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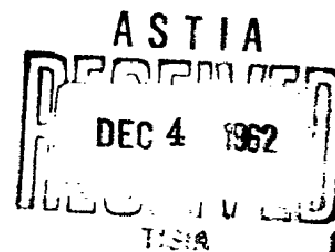
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IDENTIFICATION OF MICROCONSTITUENTS IN SUPERALLOYS

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INTRODUCTION

Before discussing the various methods of identifying the microconstituents in superalloys, it may be appropriate to state the nature of their influence on the properties, particularly at elevated temperatures. The superalloys enjoy an established position as structural materials within the temperature range of about 1300 to 1950 F. The excellent strength properties of these alloys within that temperature range are due to the combined effects of solid-solution strengthening, precipitation-hardening, and, to some extent, dispersion hardening.(1,2)** The creep and stress-rupture properties of many of the superalloys are also enhanced by additions of boron or zirconium, or both. The strengthening mechanism by which these elements improve the long-time properties of these alloys is not fully understood. Many investigators believe that the small and large atomic radii of boron and zirconium, respectively, result in their occupying the available vacancies and other lattice imperfections (usually at or near grain boundaries), thereby slowing down diffusion and agglomeration in these areas.(3)

Regardless of the mechanism by which the various alloys achieve their strength, all of them tend to reach nearly the same strength at temperatures of about 1950 F and above. Oxidation becomes a serious problem at about the same temperatures, i.e., 1950 F and above; up to that temperature, the superalloys as a class have good resistance to oxidation and to many other forms of corrosion.

For strength between 1300 and 1950 F, the nickel-base superalloys currently in use depend to a great extent upon the precipitation of a second phase.(1) Solid-solution strengthening and dispersion hardening also contribute but are secondary in those temperature ranges in which the precipitated second phase is operative. At temperatures above these ranges, leaner or less complex alloys are as strong as, or stronger than the superalloys. Cobalt-base alloys, on the other hand, depend upon solid solution and dispersion hardening (stable carbide networks) for a great portion of their strength, although some precipitated phases also contribute.(2) Consequently, these alloys lose a smaller proportion of their strength when a second phase is taken into solution than do the precipitation-hardening alloys, thereby retaining a relatively higher strength level above 1950 F. Iron-base superalloys employ all of the strengthening mechanisms but are not capable of retaining strength to temperature levels as high as the nickel- and cobalt-base alloys because the iron-base matrix solid solution is weaker than that of the nickel- and cobalt-base. The iron-base matrix solid solution also dissolves the precipitated second phase at a lower temperature than does the nickel-base, thereby lowering the useful upper temperature limit of these alloys.

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**References are identified on pages 20 through 22.

MICROCONSTITUENTS PRESENT IN SUPERALLOYS

The microconstituents of the nickel- and iron-base superalloys are very similar. Both series of alloys contain a nickel compound as the principal precipitate contributing to the elevated-temperature strength of the alloy. They differ somewhat in that the iron-base alloys usually contain eta phase, whereas the nickel-base alloys contain primarily the gamma-prime phase. All superalloys (cobalt-, nickel-, and iron-base) contain one or more of the carbides, and nearly all contain elements intended to strengthen the matrix solid solution.

The matrix solid solution actually acts as a reservoir for the elements taking part in the formation, deposition, and re-solution of intermetallic and refractory compounds, nearly all of which are capable of being dissolved and re-precipitated by heat treatment. One exception is titanium nitride (TiN) which is generally considered to be unaffected by heat treatment. The major microconstituents found in superalloys, together with their usual designations, are as follows:

Nickel-Base Alloys

1. Ni_3Al , gamma prime (γ)
2. Ni_3Ti , eta phase (η)
3. Carbides
 - TiC
 - $\text{M}_{23}\text{C}_6^*$
 - M_6C
 - M_7C_3
4. Nitrides
 - TiN
5. Borides
 - M_3B_2
 - M_5B_4
 - M_4B_3
6. $(\text{Fe},\text{Co})_7(\text{Mo},\text{W})_6$, mu phase (μ)

*M represents metal or mixture of metals.

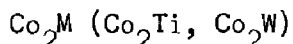
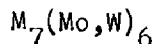
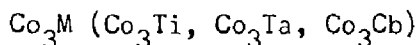
Iron-Base Alloys

1. Ni_3Ti , eta phase (η)
2. Ni_3Al , gamma prime (γ')
3. Carbide
 - TiC
 - M_6C
 - M_{23}C_6
4. Nitrides
 - TiN
5. Other Intermetallic Compounds
 - Fe_2Ti , Laves phase
 - NiTi , beta phase (β)
 - $\text{Fe}_7(\text{W},\text{Mo})_6$, mu phase (μ)
 - FeCr , sigma phase (σ)

Cobalt-Base Alloys

1. Ni_3Al , gamma prime (γ')
2. Ni_3Ti , eta phase (η)
3. Carbides
 - MC (CbC , TaC , WC)
 - Cr_7C_3
 - Cr_{23}C_6
 - M_6C
4. Cb (C,N)
5. Other Intermetallic Compounds
 - $\text{Co}_{13}\text{Cr}_{13}$, sigma phase
 - "R" phase

5. Other Intermetallic Compounds (Continued)



It is best to remember that the designations given are not always indicative of the true composition. Many of these compounds are single-phase over a range of composition, i.e., are homogeneous at compositions other than stoichiometric. Many of the compounds also have some solubility for elements other than those of the basic compound. Thus, gamma prime, designated as Ni_3Al , can have nickel atoms replaced by cobalt and chromium, and aluminum atoms can be replaced by titanium (in large amounts) and molybdenum (in small amounts). Some elements, such as iron, can replace either nickel or aluminum. Consequently, gamma prime is usually designated as $\text{Ni}_3(\text{Al}, \text{Ti})$, with the understanding that any of several other elements may also be present. Other examples of compounds having varying compositions are the carbides, M_{23}C_6 , M_6C , etc., and titanium nitride (TiN). In the carbides, the "M" radical can include chromium, tungsten, molybdenum, nickel, cobalt, and others. Titanium nitride has some solubility for columbium and carbon and could be written as $(\text{Ti}, \text{Cb})(\text{C}, \text{N})$.

