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Earl R. Parker and Victor F. Zackay

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-iii-

FUNDAMENTALS OF ALLOY DESIGN

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ABSTRACT

The status of alloy design is summarized. Progress in this area of materials science has been slow because of the complex nature of the interactions of the various factors involved in controlling the structure sensitive properties (particularly mechanical properties). Fracture characteristics are particularly sensitive to many factors, including chemical composition, thermal treatments, melting and processing practices.

The extensive storehouse of basic knowledge accumulated since World War II has not yet been used effectively to produce new alloys with properties superior to those of commercially available materials, and practically all of the alloys available today were accidentally discovered and empirically developed decades ago. The picture is slowly changing, however, and new alloys have been produced, with compositions and treatments based on the principles of materials science, although these alloys are not yet in general commercial use. Discussions of the new developments from basic investigations are discussed, with literature references cited. Much of the current alloy design work is still largely of empirical nature, and so the discussions are categorized as Basic Investigations, Semi-Empirical Research, Empirical Alloy Design, and

Alloy Development. These range from basic to technologically oriented product development. Over 50 recently published papers were used as the basis for the manuscript. These 50 were selected from a much larger number of papers reviewed for this purpose. There are 76 references included in the bibliography.

Outline

INTRODUCTION	2
BASIC INVESTIGATIONS	8
Strengthening With Second Phases	10
Particles Cut by Dislocations	17
High Temperature Strength	18
Toughness and Ductility	20
Fatigue Strength	21
Enhancing Fracture Toughness Through Microstructural Control	21
Enhancement of Notch Bar Properties at Cryogenic Temperatures	29
Design of a Creep Resistant Alloy	29
Design of Refractory Carbide Cutting Tool Alloys	31
Design of a High Field Superconducting Alloy	34
THE SEMI-EMPIRICAL APPROACH	35
EMPIRICAL ALLOY DESIGN	39
ALLOY DEVELOPMENT	42
REFERENCES	47
FIGURE CAPTIONS	55

INTRODUCTION

Learning how to design alloys from basic principles has been a goal of metallurgists for half a century. In the AIME 1932 Institute of Metals Division Lecture,¹ Paul D. Merica stated that the metallurgist "has been obliged to discover rather than to design alloys". Dr. R. F. Mehl, who delivered the 1936 Institute of Metals Division Lecture,² said "Metallurgy is in the happy state where there is much in the future, where simple facts and simple theories remain to be discovered, and where the development of the science will lead to practical applications of wide industrial consequences". Both of these men visualized that it should be possible to design alloys from basic principles, but progress has been so slow that this goal has not yet been realized in the practical sense. Virtually all of the alloys currently used for structural purposes were accidentally discovered and empirically developed decades ago.

Why has progress not been more rapid? It seems particularly strange that the extensive basic research efforts in the decades following World War II have not provided us with adequate knowledge to design alloys with desirable properties. One of the frustrating factors is that mechanical properties are highly structure sensitive, and the complex theoretical background needed for an understanding of the phenomena involved, such as fracture, has been only partially developed in a quantitative manner. Small changes in the fine details of internal structure can produce major changes in fracture strength. These fine scale features are often unresolvable with optical microscopes.

In contrast with fracture, the processes of plastic flow and the ways in which the yield strength of an alloy can be controlled are understood reasonably well. They are primarily based upon the dislocation theory (conceived in 1934), which can be applied with considerable success in designing alloys to meet specific yield strength requirements. The problem of designing alloys for structural applications resides not so much in meeting the yield strength requirement but in producing resistance to fracture at low strains. Except for rather elementary considerations, such as the variation in yield strength with the grain size for single phase alloys, or the effect of spacing of precipitated particles on the yield strength,³ available theories are inadequate to account for the microstructural effects on other properties (such as elongation and fracture strength). It was nearly two decades after dislocations were conceived to explain the low yield strength of metals that primitive explanations of the roles played by dislocations in fracture were offered; even today, our understanding of fracture phenomena is grossly inadequate.

A major research breakthrough occurred in 1957, when Hirsch and his colleagues⁴ demonstrated that it was possible to see dislocations in motion with transmission electron microscopy. Immediately thereafter, observations of moving dislocation and studies of the complex arrangements of dislocations in solid metals became widespread, and rapid progress was made in determining the characteristics of dislocations. Soon, books on this subject became available.⁴⁻⁶ Eventually, it became possible to observe directly some of the microscopic events that precede fracture. Even though important insights into the micromechanics of fracture were

obtained, the macroscopic aspects of fracture, with which engineers are concerned (such as the failures of large structures), could not be rationalized on the basis of the micromechanical studies. The gap between the micromechanics and the macromechanics of fracture still exists.

Paralleling the development of dislocation mechanics was the growth of fracture mechanics (the phenomenological approach to fracture problems). This subject was initiated by Griffith,⁷ in 1921, to explain crack propagation in elastic media. The Griffith relation is

$$\sigma_m = (2\alpha E/\pi C)^{1/2} \text{ or } \sigma_m = (G_c E/\pi C)^{1/2}$$

where σ_m is the mean tensile stress acting on a piece of material containing a small flaw in the form of a crack of length $2C$, E is Young's modulus, α is the surface energy of the material, and G_c replaces 2α when plastic flow occurs. Irwin extended the Griffith analysis⁸ to include the case where some plastic flow occurs in the vicinity of the fracture surface. In this case, the fracture energy is greater because the energy required for plastic flow is much larger than the surface energy of the material. Irwin replaced the surface energy term, α , in the Griffith equation, with the term G_c . This change constituted an extension of the Griffith's elastic theory to include fractures of metals which are relatively brittle, but in which there is a small amount of plastic flow prior to fracture. The early work of Irwin led to an extensive expansion of the subject of fracture mechanics.⁹⁻¹¹ However, continued attempts to couple dislocation mechanics and fracture mechanics have been relatively unsuccessful.

In general, the coupling of materials science and materials engineering is a problem that remains with us. Design engineers think in terms of

continuum mechanics whereas materials scientists think mainly in terms of dislocation mechanics. Since both concepts are valid and the gap between them remains essentially unbridged at present, it is necessary for those working in the field of fracture, whether they be design engineers or materials scientists, to understand both languages. Through changes in educational programs in universities, and through technical meetings, a common language is slowly developing between the two groups of workers. Before materials scientists can be effective in designing new alloys for structural applications they must understand the technological requirements as defined by design engineers. Most designs for structural applications involve the use of mechanical properties data obtained from tension tests on unnotched bars. The safe lifetime of an engineering structure cannot be predicted from such simple test data, and so it is common practice to use "factor of safety" to guard against unanticipated fracture during service. The factor of safety is a number which is divided into the yield strength of the material to obtain a service design stress. Factors of safety of the order of 2 are commonly employed in practice. In recent years the material property, K_{IC} , has become part of materials procurement specifications and is used as a quantitative design parameter in a few instances. Plane strain fracture toughness values are determined experimentally by means of uniaxial load tests on notched specimens, and are presented in terms of linear elastic fracture mechanics. The K_{IC} values are obtained with specimens and testing procedures outlined in ASTM E399-72 "Standard Method of Test for Plain Strain Fracture Toughness Testing of Metallic Materials" (1972). The plane strain fracture toughness parameter, K_{IC} , relates the size of a flaw, C , such as a fatigue

crack, to the critical stress, σ_c , that the structure can withstand without catastrophic failure. This formulation is in the following form:

$$\sigma_c = AK_{IC}(C)^{-\frac{1}{2}}$$

The constant A depends upon the geometry of the particular structure under consideration and K_{IC} is a property of the material.

Alloys must be designed for some purpose, usually of a technological nature, such as designing against fracture when a flaw or crack is present in a material. Alloys can also be designed for many other purposes, such as for good formability (ability to be shaped into complicated forms in an easy manner), to meet specific magnetic requirements, to resist radiation damage in nuclear reactors, to have unique electrical properties (e.g., superconductivity). These are but a few examples of areas where the concepts of alloy design are being applied to meet advanced technological needs.

Alloy design involves many facets--basic science, applied science, alloy theory, phase transformations, morphology of transformation products, kinetics of solid state reactions, microstructural control during solidification, thermomechanical processing, fabrication procedures, heat treatments, and testing methods. The design of a new alloy requires the availability of the newer tools of science. It is necessary to have access to both transmission electron microscopes and scanning electron microscopes for visual examination of the fine details of microstructure. Examples of other modern instruments are the electron beam microprobe, for determining local variations in chemical composition in the dimension range of a micron and Auger spectroscopic equipment, for quantitatively measuring

the degree of partitioning of elements to grain boundaries. Equally important is a knowledge of manufacturing processes, because methods of melting and processing can have major effects on the properties of any alloy. Even the economic factors must be given serious consideration. Alloys with superior properties may never be used in technological applications if the cost is substantially more than that of commercially available alloys. Cost savings is sometimes carried to an extreme by design engineers, and occasionally this results in serious service failures. The overall cost effectiveness may become negative when service failures occur. Laboratory workers, as well as design engineers, often see only one part of the complex picture of alloy design and utilization. The need for continuing education programs in this area of knowledge is strongly felt by engineers and materials scientists alike.

The field of alloy design ranges from basic investigations to product development. The following discussion is divided into four categories: Basic Investigations, Semi-Empirical Research, Empirical Alloy Design, and Alloy Development. These categories were arbitrarily selected for the purpose of grouping together discussions of recently published results that have some commonality. Overlapping between these categories exists; there was no intent to restrict the classification of any contribution to the category in which it was discussed. Some of the contributions in each of the categories involved basic investigations, and empirical and developmental work was involved in many of the cases discussed under the basic section. The principal reason for separating the discussions into categories was to provide the reader with a better overall perspective of alloy design.

The number of publications related to alloy design is not large, but the rate of publication in this field is increasing each year. About 50 recent articles provided the background information for this paper.

BASIC INVESTIGATIONS

The term Basic Investigations as used herein refers to research conducted with the objective of designing new alloys primarily by invoking the basic principles of materials science.

It is well known from both theory and experiment that a fine, uniform dispersion of second phase particles is essential for high yield and tensile strengths. Most of the recent literature contributions have been concerned with strength considerations, but designing alloys for strength alone is not sufficient to meet technological requirements. As alloys are made stronger, their toughness decreases, with the highest strength materials being as brittle as glass. The term "toughness" refers to the strength of a material when a macro defect is present (such as a weld crack, fatigue crack, slag inclusion, or a man-made notch). The presence of such defects has led to unanticipated, catastrophic service failures of machine parts and large structures (such as automobile parts, aircraft components, motor and turbine shafts, bridges, pipelines, storage tanks, and ships).

In this section, papers dealing with second phase strengthening are discussed, as well as those using spinodal decomposition of supersaturated solid solutions to produce a fine scale fluctuating structure that forms without the nucleation of a second phase. The latter method of strengthening is relatively new, and only recently have attempts to use this

phenomenon as a basis for alloy design been encouraging enough to attract the interest of potential users.

