-containing alloys should be regarded not as a dream, but as a goal to be achieved by recent advances in metallurgical processing. Furthermore, since many corrosive degradations occur on exposed surfaces, the high-silicon alloys would be the ideal choice for weld overlaying, thermal spraying and surface impregnation. In this regard, it is interesting to note that the silicon impregnation process (surface alloying with silicon in the form of 0.010- to 0.050-inch-thick layer containing ≈14% Si) was developed in the early 1930's to provide components with excellent corrosion properties and to get around the brittleness and the poor physical properties of high-silicon alloys (27). At that time, i.e., half a century ago, the strategic importance of replacing chromium with silicon (one of the most abundant elements, obtained from common silica sand) had already been recognized and proposed.

Finally, it is true that solutions to future chromium scarcities can be found by examining many of the old alloys (2). Also, new corrosion alloys containing little or no chromium may become available. Still, for a successful "chromium substitution preparedness" (1), a close interaction between materials suppliers and materials users is required.

V. SUMMARY

- Presently, it is apparent that chromium remains the most cost effective alloying element from the aspect of aqueous corrosion.

- The economical incentives appear favorable for reducing chromium consumption via the usage of high-performance alloys and the adoption of "surface protection" systems.

- High-silicon alloys offer excellent resistance to aqueous corrosion. Their implementation to conserve chromium depends on improving their mechanical properties and fabrication.

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TABLE 1: CONSUMPTION PATTERNS OF CHROMIUM IN U.S.A. (1977)

END USE	U.S. CONSUMPTION, %
METALLURGICAL	
WROUGHT AND HEAT-RESISTING STAINLESS	51.3
TOOL STEELS	1.3
WROUGHT ALLOY STEELS	9.5
CAST ALLOY STEELS	3.1
ALLOY CAST IRONS	1.8
NON-FERROUS, HIGH-PERFORMANCE ALLOYS	3.1
OTHER	1.3
	71.4
REFRACTORIES	
CHROME AND CHROME-MAGNESITE	2.2
MAGNESITE-CHROME BRICK	3.1
GRANULAR CHROME-BEARING	6.0
GRANULAR CHROMITE	2.2
	13.5
CHEMICALS	
PIGMENTS	4.0
METAL FINISHING	3.3
LEATHER TANNING	2.4
DRILLING MUDS	0.7
WOOD TREATMENT	0.9
WATER TREATMENT	0.9
CHEMICAL MANUFACTURE	1.1
TEXTILES	0.4
CATALYSTS	<0.3
OTHER	1.1
	15.1
TOTAL	100.0

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(L. Whalley, Inst. Mining & Metallurgy, Vol. 89, p. C-107, Sept. 1980)

Table 2: **IMPROVEMENT IN CORROSION RESISTANCE WITH HIGHER CHROMIUM**

UNIFORM CORROSION: 45% PHOSPHORIC ACID, UNDER HEAT-TRANSFER(*)	
Ni-22Cr-9Mo-3.5Cb+Ta (ALLOY 625)	32 MILS/YEAR
Ni-35Cr	4 MILS/YEAR
LOCALIZED CORROSION: 10% FERRIC CHLORIDE, ROOM TEMPERATURE (**)	
Fe-20Cr-35Ni-2Mo-3Cu-	PITTING/CREVICE
Fe-28Cr-2Mo	NO ATTACK
STRESS CORROSION CRACKING: UNDEAERATED WATER, 316°C(***)	
Ni-15Cr-8Fe (ALLOY 600)	CRACKING (2 WEEKS)
Ni-30Cr-9Fe (ALLOY 690)	NO CRACKING (48 WEEKS)

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TABLE 3: CORROSION RATES (MILS PER YEAR) IN PLANT PHOSPHORIC ACID

	42% P_2O_5 AT 85°C	42% P_2O_5 + 2000 PPM Cl^- AT 85°C
Ni-22Cr-20Fe-6Mo (ALLOY G)	1.2	3
Ni-30Cr-9Fe-0Mo (ALLOY 690)	0.6	192

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TABLE 4: STRESS CORROSION CRACKING DATA

50% COLD WORK, C-SHAPE SPECIMENS

	24% $CaCl_2$ AT 204°C	25% NaCl + ACETIC ACID + CO_2-H_2S AT 204°C
Fe-31Ni-27Cr-3Mo (ALLOY 28)	2/2*	1/2
Fe-42Ni-21Cr-2Mo (ALLOY 825)	0/2	0/2

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* NUMBER OF SPECIMENS CRACKED OUT OF TWO SPECIMENS TESTED.

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TABLE 5: METALLURGICAL CHROMIUM CONSERVATION

RESOURCE RECOVERY	REDUCED CONSUMPTION	SUBSTITUTION
PICKLING WASTES	EFFICIENT PROCESSING	ALTERNATE MATERIAL
FLUE DUST, MILL SCALE	HIGH-PERFORMANCE ALLOY	PARTIAL SUBSTITUTE
INDUSTRIAL SCRAP	SURFACE TREATMENT	TOTAL SUBSTITUTE

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TAB. 6: INDUSTRIAL APPLICATIONS OF "SURFACE PROTECTION" SYSTEMS IN CORROSIVE SERVICES

PROCESS	COMPONENTS	SERVICE	REMARKS
LINING	CIRCULATOR PUMP	40% P_2O_5 AT 82°C + GYPSUM + FLUOSILICATES	ORIGINAL Fe-20Cr-35Ni-2Mo-3Cu ALLOY CORRODED. WELD OVERLAY WITH ALLOY WIRE WAS UNSATISFACTORY. LINING WITH Ni-22Cr-20Fe-6Mo-2Cu ALLOY WORKED.
EXPLOSION-BONDING	AGITATION VESSEL	HCl + PHARMACEUTICAL COMPOUNDS	Ni-28Mo ALLOY EXPLOSION-BONDED TO STEEL.
WELD-OVERLAYING	TUBE SHEET	ACETIC ACID AT 130°C	ORIGINAL Fe-20Cr-35Ni-2Mo-3Cu ALLOY CORRODED. WELD OVERLAY WITH Ni-16Cr-16Mo-4W ALLOY WORKED.
THERMAL-SPRAYING	BOILER TUBES	SULFUR-BURNING OIL, ALKALI-IRON-SULFATES	SEVERE CORROSIVE ATTACK OBSERVED IN THE VICINITY OF THE TOP ROW OF BURNERS - FRONT WALL OF BOILER. METALLIZING WITH Ni-16Cr-16Mo-4W PROVIDED EXCELLENT ADHESION AND CORROSION RESISTANCE.

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TABLE 7: CORROSION RATES (MILS PER YEAR) OF Ni-9Si-3Cu ALLOY; T≃93°C

EXPOSURE	70% H_2SO_4	70% H_2SO_4 + 5% HNO_3
"FIRST" 72 HOURS	70	52
"SECOND" 72 HOURS	57	13
"THIRD" 72 HOURS	27	9
"FIRST" ADDITIONAL 240 HOURS	5	4
"SECOND" ADDITIONAL 240 HOURS	2	4

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TABLE 8: EFFECT OF SOME CORROSIVE CONDITIONS ON FE-15 SI ALLOY
LABORATORY AND WORKS SCALE TESTS

[A = <5 mpy], [B = <50 mpy], [C = <500 mpy], [D = >500 mpy]

Acids	Concentration %	Temperature	Performance
Acetic Acid	80-100	Boiling	A
Boric Acid	25	Boiling	A
Chromic Acid	50	Boiling	B
Formic Acid	5-100	15-60°C	A
Hydrofluoric Acid	70	15°C	D
Hydrochloric Acid	5	90°C	A
Nitric Acid	50	Boiling	A
Oxalic Acid	20	Boiling	A
Phosphoric Acid	All	Boiling	A
Sulfuric Acid	All	Boiling	A
Tartaric Acid	25	Boiling	A
Tannic Acid	All	Boiling	A
Mixtures			
20% H_2SO_4 + 10% HCl	-	70°C	A
H_2SO_4 + HNO_3	All	15-120°C	A
15% H_2SO_4 + H_3PO_4	-	110°C	A
5% H_2SO_4 + 10% NaCl	-	50°C	A
Potassium Chlorate + HCl	-	Boiling	A
Aniline + HCl	-	Boiling	A
Salts			
Ammonium Chloride	All	Boiling	A
Copper Chloride	10	Boiling	C
Hydrogen Sulfide	Saturated	15°C	A
Magnesium Chloride	Saturated	Boiling	A
Sodium Hypochlorite	Saturated	20°C	B
Zinc Chloride	30	Boiling	D
Others			
Bromine	Moist Vapor	15°C	B
Chlorine	Saturated H_2O	15°C	A
Iodine	Gaseous	100°C	A
Steam	-	300°C	A
Zinc	Molten	500°C	D
Aluminum	Molten	700°C	D

Table 9: **COMPARATIVE CORROSION RATES IN VARIOUS SULFURIC ACID ENVIRONMENTS**

	$35-42\%\ H_2SO_4 + Cu^{++} + Be^{++}$ 13-130 DAY EXPOSURE, T ≃ 110°C
Fe-22Cr-26Ni-5Mo	234 MPY
Ni-22Cr-20Fe-6Mo-2Cu (ALLOY G)	206 MPY
Ni-9Si-3Cu	13 MPY
	COMMERCIAL 98% H_2SO_4 24-HOUR EXPOSURE, T ≃ 110°C
Ni-22Cr-20Fe-7Mo-2Cu (ALLOY G-3)	30 MPY
Ni-20Cr-3Fe-20Mo	67 MPY
Ni-9Si-3Cu	32 MPY
	COBALT ELECTROWINNING LIQUOR (ZAMBIA) 24-HOUR AS ANODE (28 MA/CM^2), T ≃ 70°C
Ni-16Cr-16Mo-4W (ALLOY C-276)	54 MG/AMP. HR.
Ta	19 MG/AMP. HR.
Co-12Si-5Mn	9 MG/AMP. HR.

