A PERSPECTIVE OF NIOBIUM IN SUPERALLOYS

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Introduction

The central objective of this paper is to characterize the metallurgical behavior of niobium as an alloying element in austenitic superalloys.   To accomplish this, we will first define, then describe superalloys in some detail as background.   Next, niobium itself will be reviewed with respect to its properties appropriate for superalloy constitution.   Then the specific function of niobium as additive to nickel, cobalt and iron-based superalloys will be established and its broad effects summarized.

According to the book, **The Superalloys,** (1) superalloys are "alloys developed for elevated temperature service, usually based on Group VIA elements where relatively severe mechanical stressing is encountered and where high surface stability is frequently required."   In present commercial superalloys it is common to find niobium present in small-to-moderate amounts. These relatively small additions have a significant contributory effect on alloy properties, yet in the technical community there has not been a directioned attempt to collate and define these effects.   Thus, this report is an attempt to accomplish this task.

Superalloys are composed **of** a group VIIIA metal alloy base (cobalt, nickel, or iron) to which are added large and varied amounts of alloying elements, ranging up to 50-60 percent of total alloy weight.   These additions modify, improve and interact with the alloy base and with each other in a very complex fashion to provide resistance to surface attack from oxidizing and hot corroding gases, and to provide an unusual level of mechanical properties.   Alloys for gas turbine service must meet stringent criteria for tensile strength and ductility, rupture and creep strength and ductility, and mechanical and low-cycle fatigue requirements, to mention only a few. Density, thermal conductivity and expansion properties are some of the physical properties usually controlled, also.

Superalloys are materials generally used to "get the most out of" high-performance equipment; they are the work horses in the hottest parts of aircraft jet engines, industrial gas turbines and very high-temperature reactor applications. Figure **1** illustrates an aircraft engine, showing a nickel-based superalloy bucket (blade) typically utilized in the turbine section of the engine. However, superalloys are also vital in high-temperature heat exchangers for energy application, in some reactors, and in a variety of other tough-service type applications.

In this paper, we will discuss cast and wrought nickel, cobalt and iron-nickel superalloys and (as a special case) eutectic superalloys. In order to consider the role of niobium most efficiently, we will cover the field in the following order; Ni-base superalloys; Co-base superalloys; Fe-Ni-base superalloys; eutectics. A more detailed discussion of superalloys as a class follows.

<u>Superalloys: Their Metallurgy and Properties</u>

A concise definition of superalloys has been given in the introduction. In this section, an attempt will be made to review the superalloy class in a very brief fashion, ⁻ yet still crack open the door into their fascinating technological detail as background for consideration of the role of niobium. This will be done by first considering a general classification which pro-vides a broad linking of application field with alloy type, then touching in turn on their chemical constitution, solid-state phase relations, metallur-gical microstructure, processing and properties.

<u>Classification</u>

Superalloys have been spawned principally by the constant and driving force of the need of aircraft jet engines to operate at higher and higher temperatures for improved efficiency and power, augmented by the demands of industrial gas turbines, heat exchangers and reactors. Superalloys can be classified in many ways, one of which is given in Figure 2, a correlation of major energy systems with alloy types (2).

<u>Chemical Compositional Characteristics and Strengthening</u>

Superalloys are most commonly considered as either cobalt or nickel-base alloys. However, significant amounts of iron have been included with nickel to reduce cost of alloys intended for larger forgings (Fe-Ni-base alloys), although in some cases the nickel dominates; this has created an iron-base series also.

Figure **3** illustrates, in broad and qualitative fashion, the general function **of** alloying elements in the group VIIIA Ni-Co-Fe bases. The compo-sitional <u>complexity</u> is obvious and Figure *4* emphasizes the point, showing that Ni-base alloy systems are the most complicated of all alloys.

Obviously, interaction between the alloying elements and alloy base, and between alloying elements also is extremely complex. However, Table I attempts some order through collation of the behavior of the major alloying element actors. One can see that mechanical properties are developed through combinations of solid solution strengthening, coherent phase precipitation,
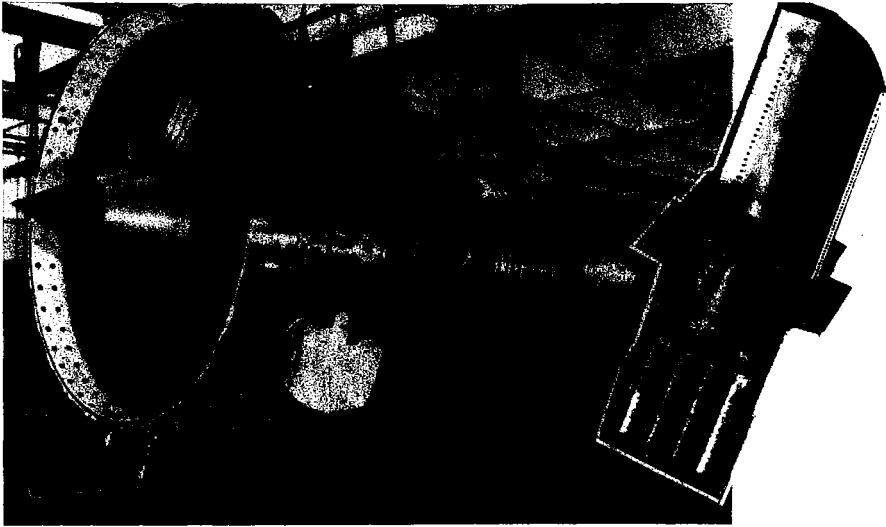
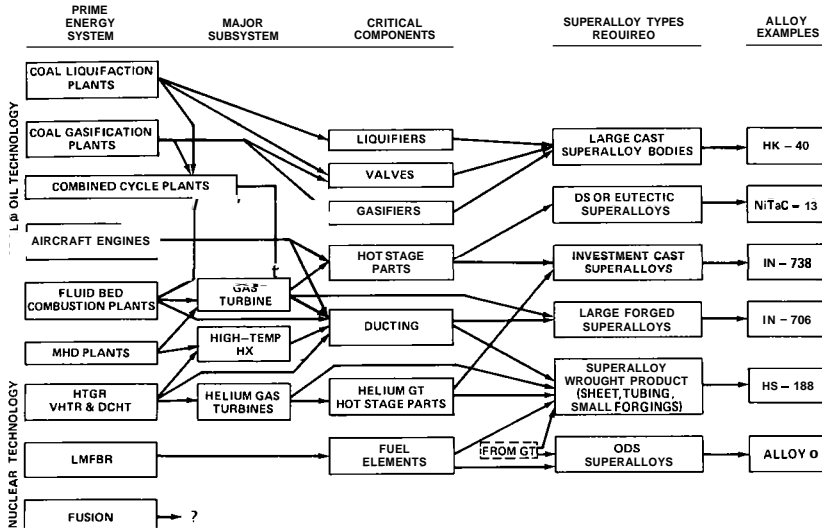Figure 1. Typical Aircraft Engine (GE-SNECMA CF-6) and Cast Superalloy Bucket (Insert).

Figure 2. A Correlation of Energy Technology, Major Plant Equipment, General Superalloy Type, and Specific Superalloy Examples.
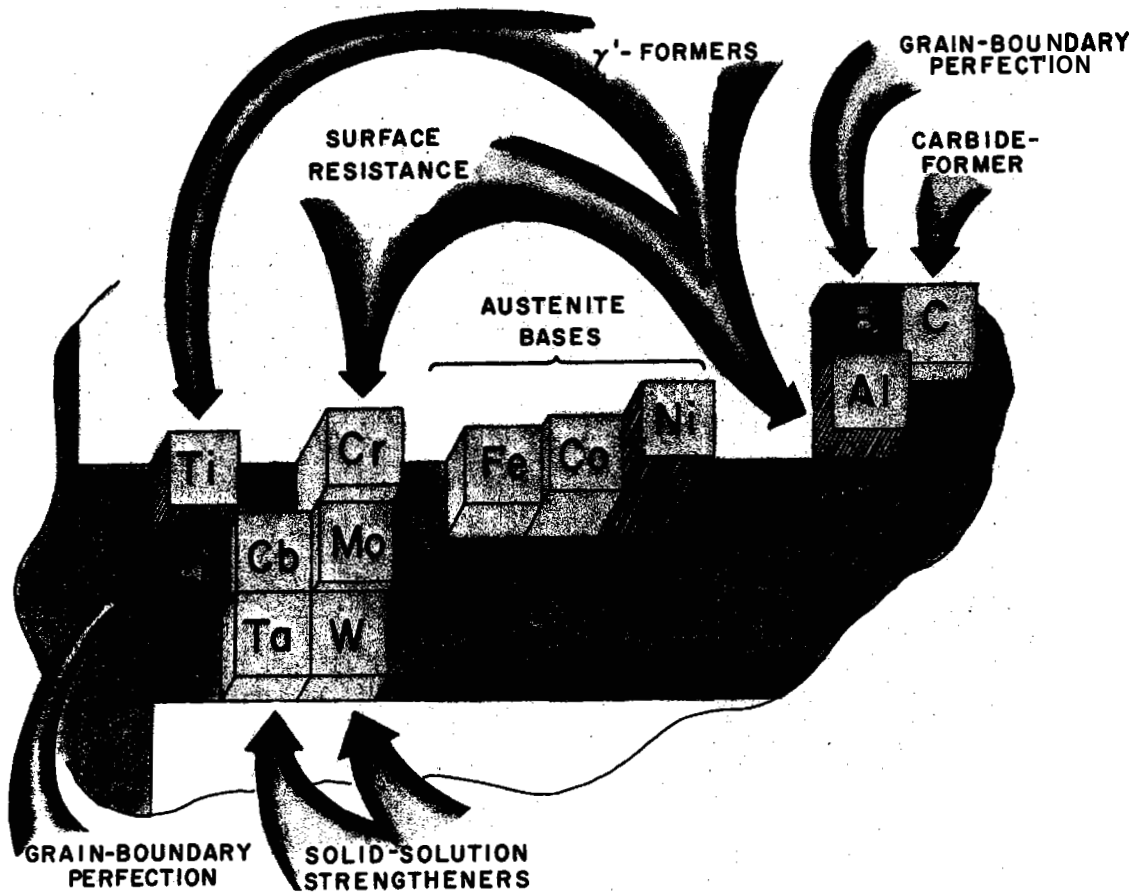
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Figure 3. Function of Elements Added for Alloying Effect in Austenitic Superalloys.

NiCrMoV	M-152	316SS	zy-II	Ti	6061	Mo-TZM	HS-188	TRW-VIA
								0.13 C
								0.13 Zr
								0.02 B
								0.5 Hf
								0.5 Re
								9.0 Ta
								0.5 Cb
								5.8 W
0.3 C	0.1 C						0.1 C	2.0 Mo
0.1 V	0.3 V	0.1 C	0.05 Ni	1.2 Mo	0.25 Cr		0.1 La	1.0 Ti
0.7 Mo	2.0 Mo	2.5 Mo	0.1 Cr	1.4 Cr	0.25 Cu	0.03 C	14 W	5.4 Al
3.5 Ni	2.5 Ni	12 Ni	0.1 Fe	1.5 Fe	0.6 Si	0.08 Zr	22 Cr	6.1 Cr
	12 Cr	17 Cr	1.5 Sn	5.0 Al	1.0 Mg	0.5 Ti		
NiCrMoV	M-152	316SS	zy-II		6061	Mo-TZM	HS-188	TRW-VIA
Fe	Fe	Fe	Zr	Ti	Al	Mo	Co	Ni

Figure 4.   Compositions of Various Alloy Groups, Showing Relative Complexity of Nickel–Base Superalloys.

carbide strengthening and grain boundary control. Some of the key precipi-
tate phases formed are also identified. It should be emphasized that Table I
is broad in its coverage and not intended to be totally inclusive.

Phase Relations

The structural matrix of all superalloys by definition is based on the
FCC γ (austenitic) lattice characteristic of Ni–, Co–, and many Fe–base
alloys. They can be considered a phase extension of the 300–Series stainless
steels. Classically, their position in the austenite field ranges back and
forth near its stability limits, depending upon the nickel, cobalt, or iron
content and the amount of counter–austenite elements added, such as BCC
chromium, molybdenum, tantalum.

Most importantly, many of these alloys are precipitation–strengthened by
the coherent FCC A_3B phase γ', formed between nickel with aluminum, titanium
or niobium. The composition is usually $Ni_3(Al,Ti,Nb)$, and the phase can
compose up to as much as 50 percent of the alloy, Phase relations for
γ' (3) are shown in Figure 5, together with a view of some typical γ' parti-
cles. Additionally, coherent phases such as γ'' (orthorhombic Ni_3Nb) can
form, and a broad range of carbides including the types MC, M_6C, and $M_{23}C_6$.
The more specific behavior of some of these species will be covered in a
detailed discussion involving niobium below.

A correlative picture of austenite phase behavior can be generated by
viewing the polar diagram of first long period elements with chromium. A
polar phase diagram is created by linking appropriate ternaries on mating
axes, and specifying a common element (such as Cr) as the focus. For super-
alloys, the first long period elements (Ni, Co, Fe, etc.) are caused to occur
in periodic order at the periphery. Fairing the ternaries allows the picture
to generate into a polar diagram (Figure 6a). It should be understood that
for superalloys this diagram refers to the FCC matrix composition only, and
not the composition of the entire alloy, including its numerous precipitate
phases.

The diagram can be tailored for greater accuracy, also. For instance, if
one utilizes Cr-15Mo as the focus instead of chromium alone, the related
group of classic Ni–base alloys Udimet–700, Rene 77, Nimonic 115, and Udimet–
500 will fall near point in Figure 6a. However, the diagram with niobium
(Figure 6b) illustrates the sharp reduction in austenite field caused by
element No. 41, and the complex series of phases then generated, –obviously
not a beneficial effect. This will be discussed later.

Table I. Summary of the Function of Alloying Elements in Superalloys.

| Metallurgical Function	Alloying Element and Phases Formed in Designated System		
	Nickel-Base	Cobalt-Base	Ni-Fe Base[a.]
Solid Solution Strengthening	Co, Cr, Mo, W, Nb, Ta	Ni, Cr, Mo, W, Nb, Ta	Fe, Cr
Coherent Phase Strengthening	Al, Ti, Mo, Nb ----------- γ'	Limited ----------	Al, Ti, Nb -------- γ', γ''
Carbide Phase Activity and Strengthening	Cr, Ti, Mo, W, Nb, Ta ----------- MC, M_6C, $M_{23}C_6$	Cr, Ti, Zr, Mo, W, Nb, Ta ---------- MC, M_6C, $M_{23}C_6$	Cr, Mo, Nb, Ti -------- MC, $M_{23}C_6$
Grain Boundary Activity	B, Zr ----------- M_3B_2	B, Zr ---------- M_3B_2	B, Zr --------
Oxidation and Corrosion Resistance	Cr, Al, Ti	Cr, Al, Y, Al	Cr, Al
Classic Alloys	Udimet 500 Inconel 738 Nimonic 80A Hastelloy X	X-40 FSX-414 MarM-509	N-155 A-286 Inconel 718 Incoloy 903

a. Either nickel or iron may predominate.
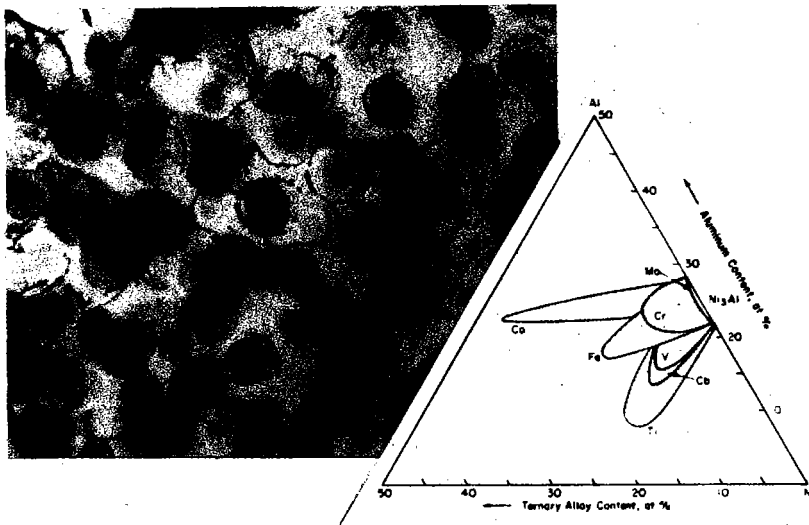
Figure 5. Ni-Al-X Phase Composition Relations, Showing
Effects of Alloying Elements on Solubilities (3).
Microstructure of γ Interacting with Disloca-
tions in Nickel Alloy U-500; 10,000X.

