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AFML-TR-69-344

Development Of Oxidation Resistant, High-Strength, Columbium-Base Alloys

AD No. ——
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D.L. Graham

STELLITE DIVISION
UNION CARBIDE CORPORATION

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Technical Report AFML-TR-69-344
January, 1970

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NOTICES

DEVELOPMENT OF OXIDATION RESISTANT HIGH-STRENGTH, COLUMBIUM-BASE ALLOYS

T. K. Roche and D. L. Graham

FOREWORD

The work described in this report was performed under Contract AF 33(615)-3856 from 1 July 1966 to 30 June 1969. The report was released for publication in December 1969.

The contract with Stellite Division, Union Carbide Corporation was initiated under Project No. 7351, "Metallic Materials," Task No. 735101, "Refractory Metals." The initial portion of the investigation was accomplished under the direction of Captain R. Kosak (MAMP), and the final portion under Mr. J. K. Elbaum (MAMP) Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

The final portion of the work was conducted by Mr. T. K. Roche of Stellite Division, Union Carbide Corporation; the earlier phases were carried out by Dr. D. Geiselman, Mr. D. L. Graham, and Mr. Roche.

The authors wish to acknowledge the assistance of the laboratory personnel of the Stellite Division, Technology Department, and particularly that of Mr. G. L. Eckert who served as project technician.

This technical report has been reviewed and is approved.

I Perlmutter
I. PERLMUTTER
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ABSTRACT

This program was carried out for the development of a fabricable columbium-base alloy with improved oxidation resistance and good strength properties at 2000°F and above for use as a blade material in gas turbine engines.

Nineteen electron beam melted ternary alloys from the Cb-W-Ta and Cb-W-Hf systems within the composition range 10-25 percent tungsten, 15-30 percent tantalum, 2-35 percent hafnium, were evaluated for fabricability, tensile and creep-rupture strength properties, and oxidation resistance. The composition Cb-15W-35Hf offered the best compromise in properties and was selected as the base for further alloying. A 1.9 percent addition of rhenium to this base did not enhance properties. Additions of 2.8 percent cobalt and nominally 5 and 10 percent titanium improved oxidation resistance but cobalt caused a pronounced depression in the solidus temperature and titanium reduced the creep-properties. Nominal additions of 1000 ppm carbon and 500 ppm carbon with 500 ppm nitrogen were not effective in restoring creep-rupture strength to the quaternary composition Cb-15W-35Hf-5Ti; an alloy containing approximately 2 percent each of aluminum and vanadium in this quaternary was the most oxidation resistant composition evaluated, but was not fabricated successfully.

The columbium alloys studied in this program did not meet the total property requisites placed upon a material for blade applications in gas turbine engines. Although the oxidation resistance and tensile properties shown by several of the Cb-W-Hf alloys were noteworthy, additional work would be required to achieve a better balance in properties for these materials.

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SECTION I

INTRODUCTION

The established trend in development of gas turbines is toward higher turbine inlet temperatures to obtain increased efficiency. The application of refractory alloys in gas turbine blades and other parts would permit higher operating temperatures than with conventional nickel- or cobalt-base superalloys. A columbium-base alloy possessing an attractive combination of fabricability and high-strength properties, together with relatively good inherent oxidation resistance, at a temperature of 2000°F or above would be expected to find significant application in gas turbine engines, and would be of considerable benefit to the advancement in performance of such engines.

Earlier work on the development of columbium-base alloys emphasized studies for improving oxidation resistance, but the alloys that were developed generally lacked either adequate fabricability or adequate strength properties at elevated temperatures. Since then, major emphasis has been placed on development of columbium-base alloys possessing excellent fabricability and weldability, along with moderately good strength properties, for use as sheet materials in aerospace applications. Oxidation resistance for these alloys has been achieved through the use of coatings, but not with 100 percent reliability. If columbium alloys could be developed that exhibited improved oxidation resistance, coating failure would not be as serious a problem and a coating-substrate system would be more reliable and resistant to catastrophic failure. It was the purpose of this program to apply existing information relative to the oxidation behavior and mechanical properties of columbium-base alloys toward the development of improved compositions possessing the desired combination of properties necessary for application in gas turbine engines.

This program had as its objective the development of at least one columbium-base alloy with the following characteristics:

(1) Oxidation resistance equivalent to that of TD nickel at 2000°F (about 1 to 2 mils loss per side in 100 hours);

(2) Ability to the fabricated;

(3) Good short-time strength properties with a minimum tensile elongation of 5 percent at room and elevated temperature;

(4) A tensile transition temperature not higher than -80°F;

(5) A density compensated rupture - strength better than 60,000 inches for 100-hour life at 2000°F (approximately equivalent to 20,000 psi rupture strength at a density of 9 gm/cc);

(6) Good thermal stability.

This report describes the results of preparing and evaluating, in light of the program objective, a large number of Cb-W-Ta and Cb-W-Hf ternary alloys and several more complex alloys based upon the composition Cb-15W-35Hf with additions of rhenium, titanium, cobalt, vanadium, aluminum, carbon, and nitrogen. Following a summary of the program in Section II, the basis for alloy selection and the experimental program are outlined in Sections III and IV. Section V covers alloy preparation, including melting and casting, fabrication, heat-treating, and phase identification studies. The description of melting and casting techniques reported in this section is quite detailed since considerable effort was devoted to this portion of the program. Mechanical property and oxidation evaluation of the alloys are reported separately in Sections VI and VII. Since results are discussed as they are presented in this report, the discussion of the program in Section VIII provides general commentary concerning the results in relation to the objective of the study. Conclusions and recommendations are presented in Section IX. The tables are collected in the Appendix followed by a listing of references and a bibliography.

SECTION II

SUMMARY

The objective of this program was the development of a fabricable columbium base alloy with improved oxidation resistance and good strength properties at 2000°F and above for use as a blade material in gas turbine engines.

Two alloy systems were selected for study: Cb-W-Ta within the composition range 10-25 percent tungsten, 15-30 percent tantalum; and Cb-W-Hf within the composition range 10-25 percent tungsten, 2-35 percent hafnium. Evaluation of these alloys led to the selection of the composition Cb-15W-35Hf as a base for further alloying since this ternary offered the best compromise in properties. Additions made to this base, both singly and in combinations, to determine their effect on property enhancement included the elements: rhenium, titanium, cobalt, aluminum, vanadium, carbon, and nitrogen.

Melting procedures for the alloys became quite involved. Nonconsumable and consumable arc melting, and electron beam melting, or their combination were used depending upon alloy composition. Where volatilization of an addition, such as titanium or aluminum, was a problem, the final ingot of the alloy was prepared by consumable arc melting under an inert atmosphere; otherwise, electron beam melting was used.

The oxidation behavior of the Cb-W-Ta and Cb-W-Hf alloys was found to be significantly different. It was found that 0.10-inch thick specimens of all the Cb-W-Ta alloys were completely penetrated by oxygen through oxide formation and contamination within 20 hours at 2000°F. On the other hand, for the same specimen thickness, alloys of the Cb-W-Hf system with moderate amounts of tungsten and fairly large amounts of hafnium contained unaffected metal even after an exposure of 65 hours at 2000°F in flowing air. This improved oxidation resistance of the Cb-W-Hf alloys resulted from a uniform, slowly advancing, internal oxidation front promoted by a high hafnium content, and an influence of tungsten in affecting the kinetics of internal oxidation and scale formation.

Although the composition Cb-15W-35Hf offered the best compromise in properties of the ternary alloys investigated, improvements in strength, ductility, and probably fabricability would be required for turbine blade applications.

Mechanical property tests on the composition Cb-15W-35Hf in the extruded, forged, and recrystallized condition showed the alloy to be brittle at room temperature with an ultimate tensile strength of 100,000 psi, whereas at 2000°F, an ultimate tensile strength of 80,000 psi, a yield strength of 70,000 psi, and an elongation of 5 percent were obtained.

However, it was indicated that ductility can be improved by suitable thermal mechanical processing since the alloy showed a tensile elongation of 15 percent at 600°F in the stress relieved condition.

Creep-rupture behavior of this basic ternary at 2000°F and 20,000 psi did not prove to be outstanding. Time to 1 percent plastic strain was 22 hours. Failure occurred in 132 hours, but elongation at failure was high, 36 percent. It was apparent, as evidenced by recrystallization accompanying the tests, that the high elongations were caused by structural instability from high diffusion rates. Therefore, improvements in creep properties could be expected by effecting an increase in the recrystallization temperature.

Further alloying of the Cb-15W-35Hf base with titanium, cobalt, aluminum, and vanadium enhanced oxidation resistance, but at the expense of other properties. For example, it was found that for titanium additions of nominally 5 and 10 percent, total penetration (metal loss plus depth of contamination) of these two alloys after oxidation for 65 hours at 2000°F was approximately 20 mils as opposed to 30 mils for the ternary base under the same conditions. However, both titanium-bearing alloys were very much weaker in creep-rupture behavior -- the time to 1 percent plastic strain at 20,000 psi and 2000°F being less than 1 hour compared with 22 hours for the base. Furthermore, additions of approximately 500 ppm nitrogen plus 500 ppm carbon and 1000 ppm carbon to the nominal composition Cb-15W-35Hf-5Ti were equally ineffective for improving the creep-rupture strength of the titanium-bearing alloy. Strength might have been benefited more by a nitrogen and/or carbon addition to the basic ternary at some sacrifice in oxidation resistance through the elimination of titanium.

A 2.8 percent cobalt addition to Cb-15W-35Hf was quite effective in improving oxidation resistance for up to 20 hours at 2000°F, but scaling rapidly increased after this time and total penetration was approximately the same as the ternary after 65 hours. The short-time improvement in oxidation resistance noted for the cobalt-bearing alloy was offset by a pronounced depression in the solidus temperature for this composition.

The most oxidation resistant composition evaluated for times up to 65 hours at 2000°F was the alloy containing approximately 2 percent each of aluminum and vanadium in the nominal base Cb-15W-35Hf-5Ti. However, this material was not fabricated successfully.

A 1.9 percent rhenium addition to the Cb-W-Hf basic ternary did not enhance properties. The rhenium-bearing alloy was more susceptible to cracking during hot forging, and showed no improvement in oxidation resistance at 2000°F with total penetration as the criterion. Also, this alloy was not appreciably more creep resistant than the Cb-15W-35Hf base for elongations up to 10 percent when tested at 2000°F and 20,000 psi.

The columbium alloys studied in this program do not meet the total property requisites placed upon a material for blade applications in gas turbine engines, but the improvement in oxidation resistance shown by several of the Cb-W-Hf alloys was noteworthy. This can be seen from the data in Table I showing a comparison between the oxidation resistance of two of the better alloys evaluated and several other columbium alloys. Likewise, strength properties are compared in Table II. Consideration of these data demonstrates the well known fact that alloying for the benefit of a particular property is usually done at the expense of another. It is evident that additional work would be required to achieve a better balance in these properties for the Cb-W-Hf alloys.

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SECTION III

ALLOY SELECTION

This program was carried out for the development of a fabricable columbium base alloy with improved oxidation resistance and good strength properties at 2000°F and above for application in gas turbine engines. Selection of the compositions investigated was based upon reported effects of alloying additions on the oxidation resistance and strength of columbium. Consideration was given also to the compositions of the more popular second generation columbium alloys. From this review the two basic systems, Cb-W-Ta and Cb-W Hf, were selected for investigation. The rationale for selection of these systems is included in the discussion below.

A considerable amount of work has been done in determining the effect of individual alloying additions on the oxidation resistance of columbium. In many investigations binary, ternary, and even more complex alloys of columbium were investigated for their oxidation characteristics.

In a review of the reaction of the refractory metals with common gases, Bacon and Moanfeldt(1) attempted to generally outline the effect of binary alloying additions on the oxidation resistance of columbium. From their summary the following general trends were noted: binary alloying additions of up to 20 percent aluminum, 1 to 35 percent iron, titanium from about 3 to 50 percent, 10 percent tungsten, and up to about 10 percent vanadium were successful in improving the oxidation resistance of columbium. These authors also concluded that ternary alloys such as Cb-9Cr-5Al, Cb-40Cr-13Al, and Cb-24Fe-22Al showed promise as oxidation-resistant compositions.

Sims, et al(2) studied the effect of binary alloy additions on the oxidation and contamination resistance of columbium. They investigated additions of titanium, chromium, zirconium, vanadium, molybdenum, tantalum, tungsten, beryllium, boron, cobalt, iron, manganese, nickel, and silicon. In oxidation tests and contamination studies of samples exposed in air at 1112, 1472, and 1832°F, four elements (titanium, vanadium, molybdenum, and chromium) were found to give the greatest improvement in oxidation resistance. Contamination, as determined by hardness penetration measurements on oxidized alloys, was reduced most markedly by zirconium and titanium. Chromium and vanadium also were effective in reducing oxygen diffusion into columbium.

In an evaluation of the oxidation resistance of binary and ternary columbium-base alloys, Wlodek(3) and others concluded that aluminum, chromium, iron, titanium, vanadium, and zirconium are effective binary additions for increasing the oxidation resistance of pure columbium. Additions of cobalt, molybdenum, tin, tantalum, and thorium also improved the oxidation resistance, but to a lesser degree.

Wlodek(4) also investigated the oxidation properties of various alloys of the Cb-Al-V ternary system. Certain compositions showed oxidation resistance considerably improved over that of columbium, and these improvements were attributed to the stabilization of a suboxide. This oxide formed a stable adherent film which greatly slowed the rate of oxidation of the alloys and reduced substantially the amount of spalling that occurred. Of the alloys investigated, the composition Cb-3Al-3V was most significantly improved in oxidation resistance over that of pure columbium.

Babitzke, et al(5) studied a large number of columbium-base alloy compositions for mechanical properties and oxidation behavior. On the basis of weight gain measurements in air, alloy compositions of Cb-24.3Hf-8.3W, Cb-25.3Hf-8.7W-4.5Ti, and Cb-24.3Hf-16.7W-4.3Ti showed attractive oxidation resistance.

Rapp and Goldberg(6) studied the oxidation kinetics of Cb-Zr and Cb-Zr-Re alloys in oxygen at 1832°F. The alloys were within the composition range Cb-(10-40)Zr and Cb-(10-27)Zr-(4-18)Re. Results of this work showed the scaling of the binary alloy, Cb-10Zr, to be about 2.3 times greater than that for pure columbium; but with increasing zirconium content, the scaling rates were reduced to values below that for pure columbium. This composition dependence of the scaling rate was partially attributed to the effect of the internal oxidation process as an internal sink for oxygen, with the formation of voluminous, and relatively impermeable ZrO_2 precipitates. Rhenium additions to binary Cb-Zr alloys caused a reduction in the thickness of the internal oxidation zones and the formation of a more adherent and much less porous external scale resulting in a decrease in the kinetics of scale formation.

In the following brief review of the effects of alloying additions on the strength of columbium, the assumption was made that the trends noted are generally accepted, and that most investigators are in agreement on the relative effects of these elements on the mechanical properties of columbium.

Tungsten is the most common alloying addition made to columbium since it is completely soluble and serves as a solid solution strengthener. The higher melting point of tungsten enhances the elevated-temperature strength of columbium-tungsten alloys by raising their melting temperature. Molybdenum has an effect very similar to that of tungsten on the mechanical properties of columbium. Tantalum has essentially the same atomic size as columbium and therefore produces very little solid solution strengthening, but slightly increases the elevated-temperature strength of columbium by raising the melting point of the alloy.

Titanium offers strength improvement when added to columbium because of atomic misfit, but when added in quantities much above 5 atomic percent causes a decrease in the elevated-temperature strength of columbium, because it lowers the melting point and the recrystallization temperature of the alloy. Vanadium has the largest atomic misfit with columbium, and therefore is the most potent strengthener of columbium on an atomic percent basis. However, it detracts from the elevated-temperature strength of columbium in the same manner as titanium when present in large amounts. Zirconium is a potent strengthener of columbium when added in small amounts because of its atomic misfit, and also because of its tendency to form interstitial compounds with the carbon, oxygen, and nitrogen present in the columbium. These compounds contribute to the strength through precipitation hardening. Zirconium has a low melting point in comparison to columbium, and therefore large additions of zirconium to columbium also detract from the elevated-temperature strength. Hafnium, a reactive metal similar to zirconium, has a similar effect on the mechanical properties of columbium. The melting point of hafnium is above that of zirconium, and therefore, it does not have as drastic an effect on the melting point of the alloy as does zirconium.

The effect of rhenium on the mechanical properties of columbium is less well known because the relatively high cost of rhenium has prevented its exploitation as an alloy addition to columbium. Chromium additions to columbium add solid solution strengthening but columbium-chromium alloys above a few percent chromium content are brittle in behavior and, therefore, not of practical interest.

An appreciation of the various alloying additions to columbium can be obtained by referring to nominal compositions of several of the more popular second generation columbium alloys. These compositions are listed in Table III. An addition of tungsten at about the 10 weight percent level is common to all of the alloys produced except one, the B-66 composition which has 5 weight percent molybdenum. Zirconium is present in all of the alloys except one, at a level of 1 to 2.5 percent. Tantalum is added to two of the alloys, and hafnium to one, while carbon at the 0.1 percent level is also present in two of the alloys represented in this table. These alloy compositions evolved from a great deal of experimental work covering a span of several years. Therefore, it appeared reasonable that certain of the additions used in these second generation alloys be considered as additions for the compositions studied on this program.

Noting the trends in the alloying behavior of columbium with various elements and the effects of these elements on the strength and oxidation resistance of columbium alloys, two basic systems, Cb-W-Ta and Cb-W-Hf, were selected for study. It was believed that the addition of tungsten in the range of 10-25 weight percent would be required for developing strength. Tantalum in the range of 15-30 weight percent was considered a desirable ternary addition for fabricability, and perhaps imparting some improvement to elevated temperature strength properties and oxidation resistance. Hafnium was selected as the other ternary addition in the range of 2-30 weight percent for hopefully improving oxidation resistance in the same manner as attributed to zirconium in the work of Rapp and Goldberg.(6) Hafnium was preferred to zirconium as an addition because of the probability of hafnium having a less deleterious effect on strength when large additions were made.

Originally it was intended that as a result of screening tests for fabricability, mechanical properties, and oxidation resistance, an optimum composition would be chosen within the above mentioned composition limits of the two selected ternary systems which could be further alloyed for enhancement of properties. However, from these initial tests it became evident from the better oxidation resistance of the Cb-W-Hf alloys that this system offered more promise for meeting the program objective. At this point work was terminated on the Cb-W-Ta alloys, and the range of investigation of alloys of the Cb-W-Hf system was extended to tungsten contents less than 10 weight percent and hafnium contents up to 35 weight percent to better establish an optimum base. Subsequently, the composition, Cb-15W-35Hf, was selected as exhibiting the best compromise in properties.

Other elements and their concentrations selected for determining their effect primarily upon the oxidation behavior of the basic ternary, Cb-15W-35Hf, included the following: 2 weight percent rhenium, 3 weight percent cobalt, and 5 and 10 weight percent titanium. Evaluation of these four alloys led to selection of the quaternary composition, Cb-15W-35Hf-5Ti, for further alloying with 2 weight percent aluminum in combination with 2 weight percent vanadium, 0.05 weight percent carbon with 0.05 weight percent nitrogen, and 0.1 weight percent carbon. Aluminum and vanadium were considered desirable additions for promoting further improvements in oxidation resistance, and carbon and nitrogen for enhancing strength.

SECTION IV

EXPERIMENTAL PROGRAM

This section presents a general outline of experimentation followed during the course of this program; a detailed description of experimental procedures is presented in the subsequent sections which treat individually the various aspects of the program, i.e. preparation and evaluation of the alloys.

This alloy development program was of the type designed for screening materials for their ability to meet a specific objective, and the processing procedures for the twenty-six alloys studied were closely aligned to production practice precluding the use of "button" melts for the evaluation of the various compositions. All of the alloys were cast as cylindrical ingots weighing approximately five pounds each.

Following the preparation of the alloy ingots, specimens from top and bottom were chemically analyzed, metallographically examined, and tested for room temperature hardness. The ingots were then conditioned for primary fabrication which was accomplished by extrusion or swaging. Secondary fabrication was usually performed by forging; however, three very fabricable compositions, Alloys No. 1 (Cb-10.3W-15.6Ta), 2 (Cb-9.8W-28.3Ta) and 6 (Cb-9.8W-1.6Hf), were reduced to final size by swaging alone. Six alloys, two from the Cb-W-Ta system and four from the Cb-W-Hf system were given no secondary fabrication. A recheck of chemical analysis was run on many of the alloys following fabrication.

Heat-treating studies were performed on the fabricated alloys to establish an annealing temperature to recrystallize the materials prior to oxidation and mechanical property evaluation. Hardness measurements and, primarily, metallographic examination were used as the criteria for recrystallization. Work was carried out to identify the phase precipitated in a typical Cb-W-high hafnium content alloy as well as the phases found in three more complex Cb-W-Hf alloys containing additions of nitrogen, carbon and cobalt.

Tensile properties of the recrystallized alloys were measured at room temperature, 2000°F, and in some cases 2200°F. Other tests, above and below room temperature, were performed to obtain an indication of the tensile transition temperature of a few of the alloys. Creep-rupture evaluation at 2000°F was performed on selected Cb-W-Hf ternary alloys and on the basic composition of nominally Cb-15W-35Hf containing additions of rhenium, titanium, carbon and nitrogen. An indication of thermal stability was obtained for the Cb-W-Hf type alloys from hardness measurements of the uncontaminated areas of the post-test oxidation specimens.

The alloys were evaluated for their oxidation resistance at 2000 and 2200°F for times of two and/or twenty hours. Some of the more oxidation resistant Cb-W-Hf compositions were tested for times of sixty-five and one-hundred hours at 2000°F. Measurements included weight gain, amount of metal loss, and depth of contamination.

A summary of the general experimental sequence used for the processing and evaluation of the various alloys is shown in the flow diagram in Figure 1.

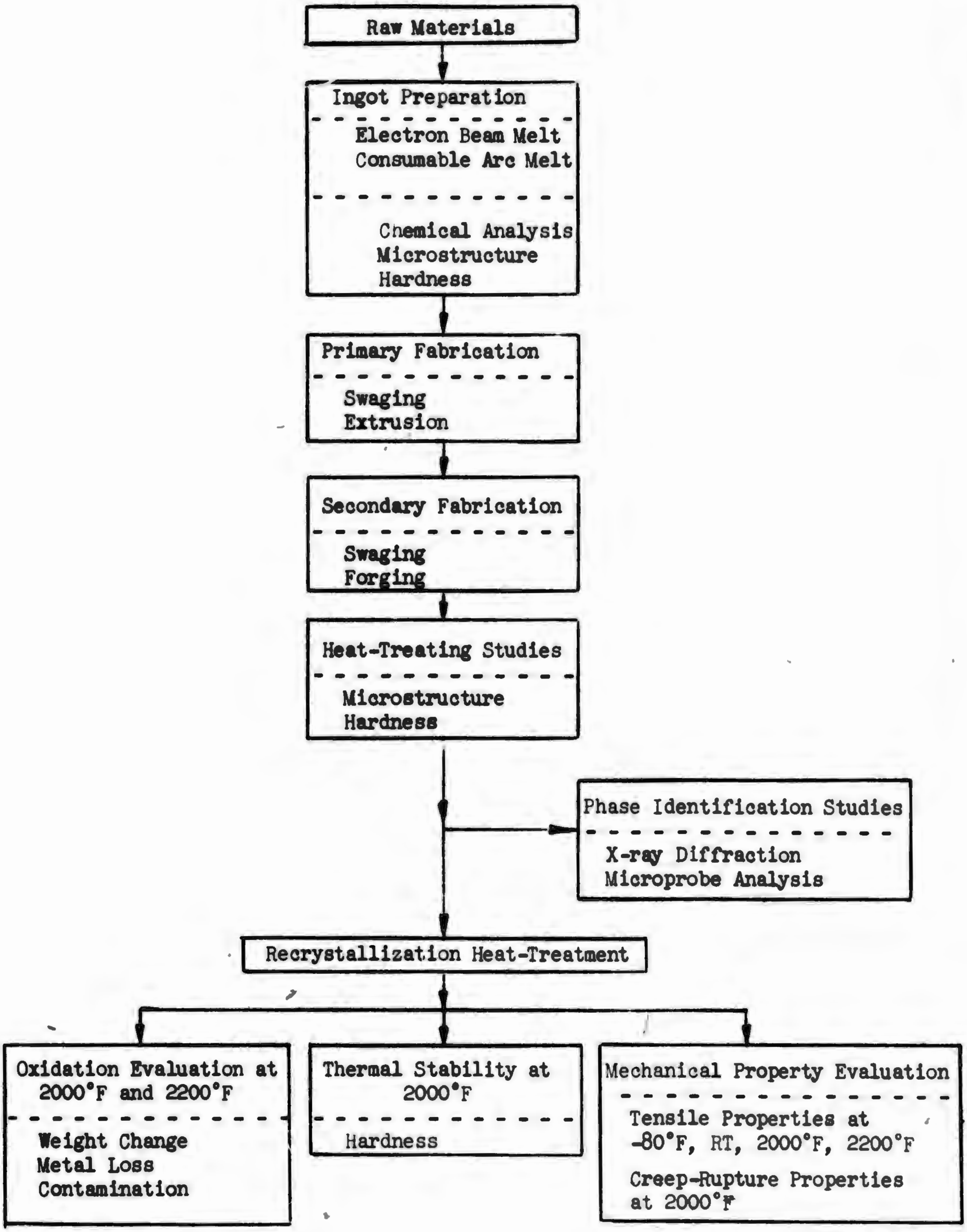

Figure 1. Outline of Experimental Program.

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SECTION V

ALLOY PREPARATION

This section presents the procedures for and results of the preparation of the alloys studied in the program. Included are a description of the melting and casting techniques utilized, the fabrication methods, and the results of studies for determining a recrystallization heat-treatment for each alloy prior to mechanical property and oxidation evaluation. In addition, the results of phase identification work carried out on several Cb-W-Hf type alloys are presented.

5.1 MELT STOCK

A listing of materials used as melt stock for the alloys is presented in Table IV. Vendors' analyses are also shown. The columbium, tungsten, and tantalum were better than 99.5 percent pure; but the hafnium contained 2.6 to 3.9 percent of zirconium. Therefore, it is to be understood that zirconium is included in the composition of the hafnium-bearing alloys up to approximately 1.4 percent, although the zirconium analyses are not reported. The source of vanadium and aluminum required for Alloy No. 28 was an electron beam melted 63Ti-37V alloy and aluminum wire, 99.9 percent pure. Rhenium added to one alloy was in the form of -325 mesh powder, and cobalt to another was in the form of strip. These two alloying additions were of commercial purity. Graphite tape was used for adding carbon to two alloys.

5.2 MELTING AND CASTING

For each of the alloys studied, an ingot weighing approximately five pounds was prepared. Melting procedures included nonconsumable and consumable arc melting and/or electron beam melting, depending upon the composition of the alloy. In those cases where volatilization of an alloy addition such as titanium or aluminum was a problem, the final ingot of the alloy was prepared by consumable arc melting under an inert atmosphere; otherwise, electron beam melting was used. Details of the various melting procedures are included in the sections which follow.

5.2.1 Cb-W-Ta Ternary Alloys

The method first proposed for preparing all of the alloys for the program involved a three-step operation: (1) preparation of buttons by nonconsumable arc melting, (2) remelting of the buttons in the nonconsumable arc furnace and drop-casting into cylindrically shaped ingots, and (3) joining the drop-cast ingots to form an electrode for consumable arc melting to produce the final ingot of each composition. Drop casting, for the most part, proved to be impractical, as will be discussed later,

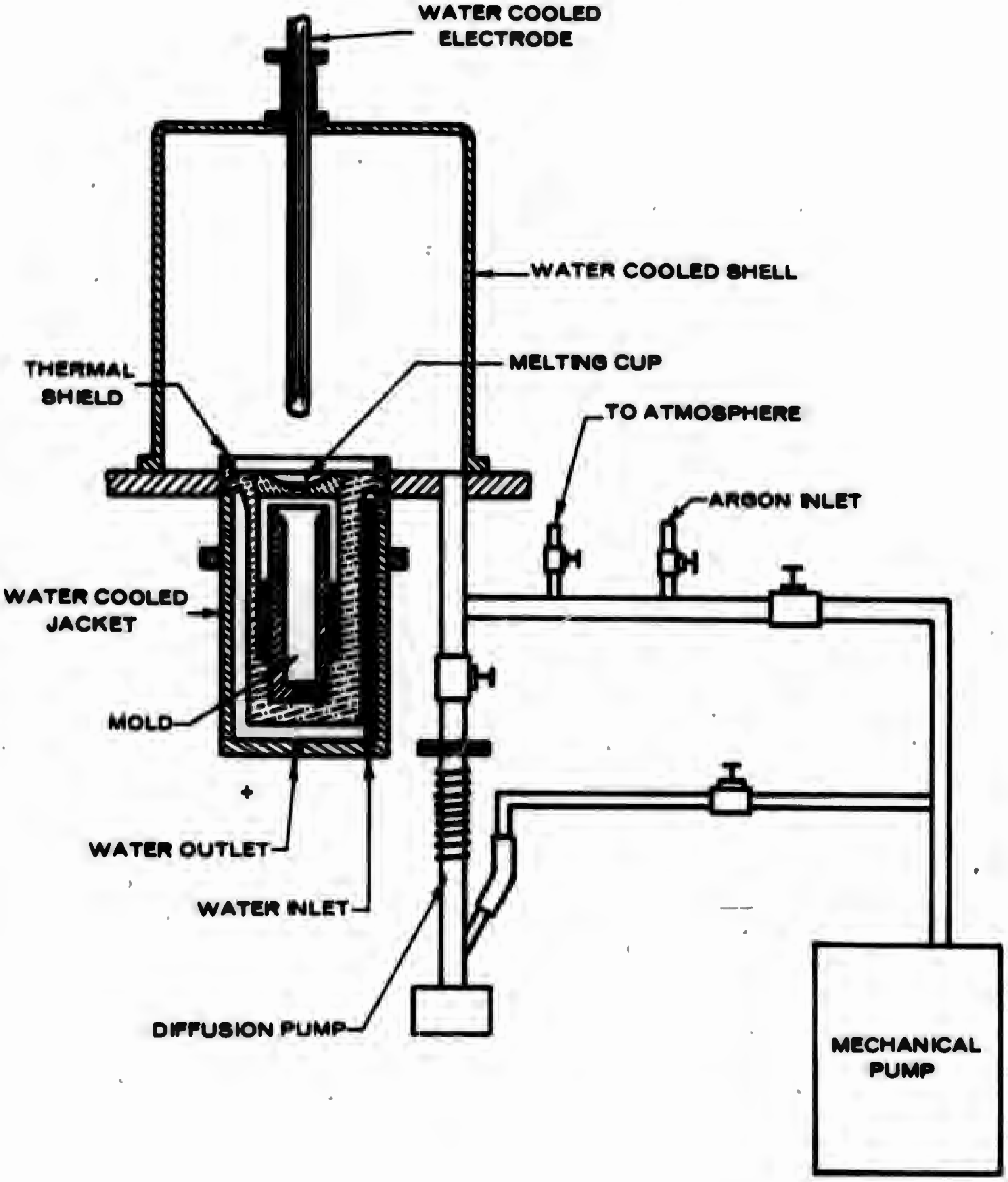
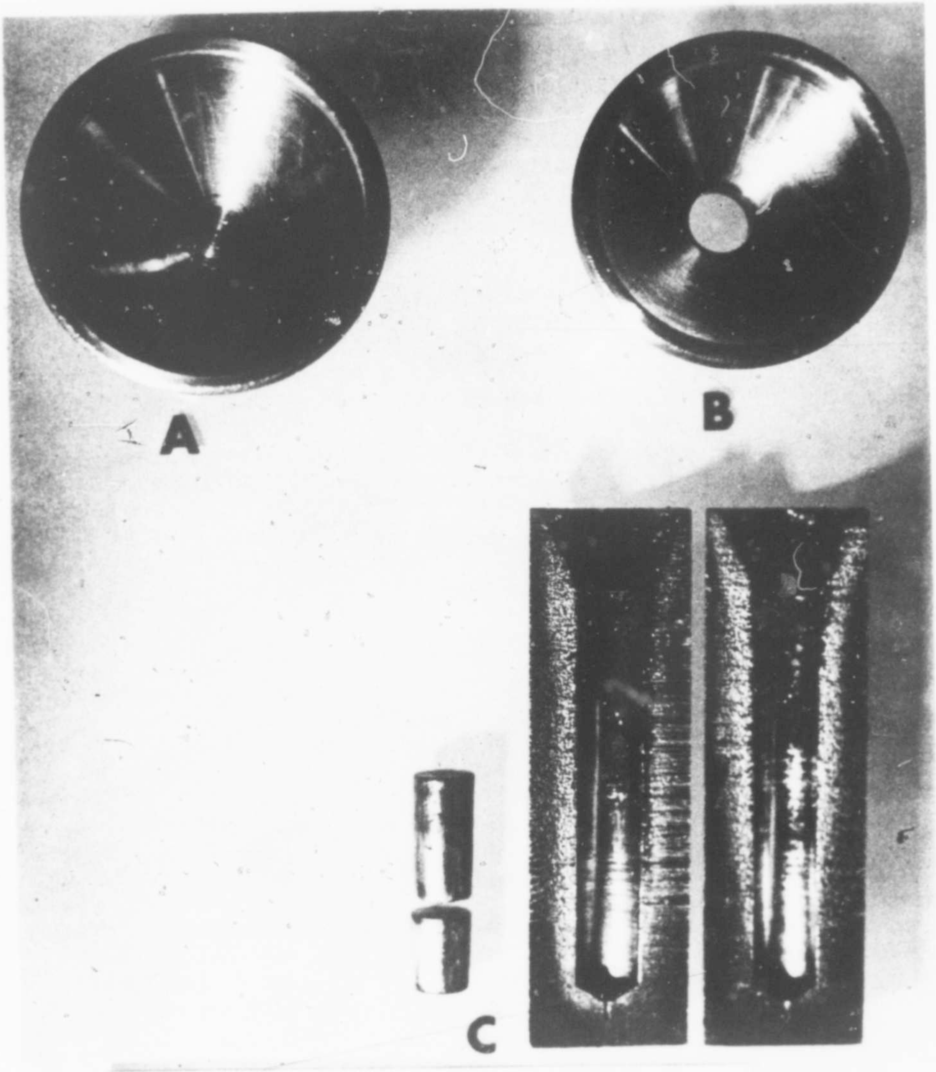


Figure 2. Schematic Diagram of Non-Consumable Arc Melting Furnace for Consolidating and Drop-Casting Alloy Buttons.



Neg. No. 20559

Figure 3. Copper Melting Cups and Drop-Cast Mold.

A. Consolidating Cup B. Remelt Cup
C. Drop-Cast Mold with Length Adjustment Plugs.

and was generally abandoned early in the program when an electron beam melting furnace became available. Nevertheless, electrodes of the five Cb-W-Ta ternary alloys which were evaluated and whose compositions represent the limits and average of the nominal range Cb-(10-25)W-(15-30)Ta were prepared by drop casting prior to electron beam melting into final ingots.

5.2.1.1 Drop-Casting

A schematic diagram of the nonconsumable arc furnace used to accomplish the button preparation and drop-casting of the Cb-W-Ta alloys is shown in Figure 2. The water-cooled base plate of the furnace accommodated the copper melting cups and drop-cast mold pictured in Figure 3. The inside of the cups was tapered, 3.0-inch diameter at the top by 1.0-inch diameter at the bottom by 1.25-inch deep. The mold was a split cylinder, 1.875-inch outside diameter by 0.75-inch inside diameter by 5.0-inch deep. Power to the furnace was supplied by two direct current welding machines connected in parallel providing a total of 2500 amperes. Before each melting operation, the furnace was evacuated to at least 5×10^{-3} mm, flushed once with high purity argon, re-evacuated, then backfilled with 127 mm (5 inches) of the inert gas.

For a typical Cb-W-Ta drop-cast ingot, the total charge, weighed to the intended composition, amounted to 1.5 pounds. In preparing the remelt button for drop-casting, portions of the columbium and tantalum strip, which had been sheared into 0.5-inch squares, and tungsten powder were placed in alternate layers in the consolidating cup (A in Figure 3) and melted. At least four separate charging and melting operations were required to "build" the button. Following the last addition, the button was homogenized by melting twice more -- once on each side. The consolidating cup was then replaced by the remelt cup (B in Figure 3) for containing the button. The cups corresponded except for the 0.75 to 1.0-inch diameter flow-through hole at the bottom of the remelt cup. Positioned beneath this cup was the drop-cast mold (C in Figure 3). After evacuating and backfilling the furnace, the button was puddled; then with a rapid increase in power to the furnace and careful manipulation of the arc, the button was melted through and cast into the mold below. A skull remained in the remelt cup.

Using the above procedure, materials such as nickel and columbium can be easily drop-cast into an ingot, 0.75-inch diameter by 5.0-inch long. Drop-casting becomes more difficult as the melting point of the material increases and it was not possible to completely fill a mold of the size described above with the Cb-W-Ta alloys. However, ingots up to 3.5-inch long could be cast. (Copper plugs shown adjacent to the drop-cast mold in Figure 3 were inserted at the bottom to adjust mold length.) Examples of 0.75-inch diameter by 2.5 and 3.5-inch long ingots of Cb-25W-30Ta are shown in Figure 4. Melting data for the 2.5-inch long ingot are presented in Table V. Typically, ingot weight was on the order of 50 percent or less of charge weight. Of course, the alloy skull remaining in the remelt cup was reclaimable.

Neg. No. 20421

Figure 4. Drop-Cast Ingots of Cb-25W-30Ta, 0.75 Inch Diameter by 2.5 and 3.5 Inches Long.

Considering that the weight desired for the final ingot of a given alloy was about 5 pounds, drop-casting did not prove to be a practical method for preparing a remelt electrode which approached this weight. For example the 3.5 pound electrode of Alloy No. 1 (Cb-10.3W-15.6Ta) shown in Figure 5 comprised nine drop-castings. To prepare a single drop-casting, a minimum of seven separate melting operations was required, in other words a total of sixty-three melting operations for the nine drop-castings. In addition, extensive material loss was incurred in machining the hot tops of the drop-castings to conform to the diameter of the ingot bodies prior to welding to form the electrode. Because of these problems, electron beam melting was phased into the program, thereby eliminating the need for drop-casting as a step in the preparation of final ingots. As previously mentioned, the remelt electrodes of the Cb-W-Ta alloys prepared by the drop-casting method served as the stock for electron beam melting of the final ingots of these alloys. Electron beam melting proved faster and assured better quality as will be described below.

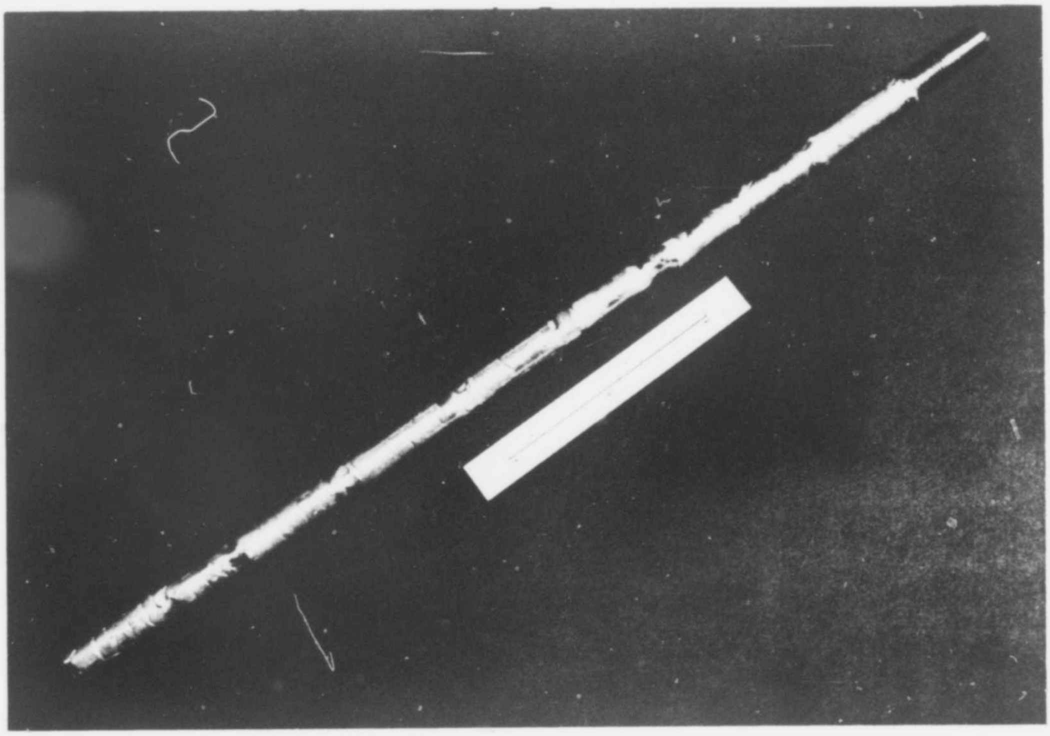
5.2.1.2 Electron Beam Melting

An exterior view of the 100 kw electron beam melting furnace is shown in Figure 6. The control panel at the left in Figure 6 contains the main power meters, gun and magnetic coil controllers (left), vacuum gages and vacuum system diagram with valve switches (right). The operator's console is attached to the door of the furnace. Situated on the console are the power and beam focusing controls for the three individual electron guns. The controls for manipulating the vertical post from which the melt stock is suspended, and the controls for retracting the ingot during the course of melting are also located here. The operator's sight-port is located above the console.

Figure 7 shows the interior of the furnace. The shell of the furnace is divided into two chambers by a plate. The bottom chamber contains the electron gun assemblies and magnetic coils. The top chamber or melt section contains the magnetic pole pieces for beam control, melt stock suspension post, and the mouth of the water-cooled copper mold. These dual chambers allow the guns to operate in a clean environment, since spatter which might occur during melting will be restricted to the top chamber. Each chamber has its own vacuum pumping system. Baffles are located in the front of the vacuum ports.

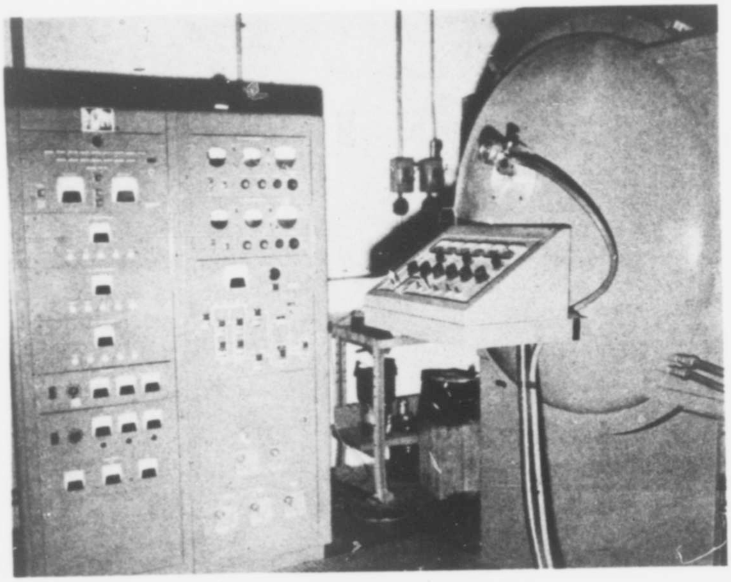
The electron beam furnace has the capability of producing nominally 0.875, 1.5, and 2.5-inch diameter by 14-inch long ingots.

Melting data for producing the final ingots of the Cb-W-Ta alloys are presented in Table VI. Since the drop-cast melt stock of these alloys had been through numerous arc-melting steps, it was felt that these alloys would be adequately homogeneous after a single electron beam melting operation. The alloys were cast into the 1.5-inch diameter mold. A typical ingot is shown in Figure 8. Side wall quality was very good. The loss in weight between melt stock and ingot noted for each alloy occurred primarily in cutting the ingot from the puller and sampling for chemical analysis and metallographic examination.