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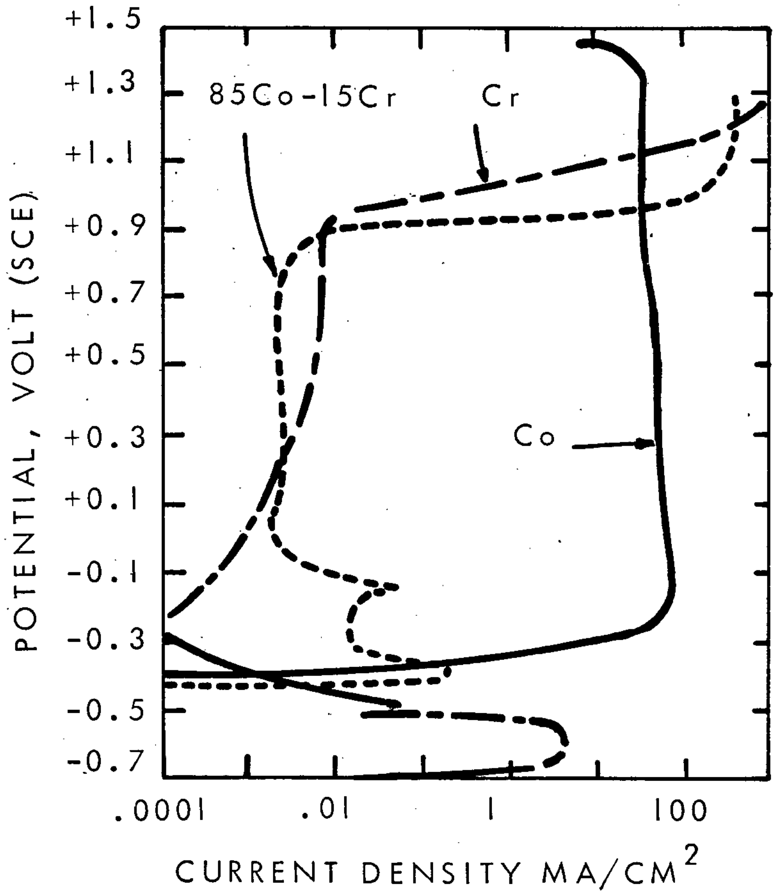

FIGURE 2: ANODIC POLARIZATION CURVES (10 mv./3 min.) FOR PURE COBALT IN H_2-SATURATED, SULPHURIC ACID SOLUTIONS AT 22°C. (G.T. SEAMAN, J.R. MYERS, and R.K. SAXER, ELECTROCHIMICA ACTA, VOLUME 12, PAGE 855, 1967)

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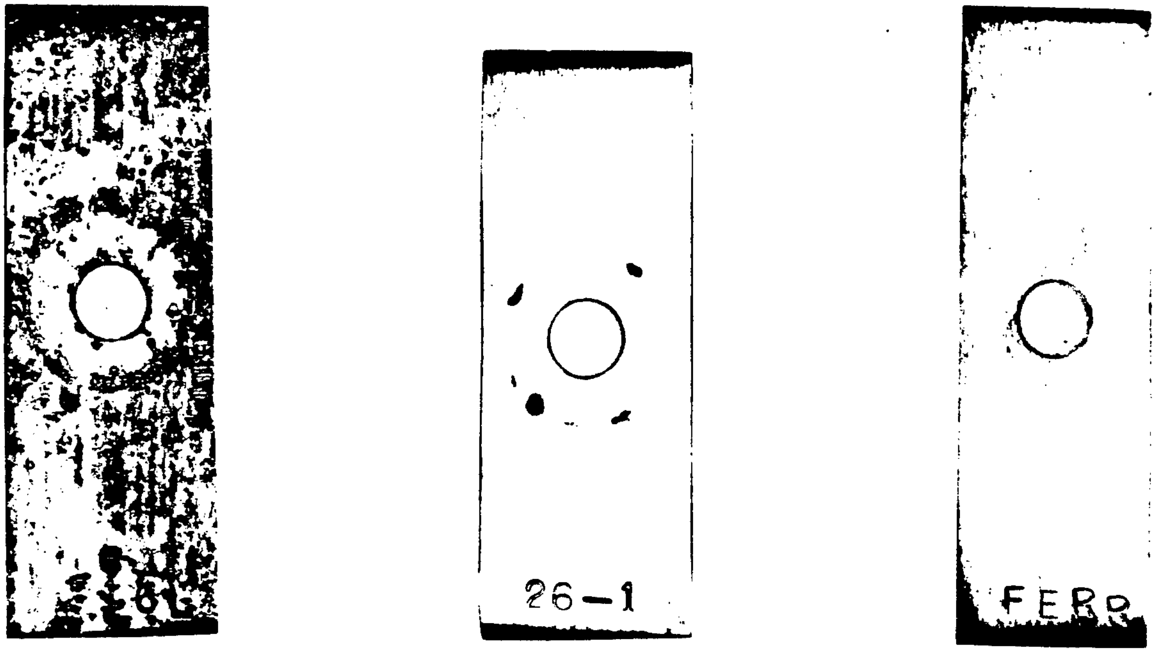


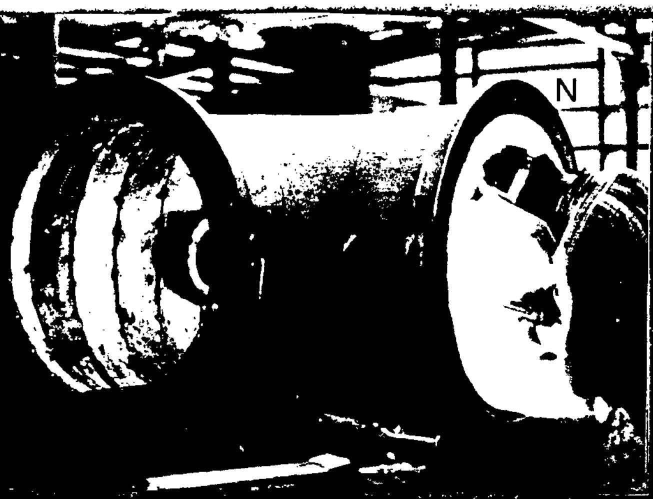
Fe-18 Cr-12 Ni-2 Mo
(Austenitic)

Fe-26 Cr-1 Mo
(Ferritic)

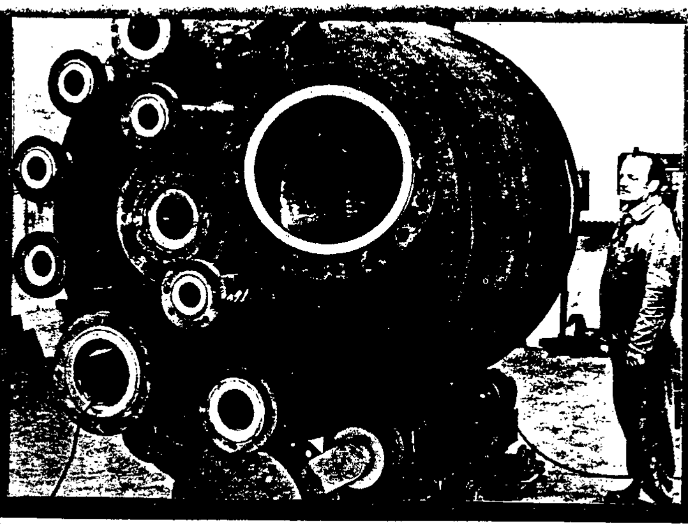
Fe-26 Cr-5 Ni-3 Mo-0.17 N
(Austenitic-Ferritic)

CREVICE CORROSION TESTS IN 10% $FeCl_3$ (RT, 5-DAY EXPOSURE)

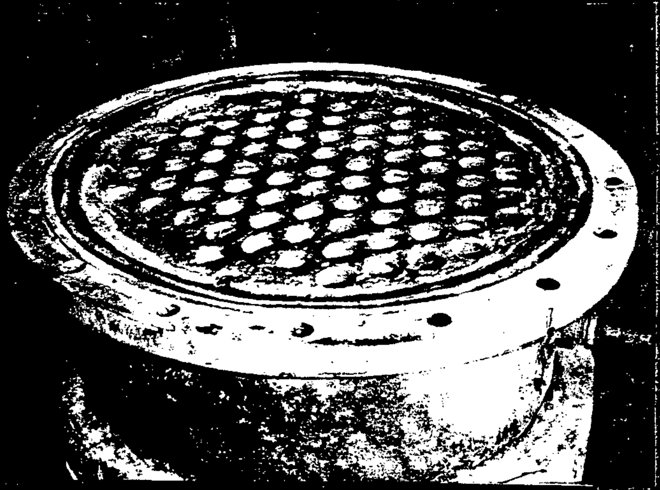
FIGURE 3



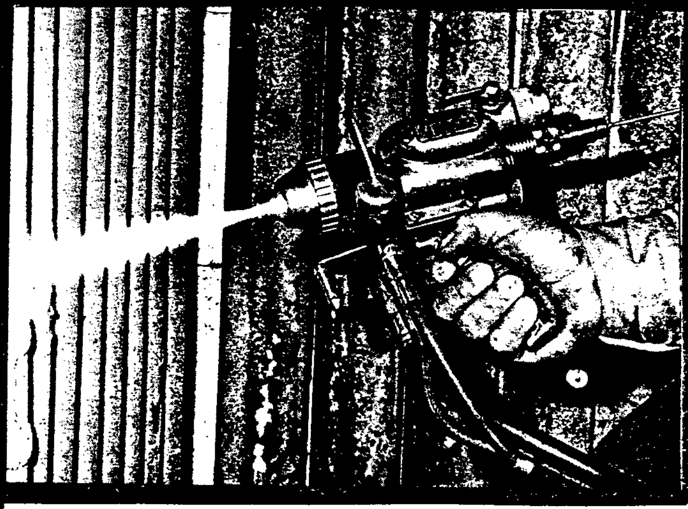
LINING CIRCULATOR PUMP
(PHOSPHORIC ACID SERVICE)



VESSEL MADE OF EXPLOSION-BONDED PLATES
(HCl + PHARMACEUTICAL COMPOUNDS)



WELD OVERLAYING TUBE SHEET
(ACETIC ACID SERVICE)



THERMAL-SPRAYING OF BOILER TUBES
(HIGH SULFUR BURNING OIL)

INDUSTRIAL APPLICATIONS OF ''SURFACE PROTECTION'' SYSTEMS

FIGURE 4:

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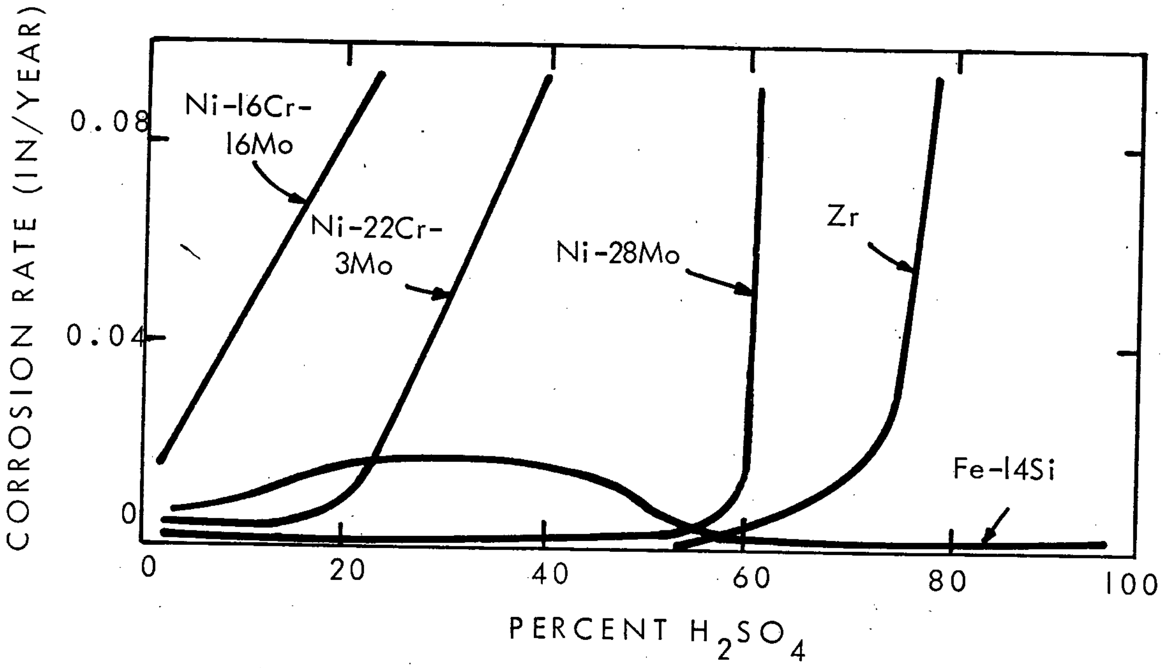

