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AN INVESTIGATION OF LAMELLAR STRUCTURES AND MINOR PHASES IN ELEVEN COBALT-BASE ALLOYS BEFORE AND AFTER HEAT TREATMENT

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AN INVESTIGATION OF LAMELLAR STRUCTURES AND MINOR PHASES IN ELEVEN COBALT-BASE ALLOYS BEFORE AND AFTER HEAT TREATMENT

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SUMMARY

An investigation was conducted to determine the occurrence and nature of lamellar structures and minor phases, by the use of metallographic and X-ray diffraction studies, of the following cobalt-base high-temperature alloys: rolled, cast, and high-carbon Stellite 21, 422-19, X-63, 6059, 61, X-40, S-816, I-336, and J.

The microstructures of as-cast alloys were generally found to contain interdendritic minor phases, many of which are low-melting eutectics; in addition, cast Stellite 21, 422-19, 61, and X-40 contained pearlitic structures. The only as-rolled alloy studied, Stellite 21, contained large carbide spheroids. Fine microconstituents in such forms as pearlite and feathery structures readily dissolved into the matrix upon solution treatment. In general, alloys with high carbon content (0.36 percent and above) and those with tantalum and niobium, contained appreciable quantities of undissolved large carbides after the solution treatment. Lamellar structures were produced in eight of the eleven alloys by heat treatments.

In molybdenum-bearing alloys it was found that the temperature at which lamellar structures first formed decreased with decreasing chromium content. Tungsten appeared to lower the temperature of lamellar precipitation, whereas nickel had no noticeable effect on the transformation.

The X-ray diffraction patterns indicated one or more of the following minor phases in each of the alloys: TaC, CbC, Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$, M_6C, Cr_2N, Cr_2O_3 type oxides, spinels, and the sigma phase. Some of the carbides listed as chromium carbides could contain carbide formers other than chromium, while other carbides could contain nitrogen. Sigma phase patterns appeared strongest when large numbers of carbides were also present and carbide precipitation may have facilitated the formation of sigma phase. The most prevalent carbide indicated was $Cr_{23}C_6$.

Sigma phase was thought to form in conjunction with or subsequent to the formation of $Cr_{23}C_6$ in heat-treated Stellite 21.

The relative quantities of the matrix phases, either the high-temperature phase, alpha (a face-centered cubic solid solution) or the lower temperature phase, beta (a hexagonal close-packed solid solution), were estimated from the X-ray diffraction patterns in each alloy in various conditions of heat treatment.

Studies of pearlitic structures indicated that one of the phases of the pearlite consisted predominantly of the carbide $Cr_{23}C_6$. The other phase of the pearlitic structure was indicated to be related to the beta matrix phase, but positive identification could not be made.

INTRODUCTION

The microstructures of several cobalt-base alloys are known to contain different carbides and, in some cases, a pearlitic structure similar to that found in steels. Several of the commercially used alloys, and in particular, Stellite 21, are known to respond to heat treatments and, in fact, the operating lives of cast, heat-treated Stellite 21 turbosupercharger blades have been doubled by suitable heat treating. The best performance of heat-treated turbosupercharger blades was associated with pearlitic microstructures (ref. 1).

Badger and Sweeney (ref. 2) observed pearlitic structures in such cobalt-base alloys as 61, 6059, and X-40 (Stellites 23, 27, and 31, respectively) and the carbides $M_{23}C_6$, M_6C, and Cr_7C_3 in Stellite 21 (where M represents any carbide-forming element). Reference 3 reports $M_{23}C_6$ and MC carbides in cobalt-base alloys; $M_{23}C_6$, M_6C, Cr_7C_3, and the sigma phase were found in Stellite 21 and Stellite 21 type alloys (ref. 4). Such carbides as Cr_3C_2, $Cr_{23}C_6$, M_6C, Cr_7C_3, and MC were observed in one or more alloys such as Stellite 21 type alloys, 422-19, and J (ref. 5). Also introduced in reference 5 is a concept of carbide decomposition: Cr_7C_3, which is rich in carbon, was believed to undergo the following decomposition upon aging:

$$Cr_7C_3 \longrightarrow Cr_{23}C_6 + \text{free carbon}$$

$$\text{Free carbon} + Cr \longrightarrow \text{additional } Cr_{23}C_6$$

The matrix phases of several of these alloys are known (refs. 2, 4, and 6) to be either face-centered cubic (alpha) or hexagonal close-packed (beta).

The investigation reported herein was conducted to determine the occurrence and nature of lamellar structures and minor phases in the following cobalt-based alloys: rolled, cast (AMS 5385A), and high-carbon Stellite 21, 422-19 (AMS 5380), X-63, 6059 (AMS 5378), 61 (AMS 5375), X-40 (AMS 5382), S-816 (AMS 5765), I-336, and J. It was intended to determine if the beta phase (hexagonal close packed) or carbon is necessary for pearlite formation and if pearlitic structures were the result of a eutectoid decomposition, and also to consider the effects of the principal alloying elements on the formation of lamellar structure.

MATERIALS, APPARATUS, AND PROCEDURE

Materials. - Chemical compositions of the eleven alloys investigated are listed in table I and were, for the most part, supplied by the manufacturers. Specimens were cut from roots of cast turbine blades in the cases of alloys 2, 3, 5, 9, and 11 (table I); from cylindrically shaped castings for alloys 4, 6, 7, 8, and 10; and from rolled bar stock for alloy 1. All specimens were approximately 3/16 inch thick and 0.2 inch square in cross-sectional area.

Heat treatment. - The specimens were separated into six groups, each group containing one specimen from each of the eleven alloys. One group was examined in the as-received condition. Each of the remaining five groups, hereinafter designated as A, B, C, D, and E was fastened together with Inconel wire strung through 1/16-inch holes and heat-treated in a zircon combustion tube furnace in a dried argon atmosphere. The specimens were found to be lightly scaled and the edges decarburized as a result of loading and unloading the furnace. The temperature of the specimens was controlled to within $\pm 5^{\circ}$ F by means of platinum - platinum-rhodium thermocouples.

Groups A, B, C, and D were simultaneously solution-treated at a temperature of 2250° F for $41\frac{1}{4}$ hours and subsequently cooled to various isothermal levels as the furnace temperature was lowered in the steps indicated by figure 1. Group A was removed after the solution treatment and quenched in brine, whereas groups B, C, and D were quenched in brine from 2000°, 1900°, and 1800° F, respectively, after being held for 2 hours at their respective temperatures. Because of an accident, group E was homogenized for 17 hours rather than 41 hours and subsequently heat-treated as shown in figure 1.

Metallographic examinations of the heat-treated specimens just described indicated that longer times at temperatures below 1800° F might produce more precipitation in alloys X-63, 6059, and 61, and that a lower solution-treating temperature would lessen the extent of eutectic melting which had occurred in alloy J at 2250° F. Therefore, these alloys were reheat-treated (groups F and G) as shown in figure 2. In this series of heat treatments, an Inconel (rather than a zircon) combustion tube was used as the heat-treating chamber of the furnace to decrease decarburization of specimens.

Metallographic examinations. - Specimens were prepared for examination by standard metallographic techniques. The photomicrographs of figures 3 to 13 were originally made at the magnifications indicated under each figure. However, a reduction of 20 percent was made during publication.

X-ray diffraction studies. - To identify the crystal structures of matrix and minor phases, X-ray diffraction patterns were obtained from as-received and heat-treated specimens E with only a few exceptions. The E specimens were chosen because they contained the greatest quantities of precipitates as shown by metallographic examinations.

Powders for the X-ray diffraction studies were ground from specimens with a small tungsten carbide burr mounted in a high-speed drill press and were stress-relief annealed at 1500° F for 1/2 hour in evacuated quartz tubes (0.5 micron pressure). A temperature of 1500° F would appear high; however, this stress-relieving treatment was of such duration that the X-ray results were found to be unchanged. The annealed powders were mounted on a fine quartz fiber and patterns were obtained with a 143.2-millimeter-diameter Debey-Scherrer powder camera and chromium radiation. Exposure times of 25 to 40 hours were used and one third of the width of each pattern was filtered with a vanadium oxide coated paper strip. The patterns were measured with a vernier scale to the nearest 0.1 millimeter. The Straumanis technique (ref. 7) was used to compensate for film shrinkage.

Identifications of minor phases were made by comparing the patterns obtained with standard patterns of carbides and intermetallic compounds that appeared reasonable on the basis of composition and which are listed in the A.S.T.M. card index or in the literature (see table II). Only the stronger lines of the standard patterns were used for the comparisons. The analysis of the patterns were difficult because of the weakness, the great number, and the overlapping of the diffraction lines. These difficulties prohibit positive statements that every minor phase listed in the results (table VIII) actually was present.

Concentration techniques attempted. - Attempts to strengthen the minor phase lines relative to matrix-phase lines in order to permit more positive identifications were also made. Such techniques as sieving of powders and partial digestion of powders were tried but, in general, the patterns were not improved. A method which consisted in polishing and relief etching specimens to cause minor phases to stand in relief, followed by grinding with a burr, did strengthen the minor phase lines but analysis of the patterns did not result in the detection of additional minor phases.

Supplementary X-ray studies of heat-treated, rolled Stellite 21. - Rolled Stellite 21 in various heat-treated conditions was selected for a more detailed investigation as a "typical" cobalt-base alloy. Furthermore, since it was hot-rolled, its fine grain size (A.S.T.M. 7-8) would permit better control of the microstructures by heat-treating.

As shown in table III, powder specimens given heat treatments M, O, P, R, and S were obtained from heat-treated metallic slugs by grinding with the tungsten carbide burr. As was previously described, these powders were annealed at 1500° F for 30 minutes. Specimens given heat treatments L, N, and Q were solution-treated as slugs but the powders ground from the solution-treated slugs were sealed in evacuated quartz tubes and again solution-treated and isothermally transformed in the powdered form.

Stain etching and heat tinting. - To supplement the X-ray data, an attempt was made to verify metallographically the presence of different carbides and the sigma phase. Three types of stain etchant were selected from the literature (table IV). The first etchant was intended to color the sigma phase; the second to differentiate between carbides and the sigma phase, and the third to differentiate among and to identify the carbides. Heat tinting as described in reference 5 but more nearly approaching the method described in reference 4 was also used. The specimens that were selected for stain etching and heat tinting and the reasons for their selection are shown in table V.

RESULTS

Microstructures. - Microstructures of as-received specimens, those solution-treated (heat treatment A), and those given heat treatment E are shown in figures 3 to 13. The as-received specimen of Stellite 21 in the as-rolled condition was found to be extremely fine grained (A.S.T.M. 7-8) and to consist of equiaxed grains, massive carbides, and fine, difficult-to-resolve precipitates in the grain boundaries. The rest of the as-received specimens were in the as-cast condition and contained, in most cases, interdendritic minor phases, many of which were low-melting eutectics. Pearlitic structures were found in the following alloys in the as-cast condition:

Relative quantity of pearlitic structure	Alloy	Fig.
Large	Cast Stellite 21	4(a)
Large	422-19	6(a)
Small	High-carbon Stellite 21	5(a)
Trace	61	9(a)
Trace	X-40	10(a)

Relative amounts of pearlitic structure were visually estimated and are arbitrarily defined as follows: large quantity, greater than 5 percent, small quantity, trace to 5 percent; trace, able to detect presence of structure. No pearlitic or feathery structures were found in the other as-cast alloys, nor were any present in the as-rolled Stellite 21.

The solution treatment at 2250° F for 41 hours dissolved most of the minor phases in the alloys rolled, cast, and high-carbon Stellite 21, and X-63 (figs. 3, 4, 5, and 7). In the other alloys, particularly those containing niobium, tantalum, and large amounts of tungsten, the quantities of minor phases dissolved by the solution treatment were less (figs. 6, 8, 9, and 10). The solution treatment used was rather ineffective for alloys I-336 and S-816 inasmuch as large portions of the minor phases remained undissolved, (figs. 11 and 12). Solution treatment at 2250° F of the J alloy produced eutectic melting (fig. 13(b)). However, the eutectic and most of the minor phases present at higher temperatures in the J alloy were dissolved in the matrix at lower temperatures (fig. 13(c)).

Table VI shows the relative quantities of lamellar structures formed in the alloys by the heat treatments. Heat treatment E produced the maximum quantities of lamellar structures in the form of pearlitic and feathery precipitates after the specimens had been homogenized. The following alloys were found to contain such structures:

Alloy	Relative quantity of pearlitic structure	Relative quantity of feathery structure	Fig.
Rolled Stellite 21	Large	Large	3(c)
Cast Stellite 21	Large	Large	4(c)
High-carbon Stellite 21	Large	Large	5(c)
422-19	Small	Small	6(c)
X-63	-----	Small	7(c)
6059	Small	Small	8(c)
61	-----	Small	9(c)
X-40	Large	-----	10(c)

Thus, it was possible to produce pearlitic or feathery structures in three alloys, rolled Stellite 21, X-63, and 6059, that contained no such structures before heat treatment. Alloy 61 contained a trace of pearlitic structure before heat treatment but only the feathery structure after heat treatment. The quantity of pearlitic structure produced in heat-treated X-40 was much greater than that found in the as-cast structure. A few alloys contained traces of Widmanstätten structures and the J alloy contained a few areas with lamellar precipitates such as shown in figure 13(c).

The photomicrographs of specimens solution-treated at 2250° F followed by transformation treatments at 1800°, 1700°, 1500°, 1400°, and 1200° F (heat treatments F) are shown in figure 14. Compared with the specimens given heat treatments B through E, X-63 (fig 14(a)) contains more precipitation in the form of a Widmanstätten structure; 6059 (fig. 14(b)) contains more salt-and-pepper precipitation; alloy 61 (fig. 14(c)) contains more precipitation in the matrix, including precipitation in slip lines. Solution treatment at 2250° F produced eutectic melting in alloy J and, therefore, a solution-treating temperature of 2150° F was used (heat treatment G). The lower temperature eliminated the eutectic melting but was not very effective as a solution treatment (fig. 14(d)).

X-Ray Diffraction Results

Matrix phases. - The percentages of the alpha (face-centered cubic) and beta (hexagonal close-packed) matrix phases were visually estimated from the intensities of the diffraction lines (table VII).

Minor phases. - The results of the X-ray diffraction analyses of eleven alloys are given in table VIII. Several types of carbide, with high and low metal-to-carbon ratios, were indicated to be present in several of the alloys. The carbides $Cr_{23}C_6$ and M_6C were frequently indicated, while evidence of Cr_3C_2 and Cr_7C_3 were somewhat less prevalent. In those alloys containing niobium or tantalum (S-816, I-336, and J) carbides such as CbC and TaC were found. The sigma phase and the nitride Cr_2N appeared to be present in many specimens. In the specimens given heat treatments F and G, most of the phase indications were more conclusive than in the comparable specimens given heat treatment E.

It should again be noted that some of the carbides listed as chromium carbides undoubtedly contained other elements replacing part of the chromium. Also carbides such as CbC and TaC could have contained large percentages of nitrogen, substituting for some of the carbon.

Many of the X-ray patterns obtained were found to contain large numbers of diffraction lines, frequently 30 or more and occasionally as many as 60. In comparing the large numbers of diffraction lines for a given specimen with the large numbers of standard patterns listed in table II, it frequently was found that several phases other than those presented in table VIII could be considered present or possible in the alloy under consideration. However, these indications could never be considered better than questionable because the standard patterns of these phases either had no unique lines, (too many overlapping d-values), too few strong lines for satisfactory indications, or both, and therefore are not presented.

The results of the supplementary X-ray identification of minor phases in heat-treated rolled Stellite 21 are shown in table IX. No certain evidence of any minor constituents were found in the solution-treated specimen (treatment L) but some of the diffraction lines found in the X-ray pattern indicated that M_6C and $Cr_{23}C_6$ may not have completely dissolved during the 16-hour solution treatment. Evidence of the formation of $Cr_{23}C_6$ and sigma phase were found in the specimens isothermally transformed for very short periods of time (15 min) at 1950° and 1500° F (treatments P and M). The carbide M_6C possibly was present in the specimen heat-treated at 1950° F. The specimens given the long-time isothermal-transformation treatments of 72 hours at 1950° and 1500° F (treatments R and O) appeared to contain the same minor constituents as the specimens heat-treated at these temperatures for 15 minutes. However, some evidence of the presence of the high-carbon carbide Cr_7C_3 was found. The specimens which were solution-treated and isothermally transformed in the powdered state (treatments N and Q) appeared to contain the same carbides as the specimens heat-treated prior to obtaining powdered specimens (treatments M, O, P, and R). The X-ray pattern from the specimen isothermally transformed at 1500° F for 2 hours (treatment Q) contained evidence of the presence of sigma phase but no evidence was found in the specimen transformed 2 hours at 1950° F (treatment N). The pattern from the specimen given heat treatment S (selected because of the unusually large quantity of pearlite in the microstructure) gave strong indications of $Cr_{23}C_6$ and sigma and a possible indication of Cr_3C_2.

Stain-etching and heat-tinting results. - Metallographic examinations of stain-etched and heat-tinted specimens of rolled and cast Stellite 21, X-40, and J were made and the results of the observations are tabulated in table X. In this table, the colors and their interpretations for different microstructures have been recorded. Photomicrographs are shown in figure 15. The colors have been reported in the literature to represent particular minor phases but these color identifications need not necessarily apply to the alloys investigated.