Microstructure

Superalloy microstructure is fascinatingly illustrative of not only the
strengthening from the variety of GCP and carbide phases present, but is the
key element in successful processing, and the prime visage tool for the great
developments in powder metallurgy and controlled solidification processing
now occurring. Unfortunately, this brief review cannot consider all this
technology so Figure 7 is given to show the classic features present in
investment-cast alloys, and Figure 8 an example for typical forged alloys
(2). The discussion below will identify additional microstructural features,
particularly where niobium is involved.

Processing

Until about 1960, superalloys consisted of but two principle classes
derived from processing, - "cast" and "wrought" - as illustrated directly
previously. In contemporary practice, castings are made by the investment
casting (lost wax) process often in vacuum. Highly complex shapes are
possible (as in the bucket of Figure 1) and are utilized to take advantage of
design factors such as air cooling in gas turbine rotating and static hard-
ware. Wrought products are produced by a variety of working techniques to
make sheet, bar, large wheels and complex parts. Precision forging is
utilized for turbine blades, but complex shape needs somewhat limit this
approach.

However, "cast" and "wrought" classes are no longer all-inclusive. We
are now in the "Age of Processing" in superalloys. Special processing
techniques are being used to extend superalloy properties to previously-
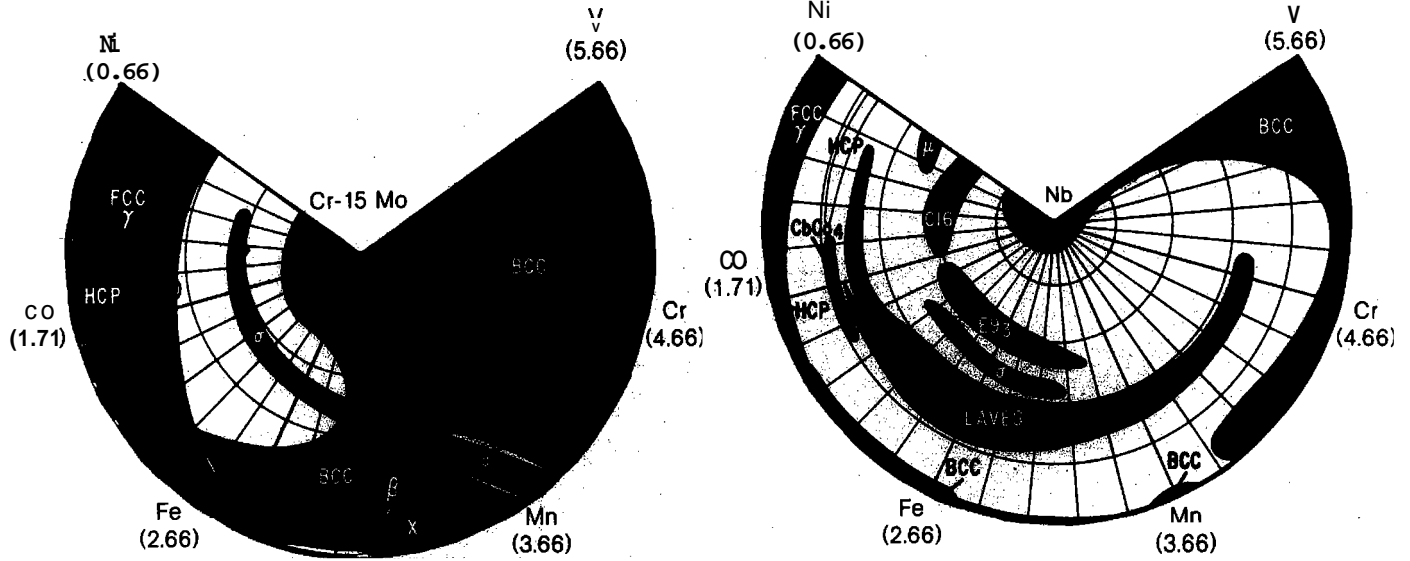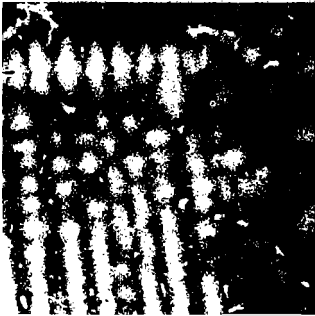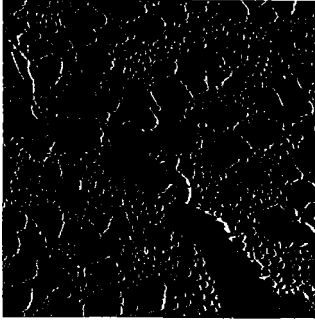unknown limits. In very brief review, some of these are:

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Figure 6. Polar Phase Diagrams for First Long Period Elements vs. Cr-14Mo (left) and Niobium (right).

A. SECTION OF INVESTMENT CASTING, SHOWING DENDRITIC STRUCTURE AND PRIMARY γ' ISLANDS. 50X

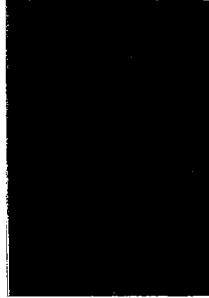B. GRAIN BOUNDARY STRUCTURE WITH CARBIDES, γ' DISPERSION, AND PRIMARY γ'. 500X

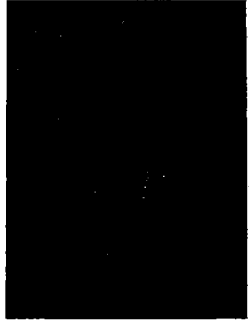C. γ' DEVELOPMENT AND CARBIDES ALONG A GRAIN BOUNDARY. 10,000X

Figure 7. Microstructure of Investment – Cast Superalloy IN-738 (2.0% Nb) at Increasing Magnification, Left to Right (2).

B. OPTIMIZED MICROSTRUCTURE FOLLOWING RUPTURE TESTING. SOLUTIONED AT 1650°F; AGED AT 1325°F AND 1100°F. 500X

C. SAME AS FIG. B. NOTE UNIFORM γ' AND GLOBULAR PHASES. 4250X

D. MICROSTRUCTURE FOLLOWING RUPTURE TESTING. SOLUTIONED AT 1800°F; AGED AT 1550°F, 1325F, AND 1150°F. 8000X

Figure 8. Microstructure of Forged Iron-Nickel-base Superalloy IN-706 (2.75% Nb) at Increasing Magnification, Left to Right (2).

o   Powder Metallurgy - to obtain fine-grain ductile structures, and
    to create oxide dispersion strengthening (ODS).

o   Micrograin Processing - where extremely fine-grained powder is used
    to generate unusual structures and ductility.

o   Directional Solidification (DS) - grains elongated to the full height
    of the part to reduce thermal fatigue initiation. DS allows strength-
    ening by eutectically-formed phases, and is becoming commercial.

o   Single Crystals - Wherein the entire complex part is one cast crystal.
    This tends to eliminate thermal fatigue failures and maximizes creep
    properties.

o   Coating and Cladding - to protect alloy surface attack from oxidation
    and hot corrosion.

   Where appropriate, these processes will be explored briefly in this text.

Properties

     Superalloys are characterized principally by high tensile and creep
properties up to greater proportions of their melting points than all other
alloy systems.   In addition, they possess good-to-outstanding surface stabil-
ity in simple oxidizing atmospheres.   Together, these characteristics have
combined to create a large group of materials which absolutely dominate high-
temperature service needs up to the 1200-1300 C (2000-2200 F) surface range.
Figure 9 illustrates these properties.   While some refractory metals have
greater strength capability, their surface stability in oxidizing atmospheres
is horrendous, prohibiting practical service.   Ultimately, a few precious
metal alloys have greater atmospheric resistance than superalloys, but these
systems are relatively weak and, of course, they are prohibitively costly.
Thus, superalloy systems posses the best combination of properties.   In point
of fact, superalloys are the only usable and durable alloys available for
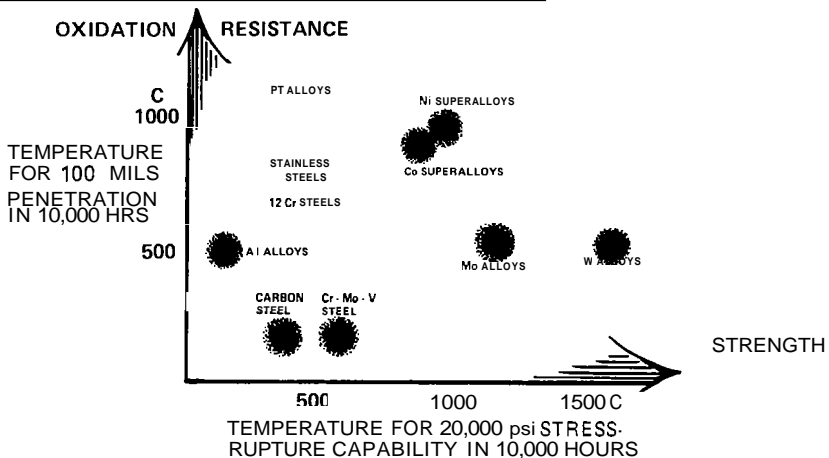high-stressed high-temperature oxidizing service.

Figure 9.   Comparison of the Surface Stability and Strength
            Characteristics of Superalloys with Other Alloy
            Systems.

In a more broad sense, of course, specific application requires many different properties, and alloy types and classes are often tailored to these needs. Alloys for gas turbine nozzle guide-vane service for instance, require creep strength, corrosion resistance and must be weldable. Alloys for aircraft engine buckets (blades) are dominated by both thermal fatigue and tensile properties, but also must be protected from corroding atmospheres. Nuclear alloys must be free of cobalt and tungsten, but still poses great creep resistance and surface stability properties in the presence of a nuclear flux.

In order to achieve all these properties, and continue to demonstrate continued improved performance, many critical component applications now utilize two or more superalloy compositions bonded together to optimize performance. The most predominant examples are alloys of great strength protected by corrosion-resistant coatings or claddings.

Niobium: Its Properties for Use in Superalloys

In the immediately preceding discussion, it was pointed out that austenitic (FCC) superalloys are strengthened principally by addition of elements in solid solution to strain the lattice, by precipitation of finely divided coherent phases such as γ' and γ'', and presence or precipitation of several types of carbide phases, usually incoherent. The behavior of alloying elements at grain boundaries and their effects on oxidation and corrosion resistance are also important, -often vital. Alloying elements are used to form special structures as well, such as in eutectic strengthening.

In this complex array **of** factors, the obvious question for us then is "What might niobium have to offer as an alloying element?"

The first consideration is a generality that hardly needs review. Niobium is a refractory metal, one of the "big four" together with molybdenum, tungsten and tantalum. All of these elements are added to one superalloy or another, singly or multiply, where they strengthen the alloys by either carbide phase formation and by solid solution strengthening or by both. With that start, a review of the properties of niobium pertinent to superalloy use follows. Niobium will be discussed with considerable reference to other refractory metals.

Periodic, Atomic and Physical Properties

Figure 10a shows niobium (columbium) in its periodic system relationships. It is apparent that niobium, positioned in Group VA, is of lower modulus and melting point than Mo, W, or Ta. It is also less dense. As a BCC metal, it forms continuous solid solutions with many other BCC metals, including β-Ti. However, for effective solid-solution strengthening, high modulus and high melting point are desirable. Since niobium has relatively low melting point and modulus (Figure 10c, Table II), it would not be expected to be as effective as the other refractory metals under equivalent alloying conditions. Atom size (Figure 10d) is another factor in solid-solution strengthening, effecting relative solubility. Table II identifies the solubility limit of the major refractory metals in superalloy matrixes, showing niobium to be the most limited. The atomic mismatch (calculated from Figure 10) confirms that niobium creates too much mismatch to enter solution extensively. Figure 6 shows the strong effect of niobium to restrict the extent of austenite, and its great tendency to form a variety of phases with First Long Period elements.

Figure 10(a). Periodic System of the Elements.
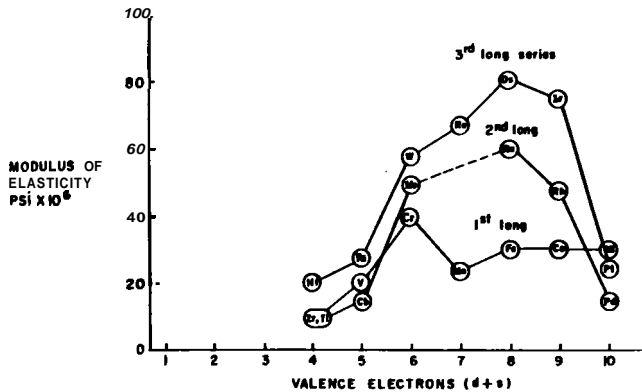
Figure 10(b). Elasticity Moduli of the Three
Long Periods of Elements.

Figure 10. Atomic and Physical Properties and Relationships
of Niobium (Columbium) to Other Elements.
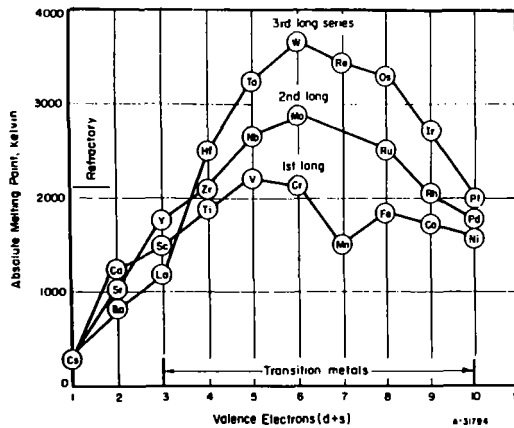
Figure 10(c). Melting Points of the Three Long Periods of Elements.

Figure 10(d). Atomic Radii of the Three Long Periods of Elements.

Figure 10. Atomic and Physical Properties and Relationships
of Niobium (Columbium) to Other Elements.

Table II. Factors Relating to Potential Solid Solution Strengthening by
Niobium and Other Refractory Metals in Austenitic Matrices.

	Solvate Element			
	Nb	Ta	Mo	W
Solubility Limit w/o, at 1000–1200 C				
IN: Fe	2	2	3	2
Fe-20Cr	10	NA	10	25
co	4	5	10	13
Co-20Cr	3	7	13	19
Ni	10	12	26	17
Ni-20Cr	7	12	23	33
Atom Size Mismatch, %				
VS: Fe	10.8	10.6	5.7	6.3
co	14.0	13.8	8.8	9.4
Ni	14.7	14.4	9.4	10.0
Elasticity Modulus, E				
psi x 10^6	15	27	50	50
n/m^2 x 10^6	100	185	345	345

Chemical and Phase-Forming Properties

The periodic system (Figure 10a) shows that niobium is the most electro-positive of the refractory metals. This indicates niobium could have a strong affinity for formation of A_3B-type GCP phases. Indeed, discussion of nickel alloys below will show that niobium substitutes for aluminum in γ' (Ni_3Al) in a very similar fashion as does titanium. In fact, its behavior in this respect is the most complex of any element added to superalloys. Niobium promotes at least 3 different strengthening phases (MC carbides, γ', and γ'') and clearly is the unique driver in formation of the γ'', the BCT Ni_3Nb strengthener in many iron-nickel forging alloys.