FIGURE 5: **CORROSION OF SOME METALS AND ALLOYS IN BOILING SULFURIC ACID. (W. BARKER ET AL., BR. CORROS. J., VOL. 5, P. 76, 1970)**

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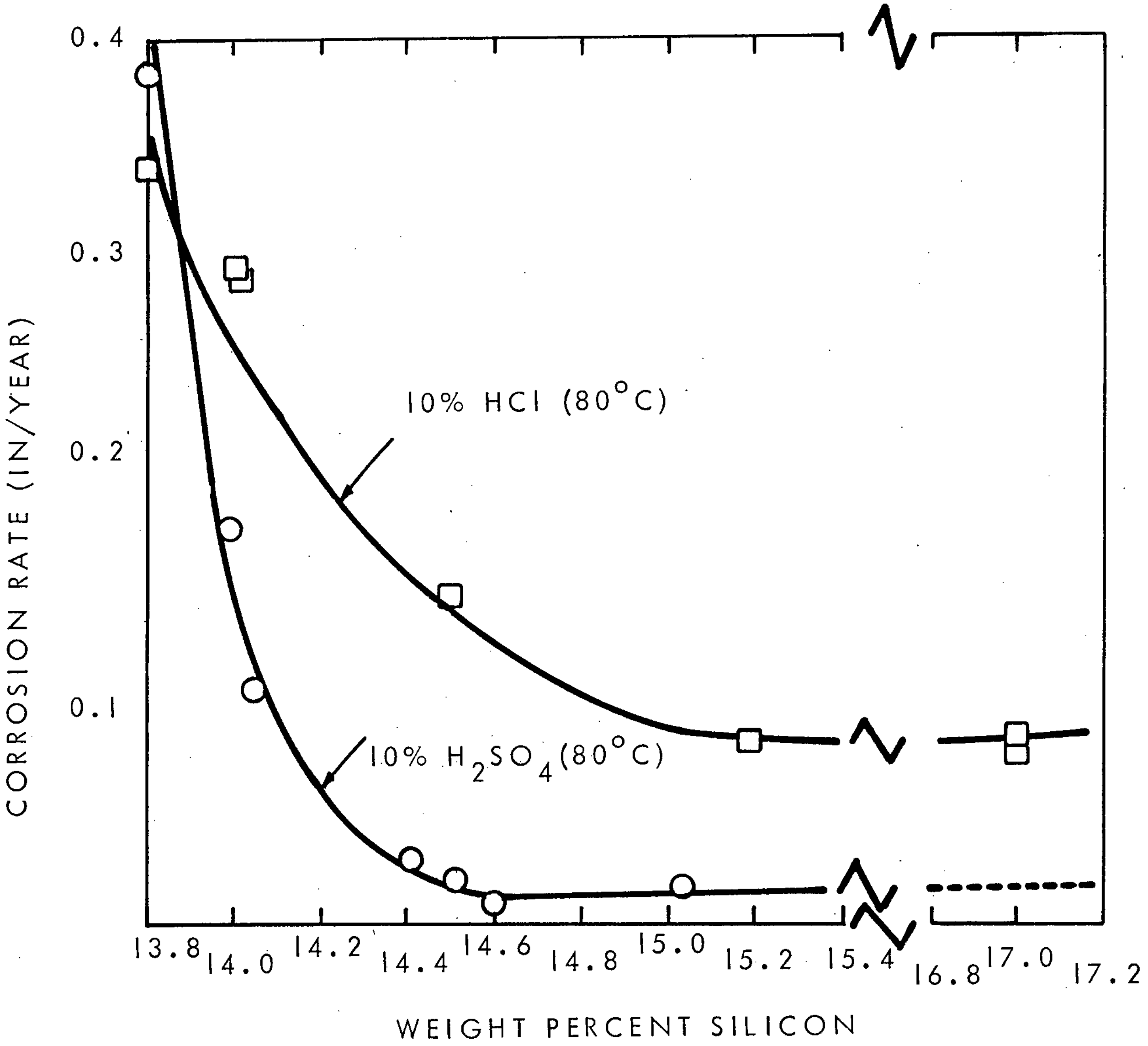

FIGURE 6: **THE EFFECT OF SILICON ON CORROSION RESISTANCE OF IRON. (H.H. UHLIG, CORROSION HANDBOOK, P. 202, 1948)**

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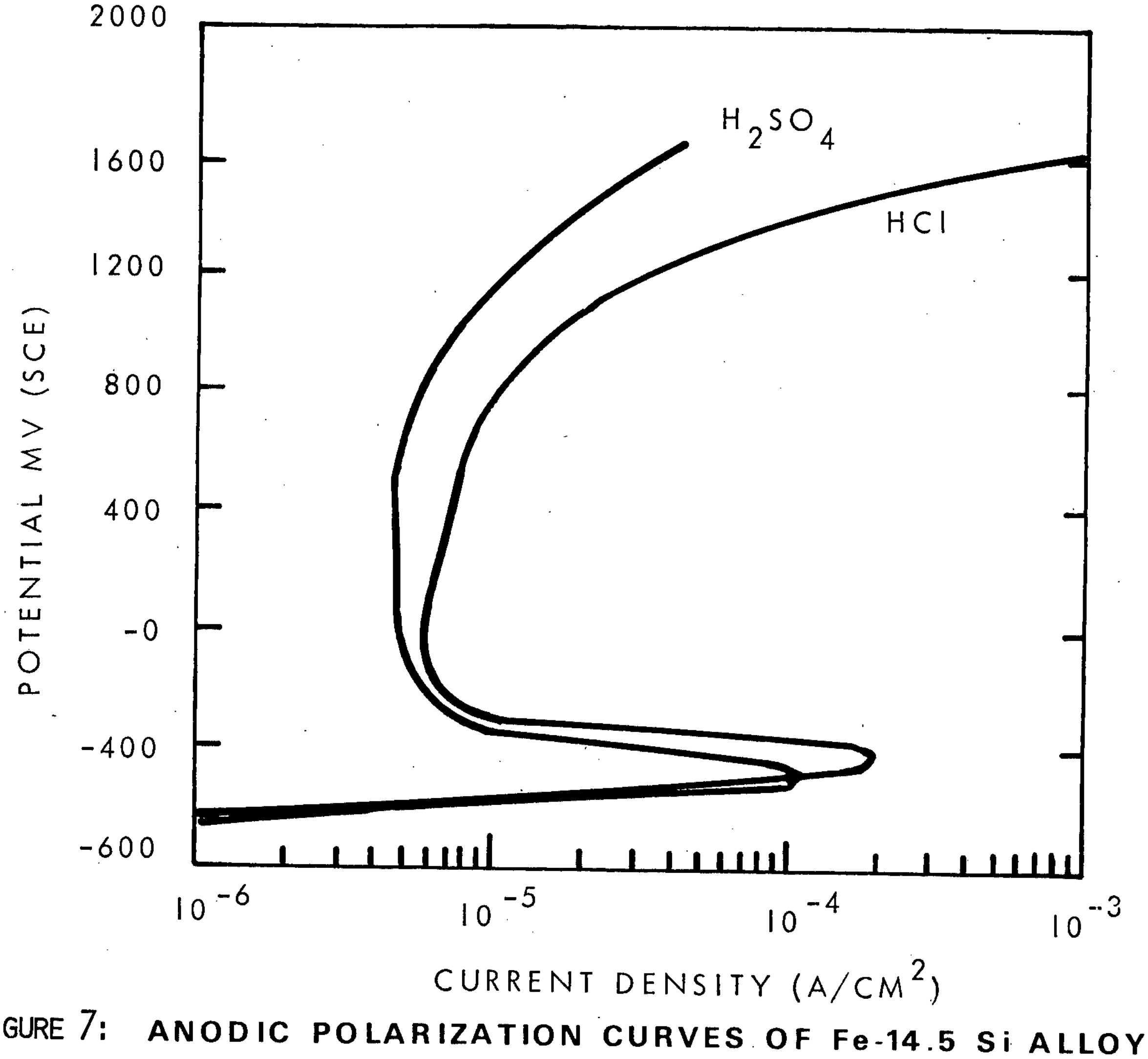

FIGURE 7: **ANODIC POLARIZATION CURVES OF Fe-14.5 Si ALLOY (30 MV. MIN.)**

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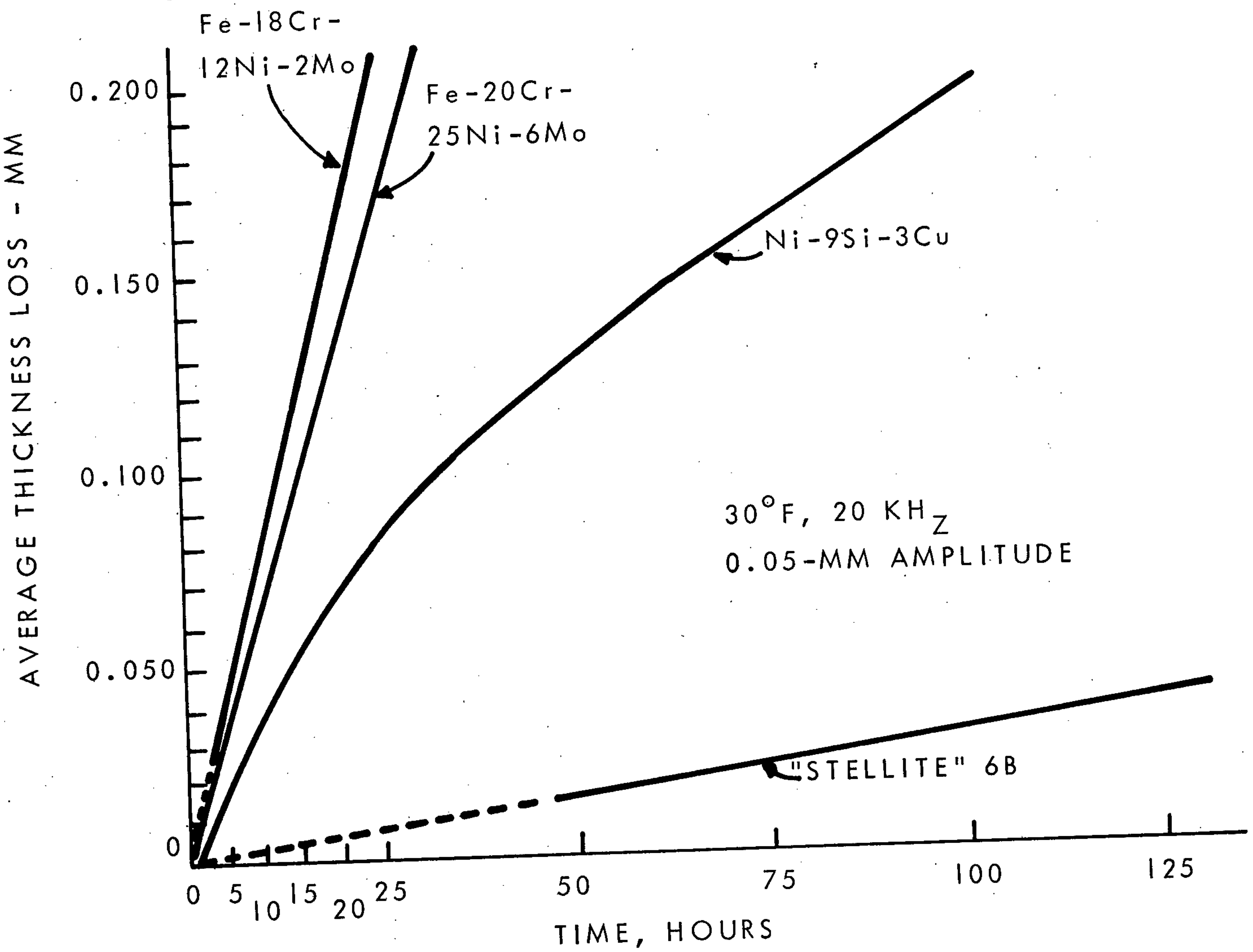