DISCUSSION OF RESULTS

Response of alloys to solution treatment. - Pearlitic structures, feathery structures, and small precipitates observed in several alloys (cast and high-carbon Stellite 21, 422-19, 61, and X-40) were readily dissolved by solution-treating 41 hours at 2250° F. In these alloys, as well as others, more massive minor constituents were not completely dissolved by the solution treatment. Except for X-63, the alloys containing molybdenum and tungsten with carbon content 0.36 percent and above contained appreciable quantities of undissolved massive minor phases after solution treatment. It should be noted that X-63 has the lowest ratio of carbide-forming elements to matrix-forming elements of any alloy in this group and perhaps this explains its better response to solution treatment. Nickel, a weak carbide former, did not appear to influence the solubility of massive minor constituents at 2250° F. The as-cast microconstituents in the tantalum- and niobium-bearing alloys were relatively unaffected by solution treatment (figs. 11, 12, and 14(d)). The solution treatment produced some evidence of incipient overheating or eutectic melting in the form of rosettes in several specimens, for example, in alloys Stellite 21, 422-19, 6059, X-63 and 61; but, for purposes of this report, incipient eutectic melting was ignored in the analysis of the microstructures. In the case of alloy J, however, extensive eutectic melting occurred and an intergranular network of eutectic was formed. A picture of the J-alloy structure after lower temperature solution-treatment (which avoided the eutectic melting) and stepwise isothermal treatments is shown in (fig. 14(d)).

Pearlitic structures in alloys. - Previously Badger and Sweeney showed that the pearlitic structures in as-cast Stellite 21 may be dissolved by solution-treating at 2375° F and subsequently reformed by furnace cooling (ref. 2); the time of the solution treatment was not given, however. In addition, this structure was previously produced during an investigation (ref. 1) with Stellite 21 turbine blades at the Lewis laboratory, by solution-treating for $1\frac{1}{2}$ hours at 2250° F and furnace cooling. In either case, it is uncertain whether reasonably complete homogenization took place and, therefore, it was not known whether an alloy of Stellite 21 composition would decompose and form similar lamellar structures upon cooling if it were originally thoroughly homogenized. The results of heat treatment given to rolled, fine-grained Stellite 21 do show that the lamellar structure can be considered to be the decomposition product of homogenous solid solution rather than the product resulting from a heterogeneous as-cast structure. The rolled, fine-grained Stellite 21 was solution-treated for 41 hours at 2250° F. This treatment was considered sufficient to homogenize the alloy. Large quantities of lamellar structure were produced upon cooling (in stepwise fashion) from the solution-treating temperature. Similar transformations were observed in several as-cast alloys, although the homogenization of these alloys was not as complete as for the rolled Stellite 21.

Possible Relations of Lamellar Structures

Composition and temperature. - An attempt to determine the possible relations between alloy compositions and the temperatures at which lamellar structures (pearlitic and feathery structures) are formed in cobalt-base alloys was made. The alloys under consideration may be classified on the basis of composition into the following groups:

Group	Alloys
Molybdenum bearing	Rolled, cast and high-carbon Stellite 21, 422-19, X-63 and 6059
Tungsten bearing	61 and X-40
Tantalum or niobium bearing	I-336, S-816, and J

If the maximum temperature at which lamellar structures are formed (see table VI) are compared with the chemical compositions of the alloys shown in table I, and if these groupings of the alloys are considered the following observations may be made:

Molybdenum-bearing alloys. - From table VI it may be seen that rolled, cast, and high-carbon Stellite 21, and 422-19 contained lamellar structures after heat treatment at 2000° F and that alloys X-63 and 6059 contained lamellar structures after heat-treatment at 1800° F or less. It was impossible to correlate the carbon, nickel, or molybdenum contents of these alloys to the transformation temperature. A possible correlation between the temperatures at which lamellar structures first formed and the chromium contents of these alloys was observed, however. The chromium compositions ranged from 22.6 to 28.8 percent. With a chromium content of 25.6 percent or more, lamellar structures formed in less than 2 hours at a temperature as high as 2000° F. The two alloys with less than 24 percent chromium (X-63 and 6059) formed no lamellar structures until 1800° F or less was reached. Thus it appears that as the chromium content of the molybdenum-bearing alloys decreased, the transformation temperatures of the lamellar structures decreased (at least, for 2-hr isothermal transformation treatments).

Tungsten-bearing alloys. - The carbon content in the tungsten-bearing alloys ranges from 0.40 to 0.49 percent, the nickel from 1 to 10 percent, the tungsten from 5 to 7.6 percent, and the chromium from 24 to 26 percent. Again, neither carbon nor nickel can be correlated with transformation temperatures. If the tungsten-bearing alloys behaved as did the molybdenum-bearing alloys with chromium content, alloy 61 would be expected to transform at 1800° F or below, while X-40 would be expected to transform at 2000° F. However, X-40 did not transform as expected and thus it appears that tungsten lowered the transformation temperatures.

Tantalum- and niobium-bearing alloys. - The niobium-bearing alloys, S-816 and I-336, behaved differently from the other alloys in that no feathery or pearlitic structures developed upon heat treatment. The tantalum-bearing alloy examined (J) contained a small quantity of lamellar Widmanstätten structure (fig. 14(d)).

X-ray diffraction studies of minor phases. - Perhaps as important as the specific X-ray diffraction identification of minor phases, is the fact that large numbers of these phases were indicated to be present or possible in many of these cobalt-base alloys in as-cast and heat-treated conditions. Several carbides with different metal-to-carbon ratios such as MC, Cr_3C_2, Cr_7C_3, and M_6C were indicated to coexist in the same alloy. The nitride Cr_2N was frequently indicated as were oxides (Cr_2O_3 or spinel types). Indications of the sigma phase were found in almost every alloy investigated, and sigma as a precipitant may significantly affect the physical properties of this class of alloys. It appeared that heat treatments produced more sigma phase than was found in as-cast structures. Precipitation of carbides would tend to deplete alloys of the cobalt-base type of chromium and molybdenum (or tungsten). However, in spite of chromium depletion by carbide precipitation in high-chromium steels, the precipitation of carbides promote the formation of sigma phase (ref. 8). In the discussion following this article, Foley and the authors indicated their belief that the straining of the matrix lattice by precipitation of carbides promoted sigma precipitation in the vicinity of the carbides. The results of this investigation indicate that sigma is associated with large quantities of carbides.

Table XI shows the minor phases detected in cobalt-base high-temperature alloys by other investigators. Most of the results shown were obtained using electrolytic digestion techniques to concentrate minor phases. The results of table VIII agree rather well with those shown in table XI. In those investigations where digestion methods were used, no sigma phase was found, presumably because sigma would dissolve in the electrolytes. It is interesting to note that the carbide Cr_3C_2 indicated to be possible or present in several of the alloys studied herein, has been reported in a very high-carbon (3.21 percent) Stellite 21 type cobalt-base alloy (ref. 5). If as postulated in reference 5 (see p. 2 of this report), a high-carbon carbide such as Cr_7C_3 decomposes to a lower-carbon carbide plus free carbon on heating or aging heat treatments, Cr_3C_2 which contains more carbon than Cr_7C_3 may also similarly decompose. This concept of carbide decomposition and aging as a result of the decomposition may prove worthy of further investigation. Some of the evidence of the presence of Cr_3C_2 and Cr_7C_3 presented in tables VIII and IX would indicate that these high-carbon carbides do not always decompose upon heat treatment at isothermal or aging temperatures. It may be possible to determine with greater certainty the presence of such high-carbon carbides in these alloys by using digestion techniques similar to those used by others. It would seem desirable to use an electrolyte which is less corrosive than aqueous acid or basic solutions, possibly a bromine-methanol solution such as that used by Kinsel to extract carbides for electron microscopy (ref. 9).

The microstructure of as-rolled Stellite 21 etched conventionally or stain etched and heat tinted is shown in figures 3 and 15(a). The large spheroidized microconstituents which are evident in the photomicrographs could be either $Cr_{23}C_6$ or sigma from the weak X-ray indications of both shown in table IX. The appearance of the structure upon heat tinting indicate that the large particles are probably $Cr_{23}C_6$. Additional unpublished work with concentrated powders (the carbides were segregated by electrolytic digestion in a nonacidic solution) indicated the principal carbide to be $Cr_{23}C_6$.

Upon solution treatment of rolled Stellite 21 at 2250° F for 41 hours, most of these particles dissolve in the matrix (fig. 3(b)) and, therefore, no X-ray patterns were made of the specimen. An X-ray diffraction pattern obtained from a specimen which was solution-treated for 16 hours at 2250° F indicated that $Cr_{23}C_6$ and M_6C may have been residual carbides, although the indications were extremely weak.

The presence of $Cr_{23}C_6$ was indicated in all the rolled Stellite 21 specimens transformed at 1950° and 1500° F. Both M_6C and sigma were indicated in almost every specimen, and Cr_7C_3 was indicated in the specimens transformed for 72 hours at 1950° and 1500° F. The strength of the X-ray indications for $Cr_{23}C_6$ indicate that this phase is the predominant minor constituent in heat-treated Stellite 21. The M_6C may, of course, precipitate directly from the face-centered cubic solid solution, but on the other hand, it may be, in part, a residual carbide or a transformation product of $Cr_{23}C_6$ (more correctly $M_{23}C_6$). The latter change would involve the diffusion of only a few atoms of molybdenum or other carbide formers (ref. 10). Sigma precipitation may have occurred in conjunction with, or subsequent to, carbide precipitation.

The chromium nitride gamma CrN, M_2C (W_2C or Mo_2C), and M_3C type carbides might have been present in some of the alloys; however, there were too few significant lines in the standard patterns to list the phases in the tables. The Co_7W_6 (which could have an isomorph of the approximate stoichiometric composition Co_7Mo_6 in the molybdenum-bearing alloys) has few strong lines and these coincide with sigma lines; Co_3W

(or possibly Co_3Mo) has one d-value which appeared unique, but this value is in a range in which the accuracy of the d-value measurements is poor.

On the basis of X-ray diffraction patterns, the possibility existed that WC (or MoC) was present in almost every specimen. The numerous indications of this carbide suggested that the powders were being contaminated by the tungsten carbide burr, but the use of a diamond burr instead of the tungsten carbide burr did not affect the results. Also, the strong lines of standard WC patterns overlapped standard spinel patterns and, therefore, the two phases could not be differentiated.

Stain etching and heat tinting. - The results of stain etching and heat tinting are helpful but not easily evaluated, because of several inherent difficulties. The colors of fine precipitates or thin pearlitic lamellae are not discernible. The colors of large phases depend upon the chemical composition, which, in turn, depends upon the heat treatment given the specimen. For example, a chromium-rich carbide of the $Cr_{23}C_6$ type would be expected to react to chemical attack differently from chromium-poor $Cr_{23}C_6$. Coring of carbides was sometimes observed and, in addition, minor phases frequently seemed to be surrounded with a band of different material which was visible either under oblique light at high magnification or polarized light. However, such banding may have been the result of optical effects.

In order to discuss more readily the stain-etching and heat-tinting results previously presented, reference may again be made to tables IV, V, and X. (In the case of rolled Stellite, Badger and Sweeney's etchant indicated M_6C to be present although X-ray diffraction results indicated the carbide to be $Cr_{23}C_6$.) In the case of as-cast Stellite 21, Badger and Sweeney's etchant indicated only M_6C to be present although again no X-ray evidence confirmed this (table VIII). Furthermore, the eutectic which could contain several carbides was eaten out (fig. 15(b)). Heat tinting showed clear black-and-white detail in the eutectic areas. According to reference 4, the white color indicates the carbide $M_{23}C_6$, which was shown to be present by X-ray diffraction. In heat-treated (E treatment) rolled Stellite 21, Beck's etchant showed a few blue dots indicating sigma phase, but such a small quantity of sigma phase could not have shown up in X-ray patterns. The etchant to differentiate between carbides and the sigma-phase showed only one color (yellow brown) indicating carbides, and similarly Badger and Sweeney's etchant showed only one color (blue) indicating M_6C. This tendency to stain or heat tint everything one color seemed fairly evident in the case of the Stellite 21 alloys.

Alloy J, however, shows several distinct differences in minor phase colors and has at least three and probably four significant minor phases.

Although the stain-etching and heat-tinting results were not completely satisfactory, these methods did leave certain impressions with the authors. The first is that sometimes the numbers of minor phases present are indicated by the etchants. Second, grain boundary precipitates and many massive constituents appear to be $Cr_{23}C_6$.

Phases of pearlitic structures. - The X-ray data obtained herein were studied in an attempt to determine the identity of the pearlitic constituents. Specimens known to contain appreciable quantities of pearlite were indicated to contain the carbide $Cr_{23}C_6$. For example, a specimen of cast Stellite 21, solution-treated and isothermally transformed 2 hours at 2000° F (heat treatment B) was indicated to contain this carbide and no others. Other specimens known to contain appreciable quantities of pearlite were specimens of rolled, heat-treated Stellite 21. However, all these specimens were indicated to contain M_6C and/or sigma, in addition to $Cr_{23}C_6$ (table X). Thus, the carbide portion of the pearlitic lamellae could also contain M_6C. It is not known whether M_6C precipitates along with the carbides $Cr_{23}C_6$, whether it is a residual carbide following solution treatment, or whether it forms from $Cr_{23}C_6$ by diffusion of alloying elements to the $Cr_{23}C_6$ precipitants. Stain-etching and heat-tinting results indicated that when the pearlite is formed from face-centered cubic solid solution, $Cr_{23}C_6$ is the carbide constituent. These observations partially confirm the work of reference 11 which reports that the pearlite consisted of lamellae of Cr_4C ($Cr_{23}C_6$) and a cobalt-rich solid solution.

With regard to the formation of the sigma phase, which was observed in the alloys and, in particular, in the specimens of heat-treated Stellite 21, it is possible, on the basis of X-ray evidence alone, to show that sigma was not always found where the carbides $Cr_{23}C_6$ and/or M_6C were detected in specimens known to contain appreciable quantities of pearlite. For example, no indications of the presence of sigma phases were found in the rolled and high-carbon Stellites 21 and the 422-19 (table VIII, heat treatments B, E, and E, respectively). Metallographic examinations made of numerous specimens of Stellite 21 have indicated that the solid-solution phase of the pearlitic lamellae does not consist of a phase such as sigma, nor do stain-etchant and heat-tinting results. From observations of the paths of growth of pearlitic lamellae, from stain-etching characteristics, and from microhardness tests made over a period of time, the phase other than the carbide in the pearlitic structure is not believed to be sigma but one of the matrix phases.

No concrete evidence was obtained to prove that the solid-solution lamellae of the pearlite consisted of beta or that the structure is a eutectoid. It is reported in reference 2 that the pearlitic structures grew near areas of beta. However, the results of this investigation show that this statement is not necessarily always the case. By reference to tables VI and VII, it may be seen that rolled Stellite 21 (heat-treatment B), high-carbon Stellite 21 (as cast), and 422-19 (as-cast and heat-treatment E) which were known to contain appreciable quantities of pearlite contain little or no beta phase. Also, beta formed in alloys where no pearlitic structures were found. Although the pearlitic structure and beta did not always coexist in a given specimen, if the maximum quantity of beta that formed in a given alloy is compared with the maximum quantity of pearlite that formed, it may be observed that, with the heat-treatments investigated, little or no pearlitic structure could be formed in alloys that were not capable of forming detectable quantities of the beta phase (table XII).

SUMMARY OF RESULTS

The results of this investigation to determine the occurrence and nature of lamellar structures and minor phases in the cobalt-based alloys rolled, cast, and high-carbon Stellite 21, 422-19, X-63, 6059, 61, X-40, I-3336, S-816, and J may be summarized as follows:

1. The microstructures of as-cast alloys generally contained interdendritic minor phases, many of which are low-melting eutectics; in addition, cast Stellite 21, 422-19, 61, and X-40 contained pearlitic structures. The only as-rolled alloy studied, Stellite 21, was very fine grained and contained large carbide spheroids.

2. The effect of solution-treatment of 2250° F may be summarized as follows: Small or fine microconstituents in the structural forms of pearlite, Widmanstätten structures, and general precipitation readily dissolved into the matrices of the alloys during solution treating. Except for alloy X-63, the specimens with carbon contents of 0.36 percent and above contained appreciable quantities of undissolved carbides after solution-treating. In the tantalum- and niobium-bearing alloys, I-336, S-816, and J, the microconstituents did not dissolve appreciably into the matrix.

3. Lamellar structures were produced in eight of the eleven alloys investigated after homogenization at a nominal temperature of 2250° F for 41 hours and cooling by interrupted-cooling method. The eight alloys are rolled, cast, high-carbon Stellite 21, 422-19, X-63, 6059, 61, and X-40. Only three of these alloys, cast and high-carbon Stellite 21, and 422-19 contained appreciable quantities of lamellar structures in the as-cast condition. Two types of lamellar structure were formed, a

pearlitic structure and a feathery (Widmanstätten) structure. No pearlitic or feathery structures were observed in alloys I-336, S-816, or J.

4. A possible correlation was observed between the chromium composition of the molybdenum-bearing cobalt-base alloys studied and the temperatures at which lamellar structures (pearlitic or feathery) first formed on stepwise cooling to various isothermal levels. The temperature of transformation decreased with decreasing chromium content. Tungsten appeared to lower the transformation temperature of lamellar structures, whereas nickel had no noticeable effect on the transformation.