On the other hand, eta phase (Ni_3Ti) has no significant solubility for any of the other elements found in superalloys and exists as the stoichiometric composition.

The variable composition of many of the phases in superalloys makes identification difficult. Addition of solute atoms increases the lattice parameters of the compounds and also often changes the size and shape of the phase in the microstructure. Gamma prime, for example, exists in shapes from cubic to spherical, in sizes from only a few angstroms up to thousands of angstroms, and with lattice parameters from 3.561 Å for the Ni_3Al stoichiometric composition to 3.605 or greater for the complex $(\text{Ni}, \text{Co})_3(\text{Al}, \text{Ti})$ compounds. Fortunately, the interplanar spacings remain relatively unchanged and the compounds can be identified using the ASTM card index.

METHODS OF ANALYSIS

Many methods are available to anyone desiring to identify the microconstituents in superalloys. The necessary skills and relative costs vary tremendously as the methods progress from simple examination with an optical microscope to complex electron transmission, X-ray diffraction, and electron-beam microprobe techniques.

Simple optical-microscopic examination can be very useful once a correlation is made between visual examination and positive phase identification by a more detailed analysis. Many of the more important microconstituents in superalloys are readily recognizable under the microscope once their identity has been established.

The difficult part of phase identification is not the analysis itself but, rather, the isolation and separation of the phase whose identity is desired. Actual identification is readily accomplished by well-established X-ray and electron-diffraction techniques. On the other hand, isolation of the desired phases is very difficult because of the small size and, in some cases, the relative scarcity of the particles. Also, many of the phases are of variable composition, and the actual composition will vary from alloy to alloy and with time and temperature experienced in heat treatment or service.

To obtain material for identification, some form of extraction technique is usually used. The most popular method is to dissolve the matrix in a suitable solution, leaving the particles of other phases as a residue, which can be analyzed chemically and by X-ray diffraction.(4-16) By appropriate choice of reagents, residues high in selected phases can be obtained. In some cases, phases can be identified in situ by use of the electron-beam microanalyzer. This instrument can be used to identify the composition of intermetallic compounds and phases but, unfortunately, the mechanics of the instrument limit its use at the present time to the elements with atomic numbers greater than that of sodium on the periodic chart. Thus, carbon, nitrogen, and boron, the very elements that form a large number of the compounds in superalloys, are eliminated from the analysis.

Fletcher, et al., described a method of detecting minor phases in cobalt-base alloys without extraction of the phases from the matrix.(17) The samples were metallographically polished on two intersecting faces. Each sample was mounted in a small Debye camera so that the corner formed by the polished surfaces was accurately located at the center of the camera and in a position for the X-ray beam to strike perpendicular to the edge.

A relatively new method has been developed whereby one may examine the general microstructure and phase composition of the same metallographic field. The technique is called "extraction replica" and permits electron microscopy of the microstructure and X-ray analysis of isolated particles of selected microconstituents within the same structure.(18,19) Basically the process produces both a standard replica of the microstructure and actual particles of the selected second phase. This technique has proved very useful in studies of the complex carbides. The mechanics of the technique include the preparation of a sample as one would for electron microscopy(20-24) and application of a collodion coating. The sample is then immersed in an acid (usually H_2SO_4 or a solution of 5 ml CHI + 1 g picric acid + 100 ml ethyl alcohol) until the collodion replica floats free, taking with it some imbedded particles etched free from the samples. In final form, the sample to be studied is composed of a collodion replica of the microstructure with actual particles of a desired phase imbedded in it.

MICROCONSTITUENTS

Gamma Prime, γ Ni₃Al

Gamma prime is easily the most abundant and most important microconstituent in nickel- and iron-base superalloys. It has a face-centered-cubic crystal lattice that varies only slightly in size (roughly 0 to 0.5 per cent) from that of the matrix solid solution (generally designated as gamma, γ). In fact, the high degree of similarity, and resultant coherency, of gamma and gamma prime is the principal source of strength of the alloys.

Gamma prime, particularly in the overaged condition, can be seen through the optical microscope as a fine precipitate distributed throughout the microstructure. Some gamma prime is almost always visible, the precipitation rate being so rapid that it is almost impossible to prevent the formation of gamma prime by rapid quenching. The temperature range within which gamma prime exists varies with the composition of the alloy but, in general, gamma prime can be seen in alloys heated in the range from about 1200 to 2200 F; the amount will vary with time at temperature. The solution temperature of gamma prime also varies with the composition of the alloys, generally being higher with increasing amounts of aluminum and titanium and also with increasing complexity of the matrix solid solution. In presently used alloys, the gamma-prime solution temperature varies between 1900 and 2200 F.

With the electron microscope, gamma prime can be seen as discrete particles varying in shape from spherical to cubical. Most often it appears in the general shape of rough flagstones. The size will vary with time at temperature and can vary from tens of angstroms to several thousand angstroms. In many cases the gamma prime will appear to precipitate along specific crystal planes, showing crystallographic orientation.

The etching techniques and etchants most often used for both optical and electron microscopy of gamma prime are: (1) immersion, a solution of 3 parts glycerol, 2 parts HCl, and 1 part HNO₃ (glyceregia) and (2) electrolytic, a solution of 5 parts HF, 10 parts glycerol, and 85 parts ethyl alcohol (some water may be substituted). Current densities in the range of 0.25 to 1.0 amp/square inch at 6 to 12 volts can be used in electrolytic etching. Using these methods, the gamma-prime precipitate will be in relief. Other etchants that can be used are listed in the appendix.

Gamma prime can be positively identified using extraction and X-ray diffraction techniques. Two of the electrolytes that can be used for the electrolytic digestion of residues are (1) a 7 to 12 per cent solution of HCl in methanol, and (2) 10 to 20 per cent of H₃PO₄ in water. Solution (1) dissolves gamma prime, whereas Solution (2) generally leaves both gamma prime and various carbides in the residue. The extraction requires long times (up to 48 hours) at low current densities (less than 1 amp/square inch).