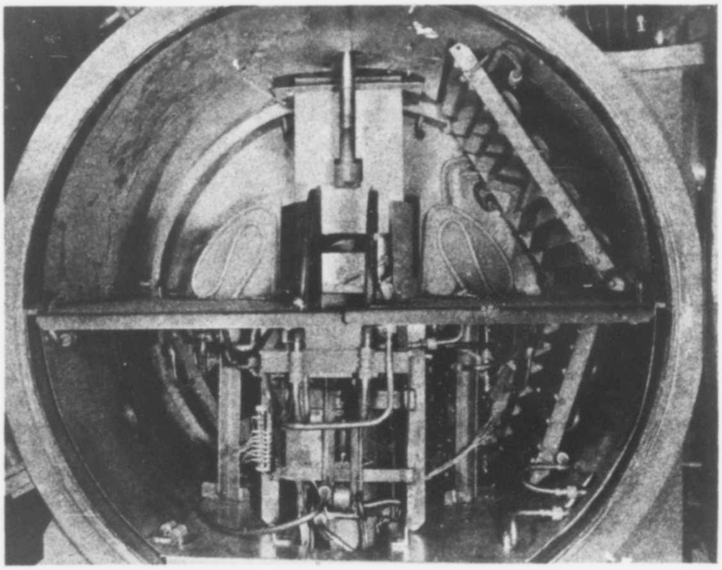
Neg. No. 20745

Figure 5. Remelt Electrode of Alloy No. 1 (Cb-10.3W-15.6Ta) Prepared from 0.75-Inch Diameter Drop-Cast Ingots.



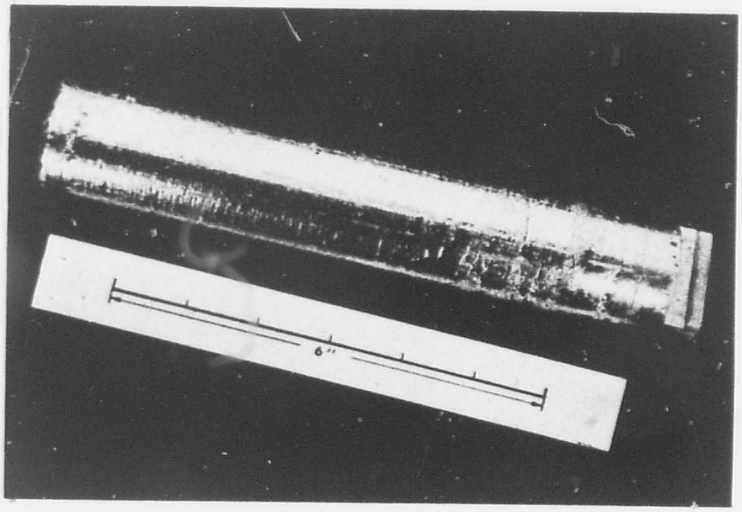
Neg. No. 22551

Figure 6. Exterior of 100 kw. Electron Beam Melting Furnace.



Neg. No. 22549

Figure 7. Interior of 100 kw. Electron Beam Melting Furnace.



Neg. No. 22397

Figure 8. Typical 1.5-Inch Diameter Electron Beam Melted Ingot.

5.2.1.3 Chemical Analysis

The procedure used for preparing the drop-cast ingots of the Cb-W-Ta alloys resulted in a contamination problem. Analyses obtained on several of the drop-cast ingots showed relatively high interstitial content, particularly carbon and oxygen. These analyses have been compared with a calculated level of interstitials which might be expected in the alloys based upon the vendors' analyses of the melt stock, assuming that the melting operation would have caused no change in interstitial content. The results of this comparison are shown in Table VII. Even though the drop-cast ingots were relatively high in interstitial content, it was felt that purification would be achieved when these were electron beam melted into the final ingots. This was found to be the case in samples taken from the top and bottom of the ingots. Results are shown in Table VIII. Furthermore, with few exceptions, the average analysis, i.e. the average of the major element contents at the top and bottom of the ingots, was in good agreement with the intended compositions of the alloys.

5.2.1.4 Hardness

Room temperature Rockwell and diamond pyramid hardness measurements were made on specimens cut from the top and bottom of each ingot. A Kentron microhardness tester was used for the diamond pyramid hardness determinations. Each hardness value presented in Table VIII represents the average of three readings. Hardness increased appreciably with tungsten content, whereas the effect of tantalum was relatively insignificant.

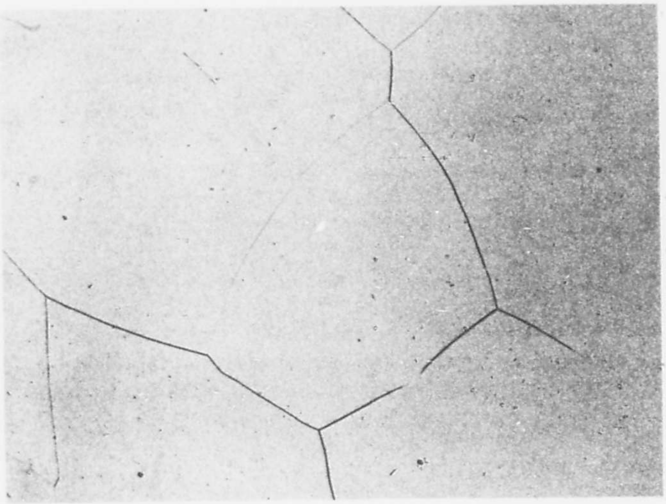
5.2.1.5 Metallography

As expected, metallographic examination of the top and bottom of the Cb-W-Ta alloy ingots revealed all these alloys to be solid solutions. Typical examples are seen in Figure 9, which are the microstructures of Alloys No. 1 (Cb-10.3W-15.6Ta) and 4 (Cb-24.6W-31.6Ta). These alloys represent the limits of the composition range investigated in this system.

5.2.2 Cb-W-Hf Ternary Alloys

The final ingots of the Cb-W-Hf ternary alloys, whose compositions are listed in Table IX were made by electron beam melting. For all but one of the compositions, Alloy No. 6 (Cb-9.8W-1.6Hf), melt stock was prepared using a powder metallurgy approach. The melt stock for Alloy No. 6 was prepared by the same drop-cast method used for the Cb-W-Ta compositions. For the powder metallurgy method, the 0.030-inch thick strip of columbium was reduced to -10 mesh powder by hydriding, crushing, and dehydriding. The hafnium crystal bar was milled into chips under a soluble oil coolant stream then thoroughly rinsed in acetone. For each composition, a five to seven-pound mix of the columbium powder, hafnium millings, and tungsten powder was blended, then cold compacted at 50,000 psi into a bar approximately 10.1 in. by 1.5 in. by 1.0 in. for subsequent electron beam melting. For several of the alloys, one-half of the hafnium added was in the form of strips, sheared into 0.25-inch widths, and buried in the pressed compacts.

(a) Neg. No. 22344
Alloy No. 1



(b) Neg. No. 22349
Alloy No. 4

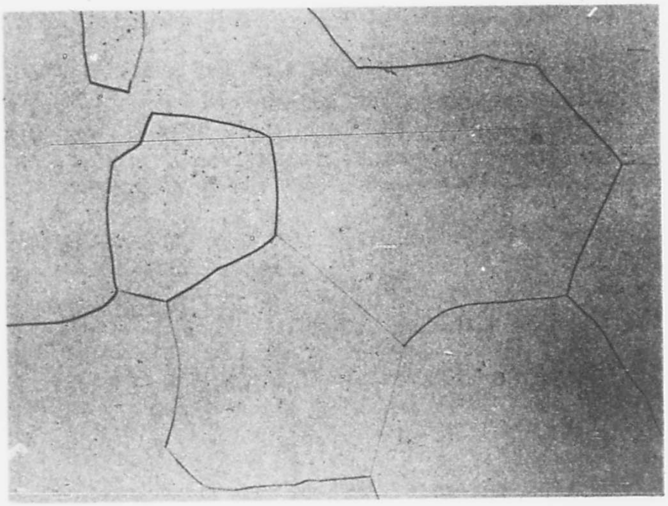


Figure 9. As-Cast Microstructures of Electron Beam Melted Alloys No. 1 (Cb-10.3W-15.6Ta) and No. 4 (Cb-24.6W-31.6Ta).

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF

Melting data for the Cb-W-Hf alloy ingots are shown in Table IX. All of the alloys, except Alloy No. 6 (Cb-9.8W-1.6Hf) were at least double electron beam melted to promote complete alloying and uniformity of composition along the length of the ingot. For multiple electron beam melting the ingot produced by the previous electron beam melt was cut in half longitudinally, one of the halves was reversed end for end and tack welded to the other forming a cylinder for remelting. The final ingots of these alloys were nominally 1.5-inch diameter (see Figure 8) except for Alloys No. 21 (Cb-14.4W-35.9Hf) and 22 (Cb-12.1W-35.5Hf) which were nominally 2.5-inch diameter - a size better suited for extrusion at the Wright Field facility as will be discussed later. The 2.5-inch diameter ingot of Alloy No. 21 (Cb-14.4W-35.9Hf) is shown in Figure 10.

5.2.2.1 Chemical Analysis

It was found, as seen from the data in Table X, that the preparation of the columbium powder and the hafnium millings resulted in a certain amount of contamination of the materials, particularly with regard to oxygen content. This contamination was removed during electron beam melting based on the interstitial contents of the electron beam ingots presented in Table XI. With several exceptions the analyses for the major elements were in fair agreement with the weighed compositions. Anomalies, where noted, may be explained by a combination of effects: powder losses from the compacts due to handling, spatter and volatilization losses during melting and perhaps segregation in the analytical specimens. An example of volatilization losses can be cited in the case of Alloy No. 21 (Cb-14.4W-35.9Hf). Following the first melting of this alloy an 18 gram deposit collected from the mold lip was checked qualitatively by X-ray fluorescence analysis and found to be enriched in hafnium and to contain only small amounts of columbium and tungsten.

A reanalysis was performed on some of the alloys after hot working. These results, also included in Table XI, are considered to represent the best sampling for these alloys because of homogenization which accompanies hot-working.

5.2.2.2 Hardness

The hardness of the Cb-W-Hf alloy ingots is reported in Table XI. Both tungsten and hafnium increased the hardness of the alloys markedly.

5.2.2.3 Metallography

Typical microstructures of the cast Cb-W-Hf alloys are shown in Figures 11 and 12 and point out an effect of high hafnium contents in promoting the formation of a second phase at grain and subgrain boundaries. With the low hafnium content alloys, 1.6 and 4.4 percent, seen in Figure 11, essentially no change in microstructure was observed by raising the tungsten level from 9.8 to 24.1 percent. Both of these alloys contained a minimal amount of precipitate in their structures. However, as the hafnium content was increased to within the range 18.7 to 35.9 a larger amount of second phase precipitated -- the amount being relatively independent of tungsten

Figure 10. 2.5-Inch Diameter Electron Beam Melted Ingot of Alloy No. 21 (Cb-14.4W-35.9Hf).

(a) Neg. No. 22354
Alloy No. 6

(b) Neg. No. 22617
Alloy No. 8

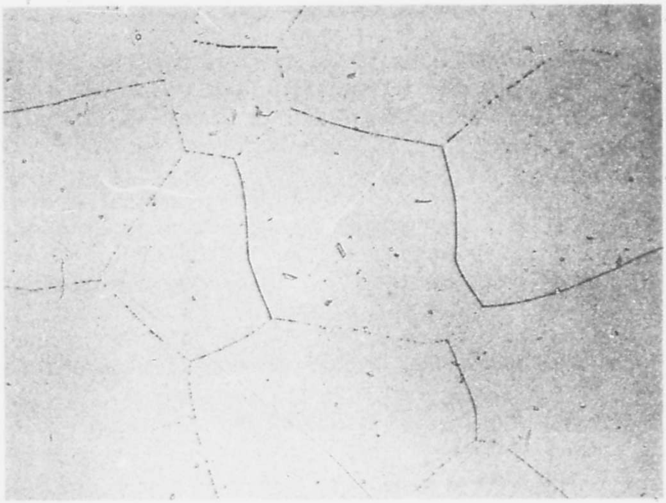


Figure 11. As-Cast Microstructures of Electron Beam Melted Alloys No. 6 (Cb-9.8W-1.6Hf) and No. 8 (Cb-24.1W-4.4Hf).

Magnification: 200X   Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF

content of the alloys over the range investigated. This effect is shown by the series of microstructures arranged in order of increasing hafnium content in Figure 12.

No phase identification studies were performed on the cast alloys, but a carbide was identified in wrought Alloy No. 7 (Cb-10.6W-30.8Hf). This result will be described later.

5.2.3 Cb-15W-35Hf with Additions of Rhenium, Titanium, Cobalt, Aluminum, Vanadium, Carbon, and Nitrogen

Evaluation of alloys within the Cb-W-Hf system for fabricability, oxidation behavior, and strength led to the selection of the nominal composition, Cb-15W-35Hf, as a base for further alloying since this ternary seemed to offer the best compromise in properties. Additions made to this base, both singly and in combinations, to determine their effect on property enhancement included the elements: rhenium, titanium, cobalt, aluminum, vanadium, carbon, and nitrogen. Seven alloys were investigated. Their preparation in all but one case involved the dual procedure of electron beam melting followed by consumable arc melting to insure better recovery of the addition(s) with high vapor pressure. Details of the preparation of the remelt electrodes required for consumable arc melting are presented below.

5.2.3.1 Melt Stock Preparation

Electrodes for consumable arc melting the various alloys were made up of electron beam melted master alloy stock of a Cb-W or Cb-W-Hf alloy plus "tacked on" strips of the other additions. The master alloy contained all of the tungsten required in the final composition.

The design of the electrodes for consumable arc melting was determined not only by alloy composition, but also by the fact that the final ingot size was 2.25-inch diameter. With this diameter ingot, the maximum cross sectional dimension of the electrode was limited to 1.25-inch, thus allowing a minimum of 0.5-inch clearance between electrode and mold wall during melting. Electrode length was within the range 20 to 28 inches. The cross sectional shape was either rectangular or circular.

Alloy No. 23 (Cb-15W-37Hf-2Re)*

Since the rhenium addition to this alloy did not present a vapor pressure problem, the final ingot was produced by electron beam melting -- the melt stock being prepared by the powder metallurgy method used for the Cb-W-Hf ternary alloys. The total charge weight was seven pounds made up of columbium, tungsten, and rhenium powders, hafnium crystal bar millings, and hafnium strips. The blended powders and millings were all

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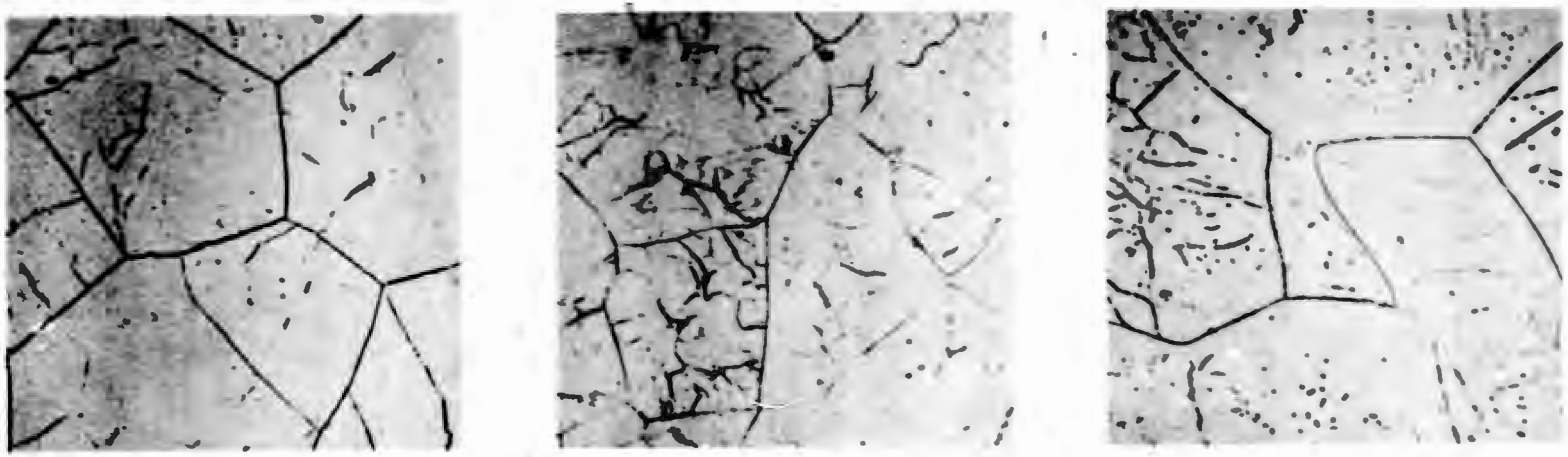
* Weighed Composition



(a) Neg. No. 22311
Alloy No. 10

(b) Neg. No. 24462
Alloy No. 32

(c) Neg. No. 23719
Alloy No. 12

(d) Neg. No. 22619
Alloy No. 9

(e) Neg. No. 22305
Alloy No. 7

(f) Neg. No. 29167
Alloy No. 21

Figure 12. As-cast Microstructures of Electron Beam Melted Alloys No. 10(Cb-14.7W-18.7Hf), 32(Cb-20.2W-21.6Hf), 12(Cb-6.3W-26.3Hf), 9(Cb-23.0W-26.5Hf), 7(Cb-10.6W-30.8Hf) and 21(Cb-14.4W-35.9Hf).

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF

pressed into a bar with the hafnium strips buried inside, uniformly along the length.

Alloys No. 24 (Cb-15W-36Hf-5.5Ti),* 25 (Cb-15W-36Hf-11Ti),* and 26 (Cb-15W-36Hf-3Co)*

The electrodes of Alloys No. 24, 25, and 26 were constructed of a master alloy of nominal composition Cb-30W and strips of the other additions. The master alloy was electron beam melted into a 2.5-inch diameter ingot which was subsequently side forged at 2700°F to a slab approximately 0.9-inch thick, then conditioned to 0.8-inch thick. Since this material provided the source for all the tungsten in each of the three alloys, this element became the reference in calculating the design of the electrodes. The stepwise procedure in making the design calculations of an electrode knowing the aim composition and weight of the alloy desired was as follows:

(1) From a calculated density of the Cb-W master alloy and with two dimensions (width and length) of the electrode fixed, the approximate thickness of master alloy was calculated which would contain the tungsten for the final alloy.

(2) The master alloy was cut to the calculated thickness and weighed. The actual weight of tungsten contained in the master alloy was then calculated from the analyzed composition of the master alloy (Cb-28.9W).

(3) With the actual weight of tungsten as a base, and the aim concentration of tungsten in the final alloy known, the exact electrode weight was calculated. The required weights of the other additions, knowing their aim concentrations in the final alloy, were then determined.

(4) The dimensions of the strips of the other alloying additions were calculated which would distribute their required weights uniformly along the electrode length.

A diagram of the cross section of the electrodes prepared of Alloys No. 24, 25, and 26 and a tabulation of the component weights for these electrodes are shown in Figures 13, 14, and 15. After assembly, the components of each electrode were tack welded together in a dry box under an inert atmosphere.

Alloys No. 27 (Cb-15W-36Hf-5.5Ti-0.07N-0.05C),* and 29 (Cb-15W-35.5Hf-5.5Ti-0.1C)*

Electrodes weighing approximately six pounds were prepared for Alloys No. 27 and 29. For each of these compositions Cb-W-Hf master alloys

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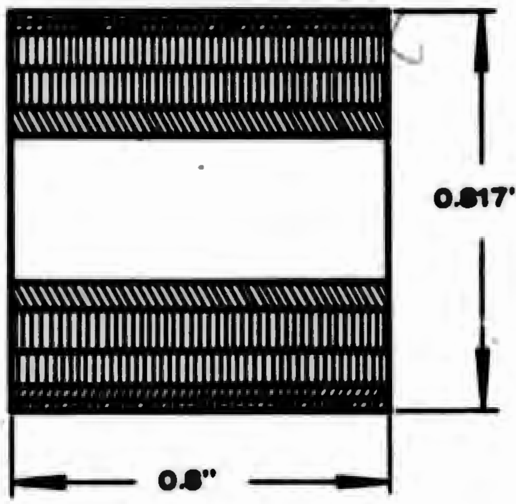
* Weighed Composition



Legend

☐ 0.421-in. thick Cb-28.9W

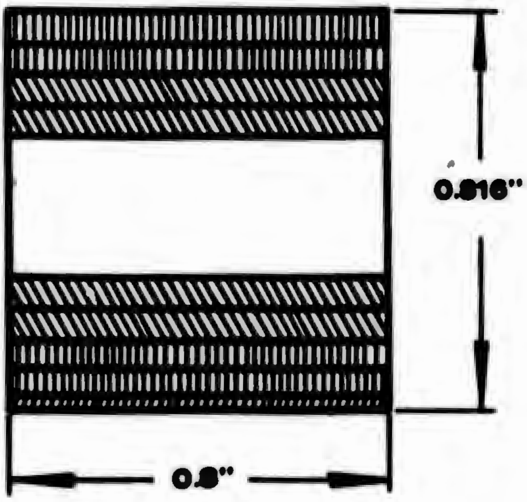
▧ 0.050-in. thick Ti strip

▥ 0.058-in. thick Hf strip

▨ 0.016-in. thick Cb strip

Electrode Component	Weight							
	Cb		W		Hf		Ti	
	gms	lbs.	gms	lbs.	gms	lbs.	gms	lbs.
Cb-28.9W	1138.3	2.51	462.7	1.02				
Cb Strip	204.4	0.45						
Ti Strip							167.8	0.37
Hf Strip					1111.3	2.45		
Total	1342.7	2.96	462.7	1.02	1111.3	2.45	167.8	0.37

Figure 13. Schematic Diagram of Cross Section of 28-In. Long Electrode of Alloy No. 24 (Cb-15W-36Hf-5.5Ti) for Consumable Arc Melting.



Legend

☐ 0.396-in. thick Cb-28.9W

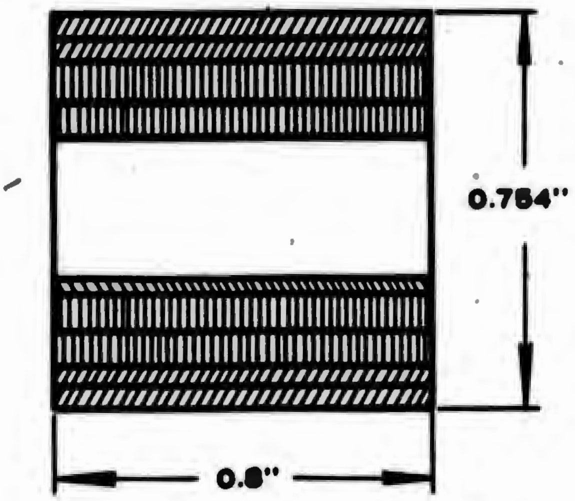
▧ 0.048-in. thick Ti strip

▥ 0.054-in. thick Hf strip

▨ 0.010-in. thick Cb strip

Electrode Component	Weight							
	Cb		W		Hf		Ti	
	gms	lbs.	gms	lbs.	gms	lbs.	gms	lbs.
Cb-28.9W	1071.4	2.36	435.5	0.96				
Cb Strip	30.8	0.07						
Ti Strip							322.0	0.71
Hf Strip	—	—	—	—	1043.3	2.30	—	—
Total	1102.2	2.43	435.5	0.96	1043.3	2.30	322.0	0.71

Figure 14. Schematic Diagram of Cross Section of 28-In. Long Electrode of Alloy No. 25 (Cb-15W-36Hf-11Ti) for Consumable Arc Melting.



Legend

□ 0.413-in. thick Cb-28.9W

▧ 0.028-in. thick Co strip

▥ 0.056-in. thick Hf strip

▨ 0.022-in. thick Cb strip

Electrode Component	Weight							
	Cb		W		Hf		Co	
	gms	lbs.	gms	lbs.	gms	lbs.	gms	lbs.
Cb-28.9W	1104.8	2.44	449.1	0.99				
Cb Strip	274.1	0.60						
Co Strip							90.7	0.20
Hf Strip					1075.0	2.37		
Total	1378.9	3.04	449.1	0.99	1075.0	2.37	90.7	0.20

Figure 15. Schematic Diagram of Cross Section of 27.7-In. Long Electrode of Alloy No. 26 (Cb-15W-36Hf-3Co) for Consumable Arc Melting.

containing all of the tungsten, essentially all of the columbium, and about one-half of the hafnium were electron beam melted directly into 0.875-inch diameter rounds. Two individual master alloy ingots or a total length of approximately 20 inches were melted for each electrode. This procedure for preparing the master alloys proved simpler than that used for Alloys No. 24, 25, and 26 since fabrication, conditioning, and cutting operations were eliminated.

The calculations made for electrode construction followed the same line of reasoning used for Alloys No. 24, 25, and 26, that is, the tungsten in the master alloy was used as the reference element but its concentration was assumed to be the amount added rather than being determined from an actual analysis of the master alloy. The titanium strip added to the electrode of each alloy was wide enough to be formed into a segment of a circle along the length so as to fit relatively snug to the master alloy core. The narrowed hafnium strips representing the balance of the hafnium required, were positioned between the titanium strips. Carbon was added in the form of graphite tape held in place along the electrode by its location beneath the titanium strips. No melting losses were anticipated in making the carbon addition to either alloy. Therefore, this element was added in the amount required after taking into account the carbon added through the other melt stock.

The nitrogen addition to Alloy No. 27 was made from nitrided columbium strips. Nitriding was accomplished by induction heating the strips in a nitrogen atmosphere at 3000°F for two hours. The resulting nitrogen pick up amounted to 22 milligrams per square centimeter for the 0.275-inch (0.698 cm) wide by 0.031-inch (0.078 cm) thick by 21-inch (53.34 cm) total length of strips treated - equivalent to a 1.79 gram nitrogen addition to the electrode. This amount of nitrogen together with that contained in the melt stock was approximately equal to a 40 percent excess of nitrogen in the electrode to allow for losses during melting in arriving at a 500 ppm concentration of this element in the final ingot. Like the graphite cloth, the nitrided columbium strips were held in place beneath the titanium.

A cross-sectional diagram of the electrodes of Alloys No. 27 and 29 and tabulated component weights are shown in Figures 16 and 17, respectively. The actual electrode of Alloy No. 29 is pictured in Figure 18 prior to being tack welded.

Alloy No. 28 (Cb-15W-35.5Hf-5.3Ti-2.5Al-2.2V)*

Of the electrodes constructed for consumable arc melting, that of Alloy No. 28 was the most involved primarily due to the addition of aluminum with its low melting point to this composition. The basic procedure used for constructing the electrode of this alloy was essentially the

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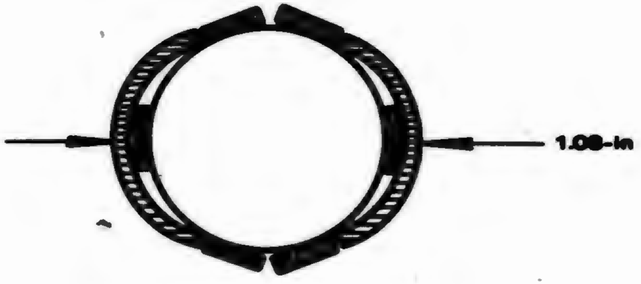
* Weighed Composition



Legend

○ 0.875-in. diam. 55.9Cb-19.7W-24.4Hf

▤ 0.584-in. wide x 0.082-in. thick Ti strip

▥ 0.328-in. wide x 0.079-in. thick Hf strip

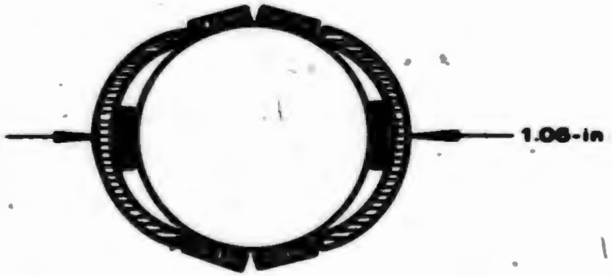
▨ 0.275-in. wide x 0.0315-in. thick nitrided Cb strip

■ 0.312-in. wide x 0.015-in. thick Graphite tape

Electrode Component	Weight									
	Cb		W		Hf		Ti		N	C
	gms	lbs.	gms	lbs.	gms	lbs.	gms	lbs.	gms	gms
Cb-19.7W-24.4Hf	1169.6	2.58	412.2	0.91	510.5	1.13			0.105*	0.105*
Ti strip							151.7	0.33	0.02	0.076
Hf strip					466.8	1.03			0.007	0.039
Nitrided Cb strip	23.6	0.05							1.79	
Graphite tape										1.22
Total	1193.2	2.63	412.2	0.91	977.3	2.16	151.7	0.33	1.922	1.44

* Assumed analysis of Cb-19.7W-24.4Hf master alloy was 50 ppm N and 50 ppm C.

Figure 16. Schematic Diagram of Cross Section of 21-in. Long Electrode of Alloy No. 27 (Cb-15W-36Hf-5.5Ti-0.07N-0.05C) for Consumable Arc Melting.



Legend

○ 0.875-in. diam. 57.1Cb-19.2W-23.7Hf

▤ 0.578-in. wide x 0.082-in. thick Ti strip

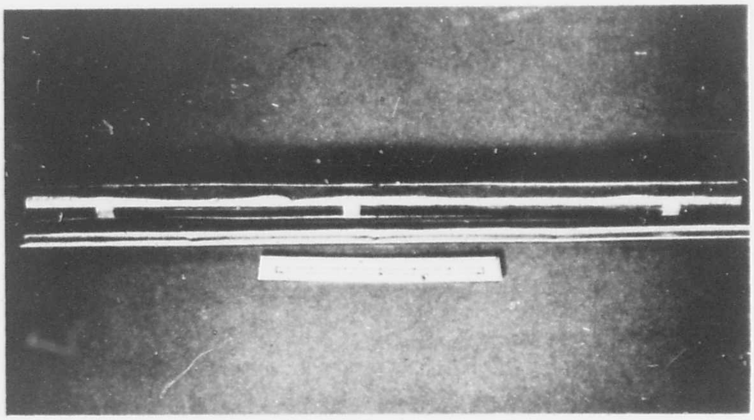
▥ 0.324-in. wide x 0.079-in. thick Hf strip

■ 0.312-in. wide x 0.015-in. thick graphite tape

Electrode Component	Weight								
	Cb		W		Hf		Ti		C
	gms	lbs.	gms	lbs.	gms	lbs.	gms	lbs.	gms
Cb-19.2W-23.7Hf	1242.7	2.74	417.9	0.92	515.8	1.14			0.109*
Ti Strip							153.1	0.34	0.077
Hf Strip					480.7	1.06			0.04
Graphite Tape									2.70
Total	1242.7	2.74	417.9	0.92	996.5	2.20	153.1	0.34	2.926

* Assumed analysis of Cb-19.2W-23.7Hf master alloy was 50 ppm C.

Figure 17. Schematic Diagram of Cross Section of 21.875-In. Long Electrode of Alloy No. 29 (Cb-15W-35.5Hf-5.5Ti-0.1C) for Consumable Arc Melting.



Neg. No. 27388

Electron Beam Melted Master Alloy Core, Cb-19.2W-23.7Hf;
Titanium Strips; Hafnium Strips; and Graphite Tape

Figure 18. Partially Assembled Electrode of Alloy No. 29 (Cb-15W-35.5Hf-5.5Ti-0.1C) for Consumable Arc Melting.

same as that used for Alloys No. 27 and 29; however, in this case four master alloys were used. The first was a 0.875-inch diameter by 20-inch long electron beam melted Cb-W-Hf alloy again containing all of the tungsten and about one-half of the hafnium for the final composition. The other three, prepared by the drop-casting procedure described previously, were of the following compositions: 50.4Ti-29.6V-20Al, 50Ti-40Hf-10Al, and 80Hf-20Al. The compositions of the drop-cast master alloys were calculated as to contain all of the titanium, vanadium, and aluminum, and another portion of the hafnium for the final alloy. These three master alloys were brittle and it was not possible to machine uniformly dimensioned strips for tacking onto the columbium-tungsten-hafnium master alloy. Therefore, these alloys were crushed in an argon atmosphere to -10 mesh powder, cold pressed at 50,000 psi into rectangular shape, and vacuum sintered. Sintering of the compacts of the alloy 50.4Ti-29.6V-20Al was carried out at 2500°F for one hour. The other compacts - a blend of 51.4 weight percent of the alloy 50Ti-40Hf-10Al and 48.6 weight percent of the alloy 80Hf-20Al - were sintered at 2350°F for the same time. These compacts, three strips of hafnium, and the Cb-W-Hf alloy core comprised all of the components for the electrode.

A schematic diagram of the cross section of the electrode of Alloy No. 28 is shown in Figure 19 along with a tabulation of the weights of the various components. These components are displayed in Figure 20. Assembly of the electrode was accomplished by attaching the sintered powder compacts and hafnium strips to the Cb-W-Hf alloy core with tantalum wires as shown in Figure 20. The wires were removed following the tack welding operation.

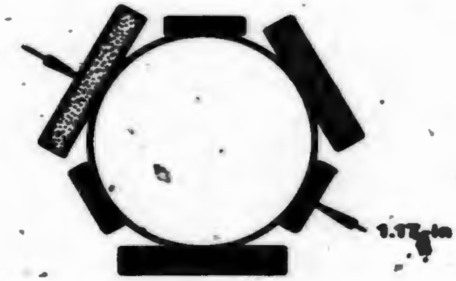
5.2.3.2 Consumable Arc Melting

Consumable arc melting of the previously described electrodes was accomplished in the 10,000 amp furnace shown in Figure 21. The electrodes were melted into a 2.25-inch diameter, water cooled, copper mold with a columbium or tantalum starter pad at the bottom. The furnace atmosphere was a gas mixture of 20 mm argon plus 5 mm helium.

Melting data for the alloys can be found in Table XII. As can be seen, melt rates were relatively fast at approximately 2000 amps and 20 volts d.c. Figure 22 shows typical ingot appearance after being cropped from the pad. Sidewall quality was good.

5.2.3.3 Chemical Analysis

Table XIII presents the chemical analyses of the ingots of the arc melted alloys and the fabricated products. The analyses were in fair agreement with the nominal chemistries although the values for tungsten and titanium were slightly higher than intended. Also to be noted is that these alloys contain higher levels of oxygen than the Cb-W-Hf ternary alloys prepared by electron beam melting.

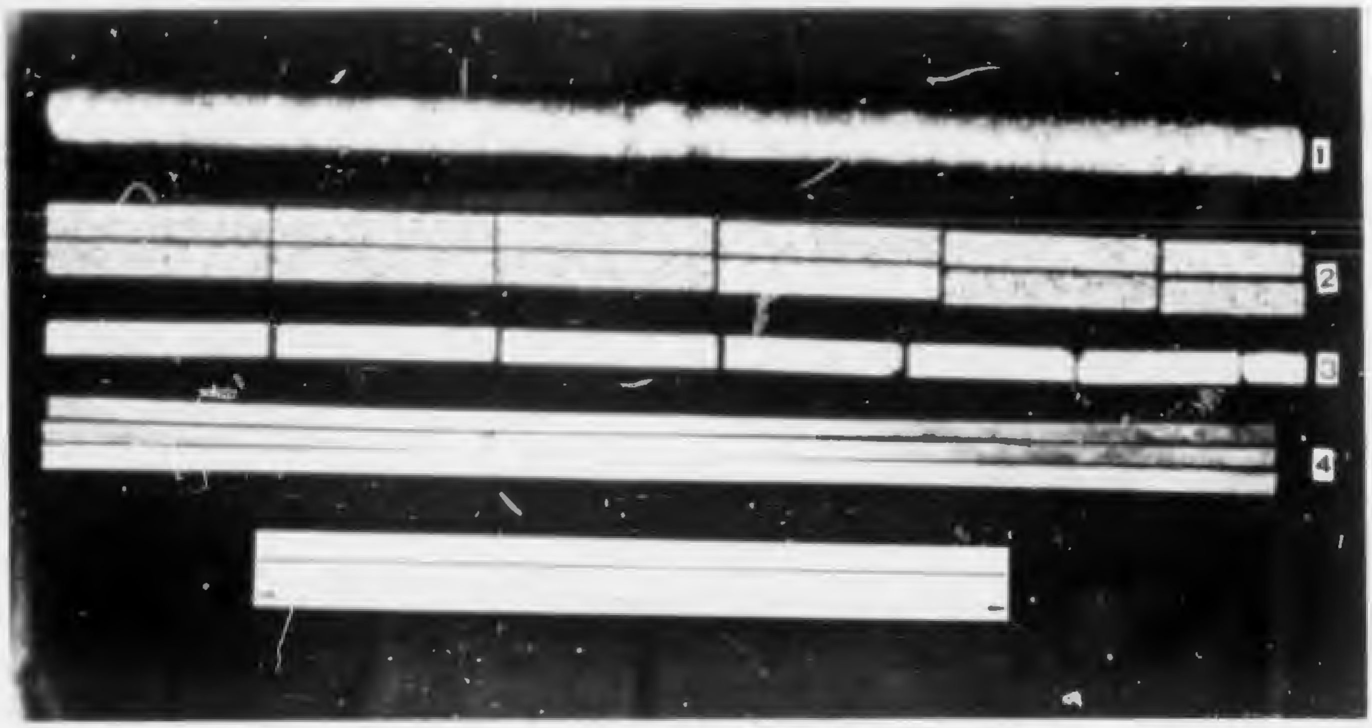


Legend

○	0.875-in. diam. 54.4Cb-20.3W-25.3Hf
▥	0.364-in. wide x 0.079-in. thick Hf strip
▤	0.5-in. wide x 0.200-in. thick compacts of 50.4Ti-29.6V-20Al
▨	0.5-in. wide x 0.220-in. thick compacts of 51.4% (50Ti-40Hf-10Al) - 48.6% (80Hf-20Al)

Electrode Component	Weight											
	Cb		W		Hf		Ti		Al		V	
	gms	lbs.	gms	lbs.	gms	lbs.	gms	lbs.	gms	lbs.	gms	lbs.
Cb-20.3W-25.3Hf	1099.2	2.42	410.2	0.90	511.2	1.13						
Hf Strip					367.4	0.81						
50.4Ti-29.6V-20Al							102.0	0.23	40.5	0.09	59.9	0.13
50Ti-40Hf-10Al					36.4	0.08	45.5	0.10	9.1	0.02		
80Hf-20Al					68.8	0.15			17.2	0.04		
Total	1099.2	2.42	410.2	0.90	983.8	2.17	147.5	0.33	66.8	0.15	59.9	0.13

Figure 19. Schematic Diagram of Cross Section of 19.875-In. Long Electrode of Alloy No. 28 (Cb-15W-35.5Hf-5.3Ti-2.5Al-2.2V) for Consumable Arc Melting.



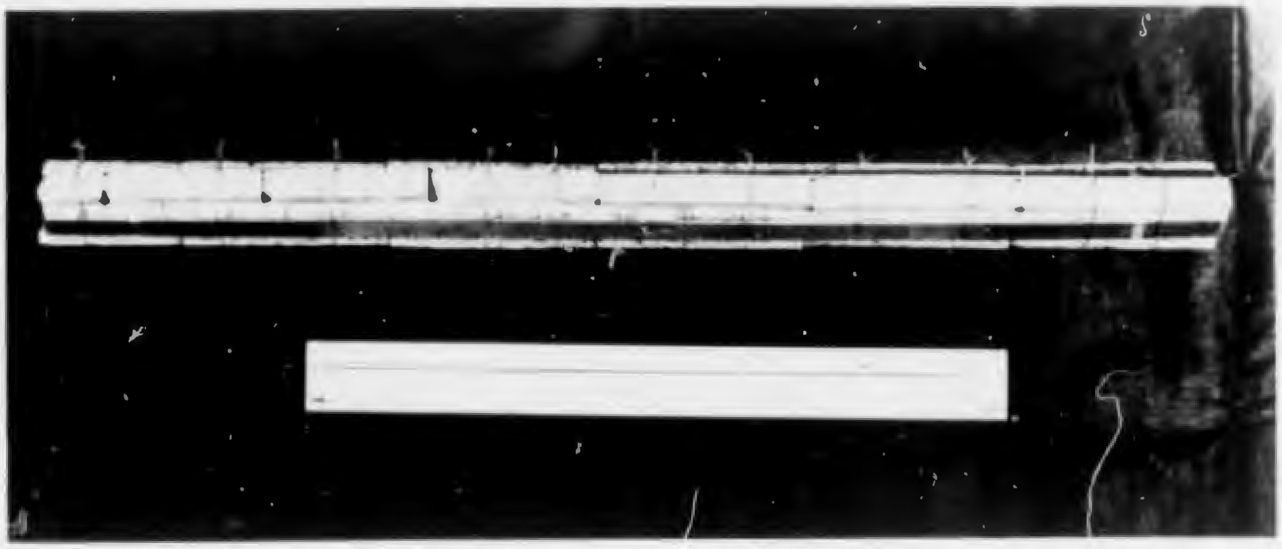
(a) Electrode Components Neg. No. 27576

(1) Electron Beam Melted Master Alloy, Cb-20.3W-25.3Hf

(2) Sintered Powder Compacts of Prealloyed Ti-29.8V-20Al

(3) Sintered Powder Compacts of Blended Prealloyed 51.4%(Ti-40Hf-10Al) - 48.6%(Hf-20Al)

(4) Hafnium Strips



(b) Assembled Electrode Prior to Tack Welding Neg. No. 27577

Figure 20. Electrode of Alloy No. 28(Cb-15W-35.5Hf-5.3Ti-2.5Al-2.2V) for Consumable Arc Melting.

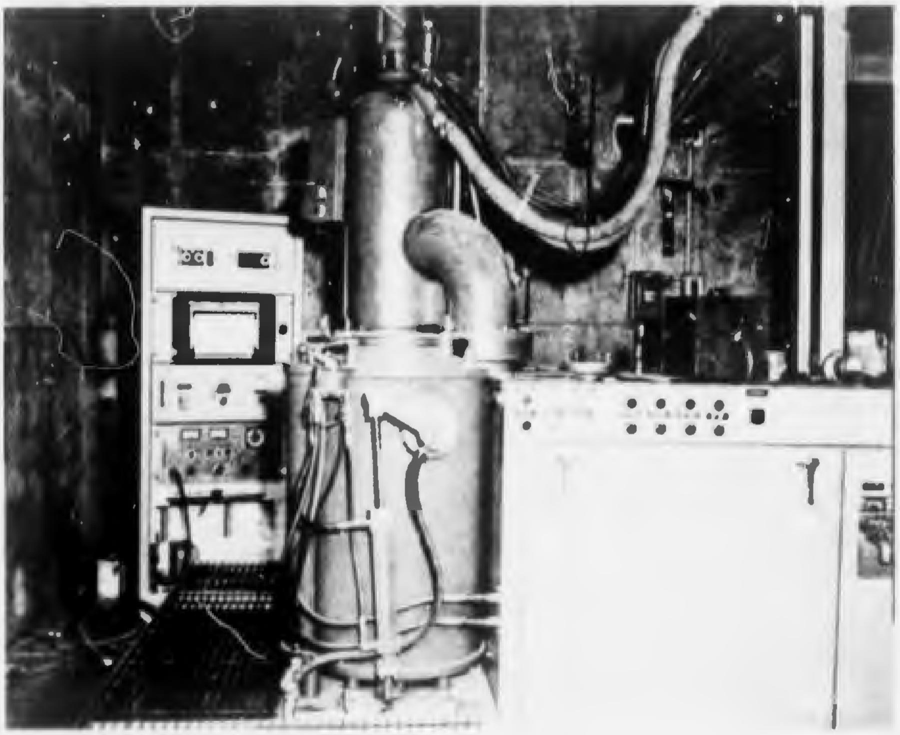
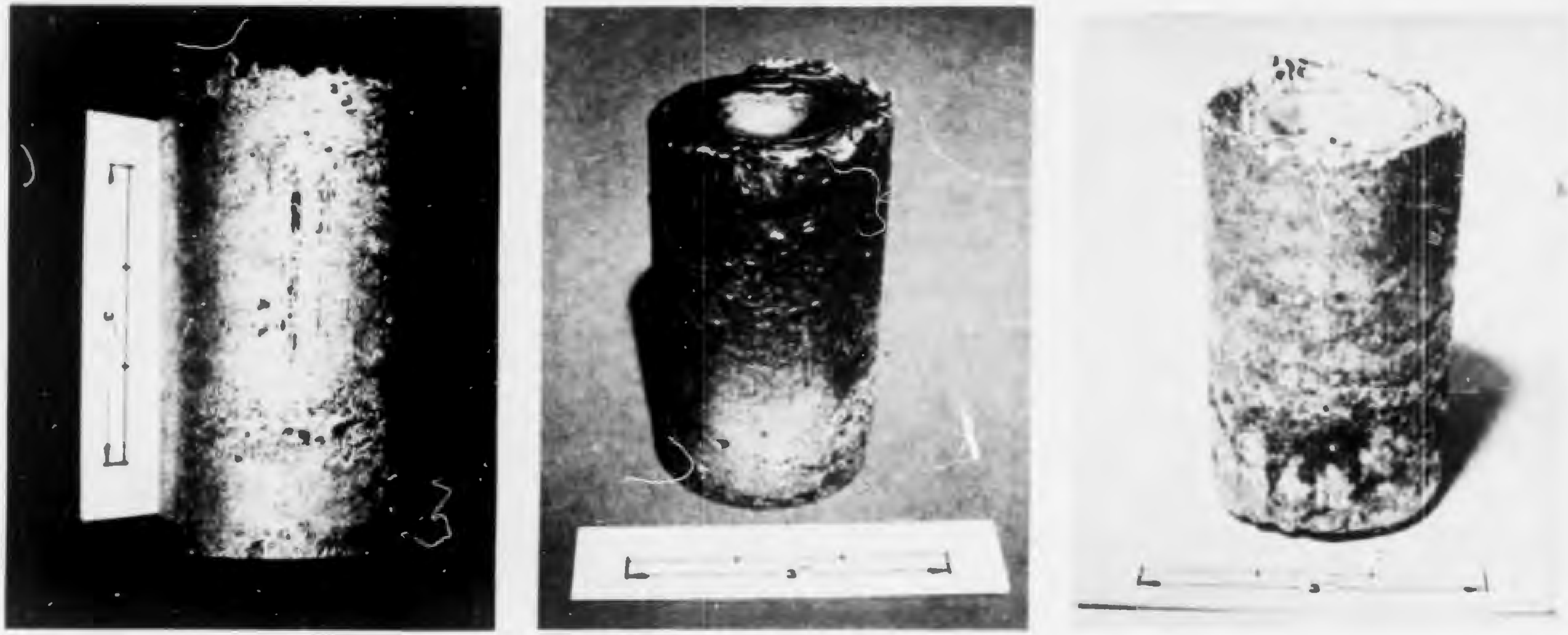


Figure 21. Exterior of 10,000 Amp Consumable Arc Melting Furnace.