5. One or more of the following minor phases were indicated to be present or possible by X-ray diffraction in each of the alloys: TaC, CbC, Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$, M_6C, Cr_2N, Cr_2O_3 type oxides, spinels, and the sigma phase. Some of the carbides listed as chromium carbides could contain other carbide formers than chromium, while other carbides could contain appreciable percentages of nitrogen.

6. X-ray diffraction results indicated that the sigma phase was present in most of the specimens studied. Although sigma phase has been observed in Stellite 21 by others, its presence has not been reported previously in so many of these alloys. Sigma phase patterns appeared strongest where large numbers of carbides were also present and formation of the sigma phase may have been facilited by carbide precipitation.

7. X-ray diffraction methods indicated that $Cr_{23}C_6$ was the most prevalent carbide in the alloys studied. In heat-treated, rolled Stellite 21 specimens, $Cr_{23}C_6$ appeared to be the most prevalent carbide, although M_6C was almost as frequently indicated. Sigma found in heat-treated Stellite 21, was thought to form in conjunction with, or subsequent to, the formation of the carbide $Cr_{23}C_6$.

8. Stain etching and heat tinting were used as auxiliary methods to the X-ray diffraction studies. In several cases the results proved helpful: A number of minor phases were shown to be present in alloy J, and, in Stellite 21, grain boundaries, massive carbides, and pearlitic lamellae were indicated to be $Cr_{23}C_6$. Coring of carbides was also revealed by these methods.

9. X-ray diffraction results and metallographic examinations of stain-etched and heat-tinted specimens indicated that one of the two phases of the pearlite consisted predominantly of $Cr_{23}C_6$. The M_6C carbide was also detected in many specimens of heat-treated Stellite 21 and possibly was formed from transformation of $Cr_{23}C_6$ lamellae.

10. The relative quantities of the matrix phases of each alloy studied, in various conditions of heat treatment, were estimated from the X-ray diffraction patterns. The matrices were known to be either the high-temperature phase, alpha (a face-centered cubic solid solution) or the lower temperature phase, beta (a hexagonal close-packed solid solution). It was found that in most cases little or no pearlite formed in these alloys where beta was not detected. However, beta formed in alloys where pearlite did not form.

11. Studies of pearlitic structures indicated that one of the phases (one of the two lamellae) in the structure consisted of the carbide $Cr_{23}C_6$. The other lamella was indicated to be related to the presence of the beta or hexagonal close-packed matrix phase; however, positive identification of this lamella could not be made. Therefore, it was impossible to show that the pearlite results from a euctectoid decomposition.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 15, 1953

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TABLE I. - CHEMICAL ANALYSES OF ALLOYS INVESTIGATED

Alloy		Chemical composition, percent by weight										
		Cr	Ni	Mo	W	C	Cb	Fe	Si	Mn	Miscel-laneous	Co (Balance)
1	Rolled Stellite 21	28.75	3.01	5.52	-----	0.29	----	0.33	0.44	0.56	-------	61.10
2[a]	Cast Stellite 21	27.5	2.5	5.5	-----	0.28	----	2 max.	----	----	-------	62.22
3[b]	High-carbon Stellite 21	26.84	2.50	5.54	-----	0.36	----	1.07	0.72	0.65	-------	62.32
4[b]	422-19	25.58	14.62	6.30	-----	0.44	----	1.43	0.69	0.65	-------	50.29
5[b]	X-63	22.63	10.64	5.62	-----	0.4	----	0.98	0.65	0.60	-------	58.48
6[c]	6059	24.03	32.68	5.76	-----	0.39	----	1.12	0.62	0.65	-------	34.75
7[b]	61	24.28	1.02	----	5.05	0.40	----	0.95	0.58	0.70	-------	67.02
8	X-40	26.10	10.44	0.36	7.59	0.49	----	0.99	0.63	0.59	P, 0.018 S, 0.012	52.79
9[b]	I-336	18.65	14.99	----	11.44	0.51	0.99	1.31	0.56	0.54	-------	51.00
10	S-816	19.87	19.64	4.16	3.89	0.40	3.81	3.02	0.73	0.94	-------	43.54
11[d]	J	23	6	6	-----	0.70	----	-----	----	1.0	Ta, 2.0	61.30

[a] Composition from medium value of specifications AMS 5385.

[b] Average of two heats.

[c] Average of three heats.

[d] Nominal composition.

TABLE II. - X-RAY DIFFRACTION PATTERN

STANDARDS USED FOR COMPARISON

Compounds checked (standards)	Number of standards checked	Source or reference
$FeO \cdot Cr_2O_3$ (spinel)	2	ASTM card index
$CoOCr_2O_3$(spinel)	1	ASTM card index
Cr_2O_3	3	ASTM card index
Cr_3C_2	2	ASTM card index
Cr_7C_3 or Mn_7C_3	1	ASTM card index
Co_4W_2C (M_6C)	1	ASTM card index
Fe_3W_3C or Fe_3Mo_3C or $Fe_4W_2C \cdot (M_6C)$	1	ASTM card index
M_6C	1	Ref. 3
Sigma (or gamma) Co_2Cr_3	1	Diffraction standard obtained from specimen given to NACA by Battelle Memorial Institute
Sigma (Co-Cr-Mo)[a]	1	Ref. 12
Sigma (Co-Cr-Ni)[a]	1	Ref. 12
Sigma (FeCr)	1	Ref. 13
Sigma (CoCr)	1	Ref. 14
Sigma (Fe-Cr-Ni)	1	Ref. 13
Co_7W_6	1	ASTM card index
Co_3W	1	ASTM card index
$Cr_{23}C_6$	2	ASTM card index
Mo_2C	2	ASTM card index
Cr_2N and βCr_2N	2	ASTM card index
Co_3C	1	ASTM card index
Fe_3C	1	ASTM card index
WC	2	ASTM card index
αW_2C	1	ASTM card index
βW_2C	1	ASTM card index
CbN	1	ASTM card index
CbC	2	ASTM card index
TaC	2	ASTM card index

[a] Either one pattern or the other was checked.

TABLE III. - HEAT TREATMENTS GIVEN ROLLED STELLITE 21 SPECIMENS PRIOR TO X-RAY DIFFRACTION STUDIES

Heat treatment	Solution treatment	Isothermal transformation		Aging treatment	
		Temperature, °F	Time, hr	Temperature, °F	Time, hr
L	(1) 2250° F; 16 hr; water quench (2) Grind, X-ray powders (3) Heat-treat powders 2250° F; 1/4 hr; water quench				
M	2250° F; 69 hr	1950	1/4		
N	(1) 2250° F; 16 hr; water quench (2) Grind, X-ray powders (3) Heat-treat powders 2250° F; 1/4 hr	1950	2		
O	2250° F; 69 hr	1950	72		
P	2250° F; 72 hr	1500	1/4		
Q	(1) 2250° F; 16 hr; water quench (2) Grind, X-ray powders (3) Heat-treat powders 2250° F; 1/4 hr	1500	2		
R	2250° F; 72 hr	1500	72		
S	2250° F; 46 hr	1850	$1\frac{1}{2}$	1500	2

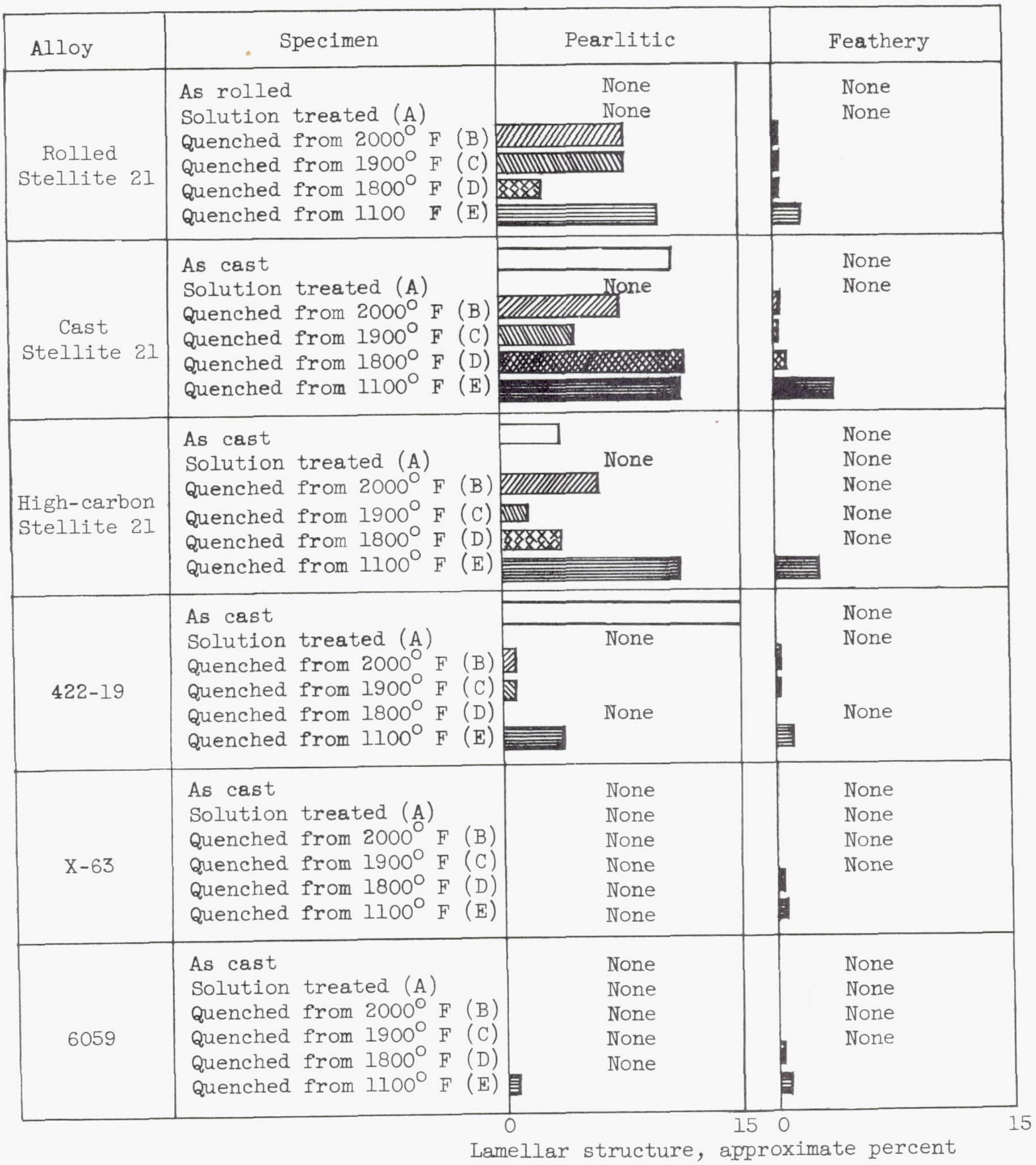
TABLE IV. - STAIN ETCHANTS AND HEAT TINTING

Coloring process	Method	Purpose	Source of methods	First etchant		Staining method		Colors of minor phases obtained by previous investigators
				Solution	Method	Solution	Method	
1	Etch	To stain sigma	Rideout and Beck (ref. 13) (Cr, Ni, Mo alloys)	8 Percent oxalic acid; 92 percent water	Electrolytic etch; 8-10 sec; 6 volts; room temperature	5 g $KMnO_4$; 5 g NaOH; 90 ml water	Immerse 10-20 sec; room temperature	Sigma: bright green or red to purple
2	Etch	To differentiate between carbides and sigmaphase	Batelle (ref. 4) for Stellite 21 type alloy	10 percent NaCN; 90 percent water	Electrolytic etch; 10-20 sec; 1.5 volts	Murakami's 10 g $K_3Fe(CN)_6$; 10 g KOH; 100 ml water	Immerse 2-4 sec; room temperature	Carbides: straw to yellow brown or buff Gamma (sigma): grey to blue or greenish grey
3	Etch	To identify carbides	Badger and Sweeney (ref. 2) for Stellite 21 and Co-Cr base alloys	2 percent chromic acid; 98 percent water	Light electrolytic etch	1 part (20 percent $KMnO_4$, 80 percent water) + 1 part (8 percent NaOH 92 percent water)	Immerse 7 sec; room temperature	$Cr_{23}C_6$: brown Cr_7C_3: pale yellow to light tan M_6C: red, green, yellow, blue (also reticulation)
4	Heat tint	To identify carbides and sigma-phase	Batelle (ref. 4) Also see Lane and Grant (ref. 5)	5 percent HCl; 95 percent H_2O	Electrolytic (light); 1 sec; 5 volts	(1) Heat polished specimen to dull red (2) Held at temperature until surface becomes colored (3) Air cooled or Hg quenched		Sigma: dark-medium brown $Cr_{23}C_6$: white M_6C: dark Note: M_6C and sigma cannot be differentiated in same structure

TABLE V. - ALLOYS STAIN ETCHED AND HEAT TINTED

Alloy	Condition or heat treatment	Reason for selecting alloy
Rolled Stellite 21	As rolled	Relatively few visible microconstituents, should be able to compare results readily with X-ray results
Rolled Stellite 21	Heat treatment E	To observe different microconstituents formed at very high temperature of 2000° F
Cast Stellite 21	As cast	Typical alloy
Cast Stellite 21	Heat treatment B	Extremely high transformation temperature of 2000° F produced coarsely lamellar pearlite. To identify lamellae
X-40	Heat treatment E	Typical alloy
J	As cast	To observe microconstituents in an alloy containing Ta

TABLE VI. - LAMELLAR STRUCTURES OBSERVED IN METALLOGRAPHIC SPECIMENS



Alloy	Specimen	Pearlitic	Feathery
Rolled Stellite 21	As rolled	None	None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)		
	Quenched from 1900° F (C)		
	Quenched from 1800° F (D)		
	Quenched from 1100 F (E)		
Cast Stellite 21	As cast		None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)		
	Quenched from 1900° F (C)		
	Quenched from 1800° F (D)		
	Quenched from 1100° F (E)		
High-carbon Stellite 21	As cast		None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)		None
	Quenched from 1900° F (C)		None
	Quenched from 1800° F (D)		None
	Quenched from 1100° F (E)		
422-19	As cast		None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)		
	Quenched from 1900° F (C)		
	Quenched from 1800° F (D)	None	None
	Quenched from 1100° F (E)		
X-63	As cast	None	None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)	None	None
	Quenched from 1900° F (C)	None	None
	Quenched from 1800° F (D)	None	
	Quenched from 1100° F (E)	None	
6059	As cast	None	None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)	None	None
	Quenched from 1900° F (C)	None	None
	Quenched from 1800° F (D)	None	
	Quenched from 1100° F (E)		

Lamellar structure, approximate percent

TABLE VI. - Concluded. LAMELLAR STRUCTURES OBSERVED IN METALLOGRAPHIC SPECIMENS

Alloy	Specimen	Pearlitic	Feathery
61	As cast	▯	None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)	None	None
	Quenched from 1900° F (C)	None	None
	Quenched from 1800° F (D)	None	▮
	Quenched from 1100° F (E)	None	▤
X-40	As cast	▯	None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)	None	None
	Quenched from 1900° F (C)	None	None
	Quenched from 1800° F (D)	None	None
	Quenched from 1100° F (E)	▤	None
S-816	As cast	None	None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)	None	None
	Quenched from 1900° F (C)	None	None
	Quenched from 1800° F (D)	None	None
	Quenched from 1100° F (E)	None	None
I-336	As cast	None	None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)	None	None
	Quenched from 1900° F (C)	None	None
	Quenched from 1800° F (D)	None	None
	Quenched from 1100° F (E)	None	None
J	As cast	None	None
	Solution treated (A)	None	None
	Quenched from 2000° F (B)	None	None
	Quenched from 1900° F (C)	None	None
	Quenched from 1800° F (D)	None	None
	Quenched from 1100° F (E)	Few precipitates	Few precipitates

0 15 0 15

Lamellar structure, approximate percent

see errata #1

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TABLE VII. - PERCENTAGES OF MATRIX PHASES AS DETERMINED BY X-RAY DIFFRACTION

[Percentages visually estimated.]

Alloy	As received		Heat treated		
	Alpha	Beta	Treatment	Alpha	Beta
Rolled Stellite 21	30	70	E	5	95
			L	100	0
			M	50	50
			N	95	5
			O	Trace	>90
			P		0
			Q		0
			R		90
			S		50
Cast Stellite 21	40	60	B	100	0
Cast high-carbon Stellite 21	100	0	E	20	80
422-19	>90	Trace	E	>90	Trace[a]
X-63	90	10	E	90	Trace[a]
			F	100	0
6059	100	0	E	100	0
			F	100	0
61	>90	Trace	E	60	40
			F	100	0
X-40	100		E	100	0
			E[b]	80	20
I-336	100		E	100	0
S-816	100		E	100	0
J	100		E	80	20
			G	100	0

[a] Questionable traces.

[b] Recheck; partially digested powders.