FIGURE 8: **CAVITATION-ERROSION BEHAVIOR IN DEIONIZED WATER**

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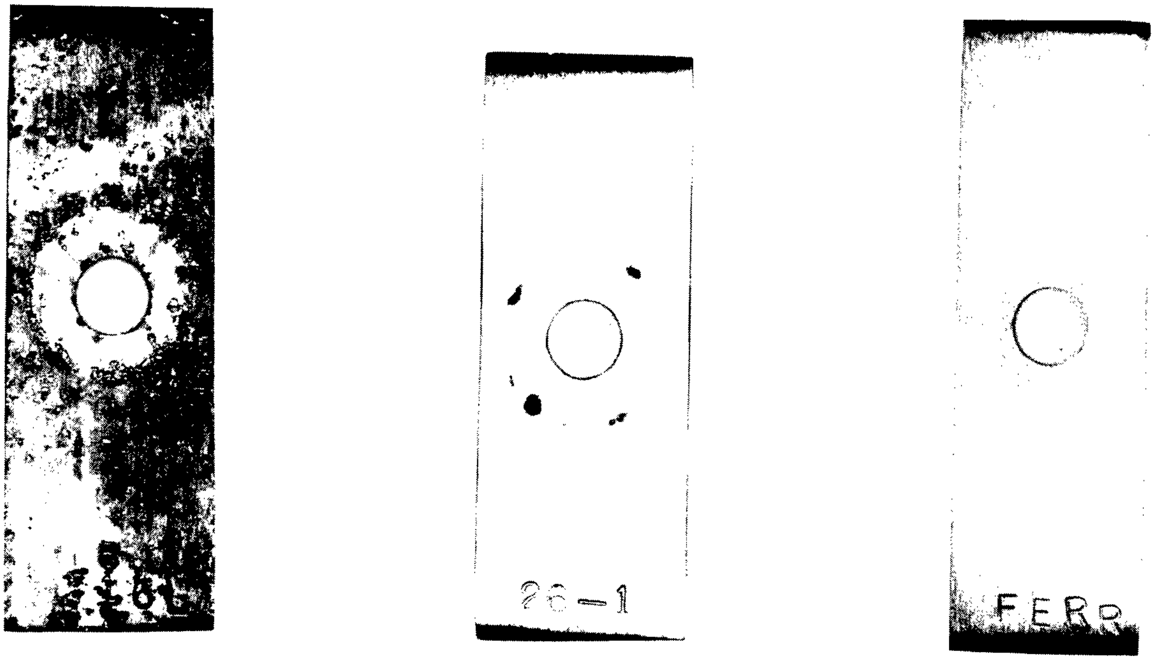

Fe-18 Cr-12 Ni-2 Mo
(Austenitic)

Fe-26 Cr-1 Mo
(Ferritic)

Fe-26 Cr-5 Ni-3 Mo-0.17 N
(Austenitic-Ferritic)

CREVICE CORROSION TESTS IN 10% $FeCl_3$ (RT, 5-DAY EXPOSURE)

FIGURE 3

POTENTIODYNAMIC CORROSION BEHAVIOR FOR SEVERAL Fe-Mn-Al AUSTENITIC STEELS

By

R. Wang* and R.A. Rapp**

ABSTRACT

Several compositions of Fe-Mn-Al austenitic steels were studied in potentiodynamic corrosion tests in artificial seawater. The 10 wt% Al steel has good performance with a corrosion rate lower than type 321 and slightly higher than type 316 austenitic stainless steels in artificial seawater.

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INTRODUCTION

Steels with 30 wt% Mn, 1 wt% C and 8 - 10 wt% Al have an austenitic structure and good mechanical properties, especially a higher ratio of strength-to-weight than Fe-Ni-Cr austenitic steels[1]. Because of their good high temperature resistance and spalling resistance, Fe-Mn-Al steels have been used to make bottom plates[2] for heat treatment furnaces and may be used as engine material for guided missiles[3], instead of Fe-Ni-Cr stainless steels. A new problem for research is to determine whether these steels could be used as corrosion-resistant steels in marine applications. A sea-going fishing vessel with a propeller made of Fe-Mn-Al steel was launched on August 10, 1980[4], which introduced a new use for these marine corrosion-resistant steels without Ni and Cr.

To understand better the marine corrosion behavior of Fe-Mn-Al steels and the effects of Al, C, and Si content, several tests have been conducted. In this paper, the potentiodynamic polarization curves and resulting values for the corrosion potential, E_{corr}, and the corrosion current, I_{corr}, and the linear corrosion rate, R_{corr} were determined in artificial seawater (Table 1) for seven compositions of Fe-Mn-Al steel with a constant 30% Mn content. These values are compared with type 321 and type 316 austenitic stainless steels.

POTENTIODYNAMIC CORROSION STUDIES

The fully austenitic Fe-Mn-Al steels listed in Table 2 were provided by S. K. Banerji, Foote Mineral Company. Alloys 3 and 9 were studied in the cast condition; the other alloys were in the as-rolled condition. All the alloys were tested in artificial seawater of pH 8 (Table 1). A Princeton Model 350 Corrosion Measurement System was used for testing. Specimens were mounted in epoxy, ground, and fine polished with 0.05μ alumina powder. A specimen was tested after it had been immersed in a testing cell for thirty minutes to reach a stable rest potential. The test solution was aerated artificial seawater. All the potentiodynamic polarization tests were started from -0.250V below E_{corr} and stopped at +0.50V (SCE). The scan rate was 1 mV/sec. The potentiodynamic polarization curves of several samples in artificial seawater or in 1 N H_2SO_4 are shown in Figs. 1 to 8. The corrosion potentials, the corrosion currents, and the calculated linear corrosion rates (R_{corr}) for the alloys are listed in Table 2. The Model 350 instrument provided the evaluation for I_{corr}, E_{corr}, and R_{corr} by extrapolating the Tafel portions of the polarization curves to provide an intersection.

ANALYSES OF THE DATA

1. The effect of Al content:

According to the data listed in Table 2, the Al content greatly affects the marine corrosion resistance of steels. The higher the Al content the higher the marine corrosion resistance, as indicated by alloy 3 with a nominal composition Fe-30 Mn-10 Al. The linear corrosion rate for this alloy is the lowest among the seven Mn-Al steels studied here. The linear corrosion rate of alloy 3 is somewhat higher than that for the 316 stainless steel, but lower than that for the 321 stainless steel. But differences on the order of a factor of two would not be considered very significant for such studies. From the data for the linear corrosion rates, sample 3 with 30 Mn and 10 Al has good corrosion resistance in artificial seawater. Nevertheless, both an increase in silicon content and a decrease in carbon content would probably provide further improvement in behavior, as explained below. Except for sample 3, the linear corrosion rates of the other six Mn-Al steel compositions are all higher than the 321 and 316 stainless steels. The higher the Al content, the higher E_{corr}. As the Al weight percent is increased from 6.67% to 8.28% and 9.75%, E_{corr} increases from -0.740V to -0.679V and-0.512V, indicating that passivation is more complete so that the more oxidizing potential is stable.

2. The effect of Si content:

The addition of Si to the Mn-Al steels improves their marine corrosion resistance. For example, alloys 4, 7, and 8 have essentially the same C, Mn and Al contents, but differ only in Si content with 0.23% Si, 1.45% Si, and 1.54% Si, respectively; correspondingly, the linear corrosion rate R_{corr} is decreased from 0.1877 to 0.0738 to 0.0504 mm/year. Many papers have shown the favorable effects of Si content on the corrosion behavior of steel[5-8]. Some authors recognized that Si can elevate the corrosion potential of the steel. From our studies, the Si addition in the three alloys 4, 7 and 8 only slightly raised the values of E_{corr} with -0.662V, -0.659V and -0.626V, respectively. In agreement with reference 7, Si seems to improve the corrosion behavior mostly by improving the protective property of the surface film.

3. The effect of C content:

The negative effect of C content is obvious. Alloys 4, 5 and 6 have the same Al, Mn, and Si content with only different C contents; as seen in Table 2, the lower the C content, the lower R_{corr}. Alloy 9 has a lower Al content than alloys 4 or 5, but much less C content. Therefore, R_{corr} is lower for alloy 9 than for alloys 4 and 5.

ANALYSES OF THE POLARIZATION CURVES

None of the polarization curves for the Mn-Al steels, nor for 316 or 321 stainless steels, show any extended passive region in artificial seawater. But as the Al content is increased (see Fig. 9 comparison of alloy 3 with alloy 5) and the Si content is increased (see Fig. 10 comparison of alloy 8 with alloy 5) or the C content is decreased (see Fig. 11 comparison of alloy 6 with alloy 5), some partial passivation becomes obvious. The polarization plot for alloy 3 (30 Mn - 10 Al steel) is quite similar to that for the 316 stainless steel (see Fig. 12).

Figure 7 is the polarization curve for alloy 3 (30 Mn - 10 Al) in 1N H_2SO_4; there is clearly a passive region within the potential range of +0.5V to +1.5V. Figure 8 is the polarization curve for alloy 1 (316 stainless steel) in 1N H_2SO_4; the 316 alloy is clearly superior to the alloy 3 in 1N H_2SO_4, as seen in Fig. 13.

Figure 14 shows repeated polarization curves for alloy 3, including one run which followed a preanodizing treatment. Figure 15 shows a comparison of several Mn-Al steels with 316 in artificial seawater.

CONCLUSION

1. Al favorably affects the marine corrosion resistance of Fe-Mn-Al austenitic steels; up to 10% Al, the higher the Al content, the lower the corrosion rate. The corrosion rate of Fe-30 Mn-10 Al austenitic steel is somewhat lower than that for type 321 but higher than that for type 316

austenitic stainless steels in artificial seawater. To satisfy the requirement for improved marine corrosion resistance, the Al content should be 10% weight percent or perhaps higher.

2. Si has a favorable effect on the marine corrosion resistance of Fe-Mn-Al-Si austenitic steels.

3. For Fe-Mn-Al alloys, as for the Fe-Cr-Ni steel system, carbon does not have a favorable effect on marine corrosion resistance. If the single-phase austenite structure can be stabilized by other alloy additions, the carbon content should be kept as low as possible.

4. Although alloy 3 exhibited reasonable marine corrosion resistance, further adjustment of the composition (increasing silicon, decreasing carbon contents) should provide further improvement.