(a) Neg. No. 26768
Alloy No. 25

(b) Neg. No. 27387
Alloy No. 27

(c) Neg. No. 27592
Alloy No. 28

Figure 22. 2.25-inch Diameter Consumable Arc Melted Ingots of Alloys No. 25 (Cb-16.7W-35.2Hf-11.0Ti), 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C), and 28 (Cb-15.6W-34.5Hf-5.0Ti-2.0Al-1.9V).

5.2.3.4 Hardness

Hardness measurements on specimens taken from top and bottom of the ingots are included in Table XIII. Relative to the electron beam melted base composition, Alloy No. 21 (Cb-14.4W-35.9Hf), the hardness of these alloys was higher which could be expected, in part, from their higher interstitial contents. Alloy No. 28 (Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V) showed the highest hardness of all the compositions evaluated. No doubt, the aluminum and vanadium are contributing to hardness; but the alloy, also, contained a high level of oxygen.

5.2.3.5 Metallography

Microstructures of the ingots of these more complex alloys are shown in Figures 23, 24, 25, and 26. The structure of the rhenium-bearing composition, Alloy No. 23, was identical to that observed for the Cb-W-high hafnium content ternaries, i.e., the presence of a second phase at grain and subgrain boundaries. Titanium added in Alloys No. 24 and 25 resulted in a cleaner microstructure for these compositions relative to the basic Alloy No. 21 (Cb-14.4W-35.9Hf). The 2.8 percent cobalt addition in Alloy No. 26 caused the formation of an intercellular second phase which was subsequently shown to be enriched in cobalt and hafnium. These results of phase identification are described later. Intentional additions of carbon + nitrogen in Alloy No. 27 and carbon in Alloy No. 29 complexed the microstructures of these alloys. Phase identification studies on wrought specimens of these compositions revealed the presence of interstitial compounds. Alloy No. 28 presented the dirtiest as-cast microstructure probably due to a high oxygen content in the presence of strong "getter-type" elements, Hf, Ti, Al, and V. No phase identification work was performed on this alloy.

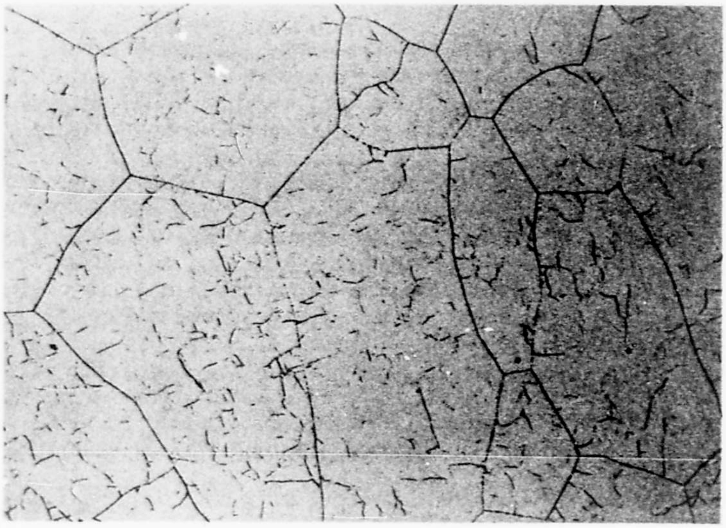
5.3 FABRICATION

Fabrication of the alloys was accomplished by extrusion, forging, and swaging procedures -- the details of which are described in the sections which follow.

5.3.1 Cb-W-Ta Ternary Alloys

5.3.1.1 Swaging

Alloys No. 1 (Cb-10.3W-15.6Ta) and 2 (Cb-9.8W-28.3Ta) were fabricated to nominally 0.250-inch diameter rod by hot and warm swaging. Three swaging billets of each alloy were prepared. Each billet was made up of a 1.5-inch long section of ingot machined to 1.285-inch diameter. This piece was wrapped in 0.005-inch thick tantalum foil and canned in a 1.5-inch O.D. x 0.093-inch wall HASTELLOY alloy X capsule. The capsule was sealed by welding a HASTELLOY alloy X cap to the open end. This welding operation was performed in a dry box under a slight partial pressure of argon. A HASTELLOY alloy X rod was welded to one end of the capsule to facilitate handling. The billets were hot swaged at 2150°F at an average reduction in diameter of 0.042-inch per pass with a 10

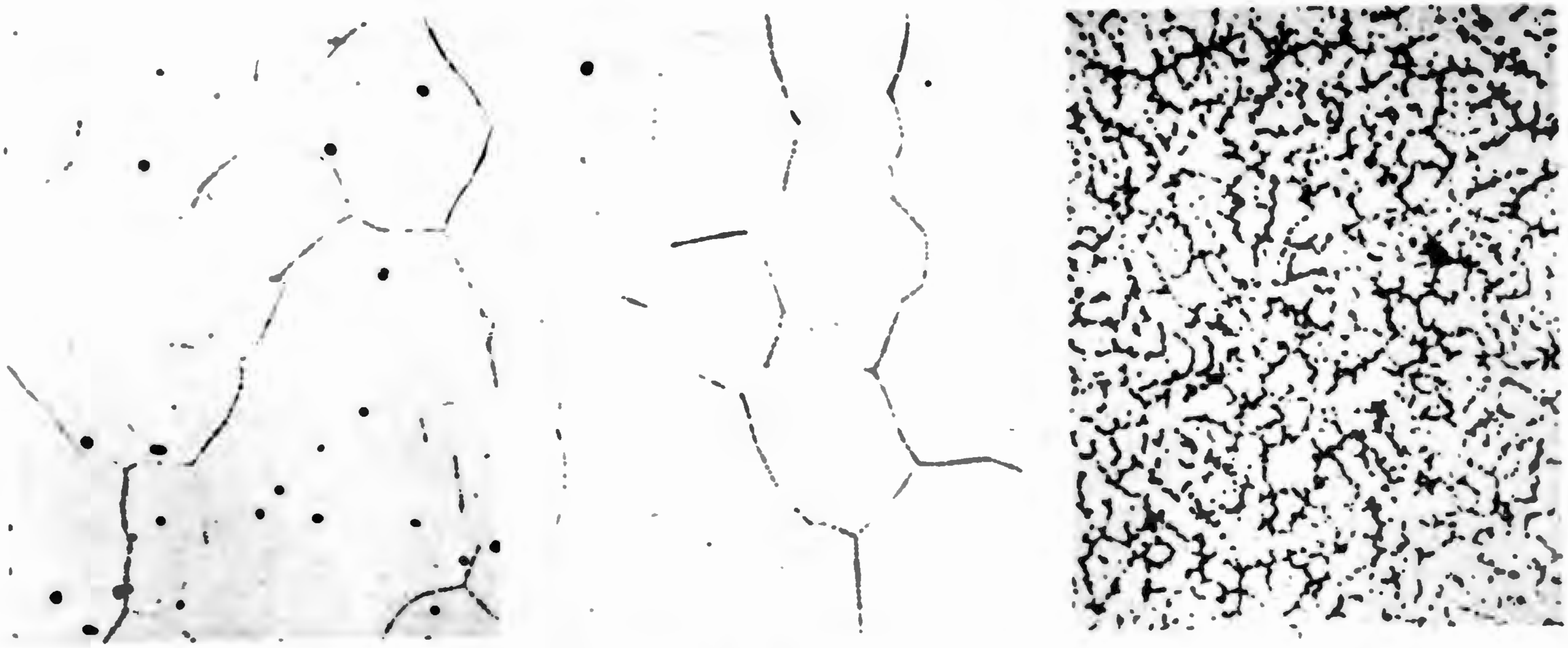


Neg. No. 25417

Figure 23. As-Cast Microstructure of Electron Beam Melted Alloy No. 23 (Cb-15.1W-34.8Hf-1.9Re).

Magnification: 200X

Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF



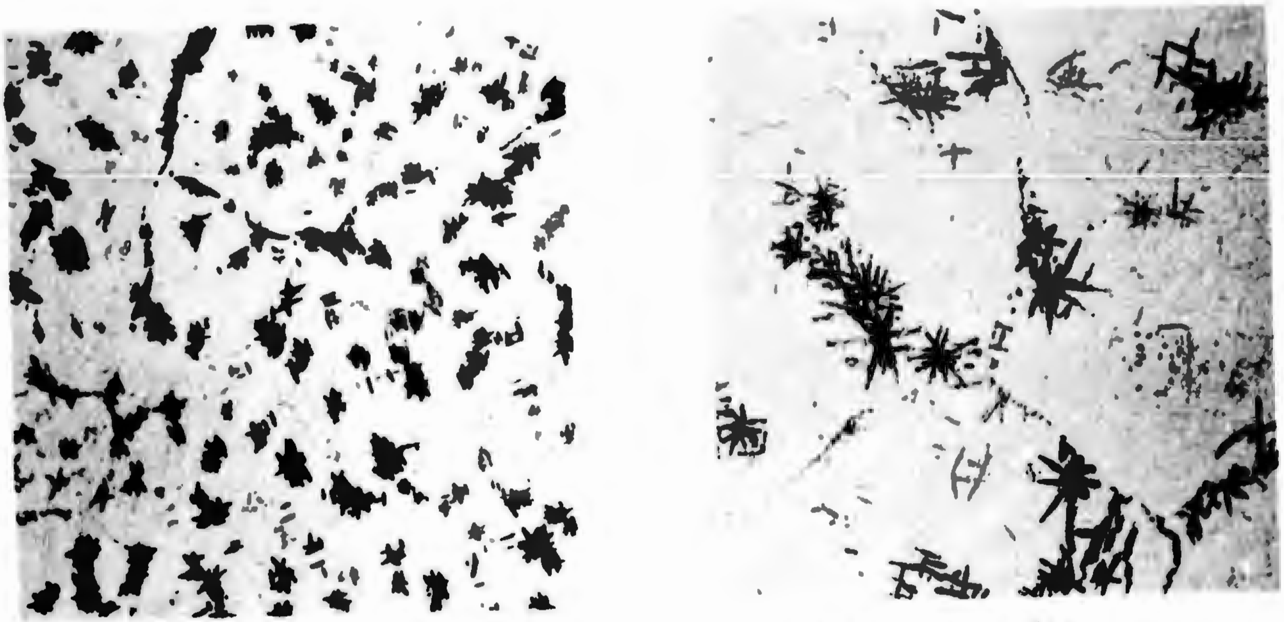
(a) Neg. No. 26752
Alloy No. 24

(b) Neg. No. 26753
Alloy No. 25

(c) Neg. No. 26754
Alloy No. 26

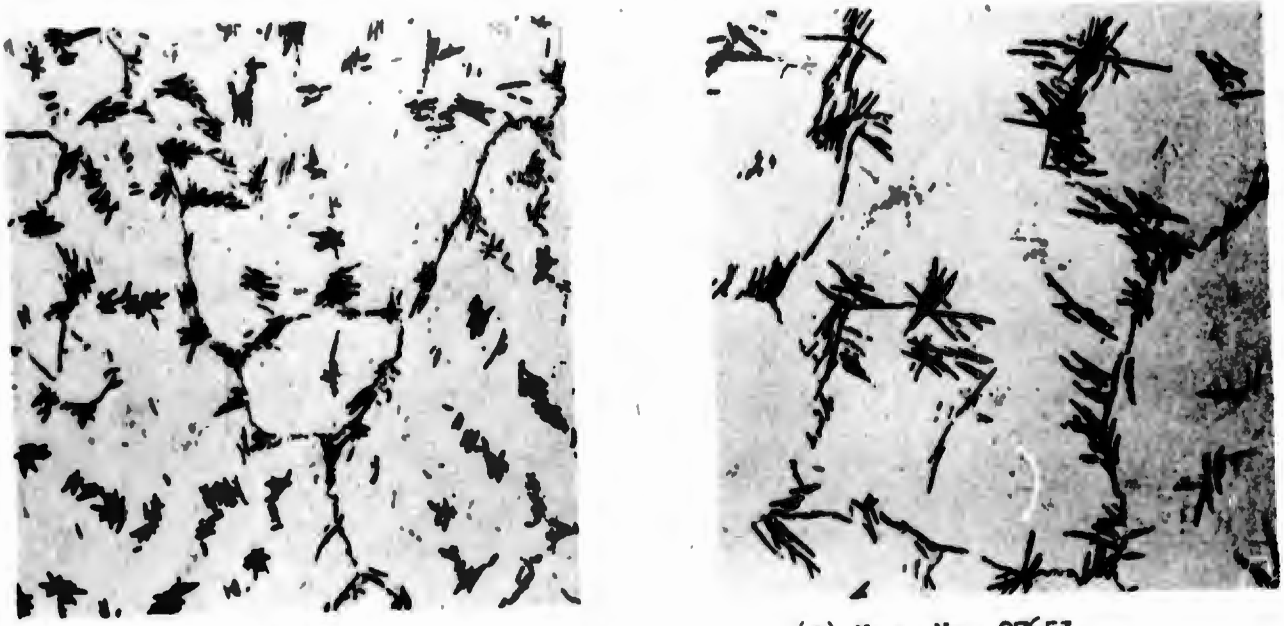
Figure 24. As-Cast Microstructures of Consumable Arc Melted Alloys No. 24 (Cb-16.9W-33.2Hf-6.3Ti), 25 (Cb-16.7W-35.2Hf-11.0Ti), and 26 (Cb-17.5W-33.5Hf-2.8Co).

Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 drops HF



(a) Neg. No. 27651
Alloy No. 27
Magnification: 200X

(b) Neg. No. 27650
Alloy No. 27
Magnification: 500X

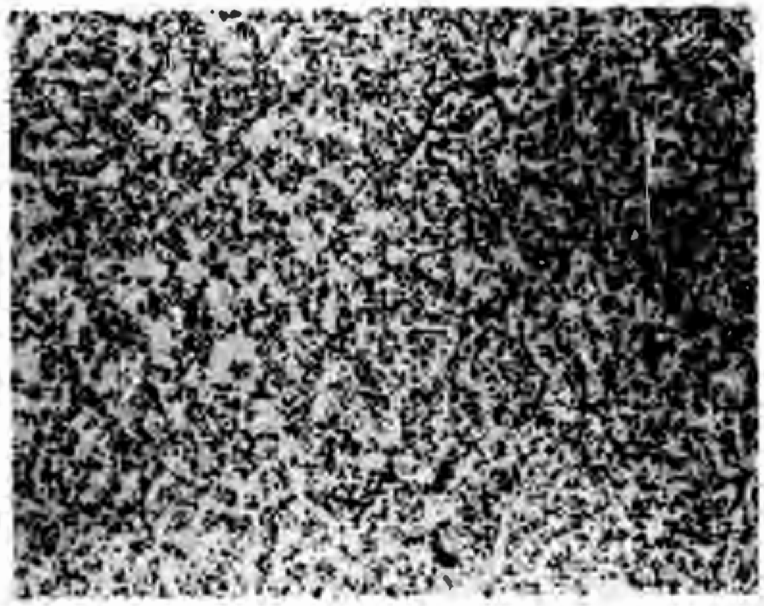


(c) Neg. No. 27652
Alloy No. 29
Magnification: 200X

(d) Neg. No. 27653
Alloy No. 29
Magnification: 500X

Figure 25. As-Cast Microstructures of Consumable Arc Melted Alloys No. 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C) and 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C).

Etchant: 50p Lactic Acid -
3p HNO_3 - 2 drops HF



Neg. No. 27720

Figure 26. As-Cast Microstructure of Consumable Arc Melted Alloy No. 28 (Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V).

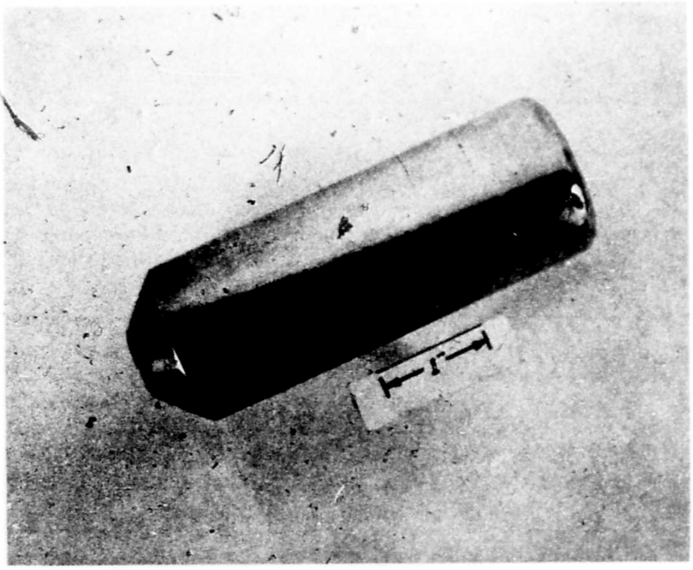
Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 drops HF

minute reheat between each pass. Hot swaging was continued until failure of the HASTELLOY alloy X was imminent as determined visually. At this stage the canning material was removed, the columbium alloy was conditioned by machining, then rewrapped in tantalum foil and vacuum annealed one hour at 2400°F. Final swaging followed at 500°F on the bare alloy at a reduction of 0.063-inch in diameter per pass to a size of 0.5-inch diameter, then a reduction of 0.031-inch in diameter per pass to final size. A detailed summary of these fabrication steps carried out on representative billets of Alloys No. 1 (Cb-10.3W-15.6Ta) and 2 (Cb-9.8W-28.3Ta) is presented in Table XIV. Gas and carbon analyses were obtained on specimens of the alloys after fabrication. The results are shown in Table XV. Little change in the level of interstitials was noted when compared with the results obtained on the ingots.

An attempt was made to fabricate one billet of Alloy No. 3 (Cb-25.1W-15.8Ta) and three billets of Alloy No. 5 (Cb-16.5W-23.8Ta) by the swaging procedures outlined above. The billet of Alloy No. 3 was reduced 32.5 percent in area by hot swaging; however, cracking was observed at one end after removing the HASTELLOY alloy X can. The remainder of the ingot of this alloy was successfully fabricated by extrusion. It was possible to reduce the three billets of Alloy No. 5 by 49.9, 45.2, and 22.6 percent in area by hot swaging. Following a one-hour vacuum anneal at 3000°F, the bars were warm swaged, but cracking occurred before significant reductions were accomplished. The bars were reconsolidated into an ingot by electron beam melting for subsequent extrusion.

5.3.1.2 Extrusion and Forging

Extrusion of Alloys No. 3 (Cb-25.1W-15.8Ta), 4 (Cb-24.6W-31.6Ta), and 5 (Cb-16.9W-23.8Ta) was performed on a 300-ton horizontal press at Materials Systems Division, Union Carbide Corporation. This press is tooled to accommodate either a 1.5 or 2.5-inch diameter billet. Billets of these alloys were prepared by machining the ingot stock to 1.245-inch diameter and encapsulating in 1.475-inch diameter by 0.115-inch wall molybdenum cans turned from bar stock. The cans were sealed by welding a molybdenum cap to the open end in a dry box under a slight partial pressure of argon. A typical billet is shown in Figure 27. The billets were induction heated under an argon atmosphere for extrusion. Temperatures were read by sighting through a glass window in the top of the heater with an optical pyrometer. Before extrusion, the press container and die were preheated to 600°F. FISKE-604, a commercially available lubricant of graphite suspended in a calcium base grease, was swabbed in the container and on the die. Additional lubrication was provided by liquid MoO_3 which formed on the billets during transfer from heater to press. A 0.75-inch diameter, 90° included angle, zirconia coated tool steel die was used for all extrusions -- producing an extrusion ratio of 4:1. Extrusion pressure on the billet was calculated from the pressure exerted on the 12-inch diameter piston actuating the ram. Extrusion rate was 1-inch of billet length per second.



Neg. No. 22488

Figure 27. Typical 1.4-inch Diameter Extrusion Billet of Columbium Alloy Canned in Molybdenum

Data for the extrusion of the Cb-W-Ta alloys are presented in Table XVI. No difficulties were encountered extruding these alloys at a temperature of nominally 2500°F (uncorrected optical pyrometer reading); however, near maximum permissible pressure was required for the extrusion of Alloys No. 3 and 4. Alloy No. 5 extruded more easily as a result of the lower tungsten content of this alloy.

No secondary fabrication was performed on Alloys No. 3 and 4, and after extrusion, these alloy rods were decanned mechanically and by pickling in a solution of one part HCl - one part HNO_3. With the molybdenum can in place the extrusion of Alloy No. 5 was vacuum annealed one hour at 3000°F, then hammer forged at 2300°F from 0.75-inch diameter to a thickness of approximately 0.33-inch in four passes. Protection of the can against oxidation during the forging operation was afforded by a coating of 7052 powdered glass suspended in a neutralized solution of Carbopol 934 in water. Forging results were good. The product after removing the molybdenum can is shown in Figure 28.

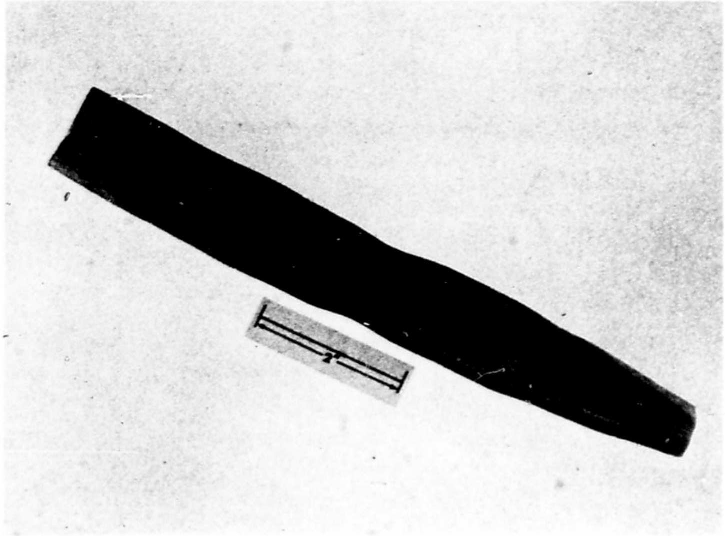
5.3.2 Cb-W-Hf Ternary Alloys

5.3.2.1 Swaging

Alloy No. 6 (Cb-9.8W-1.6Hf) was hot and warm swaged to nominally 0.250-inch diameter rod using the identical procedure as previously described for Alloys No. 1 (Cb-10.3W-15.6Ta) and 2 (Cb-9.8W-28.3Ta). Table XIV summarizes these fabrication steps for Alloy No. 6. Hot swaging of a billet of Alloys No. 7 (Cb-10.6W-30.8Hf) and 10 (Cb-14.7W-18.7Hf) was attempted; but the stiffness of these alloys at 2150°F limited their reduction in area to less than 10 percent before failure of the canned material. These billets were conditioned and recanned for extrusion.

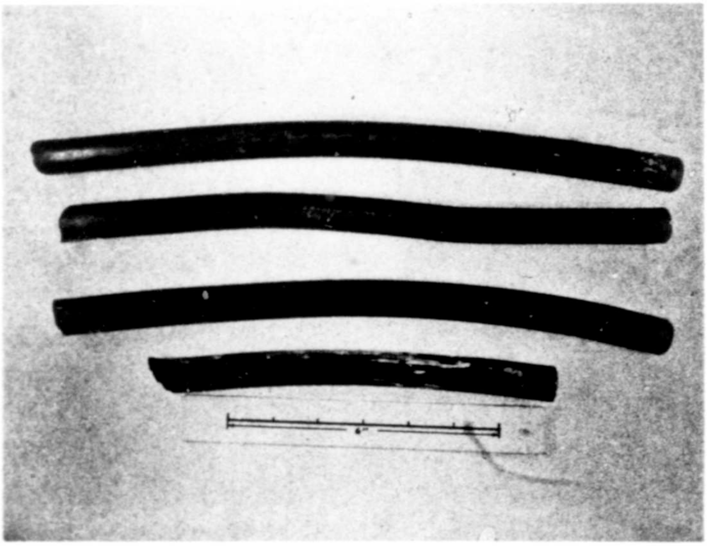
5.3.2.2 Extrusion and Forging

Alloys No. 7 through 14 and 30 through 32 were extruded on the 300-ton horizontal press at Materials Systems Division, Union Carbide Corporation. Billet preparation and extrusion procedures were as previously described for the Cb-W-Ta ternary alloys. Data for the extrusion of these Cb-W-Hf ternary alloys can be found in Table XVII. For the conditions used, extrusions could be made of those alloys with approximately 15 percent or less of tungsten and containing up to approximately 35 percent hafnium (the concentration limit of this element investigated). Only one alloy was extruded successfully with a tungsten content in excess of 20 percent. This was Alloy No. 8 (Cb-24.1W-4.4Hf) with a low hafnium content. Examples of these extrusions are shown in Figure 29. Alloys No. 9 (Cb-23.0W-26.5Hf) and 32 (Cb-20.2W-21.6Hf) were the most resistant to fabrication -- both failed to extrude. Two attempts were made to extrude each of the two billets of Alloy No. 9 within the temperature range 2600°F - 3020°F and one attempt was made to extrude the one billet of Alloy No. 32 at 2915°F (uncorrected optical pyrometer readings). A stalled billet of Alloy No. 9 can be seen in Figure 30.



Neg. No. 22892

Figure 28. Hammer Forging of Alloy No. 5(Cb-16.9W-23.8Ta) after Removing Molybdenum Can. Forged from 0.75-inch Diameter to 0.33-inch Thick at 2300°F



Neg. No. 22564

Figure 29. 0.75-inch Diameter Extrusions of Cb-W-Hf Alloys Canned in Molybdenum. Top to Bottom: Alloy No. 7 (Cb-10.6W-30.8Hf), same, Alloy No. 8 (Cb-24.1W-4.4Hf), and Alloy No. 10(Cb-14.7W-18.7Hf).

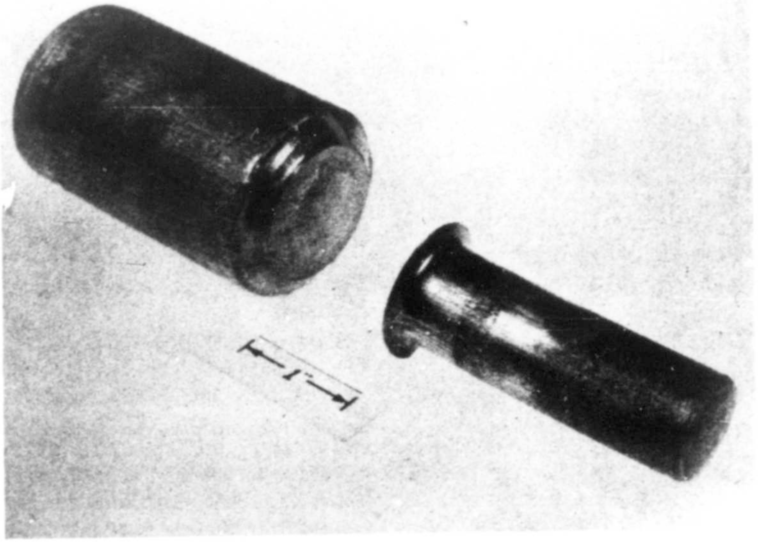


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Figure 30. Stalled Extrusion Billet, 1.4-inch Diameter, of Alloy No. 9 (Cb-23.0W-26.5Hf) Canned in Molybdenum.

The facilities of the Air Force Materials Laboratory, W-PAFB, Ohio, were used for the extrusion of Alloys No. 21 (Cb-14.4W-35.9Hf) and 22 (Cb-12.1W-35.5Hf). The press located there is a variable speed, horizontal-type with a peak capacity of 700-tons. The container diameter is 3.072-inches. One billet of each of these alloys was prepared by machining the electron beam melted ingot to 2.34-inch diameter and encapsulating in sintered molybdenum sleeves turned to 2.93-inch outside diameter by 2.345-inch inside diameter. The cans were closed by pinning molybdenum caps to each end. Before extrusion, the billets were coated with 7052 powdered glass suspended in a neutralized solution of Carbopol 934 in water.(7) The bottom of each billet was left uncoated. Heating the billets to the extrusion temperature caused the glass coating to melt and serve as a lubricant. Billet heating was accomplished in a 30 kw induction furnace under an argon atmosphere. Temperature was measured with a W/W-26Re thermocouple contacting the bottom of the billet. The press container and die, lubricated with FISKE-604 grease, were preheated to 500°F before extrusion. A 1.0-inch by 2.0 inch rectangular shaped, 90° included angle, zirconia coated, H-12 tool steel die was used -- producing an extrusion ratio of about 4:1. Extrusion pressure on the billet was recorded. In keeping with standard practice at AFML a tapered, mild steel, glass coated (0010 glass) nose block preheated to 1600°F was extruded in front of the billet.

Extrusion data for Alloys No. 21 and 22 are presented in Table XVIII. Results were good in both cases. A higher extrusion temperature was selected for Alloy No. 21 in view of the higher tungsten content of this material. Nevertheless, greater extrusion pressure was required for this alloy than for Alloy No. 22; and the pressure differential between the two extrusions undoubtedly would have been greater if Alloy No. 22 had been extruded at a slower rate since extrusion pressure increases with rate. In comparing the data for these alloys with the data obtained on Alloy No. 31 (Cb-15.1W-34.1Hf), a similar composition extruded to 0.75-inch diameter bar at Materials Systems Division, it is expected that improved lubrication practice and better heat retention in the larger billets of Alloys No. 21 and 22 extruded at AFML were two primary reasons for the lower extrusion pressure noted for these two alloys.

Secondary fabrication by forging was carried out on the Cb-W-Hf ternary compositions, except for Alloys No. 7 (Cb-10.6W-30.8Hf), 8 (Cb-24.1W-4.4Hf), and 10 (Cb-14.7W-18.7Hf) which were decanned and prepared for heat-treating studies after extrusion. Alloys No. 11 through 14, 30, and 31 were conditioned where necessary, vacuum annealed 1 hour at 3000°F, coated with glass, then hammer forged at 2300°F. Alloys No. 11 through 14 were easily reduced from 0.75-inch diameter to approximately 0.350-inch thick in three passes with a 15-minute heat between each pass. With this procedure Alloys No. 30 and 31 showed moderate to severe cracking; however, the product of Alloy No. 30 was of sufficient quality for obtaining specimens for mechanical property evaluation.

An attempt was made to hammer forge the stalled extrusion billets of Alloys No. 9 and 32, also, at 2300°F. Severe cracking resulted for both compositions.

Press forging was carried out on the 1-inch by 2-inch rectangular extrusions of Alloys No. 21 and 22. The protective molybdenum can was left in place on each extrusion, and a glass coating was reapplied to the surface. Forging was performed at 2575°F after soaking the bars 1-1/4 hours at temperature. The furnace atmosphere was argon. Alloy No. 22 was reduced to a slab 0.435 by 2.7 by 12 inches (dimensions after decanning) in one pass; and Alloy No. 21 to a slab 0.490 by 2.3 by 12.5 inches (dimensions after decanning) in two passes with a 20 minute reheat between passes. The appearance of these alloy forgings can be seen in Figure 31.

From the results of secondary fabrication of the Cb-W-Hf ternary alloys it is apparent that press forging was preferred to hammer forging.

5.3.3 Cb-15W-35Hf with Additions of Rhenium, Titanium, Cobalt, Aluminum, Vanadium, Carbon and Nitrogen

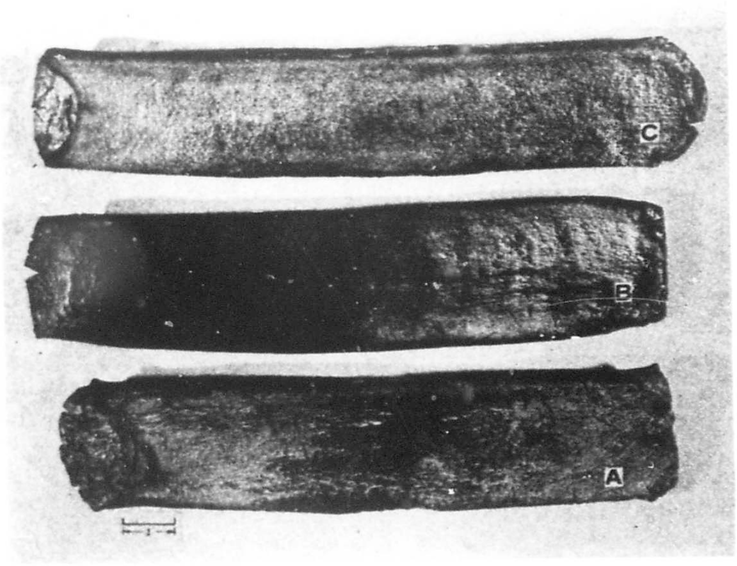
5.3.3.1 Extrusion and Forging

One billet of each of the Alloys No. 23 through 29 was prepared from their respective ingots for extrusion at the Wright Field facility. The electron beam melted ingot of Alloy No. 23 (Cb-15.1W-34.8Hf-1.9Re) was machined from 2.44 to 2.34-inch diameter, and the consumable arc melted ingots of Alloys No. 24 through 29 were machined from 2.25 to approximately 2.1-inch diameter before encapsulating in molybdenum. Extrusion procedures were the same as described for Alloys No. 21 and 22.

The extrusion data for these alloys are summarized in Table XIX. Extrusion temperature for these alloys was kept constant at 2800°F except for the rhenium-bearing composition, Alloy No. 23, which was extruded at 3500°F. All of the alloys containing titanium, regardless of the other additions, required a lower extrusion pressure than their ternary base, Alloy No. 21, even though the base was extruded 200°F higher in temperature, i.e., 3000°F. The pressure requirement for the cobalt-bearing Alloy No. 26 (Cb-17.5W-33.5Hf-2.8Co) was appreciably lower than for the other alloys -- later attributed to the fact that this composition was extruded above its solidus temperature. Furthermore, this fact accounted for the defects observed radiographically in the extruded bar of this alloy. The bar of Alloy No. 26 was decanned after extrusion and its very irregular surface is clearly evident in Figure 32. Inspection of the bars of the other alloys showed these to be radiographically sound.

Alloy No. 23 (Cb-15.1W-34.8Hf-1.9Re) was press forged after extrusion according to the practice described for Alloys No. 21 (Cb-14.4W-35.9Hf) and 22 (Cb-12.1W-35.5Hf). The 1-inch by 2-inch rectangular extruded bar was reduced to a slab 0.450 by 2.7 by 11.2-inches (dimensions after decanning) in two passes. The forged slab of this alloy, shown in Figure 31, edge cracked slightly more than the ternary Alloy No. 21 and 22 reflecting the effect of rhenium on fabricability.

Hammer forging was used as the means of secondary fabrication for Alloys No. 24 (Cb-16.9W-33.2Hf-6.3Ti) and 25 (Cb-16.7W-35.2Hf-11.0Ti). The



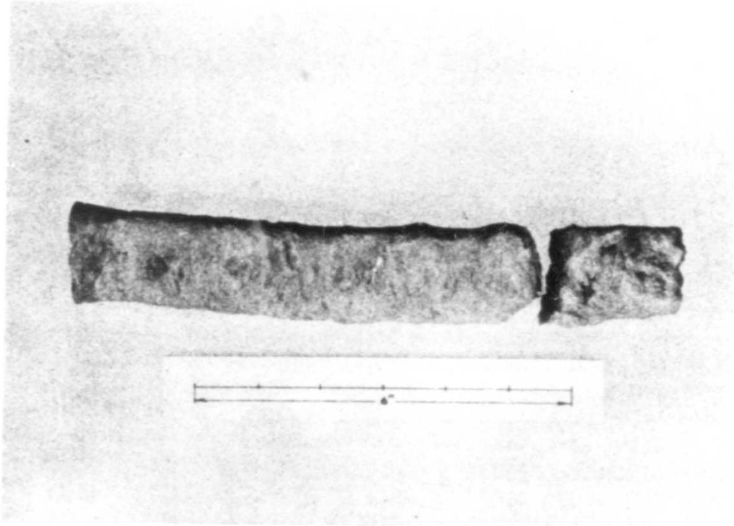
Neg. No. 25559

Figure 31. Press Forgings of Cb-W-Hf Alloys After Removing Molybdenum Cans.

A. Alloy No. 23(Cb-15.1W-34.8Hf-1.9Re) Forged from Approx. 1.0-inch Thick to 0.5-inch Thick at 2575°F.

B. Alloy No. 22(Cb-12.1W-35.5Hf) Forged from Approx. 1.0-inch Thick to 0.5-inch Thick at 2575°F.

C. Alloy No. 21(Cb-14.4W-35.9Hf) Forged from Approx. 1.0-inch Thick to 0.5-inch Thick at 2575°F.



Neg. No. 26863

Figure 32. Extrusion of Alloy No. 26(Cb-17.5W-33.5Hf-2.8Co) After Removing Molybdenum Can. Extruded at 2800°F.

extruded bars were glassed then forged at 2300°F after soaking 1-1/2 hours at temperature. Each bar was given four passes with a ten-minute reheat between each pass. Forging was stopped at this point due to development of deep edge cracks in both alloys as seen in Figure 33. After decanning, Alloy No. 24 was approximately 0.310-inch thick; and Alloy No. 25 was approximately 0.425-inch thick. Improved forging results no doubt would have been obtained had the alloys been pressed rather than hammered.

The 1-inch by 2-inch rectangular extrusions of Alloys No. 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C), 29(Cb-15.0W-35.6Hf-6.4Ti-0.11C) and 28 (Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V) were glassed and press forged at 2400°F after soaking 1 hour at temperature. Alloys No. 27 and 29 were pressed to slabs 0.36 by 2.5 by 9.5-inches and 0.33 by 1.8 by 11.5-inches, respectively (dimensions after decanning). Both alloys showed evidence of minor edge cracking as seen in Figure 34. Although as previously indicated, radiographic inspection of the extrusion of Alloy No. 28 revealed no defects in this material, forging to a slab 0.25 to 0.37-inch thick resulted in the product shown in Figure 35. The alloy fabricated poorly -- the surface of the slab was very irregular and cracking was extensive. No property evaluation was made of the forging of this composition.

5.4 HEAT-TREATING STUDIES

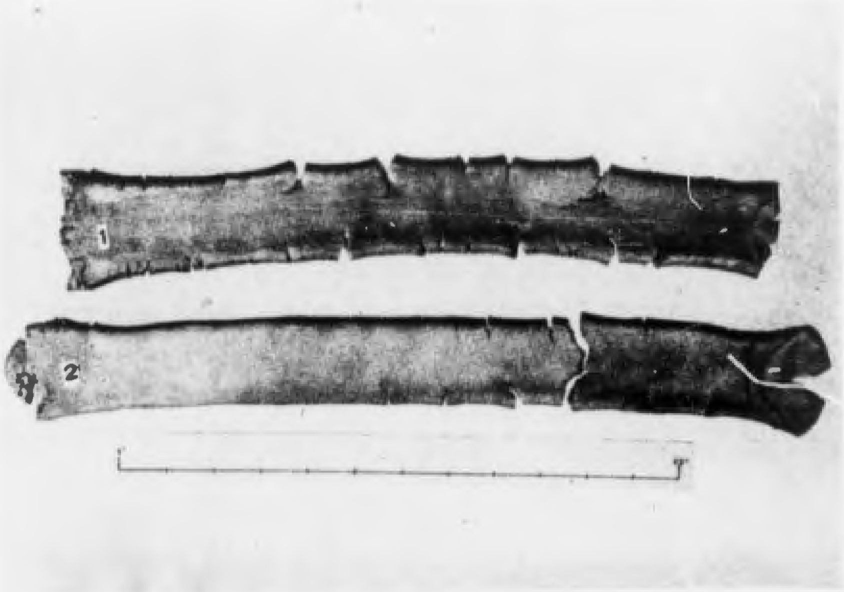
Heat-treatments were carried out on the fabricated alloys for the purpose of establishing an annealing temperature for fully recrystallizing the materials prior to mechanical property and oxidation evaluation. Test specimens were cut, wrapped in tantalum foil, and then given one-hour vacuum heat-treatments generally within the temperature range 2000-3000°F at 200°F intervals. However, some of the alloys were heat-treated as high as 3600°F in these tests. Metallographic examination was the principal means used for investigating recrystallization behavior, but hardness measurements were also taken on the test coupons. An effort was made to select a recrystallization heat-treatment which would yield a relatively constant grain size for all of the alloys.

5.4.1 Cb-W-Ta Ternary Alloys

Table XX presents the results of hardness measurements and metallographic notes taken on the specimens of the Cb-W-Ta ternaries. From these data the selected one-hour heat-treating temperature for each of the Cb-W-Ta alloys can be found in Table XXI. Microstructures corresponding to all of the heat-treatments performed on Alloy No. 1 (Cb-10.3W-15.6Ta) and 4 (Cb-24.6W-31.6Ta) are shown in Figures 36 and 37. All of the Cb-W-Ta alloys were clean solid solutions.

5.4.2 Cb-W-Hf Ternary Alloys

Hardness measurements and metallographic notes from the recrystallization test specimens of the Cb-W-Hf ternary alloys are tabulated in Table XXII; and the recrystallization heat-treatments selected for the alloys can be



Neg. No. 26864

Figure 33. Hammer Forgings of Cb-W-Hf-Ti Alloys after Removing Molybdenum Cans.

1. Alloy No. 24 (Cb-16.9W-33.2Hf-6.3Ti) Forged from Approximately 1.0-inch Thick to 0.3-inch Thick at 2300°F.
2. Alloy No. 25 (Cb-16.7W-35.2Hf-11.0Ti) Forged from Approximately 1.0-inch Thick to 0.4-inch Thick at 2300°F.