It is much easier to obtain major changes in the microstructure of metals such as iron and titanium, that undergo phase transformations during heating and cooling, than it is in alloys such as those of aluminum and nickel, which retain the same crystal structure at all temperatures below the melting point. Because the number of possible morphological variations is so great, and the reaction kinetics are so variable, in alloys that undergo allotropic transformations, the relevant theories for such alloys are more complex than those related to the simpler systems. Steels are in the more complex category. They often contain a few percent of elements other than iron and carbon, such as chromium, nickel, and molybdenum. The numerous variety of steels commercially available today have all been in common use for decades. All of the variations resulted from trial and error experimentation. Not a single commercial steel was designed from the basic principles of materials science. However, this does not mean that no basic investigations have been conducted on steels—quite to the contrary; a great deal of first rate research on iron-base alloys has been reported during the past three decades. The important point is that the results of the basic research are only now being utilized to improve the properties of existing alloys (which was long thought to be a fruitless line of research) as well as to design new alloys. Progress in steel research is discussed in this section.

Also included is a discussion of the use of powder metallurgy techniques to produce a high field superconducting wire with a microstructure dictated by theoretical requirements.

Strengthening With Second Phases

Two recent papers, both by R. F. Decker,^{3,12} are concerned with alloy design using second phases to increase strength. In his paper on "Strengthening Mechanisms in Nickel Base Superalloys",¹² Decker reviewed the role of the γ' phase $[\text{Ni}_3(\text{Al},\text{Ti})]$ in the γ (face centered cubic) matrix. The strengthening provided by the presence of the γ' phase is due to several factors, including anti-phase boundary and fault hardening, γ' strength, coherency strains, volume percent of γ' , and the γ - γ' modulus mismatch.

Nickel-base hardenable alloys were discovered four decades ago. In the intervening time they have assumed important roles in advanced technological applications, particularly in the aircraft and power generation fields. These alloys have permitted equipment to operate at higher temperatures with greater efficiency than was possible before. They are called "superalloys" and they constitute about 50% of the weight of advanced aircraft gas turbines. There are about 40 different compositional variations of the nickel base alloys in use today. Most of these consist of a nickel-chromium matrix, hardened by the γ' precipitate. Other additions consist of cobalt, iron, tungsten, molybdenum, vanadium, niobium, tantalum, boron, zirconium, and carbon. All of these different alloys have evolved from empirical research. During the past two decades, many basic investigations have been conducted on the superalloys, but the main objective has been to understand the mechanisms whereby the presence of the γ' precipitate produces the useful properties.

The formation of the γ' precipitate is limited to high nickel matrices. Both γ and γ' phases are face centered cubic, with lattice mismatches of less than 1 pct. The γ' phase can form in the lattice of the matrix as a coherent precipitate with low surface energy, and γ' has long time stability at temperatures ranging up to about 1800°F.

The γ' phase has unique characteristics. It has an ordered $L1_2$ structure which contributes strengthening to the alloy because it contains anti-phase boundaries. Research has shown that this unique phase actually becomes stronger as the temperature is increased. This is in sharp contrast to the effect of temperature on the strength of practically all other metallic types of phases. Also, γ' has an inherent ductility; dislocations can pass through the crystals of this phase at moderate stresses and temperatures. This prevents severe embrittlement when the phase forms at grain boundaries, in contrast to the brittleness resulting from the formation of sigma and Laves phases at grain boundaries.

A theory of hardening due to coherent, ordered γ' has been devised. Dislocations ($\bar{b} = a/2\langle 110 \rangle$) move in pairs during shearing. The motion of the leading dislocation is impeded because it must create an anti-phase boundary in the ordered structure, whereas the motion of the trailing dislocation is assisted because it annihilates the anti-phase boundary created by the leading dislocation. The creation of the anti-phase boundary provides an increment of strengthening for which Gleiter and Hornbogen¹³ derived a mathematical relationship. In this theory, the incremental increase in the flow stress is equal to the anti-phase boundary energy divided by two Burger's vectors.

Coherency strains play an important role in the strengthening of superalloys. Decker and Mihalisin¹⁴ isolated and measured coherency strain effects in nickel-aluminum-ternary element alloys. By varying the alloy content, they increased the γ - γ' mismatch from less than 0.2 to 0.8 pct. This added 200 Vickers hardness points, or about 100,000 psi to the yield strength. This result was in excellent agreement with the theory of Gerold and Haberkorn¹⁵ for coherency strain hardening.

The magnitude of the coherency strain can be adjusted by controlling the chemical composition of the alloy. Both titanium and niobium increase coherency strains because they partition to the γ' phase and expand its lattice constant. Chromium, molybdenum, and iron decrease coherency strains because they partition to the matrix where they expand the lattice. The alloys that maximize the coherency strains are molybdenum-free and contain a high ratio of titanium to aluminum.

Theoretical considerations¹⁶ indicate that a modulus mismatch between γ and γ' would contribute to the hardening during dislocation cutting. This conclusion has not yet been checked because of the lack of modulus data for alloyed γ' .

When the particles of the γ' phase become larger, it becomes increasingly difficult for dislocations to pass through them. Beyond a certain size of particle, bypassing, rather than cutting, will occur either by looping or by dislocation climb. The incremental increase in the flow stress required for dislocation looping is predictable from the Foreman and Makin¹⁷ modification of the theory of Orowan.¹⁸ Decreasing the inter-particle spacing or increasing the γ' particle size would increase the

flow stress. Increasing the coherency strains by introducing alloying elements that would increase the lattice mismatch would provide additional strengthening by making the particles appear to be larger to dislocations.

The strain hardening rate is increased when dislocations, looping around particles, leave rings surrounding them. This makes the particles appear to be larger to the dislocations that follow.

The more general topic of second phase strengthening was presented in an excellent paper by Decker entitled "Alloy Design, Using Second Phases".³ This paper was the 1973 Institute of Metals Lecture of the Metallurgical Society of AIME. Decker discussed processes for introducing second phases, the selection of second phases, the design of second phase morphology, the use of second phases for controlling grain size, the importance of stabilizing dislocation networks by second phase particles, the effects on toughness and ductility, optimizing the combination of high strength with high toughness, fatigue, and stress corrosion cracking. Decker classified the processes used to introduce second phase particles as gas-solid, liquid-solid, and solid-solid. The gas-solid reactions are carburizing, nitriding, internal oxidation, and vapor deposition. Liquid-solid methods involve eutectic reactions, electro-deposition, co-precipitation of gels, melt suspensions, atomizing, and splat cooling. Solid state reactions include eutectoid decomposition, sloping solvus precipitation, spinodal decomposition, short range order, and powder metallurgy methods.

Factors to be considered in the selection of second phases included cost of alloying elements, hardness of the second phase at the service temperature, modulus of elasticity, ability to bond strongly to the

matrix, ductility and toughness, crystal structure and lattice spacing, and a tendency to order and form antiphase boundaries. The size, shape, and volume fraction of second phase particles are major design options in controlling the properties of alloys.

Most of the alloy systems involve heterogeneous nucleation, often catalyzed by preferred sites,²¹ such as dislocations, stacking faults, and grain boundaries. The rates of nucleation increase with increasing density of such sites and with the degree of supersaturation. The nucleation rate is highest at some reaction temperature of optimum undercooling. The imperfect status of the lattice at the preferred nucleation sites provides regions in which the free energy for formation of nuclei is less than it is within the volume of perfect crystals. Such sites are also regions in which larger or smaller size atoms tend to concentrate, because the lattice strains around such atoms are reduced when they are so concentrated. Nucleation is favored in these regions of higher concentration because of the existing, higher degree of supersaturation.

Dislocations are very effective in speeding up precipitation reactions. Decker illustrated this for an iron-base alloy containing 8%Ni and 13%Mo, for which the aging time was reduced 25-fold by increasing the dislocation density of the ferrite from 10^8 to $10^{10}/\text{cm}^2$ by cold working. A very high density of dislocations ($5 \times 10^{11}/\text{cm}^2$) was obtained in another investigation by a martensite transformation in an iron-base alloy containing 18%Ni7%Co5%Mo.²² This material, with its higher dislocation density, aged 100 times faster than the cold worked 8%Ni13%Mo alloy.

The shape of second phase particles is controlled by surface and strain energy considerations, with elastic anisotropy playing a major role.

Most second phases are incoherent and are shaped like plates or rods to reduce strain energy. Spheroids have the minimum surface and tend to form when the second phases are coherent and the strain energy is low. In eutectic and eutectoid systems the shape of the second phase particles is generally that of plates or rods, even when the transformation is isothermal. When the temperature gradients are high during the transformation, the plates, or rods, are more perfectly formed than is the case for isothermal transformation. The rods and plates will eventually break up into spheroids when the alloy is heated below the eutectoid temperature for a long period of time. Plastic deformation, either hot or cold, accelerates the spheroidization process.²³ The average size of the spheroidal particles in an alloy will gradually increase if the alloy is held at a constant high temperature for a long period of time. The growth kinetics commonly follow the Wagner-Ostwald ripening relationship with the radius increasing as the one-third power of time. The rate of growth is also affected by surface energy, diffusion coefficient, the concentration of the second phase elements in the matrix, and the temperature.³ It is interesting to note that the time dependence of growth of second phase particles at grain boundaries is different from that of particles within the grains, the radius being proportional to the one-fourth power of time.

Particles Cut by Dislocations

When the second phase particles are small, or through which dislocations can move, the particles strengthen by one or a combination of four mechanisms:³

- (1) Anti-phase-boundary (APB) or fault energy (Γ)

$$\Delta\sigma_{\text{APB or } \Gamma} = \frac{0.56f^{1/3}r^{1/2}(\gamma_{\text{APB}} \text{ or } \Gamma)^{3/2}}{G^{1/2} b^2}$$

where

γ_{APB} = anti-phase-boundary energy

Γ = fault energy

G = shear modulus

b = Burgers vector

f = volume fraction

r = radius of particles

- (2) Lattice-mismatch

$$\Delta\sigma_{\epsilon_c} = \frac{6G(rf)^{1/2}}{b} \epsilon_c^{3/2}$$

where ϵ_c is the coherency strain

- (3) Modulus mismatch

$$\Delta\sigma_E = \frac{0.8Gb}{\lambda_d} \left(1 - \frac{E_1}{E_2}\right)^{1/2}$$

where λ_d = interparticle spacing

E_1 = modulus of soft phase

E_2 = modulus of hard phase

(4) Peierls force mismatch

$$\sigma_{PF} = 5.2 \frac{f^{1/2} r^{1/2}}{G^{1/2} b^2} (\sigma_p - \sigma_m)$$

where σ_p = strength of particles

σ_m = strength of matrix

The cutting mechanisms described above show that the flow stress will increase as the particle size becomes larger. At some point, however, the particles become so strong that they resist cutting. This critical particle size varies with different alloys and depends upon how strong the particles are. The particles may be so strong (e.g. carbides), that even the tiniest particles cannot be traversed by dislocations. For particles that cannot be cut, the Orowan-Ashby equation applies.²⁵

$$\sigma_{OA} = \frac{0.13Gb}{\lambda_d} \frac{r}{n b}$$

When the cutting process cannot occur, dislocations bypass particles by passing between them, leaving residual dislocation loops around each particle. This mechanism is simpler than cutting.