Once isolated, the gamma prime can be identified by characteristic X-ray diffraction patterns. The ASTM card index, Number 9-97, for pure Ni_3Al gives the following:

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
2.07	100	111
1.80	70	200
1.27	50	220

System - cubic

$$a_0 = 3.561 \text{ \AA}$$

The lattice spacing (a_0) changes with composition, titanium being the major solute element. Wilde and Grant report 3.561 Å as the observed lattice parameter for pure Ni_3Al , and 3.586 Å as the parameter for $\text{Ni}_3(\text{Al}_{0.5}\text{Ti}_{0.5})$, the latter being gamma prime with one-half the aluminum replaced by titanium.(16)

Early work by Nordheim and Grant showed that up to 65 per cent of the aluminum atoms in Ni_3Al could be replaced by titanium.(21) Later work by Decker, et al., showed that all of the aluminum could be replaced by titanium.(25) Other elements, such as chromium, cobalt, and iron, also are soluble to some degree in gamma prime and also affect the lattice parameter, although titanium is the most influential in this respect.

Eta, Ni_3Ti , 77

Eta phase exists in iron-, cobalt-, and nickel-base superalloys, particularly in the alloys having high titanium/aluminum ratios and those that have been exposed for long times at temperature. As seen by optical and electron microscopy, eta is an acicular compound that precipitates in a Widmanstätten pattern. In contrast to gamma prime, eta has a hexagonal crystal structure and has no solubility for other elements. Despite its hexagonal structure, eta is generally thought to be coherent with the matrix when the compound is first formed. Coherency is forced registry between pre-precipitate and matrix solid solutions. Upon further enrichment by titanium atoms, to near the stoichiometric composition, eta transforms to the hexagonal, acicular compound. Eta does not precipitate as rapidly as gamma prime and also tends to coalesce more rapidly and into larger particles than does gamma prime. Thus, eta is said to overage more rapidly than Ni_3Al .

The same etchants used for gamma prime can be used to delineate eta. Identification can be made by X-ray diffraction. ASTM card index Number 5-0723 includes the following:

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
1.95	100	202
2.13	50	201
2.07	50	004

System - hexagonal

$$a_0 = 5.093 \text{ \AA}, c_0 = 8.276 \text{ \AA}$$

Because eta has no significant solubility for other elements found in superalloys, the lattice parameter should not change.

Ni₃Cb

This phase jumped into prominence with the introduction of Inconel 718 by the International Nickel Company, Inc. This alloy contains about 5.3 per cent of columbium plus tantalum and only small amounts of aluminum and titanium, the elements usually used as "hardeners" in superalloys. Consequently it was thought that Ni₃Cb might be the hardening constituent. At the present time, the alloy is still relatively new and metallographic examinations have not definitely established the importance of various phases with regard to strength considerations. The Ni₃Cb phase, however, has been isolated and identified. It has an orthorhombic structure and exists in Inconel 718 in an acicular form within the temperature range of about 1500 to 1800 F, which is the overaged condition, when the strength of the alloy is considerably reduced from its maximum. Hansen and Anderko give the lattice parameters as $a_0 = 5.106 \text{ \AA}$, $b_0 = 4.251 \text{ \AA}$, and $c_0 = 4.556 \text{ \AA}$. Kaufman and Palty(24) give the following X-ray intensities based on the γ Cu₃Ti compound which is isomorphous with Ni₃Cb:

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
1.973	100	211
2.008	60	012
2.126	40	020

The electrolytes used during the extraction of residues were the same as those used for the gamma-prime studies (10 per cent of HCl in alcohol and 10 per cent of H₃PO₄ in water). For optical examination, etching was done electrolytically with a 5 per cent chromic acid solution.

Carbides

Carbides are important microconstituents in all of the superalloys, iron-, cobalt-, and nickel-base alike. Fortunately, only about four carbides

can be considered influential. These are MC, $M_{23}C_6$, M_6C , and M_7C_3 , with M representing one or more metallic elements. In cobalt-base alloys, the carbides are considered to be a major source of strengthening, forming a network structure that inhibits plastic deformation. They also serve to strengthen alloys by dispersion hardening; they are dispersed randomly throughout the structure.

All of the carbides of interest respond to heat treatment; none are inert to the matrix solid solution. They also are of variable composition, although certain elements tend to form one or another of the carbides. For example, chromium prefers the $M_{23}C_6$ and M_7C_3 carbide forms and precipitates only weakly in the M_6C - and MC-type carbides. Titanium, on the other hand, prefers the MC form to the exclusion of the others.

By optical and electron microscopy, the carbides can be revealed with many etchants including: (1) glyceric acid, (2) HF + glycerol + ethyl alcohol, (3) a solution of 92 per cent of HCl, 5 per cent of H_2SO_4 and 3 per cent of HNO_3 , or (4) electrolytically with 10 per cent chromic acid. These reagents will reveal the carbides, and the general structure, in relief.

As stated in the section on gamma prime (Ni_3Al), the electrolytic extraction of the carbides can be done with a 7 to 10 per cent solution of HCl in methanol. The solution developed by Mahla and Nielson, 50 parts of a 10 per cent solution of bromine plus 50 parts of methanol, also can be used.(8) The 20 per cent solution of H_3PO_4 in water is not recommended because it takes the $M_{23}C_6$ carbides into solution.(12) In the following sections, identification data will be given for each carbide form along with some comments on its general behavior.

MC

In superalloys, the MC carbide is predominantly TiC; this compound has some solubility for nitrogen, zirconium, and molybdenum. Titanium carbide is a phase of variable composition and can exist over a wide range of titanium contents. It also exists within wide temperature limits, usually starting to go into solution at about 1800 F. Radavich, along with Wilson(6) and Coutts(14), has shown that TiC decomposes into $M_{23}C_6$ with exposure to temperatures near 1800 F.