(a) Neg. No. 27710
Top View

(b) Neg. No. 27711
Edge View

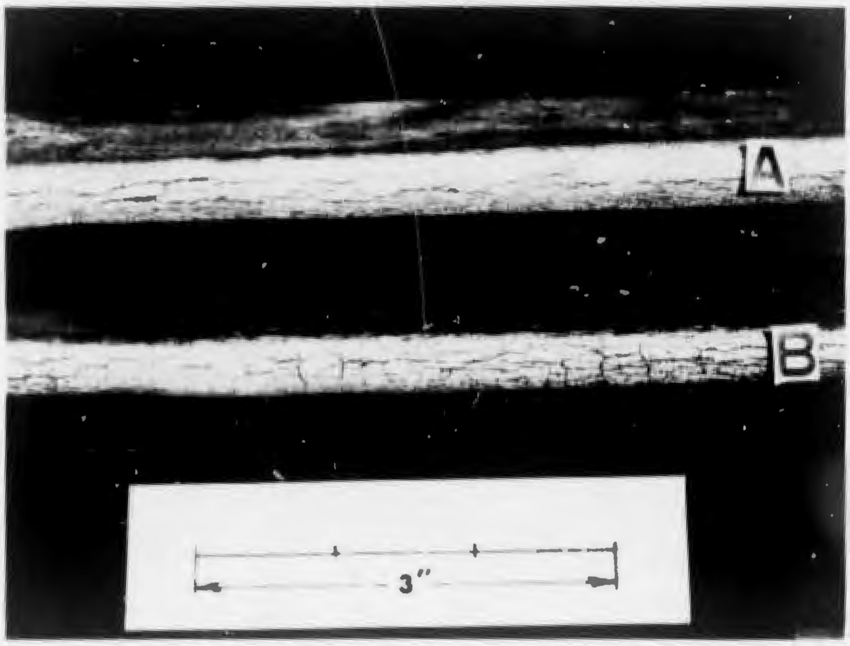


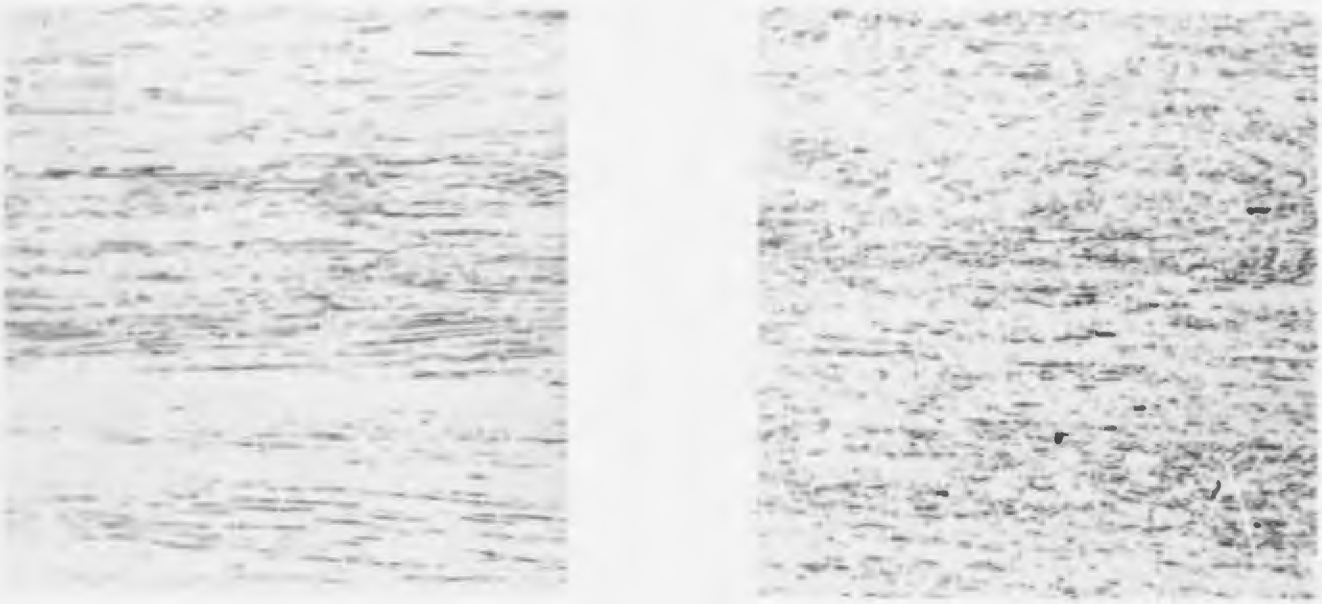
Figure 34. Press Forgings of Cb-W-Hf-Ti-N-C Alloys after Removing Molybdenum Cans.

A. Alloy No. 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C) Forged from Approximately 1.0-Inch Thick to 0.35-Inch Thick at 2400°F.

B. Alloy No. 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) Forged from Approximately 1.0-Inch Thick to 0.35-Inch Thick at 2400°F.

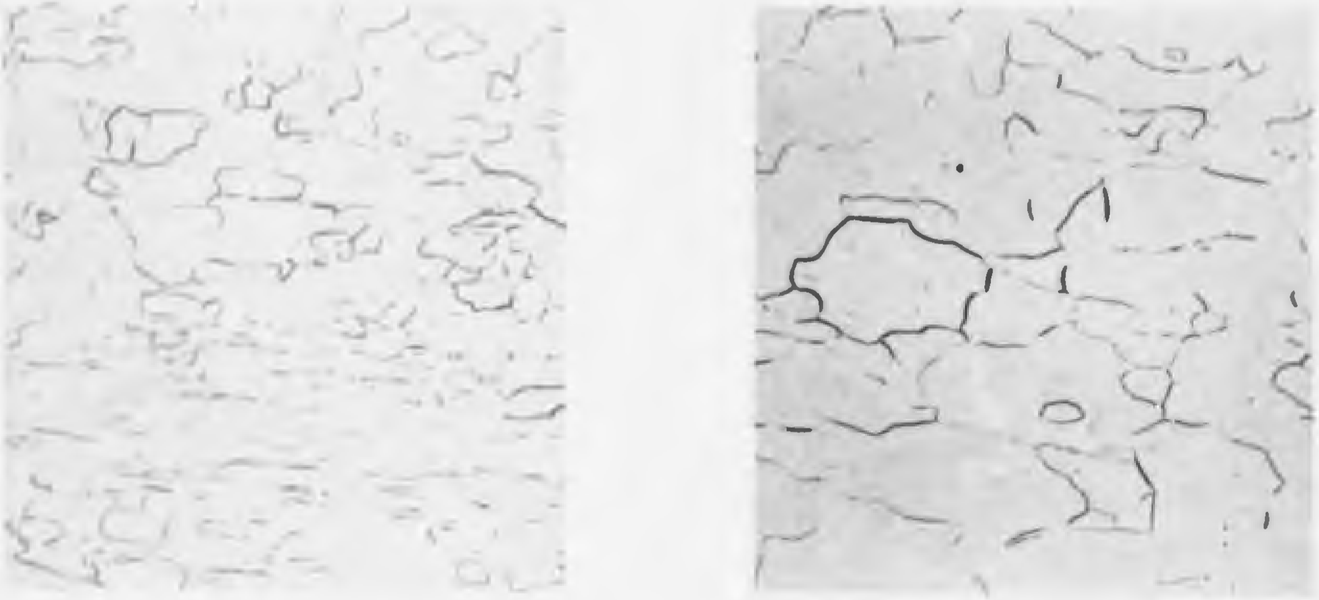
Neg. No. 27712

Figure 35. Press Forging of Alloy No. 28(Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V) after Removing Molybdenum Can. Forged from Approximately 1.0-inch Thick to 0.3-inch Thick at 2400°F.



(a) Neg. No. 22594
As-Swaged

(b) Neg. No. 22595
One Hour at 2000°F

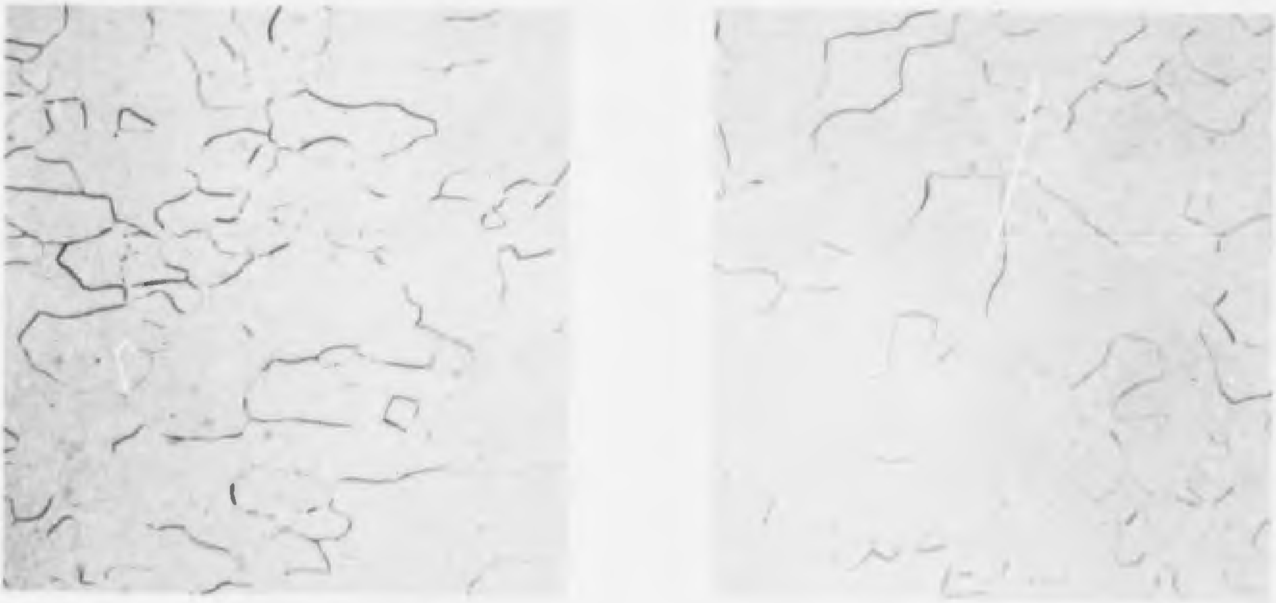


(c) Neg. No. 22596
One Hour at 2200°F

(d) Neg. No. 22597
One Hour at 2400°F

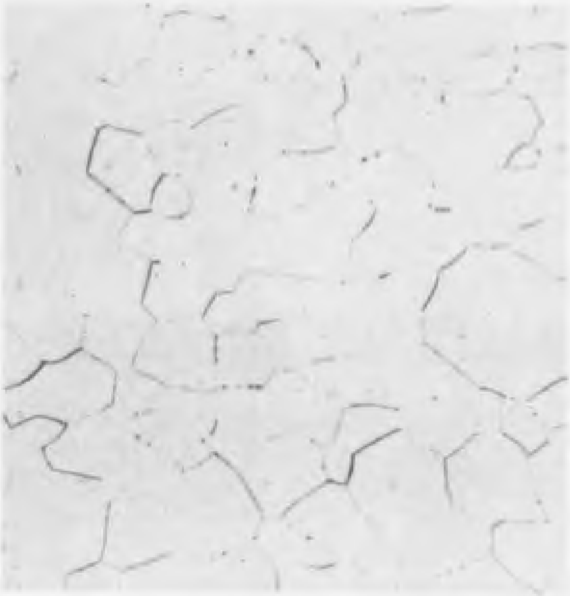
Figure 56. Microstructure of Alloy No. 1 (Cb-10.3W-15.6Ta) Warm Swaged at 500°F then Heat-Treated One Hour at Indicated Temperatures.

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF



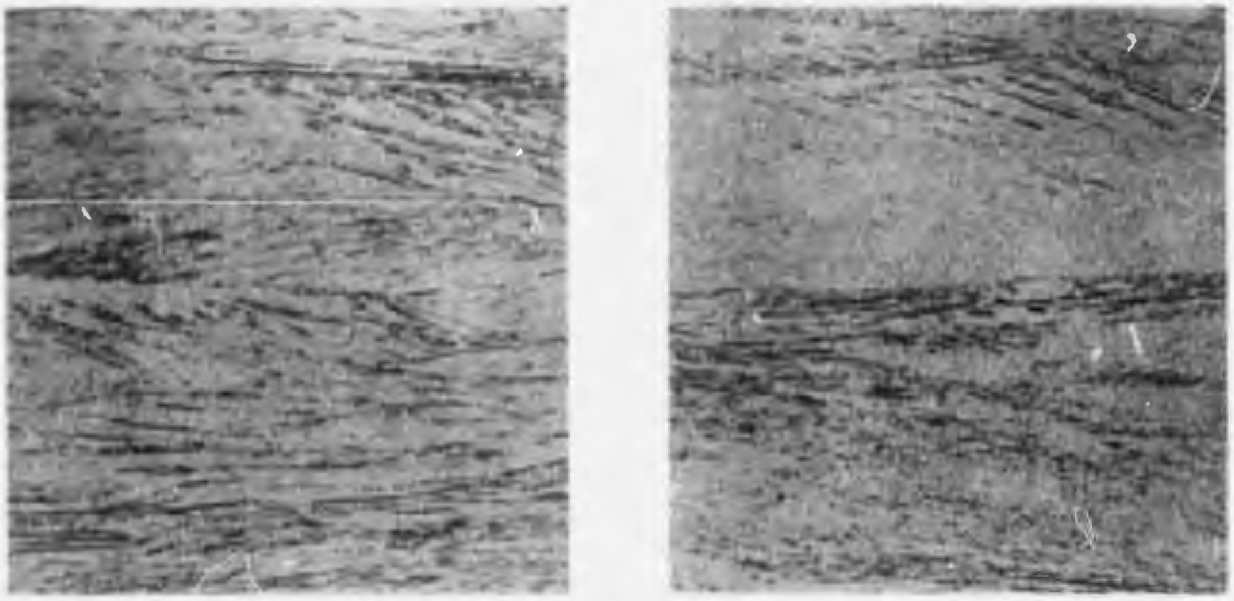
(e) Neg. No. 22598
One Hour at 2600°F

(f) Neg. No. 22599
One Hour at 2800°F



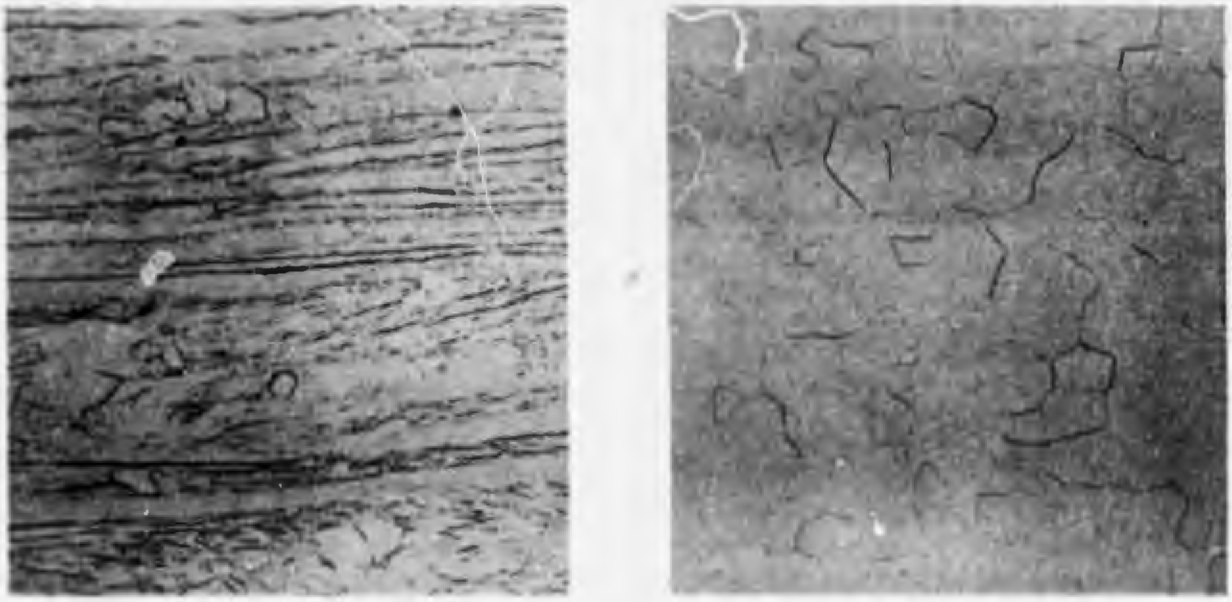
(g) Neg. No. 22600
One Hour at 3000°F

Figure 36. (continued)



(a) Neg. No. 22718
As-Extruded

(b) Neg. No. 22725
One Hour at 2200°F

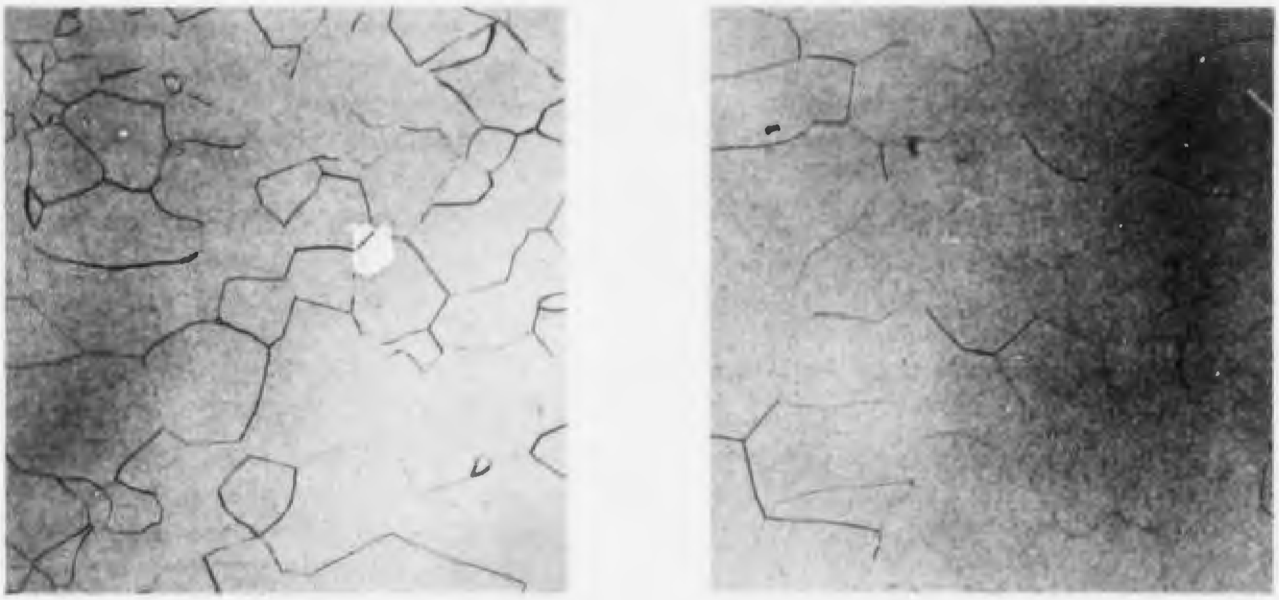


(c) Neg. No. 22726
One Hour at 2600°F

(d) Neg. No. 22805
One Hour at 3000°F

Figure 37. Microstructure of Alloy No. 4 (Cb-24.6W-31.6Ta) Extruded at 2500°F then Heat Treated One Hour at Indicated Temperatures.

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF



(e) Neg. No. 23945
One Hour at 3200°F

(f) Neg. No. 22806
One Hour at 3400°F

(g) Neg. No. 22807
One Hour at 3600°F

Figure 37. (continued)

found in Table XXIII. Typical microstructures of these alloys resulting from the heat-treatments are shown in Figures 38 through 41. Alloys No. 6 and 8, with low hafnium contents, were relatively clean alloys, whereas, the compositions with higher hafnium contents contained noticeable quantities of second phase precipitates throughout.

5.4.3 Cb-15W-35Hf with Additions of Rhenium, Titanium, Cobalt, Aluminum Vanadium, Carbon and Nitrogen

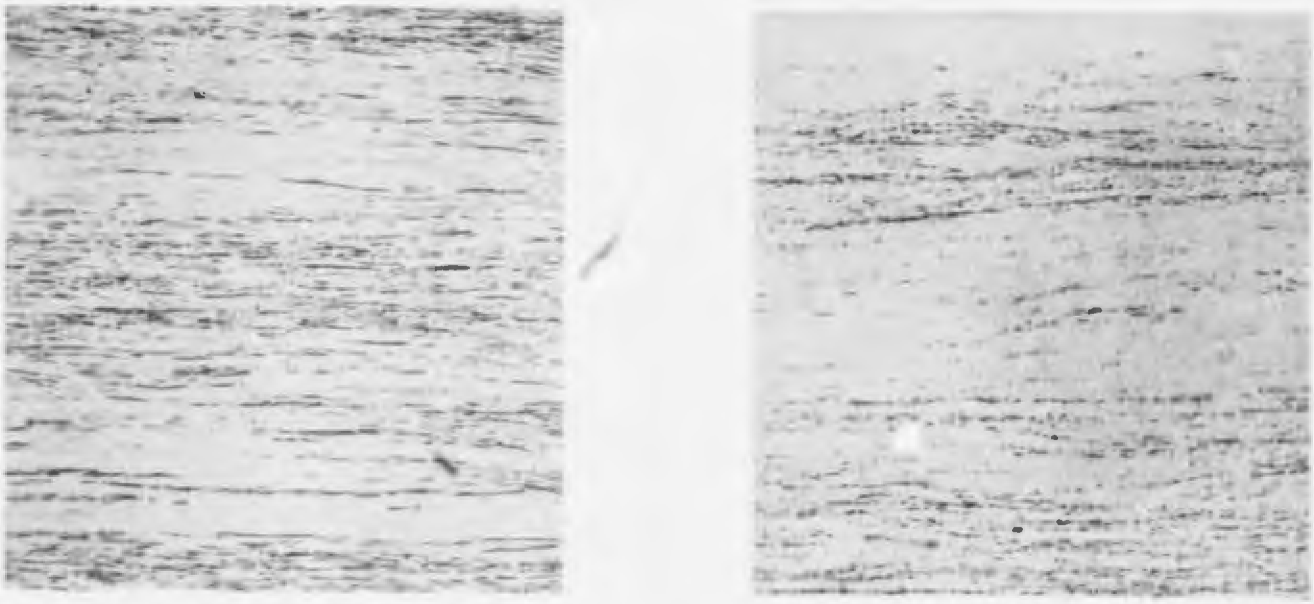
Recrystallization data for these more complex alloys are seen in Table XXIV, and the heat-treatments selected to recrystallize these materials are summarized in Table XXV. Representative microstructures can be found in Figures 42 through 46. There were some noticeable differences in the response of several of these alloys to heat-treatments as a result of composition. The large quantities of dispersed phase(s) from the interstitial additions to Alloys No. 27 and 29 caused a decrease in recrystallized grain size compared to the other materials. In the case of the heat-treatments carried out on the cobalt containing Alloy No. 26, visual inspection of the specimens revealed melting to have occurred as low as 2400°F. An example of the melting of this alloy at 2600°F is evident from the appearance of the specimen shown in Figure 47. This observation explains the extrusion results on Alloy No. 26; i.e. very irregular surface, since the extrusion temperature was 2800°F.

5.5 PHASE IDENTIFICATION STUDIES

Work was carried out to identify the phase precipitated in the Cb-W high hafnium content alloys, and the phase(s) present in the alloys containing intentional additions of carbon + nitrogen in Alloy No. 27 and carbon in Alloy No. 29. Also, a qualitative identification was made of the low melting phase observed in the Co containing Alloy No. 26.

5.5.1 Alloys No. 7 (Cb-10.6W-30.8Hf), 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C) and 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C)

A sample of Alloy No. 7 annealed one hour at 3000°F and with a microstructure as shown in Figure 39 was dissolved in a bromine-methanol solution. X-ray diffraction analysis suggested the residue to be a fcc carbide, perhaps CbC·HfC, with a lattice parameter of 4.57 angstrom units. This value is similar to the lattice parameter reported for CbC·ZrC. HfW_2 was sought but not found. Identification of a carbide phase was somewhat surprising in view of an analyzed carbon content of 30-40 ppm for the alloy; however, additional evidence was obtained by microprobe analysis to indicate that the precipitate was not HfW_2. A traverse made across stringers of the precipitate present in a specimen of the alloy annealed one hour at 2600°F (approximately 75 percent recrystallized as shown in Figure 39) revealed the stringers to be enriched in hafnium and depleted in tungsten relative to the matrix. Enrichment in tungsten would be expected if HfW_2 were present.



(a) Neg. No. 22601
As-Swaged

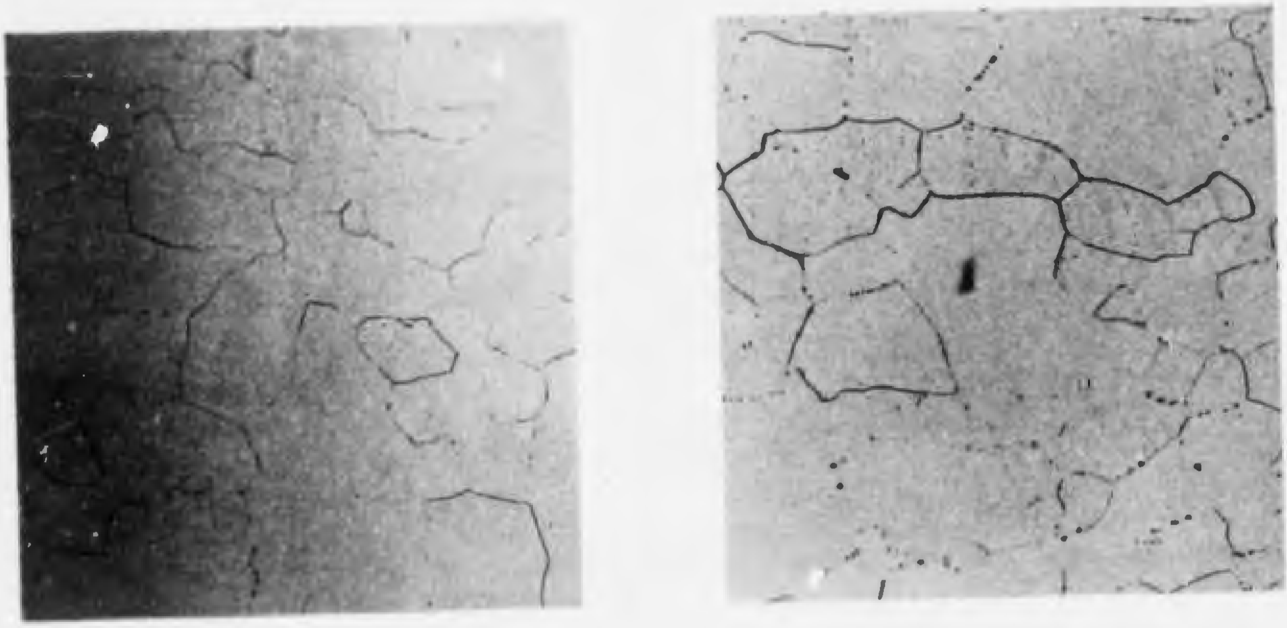
(b) Neg. No. 22602
One Hour at 2000°F

(c) Neg. No. 22603
One Hour at 2200°F

(d) Neg. No. 22604
One Hour at 2400°F

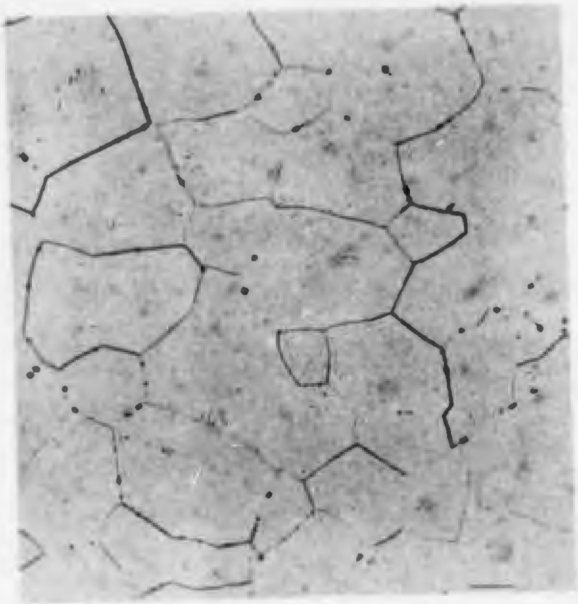
Figure 38. Microstructure of Alloy No. 6 (Cb-9.8W-1.6Hf) Warm Swaged at 500°F then Heat-Treated One Hour at Indicated Temperatures.

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF



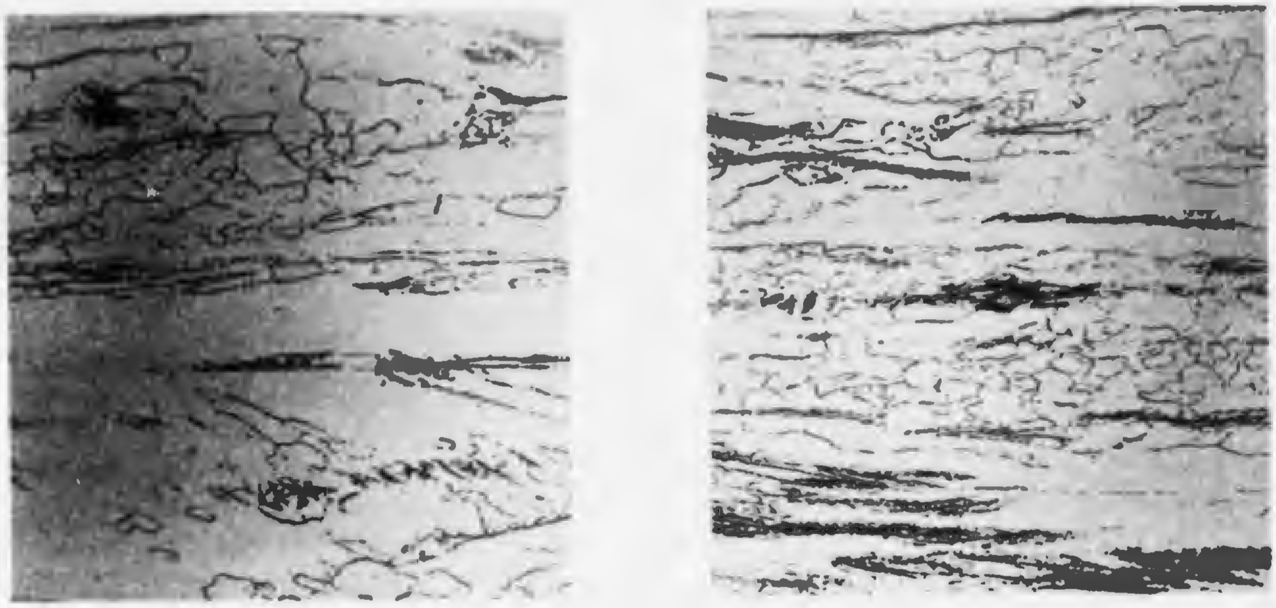
(e) Neg. No. 22605
One Hour at 2600°F

(f) Neg. No. 22606
One Hour at 2800°F



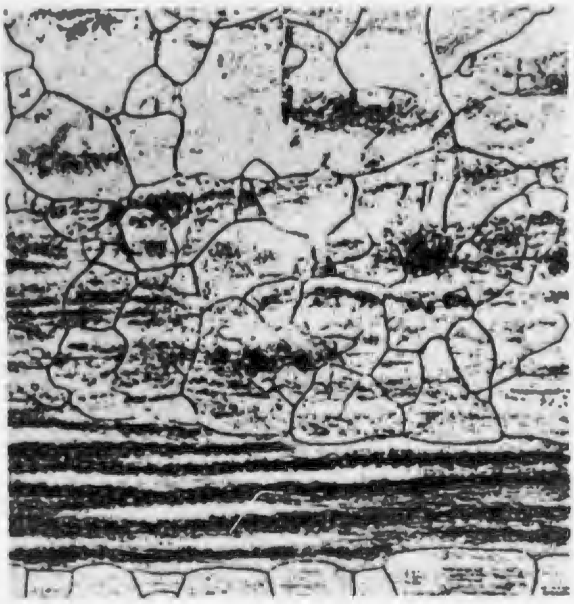
(g) Neg. No. 22607
One Hour at 3000°F

Figure 38. (continued)



(a) Neg. No. 22719
As-Extruded

(b) Neg. No. 22728
One Hour at 2200°F



(c) Neg. No. 22729
One Hour at 2600°F

Figure 39. Microstructure of Alloy No. 7 (Cb-10.6W-30.8Hf) Extruded at 2690°F then Heat-Treated One Hour at Indicated Temperatures.

Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 drops HF

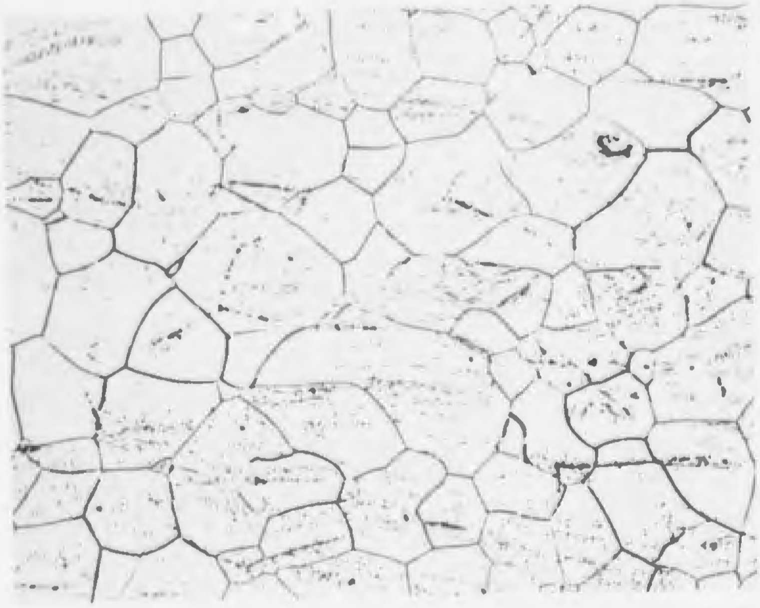
(d) Neg. No. 22727
One Hour at 2800°F

(e) Neg. No. 22800
One Hour at 3000°F

(f) Neg. No. 22801
One Hour at 3200°F

Figure 39. (continued)

(a) Neg. No. 23901
As-Forged

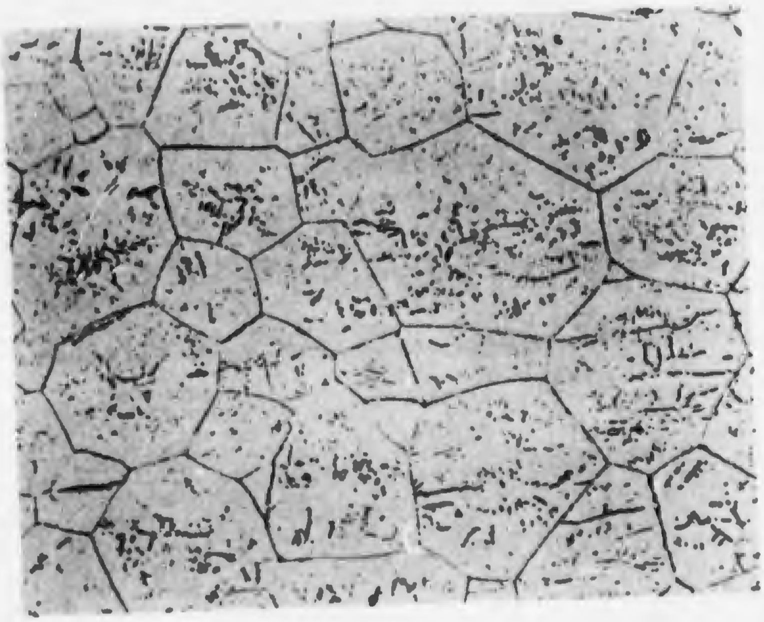


(b) Neg. No. 24919
Recrystallized

Figure 40. Microstructure of Alloy No. 13 (Cb-4.0W-34.4Hf) Hammer Forged at 2300°F then Recrystallized One Hour at 2500°F.

Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 drops HF

(a) Neg. No. 26388
As-Forged

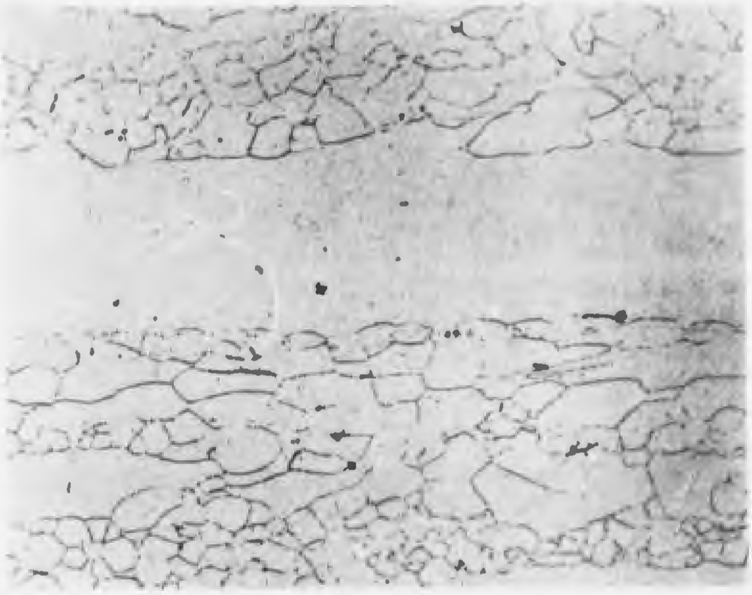


(b) Neg. No. 26390
Recrystallized

Figure 41. Microstructure of Alloy No. 21 (Cb-14.4W-35.9Hf) Press Forged at 2575°F then Recrystallized One Hour at 3000°F.

Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 drops HF

(a) Neg. No. 26392
As-Forged

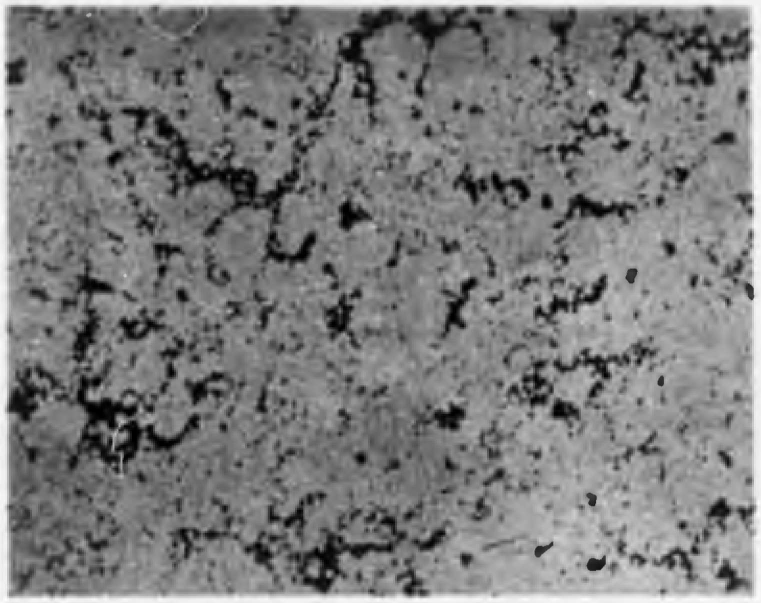


(b) Neg. No. 26393
Recrystallized

Figure 42. Microstructure of Alloy No. 23 (Cb-15.1W-34.8Hf-1.9Re) Press Forged at 2575°F then Recrystallized One Hour at 3000°F.

Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 drops HF

(a) Neg. No. 27237
As-Extruded



(b) Neg. No. 27241
One Hour at 2600°F

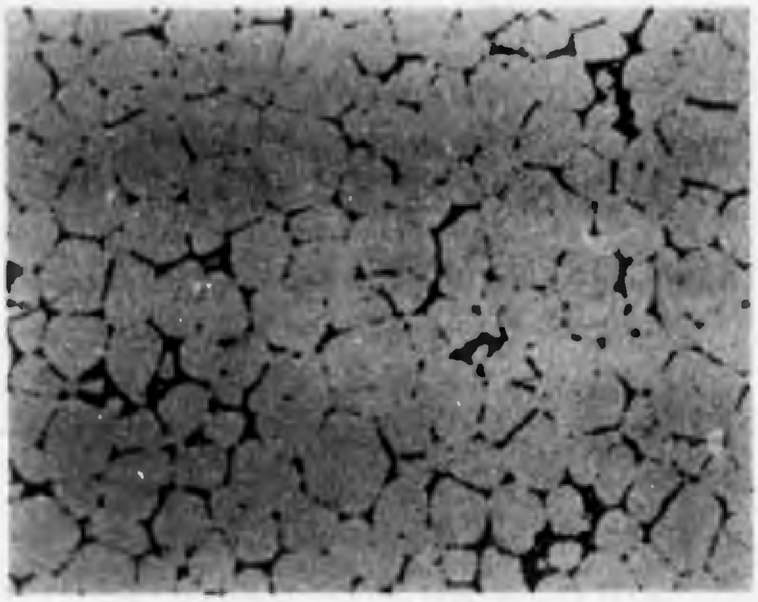


Figure 43. Microstructure of Alloy No. 26 (Cb-17.5W-33.5Hf-2.8Co) Extruded at 2800°F then Heat-Treated One Hour at 2600°F.

Magnification: 200X Etchant. 50p Lactic Acid - 3p HNO_3 - 2 drops HF

(a) Neg. No. 27718
As-Forged

(b) Neg. No. 27743
One Hour at 2000°F

(c) Neg. No. 27744
One Hour at 2200°F

(d) Neg. No. 27745
One Hour at 2400°F

Figure 44. Microstructure of Alloy No. 27 (Cb-15.5W-56.0Hf-6.6Ti-0.048N-0.052C) Press Forged at 2400°F then Heat-Treated One Hour at Indicated Temperatures.