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TABLE 1. THE COMPOSITION OF ARTIFICIAL SEAWATER

FORMULA:

1.	Dist. Water	999 ml
2.	$NaCl$	2.0%
3.	$MgSO_4 \cdot 7H_2O$	0.5%
4.	K_3PO_4	0.01%
5.	NH_4NO_3	0.02%
6.	$K_3C_6H_5O_7 \cdot H_2O$	0.05%
7.	$CaCl_2 \cdot 6H_2O$	0.01%
8.	KCl	0.06%
9.	$NaHCO_3$	0.02%
10.	KBr	0.01%
11.	NaF	0.003%
12.	$SrCl_2 \cdot 6H_2O$	0.004%
13.	Micronutrients	1.0 ml.
a.	EDTA	0.5 mg/ml
b.	$ZnSO_4 \cdot 7H_2O$	2.5 mg/ml
c.	$FeSO_4 \cdot 7H_2O$	1.0 mg/ml
d.	$MnSO_4 \cdot H_2O$	0.5 mg/ml
e.	$CuSO_4 \cdot 7H_2O$	0.1 mg/ml
f.	$CoSO_4 \cdot 7H_2O$	0.05 mg/ml
g.	H_3BO_3	0.02 mg/ml

(Constituents a through g represent the micronutrients)

TABLE 2: MAIN COMPOSITION AND CORROSION DATA OF THE TESTED SAMPLES

No.	Code Name	Main Composition Weight %								Corr. Potential E_{corr} (V)	Corr. Current I_{corr} $\mu A/cm^2$	Equiv. Weight g/equ.	Density g/cm^2	Linear Corr. Rate (mpy)	Linear Corr. Rate mm/year
		C	Mn	Al	Si	Cr	Ni	Mo	Other						
1	316	0.025	1.62		0.46	17.37	10.84	2.15	0.40 Cu	-0.414	0.785	25.88	7.83	0.339	0.0085
2	321	0.08				18.59	9.63		1.07 Ti	-0.444	2.905	26.02	7.84	1.253	0.032
3	11-1-1A (Cast)	1.01	30.15	9.75	0.12					-0.512	1.740	23.27	7.17	0.735	0.019
4	11-10-3C	1.05	30.60	8.39	0.23					-0.622	17.520	23.84	7.27	7.465	0.188
5	8-24-1	1.24	30.10	8.33	0.12					-0.667	81.740	23.84	7.26	34.84	0.877
6	10-28-1	0.52	29.81	8.28	0.02					-0.679	7.73	23.84	7.28	3.241	0.083
7	11-10-4	1.05	30.5	8.37	1.45					-0.659	6.98	23.37	7.22	2.934	0.074
8	8-24-2	1.07	30.10	8.32	1.54					-0.626	4.76	23.37	7.22	2.002	0.050
9	2-2-1 (Cast)	0.06	30.32	6.68	0.08				0.2 N	-0.740	10.11	25.42	7.40	4.514	0.113

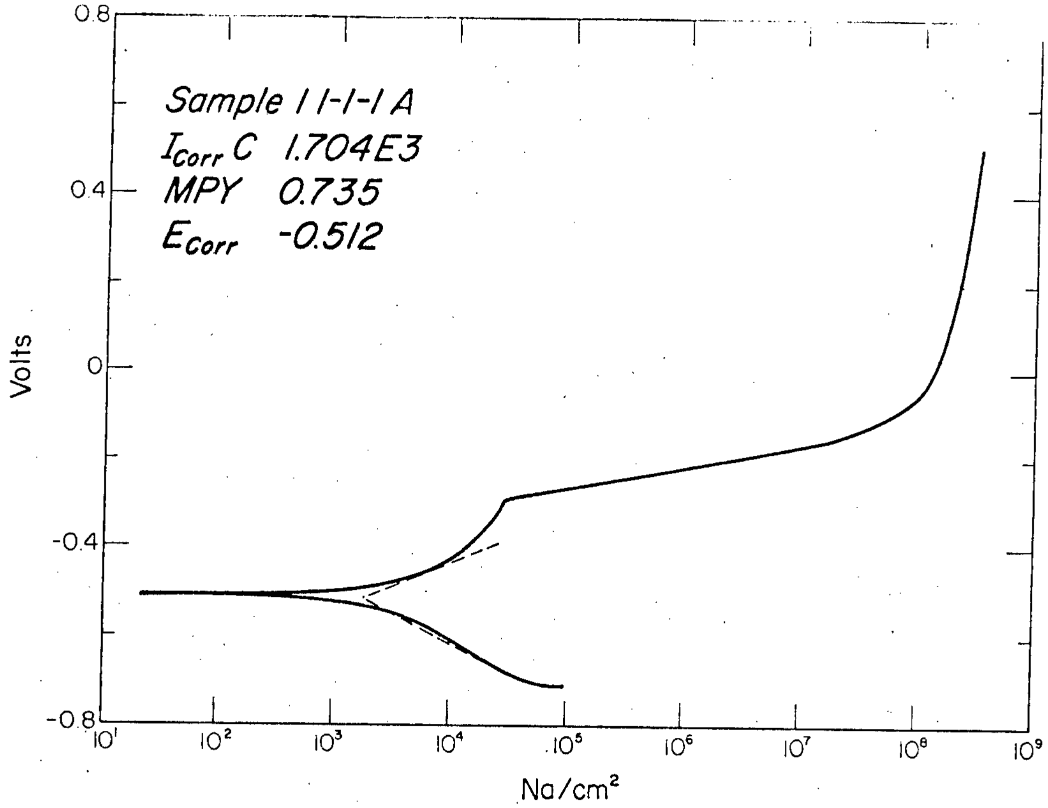

Figure 1: Polarization Curve for Alloy 3 (1.01% C, 0.12% Si, 9.75% Al) in Artificial Seawater.

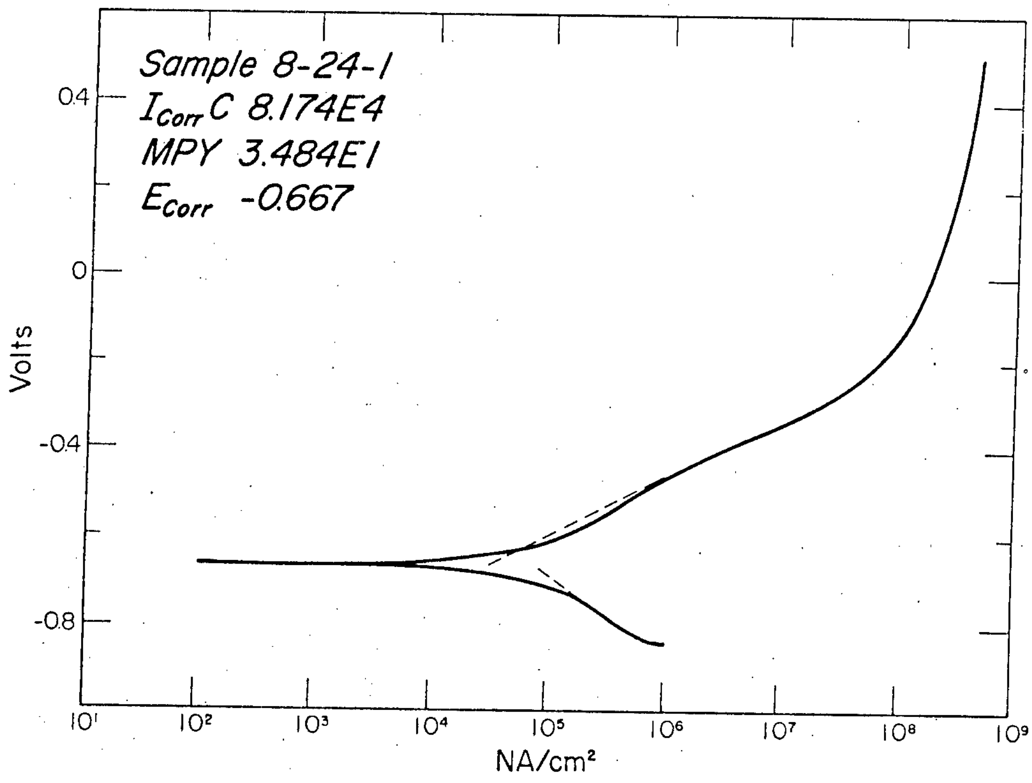

Figure 2: Polarization Curve for Alloy 5 (1.24% C, 0.12% Si, 8.33% Al) in Artificial Seawater.

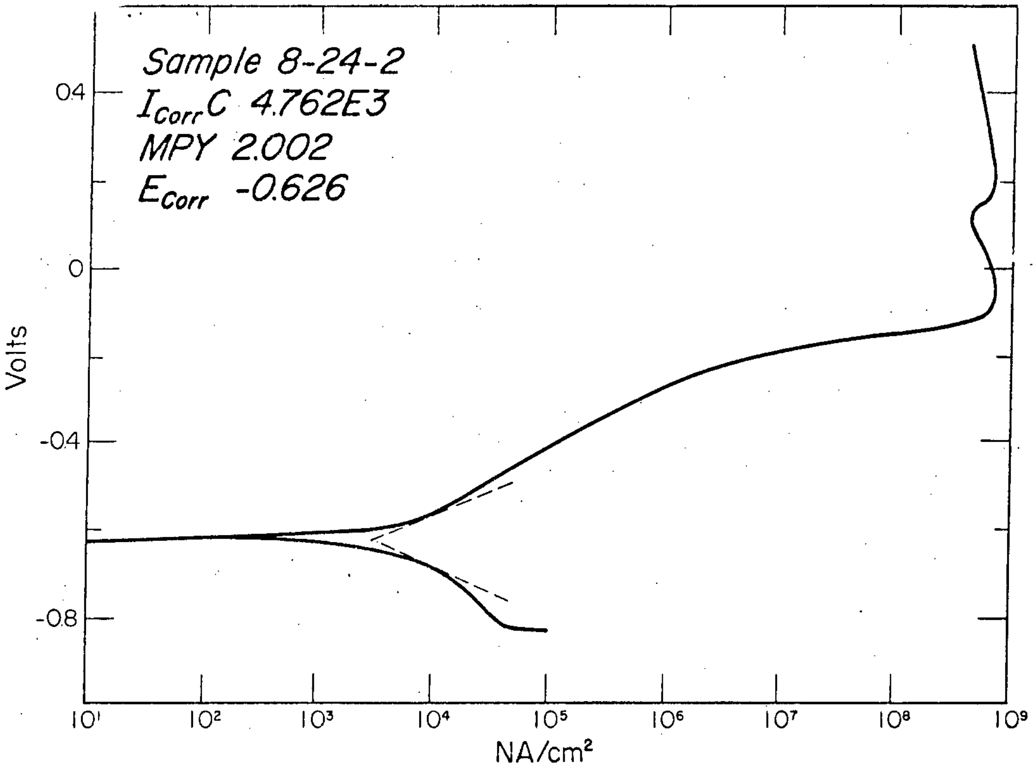

Figure 3: Polarization Curve for Alloy 8 (1.07% C, 1.54% Si, 8.32% Al), in Artificial Seawater.