High Temperature Strength

At high temperatures (above about 0.5 of the melting temperature in degrees K), thermally activated recovery processes occur at stresses lower than the short time yield strength. Within particles disordered by moving dislocations, reordering occurs because of diffusion. This effectively diminishes the incremental increase in strength provided by anti-phase boundaries. When the second phase particles contain slowly diffusing

components, such as Mo, creep is retarded. Dislocations can cross-slip or climb over uncut particles, and creep can occur at stress levels below the Crowan flow stress. Networks of dislocations form in the matrix during the creep. The presence of second phase particles causes the dislocation network spacing to be smaller, sometimes to the point where available vacancies are insufficient to satisfy the climb requirements of slip dislocations piled up at particles. When this occurs, higher activation energies are observed, and interstitial atom movement is thought to be involved.²⁶ The interfaces between adjoining grains are high energy surfaces consisting mainly of vacancies and fragments of dislocations. Boundaries are both sinks and sources of vacancies.

At high temperatures (above about 0.7 of the melting point in °K) grain boundaries often undergo sliding. The creep strain caused by grain boundary sliding can, in an extreme case, be as high as 90% of the total creep.²⁷⁻²⁹ Increasing the grain size reduces the grain boundary area, which results in a reduction of the creep rate at a given stress. Thus the alloy design concept that higher strength is associated with finer grain size, applicable at low temperatures, must be revised for elevated temperatures where higher strength is associated with larger grain sizes.

An optimum design for creep is one in which the grain boundaries are all parallel to the direction of loading, so that none of the boundaries are subjected to shear stresses. This is the case for the high strength directionally solidified gas turbine blades. With these long slender grains, the distance between boundaries has the same effect at high temperatures that it has at low temperatures, namely that higher strengths are produced by shorter interboundary distances.

In an article by Duhl, Erickson and Sullivan, entitled "Advances in Directional Solidification Spur Usage in Turbine Airfoil Shapes",²⁰ the authors pointed out that the directional solidification of superalloy airfoil shapes, which has been under development at Pratt and Whitney Aircraft since 1965, has continuously evolved, until at present the technique is being used to cast a variety of advanced turbine airfoils for both commercial and military applications. Directional solidification eliminates transverse grain boundaries which are sites for microcrack formation in service. This development is an excellent illustration of the need for combining a knowledge of microstructure and micromechanics of fracture with methods of manufacturing in order to produce alloys with superior properties for a specific application. In recent years, research in directional solidification has been focused on improving production rates, resulting in the development of a high rate solidification process. Also, empirical experiments have shown that additions of hafnium to nickel base superalloy compositions produce an enhancement of transverse ductility. In the faster technique the solidification front advances upward in the casting because of heat conduction of a chill plate located at the base. This alloy development was assisted by heat transfer analyses using a computer program. The strengthening of superalloys by the coherent γ' phase represents a relatively simple, but very important case of alloy research.

Toughness and Ductility

When second phase particles are added to a ductile matrix to increase the strength, the toughness and ductility decrease, generally in proportion to the volume fraction of the second phase. The reduction in ductility can be minimized by controlling the shape, size, spacing, and deformability of the particles. Particle cracking tends to occur with non-metallic and brittle intermetallic particles. The stress required to crack a particle is inversely proportional to the square root of the particle radius. Thus small particles are better for resisting crack initiation due to stress concentrations at the interface of the particle and the matrix. In steels, spheroids of Fe_3C with radii equal to or less than 0.3 microns resist cracking while larger ones tend to crack during tensile deformation.³⁰ Sulfides and oxides have smaller critical sizes. An equally important factor in controlling toughness and ductility is the grain size, or the mean free path for dislocation movement. Reducing the dislocation mean free path can have a very large effect upon the fracture toughness of a material. The effect of such reductions is to reduce the stress concentrations at the ends of slip bands where dislocations are forced to pile up against barriers. The stress concentration is generally considered to be inversely proportional to the square root of the free slip distance.

Soft phases may provide marked improvements in toughness. For example, in a titanium alloy having a β matrix, the presence of a grain boundary envelope of α will improve the fracture toughness when the envelope is more than 3 microns thick, but no additional improvement occurs above about 5 microns.³¹ Another example is that of the 9%Ni steel, the

Charpy impact value being enhanced by the presence of 10% austenite dispersed in ferrite.^{32,33} Additional benefits were found when finely dispersed austenite was present in quenched and tempered steels.² (This case is discussed in detail in Section F.)

The presence of a soft phase does not necessarily always have a beneficial effect on fracture toughness. It is well known that a grain boundary network of ferrite in quenched and tempered steels is detrimental. For a beneficial effect, the softer phase should be more resistant to crack propagation than the matrix so that an advancing microcrack is blunted when it contacts the softer phase.

Fatigue Strength

High cycle fatigue strength is proportional to the square root of the product of the yield strength and the modulus of elasticity.³⁴ Fatigue failures require reverse stressing, which may occur locally even when the loading is from some maximum value in tension to zero. The exact mechanism of crack nucleation due to fatigue is not yet understood clearly, but it is known that dislocation networks do form and change continuously during fatigue, eventually leading to local crack nucleation.

The dislocations that move rather freely back and forth between barriers during cyclic loading can be pinned, at least partially, by aging periodically during the fatigue loading process.^{35,36} In general, the fatigue strength is relatively insensitive to variations in microstructure, with alloys having the same yield strength (regardless of the microstructural variations) having the same fatigue properties.

Enhancing Fracture Toughness Through Microstructural Control

The evolution of a unified theory of fracture mechanics and the development of reliable test methods for obtaining accurate values of plane strain fracture toughness (K_{IC}) have provided metallurgists with a quantitative method for evaluating the effects of microstructural details on the tendency of alloys to fracture in a brittle manner. The test methods and procedures are specified by the American Society for Testing Materials.³⁷ Recent investigations of the relationships between the microstructure and fracture toughness of ultra high strength steels have been especially rewarding. The deleterious effects of sulfur and other trace impurities have been quantitatively determined.^{38,39} The influences on strength and fracture toughness of the microstructural components bainite, martensite, and tempered martensite have been well documented in recent publications.^{40,41} Retained austenite, even when present in relatively small amounts, can have a major beneficial effect on the fracture toughness of quenched steels, as was demonstrated in two recent contributions.^{42,43} In the paper by Lai et al., it was shown that the fracture toughness of AISI 4340 steel could be increased from about 39 ksi-in^{1/2} to about 65 ksi-in^{1/2} by increasing the austenitizing temperature from 870°C to 1200°C (followed by slow cooling to 870°C prior to oil quenching). The improvement in fracture toughness occurred even though the austenite grain size in the material austenitized at 1200°C was an order of magnitude larger than the grain size in the specimens treated at 870°C prior to oil quenching. No ferrite or upper bainite was present in any of the microstructures resulting from these two treatments. Transmission electron

microscopy revealed that both treatments produced mixed microstructures consisting of autotempered martensite, untempered martensite, and small amounts of lower bainite. The most striking difference found in the microstructures resulting from the two different austenitizing treatments was the amount of retained austenite. In the specimens heated to 870°C, very little retained austenite was present, whereas in the specimens given the higher temperature treatment, there were extensive networks of austenite films, 100 to 200Å thick, surrounding the martensite plates and packets of laths. The yield strength and ultimate tensile strength were substantially independent of the austenitizing temperature. The explanation for improved fracture toughness appeared to lie in two areas: there was less twinning with the higher austenitizing temperature, and there was a large increase in the amount of retained austenite. The austenite films, which are very ductile, tend to blunt any microcracks that form and also help to prevent the formation of microcracks at lath boundaries by dispersing the highly concentrated stresses that sometimes are produced at boundaries by plastic flow in the laths. The presence of retained austenite has been shown by Webster⁴⁴ to improve toughness through its crack arresting ability. In his paper, Webster described how high magnification movies were employed to follow crack propagation. He found that cracks propagated through the martensite, but were stopped upon intersecting regions of retained austenite. Upon increased loading, the cracks were found to branch out and grow around the austenitic areas.

Antolovich et al. investigated the effects of changing the microstructure of 300 grade maraging steel on fracture toughness.⁴³ They

obtained different amounts of retained austenite in an aged martensitic matrix by varying the heat treating procedure. The fracture toughness of conventionally heat treated material was found to be about $70 \text{ ksi-in}^{1/2}$ at a strength level of 280 ksi. The toughness increased to $106 \text{ ksi-in}^{1/2}$ at a strength level of 240 ksi as a result of a single thermal cycle (consisting of heating at a rate of $.33^\circ\text{C}$ per second, holding at 825°C for 2 min, and cooling to room temperature). Antolovich et al. also developed a mathematical model for predicting fracture toughness of specimens containing a mixture of different microconstituents. They obtained very close agreement between the predictions of the model and the values obtained experimentally.

Wood⁵ investigated the effect of austenitizing temperatures on the fracture toughness and microstructures of quenched and tempered low alloy steels, AISI 4130, 4330, 4140, 4340, and 3140, as well as steel 300-M. When the austenitizing temperature was raised from 870°C to 1200°C , the fracture toughnesses of all of these steels were significantly increased. For some of the steels, ice brine quenching from 1200°C (instead of oil quenching) led to a still further increase in fracture toughness. When the treatment consisting of first heating to 1200°C followed by cooling slowly in the furnace to 870°C before oil quenching was used, the resulting fracture toughnesses were not as high as those for specimens quenched directly from 1200°C , but they were higher than those obtained by using only the 870°C oil quenching treatment.