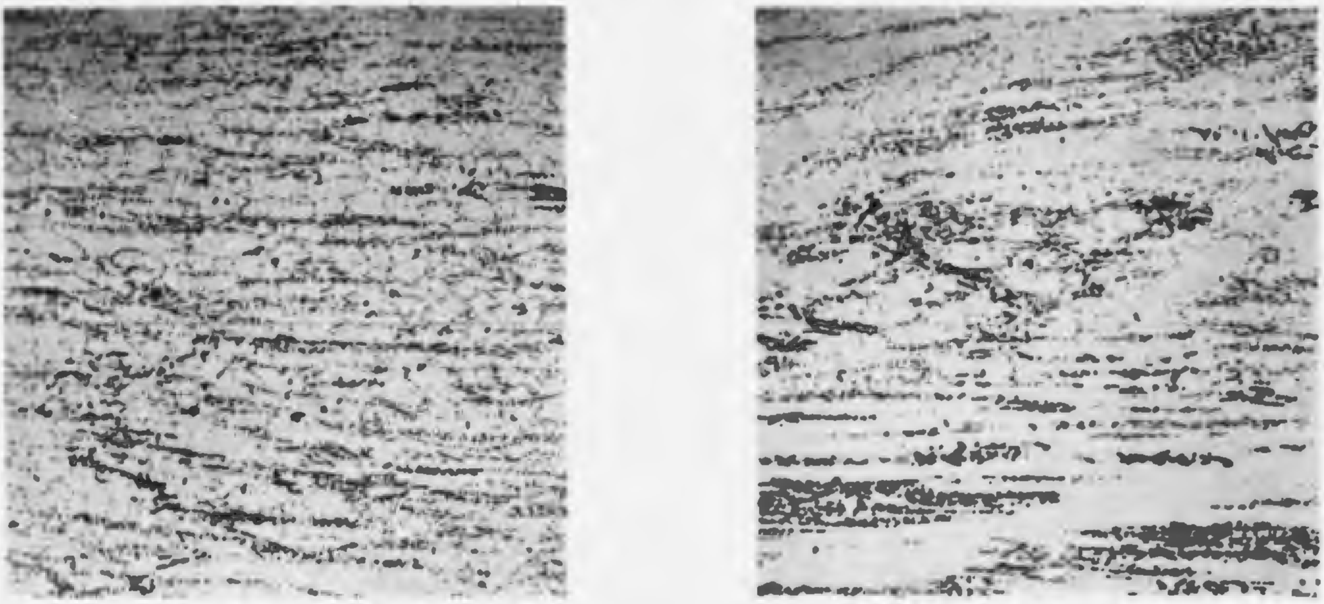
Magnification: 200X Etchant: 50p Lactic Acid -
3p HNO_3 - 2 drops HF

(e) Neg. No. 27746
One Hour at 2600°F

(f) Neg. No. 27747
One Hour at 2800°F

(g) Neg. No. 27748
One Hour at 3000°F

Figure 44. (continued)



(a) Neg. No. 27719
As-Forged

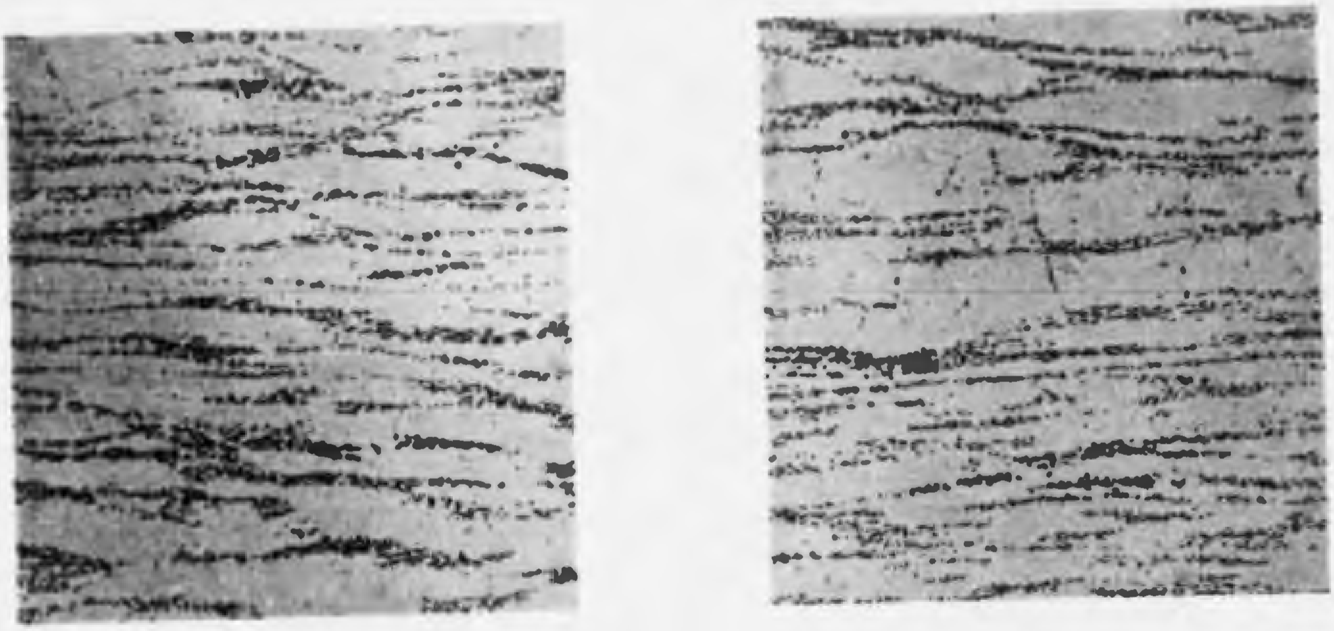
(b) Neg. No. 27749
One Hour at 2000°F

(c) Neg. No. 27750
One Hour at 2200°F

(d) Neg. No. 27751
One Hour at 2400°F

Figure 45. Microstructure of Alloy No. 29 (Cb-15.0W-35.6Hf-6.4Ti 0.11C) Press Forged at 2400°F then Heat-Treated One Hour at Indicated Temperatures.

Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 Drops HF

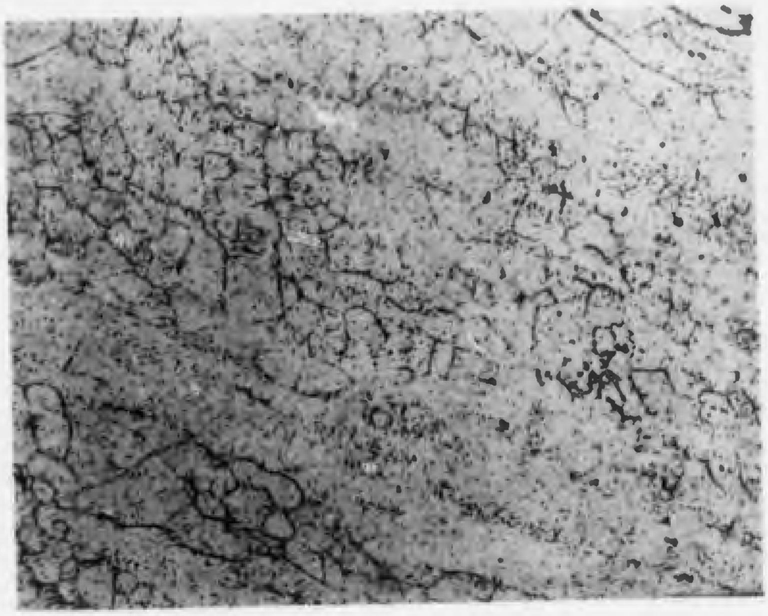


(e) Neg. No. 27752
One Hour at 2600°F

(f) Neg. No. 27753
One Hour at 2800°F

(g) Neg. No. 27754
One Hour at 3000°F

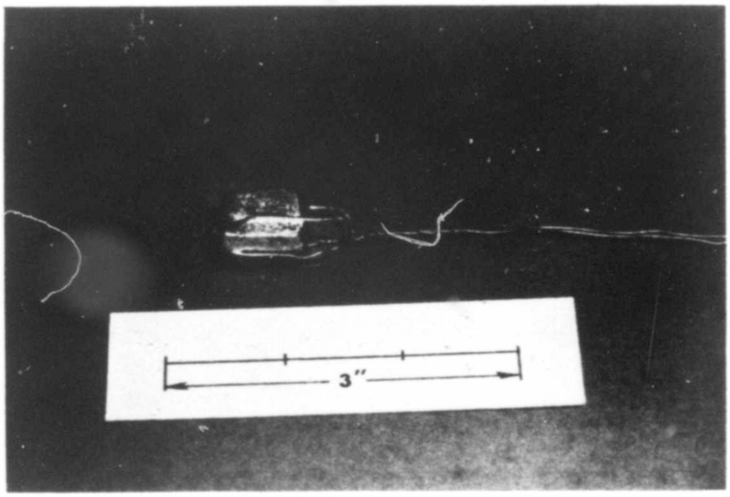
Figure 45. (continued)



Neg. No. 27717

Figure 46. Microstructure of Alloy No. 28 (Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V) Press Forged at 2400°F.

Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 Irops HF.



Neg. No. 27389

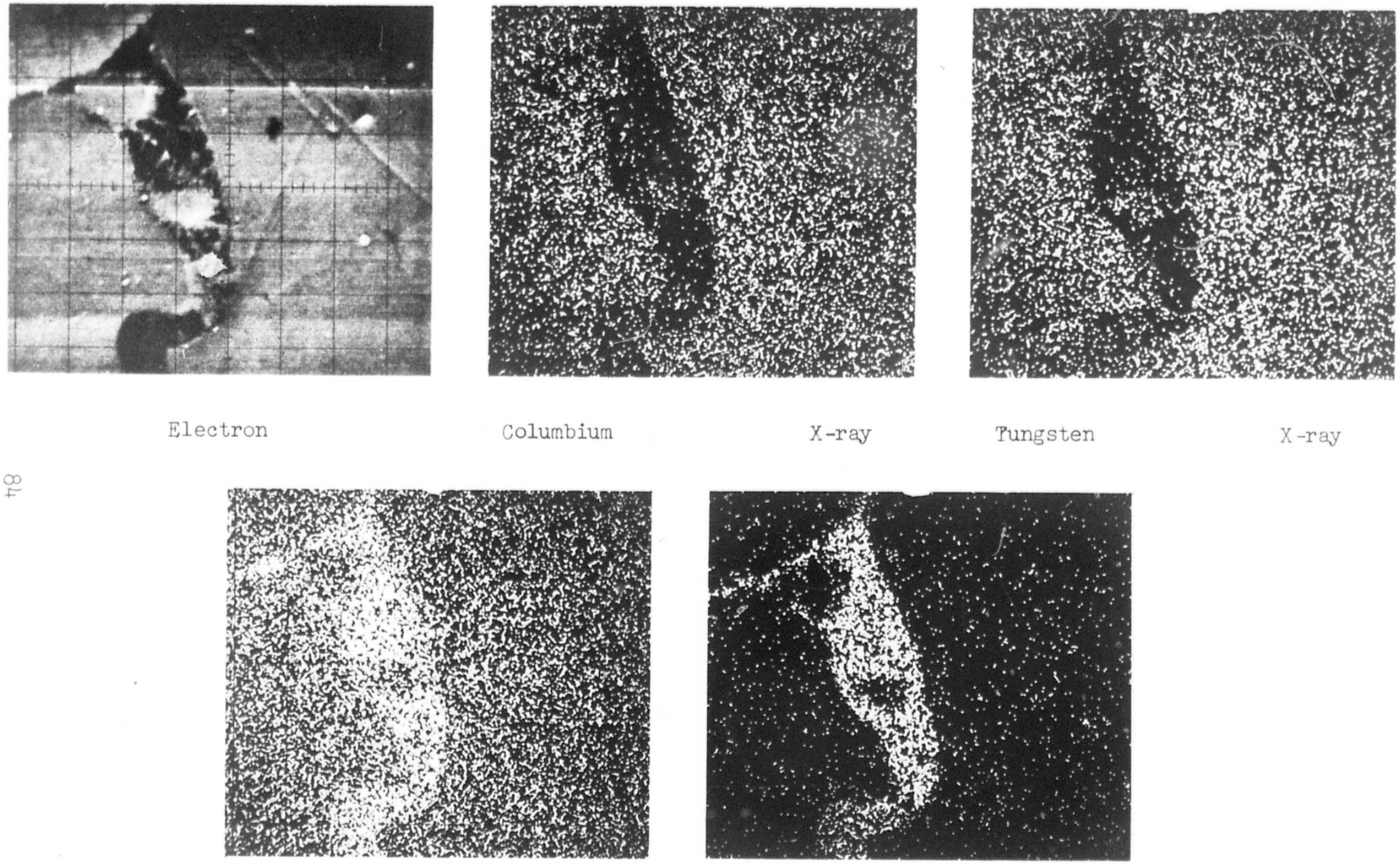
Figure 47. Specimen of Alloy No. 26 (Cb-17.5W-33.5Hf-2.8Co) Wrapped in Tantalum Foil and Heat-Treated at 2600°F. Note Melting.

Phase identification studies were attempted on forged and 2800°F annealed specimens of Alloys No. 27 and 29. The Debye-Scherrer patterns obtained on residues remaining after a bromine-methanol dissolution treatment of the specimens revealed matrix plus a carbide-type phase in each alloy and an additional unidentified fcc phase in Alloy No. 27. Measurements of the lattice parameters of these phases are tabulated below:

Alloy No.	Lattice Parameter (Å)	Probable Identification
27	3.31	BCC Matrix
	4.33	FCC
	4.56	FCC Carbide
29	3.33	BCC Matrix
	4.61	FCC Carbide

5.5.2 Alloy No. 26 (Cb-17.5W-33.5Hf-2.8Co)

The microstructure of Alloy No. 26 contained a relatively large quantity of second phase; and, as previously reported, this alloy was observed to show partial melting at a temperature as low as 2400°F. A microprobe analysis was run on this alloy, and as seen by the X-ray image photographs in Figure 48, this phase was found to be enriched in cobalt and hafnium. Since five eutectics, all existing below 2600°F, are reported in the cobalt-hafnium system(8), a convenient explanation is offered for the melting observed. Thus, the addition of only 2.8 percent cobalt in Alloy No. 26 has caused a very significant depression in the solidus temperature.



Electron Columbium X-ray Tungsten X-ray

Hafnium X-ray Cobalt X-ray

Figure 48. Back-Scattered Electron and X-ray Image Photographs of Second Phase Present in Alloy No. 26 (Cb-17.5W-33.5Hf-2.8Co).

SECTION VI

MECHANICAL PROPERTY EVALUATION

Tensile properties of the fabricated and recrystallized alloys were measured at room temperature, 2000°F, and in some cases 2200°F. Other tests, above and below room temperature, were performed to obtain an indication of the tensile transition temperature of a few of the alloys. Strength-to-weight ratios were determined.

Creep-rupture evaluation at 2000°F was performed on selected Cb-W-Hf ternary alloys and on the basic composition of nominally Cb-15W-35Hf containing additions of rhenium, titanium, carbon, and nitrogen.

An indication of thermal stability was obtained for the Cb-W-Hf type alloys from hardness measurements of the uncontaminated areas of the post-test oxidation specimens.

6.1 TENSILE PROPERTIES

For determination of tensile properties, bar-type specimens were used. Each specimen was 2.0-inch overall length with a 1.0-inch long by 0.125-inch diameter gage section and non-threaded grips. Before preparing the specimens, the alloys were given a recrystallization heat-treatment as shown in Tables XXI, XXIII, and XXV. A few tests were performed on several of the alloys in the stress-relieved condition.

Tests at room temperature and below were carried out on a Riehle Testing Machine at a crosshead speed of 0.005 inch/minute to yield, then 0.05 inch/minute to failure. For obtaining test temperatures below room temperature, liquid nitrogen was used as the coolant by being introduced into an insulated chamber surrounding the specimen. Temperature was controlled by means of a calibrated thermocouple located near the specimen. The liquid nitrogen was sprayed into the test chamber through a valve actuated by the thermocouple circuit. Operation of the valve was automatic and functioned to maintain a balanced thermocouple circuit at a value of imposed emf equivalent to the test temperature.

Tests above room temperature were carried out on an Instron Testing Machine at a crosshead speed of 0.05 inch/minute. A cold wall, tantalum resistance heated, vacuum furnace was used for heating the specimen. Temperature was controlled and recorded with Pt/Pt-13Rh thermocouples.

For determination of strength to weight ratios, density measurements were made on the mechanical property specimens of the alloys by the water displacement technique.

6.1.1 Cb-W-Ta Ternary Alloys

The results of evaluation of the tensile properties of the Cb-W-Ta ternary alloys are listed in Table XXVI. Examination of these data show that only slight additional strengthening was realized when the tantalum content was increased from approximately 15 to 30 percent in either of the base alloys of nominally Cb-10W and Cb-25W. The increase in tantalum content had essentially no effect on the ductility of either base. Increasing the tungsten content from about 10 to 25 percent resulted in significant strengthening, but shifted the ductile-brittle transition temperature from below -80°F to above room temperature, and reduced the tensile elongation at elevated temperature by about a factor of 2. As might have been expected from consideration of composition, the tensile properties of Alloy No. 5 (Cb-16.9W-23.8Ta) were intermediate between the properties of Alloy No. 1 (Cb-10.3W-15.6Ta) and Alloy No. 4 (Cb-24.6-31.6Ta). The ductile-brittle transition temperature for Alloy No. 5 was near room temperature.

6.1.2 Cb-W-Hf Ternary Alloys

The tensile properties of the Cb-W-Hf ternary alloys are presented in Table XXVII. The data show that both tungsten and hafnium were effective strengthening additions, but both elements impaired ductility when their contents increased within the approximate range of 10 to 24 percent tungsten and 2 to 35 percent hafnium. The brittleness of some of the alloys, and their sensitivity to stress concentration, led to failure of a few room-temperature test bars at the radius of the gage section. These tests have been indicated in the tabulation and the reported strength values are probably low.

The influence of hafnium as a strengthener is evident from a comparison of the elevated temperature data for Alloy No. 6 (Cb-9.8W-1.6Hf), the weakest composition, with that of Alloy No. 7 (Cb-10.6W-30.8Hf). The 2000°F and 2200°F tensile strength has increased by about three times with the increase in hafnium content from nominally 2 to 30 percent. Lowering the tungsten content to below 10 percent in the presence of relatively high hafnium contents, Alloys No. 11 through 14, did not drastically reduce strength and at the same time restored some ductility. Unfortunately these four alloys were inferior in oxidation resistance compared to the compositions with higher tungsten contents and high hafnium contents.

Late in the program limited data were obtained to indicate a possible effect of thermal mechanical processing on ductility. A test was run at 600°F on each of the Alloys No. 21 (Cb-14.4W-35.9Hf) and No. 22 (Cb-12.1W-35.5Hf) after a stress relieving heat-treatment for 1 hour at 2200°F. The microstructure of the alloys corresponded to the as-fabricated condition, i.e., partially recrystallized. The ductility of the alloys was significantly improved as shown in Table XXVII over that determined at room temperature and 2000°F following a recrystallization heat-treatment at 3000°F. Thus, grain size is probably one factor contributing to the brittleness problem, and another may be the carbide phase present in the Cb-W-high hafnium content alloys.

6.1.3 Cb-15W-35Hf with Additions of Rhenium, Titanium, Carbon and Nitrogen

Primarily from the results of oxidation evaluation, the base nominal composition, Cb-15W-35Hf, was selected for further alloying for property enhancement. The tensile properties obtained on these more complex alloys are shown in Table XXVIII and compared with tensile properties previously presented for the basic Cb-W-Hf ternary, Alloy No. 21 (Cb-14.4W-35.9Hf).

The exact effect of the 1.9 percent rhenium addition to Alloy No. 23 is uncertain due to the brittleness of the alloy and failure of the specimens at the radius. However, it was found that a 2200°F stress relief and test at 600°F did not restore ductility to any appreciable extent, as compared to this same test on Alloy No. 21.

The titanium bearing Alloys No. 24 (Cb-16.9W-33.2Hf-6.3Ti) and No. 25 (Cb-16.7W-35.2Hf-11.0Ti) were also brittle. Comparison of the 2000°F tensile properties of Alloys No. 21 and No. 25 strongly suggests a very significant reduction in strength as a result of the titanium addition.

To determine if strength could be restored by interstitial additions to the titanium containing quaternary, Alloy No. 24, a 480 ppm nitrogen + 520 ppm carbon addition, was made in Alloy No. 27 and a 1100 ppm carbon addition was made in Alloy No. 29. From the data obtained, the carbon and nitrogen additions were effective strengtheners, but the improvement at 2000°F did not result in a strength level as high as that shown by the basic ternary, Alloy No. 21, at the same temperature. These results show that strength would probably have been benefited more by a nitrogen and/or carbon addition to the basic ternary at some sacrifice in oxidation resistance through the elimination of titanium.

Comparing the room temperature data for Alloys No. 27 and No. 29, the carbon + nitrogen addition in Alloy No. 27 was a more effective strengthener than the carbon addition in Alloy No. 29. However, the strength of the two alloys was about equal at 2000°F.

To determine the effect of annealing temperature on the room temperature tensile properties of Alloys No. 27 and No. 29, forged material was annealed for 1 hour over the temperature range 2200°F to 2800°F. The results of these tests are shown in Table XXIX. No large change in strength was found for either of the alloys as a result of varying the prior annealing temperature. However, the increase in ductility to 12.7 percent of the 2200°F annealed specimen of Alloy No. 29 suggests an effect of thermal mechanical processing.

6.1.4 Thermal Stability

An indication of thermal stability of the Cb-W-Hf type alloys, ternaries and more complex compositions, was obtained from hardness measurements of the uncontaminated regions of the post-test oxidation specimens. These specimens were in the recrystallized condition prior to test. The data in Table XXX show no effect on hardness for the indicated lengths of exposure at 2000°F. Of particular interest were the data for Alloys No. 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C) and No. 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) in view of their high interstitial contents. Neither of these alloys, after a 2800°F anneal, showed any significant change in hardness for times between 4 and 100 hours at 2000°F. The results may have been different for higher solution annealing temperatures followed by low temperature aging.

6.2 CREEP-RUPTURE PROPERTIES

Because emphasis was placed upon the evaluation of Cb-W-Hf type alloys, creep-rupture testing was confined to Cb-W-Hf ternaries and several of the more highly alloyed compositions based upon Cb-15W-35Hf with additions of rhenium, titanium, carbon, and nitrogen. Of primary interest was a determination of the effect of a high hafnium content in these alloys and the effect of the above-mentioned additions to the basic ternary, on creep-rupture behavior.

Tests were carried out in vacuum at 2000°F and stress levels of 12,500 psi and 20,000 psi with the materials mostly in the recrystallized condition. The creep-rupture specimens were of the same type used for tensile testing.

The testing unit, as seen in Figure 49, was a getter-ion pumped system capable of vacuum down to the range of 10^{-10} torr. The tantalum resistance heated furnace, specimen, weight pan, and weights were all contained within the vacuum system. After loading the unit and prior to testing, the system was baked out at 500°F for at least 8 hours. During testing, temperature was measured and controlled by means of a thermocouple attached to the gage length of the specimen. Strain was measured with a cathetometer by observing the separation of the specimen grips through a window in the furnace chamber. The reference measurement, i.e., zero elongation, of the specimen was taken as the measurement made immediately upon application of the load after reaching the test temperature.

Prior to testing any of the alloys, an exposure test was performed on Alloy No. 6 (Cb-9.8W-1.6Hf) to determine the extent of contamination of this material in the vacuum environment of the equipment. A 0.25-inch diameter specimen of the alloy was exposed for 150 hours at 2000°F at an initial pressure of 8×10^{-7} torr and a final pressure of 5.8×10^{-10} torr. Pre- and post-test interstitial analyses of this specimen presented in Table XXXI showed no contamination. The most notable change was a 28 ppm reduction in nitrogen content as a result of the test.

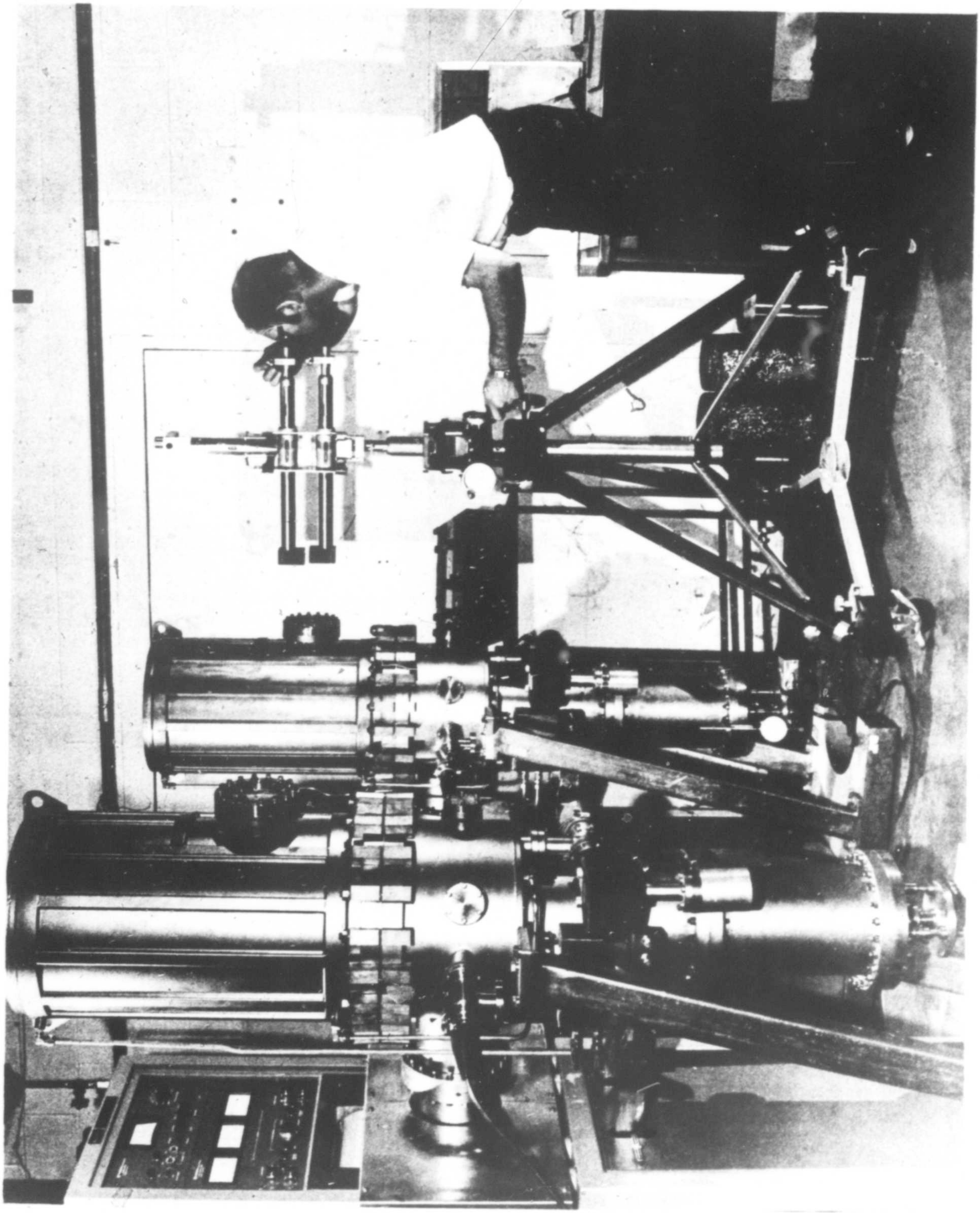


Figure 49. Ultra High Vacuum Creep Rupture Testing Units.

6.2.1 Cb-W-Hf Ternary Alloys

The creep-rupture data obtained on the Cb-W-Hf ternary compositions are summarized in Table XXXII. With the tests run on Alloy No. 6 (Cb-9.8W-1.6Hf) at 12,500 psi as a reference, it is evident that increasing the hafnium content improved creep-rupture properties as seen from a comparison with the data for Alloy No. 7 (Cb-10.6W-30.8Hf) at the same stress. The actual creep curves are plotted in Figure 50.

Alloy No. 7 was also tested at 20,000 psi and the curve is included in Figure 51. The rupture life of 92 hours approaches the target strength characteristics of 100-hour life at 2000°F. However, because of the very high rupture elongation of the alloy, strength could only be considered useful up to about 30 hours at which time the alloy entered third-stage creep. Even at a stress of 12,500 psi entry into third-stage creep began after about 40 hours.

Creep strength was improved somewhat for the high hafnium content alloys when the tungsten content was increased as seen from a comparison of the curves for Alloys No. 7 (Cb-10.6W-30.8Hf) and No. 30 (Cb-14.2W-28.8Hf) in Figure 51 and for Alloys No. 22 (Cb-12.1W-35.5Hf) and No. 21 (Cb-14.4W-35.9Hf) in Figure 52.

Metallographic examination was performed on the creep-rupture specimens of the Cb-W-Hf alloys. The post-test microstructures of both the gage and grip sections of the specimens were compared. A consistent observation for these alloys was the presence of a recrystallized structure in the region of the grain boundaries of the gage section. Examples are pointed out in Figures 53 and 54. In both of these examples, as well as the other tests, the alloys showed very high rupture elongations or extensive third-stage creep. It is reasonable to believe that this has been caused by structural instability resulting from high diffusion rates, as further evidenced by recrystallization accompanying the tests. Therefore, improvements in creep properties could be expected by effecting an increase in the recrystallization temperature.

6.2.2 Cb-15W-35Hf with Additions of Rhenium, Titanium, Carbon, and Nitrogen

Table XXXIII summarizes the creep-rupture data for the more complex alloys based upon Cb-15W-35Hf with additions of rhenium, titanium, carbon, and nitrogen. The data obtained previously on the ternary Alloy No. 21 (Cb-14.4W-35.9Hf) are included for comparison.

For the test carried out on Alloy No. 23 (Cb-15.1W-34.8Hf-1.9Re) at 20,000 psi, the strengthening effect of rhenium noted after the alloy had surpassed 1.5 percent strain was not large. The creep-rupture curve for this test can be found in Figure 55.

The most disappointing results of the various tests were those showing

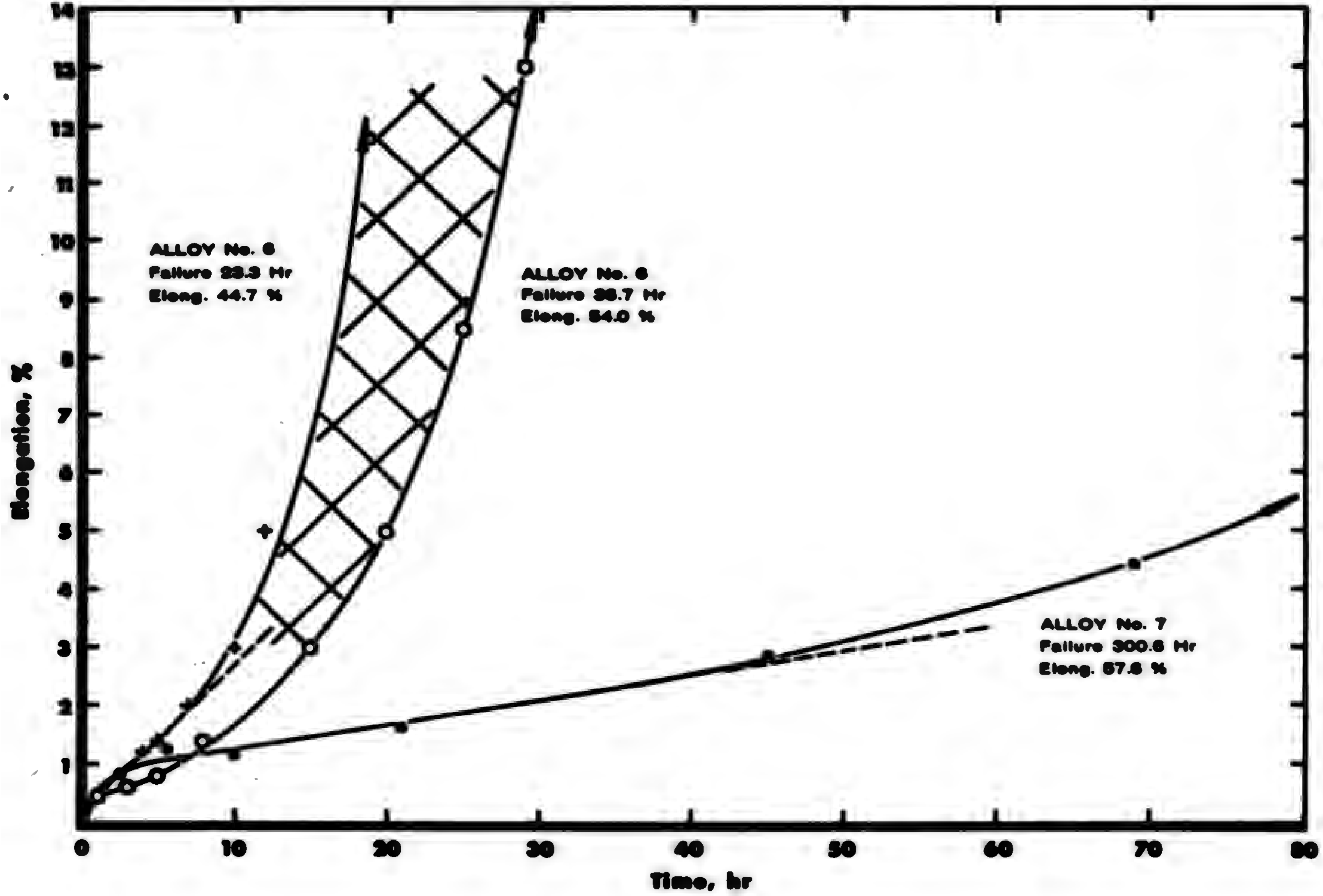


Figure 50. Creep-Rupture Curves for Recrystallized Alloys No. 6 (Cb-9.8W-1.6Hf) and 7 (Cb-10.6W-30.8Hf) Tested at 2000°F and 12,500 psi.

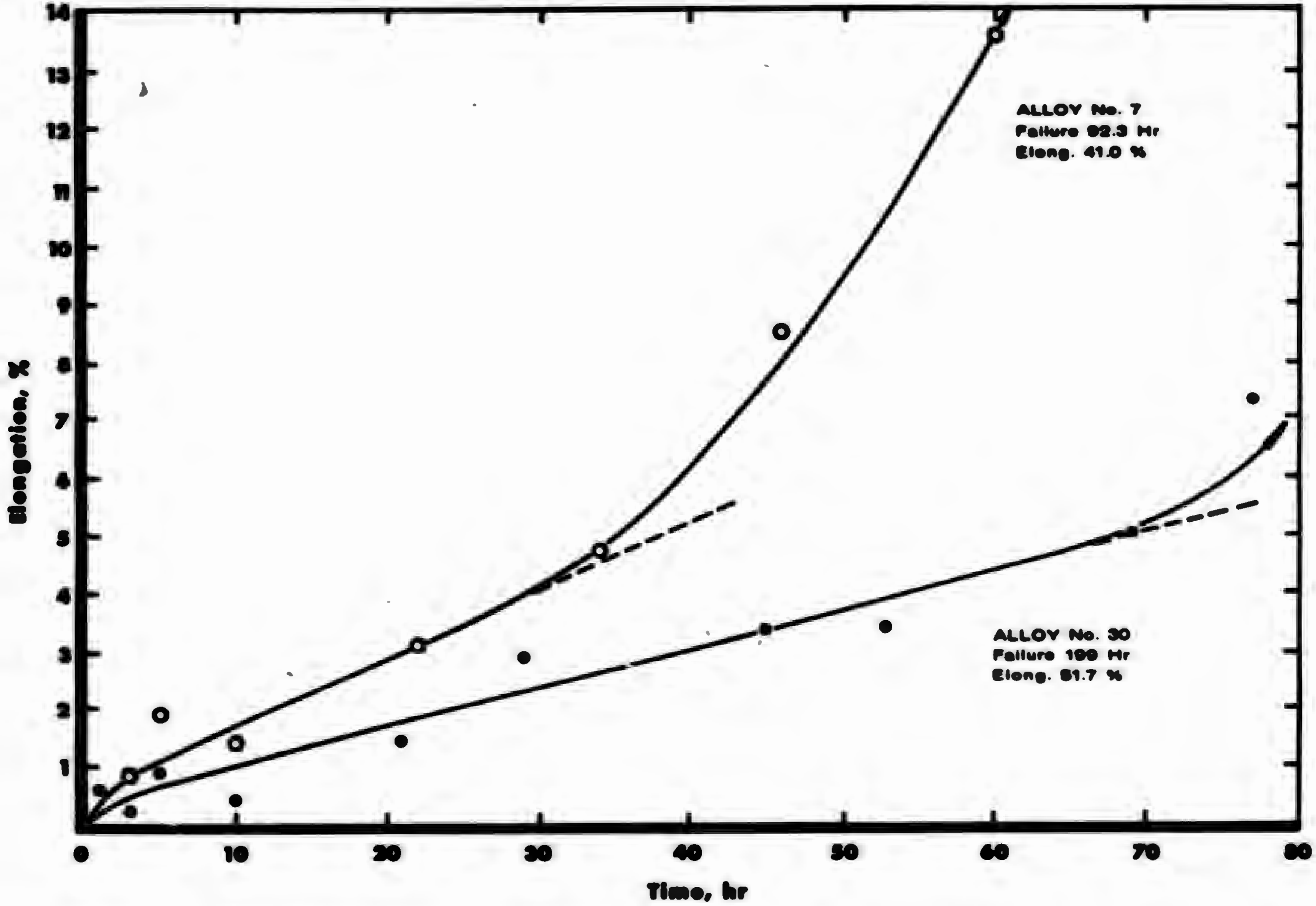


Figure 51. Creep-Rupture Curves for Recrystallized Alloys No. 7 (Cb-10.6W-30.8Hf) and 30 (Cb-14.2W-28.8Hf) Tested at 2000°F and 20,000 psi.

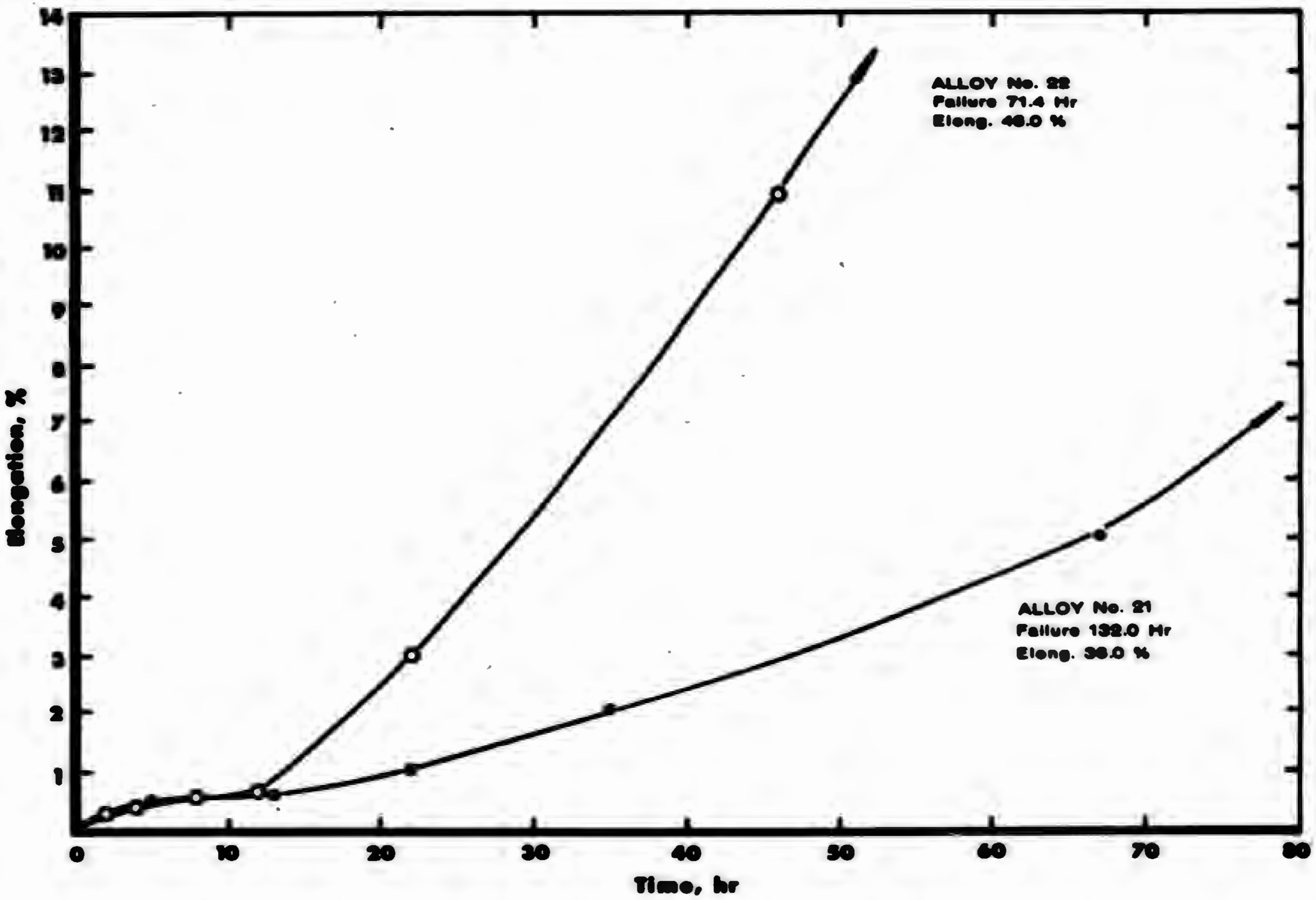
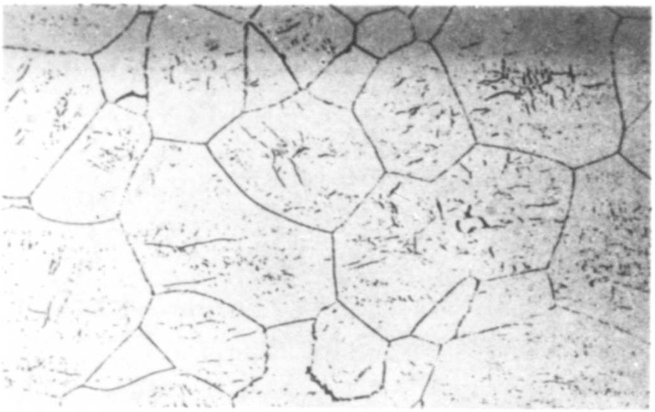
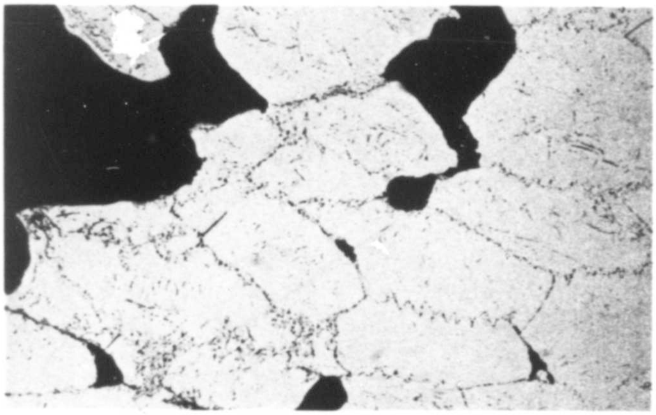


Figure 52. Creep-Rupture Curves for Recrystallized Alloys No. 22 (Cb-12.1W-35.5Hf) and 21 (Cb-14.4W-35.9Hf) Tested at 2000°F and 20,000 psi.

(a) Neg. No. 25983
Magnification: 200X
Grip Section



(b) Neg. No. 25984
Magnification: 200X
Fracture



(c) Neg. No. 25985
Magnification: 500X

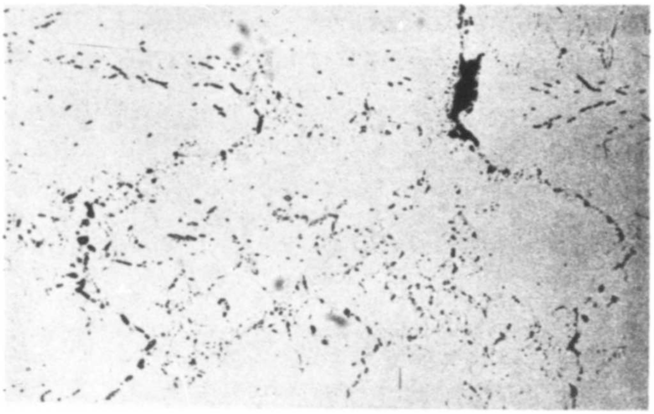
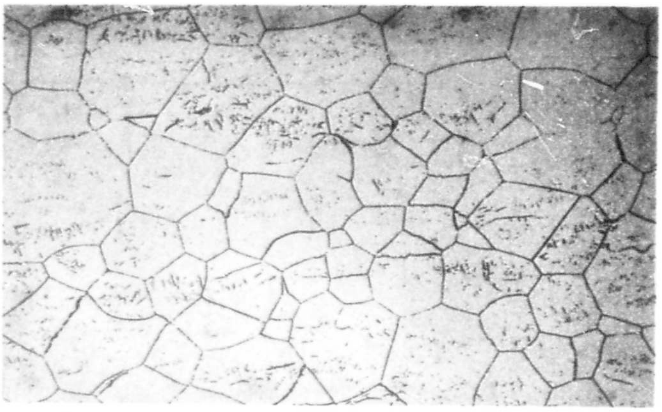


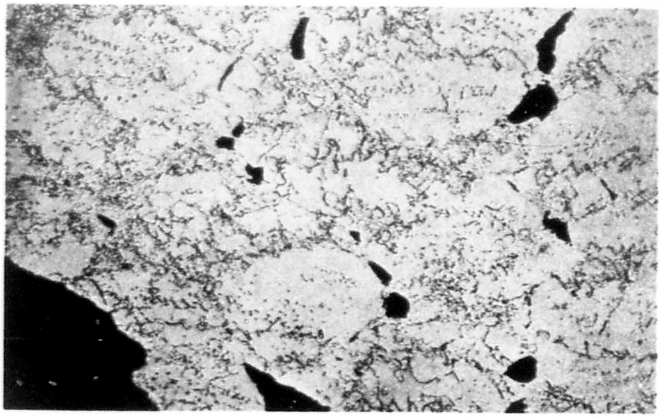
Figure 53. Microstructure of Alloy No. 7 (Cb-10.6W-30.8Hf) after Creep-Rupture Testing at 2000°F and 20,000 psi. Rupture Life: 92.3 Hours. Elongation: 41.0 Percent.

Etchant: 50p Lactic Acid - 3p HNO_3 - 2 drops HF.