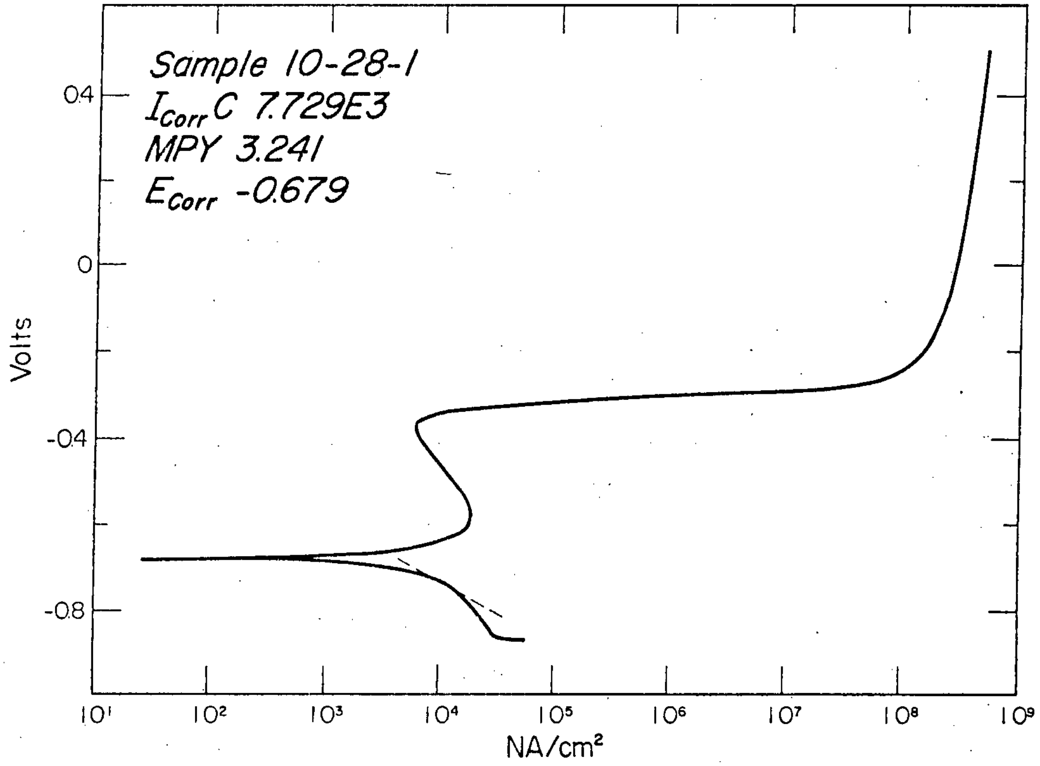

Figure 4: Polarization Curve for Alloy 6 (0.52% C, 0.02% Si, 8.28% Al) in Artificial Seawater.

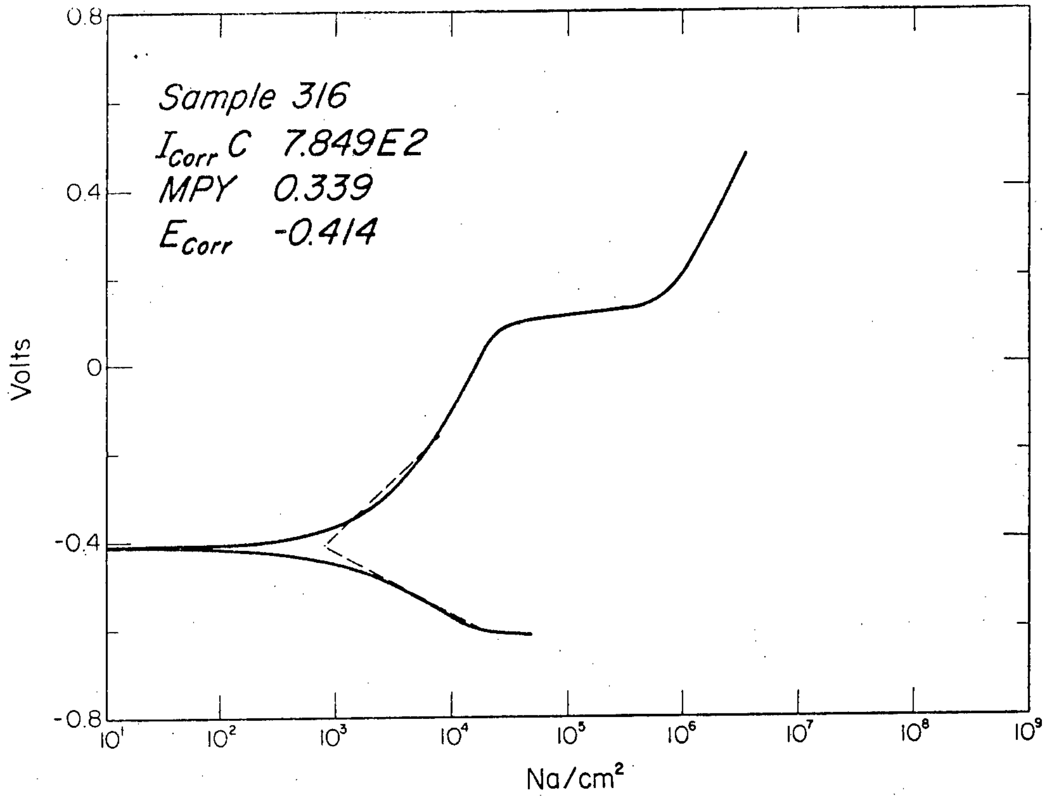

Figure 5: Polarization Curve for Alloy 1 (0.025% C, 17.37% Cr, 10.84% Ni, 2.15% Mo), in Artificial Seawater.

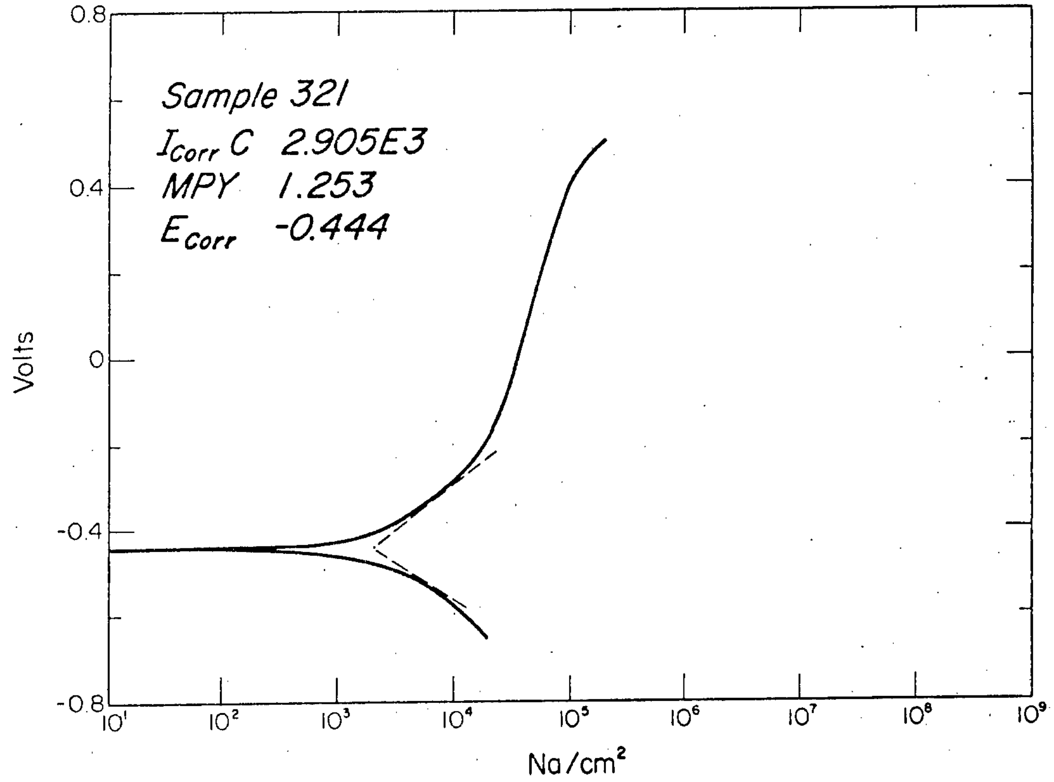

Figure 6: Polarization Curve for Alloy 2 (0.08% C, 18.59% Cr, 9.63% Ni), in Artificial Seawater.

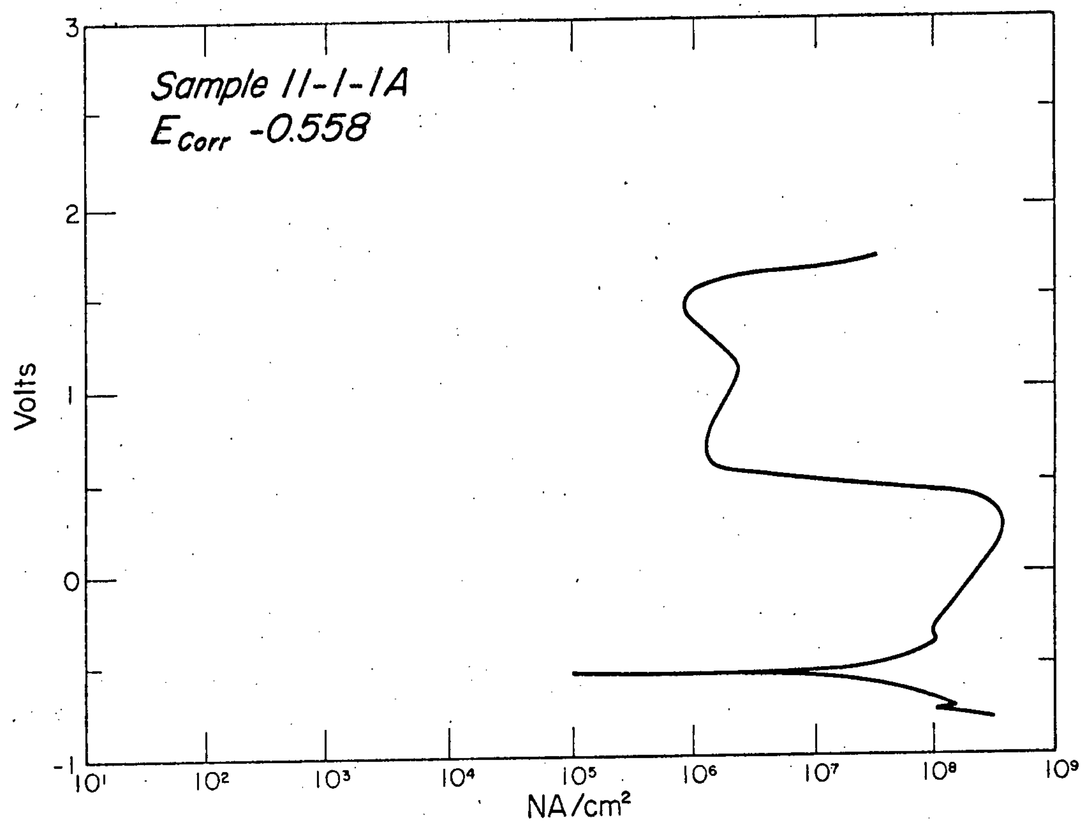

Figure 7: Polarization Curve for Alloy 3 (1.01% C, 30.60% Mn, 9.75% Al) in 1N H_2SO_4.