In a recent paper, Zackay et al.⁴⁶ discussed the influence of some microstructural features on the fracture toughness of high yield strength

steels. They showed that relatively small amounts of embrittling microconstituents, often detectable only by a combination of careful optical and electron microscopy, can have a major influence on the fracture toughness of ultra high strength steels. In an alloy steel containing 5%Mo and .3%C, undissolved carbides were detected when the steel was austenitized at a commonly used temperature of 870°C. In the as-quenched condition this steel had a fracture toughness of about 50 ksi-in^{1/2}. When the austenitizing temperature was increased to 1200°C, all carbides were dissolved and the fracture toughness doubled. Similar experiments were made with AISI 4130 and 4340 steels. In the former case, the fracture toughness was increased from 57 to 73 ksi-in^{1/2}, and in the case of the 4340, the fracture toughness was raised from 35 to 63 ksi-in^{1/2}. In both cases the steels were cooled to 870°C from 1200°C prior to oil quenching. Thus, there was no difference in cooling rates or quenching stresses in the specimens austenitized at the two different temperatures. The fracture toughness values were for specimens tested in the as-quenched condition. Additional tests were made on the specimens that had been similarly treated, but had been tempered at temperatures ranging from 100°C to 400°C. A plot of fracture toughness (K_{IC}) vs yield strength is shown in Figure 1 for quenched and tempered 4340 steel and commercial 18%Ni maraging steel. Also shown in this Figure (as circles) are the results obtained with commercial 4130 and 4340 steels and for the special 5%Mo-0.3%C steel that were austenitized at 1200°C instead of the commonly used temperature of 870°C. Simply by changing the austenitizing temperature for conventional quenched and tempered steels, it was possible to

obtain, at a given yield strength, fracture toughnesses that were equivalent to those previously obtainable only with the more expensive 18%Ni maraging steel. There are good reasons to believe that fracture toughnesses well above the maraging steel band can be obtained with quenched and tempered steels, through modifications of chemical compositions and thermal treatments. An example of what might be expected as an upper limit band is shown in Figure 2, which contains the same bands as shown in Figure 1 for the 4340 and 18Ni maraging steels. In this figure, there is a shaded area which is marked TRIP steels. This is a band obtained with experimental steels, called TRIP steels, which are metastable austenitic ultra high strength steels that transform martensitically when plastically deformed.⁴⁷ These steels contain about 0.3%C in addition to various amounts of chromium and nickel. They are thermomechanically processed at temperatures ranging from 200°C to 500°C and strains ranging up to 80% reduction in cross sectional area. They have yield strengths above 200,000 psi and fracture toughness in the neighborhood of 150 ksi-in^{1/2}, or higher. Plastic straining causes the metastable austenite to transform, and with this transformation there is associated a 3% volumetric expansion. The longitudinal portion of the strain associated with the volume change helps to spread the plastic zone over a substantially bigger volume. The volumetric expansion tends to reduce the three dimensional tensile stresses that are developed during plastic strain near the apex of a notch. This change in stress state, toward a condition which favors a more ductile performance, enhances the fracture toughness of the specimen. It is not unreasonable to assume that steels with lower

alloy content than TRIP steels, but which have TRIP characteristics, can be designed. The fracture toughnesses for such steels should fall in the region between the maraging and the TRIP steels.

The microstructures of 4130 and 4340 quenched and tempered steels were thoroughly characterized by both optical and transmission electron microscopy.^{48,49} In the 4340 steel, the 1200°C austenitizing temperature was found to eliminate virtually all of the twinned martensite plates (which are known to reduce fracture toughness), and to introduce a significant amount of retained austenite in the form of films which surrounded the martensite laths. In the case of the 4130 steels, the 870°C oil quenched specimens were found to contain mixed microstructures consisting of primary ferrite, upper bainite, lower bainite, and martensite. When the austenitizing temperature was increased to 1200°C, the austenite grain size increased from ASTM 7 to ASTM 0. In the larger grain size specimens, the amount of higher temperature austenite decomposition products were greatly reduced, particularly primary ferrite and upper bainite. The elimination of these unfavorable microstructural features produced a marked improvement in fracture toughness. However, neither the ultimate tensile strengths nor the yield strengths were significantly affected by the higher temperature austenitizing treatment. The microstructure of specimens quenched from the 1200°C temperature consisted almost entirely of untwinned lath martensite, a structure which has high toughness. The martensite was observed to be autotempered, and there were retained austenite films between the martensite laths. These features undoubtedly added to the fracture toughness. More than a dozen micrographs in each

of the Lai et al. papers provide excellent illustrations of the microstructural features of the steels investigated.

Recognition of the fact that the kinetics of austenite decomposition in the bainite and martensite temperature ranges, as well as the morphology of the decomposition products, can markedly affect the fracture toughness of a quenched steel, led to the conclusion that more precise and more rapid means for studying austenite decomposition rates were in order. A new magnetic permeability method, capable of accurately indicating decomposition rates within 2 sec. after the start of quenching to an isothermal temperature, was developed.⁵⁰ TTT curves were obtained for AISI 4340,⁵⁰ and AISI 4140, D6AC, and AMS6416 (300-M) steels.⁵¹ The kinetics of the bainitic reaction below the martensite start temperature (M_s) were determined, and the martensite transformation range was measured. The shapes of some of the TTT curves differed significantly from those previously published. Also, the effects of changing the austenitizing temperatures from 880°C to 1200°C were established for the AISI 4130 and 300-M steels. In this investigation, computeraided computational methods were used to decode, analyze and plot the austenite decomposition data.

The martensite transformation temperature ranges for most of the steels studied in the investigation had been reported in the literature. However, a number of values found in the literature were not in accord with those determined by the new magnetic technique. The new technique provided a direct experimental means for determining the range over which martensite formed. The M_s temperatures determined by the new technique

were in reasonable agreement with published values, but the percentage of martensite formed at lower temperatures differed significantly from those previously reported. Other investigators^{52,53} have suggested that the metallographic technique, used in conjunction with empirical equations and the quenched temper technique,⁵⁴ has the tendency to indicate the M_{50} and M_{90} temperatures higher than actual values. Thus the new method seems to have provided a more accurate means for studying martensite transformation behavior. Consistent with observations of others, the new method is capable of resolving the bainite C curve into two C curves, one for upper bainite and the other for lower bainite. Also, as has been observed previously, the magnetic method showed that the lower bainite reaction extends below the M_s temperature and that the lower bainite reaction is accelerated by the strains induced by the martensite transformation.

Enhancement of Notch Bar Properties at Cryogenic Temperatures

It is well known that body centered cubic metals have a marked tendency to fail in a brittle manner at cryogenic temperatures, and that this tendency is exaggerated by certain compositional and microstructural factors. Interstitial impurities, such as carbon and nitrogen, increase the tendency for body centered metals to fail by cleavage at lower temperatures. When nickel is added to iron, the temperature of transition from ductile to brittle behavior is lowered. Another important factor is that small grain size favors the retention of toughness to lower temperatures. In a recent investigation,^{54a} it was shown that an iron base alloy containing 12%Ni and 0.5%Ti could be heat treated to produce a very fine grain structure. When this was done the toughness, as measured

by the V-notch Charpy test, was shown to be high at liquid nitrogen temperature in an alloy that had a high yield strength. The results are shown schematically in Fig. 3. This Figure is a comparative plot of the yield strength and Charpy V-notch impact toughness at -196°C for two commercial cryogenic steels and for the Fe-12Ni-0.5Ti alloy. Charpy values in the neighborhood of 150 ft lbs at -196°C were obtained with grain sizes of less than 10 microns diameter. With grain sizes 25 microns or higher, the Charpy V-notch energy dropped to 25 ft lbs or less.

Design of a Creep Resistant Alloy

Most of the creep resistant materials derive their strength from a dispersed second phase which interferes with the movement of dislocations. In ferritic alloys, the dispersed phase is almost always a carbide, but in the high nickel super alloys, the phase generally of the Ni_3Al type of intermetallic compound. Carbide precipitates are not stable at elevated temperatures. They often change composition, morphology, and even crystal structure with long exposure to high temperatures. Such changes almost invariably act in the direction of increasing the creep rate at a constant stress. The concept of using more stable intermetallic compounds, rather than carbides, for enhancing elevated temperature strength is decades old, but progress toward the realization of this concept has been slow. The major deterrent to the use of intermetallic compounds has been a tendency of such compounds to precipitate as thin films on grain boundaries, which leads to severe embrittlement at room temperature.

In a recent investigation, a means was found for eliminating the embrittling grain boundary film in an ironbase alloy containing 1 at pct of Ta and 7 at pct of Cr. In this alloy, the dispersed phase was a compound Fe_2Ta , a Laves phase.⁵⁵ A brittle grain boundary network of a Laves phase formed during the initial heat treatment, but it was made to spheroidize by a thermocycling treatment consisting of heating the alloy through the $\alpha \rightarrow \gamma \rightarrow \alpha$ transformation. The thermocycling produced new irregular grain boundaries. The preexisting brittle network spheroidized relatively rapidly and was eliminated. The tensile elongation at room temperature was increased from 13 to 20% by the spheroidizing treatment. Creep and stress rupture tests were made at both 1000°F (538°C) and 1100°F (593°C) for the 1 pct Ta and 7 pct Cr alloy, and at 1100°F (593°C) for similar alloys to which .5%Mo had been added. Figure 4 shows the stress rupture plots for these alloys, along with commercial materials currently used in this temperature range. The stress rupture curves for the new alloys fall near the middle of the range of the commercial materials. The fact that these results were from preliminary experiments leads to the encouraging conclusion that, with further development, it might be possible to produce alloy variations that have properties superior to those of alloys now in commercial use.

Design of Refractory Carbide Cutting Tool Alloys

Dr. Erwin Rudy has recently devised a new method for producing superior refractory carbide cutting tool type of alloys.^{56,57} Small, effective grain sizes and resistance to grain growth can be obtained

through the use of spinodal decomposition reactions.⁵⁸⁻⁶⁰ One of the major restrictions to the use of spinodal decomposition phenomena in alloy design is the scarcity of suitable alloy systems. To undergo decomposition, alloy systems must have miscibility gaps; and useful alloys must also be comprised of materials of technological interest.

Dr. Rudy developed the thermodynamic requirements in mathematical form that define the spinodal reaction in complex multicomponent systems, such as Ti-Mo-C-N. It is well known to thermodynamists that phase equilibria in solid solutions systems are solely determined by the free energy of mixing, and are not directly affected by the stabilities of the constituent elements or phases. The ratio of atomic sizes is the most important factor contributing to positive deviation from ideality, and thus to a decrease in the stability of a solution. The atomic size ratio largely determines the extent of miscibility. The coherency stresses caused by lattice mismatch give rise to an elastic energy term, which must be added to the chemical free energy. Dr. Rudy's work showed that the most important aspect of his study concerns the thermodynamic prediction, verified by experiment on a specific system, that critical solutions phenomena can be induced by thermodynamic factors other than those associated directly with solutions formation, i.e., the free energies of mixing. In the four component system used by Rudy to check the thermodynamic predictions, intermixing of atoms on at least two different sublattice sites was required. Rudy has successfully applied his theory of the decomposition reaction in higher order carbonitride solid solutions to achieve high strength and resistance to grain growth

in alloys potentially useful as machine tool components and wear resistant alloys.

In the specific example of cemented Ti-Mo-C-N base alloys, the following considerations were considered to be important:

1. The α' -phase (Ti- and N-rich phase) has superior wear characteristics, but is very poorly wetted by iron metal base binders, thus yielding alloys with insufficient strength; the α'' -phase, on the other hand, has excellent wettability, but has inadequate wear resistance when present in cutting tool alloys.