The electropositive nature of niobium also indicates formation of rela-tively stable covalent - and ionic-bonded compounds such as carbides, ni-trides, and oxides, affecting in turn carbide stability, and also having relationships to oxidation behavior. Figure 11 summarizes stability behavior of these compounds.

Niobium Potential; Summary

As might be viewed by a superalloy development metallurgist from consid-eration of its elemental properties alone, the <u>potential</u> of niobium can be summarized as follows:

o   Its moderate melting point and low modulus suggest little or no specific potential as a solid-solution strengthener. Further, its large atom diameter mismatch suggests limited solubility potential in systems of interest.

o   Electropositive position in the periodic systems predicts formation of rather stable carbides and nitrides.

o   However, low density (for a high-melting metal) means niobium is a desirable alloying addition for rotating components.

o   Atom size and electropositive position connotes potential solubility in established GCP phases, (i.e., - Ni_3Al) and as a GCP-phase generator,

o   Moderate oxide thermodynamic stability identifies that effects on alloy oxidation and corrosion resistance may be expected, with niobium competing for surface oxide formation.

Metallurgical Behavior of Niobium in Superalloy Systems

The role of niobium will be discussed by consideration of nickel-base, cobalt-base, and iron-nickel-base alloys in turn, followed by a discussion of eutectics and of its effect on oxidation and corrosion.

Nickel-Base Alloys

A significant number of conventional nickel-base superalloys contain niobium as an alloying element. Niobium is particularly apparent in nickel-base casting alloys, where about 50 percent contain about 1.0 to 2.5 percent.

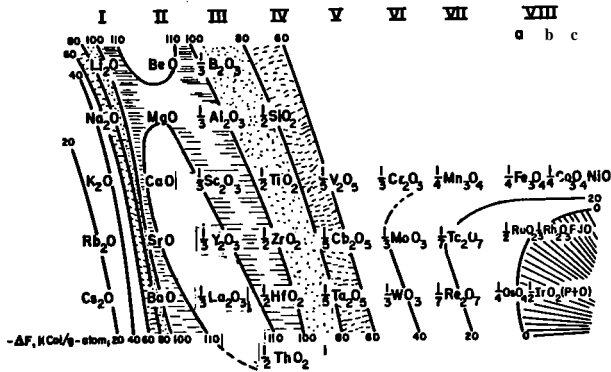Figure 11(a). Stability Relationships of Transition Metal Oxides
(solid lines are those of constant standard free
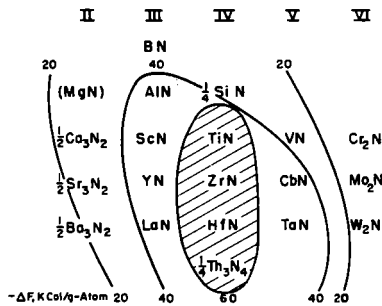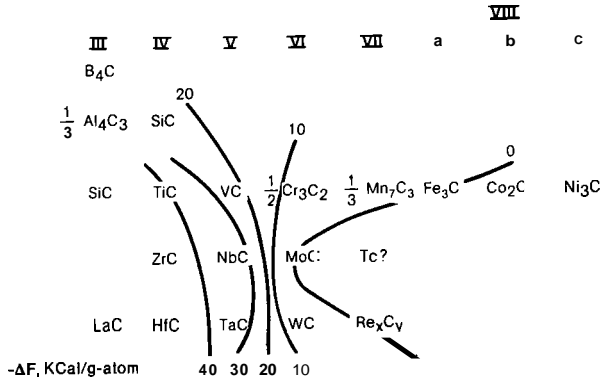energy of formation from the elements).

Figure 11(c). Stability Relationships of Refractory
Nitrides (room temperature).

Figure 11. Stability Maps of Niobium with Co-valent and Ionic Bonding
Elements (Solid Lines Are Those of Constant Standard Free
Energy of Formation from the Elements).

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A lesser proportion of wrought nickel alloys contain niobium, but amounts up to 6 percent are used, and its function is more broad and essential. Table III gives a representative list of these nickel alloys, together with a selection of contemporary alloys of importance that do not contain niobium, for comparison purposes.

Inspection of the alloy list does not reveal any obvious pattern (to this writer) of attention to niobium; it appears to have been utilized in a rather random manner in nickel alloy development. The objective here then is to determine the function of niobium in nickel alloys. Since strengthening is achieved principally by atom, particle, or defect interaction with disloca-tions through solid solution, hard particle (carbide or boride) and coherent particle effects, niobium's role will be considered for each of these latter effects in turn.

However, there are two specific phenomena of major consequence wherein niobium is a key element which must be first clarified. Niobium utilized in intermediate–temperature high–strength Fe-Ni forging alloys, such as IN-718, provokes a major strengthening effect, whereby a precipitation of γ " BCT (Ni_3Nb) occurs as a major strengthening phase. This occurs only in alloys of mixed iron and nickel content. For our purposes here, this effect is in-cluded under Fe-Ni-base alloys. Secondly, niobium plays a key role in certain eutectics, such as $\gamma-\gamma'-\delta$ or CoTaC-744; that effect is also discussed separately.

Solid Solution Strengthening. As is well known, introduction into an alloy lattice of foreign atoms can create strain by lattice expansion which interacts with dislocations. Periodic valency effect (N) can create strengthening effects, also. Altogether key factors related to the effec-tiveness of the substitute atoms are atom size mismatch with the lattice, elasticity modulus, electrical differences, and/or the effective amount of the solution element hosted by the lattice.

As summarized in Table II, niobium does not dissolve extensively in nickel, Ni-Cr or other austenitic-base systems. It is limited to the range 5–10 percent in most cases, and to ~7 percent in Ni-20 Cr at 1200 C (2200 F). Atom size mismatch, ranging from 10–15 percent, is too large to allow greater solubility. However, the large mismatch does suggest the specific effect per niobium atom might be significant. The periodic valence position of niobium at N_v = 5.66 suggests a strong relationship with stacking fault energy.

The behavior of niobium in Ni-base solid solution has been investigated and reported by Gua and Ma (4). Their pertinent study of the effect of niobium in a Ni-20Cr-base alloy is the first broad attempt at a definitive work. A vacuum-melted Ni-20Cr base alloy, mildly strengthened by γ' and carbon was alloyed with eight levels of niobium, from 0.5 to 2.46 w/o. The alloys were fabricated to rod and heat treated. The phases formed were separated and evaluated for niobium content, while lattice spacing and long-range order effects were studied by x-ray. Some physical and mechanical properties and microstructural studies also were reported.

Table IV summarizes completely the analytical results obtained; in connection with solution strengthening it shows the following:

o Slightly over half of the niobium concentrated in the FCC γ matrix. (Partitioning to γ, γ', and carbides is shown in Figure 12a).

Table III. Compositions of Selected Nickel-Base Superalloys With and Without Niobium.

Alloy (a)	C	Cr	Ni	Fe	Co	Mo	W	Cb	Ta	Ti	Al	B	Zr	Other	Form
Alloy 713C	0.12	12.5	Bal	--	--	4.2	--	2.0	--	0.8	6.1	0.012	0.10	--	C
Alloy 713LC	0.05	12.0	Bal	--	--	4.5	--	2.0	--	0.6	5.9	0.01	0.10	--	C
Astroloy	0.06	15.0	Bal	--	15	5.25	--	--	--	3.5	4.4	0.03	--	--	W
B-1900	0.1	8.0	Bal	--	10	6.0	0.1	0.1	4.3	1.0	6.0	0.015	0.08	--	C
Hastelloy alloy X	0.10	21.8	Bal	18.5	1.5	9.0	0.6	--	--	--	--	--	--	--	W
IN-I00	0.18	10.0	Bal	--	15.0	3.0	--	--	--	4.7	5.5	0.014	0.06	1.0V	C
IN-162	0.12	10	Bal	--	--	4.0	2.0	1.0	2.0	1.0	6.5	0.020	0.10	--	C
IN-738	0.17	16	Bal	--	8.5	1.75	2.6	0.9	1.7	3.4	3.4	0.01	0.10	--	C
IN-597	0.05	24.5	Bal	--	2.0	1.5	--	1.0	--	3.0	1.5	0.012	0.05	--	C
Inconel 625	0.05	21.5	Bal	2.5	--	9.0	--	3.65	--	0.2	0.2	--	--	--	W
Inconel X-750	0.04	15.5	Bal	7.0	--	--	--	1.0	--	2.5	0.7	--	--	--	W
Inconel 751	0.05	15.5	Bal	7.0	--	--	--	1.0	--	2.3	1.2	--	--	--	W
MarM-200	0.15	9.0	Bal	--	lo	--	12.5	1.8	--	2.0	5.0	0.015	0.05	--	C
MarM-211	0.15	9.0	Bal	--	10	2.5	5.5	2.7	--	2.0	5.0	0.015	0.05	--	C
MarM-246	0.15	9.0	Bal	--	10	2.5	10.0	--	1.5	1.5	5.5	0.015	0.05	--	C
Mar M-421	0.15	15.5	Bal	1.0	10	1.75	3.5	1.75	--	1.75	4.25	0.015	0.05	--	C
MarM-432	0.15	15.5	Bal	2.0	20	--	3.0	2.0	2.0	4.3	2.8	0.015	0.05	--	C
Rene 95	0.15	14	Bal	--	8.0	3.5	3.5	3.5	--	2.5	3.5	0.01	0.05	--	W
SEL	0.08	15	Bal	1.0	26	4.5	--	--	--	2.4	4.4	0.015	--	--	C
SEL-15	0.07	11	Bal	--	14.5	6.5	1.5	0.5	--	2.5	5.4	0.015	--	--	C
TAZ 8A	0.125	6.0	Bal	--	--	4.0	4.0	2.5	8.0	--	6.0	0.004	1.0	--	C
TRW 1800	0.09	13.0	Bal	--	--	--	9.0	1.5	--	0.6	6.0	0.07	0.07	--	C
TRW 1900	0.11	10.3	Bal	--	10.0	--	9.0	1.5	--	1.0	6.3	0.03	0.10	--	C
TRW VIA	0.13	6	Bal	--	7.5	2.0	5.8	0.5	9.0	1.0	5.4	0.02	0.13	0.5 Re, 0.4 Hf	C,W
Udimet 500	0.08	19	Bal	--	18.0	4	--	--	--	3.0	3.0	0.005	--	--	--
Udimet 700	0.07	15	Bal	--	18.5	5.0	--	--	--	3.5	4.4	0.025	--	--	C,W
Waspaloy B	0.07	19.5	Bal	2.0	13.5	4.3	--	--	--	3.0	1.4	0.006	0.07	--	W
Nimonic 80A	0.06	19.5	Bal	--	--	--	--	--	--	2.4	1.4	0.004	0.06	--	W
Nirnonic 115	0.15	14.5	Bal	--	13.2	3.3	--	--	--	3.7	4.9	0.16	0.04	--	W

Table IV.   Niobium Behavior in Experimental Ni–Base Austenitic Superalloys Guo and Ma *(4)*.

No.	Nb Content in the alloys wt%	γ' Content Wt%						Carbide Content Wt%				
		Ni	Cr	Nb	Al	Ti	Total	Ni	Ti	Nb	Cr	Total
1	--	9.46	0.222	--	0.666	1.387	11.74	< 0.01	0.023	--	0.520	0.543
2	0.5 I	9.40	0.467	0.138	0.710	1.404	12.12	0.01	0.066	0.103	0.168	0.337
3	1.00	10.40	0.532	0.291	0.710	1.427	13.36	0.01	0.063	0.140	0.153	0.356
4	1.24	10.75	0.554	0.469	0.702	1.475	13.95	0.0 I	0.055	0.181	0.126	0.362
5	1.53	10.80	0.55 I	0.485	0.705	1.476	14.02	0.0 I	0.054	0.170	0.129	0.352
6	1.72	10.90	0.547	0.529	0.700	1.48 I	14.15	0.0 I	0.069	0.246	0.128	0.443
7	1.94	11.70	0.608	0.628	0.710	1.489	15.14	0.01	0.06 I	0.246	0.122	0.429
8	2.46	11.80	0.580	0.739	0.745	1.522	15.39	0.0 I	0.058	0.30 I	0.122	0.48 I

| No.	Lattice Spacing a		Mismatch ε, %	Particle Radius r, Å	Long Range Order Parameter, S	Volume Fraction of γ' %	Shear Modulus, G N/mm^2
	γ'	γ					
1	3.5906	3.5634	0.76	84.5	0.79	12.56	81.7×10^3
2	3.5933	3.5666	0.75	85.5	0.82	12.98	82.4×10^3
3	3.5951	3.567 I	0.78	98.5	0.85	14.18	82.8×10^3
4	3.5965	3.5674	0.8 I	101.5	0.86	14.85	83.8×10^3
5	3.5967	3.5682	0.80	98.5	0.87	14.84	83.8×10^3
6	3.5970	3.5701	0.75	98.5	0.92	14.95	84.2×10^3
7	3.5976	3.5701	0.77	105	0.95	15.91	--
8	3.5987	3.57 13	0.77	113	1.01	16.21	85.1×10^3
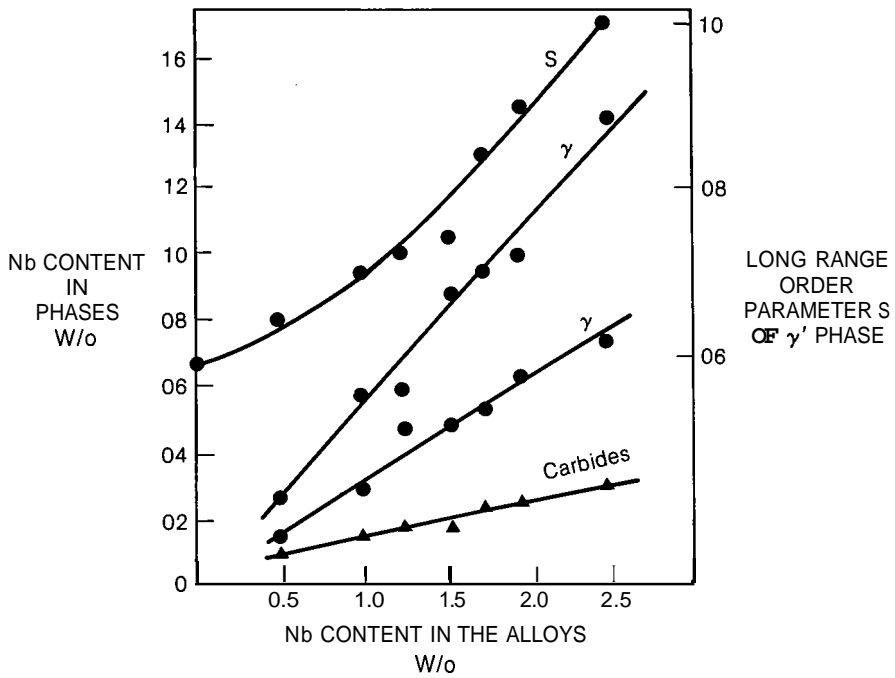
Figure 12. Partitioning of Niobium to γ, γ', and Carbides
in Ni-base Alloys with 0–3.0% Niobium. After
Gua and Mi (4).

o Niobium increased the lattice spacing of γ slightly.

o Lattice mismatch of γ to γ' increased from 0.76 at 0 percent Nb to 0.81 at 1.24 percent Nb; the mismatch then declined to nearly 0.76 at 2.5 percent Nb.

o Alloy shear modulus increased from 81.7 x 10^3 N/mm^2 to 85.0 x 10^3, –an increase of about 4 percent.