ERRATA NO. 1

NACA TN 3109

AN INVESTIGATION OF LAMELLAR STRUCTURES AND MINOR PHASES IN ELEVEN COBALT-BASE ALLOYS BEFORE AND AFTER HEAT TREATMENT

By J. W. Weeton and R. A. Signorelli

March 1954

Page 26, Table VII: The "Alpha" and "Beta" columns for "Rolled Stellite 21" should read as follows:

5	95
100	0
100	0
100	0
10	90
50	50
95	5
Trace	>90
50	50

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TABLE VIII. - X-RAY DIFFRACTION IDENTIFICATION OF MINOR PHASES IN ELEVEN ALLOYS

Alloy	Minor phases indicated[a]										
	Heat treatment designation	Cr_3C_2	Cr_7C_3	$Cr_{23}C_6$	M_6C	Sigma	Cr_2O_3	Spinels	Cr_2N	C_bC	T_aC
As received											
Rolled Stellite 21				W		W		W			
Cast Stellite 21		W	W	S		S					
Cast high-carbon Stellite 21		M		S	W	W			W		
Cast 422-19		W		M		VW		VW	W		
Cast X-63		VW		W		VW		VW	S		
Cast 6059				W		W		W	W		
Cast 61		VW		S				VW	W		
Cast X-40		VW		S		W					
Cast I-336				M					W	W	
S-816		VW		W				W	W	VW	
J		M		S	M			W			S
Heat treated											
Rolled Stellite 21	E			S		S	M	W	W		
Cast Stellite 21	B[b]			W							
Cast high-carbon Stellite 21	E	W		W			W				
Cast 422-19	E	S		M							
Cast X-63	E F	W		W M		W		W	W W		
Cast 6059	E F	W	M	W S	W	S W	W	W	W		
Cast 61	E F	W W	W	W M	W	W M		VW W			
Cast X-40	E			W	W	W		W	W		
Cast I-336	E			W	W	S		W	S	S	
S-816	E			S		W				S	
J	E			W	W	W		W	W		
J	G		W	W	M	W			M		S

[a] Indications of the presence or possible presence of minor phases in these alloys are as follows:

S Good indication of presence
M Fairly good indication of presence
W Possible
VW Minimum indication considered

[b] Specimens given heat treatments C, D, and E were used for chemical analysis; therefore, specimen B was used for X-ray diffraction.

TABLE IX. - X-RAY IDENTIFICATION OF MINOR PHASES IN ROLLED, HEAT-TREATED STELLITE 21

Heat treatment	Minor phases indicated						
	Cr_3C_2	Cr_7C_3	$Cr_{23}C_6$	M_6C	Sigma	Oxide	Cr_2N
L			VW	VW			
M[a]			S	W	M	S	M
N			S	S			M
O		VW	S	W	M	W	S
P[a]			S		M		W
Q			M	W	S	W	
R		VW	S	W	W	W	S
S	W		S		S	W	S

[a] Powder scaled during annealing.

TABLE X. - STAIN-ETCHING AND HEAT-TINTING RESULTS

Alloy	Heat treatment	Coloring process[a]	Color observed and identifications based on literature							
			Massive phases		Grain boundaries		Pearlite		Miscellaneous	
			Color	Phase	Color	Phase	Color	Phase	Color	Phase
Rolled Stellite 21		3	Blue	M_6C	Brown	$Cr_{23}C_6$				
		4	White	$Cr_{23}C_6$	Brown	Sigma				
Cast Stellite 21		3			Blue	M_6C	Blue	M_6C		
		4					White	$Cr_{23}C_6$	White Black	Eutectic: $Cr_{23}C_6$ and unknown
Rolled Stellite 21	E	1							Blue	Spots of sigma
		2	Yellow, brown	Carbides	Yellow, brown	Carbides				
		3	Blue	M_6C	Blue	M_6C	Blue	M_6C		
		4	White	$Cr_{23}C_6$						
Cast Stellite 21	B	2	Buff	Carbides	Buff	Carbides				
		3	Yellow, blue Yellow, green	M_6C Cr_7C_3	Yellow-blue Yellow-green	M_6C Cr_7C_3	Yellow, blue Yellow, green	M_6C Cr_7C_3		
		4	White	$Cr_{23}C_6$	White	$Cr_{23}C_6$	White	$Cr_{23}C_6$		
X-40	E	1							Red, violet	Sigma
		2	Yellow, red	Carbides					Blue	Sigma
		3	Brown	$Cr_{23}C_6$	Brown	$Cr_{23}C_6$	Brown	$Cr_{23}C_6$		
		4	White	$Cr_{23}C_6$						
J, cast		1								
		2	Blue	Sigma						
		3	Yellow Blue Brown	Cr_7C_3 M_6C $Cr_{23}C_6$						
		4	White	$Cr_{23}C_6$						

[a] See table IV.

TABLE XI. - MINOR PHASES DETECTED IN SEVERAL COBALT-BASE ALLOYS BY OTHER INVESTIGATORS

Alloy	Phases found	References
Stellite 21	Cr_7C_3 $M_{23}C_6$(or $Cr_{23}C_6$) M_6C Sigma	2, 4 2, 3, 4 2, 4 4
Stellite 21 - Type 0.1-0.90 percent C	Cr_7C_3 $Cr_{23}C_6$ M_6C	5 5 5
3.21 percent C	Cr_3C_2 + above carbides	5
422-19	Cr_7C_3 $Cr_{23}C_6$ M_6C	5 3, 5 5
6059	$M_{23}C_6$	3
61	$M_{23}C_6$	3
X-40	$M_{23}C_6$	3
I-336	Cb(C,N) $M_{23}C_6$ M_6C	15 15 15
S-816	CbC	3, 5, 16
J	TaC Cr_7C_3 $Cr_{23}C_6$ M_6C	5 5 5 5

[a] Phases found in one or more specimens, cast or heat treated or both.

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TABLE XII. - RELATIVE QUANTITIES OF LAMELLAR PEARLITE AND BETA

	Maximum percent β in either as-received or heat-treated specimens	Maximum quantity pearlite in as-received or heat-treated specimens
Wrought Stellite 21	95	
Stellite 21 Cast	60	
High-carbon Stellite 21	80	
422-19	Trace	
X-63	10	None
6059	0	
61	40	
X-40	20	
I336	0	None
S-816	0	None
J	20	None

0 15
Approximate percent

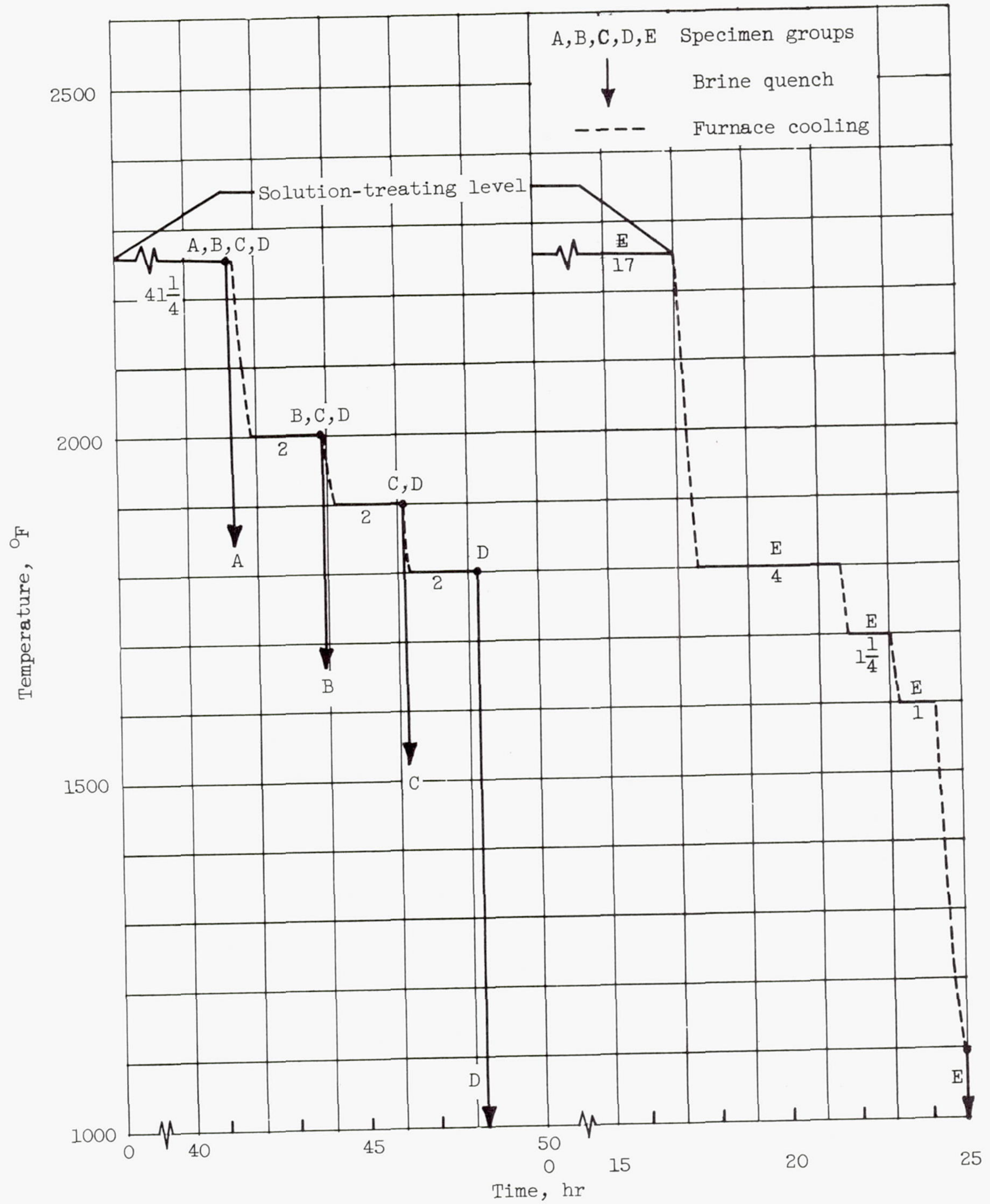


Figure 1. - Heat-treatment applied to five groups of eleven alloys.

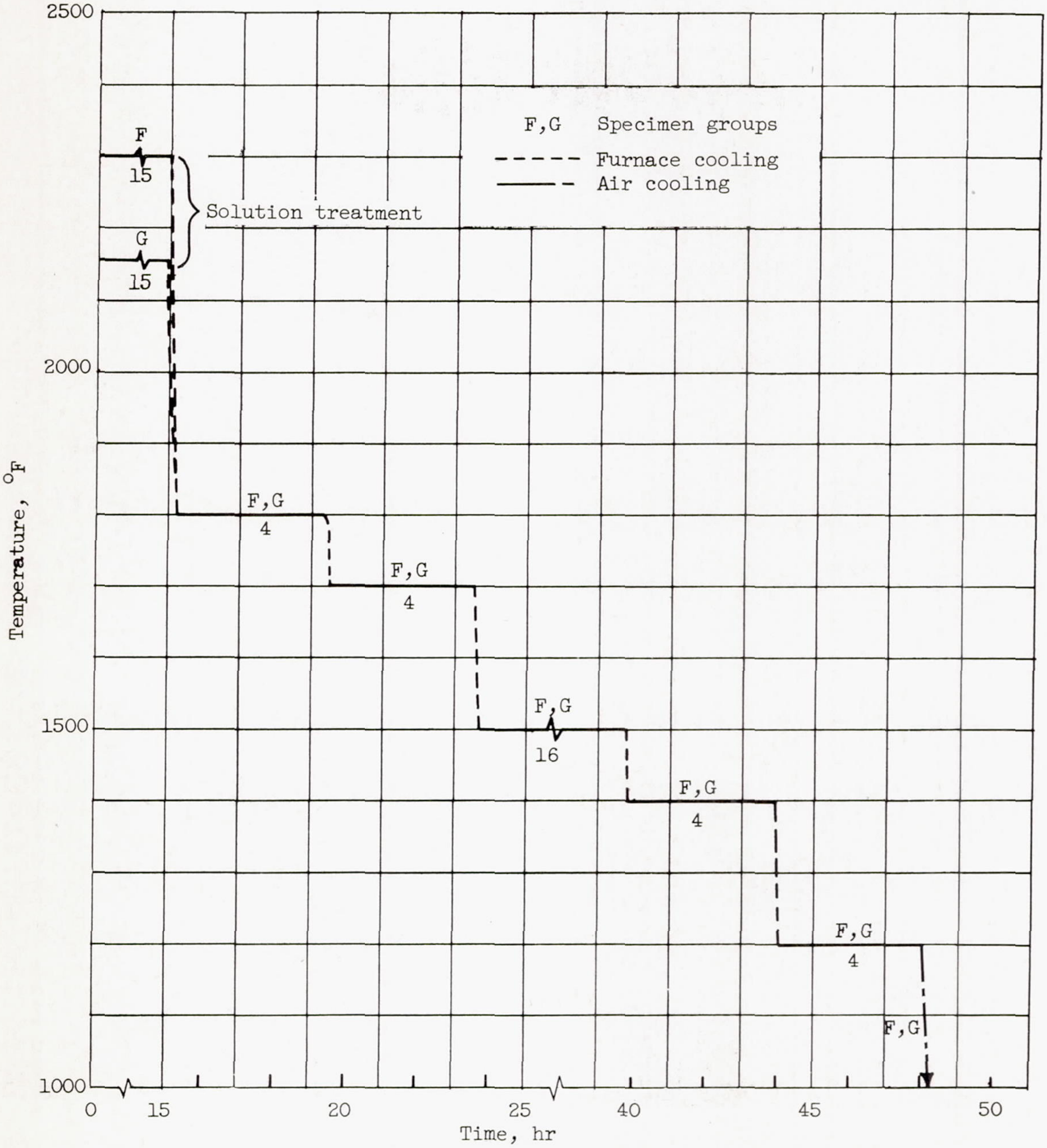
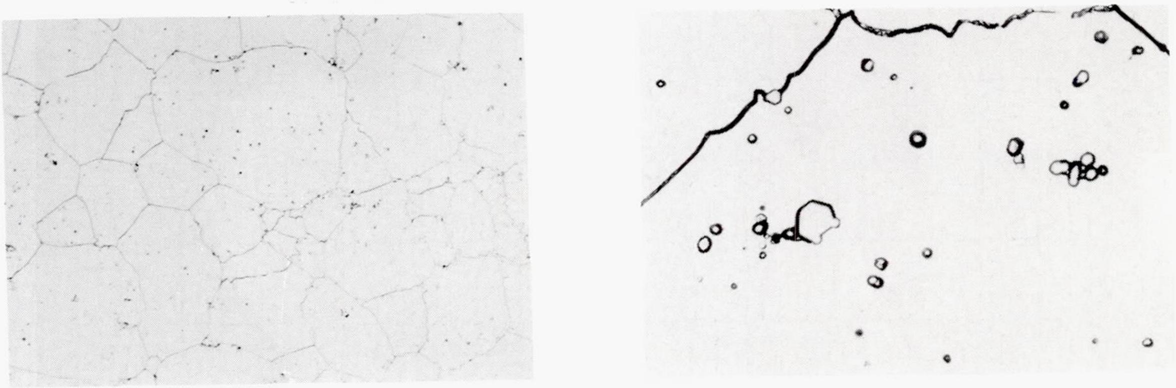


Figure 2. - Additional heat treatment. Group F: alloys X-63, 6059, and 61; group G: alloy J.

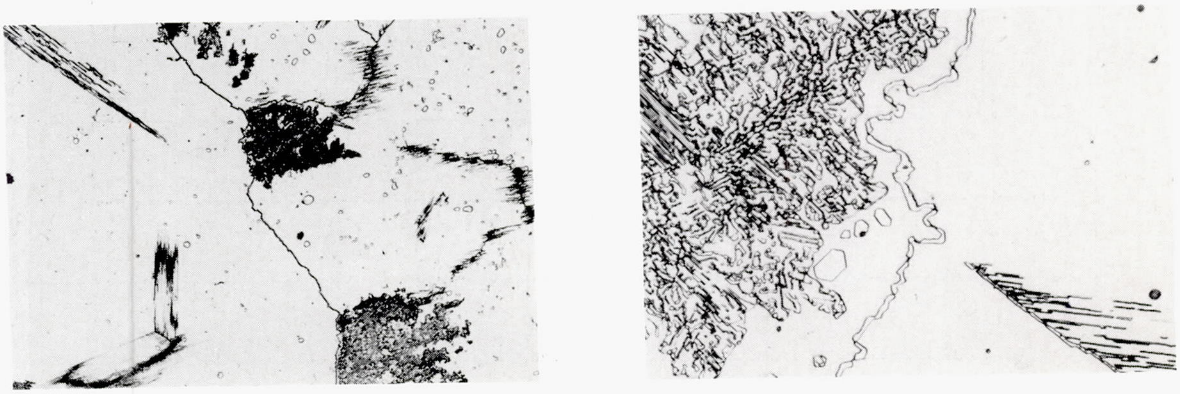
X750

(a) As-rolled condition; etchant, 5 percent aqua regia in water, electrolytic.



X100 X750

(b) Solution-treated and quenched (heat treatment A); etchant, 5 percent HCl in alcohol, electrolytic.



X100 C-27880 X750

(c) Solution-treated, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent aqua regia in water, electrolytic.

Figure 3. - Microstructures of rolled Stellite 21.