As seen unetched under the microscope, TiC is a globular, irregularly shaped particle that is gray to lavender in color. When present in extracted residue, TiC can be identified by X-ray diffraction data given on ASTM Index Card Number 6-0614. These data include:

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
2.18	100	200
2.51	80	111
1.54	50	220

System - cubic

$a_0 = 4.3285$ A at stoichiometric ratio

4.3127 A at 13.3 per cent Ti

4.3285 A at 15.3 per cent Ti

4.3291 A at 17.5 per cent Ti

Because of its solubility for nitrogen, TiC is often referred to in the literature as Ti(C,N). As will be pointed out later, this compound should not be confused with titanium nitride (TiN) that has some solubility for carbon and also is often designated Ti(C,N).

M₂₃C₆

The M₂₃C₆ carbide has been the subject of much investigation and discussion in relation to superalloys. It is the low-temperature form of the carbides and tends to form at grain boundaries. The temperature range of its existence varies with the alloy, but M₂₃C₆ generally goes into solution near 1900 F. Carbon taken into solution by high-temperature annealing often is redeposited at the grain boundaries at lower temperatures. Many investigators have correlated low ductility with grain-boundary precipitation of M₂₃C₆. Other studies have shown that the form that the M₂₃C₆ takes during precipitation at the grain boundaries is also very important. M₂₃C₆ can precipitate as films, globules, platelets, lamellae, and a cellular growth. The globular form is generally thought to be the "least undesirable" form, effecting greater ductility by shortening the length of microcracking at the grain boundaries.

The principal constituent of the metallic radical of M₂₃C₆ is chromium. Nickel, cobalt, iron, molybdenum, and tungsten can substitute for chromium. The amount of substitution reflects time at temperature and the relative abundance of each element in the alloy.

M₂₃C₆ can be identified by X-ray diffraction patterns of residues according to the following data from ASTM Index Card Number 9-122.

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
2.38	100	420
2.17	100	422
2.05	100	511

System - cubic

$$a_o = 10.638 \text{ A}$$

Naturally, the lattice parameter will change with the addition of solute atoms. Some data on this subject are given by Beattie and Ver Snyder.(26,27)

M₆C

The metallic radical of the M₆C carbide is composed predominantly of the heavy elements molybdenum and tungsten, although there is some solubility for chromium, nickel, and cobalt. Thus, it is usually found in cobalt-base superalloys (where considerable use is made of the heavy elements for solid-solution hardening) and in the nickel-base superalloys containing more than about 6 per cent of molybdenum(27) or tungsten, or both.

M₆C is stable at higher temperatures than is M₂₃C₆ and is present in the as-cast structure of many alloys. It is randomly distributed in the matrix of the as-cast alloys and has no distinguishing characteristics under the optical microscope, other than an occasional pinkish cast. The emphasis on "as-cast" M₆C stems from the fact that, according to Morris and Weisenberg, retention of as-cast M₆C is required to obtain optimum stress-rupture properties in René 41 alloy.(28) For this alloy, the solution temperature of M₆C is about 2150 F. It is imperative that annealing temperatures be kept below 2150 F or else the randomly distributed M₆C will be taken into solution and subsequently reprecipitated in the less desirable forms of intergranular M₆C and M₂₃C₆ carbides.

X-ray diffraction data for the M₆C carbide, taken from ASTM Index Card Number 11-546, are as follows:

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
2.10	100	333, 511
2.22	80	422
1.96	80	411

System - cubic

$$a_o = 10.85 \text{ A}$$

M₇C₃

For the M₇C₃ carbide, the metallic radical is again chromium with limited solubility for nickel. This carbide is not so prevalent as the previously described carbides and has been found most often in Nimonic 80 alloy and in certain cobalt-base alloys. Cr₇C₃ is stable to higher temperatures than is M₂₃C₆. Betteridge states that an intermediate solution anneal (actually a high-temperature aging) in the 1900 to 2000 F range initiates carbide precipitation as Cr₇C₃, so that less carbon is available to form the more undesirable M₂₃C₆ during a later, lower-temperature aging treatment or in service.(29) According to Hagel and Beattie, there are indications that Cr₇C₃ may transform to M₂₃C₆ after very long aging times.(12) M₇C₃ is not distinguishable from the other carbides during optical or electron microscope examination. X-ray data, as given by ASTM Card Index Number 11-550, are as follows:

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
2.04	100	421
2.28	70	411
2.12	70	202, 501

System - hexagonal

$$a_o = 13.98 \text{ \AA}, c_o = 4.523 \text{ \AA}$$

Carbides in Cobalt-Base Superalloys

As stated earlier, carbides are a major source of strengthening in cobalt-base alloys. Consequently, much work has been done on carbide identification in cobalt-base alloys by selective etching and heat tinting.

Differentiation of the various carbides present in Haynes Stellite Alloy No. 21 was discussed by Badger and Sweeney.(30) They recommend a very light electrolytic etch in 2 per cent chromic acid, followed by a 7-second etch in a solution consisting of equal parts of 20 per cent potassium permanganate solution and 8 per cent sodium hydroxide solution. In this type of etch, a selective staining action results, and the various carbides are identified as follows:

Cr₄C (actually Cr₂₃C₆), a cubic type containing both cobalt and molybdenum in solid solution, is colored brown.

Cr₇C₃, a hexagonal type containing cobalt and molybdenum in solid solution, is colored a very pale yellow to light tan.

M_3C , where M may be cobalt, chromium, or molybdenum, is not constant in color but will vary from red to green, and occasionally through yellow and blue. It is most easily identified by tiny cracks occurring in the layer deposited on it by etching.

The etchant used by Fletcher, et al., for cobalt-chromium-base alloys was not satisfactory for distinguishing carbides in carbon-bearing cobalt-chromium ternary alloys or on alloys of the Haynes Stellite No. 21 type.(31) A technique was devised in later work, however, for distinguishing between the sigma phase and carbides that contain molybdenum in solid solution and correspond roughly to the Cr_4C composition.(32) This technique consisted of an electrolytic etch in sodium cyanide solution, followed by a dip etch in Murakami's reagent under the following conditions:

Sodium cyanide, electrolytic

10 per cent aqueous solution of NaCN
1.5 volts
0.003 to 0.005 ampere
Usually 20 to 30 seconds

Murakami's reagent, dip

Potassium ferricyanide ($K_3Fe(CN)_6$), 10 g
Potassium hydroxide (KOH), 10 g
Water, 100 ml
Room temperature
2 to 4 seconds.