This problem was circumvented by choice of an alloy composition which, upon cooling, disproportionates into a fine grained agglomerate of $\alpha' + \alpha''$ phases. When combined with an iron metal binder, the α'' (which by virtue of its lower stability has a much higher solubility in the binder phase) is transported preferentially by the liquid binder phase during sintering, physically enclosing the α' -phase and separating it from the binder. The sintering and binder-hard phase bonding characteristics are in this way entirely determined by the α'' -phase.

2. Noncoherent grain boundaries between two hard phases, such as α' and α'' in our example, represent areas of high stress concentration and act as crack nucleation centers. Because these alloy types generally need considerably lower stresses to propagate cracks than those required for their initiation, freedom from crack nuclei is very important for good strength and fatigue properties.

This problem was minimized by choosing such alloy compositions, for which the lattice dimensions of the α' + α'' phases are matched to within 1%, and the thermal expansion characteristics differed by less than 10%.

3. The carbonitride alloys of the group IV metals (Ti,Zr,Hf), which are normally quite stable, are reactively attacked by iron group metals at sintering temperatures. They must be sintered under nitrogen to prevent compositional changes. Sintering under nitrogen, however, is undesirable because of the danger of gas entrapment, oxygen contamination, and poor surface quality of the sintered parts.

Because the α' phase is not in contact with the binder, and the α'' hardly contains any nitrogen, the alloys can be sintered under high vacuum.

4. Oxygen contamination in excess of 0.5% in group IV metal carbides and carbonitrides renders them unsinterable because the presence of oxygen causes poor wetting. Oxygen is well known to cause problems in the fabrication of TiC tools, and necessitates extreme care in the selection of raw materials and processing techniques.

At oxygen levels below 2%, the distribution coefficient for oxygen between the α' and α'' phases is about 40:1, so that even sizeable gross contamination will not significantly affect sinterability and final properties of the alloy. TiO has the same structure and similar parameters as TiC and TiN, and small changes in the composition of the solid solution Ti(C,N) by oxygen substitution do not noticeably affect the disproportionation behavior of the alloys and the properties of the interface α'/α'' . Figures 5, 6 and 7 illustrate the results of this research.

Design of a High Field Superconducting Alloy

One of the best high field superconducting materials is the inter-metallic compound, Nb_3Sn , which is capable of carrying a sustained current in excess of $100,000 \text{ A/cm}^2$ in magnetic fields that exceed 100 kG at 4.2°K . The difficulty of utilizing the very excellent superconducting properties of Nb_3Sn , however, is that this compound is extremely brittle. In order to make use of the extraordinary superconducting properties, it is necessary to prepare Nb_3Sn in the form of a tape or a wire. The early efforts to fabricate such wires have been reviewed by Kunzler.⁶¹ These early efforts included the cored-wire processes developed at the Bell Telephone Laboratories, and the process developed by the Radio Corporation of America involving vapor deposition of thin layer coatings. Sometimes solenoids made from such wires had to be wound before the Nb and Sn were reacted in order to avoid cracking of the Nb_3Sn during winding. Reacting Nb and Sn after winding was a costly and inconvenient procedure. A flexible tape with Nb_3Sn present as a thin layer was obtained by a diffusion process described by Benz.⁶² More recently, Pickus and his colleagues,^{63,64} in a new approach to this problem, produced a flexible composite with the Nb_3Sn phase in the form of thin, interconnected filaments, dispersed in a ductile matrix. The filaments had thicknesses of approximately 2 microns. The composite was produced by roll-compacting Nb powder to produce a tape that contained a series of interconnected pores, which were subsequently infiltrated with liquid Sn. The thickness of the roll compacted tape was about 0.020 in. After infiltrating, the

tape was reduced in thickness 75 pct or more by cold rolling. Thereafter, the Nb and Sn were reacted in the temperature range of 950 to 1000°C. Heating for 3 min or less in this temperature range produced the compound. Tapes made in this way could be wrapped around a mandrel 1 inch in diameter with no mechanical damage to the filament and with no measurable deterioration in the superconducting properties. The current densities obtained at different pulse magnetic fields with this tape are shown in Figure 8.

THE SEMI-EMPIRICAL APPROACH

In this section, as well as in the ones that follow, the material has been taken from publications that appeared in journals concerned with fabrication, treatments, and uses of metals rather than from scientific publications. The semi-empirical approach to alloy development involves work mainly concerned with the improvement of existing commercial alloys. Improvements expected from a knowledge of the basic principles of materials science are realized through modifications in chemical compositions or variations of heat treatments. An example of this kind of work is that of Denhard and Espy,⁶⁵ which was concerned with producing austenitic stainless steels with unusual mechanical and corrosion properties. The authors reported improved results with Ni-Cr stainless steels modified by additions of Mn and N. The three steels that they investigated were 18Cr-3Ni-12Mn-0.3N, 21Cr-6Ni-9Mn-0.33N, and 22Cr-13Ni-5Mn-0.3N. The commonly used austenitic stainless steels of the AISI 200 and 300 series are ductile, weldable, and have good corrosion and oxidation resistance. However, these standard steels have some drawbacks; for example, their

uses are restricted in areas where severe corrosion problems are encountered or where cold forming results in the undesirable formation of martensite. The three improved steels investigated by these authors are being produced by ARMCO Steel Corporation. They have good notch toughness, austenite stability, and corrosion resistance ranging from that of AISI 304 to well above that of AISI 316. In achieving these superior properties, good weldability was retained. The steels do not embrittle in the 800°F temperature range, and deleterious grain boundary precipitation does not occur during welding. The modified steels have yield strengths approximately twice those of the AISI 300 series steels.

In another recent paper, Sadowski related the story of the development of a stainless maraging steel.⁶⁶ This is a new patented addition to the series of maraging steels. It is designated IN-736 and contains 10%Ni-10%Cr-2%Mo. The yield strengths of this steel, in various conditions of treatment, range from 150,000 to 195,000 psi. The steel has high toughness, ranging from 48 to 150 ft lbs of Charpy V-notch impact energy, and the alloy has better atmospheric corrosion resistance than type 410 stainless steel. It is also reported to have excellent weldability. The approach in this development was to utilize a nickel steel with a low carbon martensitic matrix. To this base, molybdenum was added for strength, resistance to temper embrittlement, and for corrosion resistance. Chromium was added for corrosion resistance and strength. Optimum toughness along with high strength was obtained by utilizing small amounts of aluminum and titanium additions, and by aging at an optimum temperature. The composition was balanced so that the desirable mechanical properties could

be obtained with a simple heat treatment, consisting of solution treating plus aging. The experimental program in this case consisted of making 30 lb heats of 33 alloys with different variations of compositions. The effects of various combinations of elements were studied and the optimum heat treatments were determined empirically.

Donald Webster reported the development of a high strength stainless steel with improved toughness and ductility.⁴⁴ The highest strength stainless steels normally available commercially contain as major alloying elements, carbon, chromium, cobalt, and molybdenum. These are aircraft type steels commonly used at elevated temperatures. They are identified by Air Force specifications AFC77 and AFC260. Alloy AFC77 contains 14Cr-13Co-5Mo-0.16C. AFC260 contains 15Cr-13Co-4Mo-2Ni-0.14Nb-0.08C. Webster modified the AFC77 composition by adding 0.13 Nb, and he modified the AFC260 by increasing the niobium to 0.22 and reducing the nickel to 1.0, with the carbon content being raised to 0.16. The steels in the standard form were not designed for high toughness, but Webster showed that the toughness could be improved by the selection of a nonstandard austenitizing temperature which controlled the amount of retained austenite present after heat treatment. The objective of the new work was to produce a stainless steel with properties superior to AFC260 and AFC77 by virtue of modifying the composition slightly and taking advantage of the benefits of improved toughness associated with the retention of austenite in conjunction with small grain size. When the steels were austenitized at 1200°C, large amounts of retained austenite were present

(approximately 10% in the modified 77 alloy and 20% in the modified 260 alloy). However, the high temperature treatment produced large grains in both alloys, with resulting deterioration in some properties.

The compositional modifications made to the two alloys were designed to refine the austenite grain size and to increase the stability of the austenite after heat treatment. Benefits included increases in strength and stress corrosion resistance as well as decreased fatigue crack growth rates. The niobium addition was a convenient way to refine the austenite grain size, although for maximum grain refinement the niobium carbide dispersion had to be optimized by a preliminary austenitizing treatment at 930°C before the final higher temperature heat treatment. Improvements in fracture toughness for the 77 steel were produced by retained austenite, and motion pictures taken during crack growth showed that austenite was an effective crack stopper. Cracks growing through martensite were arrested upon reaching an area of austenite.

Speich, Dabkowski, and Porter investigated the effects of alloy modifications of the basic alloy 10Ni, 0.1-0.2C. They introduced various amounts of chromium (0 to 3%), molybdenum (0 to 2%), and cobalt (0 to 8%). They made 19 different alloys and determined the effects of various combinations of the alloying additions, and the effects of different heat treatments on the hardness, the yield strength, and the Charpy V-notch impact energy. Following quenching from the austenite temperature range, the steels were examined after tempering for 1 hr at temperatures ranging from 100 to 700°C. The authors examined the structures with transmission

electron microscopy and, using a combination of observations from the microscopy and dislocation theory, they were able to calculate the yield strength that might be expected with the observed structures. These calculations were in reasonable agreement with the values of the yield strength that were observed.

EMPIRICAL ALLOY DESIGN

Work in this area is generally carried out without employing advanced theory either to guide the research or to analyze the results. For certain purposes this is an informative and worthwhile approach to alloy problems. Recently, two articles appeared on the effect of heat treatment and minor variations in chemical compositions on the low temperature properties of 6%Ni steels.^{67,68} In the first of these, the authors described the effects of alloy additions on the toughness. They found that manganese refines the microstructure and improves toughness, but promotes susceptibility to tempered embrittlement. The addition of molybdenum and tungsten was beneficial in preventing temper brittleness when the manganese content was high; molybdenum and tungsten were also effective in producing finely dispersed and stable austenite islands. Chromium was found to be an ineffective addition. The effect of copper was similar to that of manganese. Based on their results, a modified steel was developed containing 6 pct nickel, 1 to 2 pct manganese, and 0.2 pct molybdenum or 0.45 pct tungsten. This steel was found to have improved notch toughness at -196°C . In a second paper,⁶⁸ the effect of heat treatment in the ferrite-austenite region on notched toughness of

6%Ni steel was reported. The objective of the investigation was to improve the low temperature toughness of the newly developed 6%Ni steel. The steel was partially austenitized at the temperature range where both ferrite and austenite were present before quenching. This treatment followed the conventional quenching treatment from the austenite temperature range. The reasons that the special heat treatment markedly improved the low temperature toughness were reported as follows:

1. A large amount of finely dispersed austenite in the form of small islands was formed during the heat treatment. This austenite was stable even at -196°C . Its presence interfered with propagation of brittle cracks.
2. The temper brittleness was suppressed because the embrittled prior austenite boundaries were converted to martensite by the special heat treatment.
3. The ductility of the ferrite matrix was improved because of the scavenging effect of the austenite that formed during the heat treatment. By the use of this heat treatment, the Charpy V-notch energy at -196°C was nearly doubled.