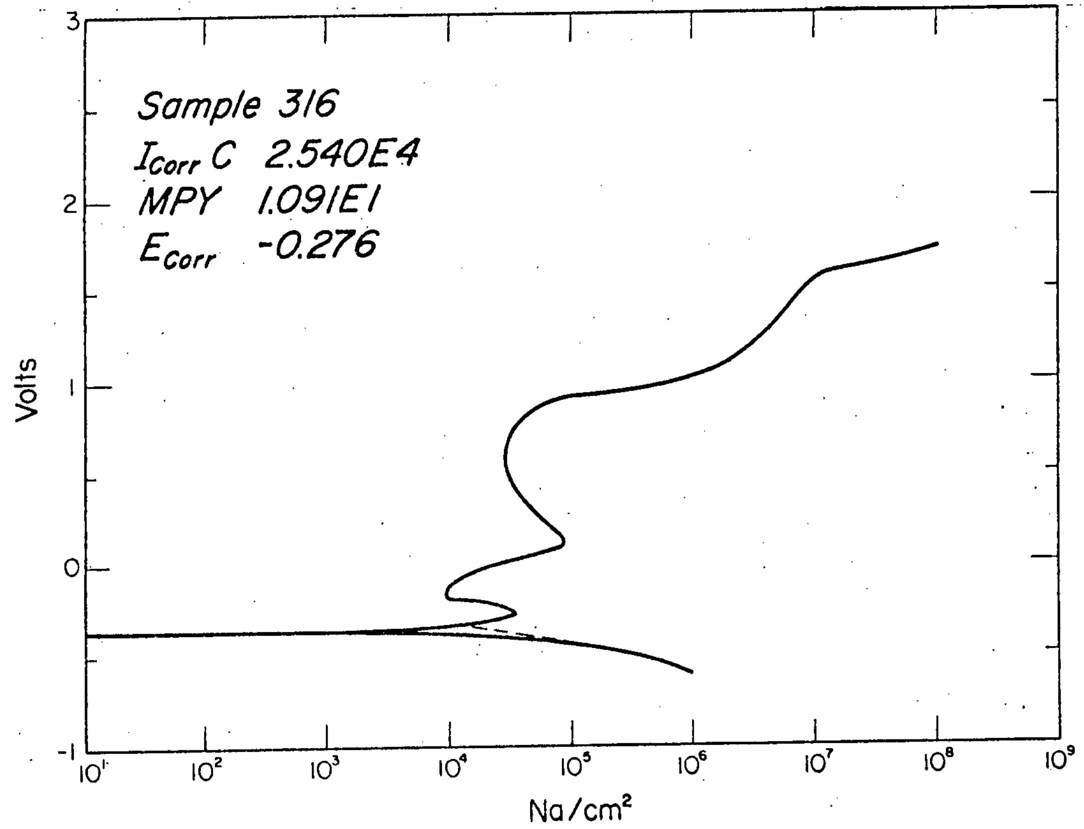

Figure 8: Polarization Curve for Alloy 1 (0.025% C, 17.37% Cr, 10.84% Ni, 2.15% Mo) in 1N H_2SO_4.

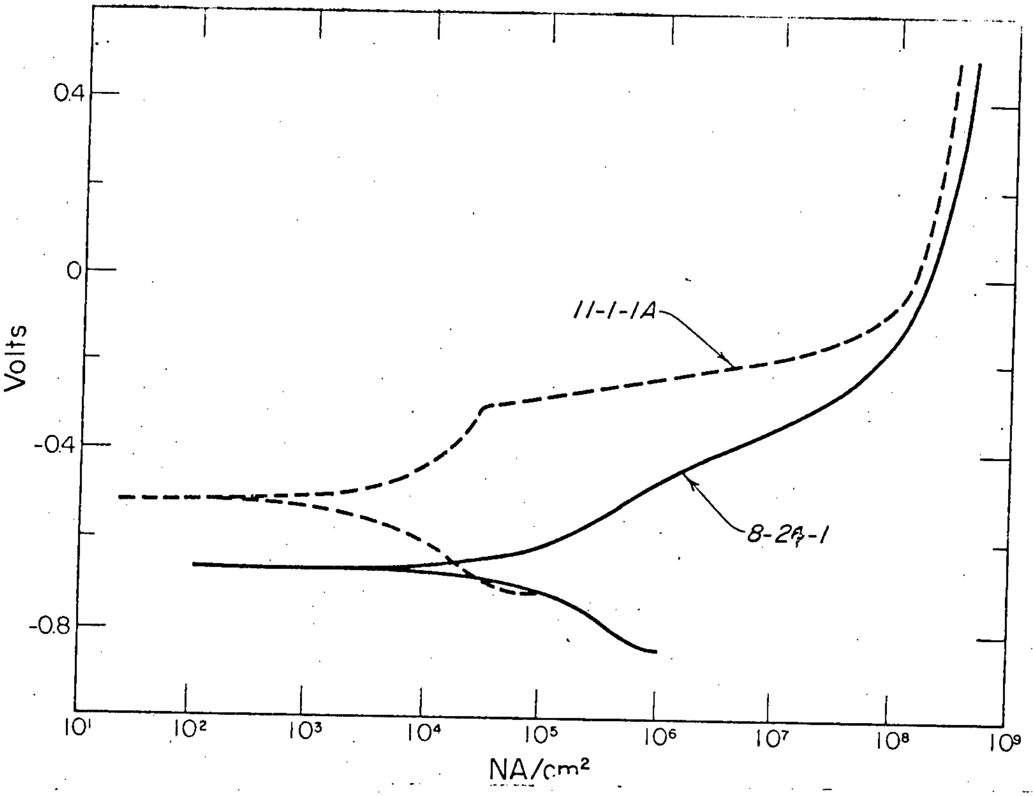

Figure 9: The Comparison of Polarization Curves for Alloy 3 with Alloy 5, in Artificial Seawater.

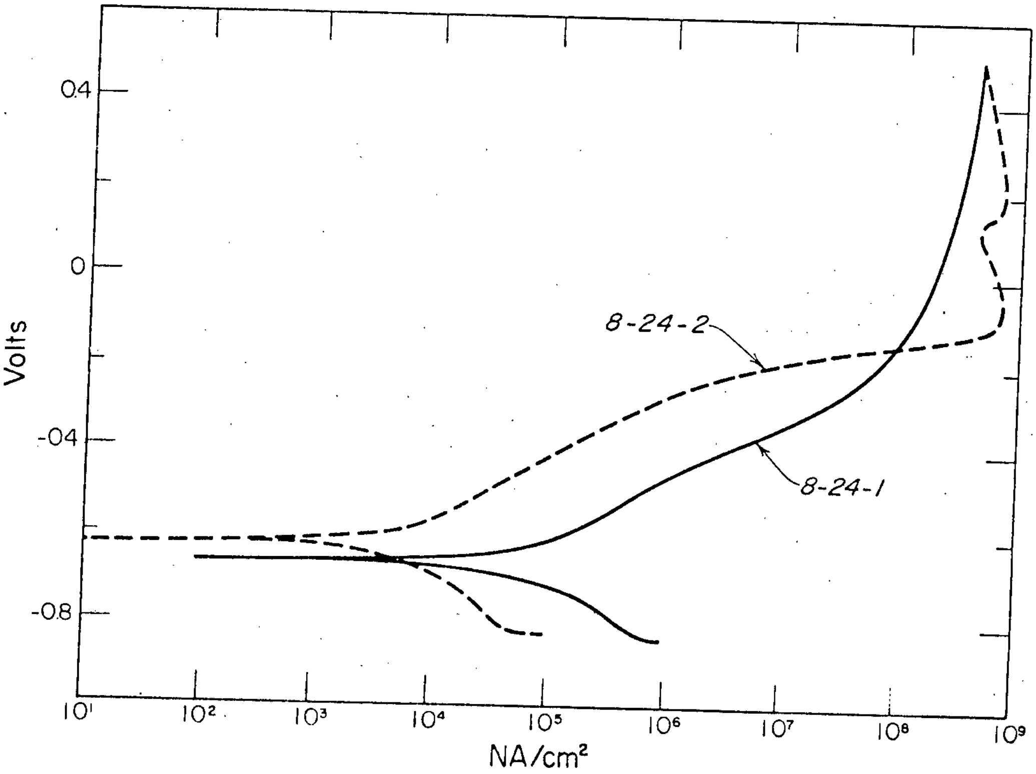

Figure 10: The Comparison of Polarization Curves for Alloy 8 with Alloy 5, in Artificial Seawater.

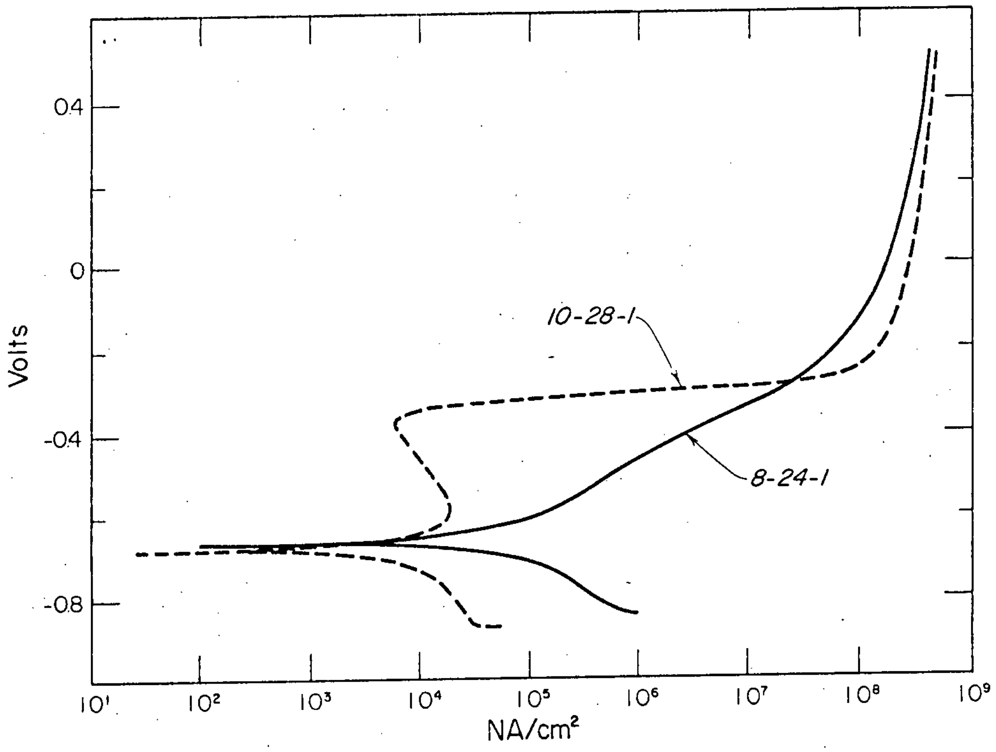

Figure 11: The Comparison of Polarization Curves for Alloy 6 with Alloy 5, in Artificial Seawater.