The electrolytic sodium cyanide outlines the carbide and sigma phases. Upon treatment with Murakami's etch, the sigma phase becomes a gray to blue-gray (occasionally a greenish-gray) and the $Cr_{23}C_6$ becomes a light straw to brownish-yellow or buff.

Attempts by Lane and Grant(33) to distinguish carbides in Vitallium-type alloys by the method of Badger and Sweeny(30) were generally unsuccessful. Although color resulted in Lane and Grant's research, they were not able to associate a color or colors with any one carbide. Etching of Vitallium-type alloys (as well as N-155, S-816, and 70 J) with a dilute acid, however, caused attack of the matrix, leaving the carbides light in color. Columbium and tantalum carbides were said to have a finer "Chinese script" structure and more relief than the chromium carbides. A slight difference in color was also noted. Electrolytic etching in a basic solution, instead of acid, attacked carbides rapidly, except for tantalum and columbium carbides.

Weeton and Signorelli(34,35) applied to Haynes Stellite No. 21 the stain-etching methods recommended by Fletcher, et al.(32), Badger and Sweeny(30), and Rideout and Beck(36). It was found, however, that the results were hard to interpret. For example, the colors of fine precipitates or thin pearlitic lamellae were not discernible. Composition, which depends also on the heat treatment, changed the colors of the large phases. Many of the colors observed by Weeton and Signorelli did not agree with the literature, if the results of X-ray diffraction analysis are taken as standards.

In the metallographic identification of M_6C -type carbides in Haynes Alloy No. 25, an electrolytic etch followed by a stain is used to darken the carbide.(37) The electrolytic etch is a 100 to 1 mixture of concentrated hydrochloric acid and 2 per cent chromic acid. The stain is a mixture of sodium hydroxide and potassium permanganate.

Heat Tinting. Spektor proposed a method of heat tinting to show up carbides in a tool steel.(38) Fletcher, et al., used a variation of this method on cobalt-base alloys.(17) In Fletcher's method, a metallographic specimen is placed, polished face up, on a piece of Inconel sheet heated by a Fischer burner to a dull red color. When the specimen becomes slightly colored, which usually takes from 1/2 to 5 minutes, it is quenched in mercury, care being taken to keep the mercury off the specimen surface. The resulting heat tint was usually enhanced when preceded by a light electrolytic etch to remove the small amount of disturbed metal remaining after polishing. Suitable etchants for this purpose were found to be 5 per cent hydrochloric acid or 10 per cent sodium cyanide.

This technique was used by Fletcher on alloys belonging to the Haynes Stellite No. 21 category. The etchant darkened particles of sigma phase to a medium-brown color, and showed coring in as-cast specimens especially well. The $M_{23}C_6$ carbides remained white under all conditions.

In similar alloys, Lane and Grant found that the M_6C was darkened by heat tinting.(33) Methods for distinguishing sigma from M_6C were not developed by either Fletcher or Lane and Grant.

The comments of Weeton and Signorelli regarding stain etching apply also to heat tinting; that is, it was often difficult to distinguish the various carbides because of the tendency to stain everything the same color.(34,35) It did appear certain, however, that the $Cr_{23}C_6$ -type of carbide remained white.

A complete list of etchants for cobalt-base alloys is included in the appendix.

Borides

Only a relatively small amount of work has been done on the borides in superalloys. Until recently, boron was not added to alloys in a quantity sufficient to form borides as separate phases. Radavich and Boesch identified a boride phase, M_3B_2 , in a nickel-base alloy containing 0.03 per cent of boron.(15) Radavich and Coutts showed that this phase becomes unstable between 1800 and 1900 F.(14,39)

The Soviets have made studies on nickel-base superalloys containing up to 0.50 per cent of boron.(9) Using an electrolyte of 50 parts of HCl, 100 parts of glycerine, and 1050 parts of methanol, the Soviets isolated borides and identified them as either M_4B_3 or M_5B_4 . The M radical contained molybdenum, chromium, tungsten, and nickel, with chromium and molybdenum being the major components. X-ray diffraction studies gave the following data:

M₄B₃ Phase

<u>"d" spacing</u>	<u>intensity</u>
1.97	strong
1.85	med. strong
1.72	med. strong
1.244	strong
1.229	strong
1.145	med. strong
1.022	med. strong

System - face-centered-
tetragonal

$$a_o = 7.71 \text{ kx}, c_o = 10.16 \text{ kx}$$

M₅B₄ Phase

<u>"d" spacing</u>	<u>intensity</u>
2.59	strong
2.12	strong
1.99	strong
1.40	strong
1.338	strong
1.279	strong
1.251	strong
1.187	strong
1.044	strong
0.965	strong

The crystal structure of the M₅B₄ phase was not definitely established.

Beattie and Hagel found the M_3B_2 phase in Incoloy 901, an iron-nickel-base superalloy containing 0.1 per cent of boron.(11) In their study, M_3B_2 had a tetragonal crystal structure with lattice parameters of about $a_0 = 5.795$ A and $b_0 = 3.135$ A. It was stable at all temperatures from 1200 through 2200 F. The borides cannot be distinguished from the carbides by light or electron microscopy.

Nitrides

The nitrides usually found in superalloys are those of titanium, columbium, and, to a lesser extent, zirconium. Actually, all three nitrides form solid solutions and would be likely to form (Ti, Cb, Zr)N or (Ti, Cb, Zr)(C,N), as all have some solubility for carbon.