Another example of useful research of the empirical type is that of Schneider and colleagues,⁶⁹ who found a process for enhancing the drawability of 430 stainless steels. The formability of 430 type stainless steels is not very good. This material normally does not flow uniformly in different directions, and causes considerable difficulty during metal forming operations. Consequently, these steels are generally employed

only for products requiring a minimum of formability. The object of the investigation was to attempt to improve the formability of these ferritic stainless steels. The investigation was centered on the development of a crystallographic preferred orientation which is known to influence the drawing characteristics. The authors attempted to optimize the crystallographic preferred orientation texture by controlled cold reduction processes. They were successful in this attempt, and they were able to translate their laboratory experiments into effective production processes in the mill. The authors obtained a patent on the process.

Tipnis and his colleagues⁷⁰ developed a new family of gear steels with improved machining characteristics. Automotive pinions, gears, and worms are used in differentials, transmissions, and steering mechanisms as structural power transmitting members. Power is transmitted through the gear teeth, which must withstand high bending loads; the teeth must resist bending and contact fatigue, as well as provide wear resistance. The steels commonly used for such applications are carburizing grades of low alloy or carbon steels. Such steels are generally made by aluminum deoxidation practices to produce fine grain structures for the best combinations of case and core properties after carburizing. Aluminum deoxidation produces numerous small, hard oxide particles that are particularly harmful to the high speed tools used for cutting gear teeth. Because of the aluminum oxide particles, these steels are difficult to machine. Consequently, it was desirable to produce a steel that did not contain such particles. Several alternative deoxidation processes for steel were considered, but the calcium deoxidation process appeared to

have the best merits. Calcium-silicon and calcium-manganese-silicon deoxidizers have been available since 1930. However, the effectiveness of such deoxidizers has remained in doubt. Several BOF, electric furnace, and open hearth furnace experimental heats were made. These heats were evaluated metallographically to study the inclusions. A calcium deoxidation practice that consistently modified the nonmetallic inclusions in the desired manner was developed. The machinability of these steels was significantly improved, and steels of this type are now marketed commercially. Over 300,000 tons of such steel was used during a single year following the development. The use of such steel resulted in substantial cost savings and productivity gains.

ALLOY DEVELOPMENT

Alloy development is usually conducted for the purpose of lowering cost or improving the properties of a commercial product. Some examples of this type of alloy work will be considered in this section.

The first of these is a powder metallurgy alloy steel designed to be used for critical components.⁷¹ Alloying powders to be used for making hot formed metal sheets present problems because the alloying elements that are used are strong oxide formers which tend to be preferentially oxidized during processing. However, the presence of alloying elements is necessary in order to have high enough hardenability, so that the part being made can be hardened properly during subsequent heat treatment. Elements that oxidize readily, such as silicon, do not contribute to hardenability in powder metallurgy parts because they are present mostly

as oxides. Alloying elements such as chromium and manganese also tend to be preferentially oxidized during processing of the powders. The alloy now being used most widely for making powder metallurgy parts is modified 4600P/M steel (0.5%Mo, 2.0%Ni). This modified composition, however, is too costly for many automotive components. Consequently, an investigation was started with the objective of developing a lower cost P/M steel which could be processed in conventional equipment and would provide consistency in end product properties. Several suitable alloy compositions were found which would serve the purpose. One of these is now in commercial use; it contains 0.35%Mn, 0.45%Ni, and 0.60%Mo.

Lenel, in a current article,⁷² described processes for producing powder metallurgy components. He stated that among developments in powder metallurgy, two technologies have recently come into commercial use and that they should find accelerated usage in the near future. These technologies are (1) hot forging of powder metallurgy preformed compacts and (2) hot consolidation techniques for highly alloyed powders, mainly superalloys and high speed steels. The hot forging of preforms is an advanced development of the conventional powder metallurgy technique of close dimensional control. The mechanical properties of compacts, such as strength and ductility, depend upon the density of the sintered compact. Close dimensional control is difficult when high density is required. One method of producing dimensional control is repressing of the compact after sintering, sometimes followed by resintering. However, the degree to which the density of sintered compacts can be increased by cold pressing is limited. The origin of hot forging of powder metallurgy

preforms comes from the technique of precision forging--i.e., hot forging to close dimensional tolerances. An important difference between the blanks made from sintered powder metals and those cut from wrought stock is their density. This difference must be taken into account in designing forging dies for powder metallurgy preforms. A major incentive for the development of new processes for powder metallurgy forming is the changing relative costs of powdered metals vs hot rolled steels. In 1967, iron powder for molding parts cost 11-1/2¢ per lb; this decreased to 9-1/2¢ per lb in 1972. During the same period, hot rolled carbon steel bars increased from 7¢ to 9¢ per lb. Similarly, the prices of prealloyed steel powder and hot rolled alloy steel bars are now approaching each other. Numerous investigations are now underway in commercial plants where hot forged P/M preforms are being considered as replacements for bar stock forgings.

Highly alloyed powders are also consolidated for the purpose of producing semifinished products that must be further formed. The problems involved in making and using highly alloyed powders are divided into three areas: (1) powder production, (2) powder consolidation, and (3) producing parts of superalloys and high speed steels by powder metallurgy methods. A number of new methods for producing highly alloyed powders in vacuum or inert atmospheres have been patented. The powders are usually consolidated by a hot pressing technique. One of the first such processes was that used for consolidating beryllium powder, which was pressed in graphite molds in vacuum at 1100°C. Another technique is to place the powders in metallic shells or cans and then extrude them together with

the can. Extrusion of superalloys at billet temperatures slightly below the recrystallization temperature leads to extrusions that have been recrystallized and have very fine grain structures (additional heating occurs during extrusion). Other types of processing are under experimentation.

High speed steels with very small grain size and with small carbide particles can be produced by the consolidated powder compact method. High speed steels, as well as superalloys, can be produced by hot consolidation from powders and have the same chemical compositions as conventional alloys. Active development work to produce products from powders to compete with those made from cast alloys is now underway.

Another example of alloy development is that of a new bearing steel which combines the desirable properties of high hardenability and low cost.⁷³ Users have felt a growing need for an economical through-hardening ball bearing steel. To meet this need, the Timken Company (the main producers of ball bearing steels) have patented a new grade called PBS-9. The test results on this steel indicate that it offers service properties equivalent to those steels now commercially available on the market, but at a lower cost. Customers using the new steel may save as much as \$70 per ton. The new steels contain about 0.9%C, 0.6%Mn, 0.3%Si, 0.3%Cr, and 0.1%Mo.

Additional examples of alloys developed to meet specific technological needs can be found in current issues of the publications cited as references for this section.

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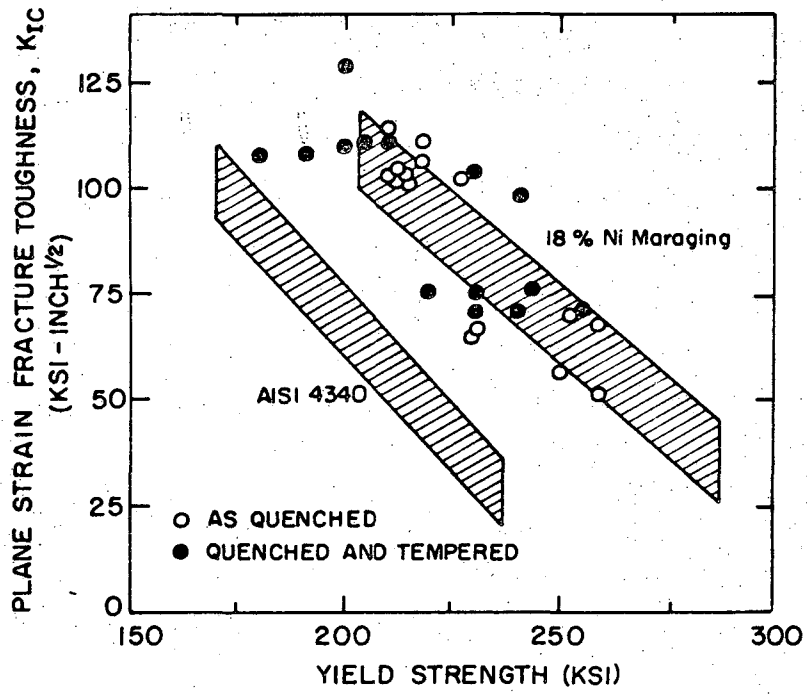
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FIGURE CAPTIONS

- Fig. 1. Plots of fracture toughness (K_{IC}) vs yield strength. The two shaded bands represent the range of values found in the literature for commercial AISI 4340 and 18%Ni maraging steels, heat treated in accordance with conventional practices. The circles are data points for commercial 4130 and 4340 steels, and for the special 5%Mo-0.3%C steel, that were austenitized at 1200°C instead of the commonly used temperature of 870°C. The higher group of points is for 4130 and 5%Mo-0.3%C steels; the lower group is for 4340 steel.
- Fig. 2. Plots of fracture toughness vs yield strength, showing bands for commercial 4340 and 18Ni maraging steel, along with the band for the metastable austenitic TRIP steels.
- Fig. 3. A comparative plot of yield strength and Charpy V-notch impact toughness at -196°C for two commercial steels and the Fe-12Ni-0.5Ti alloy. Data for the 304 and 9Ni steels were obtained from the literature. The Charpy values for the 9Ni steel can be increased to 80-90 ft by special heat treatment.
- Fig. 4. Stress-rupture curves at 1100°F for the new Fe-1Ta-7Cr and Fe-1Ta-7Cr-0.5Mo alloys. Also shown are published results for 0.3C-1Cr-1Mo-0.25V steel, 0.15C-9Cr-1Mo steel, Greek Ascoloy, and AISI 403, 410, and 422 stainless steels.
- Fig. 5. Bending strength of modified spinodal alloys ($\alpha' + \alpha''$) and of cemented titanium-carbonitride as a function of the binder content. Note: Mo exchange in spinodal alloy, 17 at pct. (Courtesy Dr. E. Rudy)

- Fig. 6 Photomicrographs showing grain growth characteristics of cemented α' and $\alpha' + \alpha''$ alloys. Top photographs: Left, $\alpha' + \text{binder}$ as sintered; Right, $(\alpha' + \alpha'') + \text{binder}$ as sintered. Bottom photographs: Left, $\alpha' + \text{binder}$ after additional heating for 64 hours at 1470°C ; Right, $(\alpha' + \alpha'') + \text{binder}$ after additional heating for 64 hours at 1470°C . Note: isolated black spots in photomicrographs are where free graphite had formed by interaction with nitrogen gas during the 64 hour treatment. (Courtesy Dr. E. Rudy).
- Fig. 7 Electron micrograph of modified spinodal Ti-Mo-C-N alloy with Ni binder. Note enclosure of α' phase by α'' , the latter forming the interface with the binder. (Courtesy Dr. E. Rudy).
- Fig. 8 Plot of overall current density of $\text{Nb}_3\text{Sn-Nb}$ composite superconducting tape produced by a powder metallurgy process is shown as a function of magnetic field (produced by a pulsed technique).