From these data, it is obvious that niobium has a definite solution strength-ening effect', and also generates significant mismatch effects between the matrix and γ'. The authors estimated lattice distortion should increase the yield strength by 44 N/mm^2 ($\sim$ 6,300 psi), one-third of the total yield strength gained. Electronic effects were not discussed.

The question still remains as to whether useable solid strengthening effects continue up to the solubility limit of about 7 percent Nb, - but it may be a moot point. The most useful effect from niobium is in carbide and coherent phase strengthening, as discussed subsequently, and effects in solution relate principally to effect on coherent phase mismatch.

Carbide Strengthening. Depending upon carbon and alloy content, a relatively complex series of carbides can be found in nickel superalloys. Their composition varies over a range from MC (such as TiC) through M_2C and $M_{23}C_6$ to M_6C. These carbides react constantly with each other and with the alloy matrix in heat treatment and in service. They provide a multitude of useful services in the alloys, including at least:

o Structure refinement during cooling from heat treatment or during fabrication.

o Grain strengthening through matrix precipitation at structural asper-**sions.**

o Grain boundary "locking" to prevent slip.

o General dislocation generation.

Among the carbides, the MC form is usually found profusely in early alloy history. During alloy thermal exposure the MC usually degenerates according to the reaction (5):

$$MC + \gamma \rightarrow M_{23}C_6 + \gamma'$$

(1)

The $M_{23}C_6$ can be located at grain boundaries, sometimes with a strong tough layer of γ' formed over it. An example of this reaction history in alloy 713C (2.0% Nb) is shown in Figure 13, taken from the classic work of Mihalisin, et al (6).

Niobium is important in this reaction, since it partitions to the MC carbides in favored fashion and is believed to be instrumental in helping control the stability (i.e., - reduces reaction rate) of the MC. Decker and Bieber (7) have analyzed MC carbide in Inco-713C to be $(Nb_{0.40}Ti_{0.09}Cr_{0.33}Mo_{0.18})C$, showing the dominant role niobium can play. Beattie (9) has identified that the stability of MC carbides varies as follows:
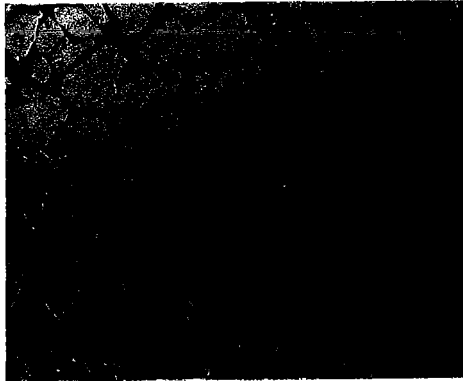
a.   As Cast; MC Carbide Particle

b.   Alloy Exposed at 1040°C (1900F) for 1000 Hrs. Showing Near-Complete MC Solution, with Surrounding $M_{23}C_6$ and γ' Formed
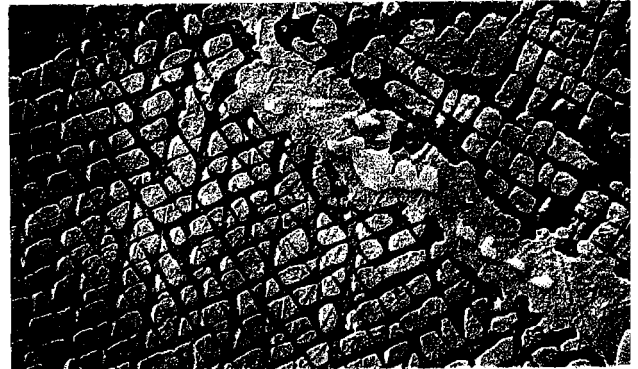

c. $M_{23}C_6$ and γ' Formed at Grain Boundary

Figure 13.   Decomposition of NbC in Alloy 713C (2.0% Nb) During Thermal Exposure, Showing Generation of $M_{23}C_6$ at Grain Boundaries. All Structures at about 10,000X. Adapted from Studies by Mihalisin, et al. (6).

(most stable) TaC-NbC-TiC-VC (least stable)

Also, when molybdenum enters the MC structure, - viz. (Ti, Mo)C, - it de-creases the stability of the TiC. Conversely, it is generally held that both tantalum and niobium stabilize MC carbide, decreasing the tendency to pursue reaction (Equation 1). This latter fact was first mentioned by Harris and Child (9) who in a detailed study of carbide-forming elements in Fe-Ni-base alloys (discussed subsequently) concluded that niobium not only formed profuse stable carbides but singularly depressed formation of chromium carbides (i.e. , $M_{23}C_6$). Further, Lund (10) reports that niobium appears to stabilize MC more strongly than tantalum. In development of alloys such as MM-200, niobium created such a stable MC carbide, viz., (Nb, Ti)C, - that reaction (Equation 1) could not proceed at all. In these cases, tantalum was added to reduce the MC stability, since (properly controlled) the reaction is considered essential for many alloys.

Certain other high-niobium alloys (such as MarM-421 and Inco-713C) show pronounced degeneration of MC (7), while some non-niobium alloys (IN-792) generate very stable MC carbides. In those cases where NbC does form and later decompose, it is highly possible that, like titanium, the niobium helps generate more γ' in the alloy through reaction (Equation 1), which can be written to include niobium approximately as follows:

$$NbC + (Ni,Cr,Al) + Cr_{23}C_6 + Ni_3Nb$$

(2)
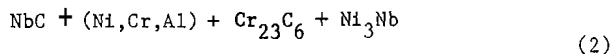
In the report of Gua and Ma (4) 15-20 percent of the niobium (Table IV) partitioned to the carbide phase. While the specific type of carbide was, unfortunately, not reported, its composition suggests an MC structure.

Coherent Phase Strengthening. As discussed near the beginning of this paper, the most significant single metallurgical strengthening phenomenon in superalloys is precipitation strengthening from the FCC-GCP phase γ', based on the composition Ni_3Al. Microstructural views of two alloys with γ' con-taining niobium are shown in Figure 14 (see also Figure 13). Gamma prime causes strengthening through generation of coherency strains with the lattice, and effects APB energy in dislocation cutting; strength of the γ' and the γ , size of the γ' and diffusivity of the γ and γ' are significant factors. Importantly, γ' forms a broad range of composition and accepts elements such as chromium and cobalt in substitution for the nickel, and titanium and niobium for the aluminum.

Superalloy metallurgists have found that additions of titanium and niobium to alloys increase the amount of γ' (there is always sufficient nickel) and change its stability characteristics as well. Guard and West-brook (3) (Figure 5) have shown the liberal amount of titanium and niobium which can substitute for aluminum. In fact, one can substitute titanium for nearly 75 percent of the aluminum, still retaining γ'. Niobium also dissolves extensively in γ', increasing the γ' volume fraction in alloys such as SEL-15, MarM-200, IN-713C and probably increases γ' solution temperatures as well (12). Mihalisin (7) analyzed γ' in 713C (Figure 13) showing the following composition $(Ni_{.98}Cr_{.02}Mo_{.004})_3(Al_{.71}Nb_{.10}Ti_{.05}Mo_{.04}Cr_{..10})$. Thus, niobium accounted for about 10 percent of the γ' precipitate on an atom concentration basis.

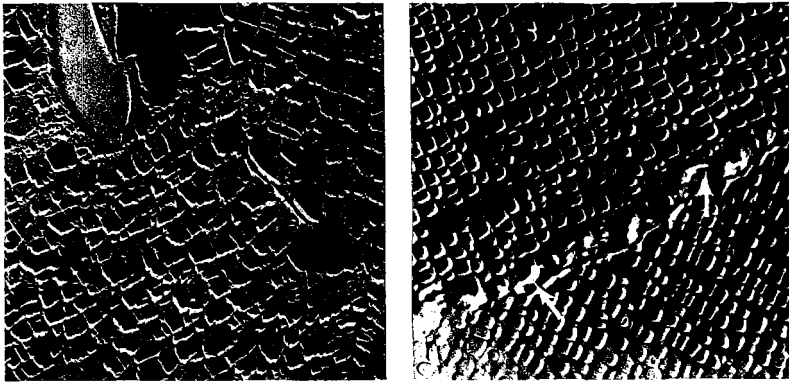Figure 14(a). Alloy MarM421 (2.3% Nb).   Figure 14(b). Alloy SM–200 (2.0%
Heated at 87 C (1600F)   Nb). As cast. 5500X.
for 1000 Hours. 4250X.   After Lund.
After Ault and Donachie (11).

Figure 14. Examples of γ' in Ni–base Alloys Containing Niobium.

Evaluation of a series of superalloys (13) showed niobium could reach 3
percent of the whole (12% of Al). While niobium did not increase γ' hardness
at room temperature, it could be a significant strengthener at high tempera-
tures (3). Further, Thornton, et al (14) have demonstrated specifically
(Figure 15) that niobium (and titanium) doubled the flow strength of γ' it-
self at useful temperatures, –600–900 C (1100–1650 F).

The study of Gua and Ma is further instructive here, also (Table IV) (4).
They found that:

o   Niobium concentrated in the γ' in approximately 2:1 ratio to the
    matrix

o   As niobium content in the alloy increased from 0 to 2.5 percent, the
    amount of γ' increased 3.7 percent n the alloy, and the volume frac-
    tion of γ' increased 30 percent, – from 12.56 to 16.21.

o   Lattice mismatch with γ increased to 0.8, then decreased to near-
    original at 0.77.

Thus, niobium significantly increases the amount of γ'. Further, the niobium
in the alloy matrix decreased aluminum and titanium solubility, allowing
still more γ' to form.

Gua and Ma also evaluated the effect of niobium on the coherent strain
field, and pointed out that while the YS increment due to coherent strain is
large, lattice mismatch change caused by the niobium is not significant in
increasing strengthening through coherent strain. However, utilizing the
value of long–range order determined, – which increased with increasing
niobium, – the APB energy was calculated and found to increase by about 60
percent. A yield strength increment calculation showed up to about half of
the gross alloy yield strength factor was due to this factor.

Nickel Alloy Summary. The significant strengthening effects of niobium
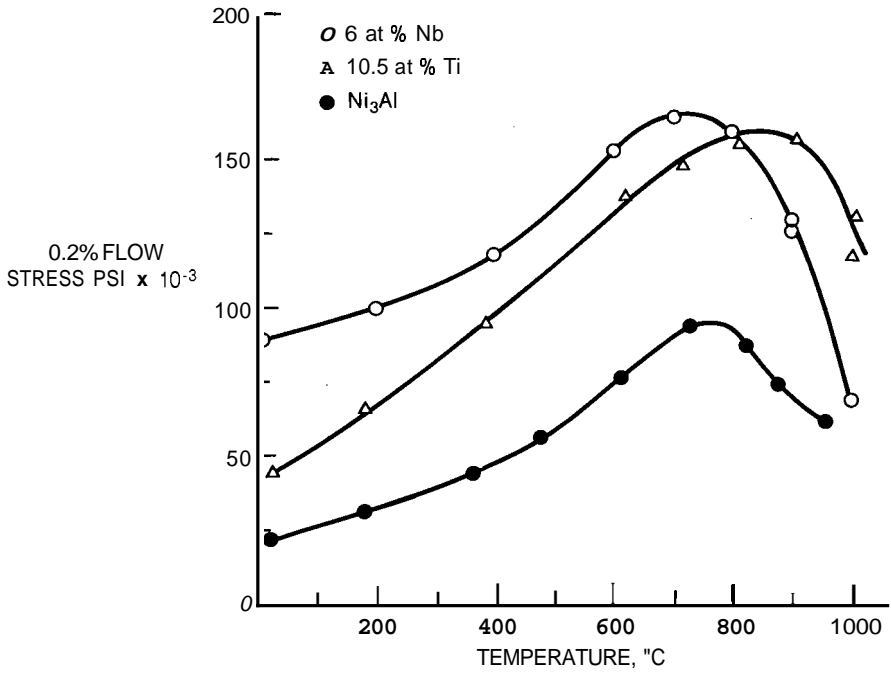in nickel–base superalloys appear to be as follows:

Figure 15. Effect of Alloying on Flow Stress of γ'.
After Thornton, et al. (14).

o   Niobium concentrates in γ', increasing volume fraction significantly

o   In γ', niobium increases the APB energy, increasing resistance to dislocation cutting, ‒ and thus increases high‒temperature strength.

o   Niobium reacts with carbon to form a very stable MC; it thus **can** be utilized to control the MC degeneration reaction (Equation 1).

Cobalt‒Base Alloys

   Niobium has been utilized as a strengthener in several commercial cobalt‒base superalloys. Analysis of its behavior is relatively simple compared to that in nickel or Ni‒Fe‒base alloys, since coherent GCP‒type phases (such as Ni_3Al) are not formed usefully. In commercial cobalt superalloy use, it appears that niobium's role is principally that of only solid‒solution strengthener or a carbide‒former. Nonetheless, niobium has been studied intensively as a potential generator of GCP‒type phases, as will be discussed below.

   Table V identifies several cobalt‒base alloys containing niobium, as well as several that do not; the latter are for baseline comparison. While not extensive in variety, 10,000‒20,000 tons of these alloys are utilized annually in industrial gas turbines, aircraft engines, furnace components, and other applications. *X-40,* WI‒52, and *FSX-414* are among the most voluminous of all superalloys cast, and S‒816 one of the earliest. Historically, investment‒cast cobalt superalloys were the first successful American jet engine alloys.

   In general, these alloys are cast readily in air or vacuum to complex shapes, possess useful creep strength to higher temperatures than most con‒ventional nickel‒base alloys, and offer excellent hot‒corrosion resistance. Niobium content ranges from about **2.0** percent to **4.0** percent in typical alloys. The behavior of niobium will be discussed by strengthening function below.

   Solid‒Solution Strengthening. Most of the cobalt‒base alloys contain several types of refractory metals. These form stable carbides early in the alloy freezing process, but are sufficiently in excess for significant solid‒solution strengthening effects also to be apparent. **An** important exception may be the alloy UMCo‒51, in which most of the niobium is present only as a carbide.

   Detailed examination of the behavior of niobium in solid‒solution strength‒ening appears limited. Solubility limits in Co‒Cr alloys appear to be about 3 percent at 1000‒1200 C (1800‒2200 *F),* Table II. This is the lowest of the group Mo, **W,** Ta, and Nb. Nb‒Co atom size mismatch is about **14** percent, ‒ much too great for extensive solutioning (Figure 11). Further, the elastic modulus (Figure 10) is low, ‒ about 14×10^6 compared to 30×10^6 for cobalt. All of these three factors are sufficient to predict poor solution‒strengthen‒ing effects. In fact, molybdenum and tungsten (and even tantalum) are much more effective solution strengtheners in cobalt. Niobium has a much more significant role in these alloys as a carbide‒forming element.

   Carbide Strengthening. As in other austenitic systems, niobium combines to form strong, stable carbides in cobalt. A prime example is S‒816, where niobium is the principal element reacting to form the primary carbide, NbC; NbC in **S‒816** is stable up to 1200 C **(2200 F),** where it is only very slightly soluble. **An** intermediate carbide, of the M_6C type is formed also, and

Table V.   Compositions of Cobalt-Base Superalloys With and Without Niobium.