All of the nitrides are chemically inert to the remainder of the alloy and do not respond to heat treatments below the alloy's melting point. Herein lies the major difference between titanium nitride (with some solubility for carbon) and titanium carbide (with some solubility for nitrogen). Both are often designated Ti(C,N), but the carbide responds to heat treatment and the nitride does not. The nitrides are formed in the liquid melt and solidify prior to solidification of the ingot. It is not surprising, therefore, to find a lesser amount of nitrides in alloys that have been carefully vacuum melted.

The nitrides are easily recognized upon optical investigation without etching; they are easily identifiable in shape and in color. From the metallographic point of view, they are the most outstanding of the microconstituents, being regular in shape and ranging from golden to orange in color. The nitrides high in carbon often have a black dot in the center of the inclusion. Most often the nitrides appear square or rectangular in shape in a metallographic specimen but occasionally they assume a hexagonal configuration, depending on the plane of polish. In any case, they always are a regular, sharp configuration rather than an irregular blob or stringer.

X-ray diffraction data for TiN are given in ASTM Index Card Number 6-0642.

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
2.12	100	200
2.44	77	111
1.50	56	220

System - cubic

$a_0 = 4.240$ A

Other Phases

Superalloys sometimes contain several phases that are of relatively minor importance. These phases generally are not desirable and do not contribute to either the strength or the ductility of the alloys. Nevertheless they often occur, being formed by the interaction of two or more of the many elements that make up the completely alloyed superalloys.

Three examples of such compounds are "mu phase" (sometimes called epsilon), one or more of the Laves phases, and sigma phase.

Mu or epsilon phase is usually designated by the empirical formula $(\text{Fe}, \text{Co})_7(\text{Mo}, \text{W})_6$ although nickel can replace iron and cobalt. The phase exists over a narrow temperature range (1700 to 1800 F for René 41) and is usually found in superalloys containing relatively large amounts of the heavy elements molybdenum and tungsten. When viewed by either light or electron microscopy, mu phase appears as coarse, irregular Widmanstätten platelets. X-ray diffraction data taken from ASTM Index Card Number 9-298 is as follows:

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
2.07	100	not given
2.37	70	not given
2.17	60	not given

Laves phases are most abundant in iron-base superalloys, and sigma phases are most often found in cobalt- and iron-base superalloys, rather than in nickel-base alloys. Laves phases are of the AB_2 type, where A is a transition element and B is an element of the IV, V, and VI groups having a large atomic diameter. Sigma is a phase formed by two transition elements and is very hard and brittle. An example of Laves phase is Fe_2Ti (hexagonal), while a typical sigma is FeCr (tetragonal).

X-ray diffraction data for Fe_2Ti from ASTM Index Card Number 3-1040 is as follows:

<u>"d" spacing</u>	<u>relative intensity</u>	<u>hkl</u>
2.04	100	not given
2.00	100	not given
1.30	85	not given

System - hexagonal

$$a_0 = 4.77 \text{ \AA}, c_0 = 7.79 \text{ \AA}$$

Both sigma and Laves phases can appear as irregular globes which are usually elongated. In some cases a Laves phase can appear as so-called "Chinese script".

Identification of Various Phases
in Cobalt-Base Superalloys

An electrolytic etching procedure for distinguishing between the phases in cobalt-rich, cobalt-chromium-base alloys containing iron, nickel, nitrogen, tungsten, and molybdenum was described by Fletcher, et al.(31) The carbon content was low in all of these alloys. The following reagents were recommended:

Reagent 1 : Ethyl alcohol, 100 cc
Ethylene glycol, 20 cc
Nitric acid, 20 cc

Potential, 1-1/2 v

Reagent 2 : Water, 100 cc
Citric acid, 5 g
Boric acid, 6 g

Potential, 3 v

Reagent 3 : 0.5 per cent solution of chromic acid in
water

Potential, 1-1/2 to 4-1/2 v

Alpha phase, the high-temperature modification of the cobalt-rich terminal solid solution, shows no structural features when lightly etched with Reagent 1, and upon prolonged etching becomes roughened without developing grain boundaries. Subsequent etching with Reagent 2 makes the roughening more conspicuous. Epsilon phase, the low-temperature modification of the cobalt-rich terminal solid solution, will, unlike the alpha phase, develop grain boundaries without roughening on prolonged etching in Reagent 1. When specimens containing mixtures of alpha and epsilon are lightly etched with Reagent 1, the alpha phase is attacked more rapidly than epsilon; when subsequently etched with Reagent 2, the alpha phase is darkened more than the epsilon phase. The sigma phase, corresponding approximately to $\text{Co}_{13}\text{Cr}_{17}$, shows little or no attack when etched in any of the three reagents described above. Both alpha and epsilon are stained yellow to buff in Reagent 3, and consequently, this reagent may be used to identify sigma in mixtures of alpha, epsilon, and sigma.

Sigma in ternary chromium-cobalt-nickel alloys was identified by Manly and Beck(40) by means of the following reagent:

Nitric acid 10 cc
Hydrochloric acid 20 cc
Glycerol 20 cc
Hydrogen peroxide (3 per cent) 10 cc
(Hydrogen peroxide is the most critical constituent.)

The specimens were dipped into the solution for 10 seconds. This reagent darkened the sigma phase to a color varying from light brown to purple, depending on the etching time, and did not attack the alpha phase (cobalt-rich terminal solid solution). Frequently, positive identification of sigma was made by observing that cracks ran through this phase but stopped at the alpha phase.

In work on the chromium-cobalt-nickel-molybdenum system at 1200 C, Rideout and Beck identified a number of phases by metallographic techniques.⁽³⁶⁾ A phase, which they labeled mu, is a solid solution based on the cobalt-molybdenum epsilon phase. It occurs in the 1200 C isothermal sections of the chromium-cobalt-molybdenum and cobalt-nickel-molybdenum ternary systems. Another phase, designated R, exists at 1200 C in the chromium-cobalt-molybdenum ternary system. To distinguish these phases, Rideout and Beck used the following procedure:

For chromium-cobalt-molybdenum alloys, the specimens were electrolytically etched in a 5 per cent phosphoric acid solution for 10 to 15 seconds at 6 volts. The specimen was removed from the etching bath and immediately immersed for 10 to 20 seconds in a staining solution consisting of 5 grams of potassium permanganate and 5 grams of sodium hydroxide dissolved in 40 ml of distilled water. The alpha phase was lightly etched, but was not stained; whereas, the sigma was lightly etched and stained colors ranging from orange to blue or purple. The R phase, while unattacked by the electrolytic etching solution, was stained yellow to rusty brown. The mu phase, if stained at all, was usually a pale blue after the treatment.