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Fig. 1

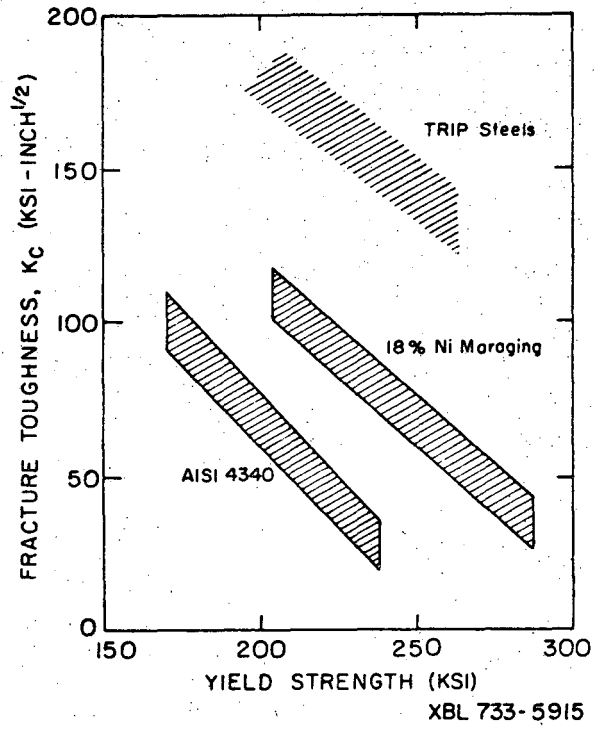
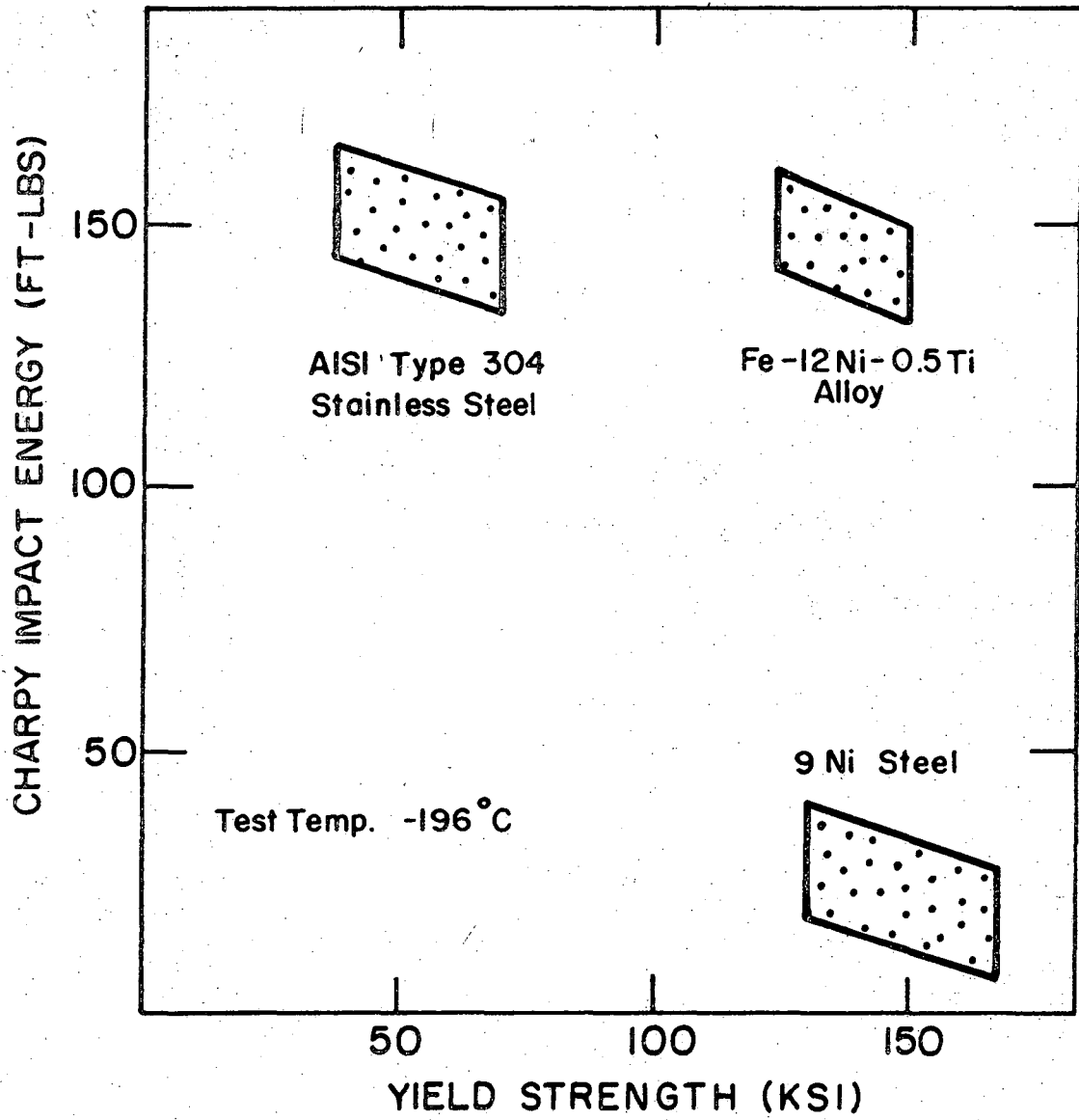
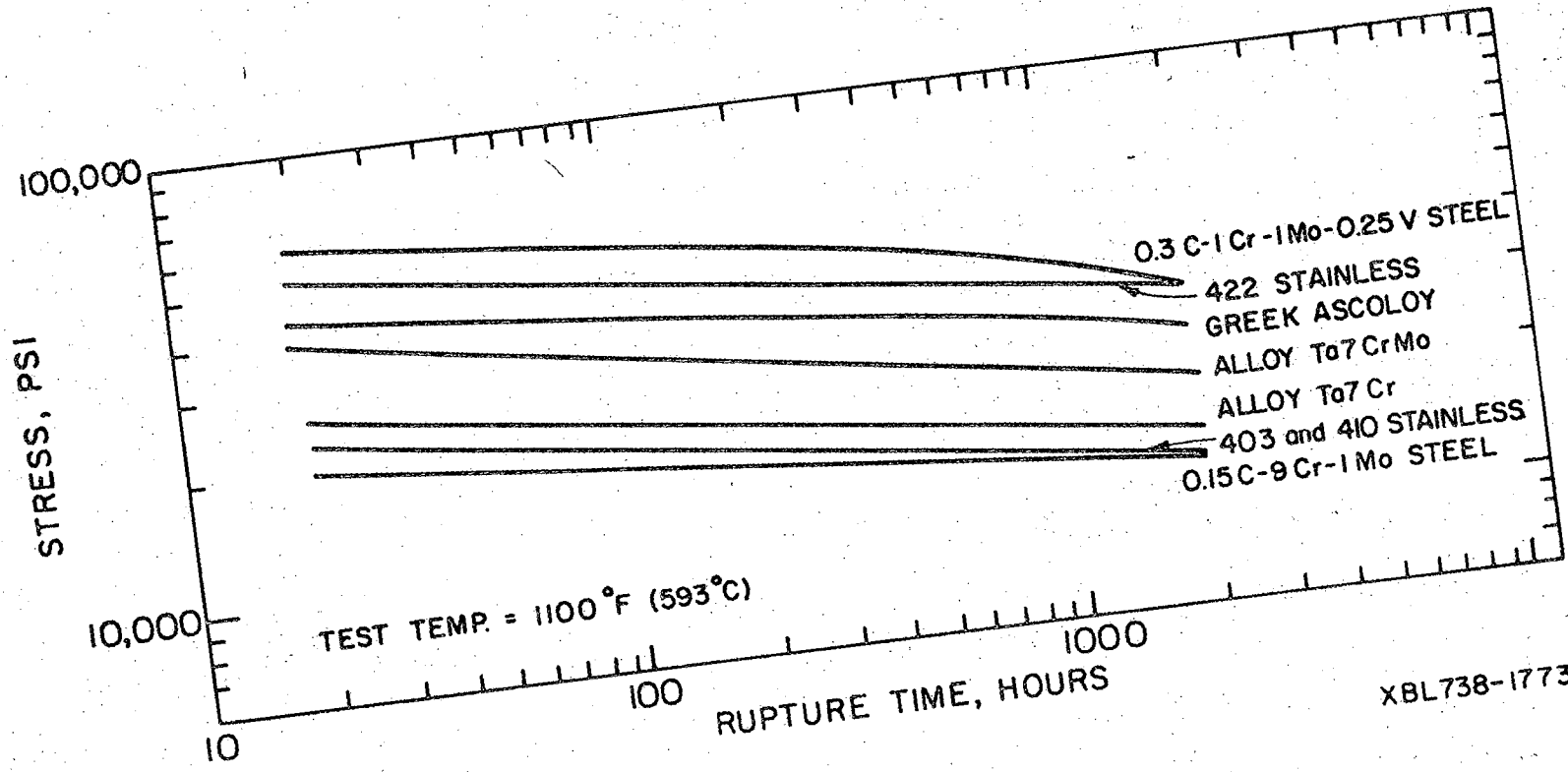