	Composition, wt%											
Name or Tradename	C	Cr	Ni	Mo	W	Nb	Ta	Ti	B	Fe	Other	Alloy Type
S-816	0.38	20	20	4	4	4	--	--	--	4	--	Wrought
WI-52	0.45	21	--	--	11	2	--	--	--	2	0.25 Mn	Cast
UM Co-51	0.3	28	--	--	--	2	--	--	--	20	--	Cast
AiResist 13	0.45	21	--	--	11	2	--	--	--	2.5	0.1 Y	Cast
X-40	0.50	25	10	--	7.5	--	--	--	--	1.5	0.75 Mn	Cast
FSX-414	0.25	29	10	--	7.5	--	--	--	0.010	--	0.75 Mn	Cast
L-605	0.10	20	10	--	15	--	--	--	--	--	--	Wrought
MarM-509	0.60	24	10	--	7	--	7.5	0.2	--	I	--	Cast

appears to be principally $(Cr,Mo)_6C$ in nature. Since MC carbide in the

alloy S-816 is a major strengthener and source of carbon for M_6C, niobium

appears to be the most significant alloy strengthener. Effects of niobium in
WI-52 and AiResist 13, - while not identical, - are quite similar. All of
this behavior is consistent with the observations of carbide stability by
Beattie (8) discussed above.

It should be clarified that in such carbide-strengthened cobalt alloys,
the MC can be large and blocky and/or "Chinese Script" in shape. One school
of thought feels that niobium promotes the blocky type, which is favored for
alloy ductility. Both MC carbides function principally as stable, thermally-
resistant sumps of carbon. During heat treatment and service they gradually
enter solution, with the carbon reprecipitating to form finely-divided lower
carbides such as M_6C and $M_{23}C_6$ by reaction with chromium and other matrix

elements. These carbides can be redissolved solutioned and precipitated.
The stable, relatively coarse NbC also acts as a grain refiner during cooling
of castings (it can precipitate in the melt prior to casting) and to refine
structure during forging, - or during cooling from heat treatments. Typical
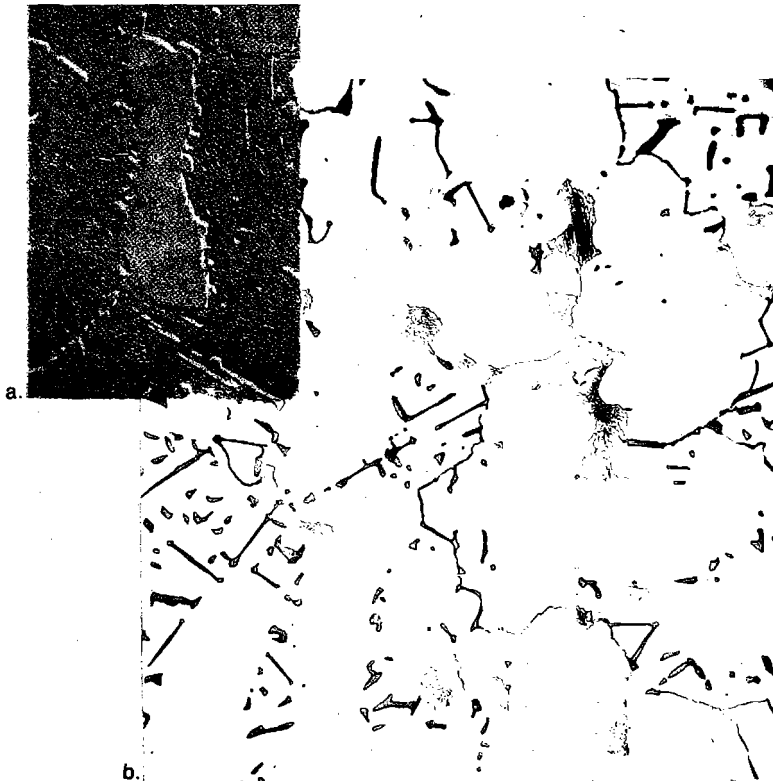structures of these carbides are shown in Figure 16.

Figure 16.   Structures Typical of Cobalt-Base Superalloys Containing Niobium.
     a.   Massive NbC Particle in S-816. 10,000X. After Beattie
     b.   General Structure Showing Angular MC Carbides, with Eutectic
        Areas $(M_{23}C_6)$ which Tend to be Devoid of Niobium. 500X.

An important application of Co–base alloys is for heavy–duty furnace parts, such as runners and tubes in the metallurgical, chemical and petro–chemical and petrochemical industries, where oxidation and corrosion resis–tance, erosion resistance, and strength are needed. UMCO–50 (50 Co, 28 Cr, 21 Fe, 0.3 C) has been utilized for many years in this service. Ultimately a niobium–containing version, UMCO–51 (Table V) was issued (16). In studies to improve the UMCO alloys, it was found that additions of niobium systematically improved the strength through interaction to form NbC–type carbides in addition to the $M_{23}C_6$ carbides already present. In fact, aging studies for 3000 hours up to 800 C (1470 F) showed increases in strength, but with no tendency towards unwanted a–phase formation, since the Phacomp phase control tool was utilized to control composition. Figure 17 shows the carbide structure obtained in one alloy, and illustrates the effects noted from systematic increases in niobium content. However, maximum properties (im–provement in both UMCO–50 and UMCO–51) are obtained by concurrently replacing a moderate amount of the cobalt with nickel. These NbC–type carbides probably also contain nitrogen, – becoming carbonitrides.

Such alloys, as noted previously, are considered a good example of the necessity for creating a major carbide reservoir by adding Nb to form ini–tially stable and relatively coarse NbC, – to subsequently degenerate slowly in service. The constant supply of carbon in turn, generates the more pervasive $M_{23}C_6$, which constantly dissolves and reprecipitates at grain boundaries, MC/matrix interfaces, stacking faults, and other structural aspersions acting as a major strengthener through $M_{23}C_6$/dislocation inter–action. The niobium, in this act of the play, will go back into solid solution.

Coherent Phase Strengthening. The success found in using coherent phases to strengthen Ni–base alloys (e.g., – γ', Ni_3Al) has been one of the most strikingly useful phenomena discovered in all metallurgy. Thus, for years alloy developers have hoped for a similar effect in cobalt alloys. However, the analog to Ni_3Al, Co_3Al per se, is not stable. A most complete search was conducted by Drapier, et al (15) who evaluated the nature and morphology of intermetallic compounds formed between cobalt and the refractory metals, – niobium, tantalum, molybdenum, and tungsten.
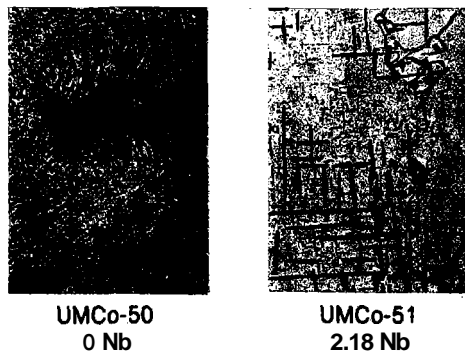

UMCo-50
0 Nb

UMCo-51
2.18 Nb

Figure 17. Effect of Niobium on the Structure of UMCo-50. 500X.

In this study, one cubic phase, α-Co_3Ta, was found to precipitate (in Co–Cr alloys) in an ordered coherent (spinodal) fashion akin to γ' (Ni_3Al). However, a–Co_3Ta is metastable, transforming to a β–Co_3Ta hexagonal form, and, has not appeared useful. Co_3Ti also forms, but it is not stable at high temperatures.

For niobium, a summary of the possible intermetallic components is reported in Table VI, showing three types of Laves phases, – Co_2Nb, Co_3Nb, and possibly Co_5Nb_2. Some age–hardening tendencies were observed by precipitation of these intermetallics in Co–base binary alloys with from 5 to 25 percent chromium in 5 percent increments. Alloys with tantalum, molybdenum, and tungsten were studied similarly.

Age–hardening effects were found in Co–Cr–Nb alloys at moderate temperatures, due to generation of a superstructure in the cubic matrix, and the hexagonal Laves phase Co_2Nb ($MgZn_2$-type) in the HCP phase. At high temperatures (1200 C) the hexagonal $MgNi_2$–type Laves phase occurred, apparently stabilized by the chromium. From all of this work the authors concluded that while some hardening occurred by addition of niobium to cobalt, overaging occurs at temperatures too low to be of interest, and tantalum, tungsten, and molybdenum generated much more provocative results. Figure 18 shows the strengthening effects of the refractory metals added to a Co–Cr base, and illustrates well that niobium has but poor potential as a strengthener through coherent phase precipitation. However, niobium was not investigated as a partial substitute for tantalum.

Cobalt Alloy Summary. Niobium has been explored rather extensively for possible use as a solid solution or coherent phase–former for strengthening Co–base alloys, and found, to date, not to be helpful in these modes. Its low modulus and limited solubility is a major factor, and A_3B–type phases are not thermally stable.

However, as for nickel alloys, niobium forms stable and refractory carbides in cobalt superalloys. These are highly effective strengtheners in widely–used commercial alloys, such as S–816, WI–52 and UMCO–51.

Iron–Nickel Alloys

For the purposes of this paper, this section refers to alloys which are based on iron (Table VII). Virtually all of these alloys contain a significant amount of nickel and in fact a few such as IN–718 and Pyromet 860 contain more nickel than iron. However, all of these alloys are characterized by metallurgical features and use patterns related to the presence of large amounts of iron, so they are chosen to be discussed as iron–nickel–base alloys. There are several generalities concerning Fe–Ni alloys that should be made at this point to clarify and shorten subsequent discussion.

o   The Fe–Ni–type alloys principally are used for forged or wrought structural applications to about 650 C (1400 F). Some are used for low–strength casting applications to higher temperatures.

o   Iron–nickel superalloys utilize niobium for strengthening more than do any other class. In some Fe–Ni alloys niobium can be called the principal strengthener.

Table VI. Intermetallic Compounds in the Co-Nb System. After Drapier (15).

Compound	% co		Stability	Structure	Lattice Parameters, a
	a/o	w/o			
Co$_2$Nb (Co$_3$Nb)	74.5–75.2	65–67.3	up to 1175 C (?)	hexag., Laves MgNi$_2$ type	a = 4.740 c = 15.45 c/a = 3.259
	73	63.3	?		a = 4.738 c = 15.46 c/a = 3.262
	73	63.3	*		a = 4.75 c = 15.56 c/a = 3.27
Co$_5$Nb$_2$ (?)	71.5 (?)	61.4 (?)	?	hexagonal	a = 5.89 c = 6.83 c/a = 1.16
Co$_2$Nb	67.4–72.7	56.8–62.7	up to 1175 C	cubic, Laves, MgCu$_2$ type	a = 6.713–6.770
	66.7	56.0	?		a = 6.759
	66.7	56.0	?		a = 6.767
Co$_2$Nb	66.7	56.0	**	hexag., Laves, MgZn$_2$ type	a = 5.190 c = 8.384 c/a = 1.615

*As stabilized by Cr
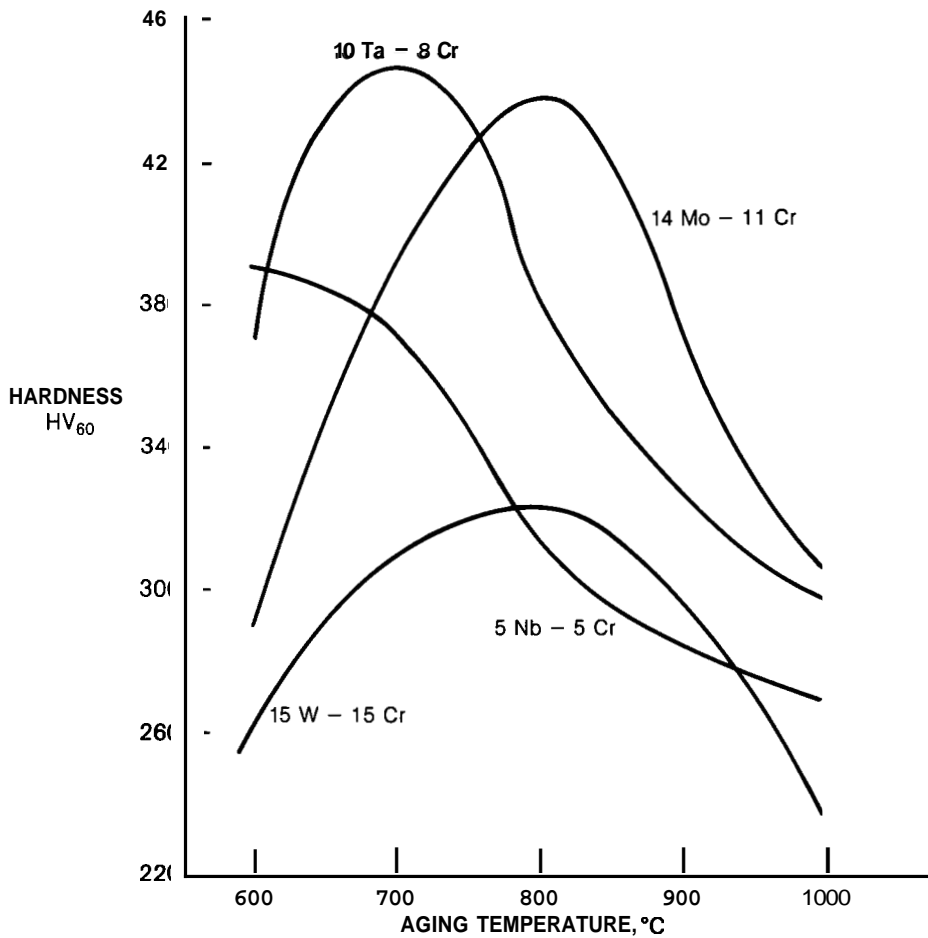**As stabilized by Ni.

Figure 18. Strengthening Effects of Nb, Ta, Mo, and W
            in Co-base Alloys with Appropriate Chromium
            Levels. Adapted from Drapier, et al. (15).

Table VII. Compositions of Selected Iron–Nickel Superalloys With and Without Niobium.

Alloy	C	Cr	Ni	Fe	Co	Ti	Al	B	Mo	W	Nb	Other	Form
A–286	0.05	15.0	26.0	Bal	--	2.00	0.20	0.005	1.25	--	--	0.3 V	W
v–57	0.05	15.0	25.5	Bal	--	3.0	0.25	0.008	1.25	--	--	0.3 V	W
Unitemp 212	0.08	16.0	25.0	Bal	--	4.00	0.15	0.060	--	--	0.50	0.05 Zr	W
Inco–901	0.05	13.5	42.7	34.0	--	2.50	0.25	0.015	6.1	--	--	--	W
Pyromet 860	0.05	14.0	42.5	Bal	4.0	3.00	1.25	0.010	6.0	--	--	--	W
IN–718	0.04	19.0	52.5	Bal	--	0.90	0.50	0.005	3.05	--	5.30	--	W,C
IN–706	0.02	16.0	40.0	Bal	--	1.70	0.30	0.004	--	--	2.75	--	W
Inco–903A	0.1	--	37.5	Bal	14.0	1.6	0.02	--	--	--	5.0	--	W
Rene 62	0.05	15.0	Bal	22.0	--	2.50	1.25	0.005	9.0	--	2.25	--	W
Udimet 630	0.04	17.0	Bal	18.0	--	1.00	0.60	0.005	3.0	3.0	6.50	--	W
D–979	0.05	15.0	45.0	Bal	--	3.00	1.00	0.010	4.0	4.0	--	--	W
CG–27	0.05	13.0	38.0	Bal	--	2.50	1.50	0.010	5.5	--	0.6	--	W
H–155	0.15	21.0	20.0	Bal	20.0	--	--	--	3.0	2.5	1.0	--	W,C
S–590	0.43	20.5	20.0	Bal	20.0	--	--	--	4.0	4.0	4.0	--	W
CRM–180	0.75	23.0	5.0	Bal	5.0	--	--	0.003	1.0	1.0	2.0	5.0 Mn	W
G–18B	0.40	13.0	13.0	Bal	--	--	--	--	2.0	2.5	3.0	--	W

o   Early alloys, such as S–590 and N–155, are strengthened only by **solu-**
    tion effects and carbide precipitation. In this respect they are
    similar to cobalt–base alloys.

o   Most significantly, alloys such as IN–718 show generation of a unique
    and vital coherent strengthening phase which depends upon niobium,
    called γ''.

o   The amount of nickel in the austenite matrix is critical. About 25
    percent is required to maintain the FCC structure and allow precipita–
    tion of γ'.