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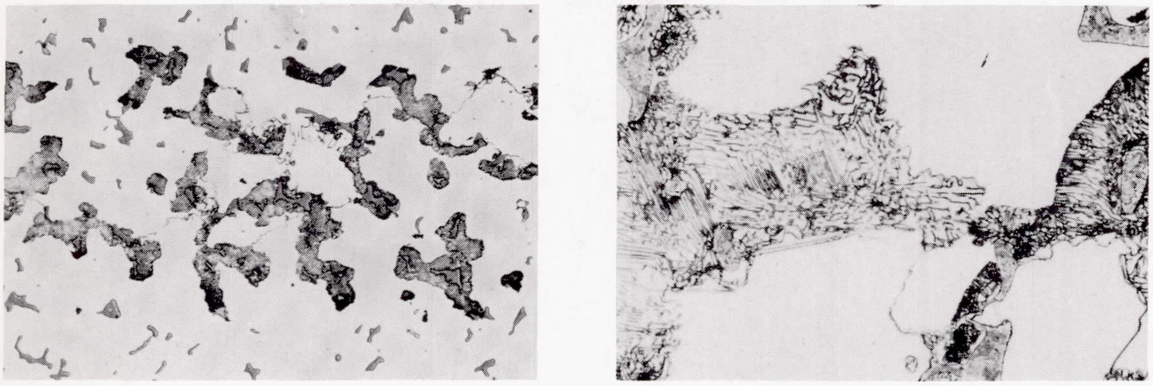
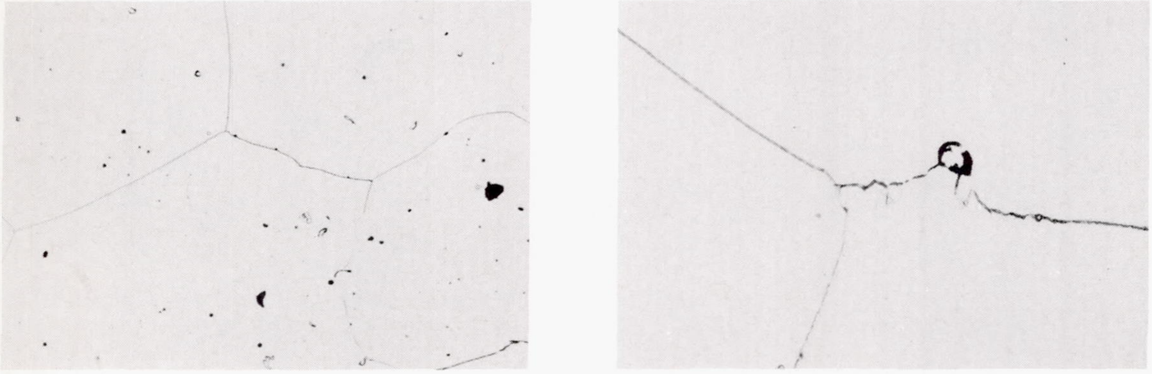
CI-5 back



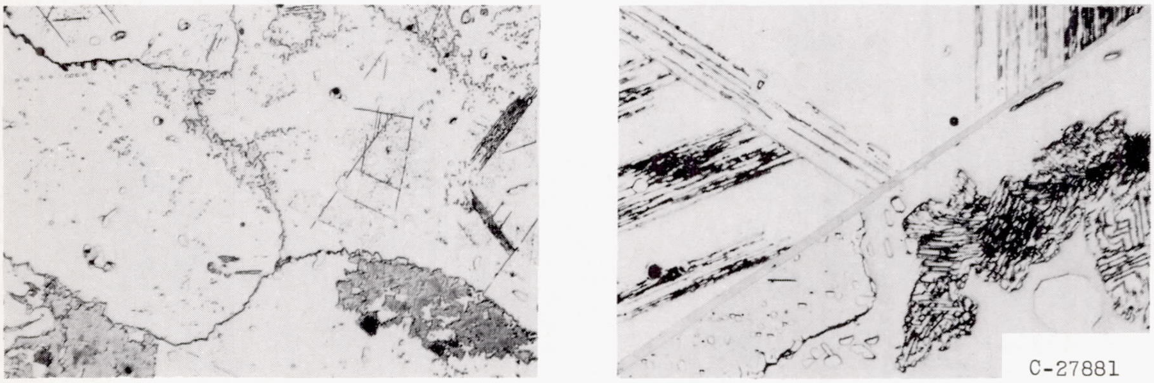
X100 X750

(a) As-cast condition; etchant, 5 percent aqua regia in water, electrolytic.



X100 X750

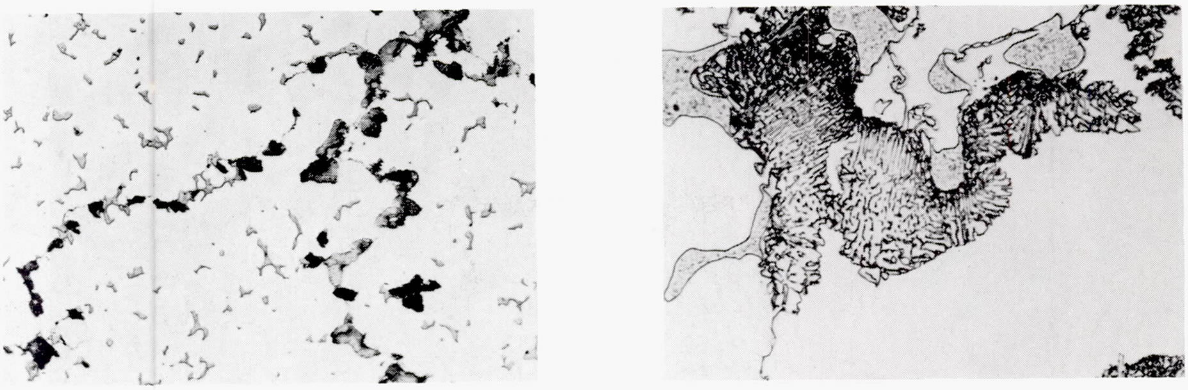
(b) Solution-treated and quenched (heat treatment A); etchant, 5 percent HCl in alcohol, electrolytic.



X100 X750

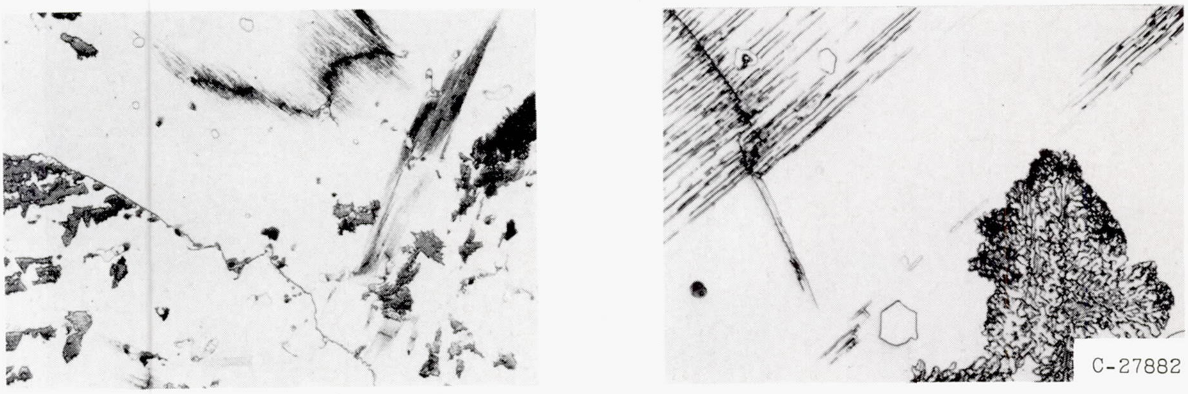
(c) Solution-treated, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent aqua regia in water, electrolytic.

Figure 4. - Microstructures of cast Stellite 21.



(a) As-cast condition; etchant, 5 percent aqua regia in water, electrolytic.

(b) Solution-treated and quenched (heat treatment A); etchant, 5 percent HCl in alcohol, electrolytic.



(c) Solution-treated, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent aqua regia in water, electrolytic.

Figure 5. - Microstructures of high-carbon Stellite 21.

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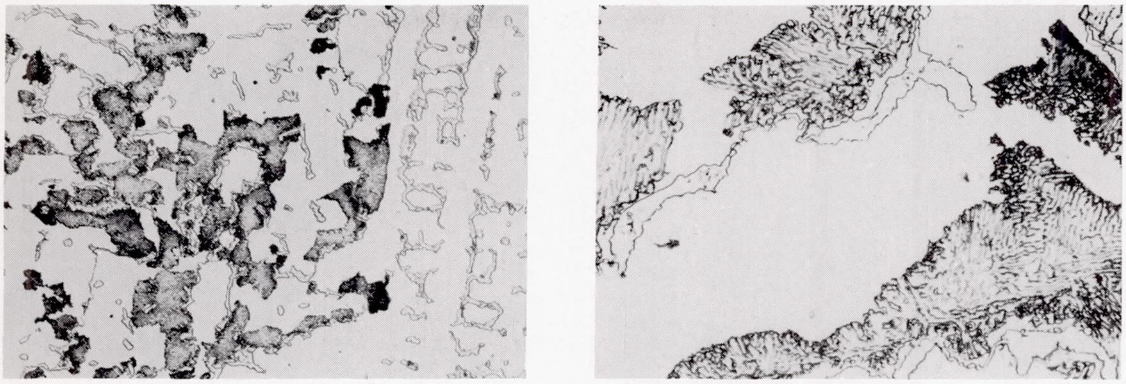
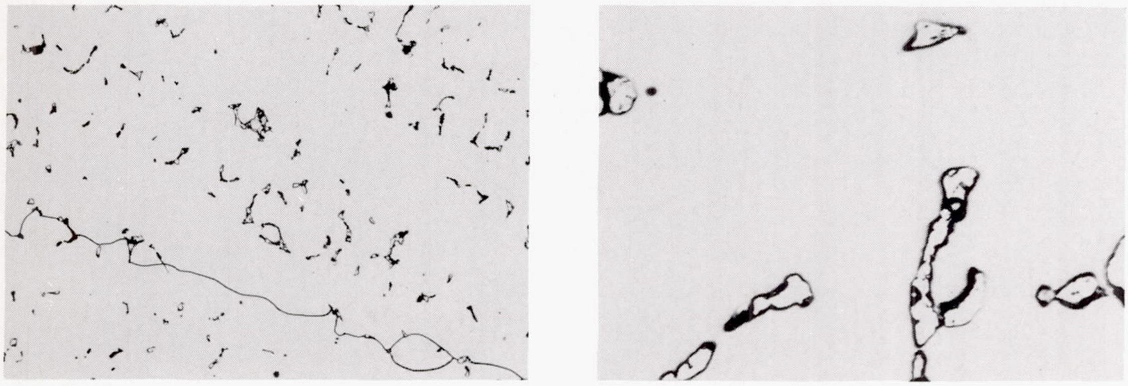


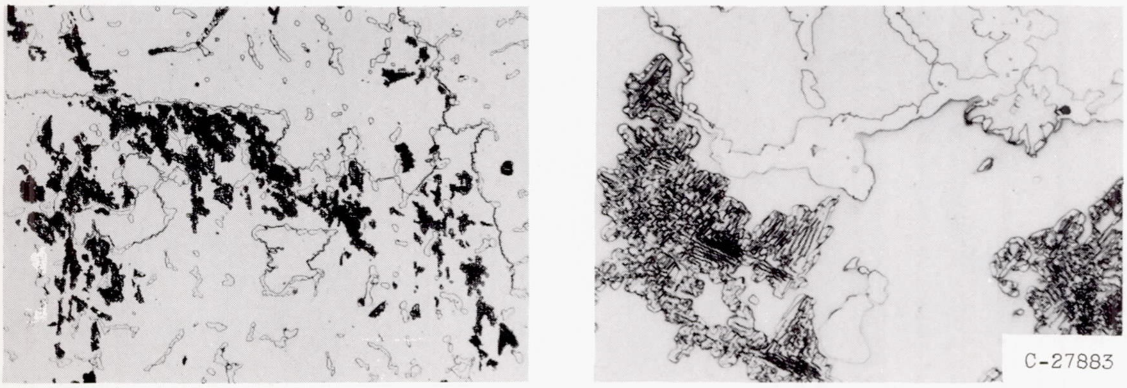
X100 X750

(a) As-cast condition; etchant, 5 percent aqua regia in water, electrolytic.



X100 X750

(b) Solution-treated and quenched (heat treatment A); etchant, 5 percent aqua regia in water, electrolytic.



X100 X750

(c) Solution-treated, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent aqua regia in water, electrolytic.

Figure 6. - Microstructures of 422-19.

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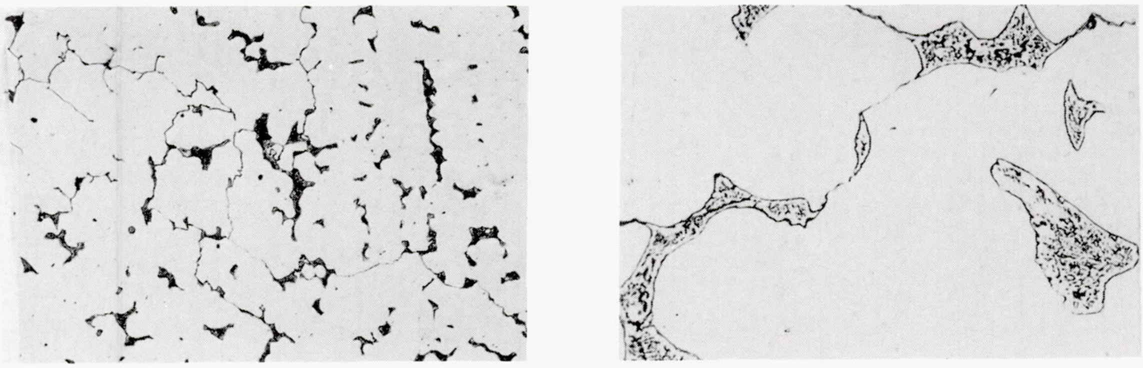
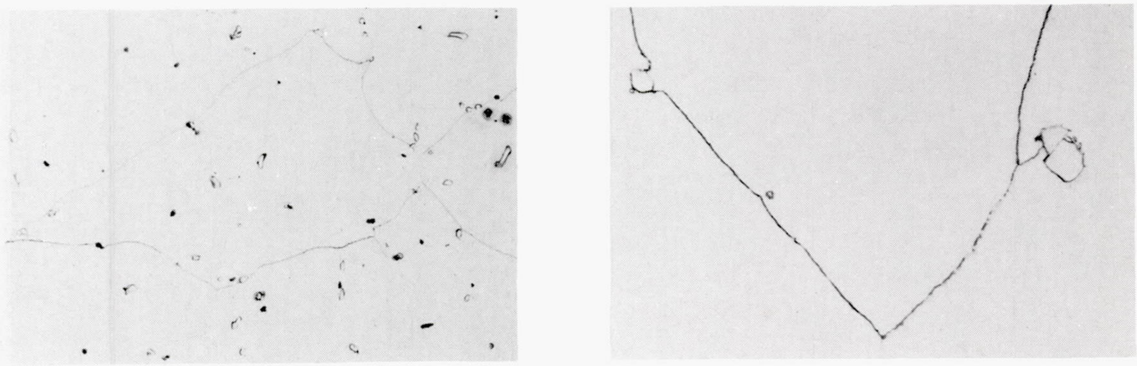


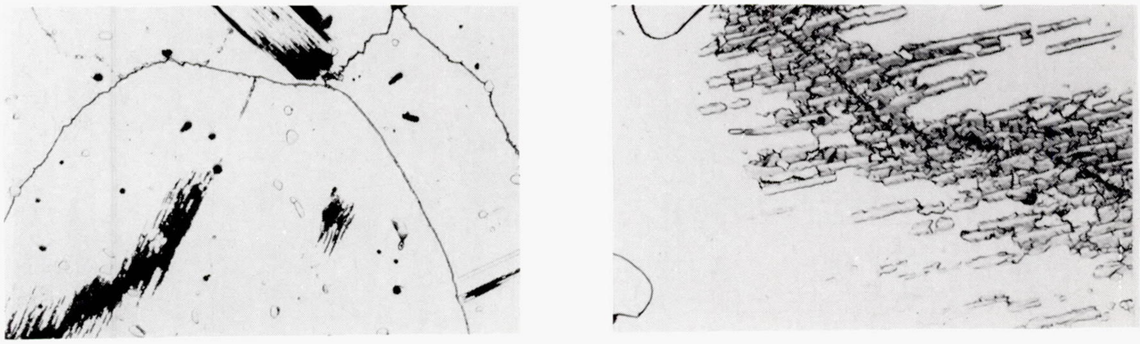
X100 X750

(a) As-cast condition; etchant, 5 percent aqua regia in water, electrolytic.



X100 X750

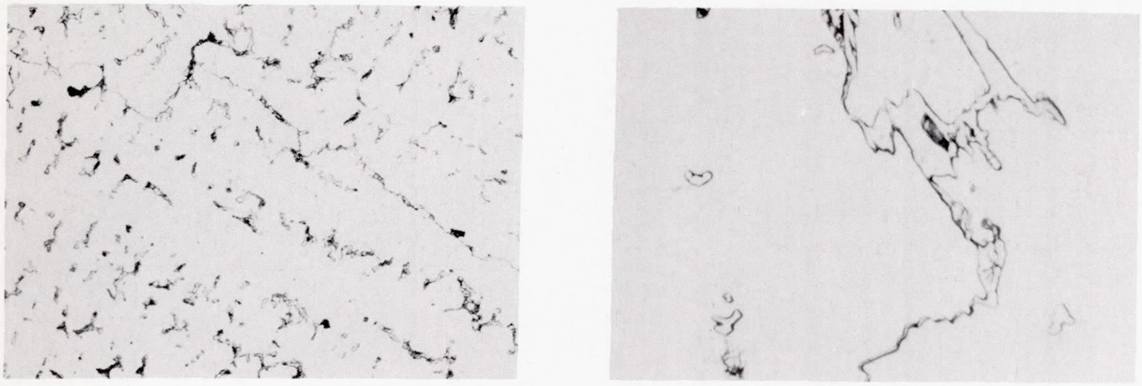
(b) Solution-treated and quenched (heat treatment A); etchant, 5 percent HCl in alcohol electrolytic.