(a) Neg. No. 25980
Magnification: 200X
Grip Section



(b) Neg. No. 25981
Magnification: 200X
Fracture



(c) Neg. No. 25982
Magnification: 500X
Gage Section

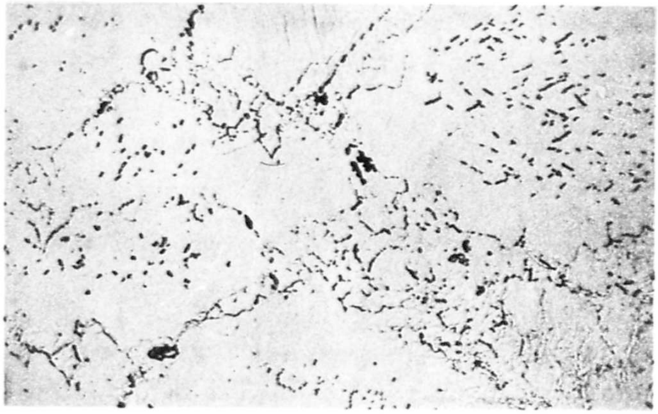


Figure 54. Microstructure of Alloy No. 30 (Cb-14.2W-28.8Hf) after Creep-Rupture Testing at 2000°F and 20,000 psi. Rupture Life: 199 Hours. Elongation: 51.7 Percent.

Etchant: 50p Lactic Acid - 3p HNO_3 - 2 drops HF.

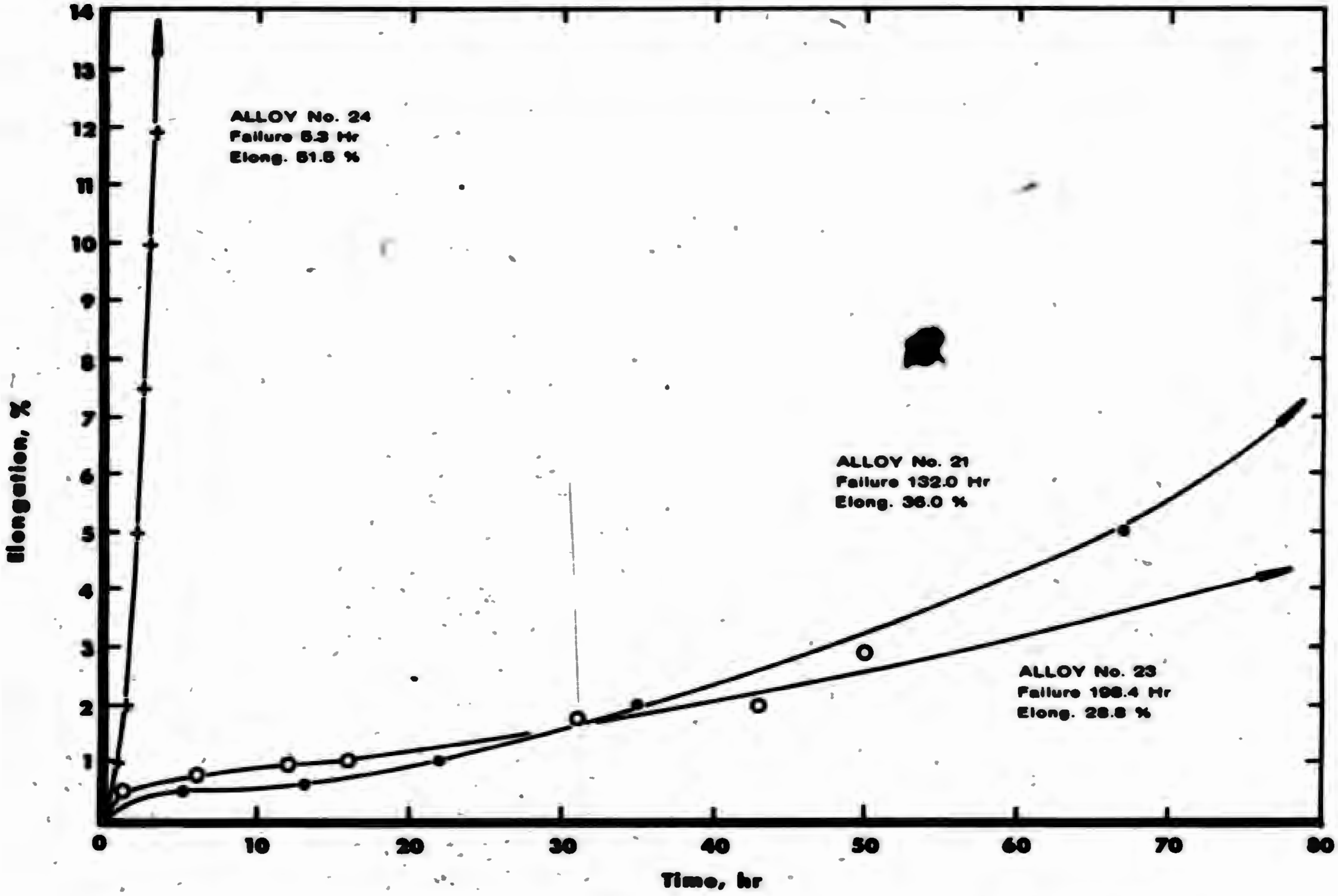


Figure 55. Creep-Rupture Curves for Recrystallized Alloys No. 21 (Cb-14.4W-35.9Hf), 23 (Cb-15.1W-34.8Hf-1.9Re), and 24 (Cb-16.9W-33.2Hf-6.3Ti) Tested at 2000°F and 20,000 psi.

the effect of titanium since this element enhanced oxidation resistance. A 6.3 percent addition of titanium in Alloy No. 24 (Cb-16.9W-33.2Hf-6.3Ti) caused a gross deterioration in creep-rupture strength. Figure 55 compares the creep curve for this alloy with the curve for Alloy No. 21 (Cb-14.4W-35.9Hf) at a stress of 20,000 psi. A further reduction in creep-rupture strength was found when the level of titanium was increased to 11.0 percent in Alloy No. 25 (Cb-16.7W-35.2Hf-11.0Ti) - see Table XXXIII.

Tests run on Alloys No. 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C) and No. 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) showed the carbon + nitrogen addition and the carbon addition alone to be equally ineffective for improving creep-rupture strength of the titanium bearing alloy. This fact is readily seen from the comparative curves plotted in Figure 56. The second phase particles in these alloys are probably too coarse to effectively enhance creep resistance.

Creep-rupture data were also obtained on Alloys No. 27 and No. 29 at a stress of 12,500 psi. These results were only slightly improved over the 20,000 psi results as seen from the data in Table XXXIII. The creep-rupture behavior of these two alloys classifies them below Alloy No. 6 (Cb-9.8W-1.6Hf) which was the lowest strength Cb-W-Hf ternary alloy evaluated during the program.

Two final creep-rupture tests were performed on Alloys No. 27 and No. 29 at 12,500 psi with the alloys in the stress-relieved condition, 1 hour at 2200°F. This heat-treatment relative to the recrystallized condition resulted in further weakening of the alloys indicative of a higher degree of instability of the alloys in the stress-relieved condition. Creep-rupture curves for Alloy No. 29 for the two conditions of heat-treatment are compared in Figure 57.

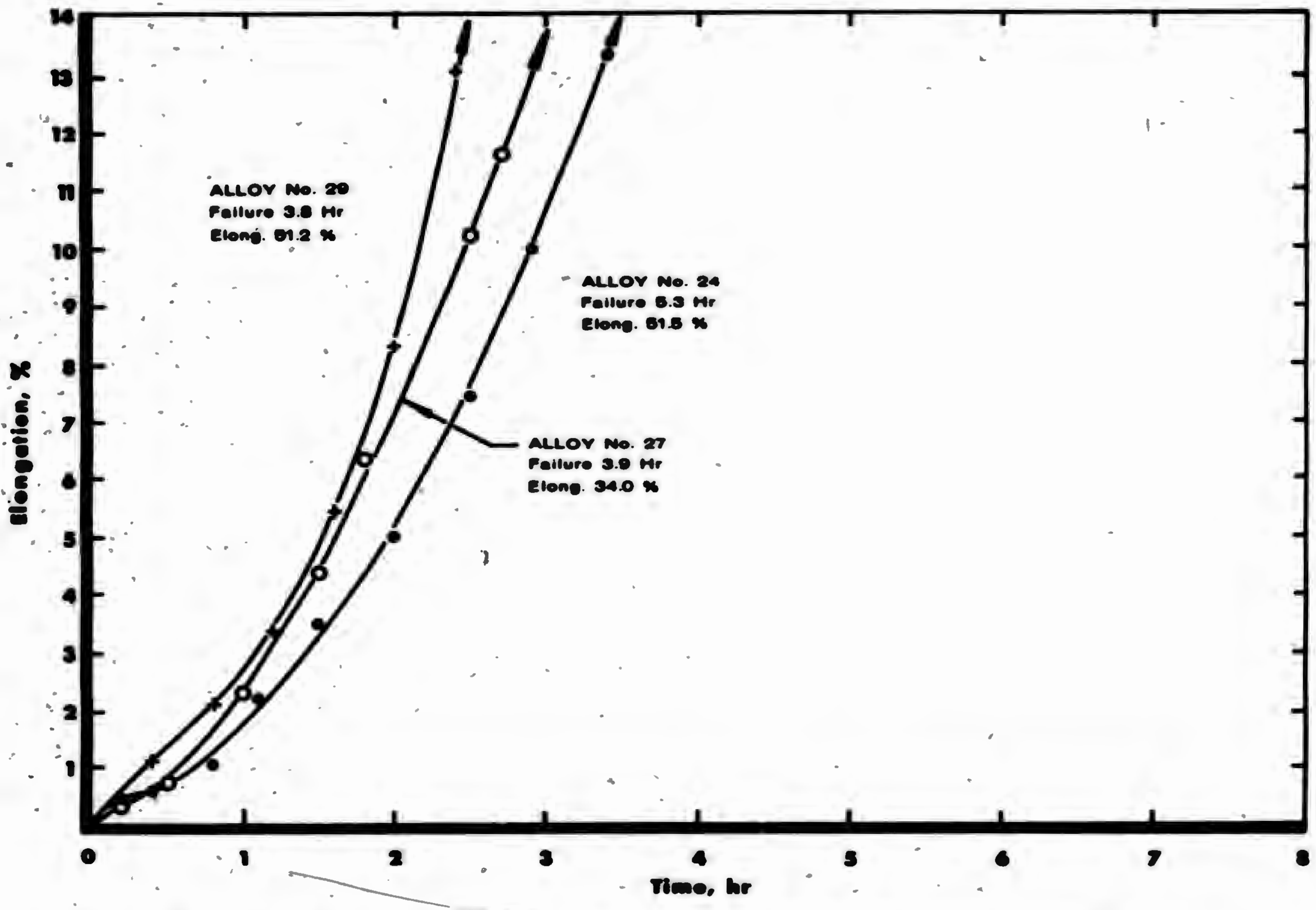


Figure 56. Creep-Rupture Curves for Recrystallized Alloys No. 24 (Cb-16.9W-33.2Hf-6.3Ti) 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C), and 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) Tested at 2000°F and 20,000 psi.

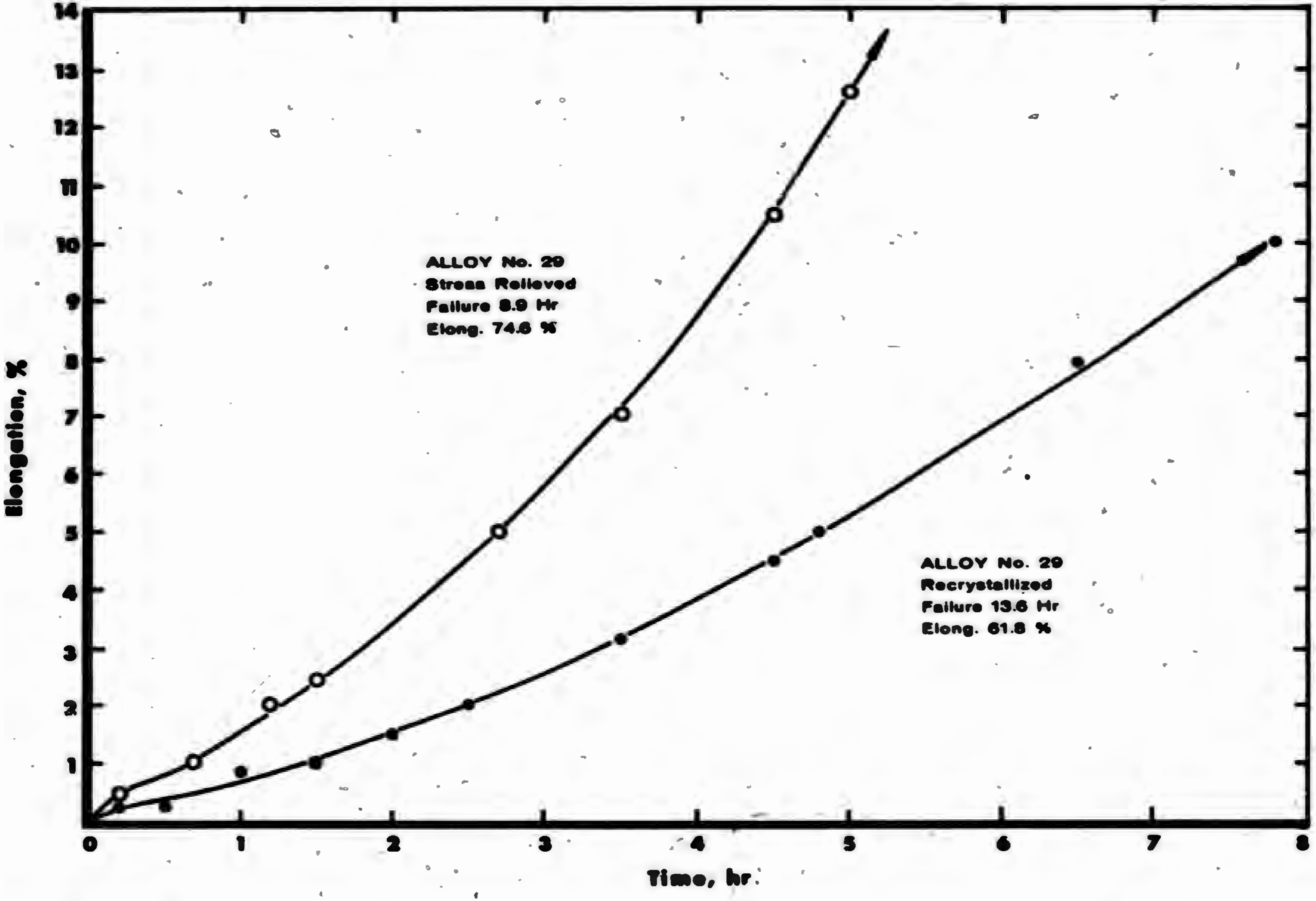


Figure 57. Creep-Rupture Curves for Stress Relieved (2200°F) and Recrystallized (2800°F) Alloy No. 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) Tested at 2000°F and 12,500 psi.

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SECTION VII

OXIDATION EVALUATION

The alloys were evaluated for their oxidation resistance at 2000 and 2200°F. Tests were conducted in flowing air (two standard cubic feet per hour) for two and/or twenty hours; and some of the more oxidation resistant Cb-W-Hf compositions were tested for times of 65 and 100 hours at 2000°F. Specimens were either cylindrical (approximately 0.25-inch diameter by 0.285- to 0.51-inch long) or rectangular (approximately 0.5-inch by 0.2-inch by 0.1- to 0.2-inch) ground from fabricated and annealed stock of the alloys. Specimens of the few alloys which were not fabricated successfully were prepared from cast material which had been given a prior homogenization treatment at 3000°F. Final surface preparation of the specimens consisted of a hand polish with 320 grit paper and a thorough rinse with acetone.

Before testing, the specimens were measured and weighed together with their alumina containment crucibles. The specimens, in open crucibles, were tested in a horizontal tube furnace. Following exposure and removal of the specimens from the furnace, the crucibles were covered immediately to prevent loss of any oxide which spalled during cooling. After cooling to room temperature, each specimen and crucible was reweighed to determine weight gain. The oxidized specimens were examined metallographically for measuring the amount of metal loss per side and determining the depth of contamination by direct measurement and/or microhardness traverses. The principal criterion used for oxidation resistance was total penetration in mils per side defined as the total measurement of metal loss + depth of contamination.

Post-test X-ray diffraction analyses, using a diffractometer, were conducted to obtain an indication of the identity of the oxidation reaction products of Alloy No. 9 (Cb-23.0W-26.5Hf). The identification of these products, present in different layers, was attempted by diffracting the surface of a metallographically mounted specimen after each successive removal of a layer by grinding. These data were assumed to typify results which could be expected from the other high-hafnium content compositions after oxidation.

7.1 Cb-W-Ta TERNARY ALLOYS

The oxidation of the five Cb-W-Ta alloys was characterized by appreciable weight gain and metal loss, high rate of oxygen contamination, and the formation of a non-adherent, voluminous, oxide scale.

The data presented in Table XXXIV for cylindrical specimens tested 2 and 20 hours at 2200°F show that Alloy No. 2 (Cb-9.8W-28.3Ta) experienced less weight gain and metal loss than the other Cb-W-Ta alloys. Alloys No. 1 (Cb-10.3-15.6Ta) and No. 5 (Cb-16.9W-23.8Ta) were the next most resistant alloys, followed by Alloy No. 3 (Cb-25.1W-15.8Ta). Alloy No. 4 (Cb-24.6W-31.6Ta), which oxidized the most rapidly of this group of alloys, was almost completely oxidized at the end of the 20-hour test. Relating these results to alloy composition, metal loss increased with increasing tungsten content. For the low tungsten content alloys, 10 percent, metal loss decreased when the tantalum content was increased from approximately 15 to 30 percent; but, this trend was reversed for the alloys with higher tungsten, 25 percent.

Although the differences in metal loss shown by the Cb-W-Ta alloys were noteworthy, the most significant result of oxidation evaluation of these materials was their very rapid contamination. In all cases, the entire cross section of the specimens was contaminated within 2 hours as indicated by microhardness traverses. Representative of these data are the traverses run on Alloy No. 5 as shown in Figure 58. It is to be expected that the large increase in hardness caused by contamination will generally have a detrimental effect on the mechanical properties of these alloys.

A microstructure of the metal-metal oxide interface for the Cb-W-Ta alloys following oxidation testing is shown in Figure 59, a photomicrograph of Alloy No. 5 after a 2-hour test at 2200°F. Typical of these alloys was the preferential oxidation in the grain boundaries and in the grains adjacent to the surface. The microstructures of the specimens oxidized for 20 hours was not appreciably different, except that the extent of the oxidization was greater.

None of the Cb-W-Ta alloys formed a very adherent oxide scale, as was evidenced by the large amount of spalling that occurred upon cooling the specimens from 2200°F to room temperature. Even though some of the scale did adhere, as is shown in Figure 59, it was generally of non-uniform thickness and discontinuous, and it is doubtful that it provided appreciable protection to the alloy.

The data obtained for 20-hour tests at 2000°F on rectangular specimens of the Cb-W-Ta alloys are shown in Table XXXV. Except for Alloy No. 2, weight gains for these compositions were slightly less at 2000°F than at 2200°F. Again, Alloy No. 4 was the least oxidation resistant of the five alloys, but the relative relationship between composition and metal loss for the others was different at 2000°F that at 2200°F. Also, the magnitude of metal loss for Alloys No. 1 and No. 2 was greater at the lower temperature. Regardless of these anomolies, it was again observed that the alloys were totally penetrated within 20 hours which, for the purpose of these tests, was considered the most significant result. The hardness traverse run on Alloy No. 5 after oxidation is presented in Figure 60. Because of the rapid oxidation and contamination of these compositions, subsequent work on alloys of the Cb-W-Ta system was terminated at this stage of the program.

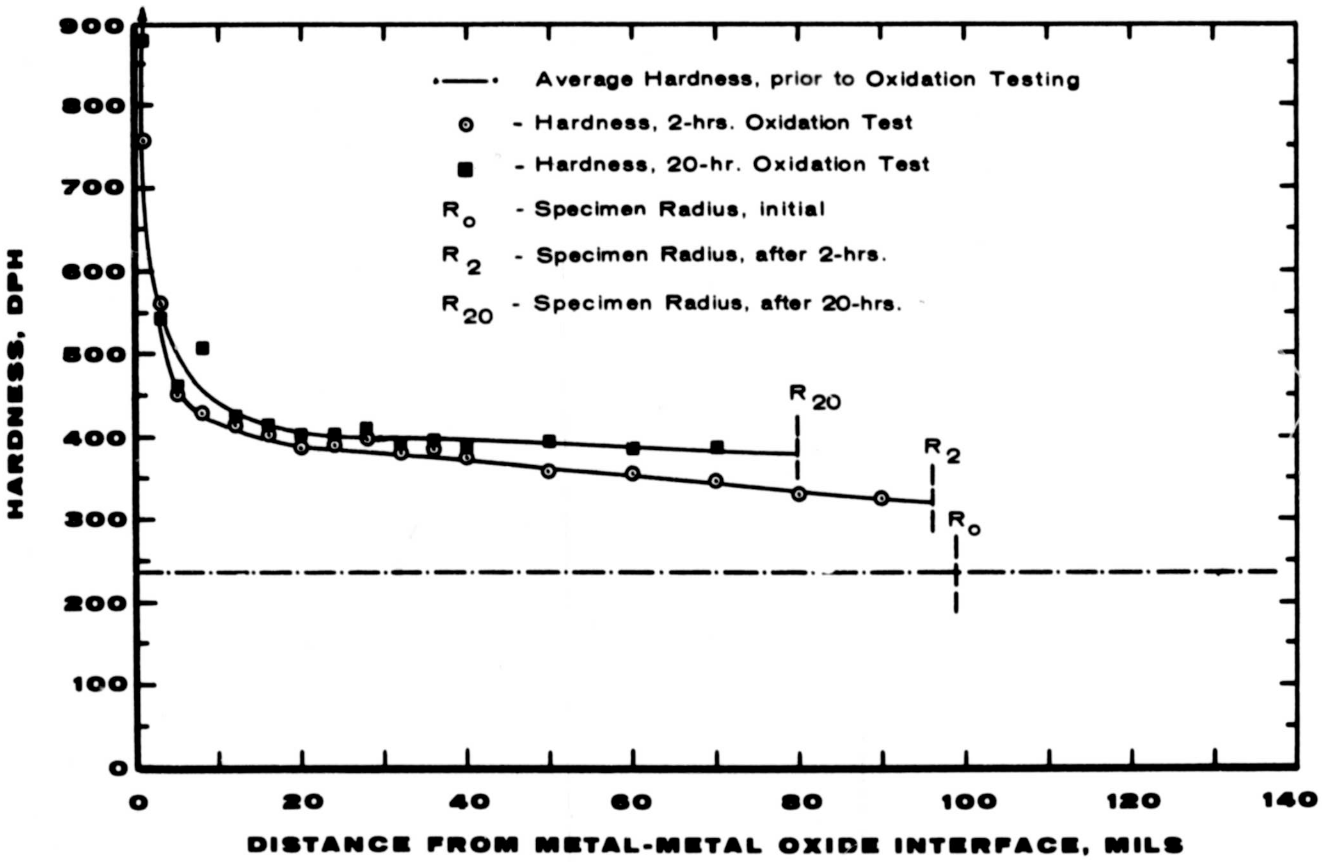
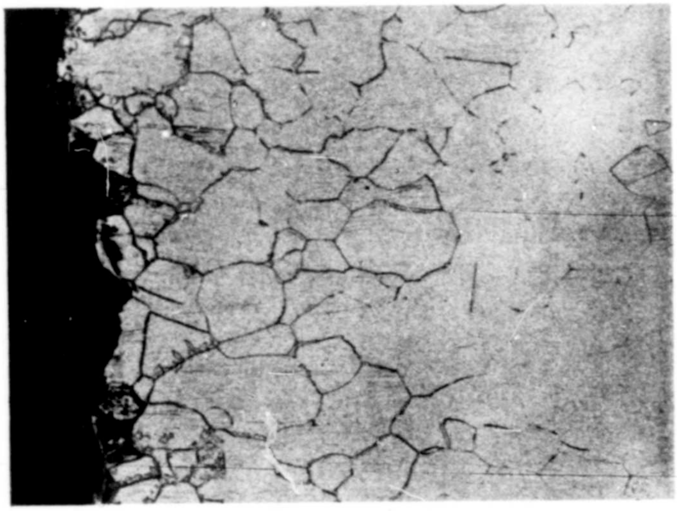


Figure 58. Contamination Hardening of Alloy No. 5 (Cb-16.9W-23.8Ta) after Air-Oxidation at 2200°F.



Neg. No. 23165

Figure 59. Microstructure of Alloy No. 5 (Cb-16.9W-23.8Ta) Air-Oxidized for Two Hours at 2200°F.

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3-10p HF

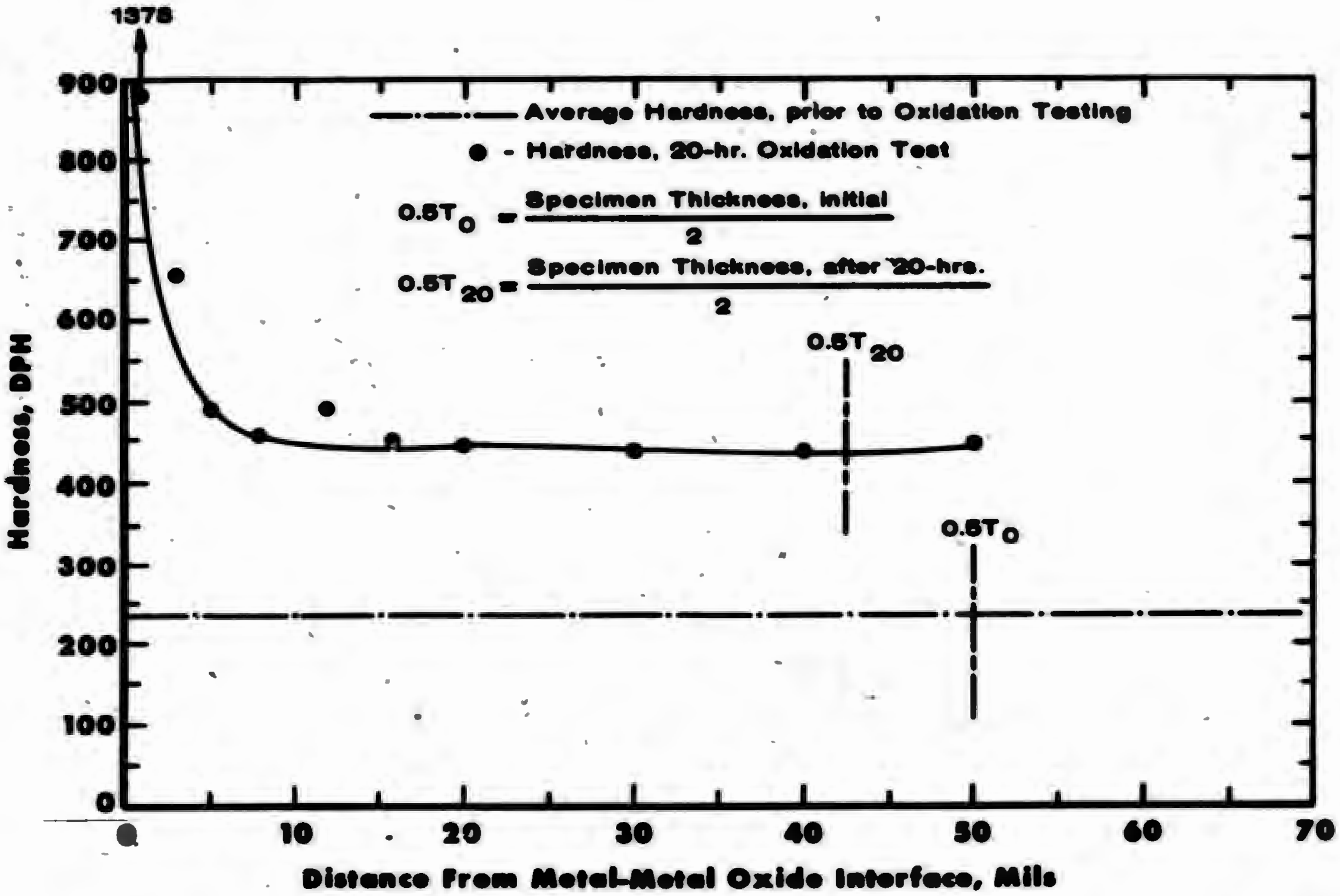


Figure 60. Contamination Hardening of Alloy No. 5 (Cb-16.9W-23.8Ta) after Air-Oxidation at 2000°F.

7.2 Cb-W-Hf TERNARY ALLOYS

The oxidation behavior of the Cb-W-Hf ternary alloys was of two types depending upon alloy composition: first, a type closely paralleling that of the Cb-W-Ta alloys discussed above and, second, a type resulting in oxidation product made up of sequential zones which included an outer oxide layer, an intermediate oxide layer, and an internally oxidized or contaminated layer followed by uncontaminated base metal. The first type was characteristic of the two alloys with low hafnium content, 2 to 4 percent, and the second type was characteristic of the other alloys which contained 18 to 35 percent hafnium.

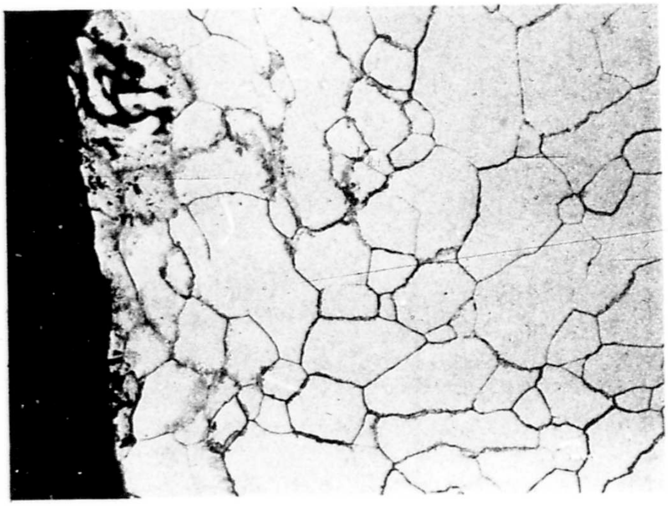
Oxidation data for the Cb-W-Hf alloys tested 2 and 20 hours at 2200°F can be found in Table XXXVI. Within the group, Alloys No. 6 through No. 10, representing the composition range Cb-(10-25)W-(2-30)Hf, the two types of oxidation behavior referred to above are evident.

The two alloys with lowest hafnium content, Alloys No. 6 (Cb-9.8W-1.6Hf) and No. 8 (Cb-24.1W-4.4Hf), experienced the highest weight gain and metal loss and were completely contaminated within 2 hours at this temperature. The microstructure of Alloy No. 8 after oxidation for 20 hours at 2200°F is presented in Figure 61. Like the Cb-W-Ta alloys, the scale has mostly spalled and oxidation has progressed in the grain boundaries and within the grains near the surface. The post test hardness traverses run on this alloy after 2 and 20 hours at this temperature and plotted in Figure 62 show complete contamination of the material for both times.

On the other hand, a very marked improvement in oxidation resistance was realized with increased hafnium content. Alloy No. 9 (Cb-23.0W-26.5Hf) was the most resistant composition -- unfortunately unfabricable. As seen in Figure 63, a photomicrograph of Alloy No. 9 after 2 hours at 2200°F, the product of oxidation is comprised of two oxide layers and an internally oxidized or contaminated layer adjacent to the base metal. These layers are separated by sharp interfaces. Spalling of the oxide on cooling the high hafnium content alloys was mostly, but not always, confined to the outer layer; however, in the area shown in Figure 63, no spalling had occurred. For the high hafnium content alloys, a dependence of spalling behavior upon tungsten content was apparent since alloys with tungsten contents less than 10 percent, Alloys No. 12 through No. 14, appeared to spall more than those compositions with greater than 10 percent tungsten. Therefore, the formation of an intermediate oxide layer on Alloys No. 12 through No. 14 was less certain because of this increased spallation tendency.

A hardness traverse across the specimen of Alloy No. 9 after oxidation for 2 hours at 2200°F (Figure 63) is plotted in Figure 64. Abrupt changes in hardness can be noted at the oxidation product interfaces with the hardness of the unaffected base metal returning to essentially the pre-test value.

The effectiveness of a high hafnium content in the Cb-W-Hf alloys for inhibiting contamination can be attributed to the stability of HfO_2, a



Neg. No. 23102

Figure 61. Microstructure of Alloy No. 8 (Cb-24.1W-4.4Hf) Air-Oxidized for Twenty Hours at 2200°F.

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF

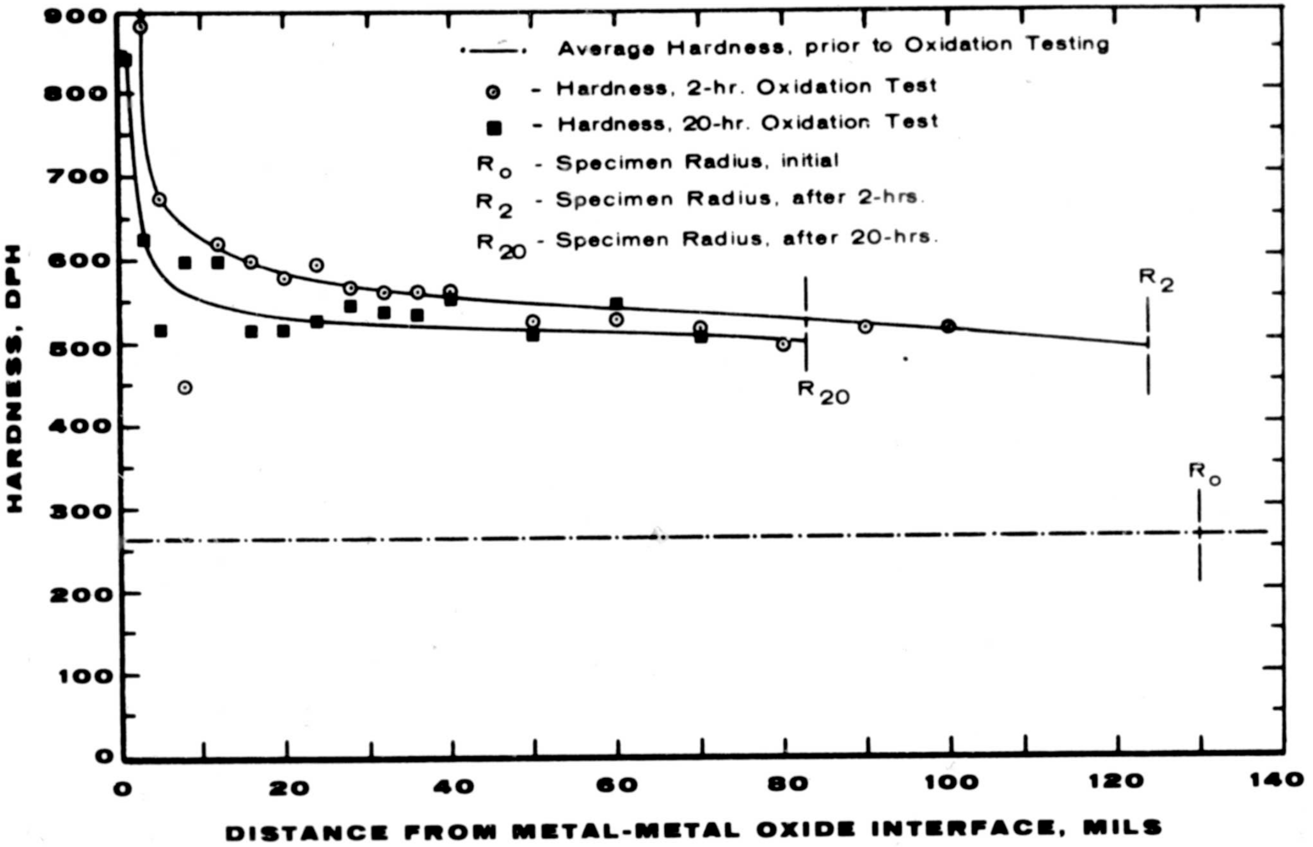
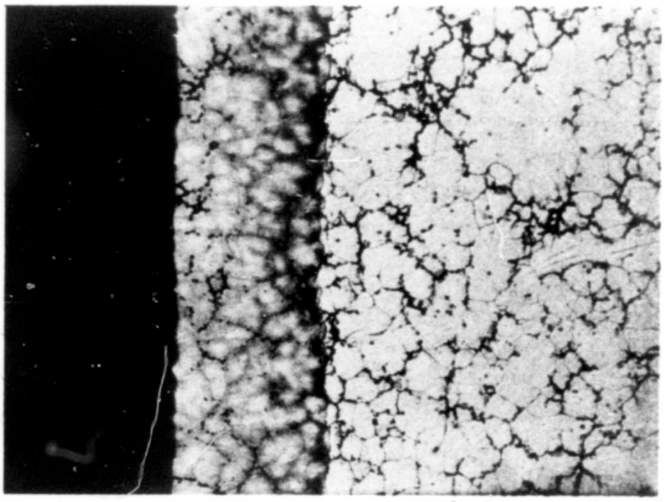


Figure 62. Contamination Hardening of Alloy No. 8 (Cb-24.1W-4.4Hf) after Air-Oxidation at 2200°F.



Neg. No. 21902

Figure 63. Microstructure of Cast Alloy No. 9 (Cb-23.0W-26.5Hf) Air-Oxidized for Two Hours at 2200°F.

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF

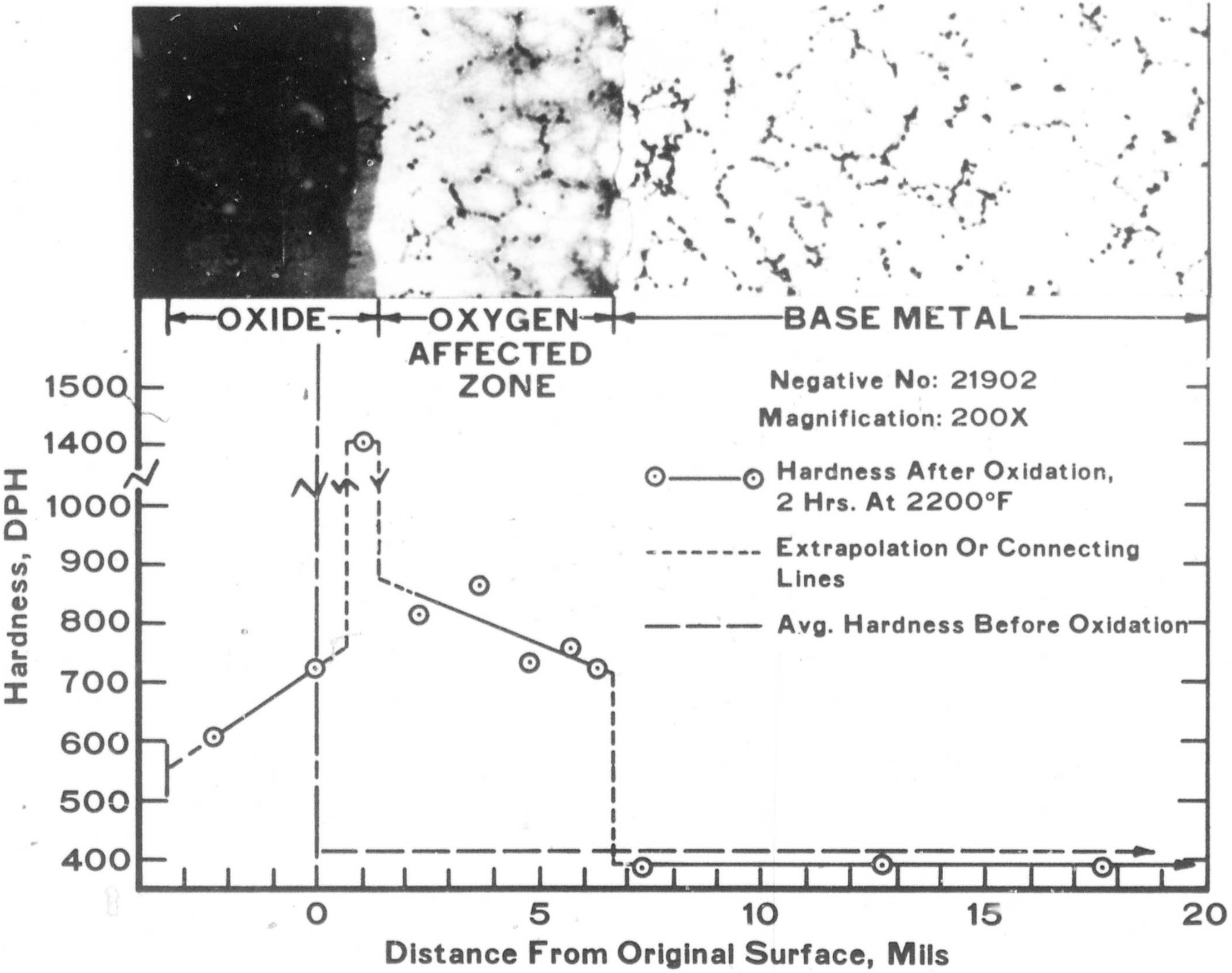


Figure 64. Hardness Traverse for Cast Alloy No. 9 (Cb-23.0W-26.5Hf) Air-Oxidized for Two Hours at 2200°F.

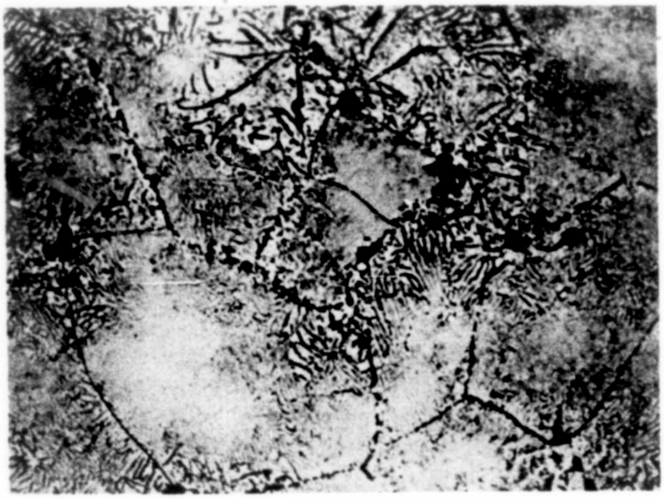
reaction product identified in the contaminated layer, as will be pointed out later. Hafnium, being less noble than either columbium or tungsten, serves as a sink for the oxygen and prevents its rapid diffusion through the parent metal. The reaction of hafnium with oxygen results in a two-phase, pearlitic-type structure of HfC_2 and the Cb-W solid solution as seen in Figure 65. Scaling of the alloy undoubtedly progresses through a series of complex reactions between oxygen, the Cb-W solid solution, and HfO_2. Hence, oxidation of these alloys proceeded by a combined mechanism of internal oxidation and scale formation.

Examination of the 20-hour, 2200°F, oxidation data for the Cb-W-Hf alloys (Table XXXVI) points to the fact that total penetration was dependent upon both the tungsten and hafnium contents. For the alloys containing greater than 20 percent hafnium, an apparent trend was a decrease in the rate of metal loss (scaling) with increasing tungsten content between 4 and 23 percent. For these same alloys the measured depth of contamination did not change much until the tungsten + hafnium content totaled approximately 50 percent, i.e., Alloys No. 9 and No. 31, at which point contamination rate decreased. These two alloys thus exhibited the best overall oxidation resistance of the ternary compositions.

The above results indicate that the permeability of the internally oxidized or contaminated zone for the diffusion of oxygen is probably significant in determining the depth of total penetration of these alloys. Other investigators have shown that tungsten additions to columbium reduce the oxygen solubility(9), which, in turn, will decrease the permeability. In the case of the Cb-W-high hafnium content alloys, following the formation of HfO_2 by internal oxidation, the matrix material in this zone can be considered a Cb-W solid solution. With increasing tungsten content of the alloys, the diffusion rate of oxygen through the matrix of this zone should decrease resulting in a decrease in the depth of contamination for a given test time. This would appear to offer a partial explanation for the improved oxidation resistance shown by Alloys No. 9 and No. 31, whose W + Hf content totaled approximately 50 percent and whose depths of contamination were less than those of the other alloys.