   <u>Solution Strengthening</u>. As with nickel– and cobalt–base alloys, solution
strengthening effects occur from additions of cobalt, chromium, molybdenum
and other refractory metals. The behavior of niobium as a solution strength–
ener was discussed in some detail for nickel–base alloys above. In recent
measurements (17) a heat of IN–718 (nominally 5.1% Nb) was found to retain
about 3 percent Nb in the austenite matrix, ‾ about the same as for nickel
alloys according to Stoloff (18). Thus, the solution strengthening effects
are probably similar. Since γ–γ' misfit is not an important source of
strengthening, effects of niobium in solution on this factor probably can be
ignored. The role of niobium in the precipitate phases themselves is far
more significant, as follows.

   <u>Carbide Strengthening</u>. The iron–nickel alloys all contain MC carbides,
formed principally with titanium but complexed by niobium and other refrac–
tory metals. Since most of the alloys are forged and MC carbides form at
very high temperature, they can be vital in structural control such as grain
refinement during fabrication or grain control in heat treatment. This is
particularly important as forged alloys are used for wheels and other large
parts. Niobium helps maintain stability of the MC carbides, but it still
degenerates to $M_{23}C_6$ or M_6C carbides in the same fashion as for nickel–base
alloys, particularly during heat treatment. The specific partitioning of
niobium to the carbides appears not to have been studied, but if behavior is
similar to nickel alloys, one can expect about 10 percent in MC.

   Among the Nb–containing Fe–Ni alloys (Table **VII)** H–155, S–590, and CRM–
180 precipitate carbides as their principal strengthening phases. The high
carbon level for this purpose is obvious. MC–type carbides, composed of
niobium, molybdenum, tungsten and chromium dominate; they precipitate at
grain boundaries, and (as 'in G–18B (9)) on matrix dislocations as well as
other aspersions in the alloy. MC carbides also are important in alloys
strengthened with γ' and γ'', where they help control grain structure.

   <u>Coherent Phase Strengthening</u>. Many Fe–Ni superalloys are characterized
uniquely by precipitation of two coherent phases, γ' and γ''. To discuss this
behavior the two phases each will be discussed briefly, then covered in
detail by discussion of IN–718 as a leading example.

   Ordered and coherent gamma prime (γ') is formed in Fe–Ni–base alloys by
reaction of <u>titanium</u> with nickel, not primarily aluminum as in nickel–base
superalloys, although aluminum participates if present. γ' precipitation
usually occurs as spherical particles. Strengthening mechanisms utilizing
γ' have been well summarized by Muzyka (19) who reports that particle size
and volume fraction are significant, while matrix coherency relationships are
not; it has also been observed (20) that APB energy contribution is about 10–
20 percent. Further, a major function of γ' is its contribution in convert–
ing to γ''.

Gamma double prime (γ") is a prime strengthener in several of the most important alloys. While identified by a variety of workers (20, 21) some still contest its existence. In any case, γ" is a BCT-type phase (like two stacked FCC γ' cells). It forms as discs or platelets in the alloy. It uniquely depends on the presence of both niobium and iron for formation; they provide needed electron-to-atom ratios and matrix-precipitation mis-match effects. Figure 11 is a summary of leading work showing the approximate quaternary phase relations between γ, γ', γ", and other neighboring phases.

Gamma double prime has been observed to form by enveloping γ' cubes on all sides (21). Once formed, it is more stable than γ'. In turn, the γ" eventually may convert to the most stable phase in this series, Ni_3Nb (δ).

Thus, depending strongly on specific alloy chemistry and heat treatment a series of irreversible (without heat treatment) reactions giving differing phases and effects can be generated (Figure 19).

$$\gamma \text{'(FCC)} \rightarrow \gamma \text{"(BCT)} \rightarrow 6 \text{ (Orthorhombic)}$$

(3)

$$\eta \text{ (HCP)}$$

(4)
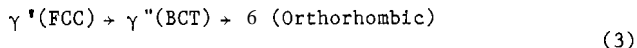
These alloys must be melted, fabricated, and heat-treated with care!

Non-Coherent Phases. Delta phase (δ) is not coherent with the matrix, and forms as plates or cells. Generally, delta does not contribute to strength and thus is to be avoided. However, it has been found possible to create overaged delta (globular or platelike) by Eiselstein (23) which can control grain size during hot working.

Eta phase (η - Table VIII) can form directly from γ' in these alloys, due also, of course, to the high levels of titanium and niobium. Characteristically, it will occur as plates or cells, the plates often growing from grain boundaries where it reduces ductility leading to undesirable properties. However, careful processing and heat treatment can cause a more blocky form to generate from cellular structure, useful in grain control in a similar fashion to 6. Since both η and δ contain niobium and titanium, they can reduce strength by robbing γ' and γ," reducing the amount present and reducing stability.

TCP Phases. In a similar fashion to the formation of σ or μ in the Ni-base alloys, the Ni-Fe alloys can form TCP phases and Laves. Laves is a common problem, related again to the presence of niobium as well as aluminum and silicon. σ has also been reported in these alloys, but the role of niobium is secondary here, since reduction of matrix nickel (by A_3B precipitation) is a major driver to form σ along with chromium and molybdenum. TCP phases form in areas of high segregation of the forming elements, so good homogenization practice can avert this problem.

In summary, as listed by Muzyka (19) the most important precipitate non-carbide phases in Fe-Ni alloys are:
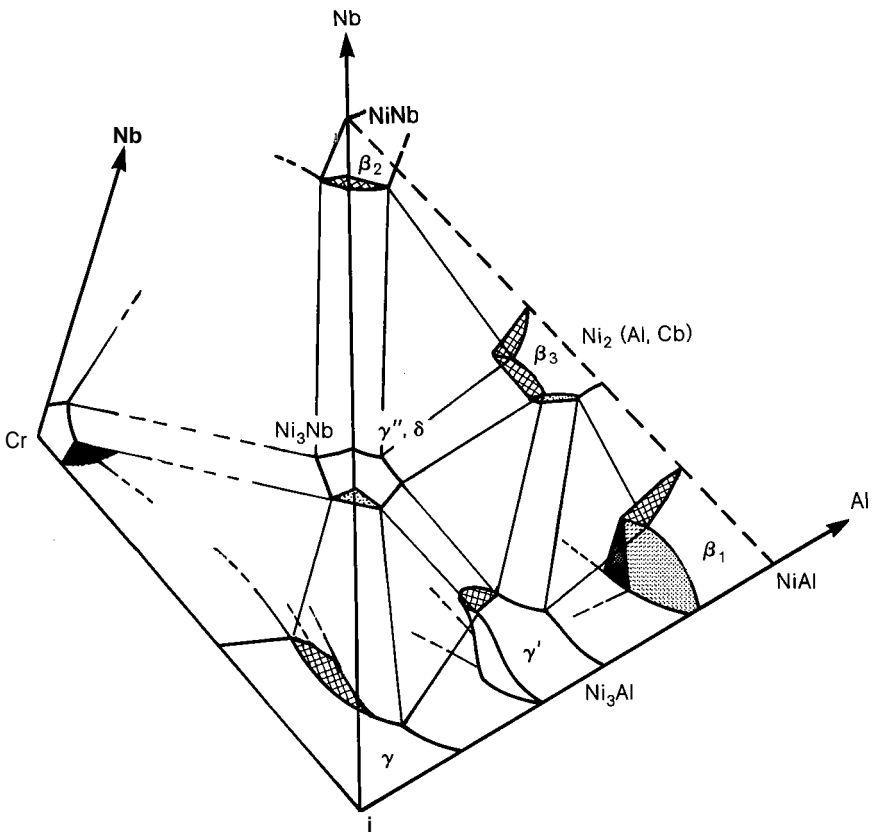
Figure 19. Sketch of Approximate Relationships Between
γ' and γ"/δ in the Ni-Al-Cr-Nb System.

Table VIII. Superalloy Phases Containing Niobium.

Name	Symbol	Nominal Chemical Formula	Crystal Type	Estimated Niobium Content
Gamma α Austenite	Y	Ni,Co,Fe Solid Solution	FCC	up to 5%
Gamma Prime	γ'	$Ni_3(Al,Ti,Nb)$	Ordered FCC	Up to 25%
Gamma Double Prime	Y"	$Ni_3(Nb,Al,Ti)$	Ordered BCT	Up to 25%
Delta	δ	$Ni_3(Nb_8Ti_2)$	Orthorhombic	Up to 25%
Eta	η	$Ni_3(Ti,Nb)$	HCP	?
MC Carbide	MC	NbC	Cubic	Up to 50%
M_6C Carbide	M_6C	$(Nb,Mo,Ni)_6C$	Complex Cubic	?
Laves	--	$(Fe,Cr)_2(Ti,Nb)$	Hexagonal $MgZn_2$	∿28%

Symbol	Structure	Composition
γ'	Ordered FCC	$Ni_3(Al, Ti)$
γ''	Ordered BCT	Ni_3Nb
Ni_3Ti (or η)	HCP	Ni_3Ti
Ni_3Nb (or δ)	Orthorhombic	Ni_3Nb

Behavior of IN-718. Alloy IN-718 is the industrially prominent example of Fe-Ni alloys which demonstrate the principles identified above; it was developed by H. L. Eiselstein (26). While alloys such as Pyromet 860, Rene 62 and Udimet 630 also demonstrate some aspects of this behavior, IN-718 dominates its present field of commercial application with an absoluteness not enjoyed by any single nickel- or cobalt-base alloy in theirs. It contains about 5 percent niobium as the most prominent strengthening addition, and currently is being developed for use in cast components in addition to its historically forged condition. Many studies have been made of the alloy. Here we will attempt to be brief.

IN-718 (Table VII) is Ni-rich with about 20 percent iron. It is used for forged turbine wheels, shafts, supports and cast frame sections in aircraft engines. A major effort in all forging or casting is to process the alloy to avoid segregation which could cause formation of deleterious Laves, μ or σ.

In forging practice IN-718 is usually fabricated by furnace heating to about 1100 C (2025 F) then rolled or forged, maintaining minimum stock temperatures of about 925 C (1700 F). The alloy is first then heat-treated by solutioning at about 950-1000 C (1750-1840 F) then aged at about 720 C (1325 F), furnace cooled to 620 C (1150 F) then cooled to room temperature. This practice avoids Laves and σ formation, generates γ' and γ'' in optimum quantities to provide maximum strength and toughness, and minimizes subsequent transformation to δ phase.

Rizzo and Buzzanell (27) showed that variations in niobium content in IN-718 had the most significant effect of all alloying elements. Their results (Figure 20) showed found steady increases in strength by increasing niobium from 3.5 to about 6.5 percent. However, additions of niobium above about 5 percent promote Laves phase and orthorhombic Ni_3Nb (δ), ~ both deleterious to alloy toughness.

The microstructure of forged IN-718 is shown in Figure 21. A typical view of the very fine A_3B phases appear in Figures 21a and b. Figure 21c shows typical phases generated by coarsening the structure.

Cast versions of IN-718 are now being developed following successful use in aircraft engine frames. Cast or ingot IN-718 has been unfortunately characterized by visible segregation "freckles", now identified as Laves phase and porosity. This inhomogeneity affects properties seriously, since the Nb (28%) and Mo (12%) locked into Laves is not then utilized for strengthening. It is possible (although difficult) to homogenize the alloy by heat treatment alone; Bouse and Schilke (17) found that a combination of hot isostatic pressing (HIP) and heat treatment (i.e., ~ four hours at 1213 C (2217 F) and 103 MPa, (15 ksi)) were effective in lowering the Laves to undetectable limits. This resulted in 600 C (110 F) increases of 0.2 percent from 780 to 920 MPa (105-125 ksi) with good retained ductility.
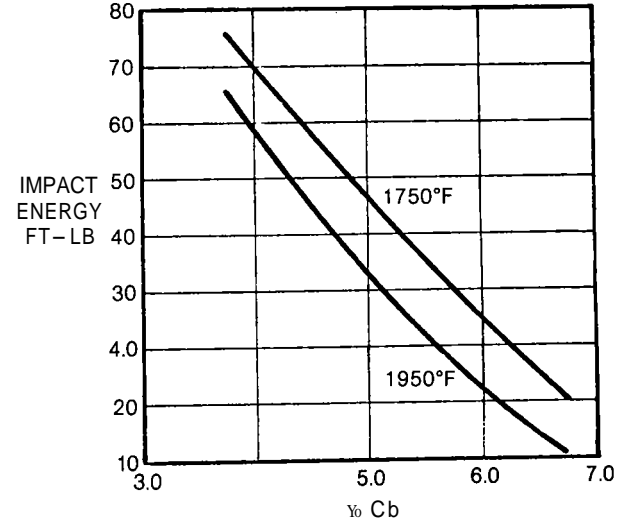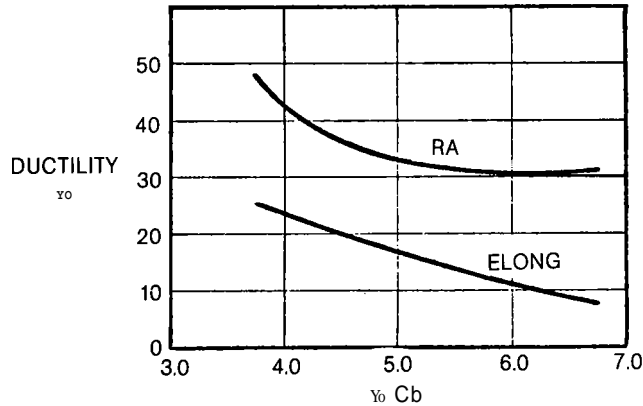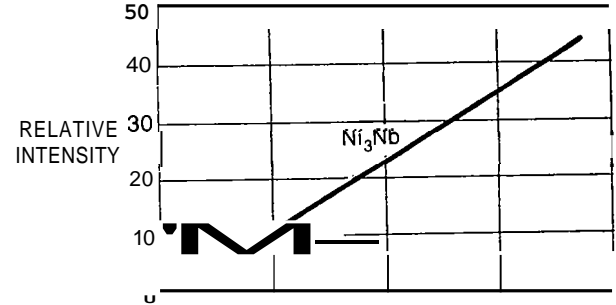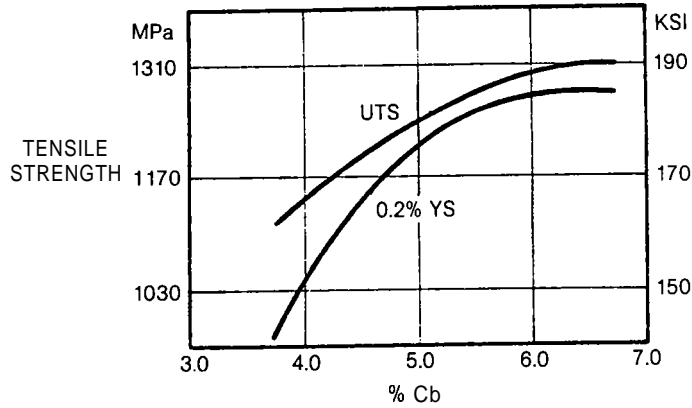
Figure 20. Effect of Nb Variations on Ni_3Nb (γ'') Level and of IN-718. After **Rizzo** and Buzzanell (27). Solutioned at 950 C (1750 F) and Aged 1500 hrs. at 650 C (1200 F).
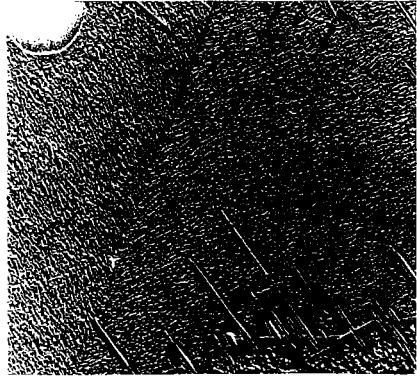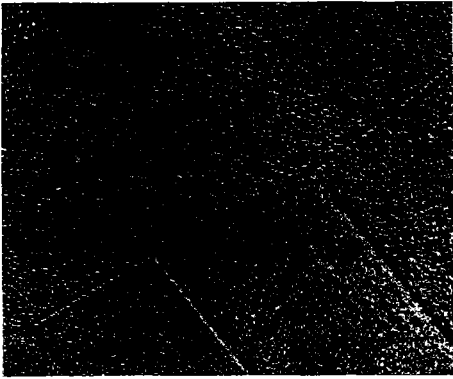
Figure 21(a). γ' and Ni_xNb (γ'') after
1 Hour at 700 C (1400 F)
i n Commercial IN–718.
7500X.