X100 C-27884 X750

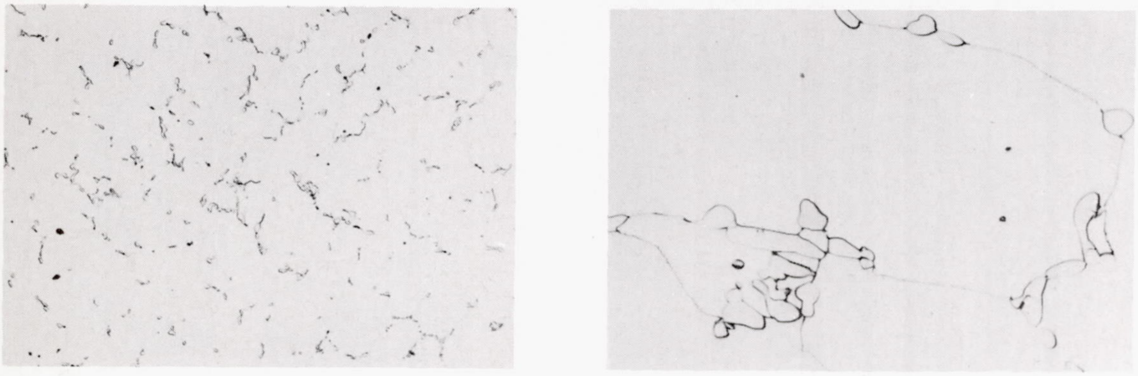
(c) Solution-treated, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent aqua regia in water, electrolytic.

Figure 7. - Microstructures of X-63.



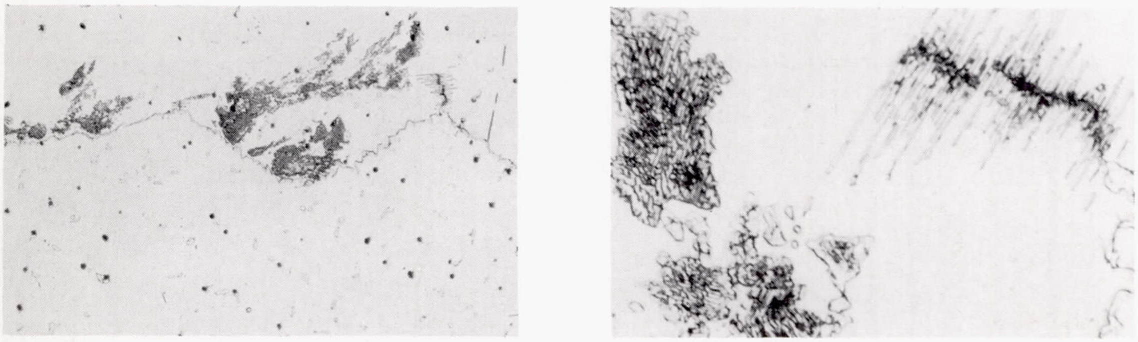
X100 X750

(a) As-cast condition; etchant, 5 percent HCl in alcohol, electrolytic.



X100 X750

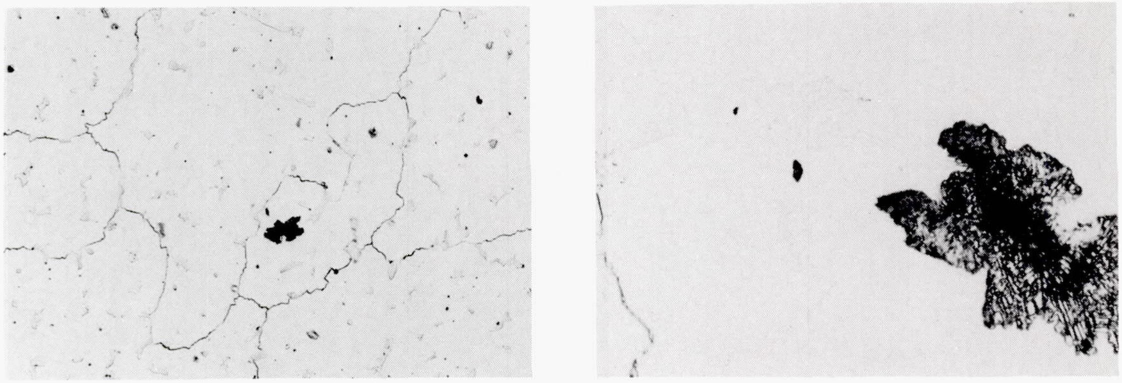
(b) Solution-treated and quenched (heat treatment A); etchant, 5 percent HCl in alcohol, electrolytic.



X100 C-27885 X750

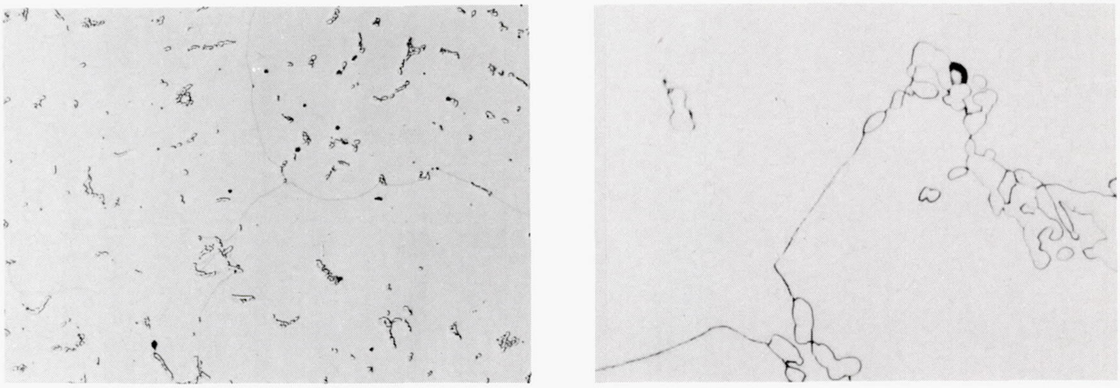
(c) Solution-treated, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent HCl in alcohol, electrolytic.

Figure 8. - Microstructures of 6059.



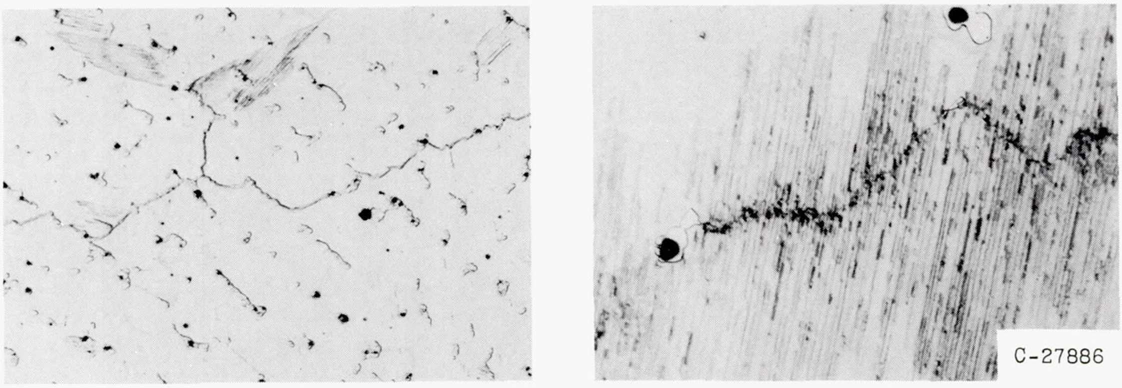
X100 X750

(a) As-cast condition; etchant, 5 percent aqua regia in water, electrolytic.



X100 X750

(b) Solution-treated and quenched (heat treatment A); etchant, 5 percent aqua regia in water, electrolytic.



X100 X750

(c) Solution-treated, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent aqua regia in water, electrolytic.

Figure 9. - Microstructures of 61.

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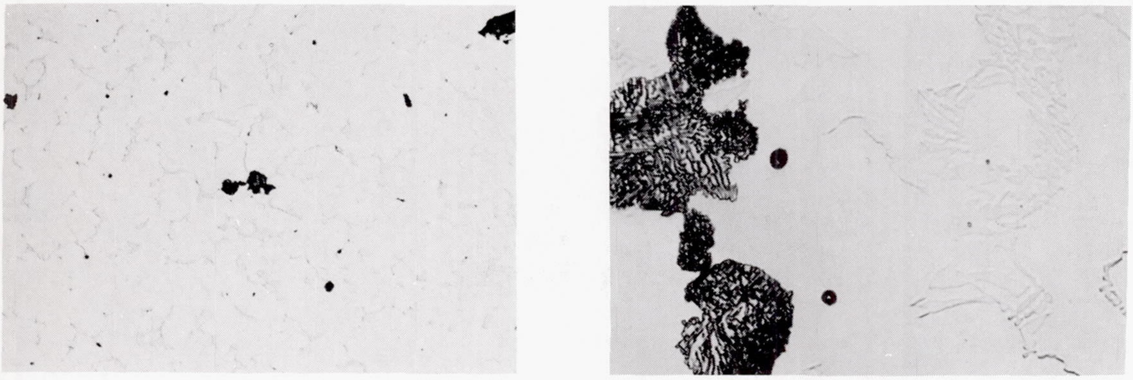
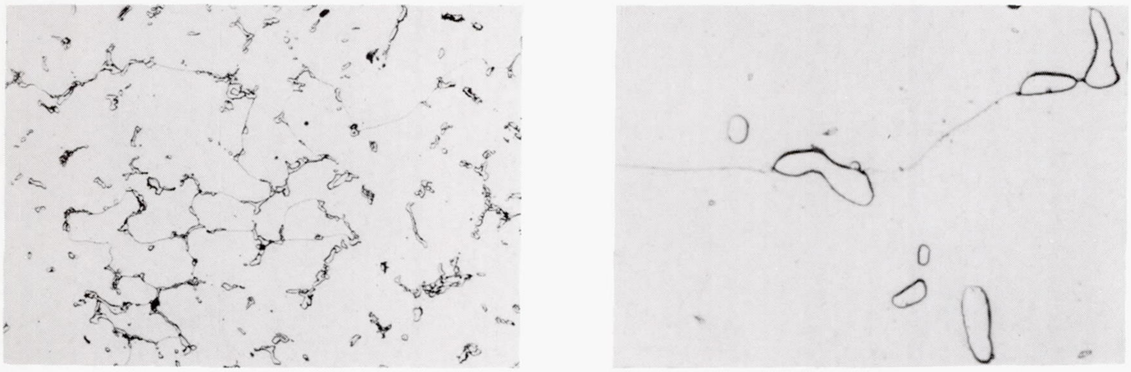
CI-6



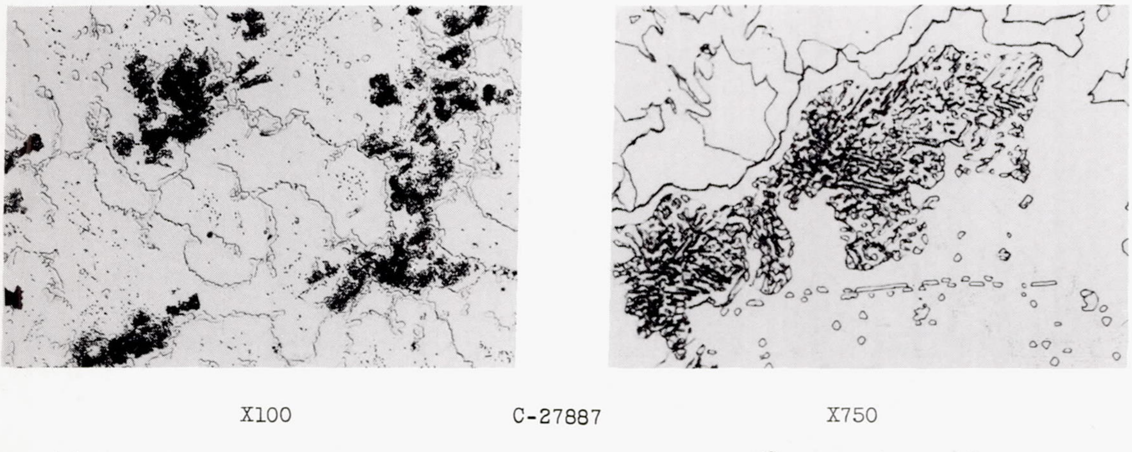
X100 X750

(a) As-cast condition; etchant, 5 percent HCl in alcohol, electrolytic.



X100 X750

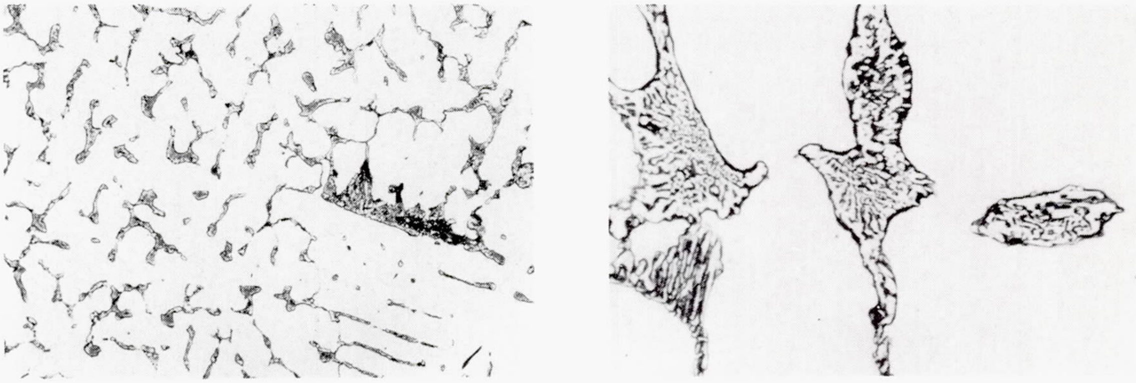
(b) Solution-treated and quenched (heat treatment A); etchant, 5 percent aqua regia in water, electrolytic.



X100 C-27887 X750

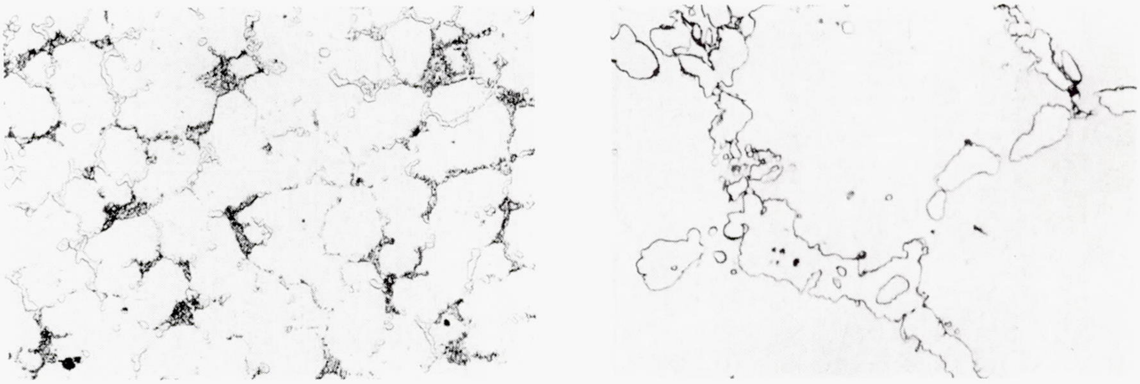
(c) Solution-treated, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent aqua regia in water, electrolytic.

Figure 10. - Microstructures of X-40.



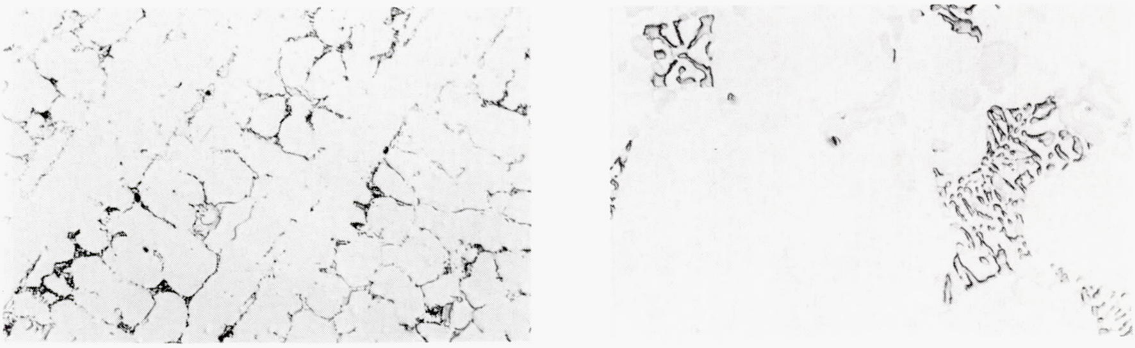
X100 X750

(a) As-cast condition; etchant, 5 percent aqua regia in water, electrolytic.