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APPENDIX

BATTELLE MEMORIAL INSTITUTE

APPENDIX

Polishing and Etching

Polishing

The polishing and etching of superalloys must be done with considerable care, particularly if electron microscopy is to be used. As is the case with most alloys, mechanical polishing leaves a layer of cold-worked material which must be removed before a representative structure can be obtained. Also, there is the likelihood that particles of some of the minor phases may be removed. Mechanical polishing does, however, result in a smooth surface with both matrix and minor phases on the same level. When the matrix is etched away, the minor phases are smooth and flat, a useful condition in light microscopy. This smooth, flat condition of minor phases may or may not be an asset for electron microscopy. In this case, more precise measurements can often be made when the larger, more abundant particles stand out in strong relief, helping to focus the electron beam.

Electrolytic polishing results in an undulating surface with the minor phases standing in relief with jagged, irregular corners. This does not interfere with electron microscopy because the depth of field is larger and the field of vision is smaller than in light microscopy. The main objection to electrolytic polishing is the possibility of contamination of the surface by adherent, insoluble products formed during electrolysis. Removal of these products often is difficult because the minor phases are in relief, thus hindering the physical removal of small particles. For best results in electrolytic polishing, a mixture of perchloric acid and organic acids is best. Two solutions that have been used with success are (1) 9 volumes of glacial acetic acid plus 1 volume of concentrated perchloric acid (68 to 72 per cent), and (2) 20 per cent solution of perchloric acid in ethyl alcohol.

Etchants Used in Optical and Electron Microscopy of Nickel-Base Superalloys

1. 50 parts aqua regia⁽⁴⁾
50 parts glycerine
(immersion)
2. 5 parts hydrofluoric acid (48 per cent)^(4,21)
10 parts glycerol
85 parts water
(electrolytic)
3. 5 parts hydrofluoric acid (48 per cent)⁽⁴⁾
10 parts glycerol
10 to 50 parts ethyl alcohol
Balance water
(electrolytic)

4. 5 parts hydrofluoric acid (48 per cent)(4)
10 parts glycerol
85 parts ethyl alcohol
(electrolytic)
5. 29 parts cupric chloride (1 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ per 5 ml of water)(20)
36 parts acetic acid (glacial)
23 parts hydrochloric acid (38 per cent)
5 parts sulfuric acid (96 per cent)
7 parts chromic acid (1 g CrO_3 per 3 ml of water)
(electrolytic)
6. 12 parts phosphoric acid (85 per cent)(20,22)
47 parts sulfuric acid (96 per cent)
41 parts nitric acid (70 per cent)
(electrolytic)
7. 11 parts phosphoric acid (85 per cent)(20)
45 parts sulfuric acid (96 per cent)
29 parts nitric acid (70 per cent)
15 parts water
(electrolytic)
8. 21 parts sulfuric acid (96 per cent)(20)
15 parts hydrochloric acid (38 per cent)
21 parts nitric acid (70 per cent)
21 parts hydrofluoric acid (48 per cent)
22 parts water
(electrolytic)
9. 40 parts cupric chloride (1 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ per 5 ml of water)(20)
40 parts hydrochloric acid (38 per cent)
20 parts hydrofluoric acid (48 per cent)
(electrolytic)
10. 2 parts sulfuric acid (96 per cent)(4)
98 parts water
(electrolytic)
11. 10 parts oxalic acid(21)
90 parts water
(electrolytic)
12. 92 parts hydrochloric acid(26)
5 parts sulfuric acid
3 parts nitric acid
(immersion)
13. 50 parts of 4 per cent NaOH solution(26)
50 parts saturated KMnO_4 solution
(immersion)

14. 10 parts chromic acid⁽²⁶⁾
90 parts water
(electrolytic)
15. 2 parts chromic acid⁽²⁶⁾
98 parts water
(electrolytic)
followed immediately by etching in
20 parts KMnO_4
8 parts NaOH
72 parts water.

Etchants for Cobalt-Base Alloys⁽⁴¹⁾

Etch	Remarks
16. 5 per cent H_2CrO_4 , electrolytic, 5 g CrO_3 , 95 cc H_2O	Use two dry cells in series, specimen as anode, carbon cathode; 1-5 sec.
17. 10 g CrO_3 , 90 cc H_2O	Use at 3 volts for 3 seconds (also 6 volts for 10 seconds).
18. 4 parts HCl , 1 part H_2O_2 (30 per cent)	Immersion for 1-10 sec; make up fresh each day.
19. $\text{HCl-H}_2\text{O}_2$	Specimen is immersed in concentrated HCl , and H_2O_2 is added dropwise until first sign of solution decomposition; then specimen is removed.
20. Saturated solution of oxalic acid	Electrolytic (sintered alloys)
21. 10 per cent oxalic acid	Electrolytic
22. 20 cc HCl , 80 cc acetic acid	Electrolytic, 6 volts
23. Heat tinting	Heat only
24. 20 per cent $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution	
25. 50:50 $\text{HNO}_3\text{-H}_2\text{O}$	
26. 0.5 g NaOH , 100 cc H_2O	Low current density, 110-volt d.c. Use 4 cp lamps in series with 2 platinum wire terminals. Flood specimen with solution. Make contact with one wire, move other around for uniform surface etching.