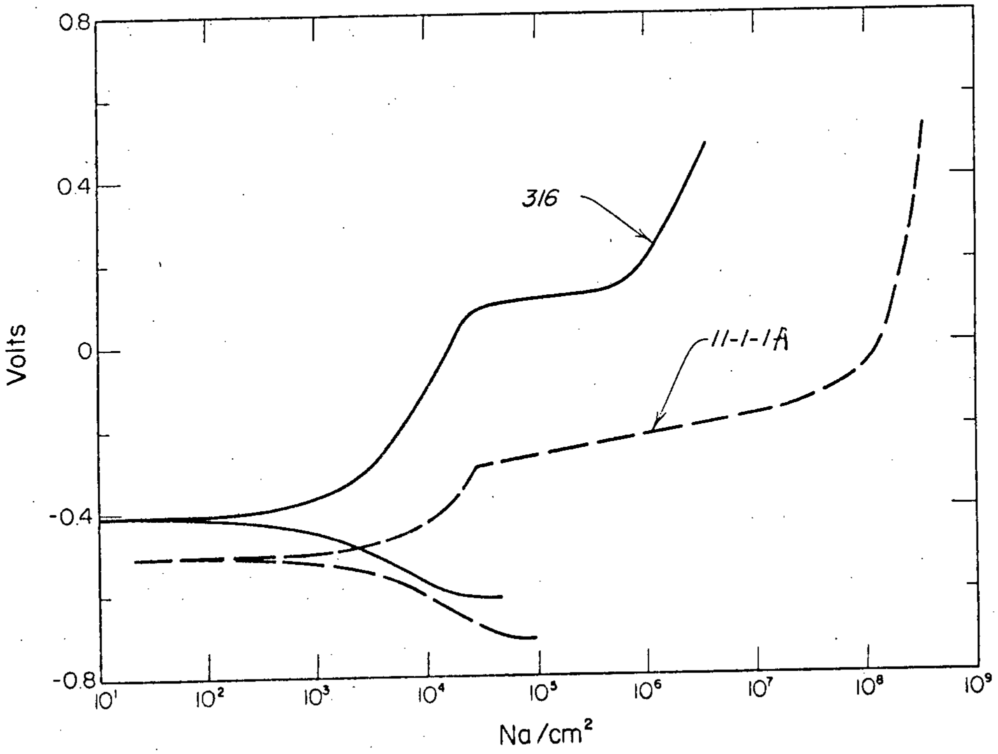

Figure 12: The Comparison of Polarization Curves for Alloy 3 with Alloy 1 in Artificial Seawater.

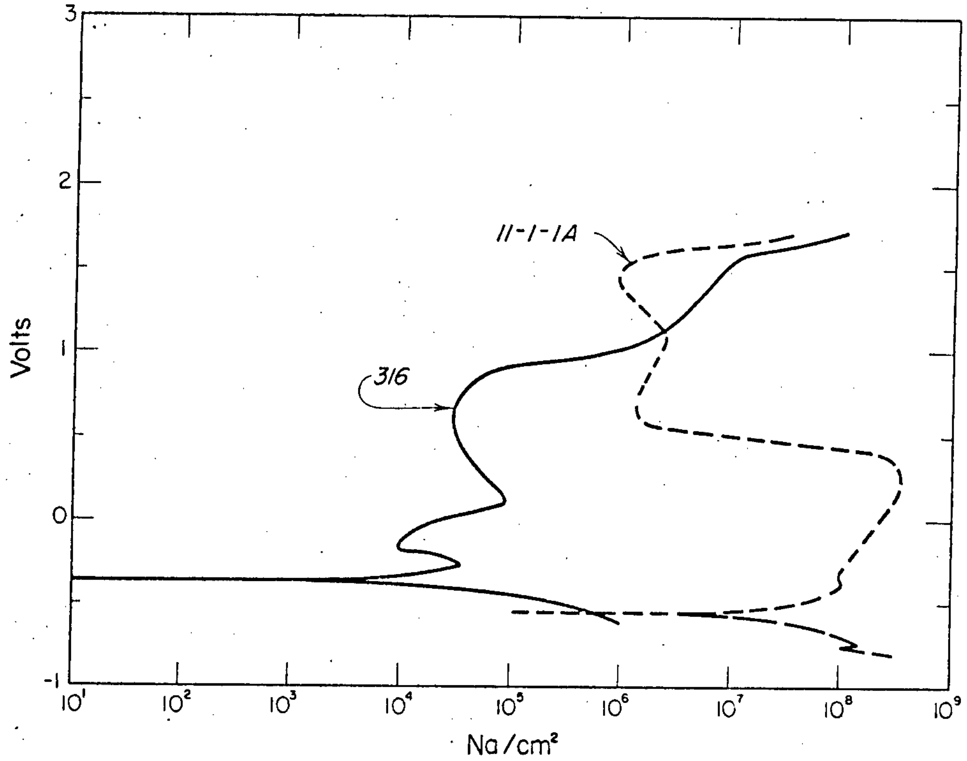

Figure 13: The Comparison of Polarization Curves for Alloy 3 with Alloy 1, in IN H_2SO_4.

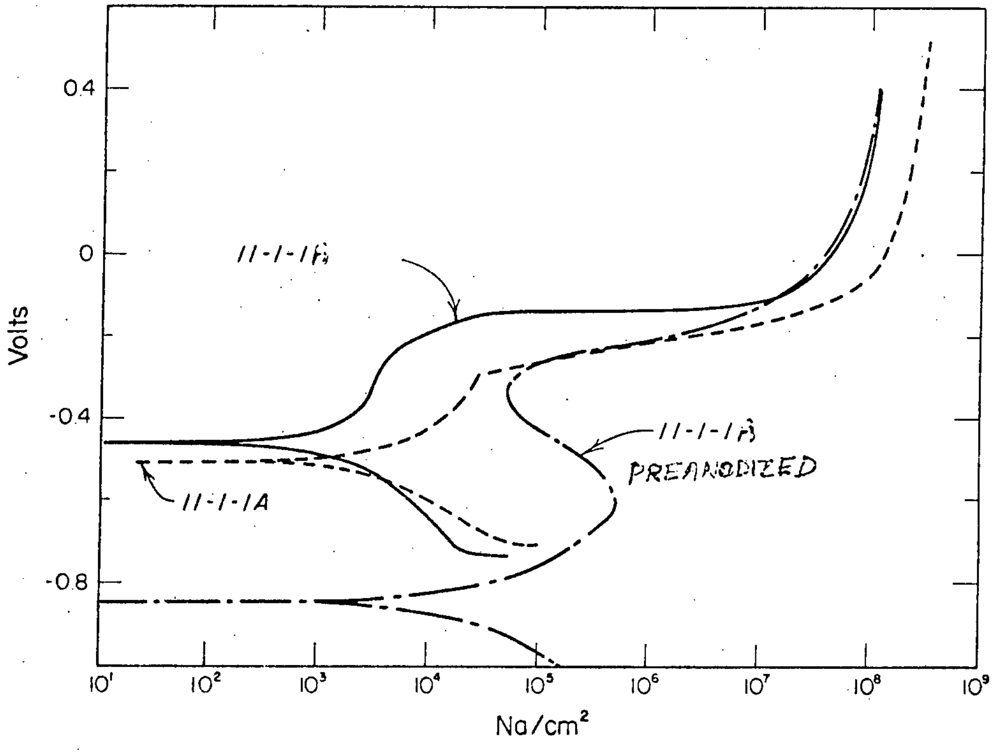

Figure 14: The Comparison of Repeated Polarization Curves for Alloy 3 in Artificial Seawater.

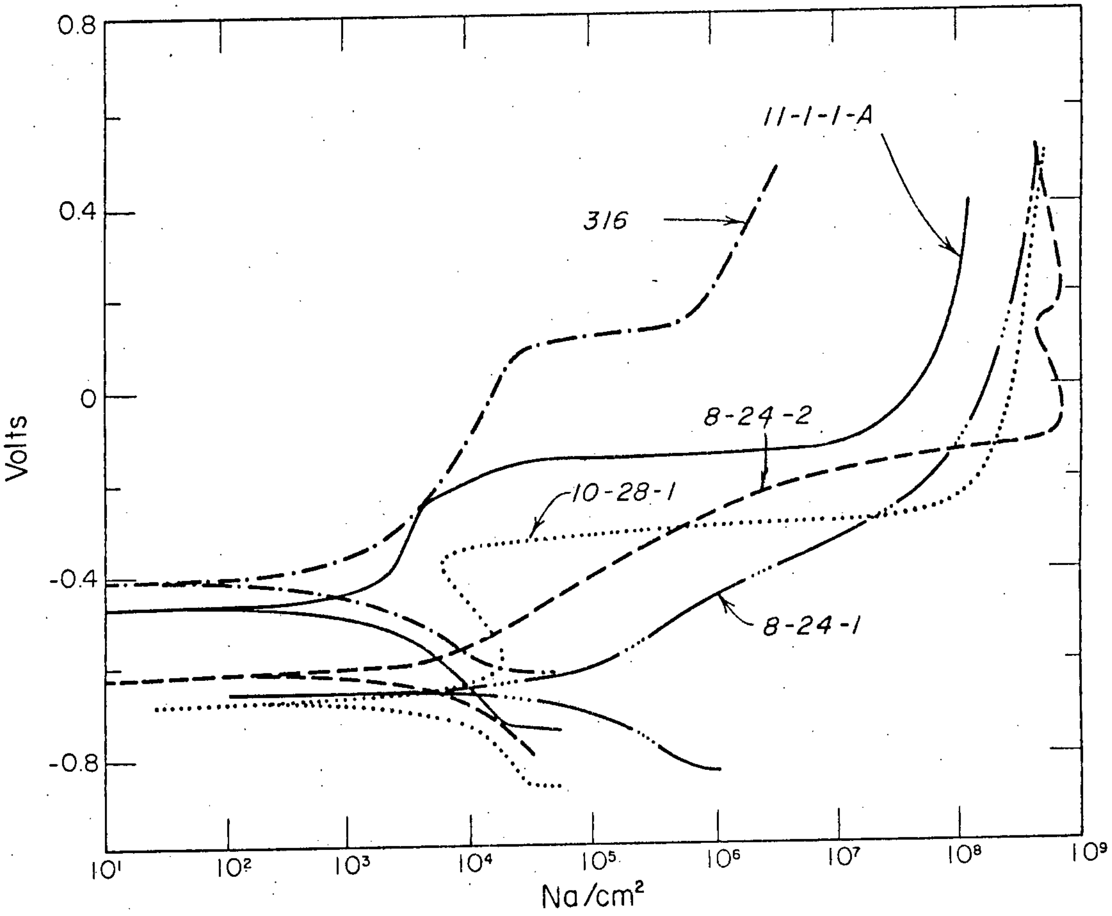

Figure 15: The Compaison of Polarization Curves of
Alloy 1, 3, 5, 6, and 8 in Artifical Seawater.

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This volume presents papers given at a public workshop sponsored jointly by the National Bureau of Standards, Bureau of Mines, Army Research Office, and Vanderbilt University. The workship "Critical Materials Requirements for Steels of the Future; Conservation and Substitution for Chromium," was held at Vanderbilt University, October 4-7, 1982; it featured 50 presentations by technical authorities from steel producing and using industries.

Volume I of this publication draws extensively on these proceedings and reviews technical opportunities for research in process improvement and in alternative materials development that would reduce U.S. dependency in critical materials. The advanced technologies reviewed in Volume I in addition to their implications for critical materials conservation represent trends leading to better quality, lower cost steel products, and therefore they may contribute positively to the industry's more immediate concern for improved markets.

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