Tables XXXVII and XXXVIII list the oxidation data for the Cb-W-Hf alloys in 20-hour tests at 2000°F. As in the evaluation at 2200°F, Alloys No. 6 and No. 8 with the lowest hafnium content again showed relatively high weight gains, but there was appreciable difference in metal loss at 2000°F between the two alloys. The higher tungsten composition, Alloy No. 8, scaled much less than the lower tungsten composition, Alloy No. 6; however, both alloys were again completely contaminated. The post-test microhardness traverse for Alloy No. 8 is plotted in Figure 66.

Of the compositions containing greater than 20 percent hafnium, those with relatively high hafnium + tungsten contents, Alloys No. 9, No. 30, No. 31, No. 32, No. 21, and No. 22, exhibited the lowest weight gains which was consistent with the data obtained at 2200°F. Inconsistencies were observed for the compositions containing relatively low tungsten content,



Neg. No. 23477

Figure 65. Internally Oxidized Zone of Cast Alloy No. 9 (Cb-23.0W-26.5Hf) Air-Oxidized for Two Hours at 2200°F.

Magnification: 1500X Etchant: 50p Acetic Acid - 50p HNO_3 - 10p HF

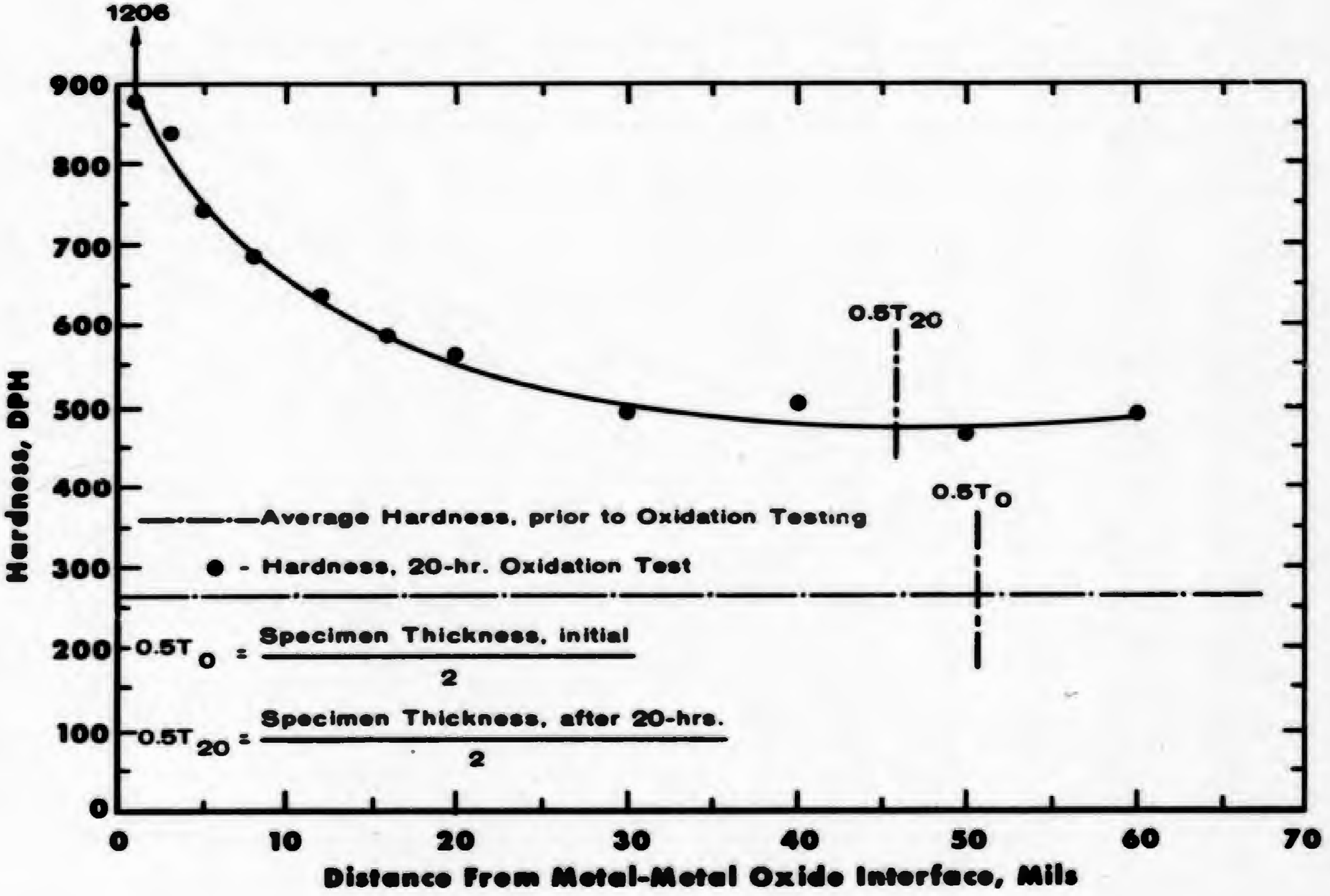


Figure 36. Contamination Hardening of Alloy No. 8 (Cb-24.1W-4.4Hf) after Air-Oxidation at 2000°F.

approximately 10 percent or less, which showed an increased weight gain at the lower temperature. In fact, the specimens of the four alloys with tungsten contents less than 10 percent were completely oxidized to scale in 20 hours at 2000°F. (Recall that at 2200°F the trend was higher scaling rates for those alloys containing greater than 20 percent hafnium when the tungsten content was less than 10 percent. This trend was magnified at 2000°F.)

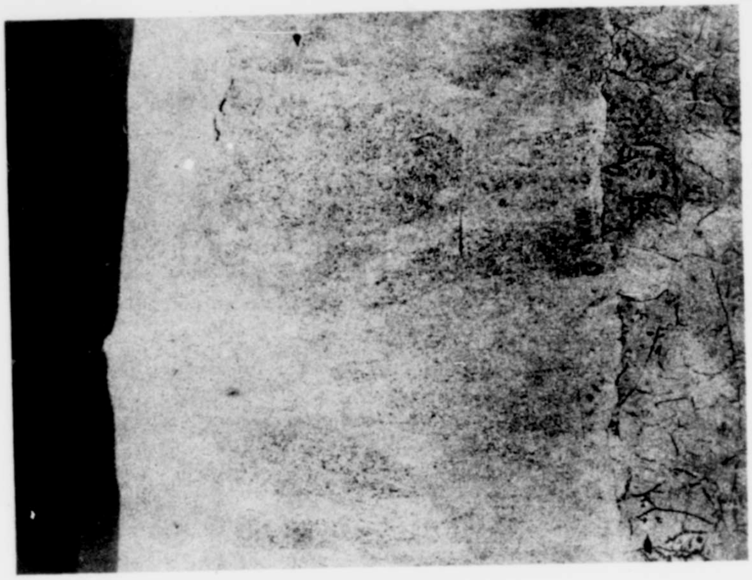
From the microhardness traverses of the 2000°F oxidized specimens, the Cb-W-Hf ternaries were found to be completely penetrated by oxygen except for Alloys No. 9, No. 31, No. 21, and No. 22 whose tungsten + hafnium contents totaled approximately 50 percent. Some of the alloys, therefore, were more severely contaminated at 2000°F than at 2200°F. The factor which may have caused this decrease in oxidation resistance at the lower temperature was a lesser tendency toward formation of the intermediate oxide layer at 2000°F than at 2200°F. An inverse relation between oxidation resistance and temperature has been observed by other investigators⑩ working on similar alloy systems and has been explained by the formation of a double oxide, $Cb_2O_5 \cdot 6HfO_2$, at higher temperatures. This oxide possibly provides a certain amount of protection against oxidation. Previous results of metallographic examination and the X-ray diffraction analysis of scales from Alloy No. 9 (to be reported) after oxidation testing at 2200°F revealed the presence of an intermediate oxide layer which appeared to be largely made up of $Cb_2O_5 \cdot 6HfO_2$. As shown in Figure 67, the post-oxidation microstructure of Alloy No. 31, the more oxidation resistant alloys formed an intermediate oxide layer at 2000°F. This layer was assumed to be $Cb_2O_5 \cdot 6HfO_2$.

A review of the data for the 20-hour, 2000°F oxidation tests for the Cb-W-Hf alloys results in the display plotted in Figure 68. The dependence of oxidation behavior on the tungsten and hafnium contents is clearly evident. These results point out the justification from oxidation evaluation and tempered by the alloys' fabrication behavior for selection of the composition, Cb-15W-35Hf, for further alloying to enhance properties.

The oxidation test time for the ternary base, Alloy No. 21, together with Alloy No. 22 was extended to 65 hours at 2000°F. Of interest is a comparison of these data with those obtained for the 20-hour tests -- see Table XXXVIII. Although exposure time varies more than a factor of 3, the total penetration of the alloys less than doubled between 20 and 65 hours. This fact suggests parabolic behavior. The microstructures of the oxidized specimens and plots of the post-test microhardness traverses for Alloy No. 21 for the two test times are shown in Figures 69 and 70.

7.2.1 Oxidation Product Identification Studies

X-ray analyses, using a diffractometer, were carried out on an oxidized specimen of Alloy No. 9 (Cb-23.0W-26.5Hf) in an attempt to identify the reaction products. The specimen had been oxidized for 20 hours at 2200°F. To detect changes in the type of oxides formed on the specimen, diffraction patterns were obtained from the surface after successive grinding



Neg. No. 24886

Figure 67. Microstructure of Alloy No. 31 (Cb-15.1W-34.1Hf) Air-Oxidized for Twenty Hours at 2000°F.

Magnification: 200X Etchant: 50p Acetic Acid - 50p HNO_3-10p HF

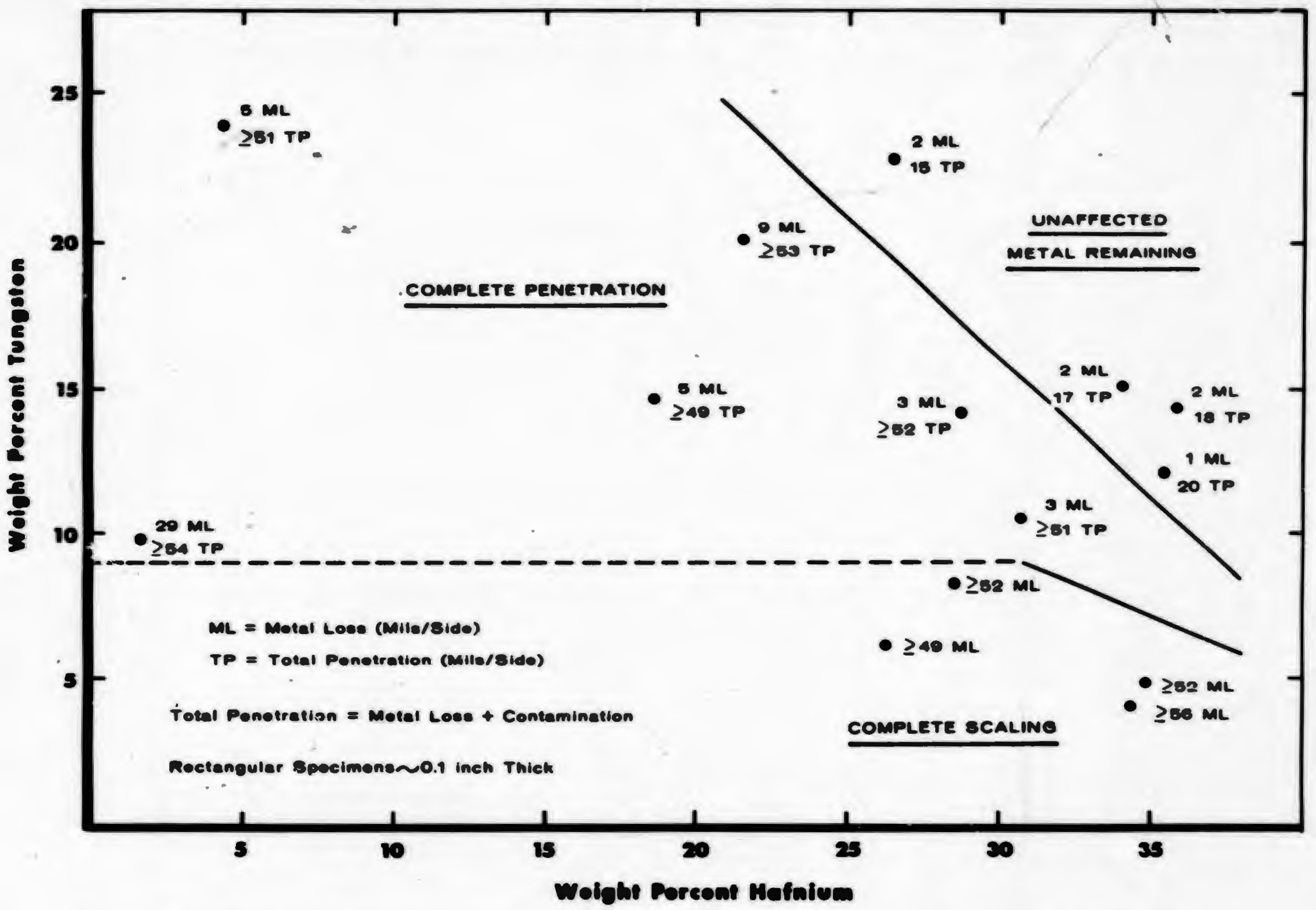
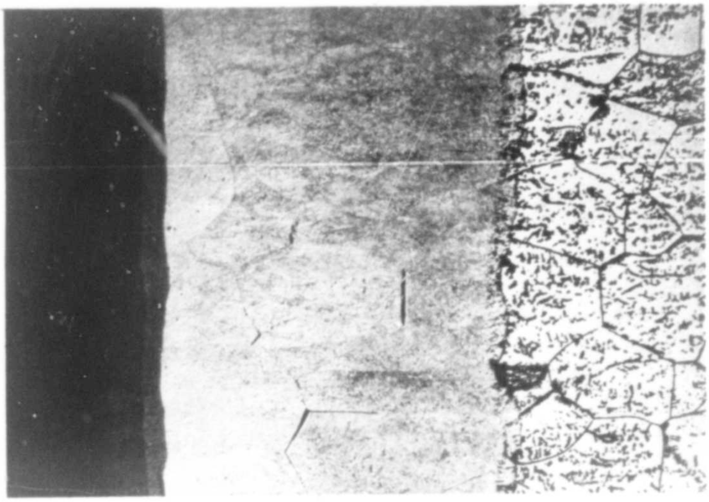


Figure 68. Effect of Tungsten and Hafnium Contents on the Oxidation Behavior of Cb-W-Hf Alloys Tested in Air for Twenty Hours at 2000°F.



(a) Neg. No. 25993
20 Hours at 2000°F

(b) Neg. No. 26035
65 Hours at 2000°F

Figure 69. Microstructure of Alloy No. 21 (Cb-14.4W-35.9Hf) Air-Oxidized for Twenty and Sixty-Five Hours at 2000°F.

Magnification: 130X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 Drops HF

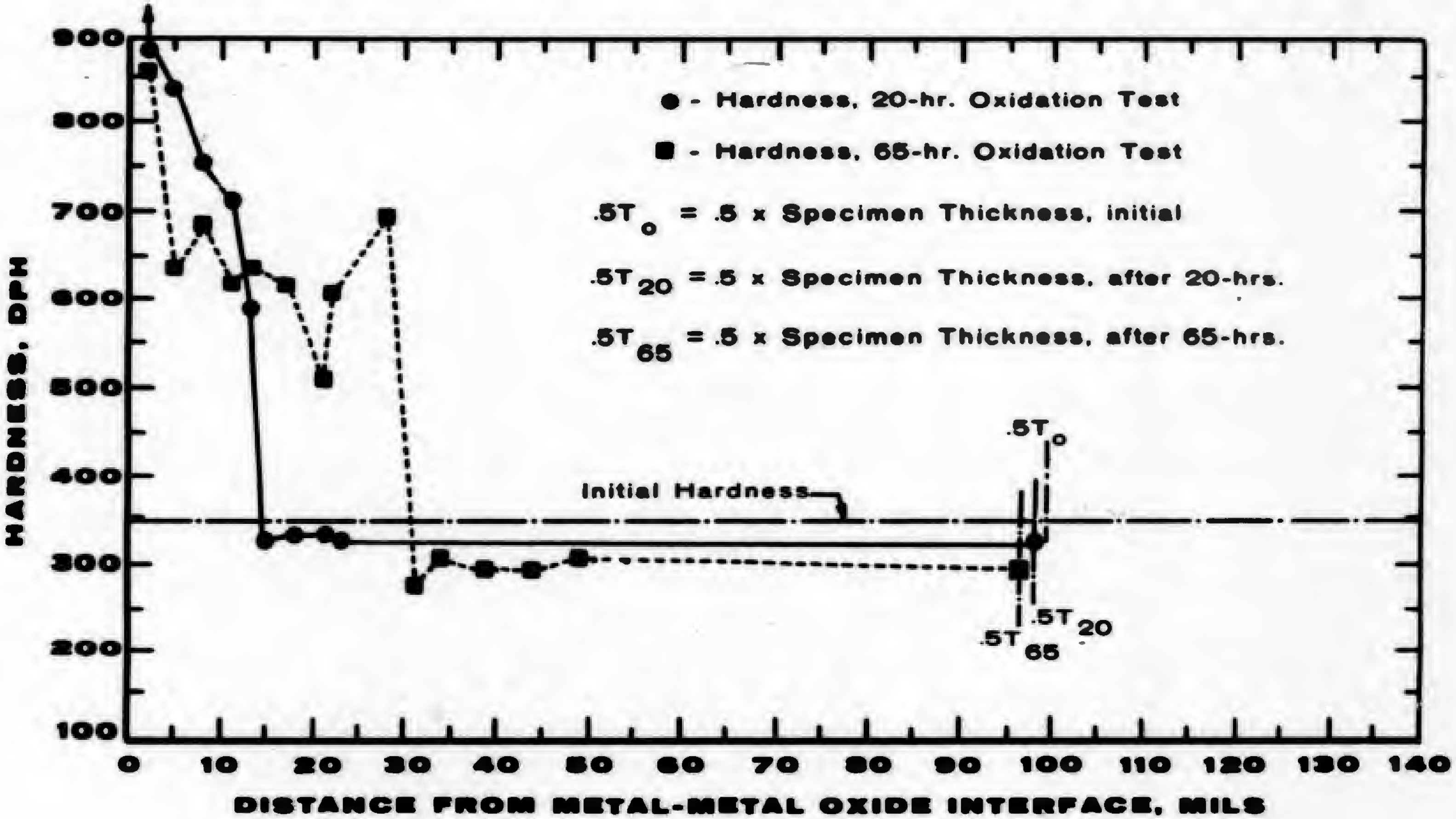


Figure 70. Contamination Hardening of Alloy No. 21 (Cb-14.4W-35.9Hf) after Air-Oxidation at 2000°F.

operations to remove various amounts of the oxidation products. The patterns were very complex, comprising more than one oxide phase, and interpretation was difficult. Emphasis in interpretation was placed upon the change in relative intensity of the prominent diffraction peaks attributed to the various oxide phases as the oxidation products were abraded from the surface of the specimen. The d-values calculated from the patterns were compared with those listed by ASTM for Cb_2O_5, $Cb_2O_5 \cdot 6ZrO_2$ (iso-structural with $Cb_2O_5 \cdot 6HfO_2$), and HfO_2. From the X-ray data shown in Table XXXIX, the significant trend was a decrease in intensity of lines attributed to Cb_2O_5-type oxides, which predominated at and near the surface, and a corresponding increase in intensity of a principal peak from $Cb_2O_5 \cdot 6HfO_2$ as up to 11 mils of oxidation product were removed. A peak suggesting the presence of HfO_2 was observed after removing 11 mils from the specimen. Intensification of HfO_2 and fading of the other oxides was seen at a depth of 18 mils. Relating metallographic examination of this specimen to the X-ray data presented here as well as the work of Kofstad and Kvernes(10), it appears that a Cb_2O_5-type oxide predominates near the surface, followed by a layer of $Cb_2O_5 \cdot 6HfO_2$, then the zone of contamination or internal oxidation with HfO_2 as the principal oxide.

7.3 Cb-15W-35Hf WITH ADDITIONS OF RHENIUM, TITANIUM, COBALT, ALUMINUM, VANADIUM, CARBON, AND NITROGEN

The seven alloys based upon the ternary composition of nominally Cb-15W-35Hf containing additions of rhenium, titanium, cobalt, aluminum, vanadium, carbon, and nitrogen were evaluated for their oxidation resistance only at 2000°F. In all cases the features of oxidation remained the same as previously reported for the base; but the magnitudes of metal loss, contamination, and total penetration were noticeably different.

The oxidation data for the more complex alloys can be found in Table XL. Data for the ternary base, Alloy No. 21, are included for comparison. Pertinent effects of the alloying additions are noted below although it is recognized that the analyzed differences in tungsten and hafnium contents of these alloys may be of significance.

The small rhenium addition in Alloy No. 23 caused an increase in the rate of scaling and a small decrease in the rate of contamination compared to Alloy No. 21; however, the resultant total penetration of the rhenium bearing alloy was slightly greater for both test times, 20 and 65 hours.

A 2.8 percent cobalt addition in Alloy No. 26 was quite effective in improving oxidation resistance for up to 20 hours, but scaling of this alloy rapidly increased after this time and total penetration was approximately the same as the ternary base after 65 hours.

Scaling rate increased with titanium content in Alloys No. 24 and No. 25. At the same time contamination rate decreased as might be expected from the chemical similarity of hafnium and titanium. The total penetration of these alloys was essentially the same from offsetting effects and both alloys were more oxidation resistant than Alloy No. 21. Because of its beneficial effect, a nominal addition of 5 percent titanium was included with those alloys containing carbon, nitrogen, aluminum, and vanadium.

The microstructures of Alloys No. 23, No. 26, No. 24, and No. 25 after oxidation testing for 65 hours at 2000°F are shown in Figures 71 and 72. The post-test hardness traverses performed on these specimens followed the same pattern as those for the ternary base (Figure 70).

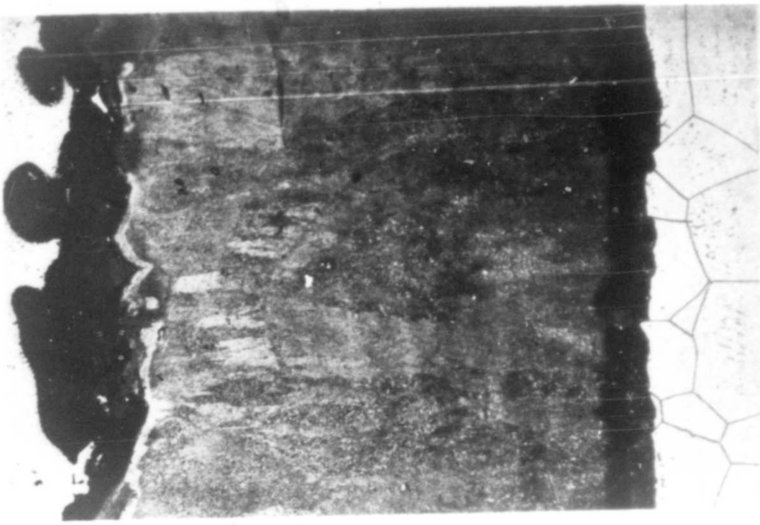
There was essentially no effect of the carbon and nitrogen additions in Alloys No. 27 and No. 29 on oxidation resistance since the data for these two alloys were comparable to that obtained on Alloy No. 24. One unexplainable deviation was the somewhat greater depth of contamination for Alloy No. 27 after 65 hours relative to the depth measured for the other two alloys.

The most oxidation resistant composition evaluated for times up to 65 hours was Alloy No. 28 by virtue of its shallow depths of contamination. Unfortunately, this material was not fabricated successfully.

Typical oxide spalling tendencies of these more highly alloyed compositions are shown in Figure 73, the actual specimens of Alloys No. 27, No. 29, and No. 28 following test.

The 2000°F oxidation data (weight gain and total penetration) for Alloys No. 21 (Cb-14.4W-35.9Hf), No. 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C), No. 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C), and No. 28 (Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V) are plotted against the square root of test time in Figures 74 and 75. Alloys No. 27 and No. 29 approximate the parabolic rate law for up to 100 hours and Alloy No. 21 for up to 65 hours. Only two data points were obtained for Alloy No. 21, however. Alloy No. 28 departed from parabolic behavior between 20 and 65 hours of test time showing an acceleration in oxidation rate.

In summary, relative to the basic ternary, the alloying additions investigated generally promoted higher scaling rates, but lesser depths of contamination. The net result was that these alloys showed improved oxidation resistance over the base except for the rhenium bearing composition.

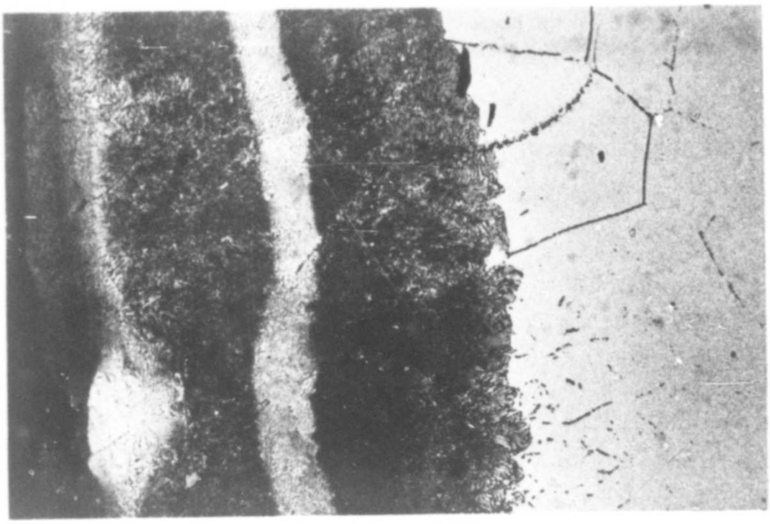


(a) Neg. No. 26037
Magnification: 130X
Alloy No. 23

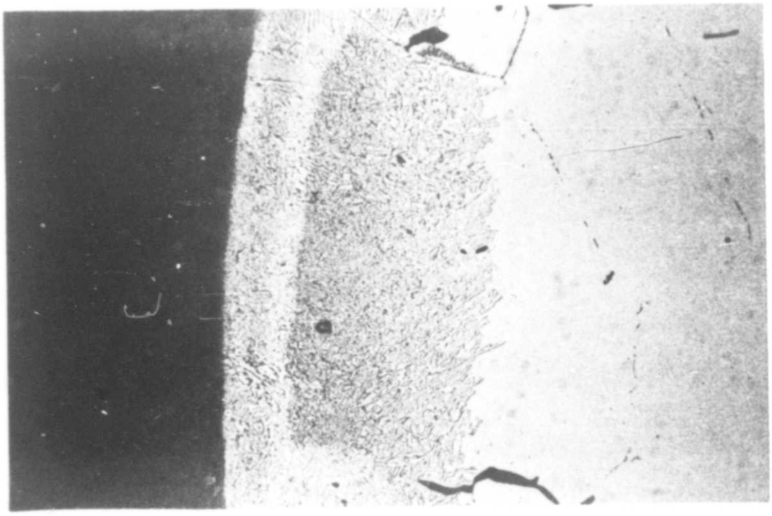
(b) Neg. No. 27125
Magnification: 280X
Alloy No. 26

Figure 71. Microstructures of Alloys No. 23 (Cb-15.1W-34.8Hf-1.9Re) and 26 (Cb-17.5W-33.5Hf-2.8Co) Air-Oxidized for Sixty-Five Hours at 2000°F.

Etchant: 50p Lactic Acid - 3p HNO_3 - 2 Drops HF



(a) Neg. No. 27123
Alloy No. 24



(b) Neg. No. 27124
Alloy No. 25

Figure 72. Microstructures of Alloys No. 24 (Cb-16.9W-33.2Hf-6.3Ti) and 25 (Cb-16.7W-35.2Hf-11.0Ti) Air-Oxidized for Sixty-Five Hours at 2000°F.

Magnification: 200X Etchant: 50p Lactic Acid - 3p HNO_3 - 2 Drops HF

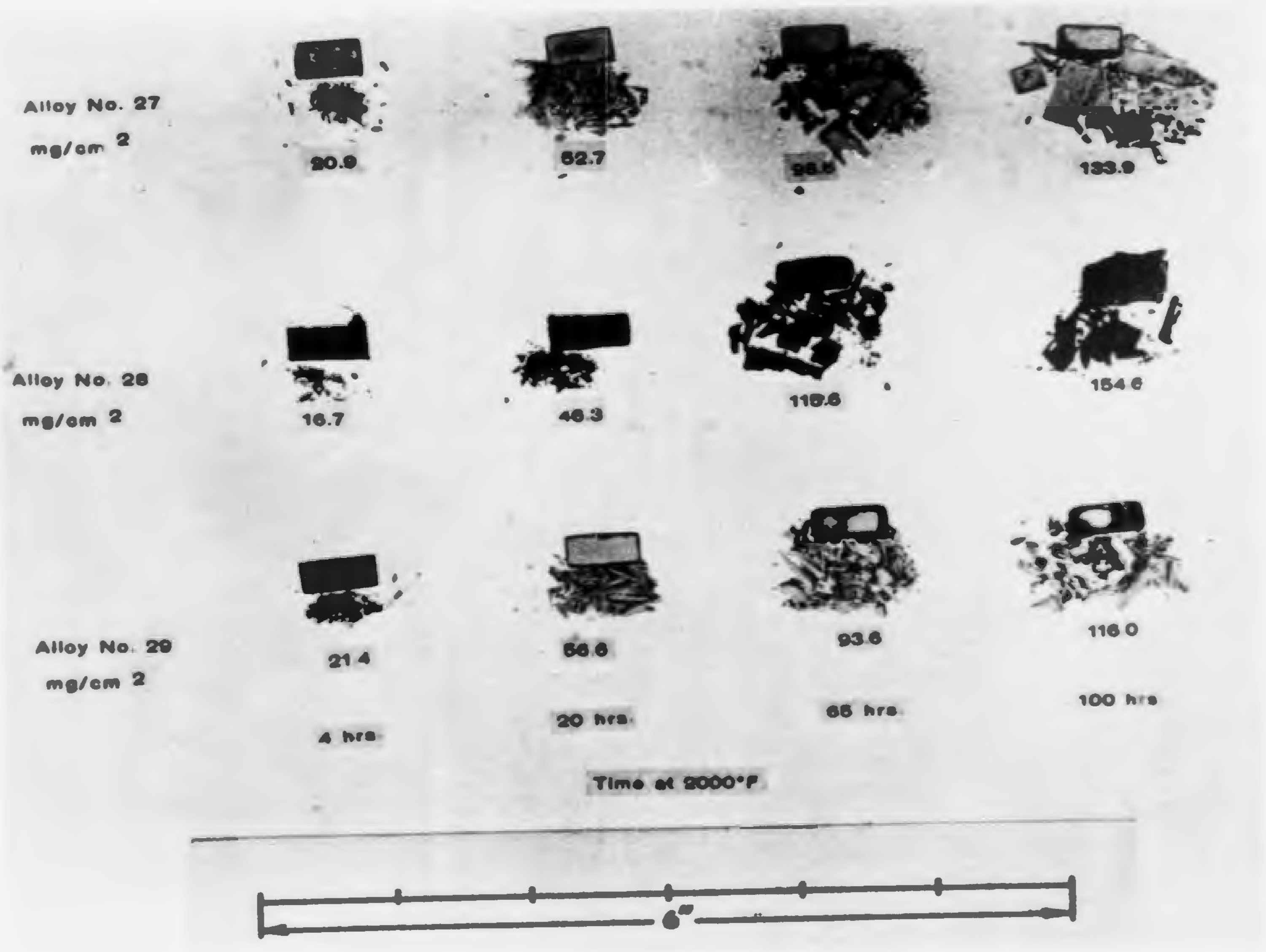


Figure 73. Specimens of Alloys No. 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C), 28 (Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V) and 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) Air-Oxidized at 2000°F.

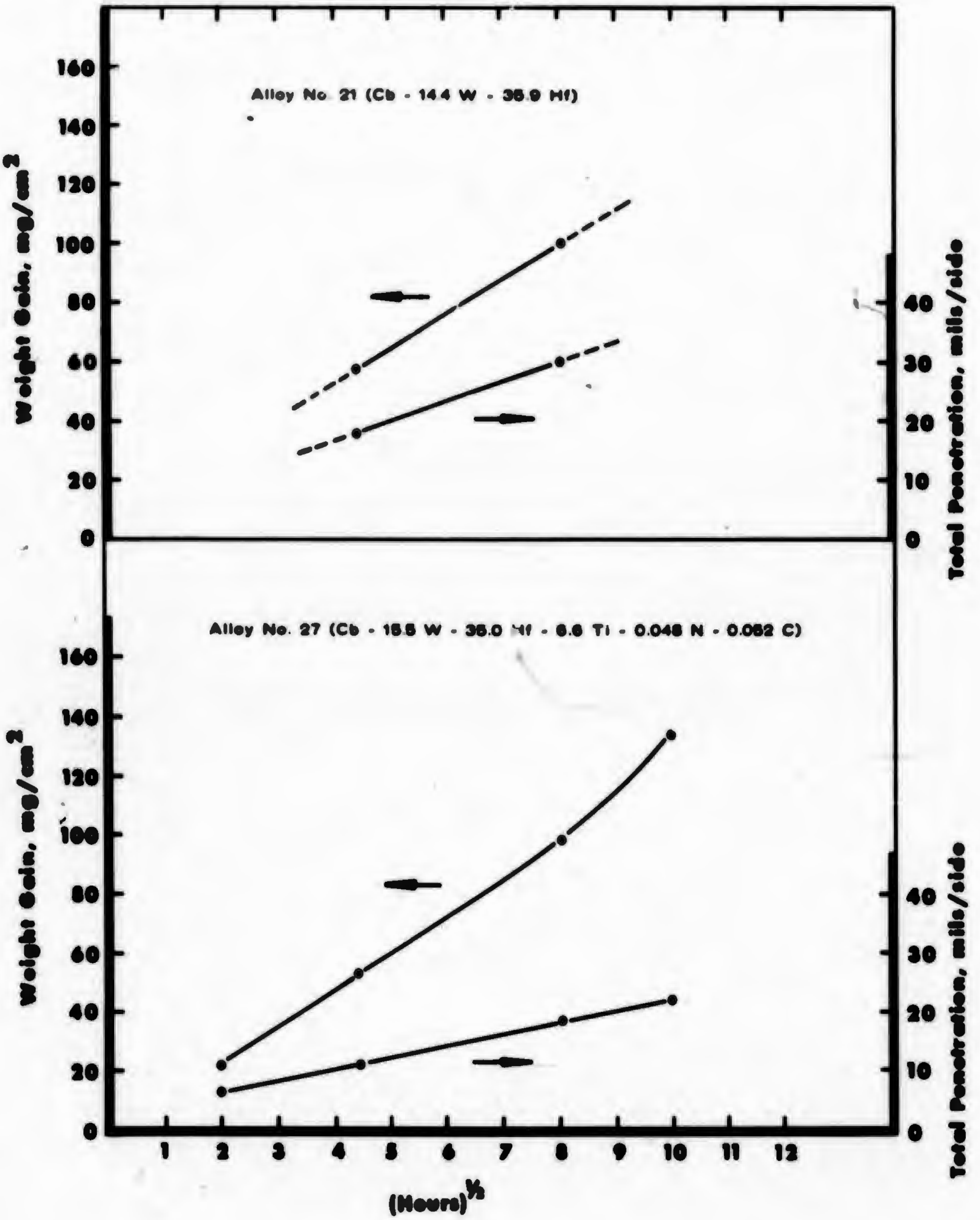


Figure 74. Weight Gain and Total Penetration for Alloys No. 21 (Cb-14.4W-35.9Hf) and 27 (Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C) Air-Oxidized at 2000°F.

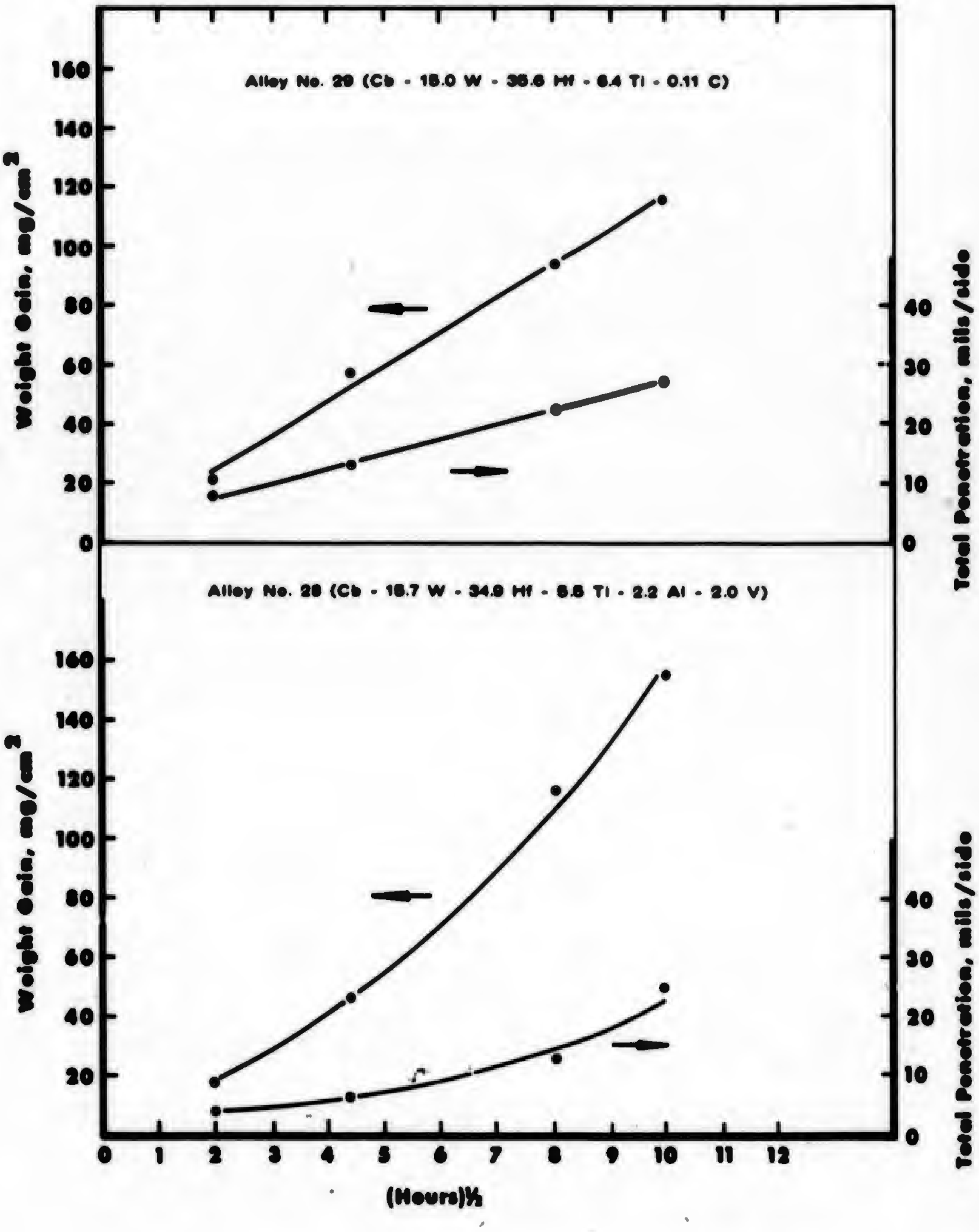


Figure 75. Weight Gain and Total Penetration for Alloys No. 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) and 28 (Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V) Air Oxidized at 2000°F.

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SECTION VIII

GENERAL DISCUSSION

In the foregoing sections of this report the results obtained on this program have been detailed with appropriate discussion; therefore, this section of the report provides general commentary concerning the results in relation to the objective of the study - development of a columbium-base alloy for use as a blade material at a temperature of at least 2000°F in gas turbine engines.

The requirements of oxidation resistance, strength, and fabricability placed upon a material for application as a turbine blade are very stringent. Most often these requirements become mutually exclusive when an attempt is made to develop acceptable total properties in a given material. This was evident for the alloys studied on this program. However, considering only oxidation resistance, improvement was appreciable for those alloys of the Cb-W-Hf system containing moderate amounts of tungsten and fairly large amounts of hafnium. The mechanism for this improvement, i.e. a uniform, slowly advancing, internal oxidation front promoted by a high hafnium content, and an influence of tungsten in affecting the kinetics of internal oxidation and scale formation, offers an interesting and perhaps realistic approach for alleviating the oxidation problem, which is characteristic of useful columbium alloys. Lack of a suitable solution to this problem is the principal deterrent in their use as turbine blade materials. Although the oxidation resistance shown by the alloy Cb-15W-35Hf probably would not be adequate for utilization of this composition in the bare condition, the safeguard this improved property would provide such an alloy for use in the coated condition could be significant.

Tungsten and hafnium are very effective short-time strengtheners of columbium, but at the expense of ductility. Proper thermal mechanical processing could minimize this effect. The creep-rupture behavior of the Cb-W-Hf alloys is not outstanding, and it was unfortunate (although not surprising) that the addition of titanium aggrevated the problem since this element provided an increase in oxidation resistance. The ineffectiveness of a nitrogen and/or carbon addition to a titanium bearing alloy for improving creep strength was unexpected. Perhaps strength would have been benefitted more by an interstitial alloying addition to the composition Cb-15W-35Hf at some sacrifice in oxidation resistance through the elimination of titanium. Again, suitable thermal mechanical processing could improve the effectiveness of these common strengthening additions.

A fabrication evaluation of the various alloys studied was not exhaustive; although it was apparent in forging operations that pressing was preferred to hammering. Good fabricability would be required of turbine blade materials unless casting be considered.

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SECTION IX

CONCLUSIONS AND RECOMMENDATIONS

From the experimental results of this program the following conclusions can be drawn:

(1) Although the columbium alloys investigated did not meet the total property requisites placed upon a material for turbine blade applications, the improvement seen in oxidation resistance by alloying columbium with tungsten and hafnium was significant.

(2) The mechanism for improved oxidation resistance of Cb-W-Hf alloys containing moderate amounts of tungsten and relatively large amounts of hafnium offers an interesting and perhaps realistic approach for alleviating the oxidation problem which is characteristic of useful columbium alloys.

(3) Within the composition limits of the Cb-W-Hf system studied, the alloy Cb-15W-35Hf presented the best compromise between oxidation resistance, fabricability, and strength properties.

(4) Although further improvement in oxidation resistance was achieved by alloying Cb-15W-35Hf with the elements titanium, aluminum, and vanadium, the improvement was obtained at the expense of strength and fabricability.

(5) Tungsten and hafnium are very effective short-time strengtheners of columbium, but at the expense of ductility when present in the amount required for significant improvement in oxidation behavior, i.e., 15 percent tungsten and 35 percent hafnium.

(6) The creep-rupture behavior of Cb-W-Hf alloys was not outstanding.

Columbium-base alloys should continue to be considered for blade applications in gas turbine engines. In this regard, the following recommendations can be made for future work in the area of Cb-W-Hf alloys:

(1) Screen additional alloys based upon the ternary composition Cb-15W-35Hf with additions of less than 5 percent titanium and less than 2 percent each of aluminum and vanadium to determine whether oxidation resistance, strength, and fabricability can be optimized.

(2) Reinvestigate the effect of additions of nitrogen and/or carbon on strength to determine if improvements can be made by suitable heat-treatment of the alloy(s).

(3) Scale-up the preparation of one or more promising alloys and characterize as follows:

   (a) Establish the temperature limits of fabrication and determine if a blade configuration can be successfully forged;

   (b) Carry out an extensive mechanical property evaluation including tensile and creep-rupture testing over a wide temperature range;

   (c) Establish the effect of thermal mechanical processing on mechanical properties;

   (d) Perform a complete study of oxidation behavior including rate studies and identification of scales;

   (e) Determine the effect of oxidation on mechanical properties;

   (f) Study coatability of the alloy(s) and the effect of coating on mechanical properties; and

   (g) Test coated alloy(s) for oxidation resistance in a high velocity gas stream.