Etch	Remarks
27. 60 cc HCl, 15 cc HNO ₃ , 15 cc H ₂ O	Age solution, immersion or electrolytic. Will reveal grain boundaries and general structure.
28. 92 per cent HCl, 5 per cent H ₂ SO ₄ , 3 per cent HNO ₃	Immerse 10 seconds
29. 5 per cent H ₂ SO ₄ in 90 to 95 per cent boric acid	Electrolytic
30. 5-10 per cent HCl, electrolytic	Use two dry cells in series, specimen as anode, carbon cathode; 1-5 sec.
31. a) H ₂ CrO ₄ , electrolytic 2 g CrO ₃ , 98 cc H ₂ O	Use four dry cells in series, specimen as anode, carbon cathode; 5-10 sec; make up fresh each day.
b) NaOH-KMnO ₄ , 1 part KMnO ₄ (20 per cent), 1 part NaOH (8 per cent)	Immersion after (a)
32. 6 per cent aqua regia, electrolytic 95 cc H ₂ O	Use four dry cells in series, specimen as anode, carbon cathode; 5-10 sec; make up fresh each day.

Electrolytes Used to Obtain Residues of Minor Phases by Selective Dissolution

- 10 parts hydrochloric acid⁽⁶⁾
90 parts methyl alcohol
(electrolytic)
- 15 parts phosphoric acid⁽⁷⁾
85 parts water
(electrolytic)
- 5 to 10 parts bromine⁽⁸⁾
100 parts methyl alcohol
(immersion)
- 10 g ammonium sulfate⁽⁹⁾
10 g citric acid
1.2 l water
(electrolytic)
- 50 parts hydrochloric acid⁽⁹⁾
100 parts glycerine
100 parts methyl alcohol
(electrolytic)

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A list of DMIC Memoranda 1-117 may be obtained from DMIC, or see previously issued memoranda.

DMIC Memorandum Number	Title
118	Review of Recent Developments in the Metallurgy of High-Strength Steels, July 21, 1961, (AD 259986 \$0.50)
119	The Emittance of Iron, Nickel, Cobalt and Their Alloys, July 25, 1961, (AD 261336 \$2.25)
120	Review of Recent Developments on Oxidation-Resistant Coatings for Refractory Metals, July 31, 1961, (AD 261293 \$0.50)
121	Fabricating and Machining Practices for the All-Beta Titanium Alloy, August 3, 1961, (AD 262496 \$0.50)
122	Review of Recent Developments in the Technology of Nickel-Base and Cobalt-Base Alloys, August 4, 1961, (AD 261292 \$0.50)
123	Review of Recent Developments in the Technology of Beryllium, August 18, 1961, (AD 262497 \$0.50)
124	Investigation of Delayed-Cracking Phenomenon in Hydrogenated Unalloyed Titanium, August 30, 1961, (AD 263164 \$0.50)
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126	A Review of Recent Developments in Titanium and Titanium Alloy Technology, September 15, 1961, (AD 263167 \$0.50)
127	Review of Recent Developments in the Technology of Tungsten, September 22, 1961, (AD 263888 \$0.50)
128	Review of Recent Developments in the Evaluation of Special Metal Properties, September 27, 1961, (AD 263994 \$0.50)
129	Review of Recent Developments in the Technology of Molybdenum and Molybdenum-Base Alloys, October 6, 1961, (AD 264291 \$0.50)
130	Review of Recent Developments in the Technology of Columbium and Tantalum, October 10, 1961, (AD 264983 \$0.50)
131	Review of Recent Developments in the Technology of High-Strength Stainless Steels, October 13, 1961, (AD 264984 \$0.50)
132	Review of Recent Developments in the Metallurgy of High-Strength Steels, October 20, 1961, (AD 265135 \$0.50)
133	Titanium in Aerospace Applications, October 24, 1961, (AD 266927 \$1.50)
134	Machining of Superalloys and Refractory Metals, October 27, 1961, (AD 268081 \$1.00)
135	Review of Recent Developments in the Technology of Nickel-Base and Cobalt-Base Alloys, October 31, 1961, (AD 266004 \$0.50)
136	Fabrication of Tungsten for Solid-Propellant Rocket Nozzles, November 2, 1961, (AD 268311 \$0.75)
137	Review of Recent Developments on Oxidation-Resistant Coatings for Refractory Metals, November 8, 1961, (AD 266469 \$0.50)
138	Review of Recent Developments in the Technology of Beryllium, November 16, 1961, (AD 267079 \$0.50)
139	Review of Recent Developments in the Technology of Tungsten, November 24, 1961, (AD 268082 \$0.50)

LIST OF DMIC MEMORANDA ISSUED
(Continued)

DMIC Memorandum Number	Title
140	Review of Recent Developments in Metals Joining, December 6, 1961, (AD 268312 \$0.50)
141	The Emittance of Chromium, Columbium, Molybdenum, Tantalum, and Tungsten, December 10, 1961, (AD 269784 \$1.25)
142	Effects of Moderately High Strain Rates on the Tensile Properties of Metals, December 18, 1961, (AD 270167 \$1.00)
143	Notes on the Forging of Refractory Metals, December 21, 1961, (AD 271030 \$1.50)
144	Review of Recent Developments in Titanium Alloy Technology, December 29, 1961, (AD 269209 \$0.50)
145	The Use of Nickel-Base Alloys in the Rotating Parts of Gas Turbines for Aerospace Applications, January 11, 1962, (AD 271174 \$0.75)
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151	Compatibility of Propellants 113 and 114B2 with Aerospace Structural Materials, April 27, 1962, (AD 275427 \$0.50)
152	Electron-Beam Welding of Tungsten, May 21, 1962, (AD 276283 \$0.50)
153	Brazing and Bonding of Columbium, Molybdenum, Tantalum, Tungsten and Graphite, June 11, 1962
154	The Effects of Decarburization on the Properties of Ultrahigh-Strength Steels, June 18, 1962
155	The Effects of Solutes on the Ductile-to-Brittle Transition in Refractory Metals, June 28, 1962
156	Properties of Mar-Aging Steels, July 2, 1962
157	A Compilation of the Tensile Properties of Tungsten, September 11, 1962
158	Summary of Briefings on Refractory Metal Fasteners, October 8, 1962
159	Nondestructive Testing of Solid-Propellant Rocket Motors, October 24, 1962
160	Identification of Microconstituents in Superalloys, November 15, 1962

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