X100 X750

(b) Heat-treated at 2250° F and quenched (heat treatment A); etchant, 5 percent aqua regia in water, electrolytic.



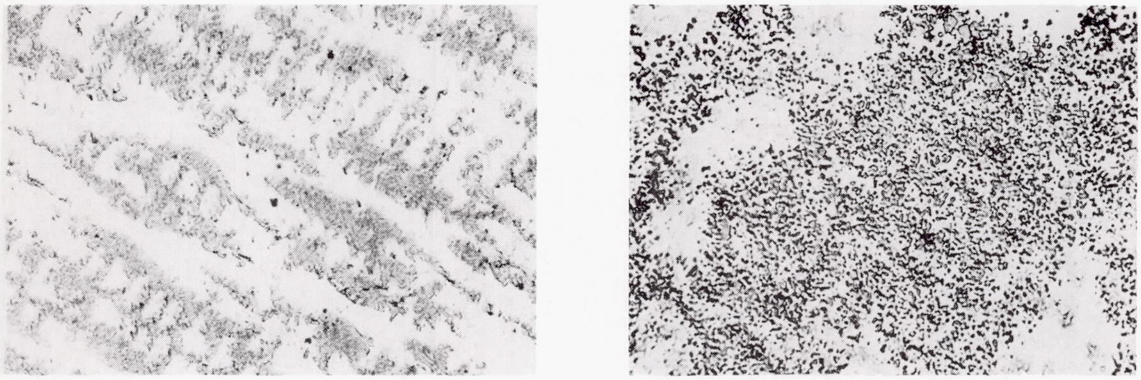
X100 C-27888 X750

(c) Heat-treated at 2250° F, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); 5 percent aqua regia in water, electrolytic.

Figure 11. - Microstructures of I336.

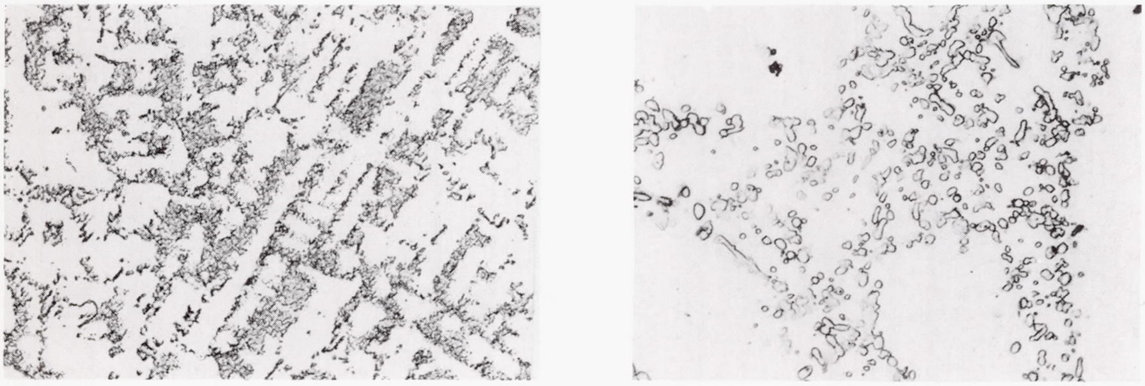
3020

CI-6 back



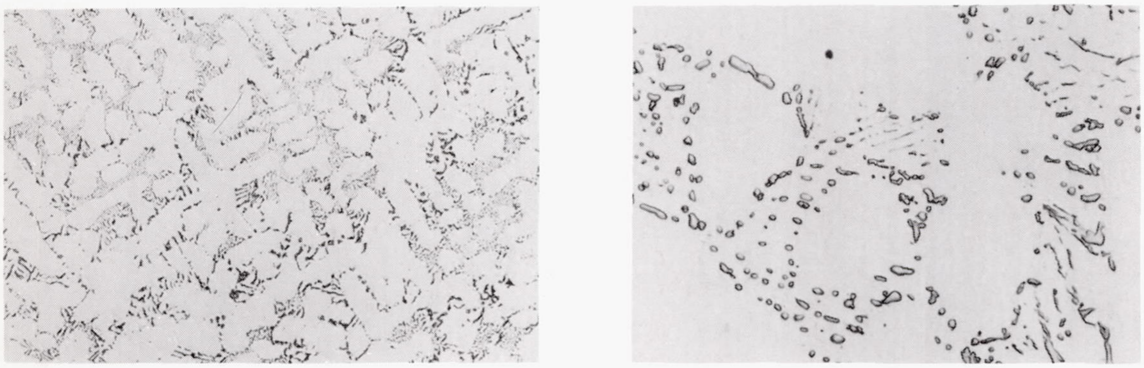
X100 X750

(a) As-cast condition; etchant, 10 percent NaCN in water, electrolytic.



X100 X750

(b) Heat-treated at 2250° F and quenched (heat treatment A); etchant, 10 percent NaCN in water, electrolytic.



X100 C-27889 X750

(c) Heat-treated at 2250° F, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent HCl in alcohol, electrolytic.

Figure 12. - Microstructures of S-816.

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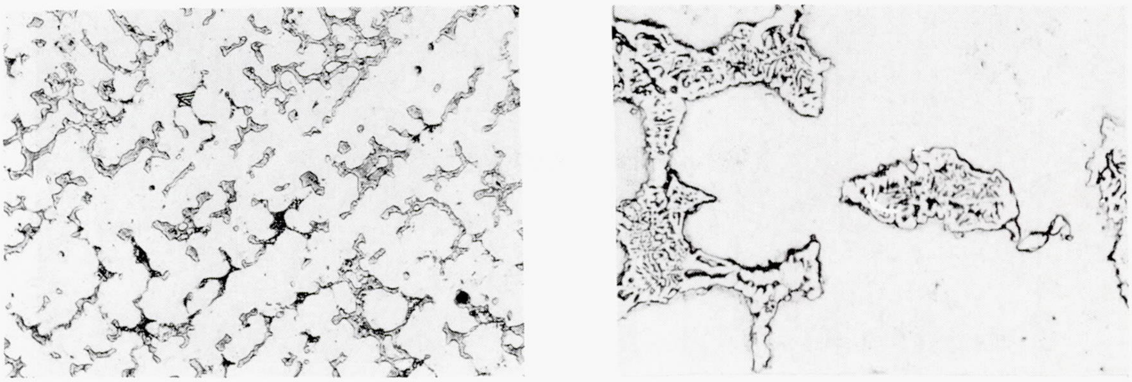
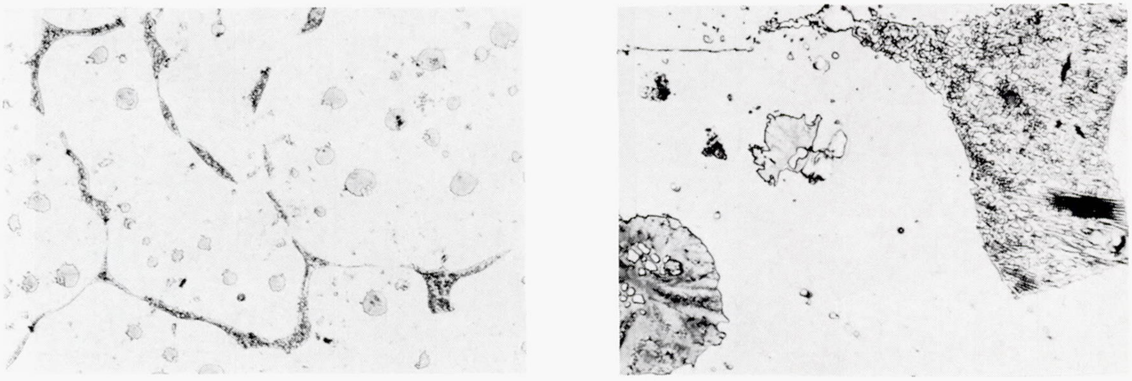


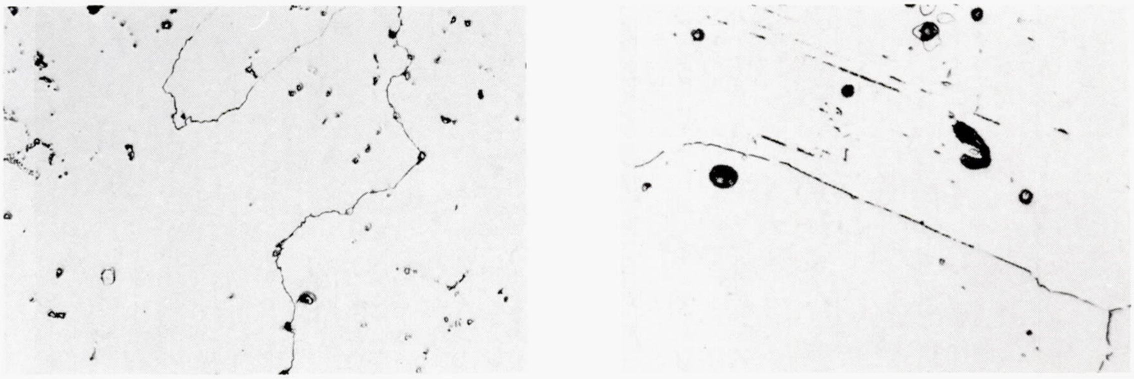
X100 X750

(a) As-cast condition; etchant, 5 percent HCl in alcohol, electrolytic.



X100 X750

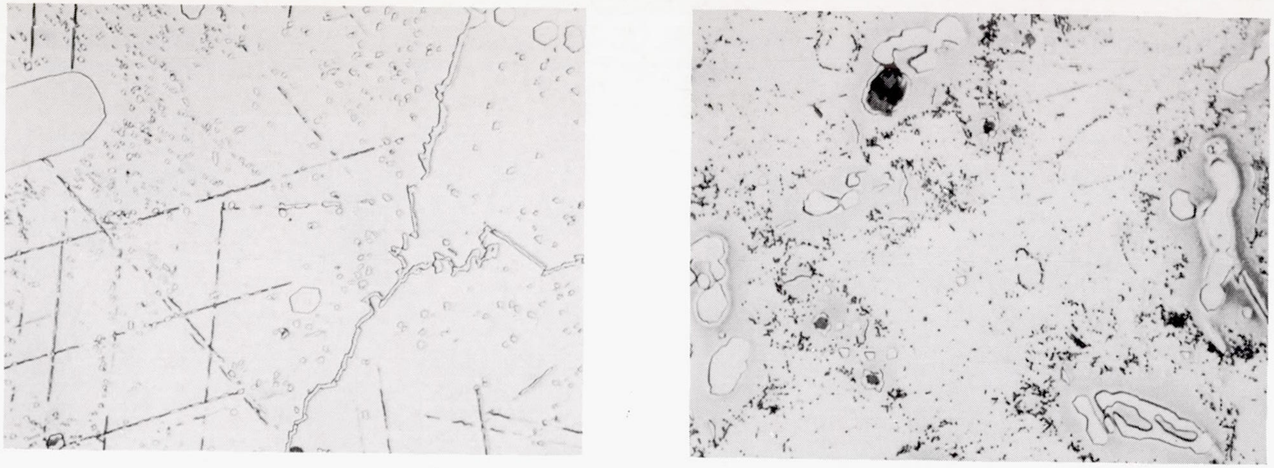
(b) Heat-treated at 2250° F and quenched (heat treatment A); etchant, 5 percent HCl in alcohol, electrolytic.



X100 C-27890 X750

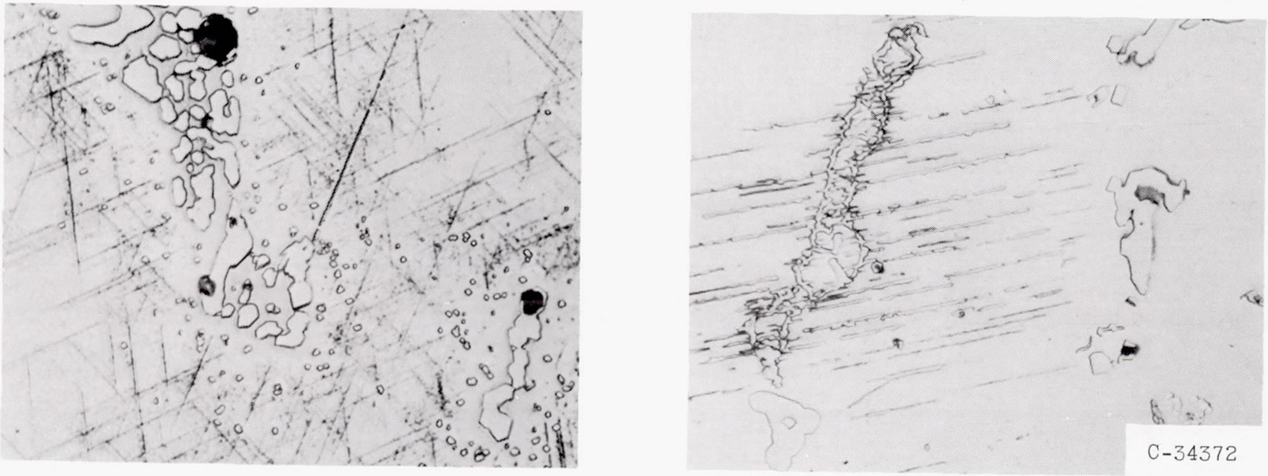
(c) Heat-treated at 2250° F, interrupted furnace cooled to 1100° F, and quenched (heat treatment E); etchant, 5 percent HCl in alcohol, electrolytic.

Figure 13. - Microstructures of J.



(a) X-63.

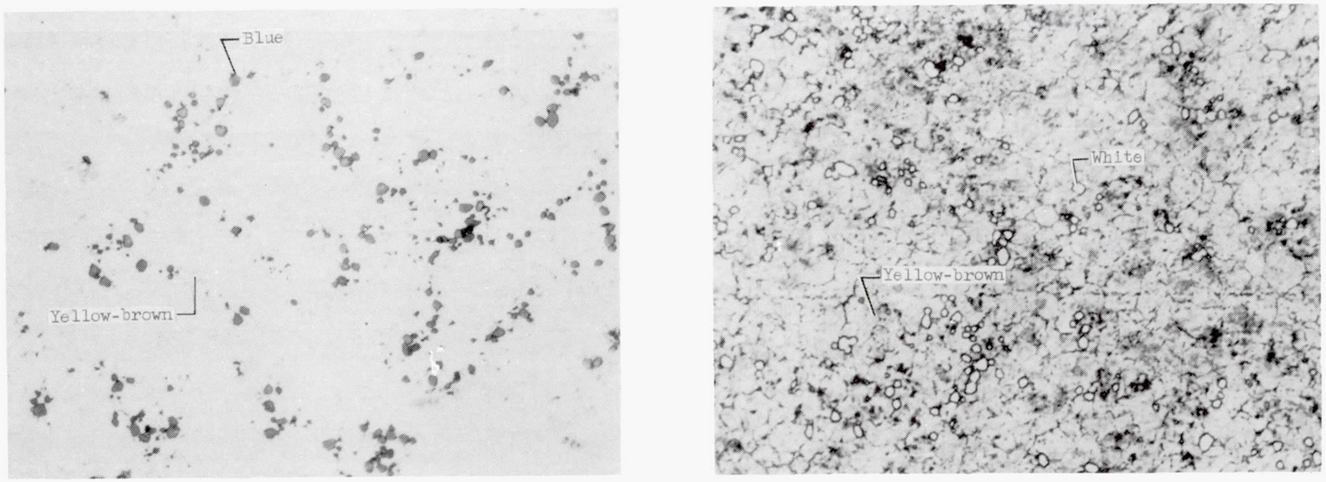
(b) 6059.



(c) 61.

(d) J.

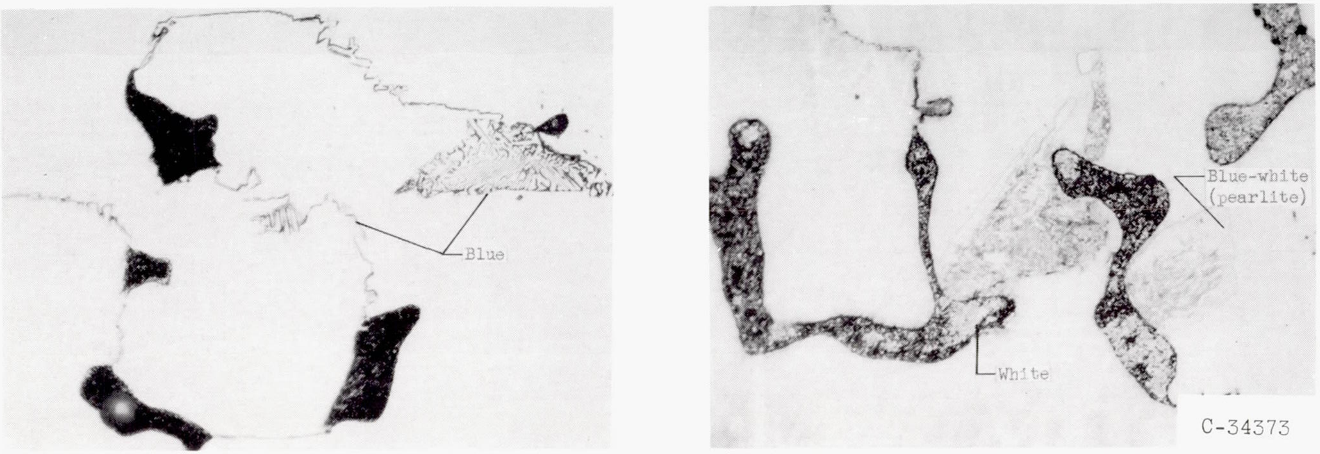
Figure 14. - Microstructures of alloys X-63, 6059, 61, and J solution-treated and isothermally transformed according to heat treatments listed in figure 2 (longer times at lower temperatures); etchant, 5 percent aqua regia in water, electrolytic; magnification, X1500.