Figure 21(b). Transformation of γ' to
Ni_xNb (γ'') with Grain-
Boundary Ni_3Nb Plates.
500 hrs. at 705 C (1300
F). 7500X.

Figure 21(c).   SCM of Large NbC Particle (center)
and Grain–Boundary Laves.   5000X.

Figure 21.   Some Microstructures Typical of IN–718.   After
Boesch (24), Stroup (28), and Biss (29).

Finally for IN-718, a summary of many studies of T-T-T relationships are given in Figure 22. It serves to summarize this brief view of IN-718 and re-emphasizes the role of niobium. The messages from Figure 22 are:

o MC (i.e., - (Nb,Ti)C) is stable at high temperatures and yields to M_6C at longer times. However, both carbides are relatively unstable at service temperatures, and will be entering into chemical reactions.

o Generation of sufficient γ'' to provide good strengthening demands relatively high niobium content, such that (Ti + Al)/Nb = 0.96. At lower Nb levels (ratio = 0.77) formation of γ'' is **much** more sluggish.

o Laves will form only if the alloy is highly segregated.

Other Alloys. Our discussion has emphasized IN-718 for the sake of brevity. However, both γ' and γ'' occur in several commercial alloys with greater iron content, such as IN-706 and IN-903A (Table VII), - a low-expansion wheel alloy. In fact, some views of γ' and γ'' in the latter alloy, resulting from a study by Bricknell and Woodford (33) are most clarifying
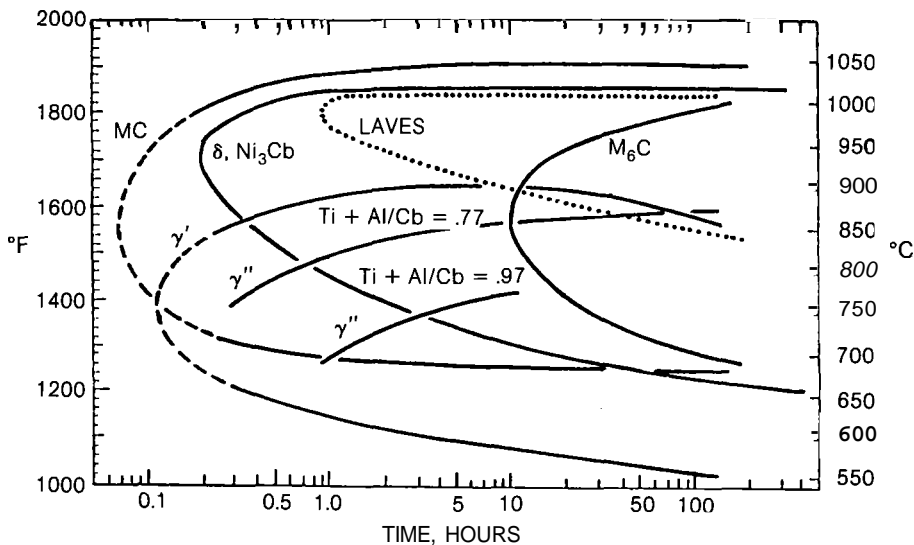

Figure 22. Time-Temperature-Transformation Diagram for Alloy 718 after Annealing in the Range 2100-2000 F/1 hr. and Water Quenched. Laves is a non-equilibrium phase that may appear in niobium-segregated areas.

Phase Transformations Determined as Follows:

γ', MC, and M_6C - Eiselstein (23)
γ'' - Cozar and Pineau (21)
δ, Ni_3Cb - Boesch and Canada (24)
Laves - Keiser and Brown (25)

1208

(Figure 23). γ'' appeared after 5.5 percent Nb was added, and a heat treat-
ment at 744 C (1375 F) 8 hrs, FC to 621 C (1150 F)/8 hrs was given.   The
cubic γ' in Figure 23a is obvious, with tiny plates of γ'' evident between and
long plates of δ-Ni_3Nb traversing the photograph.   Figure 23b reconfirms the
presence of γ'', showing another reflection.   However, it is important to note
that in this particular alloy, γ'' is not believed the principal strengthener;
it is γ'.

     Iron-Nickel Alloy Summary.   Niobium is a vital strengthener in several
Ni-Fe-base superalloys, such as IN-718 and IN-706.   In the presence of iron,
a new coherent phase γ'' is formed at the Ni_3Nb composition, which evokes
outstanding strength for use up to about 650 C (1200 F).   Niobium as Ni_3Nb
also forms delta phase (δ), which does not contribute to strengthening
significantly.

Directionally Solidified Eutectic Alloys

     Through use of the directional solidification process, there have been
recent significant American and French developments to produce naturally-
aligned fibrous or lamellar structures of superalloy materials with high
creep/rupture capability.   The structure is achieved by freezing out a stable
eutectic compound.   Typically in a nickel-or cobalt-base alloy matrix, fibers
(needles) of tantalum carbide (TaC) or niobium carbide (NbC) or lamellae
(plates) of orthogonal Ni_3Nb (δ) are formed.   In the case of nickel alloys,
γ' is usually also precipitated, and other carbides can form in most of the
alloys.

     Table IX gives a listing of some major eutectic alloys.   In the general
sense, these are not commercially available yet, but developments are now
reaching towards at least extended trial service.   For instance Brown-Boveri
company has tested a chromium carbide fiber alloy in industrial gas turbine
service for about 15000 hours, (30) and the pressure is on for aircraft
engine application.

     The leading alloys at present appear generally to be of the following
type:

   o   **NITAC.**   A TaC fiber structure in an austenitic nickel superalloy
       matrix.

   o γ/γ'-δ.   A lamellar Ni_3Nb (δ) structure in a nickel γ'-strengthened
       alloy.

   o   COTAC-744.   An NbC fiber structure in a nickel γ'-strengthened alloy.
       (Note: this alloy name is strikingly misleading, - since the word
       COTAC historically refers to TaC fiber cobalt-base alloys, with
       matrixes similar to X-40, on which much early work occurred).

     The significant role of niobium in these alloys is quite apparent.   It is
the major eutectic phase-forming element, either NbC or δ/Ni_3Nb, in two of
the three alloys.

     Structures of eutectic alloys are shown in Figure 24.   The fibers (or in
some cases lamellar plates) are obvious.   Formed eutectically, they tend to
be very stable and well-bonded to the matrix.   The structure allows much of
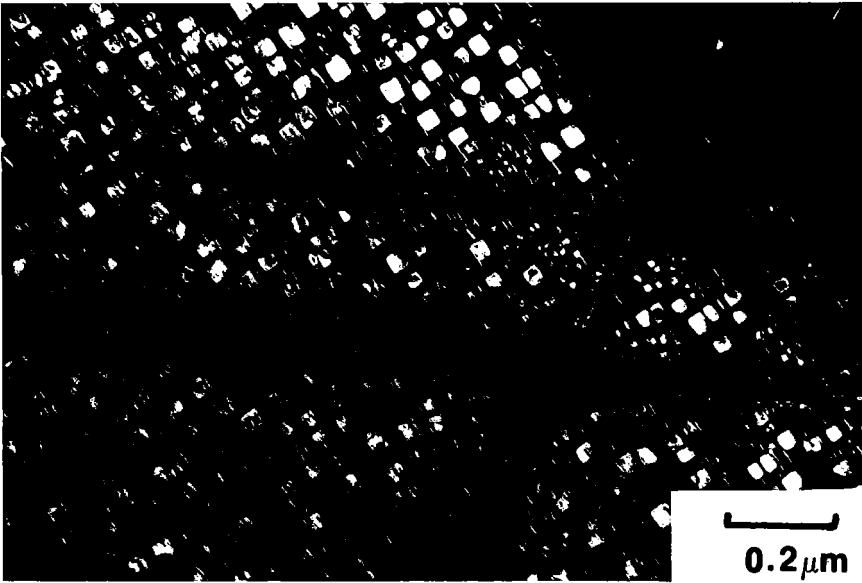the potentially great strength of the hard fibers or plates to give great

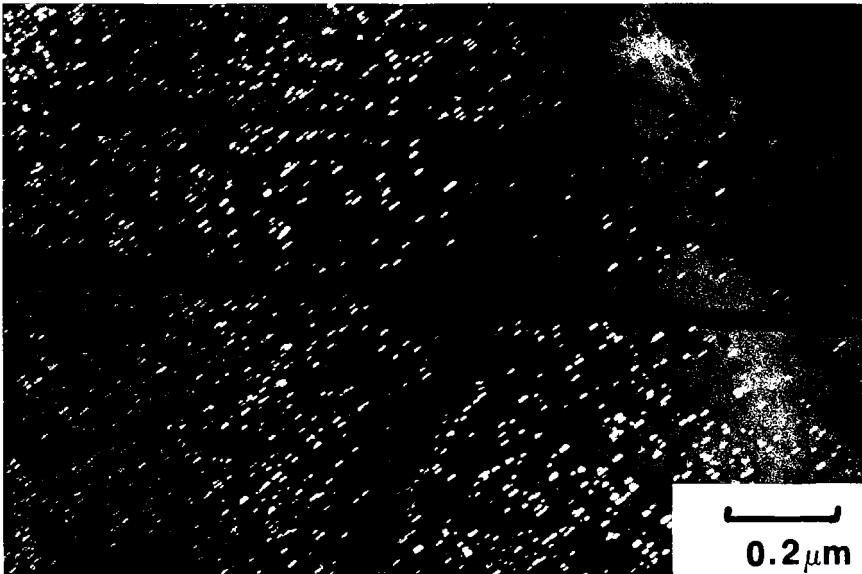Figure 23(a). IN-903A Showing Cubic γ', Plate γ'', and Large Needles of $\delta - Ni_3Nb$.

Figure 23(b). Same as 23a, Showing Another Cube Face of γ'' and the δ Needles.

Figure 23. IN-903A with Over 5.5% Nb, Heat-Treated to Produce γ'' From Bricknell, R., Personal Communication.

Table IX.   Compositions of Some Directionally Solidified Eutectic Alloys.

Alloy	Morphology	V_f	Ni	Co	Cr	w% Solute		Mo	Ta	C	Other
						Al	Nb				
Nitac	F	0.05	69	--	10	5	--	--	14.9	1.1	--
Nitac 13	F	--	63	3.3	4.4	5.4	--	--	8.1	0.54	3.1 W,6.2Re,5.6V
CoTaC	F	0.10	10	65	10	--	--	--	14	I	--
CoTaC 3 or 33*	F	0.10	10	56	20	--	--	--	13	1	--
CoTaC-744	F	--	64	10	4	6	3.8	2	--	0.47	10W
γ/γ'- 6 (6%Cr)	L	0.3	71.5	--	6	2.5	20	--	--	--	--
γ/γ'- δ (0%Cr)	L	0.3	76.5	--	--	2.5	21	--	--	--	--
γ'/γ-Mo (AG-34)	F	0.26	62.5	--	--	6.3	--	31.2	--	--	--
Y- δ	L	0.26	66.7	--	--	--	23.3	--	--	--	--
γ'-Ni$_3$Ta	L	0.35	64.1	--	--	4.9	--	31	--	--	--
Co,Cr-(Co,Cr)$_7$C$_3$	F	0.30	--	56.6	41	--	--	--	--	2.4	--

*1300 C, 2 h; 1000 C, 24 h, A.C.
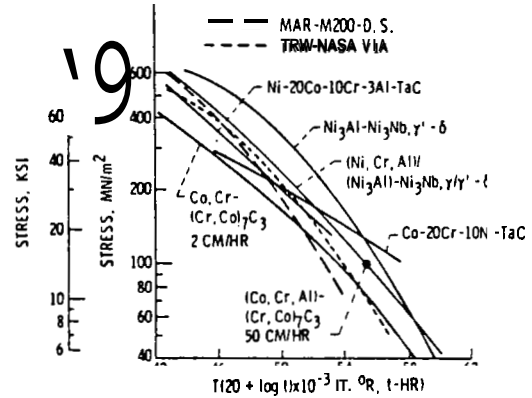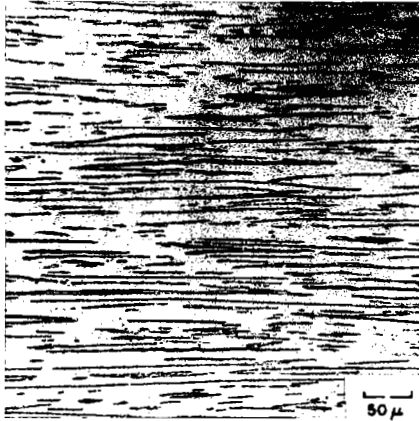
Stress rupture comparison of high temperature eutectic alloys

Figure 24. Structure of a Fiber - Strengthened Eutectic Superalloy, and a Strength
Comparison of Eutectic Alloys with Conventional Superalloys (32).

longitudinal creep capacity. Kahn (31) found the NbC fibers in COTAC-744 showed no visible damage following 2500 3-minute cycles between 1150 C and 2500 C. The lack of transverse grain boundaries reduces the potential of thermal fatigue crack initiation. The capability of some of these alloys to maintain load-carrying capability to high temperatures is shown in Figure 24. Further, they are vastly superior to conventional alloys in high-cycle fatigue (32).

Early work on carbide eutectics has showed partiality to TaC fiber structures. The potential now demonstrated by NbC shows two further advantages compared to tantalum, - greatly reduced density, and greatly reduced cost. Niobium is far more available and thus far less expensive than tantalum. However, a drawback appears to be limited oxidation and corrosion resistance, as discussed subsequently.

Eutectic Alloy Summary. Niobium is emerging as a key element in both fibrous and lamellar eutectic alloys. FCC NbC is the strengthening fibrous phase in a recent leading French alloy, CoTaC-744, and orthorhombic 6-Ni$_3$Nb is the strengthening lamellar phase in the $\gamma /\gamma '$-δ alloy system.

Effects of Niobium on Surface Stability

Discussion of this subject is divided into two sections, oxidation and hot corrosion. However, it is important to realize that hot corrosion can be considered simply as highly-enhanced oxidation caused by contaminant elements in the attacking atmosphere, such as sodium, potassium, vanadium and sulfur.