Fig. 2



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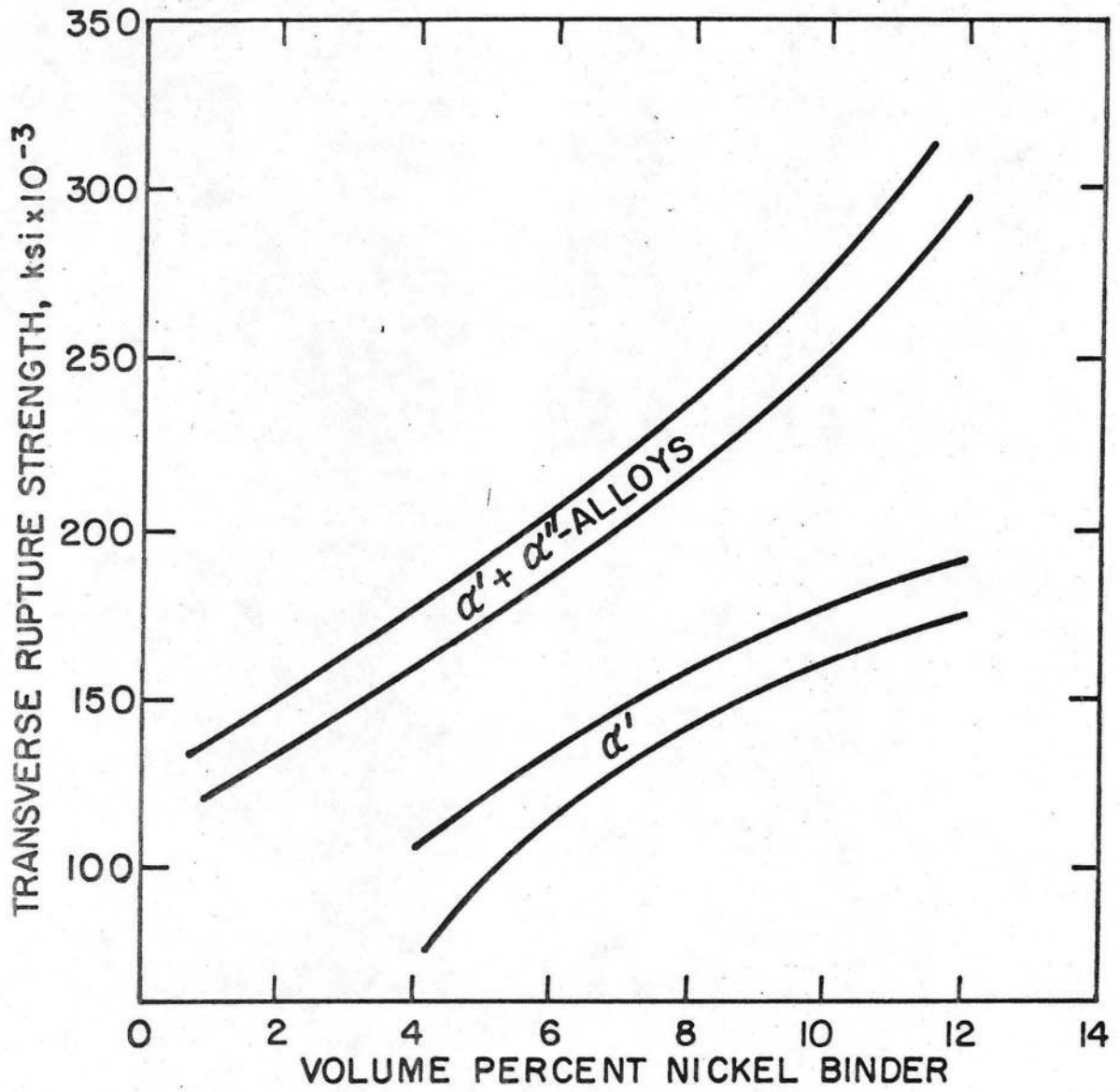
Fig. 3



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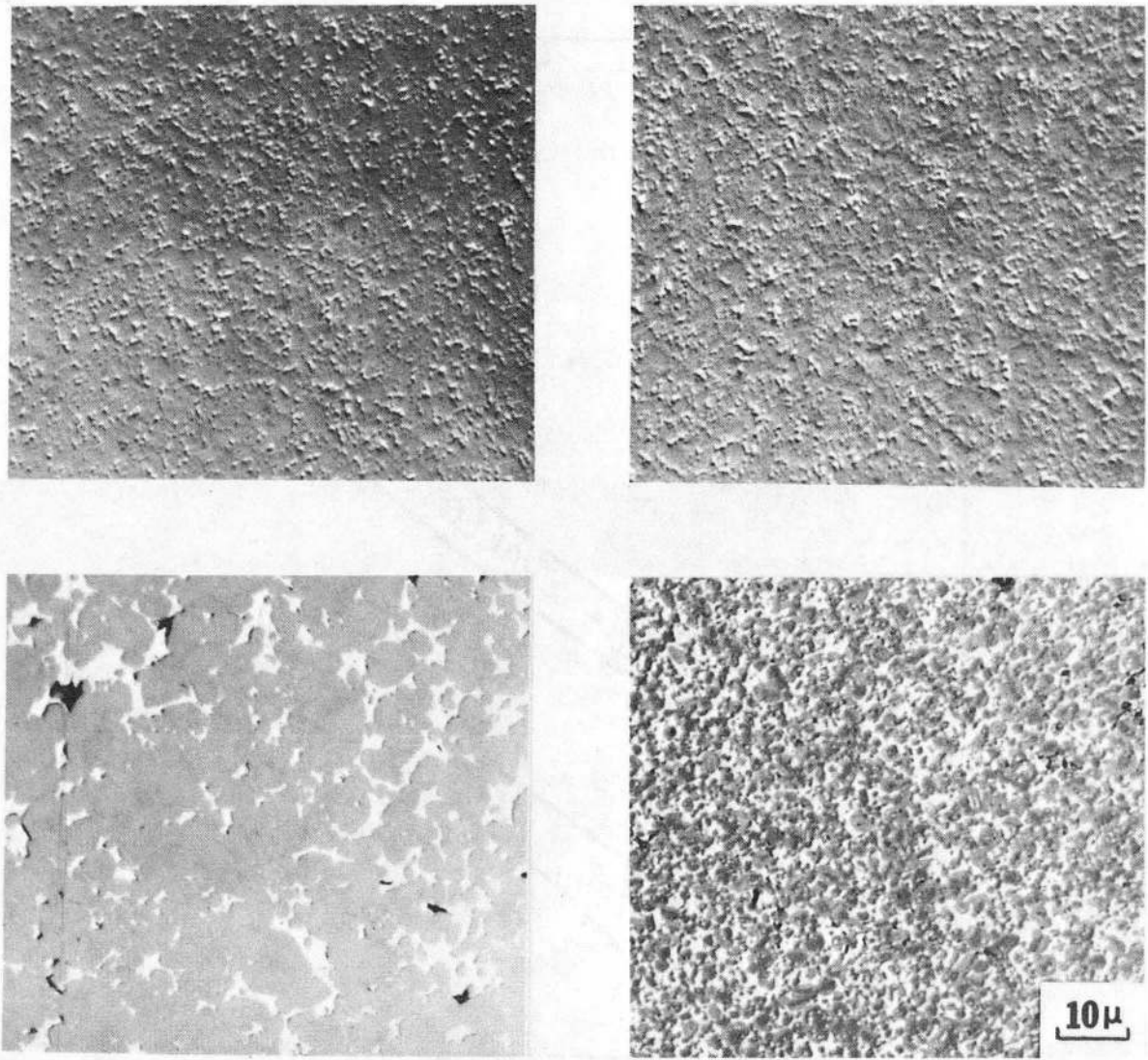
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Fig. 4



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Fig. 5



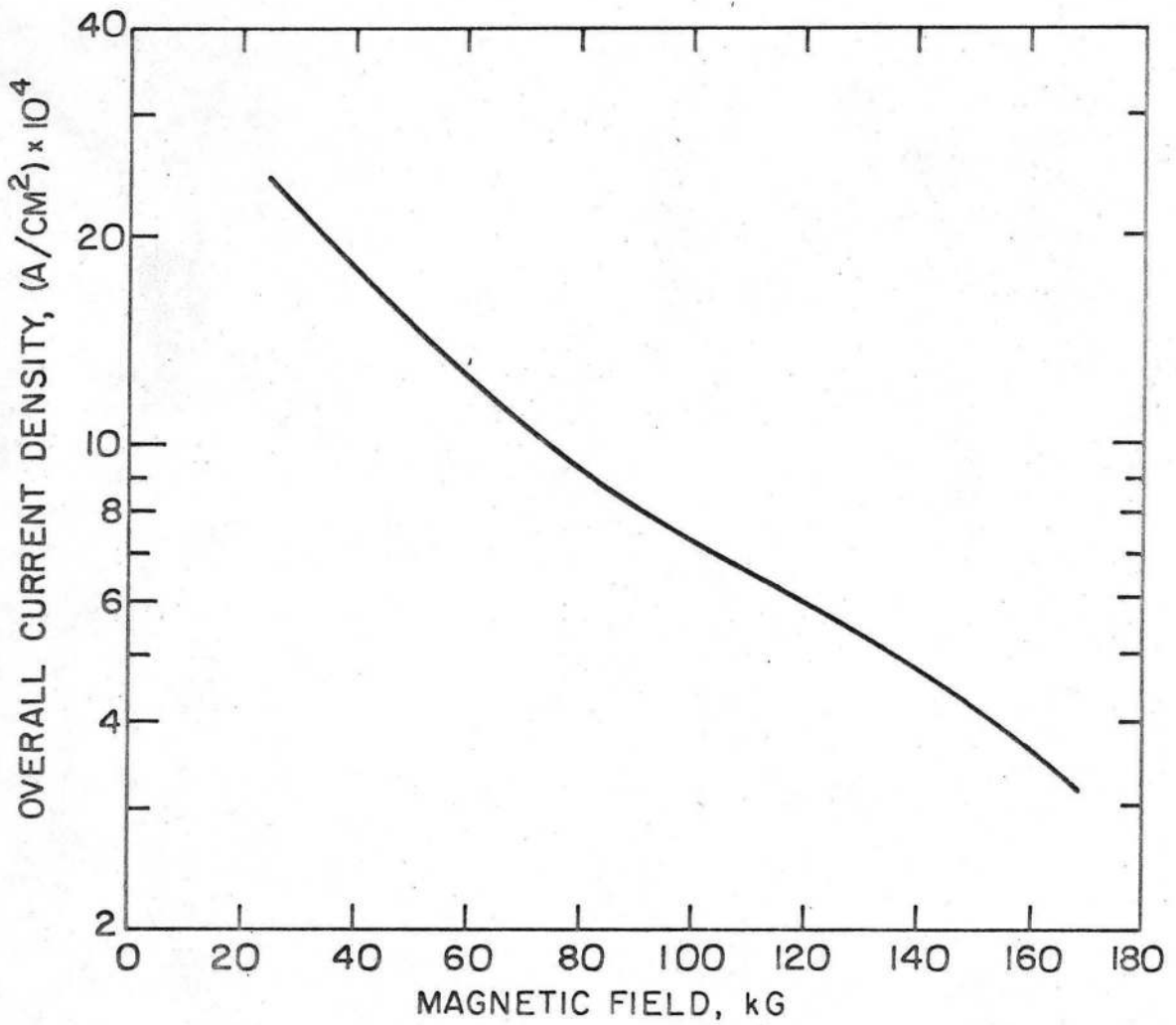
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Fig. 6



XBB 745-2980

Fig. 7



XBL 745 - 6239

Fig. 8

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