Stain etchant 3; X1000

Heat tinted; X1500

(a) Rolled Stellite 21.

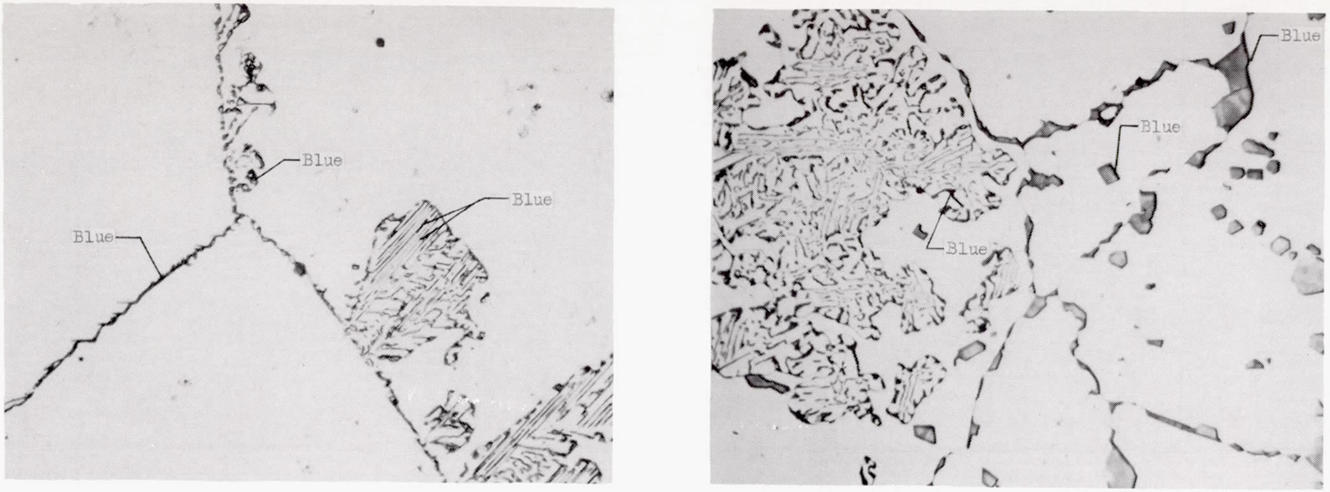


Stain etchant 3; X1000

Heat tinted; X1500

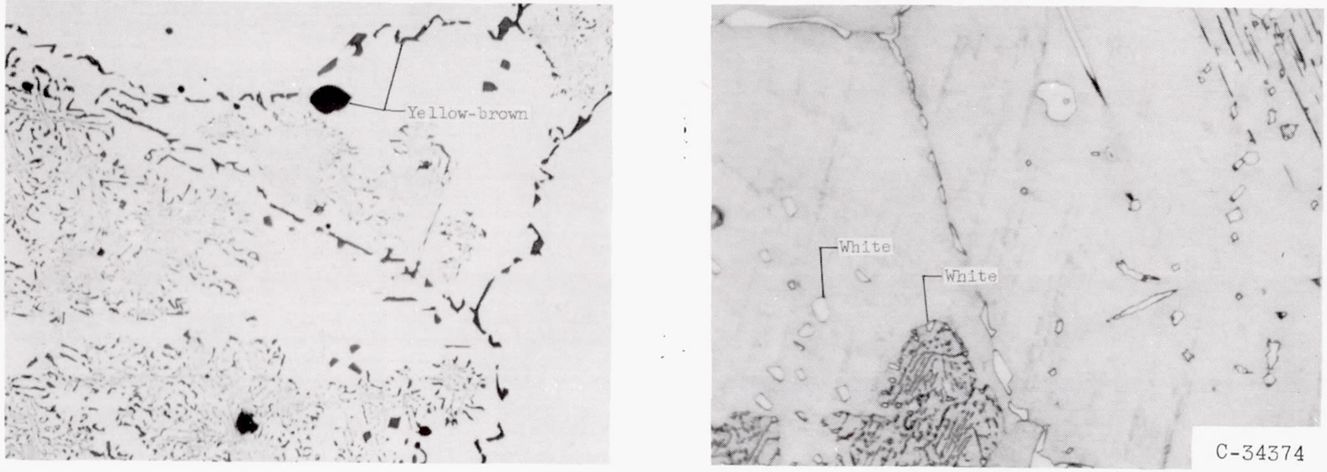
(b) Cast Stellite 21.

Figure 15. - Microstructures of various stain-etched and heat-tinted specimens.



Stain etchant 1; X1000

Stain etchant 3; X1000

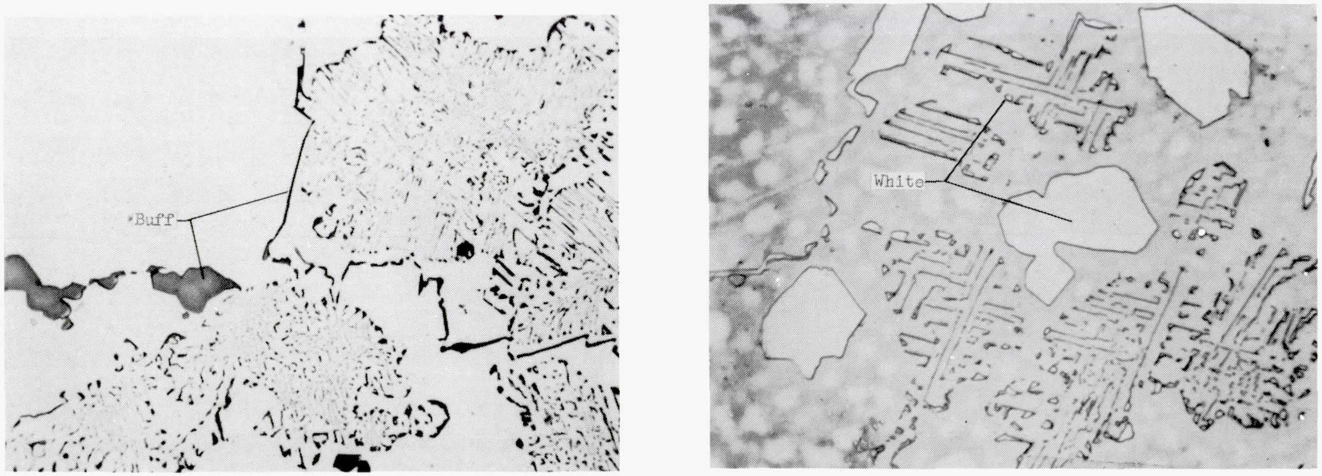


Stain etchant 2; X750

Heat tinted; X1500

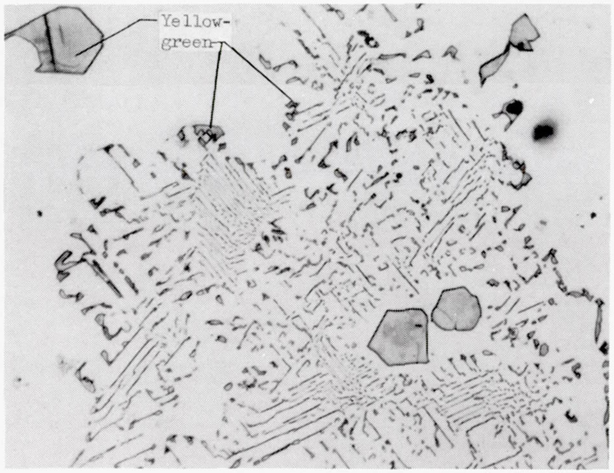
(c) Rolled Stellite 21 (heat treatment E).

Figure 15. - Continued. Microstructures of various stain-etched and heat-tinted specimens.



Stain etchant 2; X750

Heat tinted; X1500

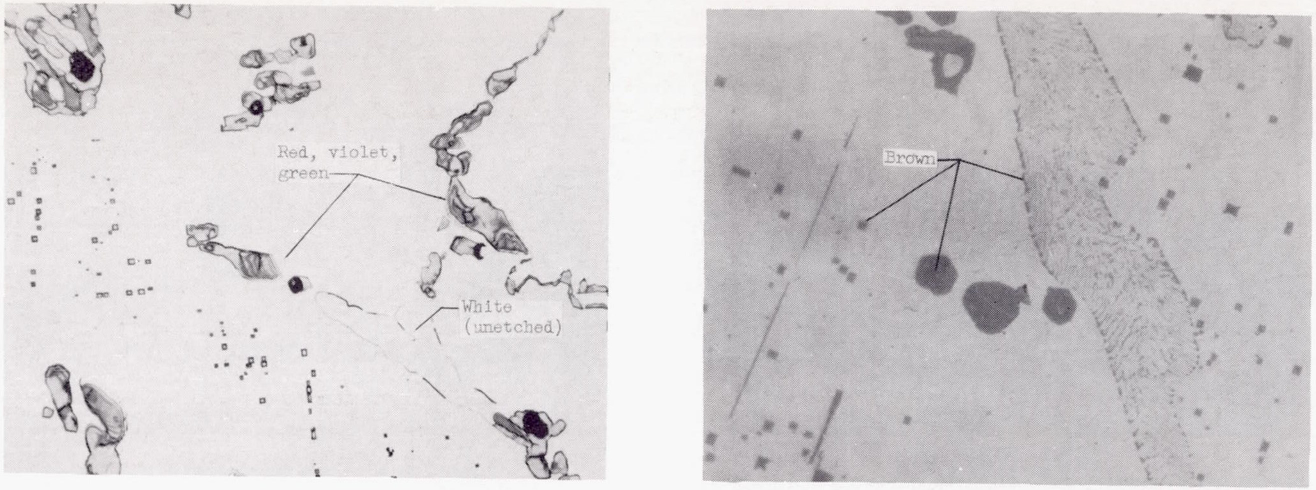


C-34375

Stain etchant 3; X1000

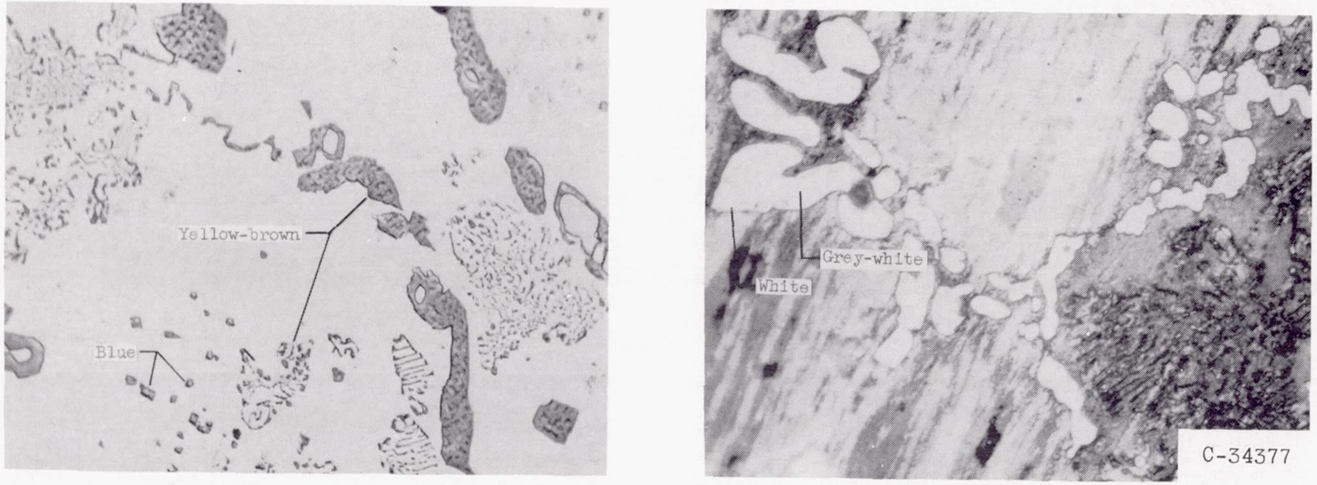
(d) Cast Stellite 21 (heat treatment B) 2 hours isothermal transformation at 2000° F.

Figure 15. - Continued. Microstructures of various stain-etched and heat-tinted specimens.



Stain etchant 1; X750

Stain etchant 3; X1500

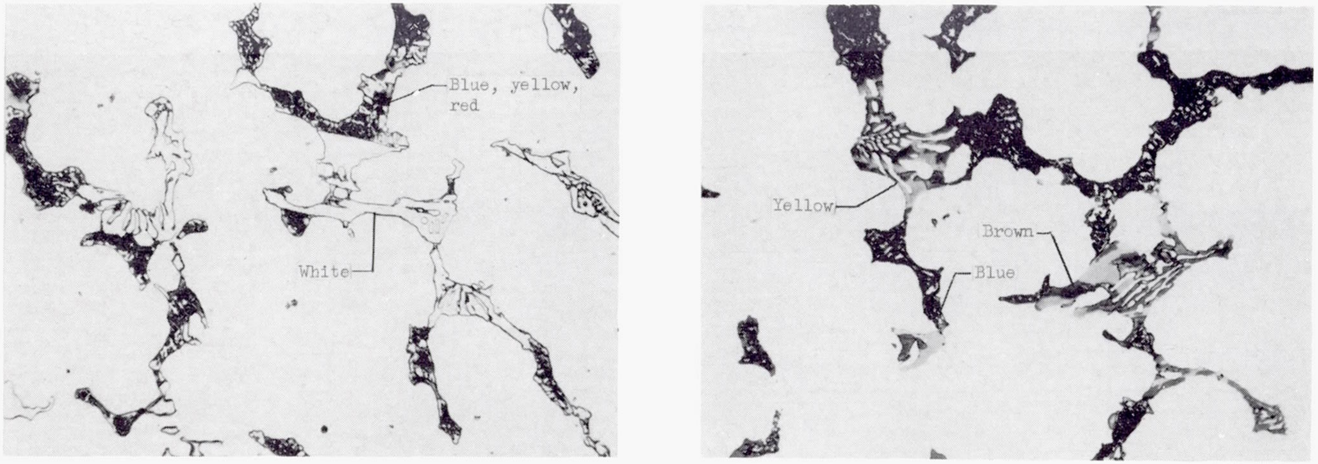


Stain etchant 2; X1000

Heat tinted; X1500

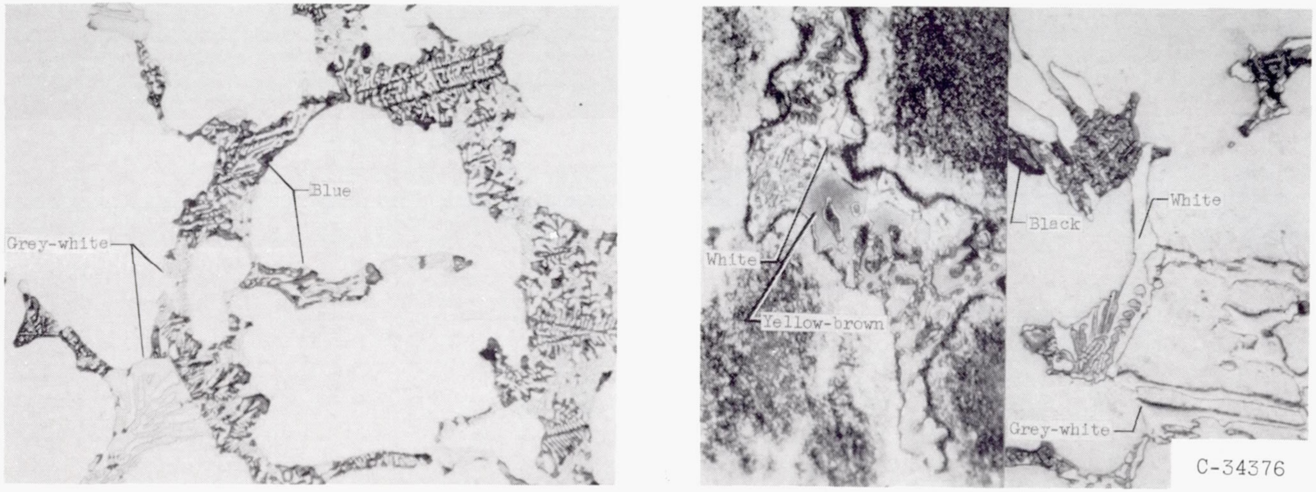
(e) Cast X-40 (heat treatment E).

Figure 15. - Continued. Microstructures of various stain-etched and heat-tinted specimens.



Stain etchant 1; X750

Stain etchant 3; X750



Stain etchant 2; X1000

Heat tinted; X1500

(f) Cast J alloy.

Figure 15. - Concluded. Microstructures of various stain-etched and heat-tinted specimens.

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