Oxidation

The broad, overall behavior of superalloys in oxidation has been noted in Figure 9. Their good high-temperature oxidation performance is a hallmark. It depends principally upon the ability to develop a stable, tenacious, tough, protective oxide film, usually provided by chromium (10-30%) and aluminum (1-6%).

Many of the multitude of elements added to superalloys affect oxidation resistance, improving or harming it for a wide variety of reasons. Small amounts of alloying elements can be significant. Thus, it is important to understand the effect of niobium, added in amounts from about 0.5 percent to 6 percent.

Unfortunately, there has been little clarifying study. Further, based on the properties of niobium as a pure metal, it is difficult to conjecture expected performance. Niobium itself readily forms a solid oxide in air, - usually a good sign for protective performance, - but the Nb_2O_5 formed (on unalloyed niobium) is of a fluffy, open-structured, nonprotective nature. Most superalloy metallurgists considered that niobium, while not observed to be harmful in oxidation, has also not been observed to be particularly helpful.

However, there have been two or three studies which, taken together, can shed some light. First, several years ago Davin, et al (34) studied Co-10Cr and Co-30Cr alloys to which a series of ternary elements, including 3 percent niobium were added. A portion of their results are shown in Figure 25. Inspection shows that molybdenum and niobium consistently promoted greatest attack. Further, the author singled out niobium as specifically causing catastrophic attack at high temperatures.
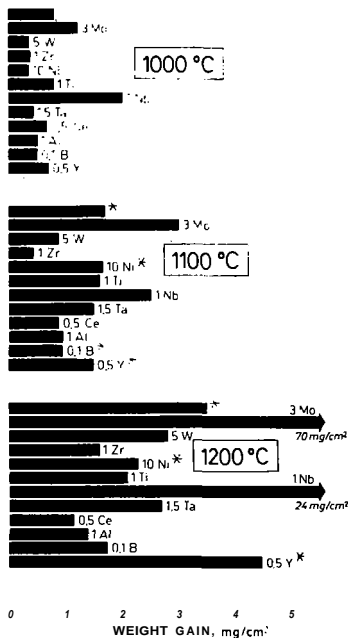
Figure 25. Air Oxidation of a Series of Co-30Cr-X
Alloys for 5 Hours. After Davin (34).

In addition, Herchenroeder (35) studied an **Fe-22Cr-20Ni-18Co-3.5Mo** alloy
(Haynes 556) as affected by a series **of** minor element additions. While it
was found that some elements such as silicon and lanthanum can create a 5X
improvement in resistance to dynamic oxidation testing conditions, niobium
had a significantly deleterious effect. For instance, in one test (1093
C/2000 F, 100 hrs) zero Nb gave 51 mg/cm^2, 0.24 Nb 111 mg/cm^2, and 0.70 Nb
261 mg/cm^2. Niobium could overpower a beneficial effect found for tantalum
but lanthanum could correct the problem. **Also** Beltran (36) states that
"Columbium is clearly harmful in oxidation" and feels that poor performance
of S-816 and WI-52 support the view.

In an interesting test by Meier (37) oxidation of a DS alloy strengthened
by δ-Ni_3Nb showed severe preferential attack of the Ni_3Nb at 700 C (1290 F)
but not 1100 C (2000 F). Figure 26 illustrates this, and shows an Ni_3Nb
denuded zone protects the alloy.

The message in this information appears clear. Niobium tends to harm
oxidation resistance, based on laboratory tests, at or above about 2 percent.
However, when attempts are made to correlate commercial alloy oxidation
performance with niobium content, the results are not consistent. For
instance IN-713C and MarM-432 (with 2% Nb) have excellent oxidation resis-
tance, superior to well-known U-500 and many other alloys. On the other
hand, U-700 (with no niobium) is excellent, and MarM-200 (1.8 Nb) is poor.
Inspection of long lists of data for many alloys still generates no correla-
tion to this writer. To cap the circumstance, IN-718 (with 5% Nb) has been
found to have better oxidation resistance (as sheet at 1000 C/1800 F) than
has Hastelloy X, an alloy utilized specifically for its fine oxidation per-
formance. Undoubtedly, the amount and balance of other elements are gener-
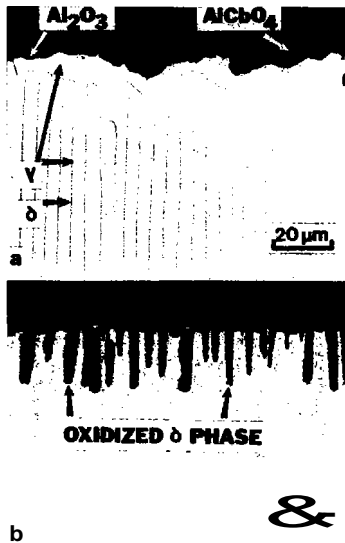ally of much more significance in causing oxidation resistance than niobium.

Figure 26.　Oxidation of Ni_3Nb - Strengthened DS Alloy at
1100 C (2000 F) Above, and 700 C (1290 F), Below.
Note Attack of Ni_3Nb.　After Meier (37).

Hot Corrosion

　　Hot corrosion attack is generally controlled in superalloys by keeping
the Ti/Al ratio at 1:1 or better, maintaining chromium content at about 15
percent, restricting molybdenum to 1–2 percent, and by adding cobalt to
nickel–based alloys.　Again, evaluation of the effect of niobium on hot
corrosion has been spotty, and it is difficult to be specific from further
literature study or experience.

　　No work studying the effect of niobium in relatively simple laboratory
systems (such as Ni/20Cr or Co-20Cr) has been seen by this author.　Reviewing
the behavior of complex commercial alloys with and without niobium also has
been a relatively fruitless task.

　　For instance, Hosier and Harris (38) studied dry sulfidation (a mild
corrosion–generating condition compared to condensing sodium sulfate) of a
series of 26 alloys at 725 C (1340 F); four of the alloys (IN–625, IN–718, X-
750 and 347 SS) contained niobium.　Their resistance to corrosion was evenly
scattered throughout the group.　On the other hand, it has been noted that
while 4 percent Nb–containing S–816 (at 870 C/1600 F) performs satisfactorily
in hot corrosion, WI–52 (2% Nb) is poor at all temperatures (36).　In a study
for the U.S.　Navy (39) niobium was present in the worst of twenty–four Ni-
base alloys.　Conversely we know that widely–used IN–738, universally well-
regarded for its high corrosion resistance, contains almost 1 percent Nb.
Further, an examination of the extensive information compiled by Stringer in
AGARD document No. 200 (40) continues to frustrate; no trend can be seen.

     Surface Stability Summary. Niobium can harm oxidation resistance signi-
ficantly in simple laboratory alloys, but the effect can be masked in many
commercial alloys. Whether niobium is helpful or harmful in hot corrosion
performance is not known, but alloying effects from other elements appear to
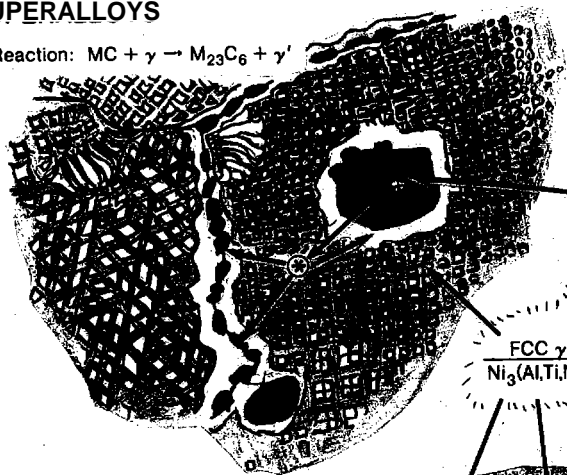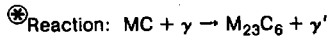mask its behavior in any case.

Niobium in Superalloys; Summary of Behavior

     Superalloys are complex FCC austenitic alloys strengthened by alloying
additions participating in complex interreactions, - including substitutional
solid solution, alloying effects at grain boundaries, formation of series of
stable and reacting carbides, and formation of a series of coherent A_3B-type
compounds in nickel- and iron-base super-alloys. The alloying additions also
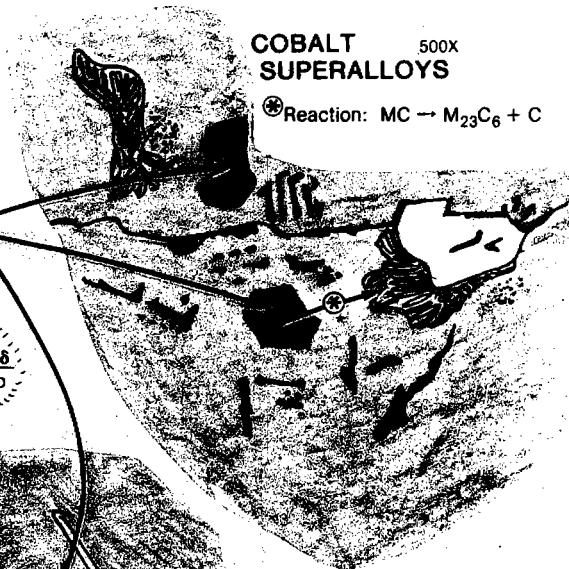affect and can control oxidation and hot corrosion properties significantly.

     Niobium has been added in amounts up to about 6 percent to about half of
the various complex cobalt, nickel and iron-nickel superalloys. Studies of a
variety of superalloys show that niobium partitions to the austenitic alloy
matrix, to the carbides, and, -when present, - the A_3B-type phases. Table
VIII summarizes the extensive phase partitioning possible by niobium, and
Figure 27 identifies by microstructure the principal phase locations. From
this review we find that niobium appears to have the following effect in
strength and surface stability in these alloys:

- o <u>Solid Solution Strengthening</u>. Due to limited solid solubility and
  unfavorable lattice mismatch, niobium has a small-to-negligible effect
  in simple solution strengthening of superalloys.

- o <u>Carbide Participation</u>. Niobium forms highly stable MC carbides, which
  are significant in helping strengthen all types of superalloys,
  particularly cobalt base. Niobium forms NbC and also enters MC
  titanium carbides (viz., - (Ti,Nb)C) in nickel alloys to affect/con-
  trol their stability, and allow needed MC degeneration reactions to
  occur. However, the complex composition of these carbides prevents
  identifying whether niobium always acts as a stabilizer. In nickel
  alloys, 15-20 percent of the niobium present partitions to carbides.

- o <u>Coherent Gamma Prime (γ') Phase.</u> In nickel alloys which form γ',
  niobium has been found to increase the volume fraction as much as 30
  percent. Niobium in solution in both the gamma matrix and the γ'
  increases AFB energy, causing a significant increase in alloy yield
  strength, - vital in dislocation particle cutting by they' particles.
  Niobium also strengthens the γ' particles themselves.

- o <u>Coherent Gamma Double Prime (γ") Phase</u>. Niobium at levels up to about
  6 percent is the principal strengthening element in Ni-Fe- or Fe-Ni-
  base alloys. It forms γ' and orthorhombic Ni_3Nb (γ"), - the latter a
  unique and important strengthener in these superalloys. Upon over-
  aging, excessive Ni_3Nb δ-phase also can form, but it is not considered
  a strengthener.

- o <u>Surface Stability</u>. Niobium appears to have a mixed or null effect on
  the oxidation and corrosion resistance of commercial resistance of
  commercial alloys and as tested in simple laboratory compositions.
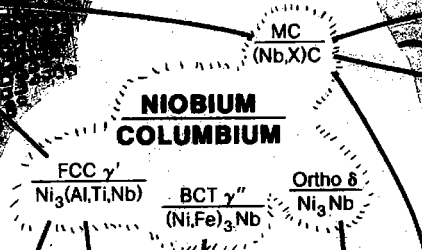 Some alloys which contain niobium demonstrate good or excellent
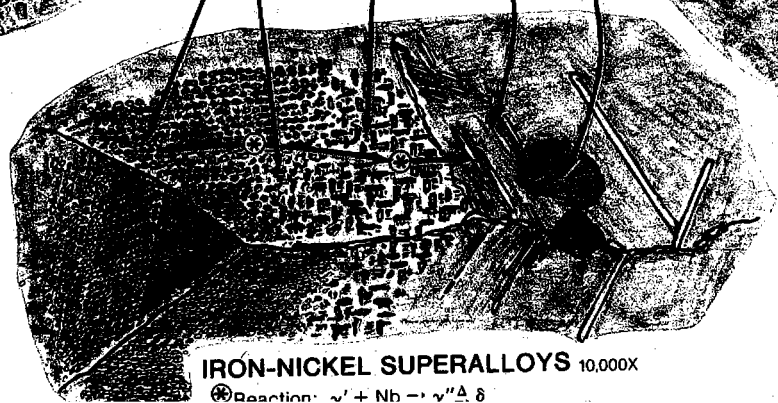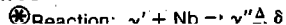
NICKEL SUPERALLOYS 10,000X

⊛Reaction: $MC + \gamma \rightarrow M_{23}C_6 + \gamma'$

COBALT SUPERALLOYS 500X

⊛Reaction: $MC \rightarrow M_{23}C_6 + C$

MC (Nb,X)C

NIOBIUM COLUMBIUM

FCC γ' / $Ni_3(Al,Ti,Nb)$

BCT γ'' / $(Ni,Fe)_3Nb$

Ortho δ / Ni_3Nb

IRON-NICKEL SUPERALLOYS 10,000X

⊛Reaction: $\gamma' + Nb \rightarrow \gamma'' \stackrel{\Delta}{\rightarrow} \delta$

Figure 27.   The Role of Niobium (Columbium) in Conventional Superalloy Microstructure.

oxidation and hot corrosion behavior, although such behavior is
usually ascribed to other alloying elements. Other alloys containing
niobium can demonstrate very poor oxidation or hot corrosion resis-
tance. In general there appears to be no evidence that niobium
improves oxidation or corrosion resistance and simple laboratory alloy
tests tend, more often than not, to show that niobium can be deleteri-
ous.

The Future in Superalloys

Perception

Over the years metallurgists have made small-to-medium additions of
niobium to conventional superalloys; these additions have been significant,
but have not been made on a systematic basis, or from broad and deep know-
ledge about its behavior. Nonetheless, advancing technology, such as that
evident in **DS** eutectics for very high temperature service, is generating an
increased role in the superalloy sun for niobium.

The major reasons are the high-temperature stability of niobium metallur-
gical compounds, and its availability. FCC NbC and orthorhombic $6-Ni_3Nb$ form
strengthening fibers or plates in eutectic alloys. In addition, the coherent
complex hexagonal phase γ'' Ni_3Nb, which provides outstanding intermediate-
temperature strengthening in iron-nickel alloys, appears prone for a greater
role in high-performance alloys.

Action

These phenomena may be the top of a small iceberg, which should be
exploited. For instance, it is perceived that:

- $\gamma''-Ni_3Nb$, singularly and modified by alloying, should be studied for
  application in a wider range of alloy base than up until now.

- Co_3Ti is moderately stable in cobalt austenitic alloy systems.
  Modifications with niobium might increase Co_3Ti stability.

- NbC will become a key fiber component in **DS** eutectics. Fundamental
  studies of its behavior, in both the "pure" and "alloyed" state are
  essential.

- $\delta-Ni_3Nb$ may have a future as a lamellar DS eutectic phase in austeni-
  tic superalloys. The fundamental properties of δ should be investi-
  gated thoroughly, and then studied for use in other alloy systems, and
  in combinations with NbC and γ''.

- Oxidation and corrosion behavior will be harmed by niobium additions.
  The fundamentals of the effects of niobium on these properties must be
  established, **so** that clear definition of the role of niobium, both
  combined and uncombined, is obtained as a guide to the next item.

- Alloying of alloy systems and of the niobium compounds in them should
  be studied, - with the objective of countering negative atmospheric-
  resistance effects,

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