APPENDIX

TABLES

TABLE I

COMPARISON OF OXIDATION RESISTANCE OF ALLOYS NO. 21 (Cb-14.4W-35.9Hf) AND 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) WITH OTHER COLUMBIUM-BASE ALLOYS

	20 hr Oxidation Behavior at 2000°F (mils/side)			65 hr Oxidation Behavior at 2000°F (mils/side)		
Alloy	Metal Loss	Contamination	Total Penetration	Metal Loss	Contamination	Total Penetration
B-66	(≥ 50)*	-	-	-	-	-
F-48	10	65	75	-	-	-
Alloy No. 21	2 (2)*	16 (22)*	18 (24)*	3	27	30
Alloy No. 29	3	10	13	5.5	17	22.5

* Data at 2200°F

B-66: Cb-5Mo-5V-1Zr

F-48: Cb-15W-5Mo-1Zr-0.06C

TABLE II

COMPARISON OF STRENGTH PROPERTIES OF ALLOYS NO. 21 (Cb-14.4W-35.9Hf) AND 29 (Cb-15.0W-35.6Hf-6.4Ti-0.11C) WITH OTHER COLUMBIUM-BASE ALLOYS

	Tensile Properties				Stress-Rupture Properties at 2000°F and 20,000 psi	
Alloy	Test Temp (°F)	UTS (psi)	YS (psi)	Elong (%)	Rupture Life (hr)	Elong (%)
Cb	RT	35,000	20,000	45	-	-
	2000	10,000	9,000	30		
B-66	RT	102,000	77,000	26		
	2000	46,000	40,000	48	30	-
F-48	RT	125,000	86,000	25		
	2000	65,000	43,000	18	>1000	-
Alloy No. 21	RT	99,700	99,700	0	132	36
	2000	79,500	69,200	4.8		
Alloy No. 29	RT	141,200	138,700	1.1		
	2000	51,600	49,100	3.8	3.8	51

B-66: Cb-5Mo-5V-1Zr

F-48: Cb-15W-5Mo-1Zr-0.06C

TABLE III

POPULAR SECOND GENERATION COLUMBIUM-BASE ALLOYS

Alloy Designation	Nominal Composition (Weight Percent)							
	Ta	W	Mo	Zr	Hf	V	C	Y
D-43	--	10	--	1	--	-	0.1	--
Cb-752	--	10	--	2.5	--	-	--	--
FS-85	27	11	--	1	--	-	--	--
B-66	--	--	5	1	--	5	--	--
C-129Y	--	10	--	--	10	-	--	0.05-0.30
Cb-132M	20	15	5	2	--	-	0.1	--

TABLE IV

VENDORS' ANALYSES OF MELT STOCK USED FOR ALLOY PREPARATION

(Weight Percent)

Columbium		Tantalum		Tungsten		Hafnium				Titanium	
0.030-in thick strip		0.030-in thick strip		-325 mesh powder		0.080-in thick strip		Crystal Bar		0.080-in thick strip	
Cb	Bal	Ta	Bal	W	99.78	Hf	Bal	Hf	Bal	Ti	Bal
Al	<0.002	Cb	0.07	Mo	0.01	Zr	2.68	Zr	3.9	Fe	0.146
B	<0.0001	Mo	<0.005	Fe	0.01	Ti	<0.002	Ti	<0.002	C	0.05
C	<0.002	W	<0.01	C	0.05	Cb	<0.005	Cb	<0.005	O	0.116
Cd	<0.0005	Fe	<0.01	O	0.03	Ta	<0.01	Ta	<0.01	H	0.0024
Co	<0.001	Cr	<0.002	S	0.005	Fe	0.11	Mo	<0.0005	N	0.013
Cr	<0.002	Ni	<0.005	SiO_2	0.01	Al	<0.002	W	<0.001		
Cu	<0.004	Zr	0.01	CaO+		Cu	<0.003	Fe	0.01		
Fe	<0.005	Ti	<0.01	Al_2O_3	0.02	C	<0.008	Cr	0.0005		
H	0.0004	Sn	<0.002			O	0.032	Ni	<0.002		
Hf	<0.008	Mn	<0.002			N	<0.002	Al	<0.002		
Mg	<0.002	C	0.002					Cu	<0.002		
Mn	<0.002	O	0.0017					U	<0.0001		
Mo	<0.002	H	0.0002					C	<0.008		
N	0.004	N	0.0024					O	<0.01		
Ni	<0.002							N	<0.0016		
O	<0.005										
Pb	<0.002										
Si	<0.005										
Sn	<0.001										
Ta	0.037										
Ti	<0.004										
V	<0.002										
W	0.008										
Zr	<0.01										

TABLE V

DATA FOR PREPARATION OF 0.75-INCH DIAMETER BY 2.5-INCHES LONG DROP-CAST INGOT OF Cb-25W-30Ta

Weight of Charge

Cb	0.675 pounds
W	0.375 "
Ta	0.450 "

TOTAL 1.5 pounds

Amperage Requirements

800 amps for 1-1/2 minutes to puddle button
1900 amps for 1/4-minute to complete drop cast

Ingot Weight (including hot top)

0.88 pound

Skull Weight

Balance

TABLE VI

DATA FOR PREPARATION OF ELECTRON BEAM MELTED INGOTS OF Cb-W-Ta ALLOYS

Alloy No.	Weighed Composition (Wt. %)	Melt Stock 0.75-in Dia Drop Castings Quantity	Melt Stock 0.75-in Dia Drop Castings Total Wt(lbs)	Power Used For EB Melting (kw)	Ingot Dimensions Dia (in)	Ingot Dimensions Length (in)	Ingot Dimensions Wt. (lbs)
1	Cb-10W-15Ta	9	3.5	35.0	1.44	4.8	2.8
2	Cb-10W-30Ta	9	3.8	29.6	1.44	4.6	2.9
3	Cb-25W-15Ta	9	3.9	55.5	1.44	4.7	3.0
4	Cb-25W-30Ta	7	3.0	51.8	1.44	2.9	2.1
5	Cb-17.5W-22.5Ta	9	4.0	46.0	1.44	5.1	3.3

Notes: Pressure during melting was 10^{-5} Torr range of vacuum.
Melt time per alloy was approximately 30 minutes.
Ingot dimensions were obtained after cutting ingot from puller and sampling top and bottom for chemical analysis and metallographic examination.

TABLE VII

COMPARISON BETWEEN CALCULATED AND ANALYZED INTERSTITIAL CONTENTS OF DROP-CAST Cb-W-Ta ALLOYS

Alloy	Calculated Composition							Analyzed Composition			
	Wt. %			ppm(1)				ppm			
No.	Cb	W	Ta	C	O	H	N	C	O	H	N
1	Bal	10	15	48	70	4	44	280	695	17	37
								390	530	10	20
2	Bal	10	30	48	65	3	41	90	472	16	86
3	Bal	25	15	90	108	3	53	170	620	14	70
4	Bal	25	30	90	103	3	50	170	348	11	41
5	Bal	22.5	17.5	70	87	2	47	130	350	3	30

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(1) Interstitial contents calculated from vendors' analyses of melt stock.

TABLE VIII

CHEMICAL ANALYSIS AND HARDNESS OF ELECTRON BEAM MELTED INGOTS OF Cb-W-Ta ALLOYS

	Weighed Composition (Weight Percent)				Chemical Analysis							Hardness	
					(Weight Percent)			(ppm)					
Alloy No.	Cb	W	Ta	Location(1)	Cb	W	Ta	C	O	H	N	Rockwell	DPH
1	Bal	10	15	T	-	9.8	15.6	30	74	3	26	B-83	169
				B	-	10.8	15.6	40	71	2	13	B-84	188
				Avg	-	10.3	15.6	35	73	3	20	B-84	179
2	Bal	10	30	T	-	9.2	27.6	40	85	2	62	B-77	188
				B	-	10.3	29.0	20	41	1	48	B-86	172
				Avg	-	9.8	28.3	30	63	2	55	B-82	180
3	Bal	25	15	T	-	25.2	15.9	-	32	2	14	C-26	306
				B	-	25.0	15.7	50	27	2	24	C-26	303
				Avg	-	25.1	15.8	50	30	2	19	C-26	305
4	Bal	25	30	T	-	24.8	33.1	20	23	2	8	C-30	319
				B	-	24.4	30.0	20	27	2	10	C-30	319
				Avg	-	24.6	31.6	20	25	2	9	C-30	319
5	Bal	17.5	22.5	T	-	16.9	25.5	20	19	2	10	B-93	237
				B	-	16.8	22.0	20	46	2	21	B-93	223
				Avg	-	16.9	23.8	20	33	2	16	B-93	230

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(1) T = Top of EB Ingot
B = Bottom of EB Ingot
Avg = Average of Top and Bottom Analyses

TABLE IX

DATA FOR PREPARATION OF ELECTRON BEAM MELTED INGOTS OF Cb-W-Hf ALLOYS

Alloy No.	Weighed Composition (Wt.%)	Melt Stock			Power Used For EB Melting (kw)	Total Times EB Melted	Ingot Dimensions (1)		
		Type	Quantity	Total Wt. (lbs)			Dia. (in)	Length (in)	Wt. (lbs)
6	Cb-10W-2Hf	Drop Castings	8	3.8	42.5	1	1.44	6.10	3.4
7	Cb-9W-32Hf	Pressed Bar	1	5.0	42.5	2	1.44	6.18	3.8
8	Cb-24W-3Hf	Pressed Bar	1	5.0	40.0	3	1.44	7.00	4.2
9	Cb-25W-32Hf	Pressed Bar	1	5.0	36.0	3	1.44	5.56	3.8
10	Cb-16W-17.5Hf	Pressed Bar	1	5.0	36.0	3	1.44	6.25	3.8
11	Cb-5W-35Hf	Pressed Bar	1	5.0	28.0	2	1.44	6.62	4.0
12	Cb-8W-25Hf	Pressed Bar	1	5.0	32.5	2	1.44	6.75	4.0
13	Cb-5W-32Hf	Pressed Bar	1	5.0	28.0	2	1.44	6.75	4.1
14	Cb-8W-30Hf	Pressed Bar	1	5.0	27.7	2	1.44	6.50	4.0
30	Cb-15W-30Hf	Pressed Bar	1	5.0	40.0	2	1.44	5.00	3.2
31	Cb-17W-36Hf	Pressed Bar	1	5.0	40.0	2	1.44	4.00	2.6
32	Cb-26W-20Hf	Pressed Bar	1	5.0	42.5	2	1.44	4.50	3.0
21	Cb-15W-37Hf	Pressed Bar	1	7.0	42.5	2	2.44	3.33	5.7
22	Cb-11W-37Hf	Pressed Bar	1	7.0	42.5	2	2.44	3.42	5.6

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(1) Ingot dimensions were obtained after cutting ingot from pad and sampling top and bottom for chemical analysis and metallographic examination.

TABLE X

INTERSTITIAL ANALYSIS OF COLUMBIUM AND HAFNIUM: AS-RECEIVED AND AFTER CONDITIONING FOR USE AS ELECTRON BEAM MELT STOCK

	As Received					After Conditioning				
		Analysis, ppm					Analysis, ppm			
Material	Form	C	O	H	N	Form	C	O	H	N
Columbium	Strip, 0.030-in. thick	<20	<50	4	40	Powder, -10 mesh	5	440	4	20
Hafnium	Crystal Bar	<80	<100	-	<16	Millings	-	164	43	44

TABLE XI

CHEMICAL ANALYSIS AND HARDNESS OF ELECTRON BEAM MELTED INGOTS AND FORGINGS OF Cb-W-Hf ALLOYS

Alloy No.	Weighed Composition (Weight Percent)			Location(1)	Chemical Analysis (Weight Percent)			Chemical Analysis (p.p.m.)				Hardness	
	Cb	W	Hf		Cb	W	Hf	C	O	H	N	Rockwell	DPH
6	Bal.	10	2	T	--	9.9	1.7	40	41	3	23	B-78	176
				B	--	9.7	1.5	40	48	3	31	B-80	167
				Avg.	--	9.8	1.6	40	46	3	27	B-79	172
7	Bal.	9	32	T	--	11.7	30.3	40	52	2	55	C-28	283
				B	--	9.5	31.3	30	87	3	88	C-29	273
				Avg.	--	10.6	30.8	35	70	3	72	C-29	278
8	Bal.	24	3	T	--	24.4	3.0	24	68	1	37	C-24	266
				B	--	23.8	5.8	17	23	1	19	C-26	276
				Avg.	--	24.1	4.4	21	46	1	28	C-25	271
9	Bal.	23	32	T	--	23.2	26.7	19	26	1	88	C-38	394
				B	--	22.7	26.2	21	24	1	77	C-38	393
				Avg.	--	23.0	26.5	20	25	1	83	C-38	394
10	Bal.	16	17.5	T	--	15.6	18.3	--	48	2	46	C-28	--
				B	--	13.8	19.0	60	9	2	38	C-30	296
				Avg.	--	14.7	18.7	60	29	2	42	C-29	296
11	Bal.	5	35	T	--	5.9	33.4	16	108	3	121	C-23	255
				B	--	7.4	34.5	41	33	6	60	C-23	257
				Avg.	--	6.7	34.0	29	71	5	91	C-23	256
				F	--	4.9	34.9						
12	Bal.	8	25	T	--	6.4	30.0	21	109	3	148	C-22	249
				B	--	6.4	29.0	24	85	1	98	C-23	254
				Avg.	--	6.4	29.5	23	97	2	123	C-23	252
				F	--	6.3	26.3						

TABLE XI (continued)

Alloy No.	Weighed Composition (Weight Percent)			Location(1)	Chemical Analysis (Weight Percent)			Chemical Analysis (p.p.m.)				Hardness	
	Cb	W	Hf		Cb	W	Hf	C	O	H	N	Rockwell	DPH
13	Bal.	5	32	T	--	4.4	39.2	26	106	2	197	C-24	261
				B	--	4.8	36.8	37	86	1	95	C-25	267
				Avg.	--	4.6	38.0	32	96	2	146	C-25	264
				F	--	4.0	34.4						
14	Bal.	8	30	T	--	7.4	30.6	42	59	2	98	C-25	267
				B	--	7.1	30.7	30	102	1	110	C-25	265
				Avg.	--	7.3	30.7	36	81	2	104	C-25	266
				F	--	8.3	28.6						
30	Bal.	15	30	T	--	14.8	29.6	81	137	4	46	C-31	311
				B	--	13.6	28.0	--	117	8	92	C-35	344
				Avg.	--	14.2	28.8	81	127	6	69	C-33	328
31	Bal.	17	36	T	--	15.2	32.9	44	70	2	21	C-33	329
				B	--	14.9	35.2	161	--	--	56	C-34	335
				Avg.	--	15.1	34.1	103	70	2	39	C-34	332
32	Bal.	26	20	T	--	17.6	23.7	65	186	4	26	C-35	342
				B	--	22.8	19.4	107	100	7	69	C-32	316
				Avg.	--	20.2	21.6	86	143	6	48	C-33	329
21	Bal.	15	37	T	--	13.1	36.9	--	--	--	--	C-33	325
				B	--	13.8	35.0	70	114	6	68		
				Avg.	--	13.5	36.0	70	114	6	68		
				F	49.2	14.4	35.9	150	103	7	96		
22	Bal.	11	37	T	--	12.1	35.1	--	--	--	--		
				B	--	15.7	27.7	25	59	40	34	C-30	301
				Avg.	--	13.9	31.4	25	59	40	34		
				F	--	12.1	35.5	60	118	7	59		

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(1) T = Top of Ingot
B = Bottom of Ingot
Avg. = Average of Top and Bottom Analyses
F = Forging

TABLE XII

DATA FOR PREPARATION OF CONSUMABLE ARC MELTED INGOTS OF NOMINALLY Cb-15W-35Hf WITH ADDITIONS OF TITANIUM, COBALT, ALUMINUM, VANADIUM, CARBON AND NITROGEN

Alloy No.	Weighed Composition (wt%)	Electrode Dimensions			Melting Data				Ingot Dimensions(2)		
		Cross Section (in)	Length (in)	Weight (lbs)	Volts (DC)	Amperes (DC)	Melt Time (min)	Melt Rate (lb/min)	Dia. (in)	Length (in)	Weight (lbs)
23	Cb-15W-37Hf-2Re	(See Note 1 below)							2.44	3.2	5.7
24	Cb-15W-36Hf-5.5Ti	0.8 x 0.81	28	6.8	19-21	1700-1950	10	0.68	2.25	4.1	6.1
25	Cb-15W-36Hf-11Ti	0.8 x 0.81	28	6.4	20-21	2000	8	0.80	2.25	3.9	5.6
26	Cb-15W-36Hf-3Co	0.8 x 0.75	27.7	6.6	20	2100	6	1.1	2.25	3.8	6.0
27	Cb-15W-36Hf-5.5Ti-0.07N-0.05C	1.08 dia	21	6.05	20	2000	4	1.5	2.25	3.5	5.2
28	Cb-15W-35.5Hf-5.3Ti-2.5Al -2.2V	1.17 dia	19.87	6.1	20	2000	4	1.5	2.25	3.9	5.3
29	Cb-15W-35.5Hf-5.5Ti-0.1C	1.06 dia	21.87	6.2	20	2000	5	1.2	2.25	3.7	5.5

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(1) Ingot of Alloy No. 23 was prepared by double electron beam melting a 7-lb. powder metallurgy compact according to procedures used for Cb-W-Hf ternary alloys.

(2) Ingot dimensions were obtained after cutting ingot from pad and sampling top and bottom for chemical analysis and metallographic examination.

TABLE XIII

CHEMICAL ANALYSIS AND HARDNESS OF CONSUMABLE ARC MELTED INGOTS AND FORGINGS OF NOMINALLY Cb-15W-35Hf WITH ADDITIONS OF TITANIUM, COBALT, ALUMINUM, VANADIUM, CARBON, AND NITROGEN

Alloy No.	Weighed Composition (Weight Percent)	Location(2)	Chemical Analysis (Weight Percent) Cb	W	Hf	Re	Ti	Co	Al	V	Chemical Analysis (p.p.m.) C	O	H	N	Hardness DPH
23(1)	Cb-15W-37Hf-2Re	T	-	14.5	37.9	2.9	-	-	-	-	-	-	-	-	
		B	Bal.	16.2	27.7	3.3	-	-	-	-	20	59	20	34	333
		Avg.	Bal.	15.4	32.8	3.1					20	59	20	34	
		F	Bal.	15.1	34.8	1.9	-	-	-	-	50	158	8	76	
24	Cb-15W-36Hf-5.5Ti	T	Bal.	16.7	34.2	-	6.5	-	-	-	40	376	17	139	356
		F	Bal.	16.9	33.2	-	6.3	-	-	-	40	238	17	67	
25	Cb-15W-36Hf-11Ti	T	Bal.	16.2	36.9	-	11.0	-	-	-	80	377	41	94	340
		F	Bal.	16.7	35.2	-	11.0	-	-	-	80	345	65	65	
26	Cb-15W-36Hf-3Co	T	Bal.	18.3	33.4	-	-	2.4	-	-	60	394	18	77	366
		E	Bal.	17.5	33.5	-	-	2.8	-	-	50	194	11	54	
27	Cb-15W-36Hf-5.5Ti-0.07N-0.05C	T	-	14.9	34.5	-	6.7	-	-	-	-	-	-	-	369
		B	-	14.8	34.4	-	7.1	-	-	-	-	-	-	-	358
		Avg.	-	14.9	34.5	-	6.9	-	-	-	-	-	-	-	364
		F	Bal.	15.5	36.0	-	6.6	-	-	-	520	331	20	480	
28	Cb-15W-35.5Hf-5.5Ti-2.5Al-2.2V	T	Bal.	15.7	35.2	-	6.0	-	2.4	2.1	160	510	12	60	440
		B	Bal.	15.6	34.5	-	5.0	-	2.0	1.9	140	640	14	60	457
		Avg.	Bal.	15.7	34.9		5.5		2.2	2.0	150	575	13	60	449
29	Cb-15W-35.5Hf-5.5Ti-0.1C	T	Bal.	15.2	33.8	-	6.9	-	-	-	1000	90	12	40	342
		B	Bal.	15.2	34.7	-	6.4	-	-	-	1100	100	11	50	340
		Avg.	Bal.	15.2	34.3	-	6.7	-	-	-	1050	95	12	45	341
		F	Bal.	15.0	35.6	-	6.4	-	-	-	1100	378	19	130	

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(1) Electron Beam Melted Ingot

(2) T = Top of Ingot
B = Bottom of Ingot
Avg. = Average of Top and Bottom Analyses
F = Forging
E = Extrusion

TABLE XIV

SEQUENCE OF FABRICATION STEPS FOR ALLOYS NO. 1(Cb-10.3W-15.6Ta), 2(Cb-9.8W-28.3Ta), AND 6(Cb-9.8W-1.6Hf) FROM INGOT TO 0.25-INCH DIAMETER ROD

	Alloy No. 1	Alloy No. 2	Alloy No. 6
Dimension of Columbium Alloy Billet*:	1.285-in.diam.	1.285-in.diam.	1.285-in.diam.
Hot Swaged at 2150°F to*:	0.643-in.diam.	0.737-in.diam.	0.683-in.diam.
Reduction in Area by Hot Swaging:	75 percent	67.1 percent	71.8 percent
Conditioned to:	0.595-in.diam.	0.636-in.diam.	0.645-in.diam.
Vacuum Annealed One Hour at:	2400°F	2400°F	2400°F
Hardness After Vacuum Annealing:	R_b 80	R_b 82.6	R_b 77.7
Warm Swaged at 500°F to:	0.253-in.diam.	0.253-in.diam.	0.253-in.diam.
Reduction in Area by Warm Swaging:	82 percent	84.3 percent	84.5 percent
Hardness After Warm Swaging:	R_b 87	R_b 88	R_b 83

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*Excluding HASTELLOY alloy X can

TABLE XV

INTERSTITIAL ANALYSIS OF ALLOYS NO. 1(Cb-10.3W-15.6Ta), 2(Cb-9.8W-28.3Ta), AND 6(Cb-9.8W-1.6Hf) AFTER FABRICATION

Alloy No.	Interstitial Analysis (ppm)			
	Carbon	Oxygen	Hydrogen	Nitrogen
1	40	55	1	36
2	20	26	2	12
6	50	63	1	66

TABLE XVI

DATA FOR EXTRUSION OF Cb-W-Ta ALLOYS

Alloy No.	Billet No.	Composition (Weight Percent)	Extrusion Temperature (°F)	Extrusion Pressure on Billet (Ksi)	Remarks
3	1	Cb-25.1W-15.8Ta	2475	192.0	Good
4	1	Cb-24.6W-31.6Ta	2500	192.0	Good
5	1	Cb-16.9W-23.8Ta	2550	122.0	Good

Notes: (1) Extrusions performed on 300T horizontal press at Materials Systems Division, UCC.

(2) Extrusion temperatures are uncorrected optical pyrometer readings.

(3) Extrusion pressures are pressures required to sustain extrusion.

(4) Billet size, including molybdenum can: 1.475-inch diameter.

(5) Die size: 0.750-inch diameter.

(6) Extrusion ratio: 4:1.

(7) Extrusion speed: 1-inch of billet length per second.

TABLE XVII

DATA FOR EXTRUSION OF Cb-W-Hf ALLOYS

Alloy No.	Billet No.	Composition (Weight Percent)	Extrusion Temperature (°F)	Extrusion Pressure on Billet (Ksi)	Remarks
7	1	Cb-10.6W-30.8Hf	2690	160.0	Good.
	2		2450	179.0	Good.
	3		2510	179.0	Good.
8	1	Cb-24.1W-4.4Hf	2500	141.0	Good.
	2		2415	128.0	Good.
9	1	Cb-23.0W-26.5Hf	2600	--	Stalled with 192.0 Ksi on billet.
	2		2760	--	Same as above.
	1		2900	--	Same as above.
	2		3020	--	Same as above.
10	1	Cb-14.7W-18.7Hf	2850	No data	Good.
	2		2550	179.0	Good.
	3		2510	179.0	Die broke. Extrusion scrapped.
11	1	Cb-4.9W-34.9Hf	2520	140.5	Slight surface cracking.
	2		2600	No data	Good.
12	1	Cb-6.3W-26.3Hf	2610	140.5	Good.
	2		2720	No data	Good.
13	1	Cb-4.0W-34.4Hf	2615	134.0	Slight surface cracking.
	2		2690	No data	Good.
14	1	Cb-8.3W-28.6Hf	2650	No data	Good.
	2		2760	No data	Good.

TABLE XVII (continued)

Alloy No.	Billet No.	Composition (Weight Percent)	Extrusion Temperature (°F)	Extrusion Pressure on Billet (Ksi)	Remarks
30	1	Cb-14.2W-28.8Hf	2750	166.0	Moderate surface cracking.
	2		2840	178.8	Slight surface cracking.
31	1	Cb-15.1W-34.1Hf	2750	217.0	Partial extrusion with moderate surface cracking.
32	1	Cb-20.2W-21.6Hf	2915	--	Stalled with 192.0 Ksi on billet.

Notes: See Table XVI

TABLE XVIII

DATA FOR EXTRUSION OF Cb-W-Hf ALLOYS

Alloy No.	Composition (Weight Percent)	Extrusion Temperature (°F)	Extrusion Pressure on Billet (Ksi)		Ram Speed (ips)	Remarks
			Maximum	Minimum		
21	Cb-14.4W-35.9Hf	3000	92.0	90.0	2.75	Good
22	Cb-12.1W-35.5Hf	2800	82.0	76.0	16.0	Good

Notes: (1) Extrusions performed on 700T horizontal press at Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

(2) Extrusion temperatures are thermocouple readings.

(3) Billet size, including molybdenum can: 2.935-inch diameter.

(4) Die size: nominal 1.0-inch by 2.0-inch rectangular.

(5) Extrusion ratio: approximately 4:1.

TABLE XIX

DATA FOR EXTRUSION OF ALLOYS OF NOMINALLY Cb-15W-35Hf WITH ADDITIONS OF RHENIUM, TITANIUM, COBALT, ALUMINUM, VANADIUM, CARBON, AND NITROGEN

Alloy No.	Composition (Weight Percent)	Extrusion Temperature (°F)	Extrusion Pressure on Billet (Ksi)		Ram Speed (ips)	Remarks
			Maximum	Minimum		
23	Cb-15.1W-34.8Hf-1.9Re	3500	76.0	72.0	3.00	Good.
24	Cb-16.9W-33.2Hf-6.3Ti	2800	74.2	62.0	2.00	Good.
25	Cb-16.7W-35.2Hf-11.0Ti	2800	81.0	68.8	1.75	Good.
26	Cb-17.5W-33.5Hf-2.8Co	2800	47.2	45.9	2.25	Defects observed radiographically.
27	Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C	2800	81.8	70.2	3.5	Good.
29	Cb-15.0W-35.6Hf-6.4Ti-0.11C	2800	81.8	70.2	3.5	Good.
28	Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V	2800	83.7	72.9	3.5	Good.

Notes: See Table XVIII

TABLE XX

EFFECT OF HEAT TREATMENT ON THE HARDNESS AND MICROSTRUCTURE OF WROUGHT Cb-W-Ta ALLOYS

Alloy No.	Composition (Weight Percent)	One Hour Annealing Temperature (°F)	Hardness (DPH)	Estimated Recrystallization (Percent)
1	Cb-10.3W-15.6Ta	As-swaged	223	Nil
		2000	195	10
		2200	179	50-75
		2400	171	100
		2600	170	100
		2800	173	100
		3000	178	100
2	Cb-9.8W-28.3Ta	As-swaged	241	Nil
		2000	206	Nil
		2200	198	25
		2400	173	50-75
		2600	171	90-95
		2800	179	100
		3000	178	100
3	Cb-25.1W-15.8Ta	As-extruded	298	3
		2200	306	3
		2600	271	50
		3000	276	100
		3400	274	100
		3600	272	100
4	Cb-24.6W-31.6Ta	As-extruded	357	Nil
		2200	346	3
		2600	348	10
		3000	314	100
		3200		100
		3400	316	100
		3600	325	100
5	Cb-16.9W-23.8Ta	As-forged	265	Nil
		2000	244	Nil
		2200	246	Nil
		2400	245	Nil
		2600	232	100
		2800	237	100
		3000	238	100
		3200	235	100

TABLE XXI

HEAT TREATMENT SELECTED TO RECRYSTALLIZE WROUGHT Cb-W-Ta ALLOYS

Alloy No.	Composition (Wt.%)	Fabrication Method	One-Hour Annealing Temperature (°F)
1	Cb-10.3W-15.6Ta	Swaging	2600
2	Cb-9.8W-28.3Ta	Swaging	2800
3	Cb-25.1W-15.8Ta	Extrusion	3000
4	Cb-24.6W-31.6Ta	Extrusion	3200
5	Cb-16.9W-23.8Ta	Extrusion & Forging	2800

TABLE XXII

EFFECT OF HEAT TREATMENT ON THE HARDNESS AND MICROSTRUCTURE OF WROUGHT Cb-W-Hf ALLOYS

Alloy No.	Composition (Weight Percent)	One Hour Annealing Temperature (°F)	Hardness (DPH)	Estimated Recrystallization (Percent)
6	Cb-9.8W-1.6Hf	As-swaged	227	Nil
		2000	187	Nil
		2200	156	50
		2400	162	90-95
		2600	150	100
		2800	164	100
		3000	162	100
7	Cb-10.6W-30.8Hf	As-extruded	292	50
		2200	267	50
		2600	274	75
		2800	270	90
		3000	261	100
		3200	263	100
8	Cb-24.1W-4.4Hf	As-extruded	317	5
		2200	285	5
		2600	264	75
		3000	263	100
		3400	266	100
		3600	269	100
10	Cb-14.7W-18.7Hf	As-extruded	293	10
		2200	285	10
		2600	264	50-75
		3000	270	100
		3400	269	100
		3600	286	100
11	Cb-4.9W-34.9Hf	As-forged	287	Nil
		2000	250	10
		2200	254	25
		2400	247	75
		2600	260	100
		2800	245	100
		3000	252	100

TABLE XXII (continued)

Alloy No.	Composition (Weight Percent)	One Hour Annealing Temperature (°F)	Hardness (DPH)	Estimated Recrystallization (Percent)
12	Cb-6.3W-26.3Hf	As-forged	266	Nil
		2000	242	Nil
		2200	239	25
		2400	238	75
		2600	240	98
		2700	255	100
		2800	239	100
		3000	239	100
13	Cb-4.0W-34.4Hf	As-forged	286	10
		2000	254	10
		2200	246	25
		2400	254	90
		2500	258	100
		2600	252	100
		2800	249	100
		3000	258	100
14	Cb-8.3W-28.6Hf	As-forged	292	Nil
		2000	263	3
		2200	257	50
		2400	258	90
		2600	265	100
		2800	265	100
		3000	267	100
30	Cb-14.2W-28.8Hf	As-forged	359	
		2200	325	100
		2600	340	100
		2800	343	100
		3000	342	100
		3200	348	100

TABLE XXII (continued)

Alloy No.	Composition (Weight Percent)	One Hour Annealing Temperature (°F)	Hardness (DPH)	Recrystallized ASTM Grain Size	Estimated Recrystallization (Percent)
21	Cb-14.4W-35.9Hf	As-forged	357	7	75
		2000	328	7	75
		2200	335	6-7	75
		2400	333	6-7	75-80
		2600	337	6	80-90
		2800	334	6	95
		3000	324	4-5	100
22	Cb-12.1W-35.5Hf	As-forged	311	7	75
		2000	304	7	75
		2200	297	7	75
		2400	311	7	80-90
		2600	304	6-7	100
		2800	289	6-7	100
		3000	298	4-5	100

TABLE XXIII

HEAT TREATMENT SELECTED TO RECRYSTALLIZE WROUGHT Cb-W-Hf ALLOYS

Alloy No.	Composition (Wt.%)	Fabrication Method	One-Hour Annealing Temperature (°F)
6	Cb-9.8W-1.6Hf	Swaging	2600
7	Cb-10.6W-30.8Hf	Extrusion	3000
8	Cb-24.1W-4.4Hf	Extrusion	3000
10	Cb-14.7W-18.7Hf	Extrusion	3000
11	Cb-4.9W-34.9Hf	Extrusion & Forging	2600
12	Cb-6.3W-26.3Hf	Extrusion & Forging	2700
13	Cb-4.0W-34.4Hf	Extrusion & Forging	2500
14	Cb-8.3W-28.6Hf	Extrusion & Forging	2600
30	Cb-14.2W-28.8Hf	Extrusion & Forging	2800
21	Cb-14.4W-35.9Hf	Extrusion & Forging	3000
22	Cb-12.1W-35.5Hf	Extrusion & Forging	3000

TABLE XXIV

EFFECT OF HEAT TREATMENT ON THE HARDNESS AND MICROSTRUCTURE OF WROUGHT ALLOYS OF NOMINALLY Cb-15W-35Hf WITH ADDITIONS OF RHENIUM, TITANIUM, COBALT, ALUMINUM, VANADIUM, CARBON, AND NITROGEN

Alloy No.	Composition (Weight Percent)	One Hour Annealing Temperature (°F)	Hardness (DPH)	Recrystallized ASTM Grain Size	Estimated Recrystallization (Percent)
21	Cb-14.4W-35.9Hf	As-forged	357	7	75
		2000	328	7	75
		2200	335	6-7	75
		2400	333	6-7	75-80
		2600	337	6	80-90
		2800	334	6	95
		3000	324	4-5	100
23	Cb-15.1W-34.8Hf-1.9Re	As-forged	364	7	75
		2000	355	7	75
		2200	355	7	75
		2400	341	6	75-80
		2600	355	6	80-90
		2800	344	6	80-90
		3000	363	3-5	98
24	Cb-16.9W-33.2Hf-6.3Ti	As-forged	333		75
		2000	344		75
		2200	332		75
		2400	341		100
		2600	349		100
		2800	336		100
		3000	359		100
25	Cb-16.7W-35.2Hf-11.0Ti	As-forged	365		75
		2000	335		75
		2200	311		95
		2400	341		100
		2600	334		100
		2800	339		100
		3000	341		100

TABLE XXIV (continued)

Alloy No.	Composition (Weight Percent)	One Hour Annealing Temperature (°F)	Hardness (DPH)	Recrystallized ASTM Grain Size	Estimated Recrystallization (Percent)
26	Cb-17.5W-33.5Hf-2.8Co	As-extruded	424	Extruded above solidus temperature	
		2000	388	-	-
		2200	393	-	-
		2400	408	Heat-treated above solidus temperature	
		2600	413	Heat-treated above solidus temperature	
27	Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C	As-forged	368	-	50
		2000	349	8	75
		2200	348	8	90
		2400	352	7-8	98
		2600	341	7-8	98
		2800	346	6-7	100
		3000	363	5-6	100
29	Cb-15.0W-35.6Hf-6.4Ti-0.11C	As-forged	335	-	90
		2000	322	8	90
		2200	322	8	98
		2400	305	7-8	98
		2600	311	7-8	100
		2800	316	6-7	100
		3000	326	5-6	100
28	Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V	As-forged	456	-	50-75

TABLE XXV

HEAT TREATMENT SELECTED TO RECRYSTALLIZE WROUGHT ALLOYS OF NOMINALLY Cb-15W-35Hf WITH ADDITIONS OF RHENIUM, TITANIUM, CARBON, AND NITROGEN

Alloy No.	Composition (Wt. %)	Fabrication Method	One-Hour Annealing Temperature (°F)
23	Cb-15.1W-34.8Hf-1.9Re	Extrusion and Forging	3000
24	Cb-16.9W-33.2Hf-6.3Ti	Extrusion and Forging	2800
25	Cb-16.7W-35.2Hf-11.0Ti	Extrusion and Forging	2600
27	Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C	Extrusion and Forging	2800
29	Cb-15.0W-35.6Hf-6.4Ti-0.11C	Extrusion and Forging	2800

TABLE XXVI

TENSILE PROPERTIES AND STRENGTH-TO-WEIGHT RATIOS FOR RECRYSTALLIZED Cb-W-Ta TERNARY ALLOYS

Alloy No.	Composition (Wt%)	Density (lb/in^3)	Test Temp., (°F)	Ultimate Tensile Strength, (psi)	UTS/Den. (in)	Yield Strength, 0.2% Offset, (psi)	YS/Den. (in)	Elong. (%)
1	Cb-10.3W-15.6Ta	0.362	-80	83,700	231,200	62,500	172,600	26.0
			Room	70,900	195,900	52,600	145,300	33.1
			2000	17,200	47,500	11,900	32,900	59.8
			2200	13,300	36,700	9,700	26,800	70.2
2	Cb-9.8W-28.3Ta	0.402	-80	95,800	238,300	79,900	198,700	25.8
			-40	85,900	213,700	-	-	22.6
			0	76,900	191,300	-	-	31.1
			Room	74,300	184,800	56,100	139,600	28.8
			2000	18,700	46,500	12,400	30,800	68.9
			2200	16,300	40,500	11,500	28,600	66.7
3	Cb-25.1W-15.8Ta	0.400	Room	95,400	238,500	95,300	238,200	0
			175	103,900	259,500	103,800	259,500	0
			2200	29,600	74,000	22,000	55,000	33.6
4	Cb-24.6W-31.6Ta	0.456	Room	99,200	217,500	99,200	217,500	0
			395	101,400	222,300	-	-	0
			2200	34,300	75,200	26,400	57,900	35.0
5	Cb-16.9W-23.8Ta	0.408	Room	85,800	210,300	75,000	183,800	2.8
			750	53,500	131,100	37,600	92,100	29.3
			1000	50,400	123,500	33,700	82,600	22.0
			2200	21,300	52,200	17,900	43,900	47.3

TABLE XXVII

TENSILE PROPERTIES AND STRENGTH-TO-WEIGHT RATIOS FOR RECRYSTALLIZED Cb-W-HF ALLOYS

Alloy No.	Composition (Weight Percent)	Density (lb/in^3)	Test Temperature (°F)	Ultimate Tensile Strength, (psi)	UTS/Den. (in)	Yield Strength, 0.2% Offset, (psi)	YS/Den. (in)	Elongation, Percent
6	Cb-9.8W-1.6HF	0.336	-80	82,500	245,500	60,200	179,100	26.4
			Room	68,300	203,300	63,200	188,100	30.1
			2000	21,800	64,900	15,500	46,100	58.4
			2200	16,000	47,600	12,600	37,500	63.2
7	Cb-10.6W-30.8HF	0.378	Room	86,600(1)	229,100	86,600	229,100	0
			2000	62,300	164,800	55,400	146,600	6.6
			2200	50,600	133,900	44,200	116,900	1.5
8	Cb-24.1W-4.4HF	0.373	Room	89,400(1)	239,700	89,400	239,700	0
			400	86,600	232,200	77,600	208,000	8.2
			2000	39,000	104,600	30,400	81,500	42.0
			2200	32,900	88,200	23,800	63,800	33.2
10	Cb-14.7W-18.7HF	0.375	Room	87,800(1)	234,100	87,800	234,100	0
			2200	49,800	132,800	42,500	113,300	10.0
11	Cb-4.9W-34.9HF	0.375	Room	110,700	295,200	100,400	267,700	5.1
			2000	57,700	153,900	51,300	136,800	5.0
			2200	46,600	124,300	43,600	116,300	4.2
12	Cb-6.3W-26.3HF	0.366	Room	105,500	288,300	95,100	259,800	3.6
			2000	53,900	147,300	45,300	123,800	19.8
			2200	44,300	121,000	39,900	109,000	14.0
13	Cb-4.0W-34.4HF	0.374	Room	107,200	286,600	95,400	255,100	18.1
			2000	56,000	149,700	49,200	131,500	8.6
			2200	41,300	110,400	37,600	100,500	17.0

TABLE XXVII (continued)

Alloy No.	Composition (Weight Percent)	Density (lb/in^3)	Test Temperature (°F)	Ultimate Tensile Strength, (psi)	UTS/Den. (in)	Yield Strength, 0.2% Offset, (psi)	YS/Den. (in)	Elongation, Percent
14	Cb-8.3W-28.6Hf	0.375	Room	112,800	300,800	104,400	278,400	2.3
			2000	55,800	148,800	48,000	128,000	10.2
			2200	44,500	118,700	40,900	109,100	11.0
21	Cb-14.4W-35.9Hf	0.396	Room	99,700(1)	251,700	99,700	251,700	0
			600(2)	146,600	370,200	109,000	275,200	15.8
			2000	79,900	200,800	69,200	174,700	4.8
22	Cb-12.1W-35.5Hf	0.386	Room	124,700	323,100	124,700	323,100	0.8
			600(2)	105,000	272,000	88,000	228,000	9.9
			2000	63,200	163,700	58,800	152,300	3.8

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(1) Broke at radius.

(2) Specimen in stress-relieved condition, i.e., 1 hour at 2200°F.

TABLE XXVIII

TENSILE PROPERTIES AND STRENGTH-TO-WEIGHT RATIOS FOR RECRYSTALLIZED ALLOYS OF NOMINALLY Cb-15W-35Hf WITH ADDITIONS OF RHENIUM, TITANIUM, CARBON, AND NITROGEN

Alloy No.	Composition (Wt.%)	Density (lb/in^3)	Test Temp., (°F)	Ultimate Tensile Strength (psi)	UTS/Den. (in.)	Yield Strength 0.2% Offset (psi)	YS/Den. (in)	Elong. (%)
21	Cb-14.4W-35.9Hf	0.396	Room	99,700(1)	251,700	99,700	251,700	0
			600(2)	146,600	370,200	109,000	275,200	15.8
			2000	79,500	200,800	69,200	174,700	4.8
23	Cb-15.1W-34.8Hf-1.9Re	0.406	Room	86,200(1)	212,300	86,200	212,300	0.7
			600(2)	119,700	294,800	114,800	282,700	1.8
			2000	67,700(1)	166,700	67,700	166,700	0.8
24	Cb-16.9W-33.2Hf-6.3Ti	0.373	Room	104,200(1)	279,300	104,200	279,300	0.9
			2000	36,400(1)	97,600	36,400	97,600	0.2
25	Cb-16.7W-35.2Hf-11.0Ti	0.356	Room	131,800	370,200	131,300	368,800	0.7
			2000	38,400	107,800	38,200	107,300	1.8
27	Cb-15.5W-36.0Hf-6.6Ti -0.048N-0.052C	0.372	Room	157,800(1)	424,200	156,000	419,300	1.5
			2000	53,500	143,800	52,300	140,600	1.1
29	Cb-15.0W-35.6Hf-6.4Ti -0.11C	0.371	Room	141,200	380,600	138,700	373,800	1.1
			2000	51,600	139,100	49,100	132,300	3.8

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(1) Broke at radius

(2) Specimen in stress-relieved condition; i.e., 1 hour at 2200°F

TABLE XXIX

EFFECT OF ONE HOUR ANNEALING TEMPERATURE ON THE ROOM TEMPERATURE TENSILE PROPERTIES OF ALLOYS NO. 27(Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C) AND 29(Cb-15.0W-35.6Hf-6.4Ti-0.11C)

Alloy No.	Annealing Temp.(°F)	Ultimate Tensile Strength (psi)	Yield Strength 0.2% Offset (psi)	Elongation (%)
27	As-forged	173,100	164,40[illegible]	1.6
	2200	159,700	158,0[illegible]	1.5
	2400	165,300	157,800	1.6
	2600	159,400(1)	157,800	0.9
	2800	157,800(1)	156,000	1.5
29	As-forged	163,100	149,000	2.4
	2200	151,900	142,600	12.7
	2400	152,600	142,000	4.7
	2600	150,500	140,300	2.1
	2800	141,200	138,700	1.1

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(1) Broke at radius

TABLE XXX

HARDNESS OF RECRYSTALLIZED Cb-W-Hf TYPE ALLOYS FOLLOWING EXPOSURE AT 2000°F

Alloy No.	Composition, (Weight Percent)	One Hour Prior Annealing Temperature (°F)	Initial Hardness (DPH)	Hardness (DPH) After Exposure at 2000°F 4	20	65	100 -- (Hrs)
9	Cb-23.0W-26.5Hf	As-cast	394		390		
31	Cb-15.1W-34.1Hf	As-cast	331		337		
21	Cb-14.4W-35.9Hf	3000	324		325	310	
23	Cb-15.1W-34.8Hf-1.9Re	3000	365		328	340	
24	Cb-16.9W-33.2Hf-6.3Ti	2800	336		330	345	
25	Cb-16.7W-35.2Hf-11.0Ti	2600	334		320	335	
27	Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C	2800	346	328	340	345	347
29	Cb-15.0W-35.6Hf-6.4Ti-0.11C	2800	316	314	323	321	325
28	Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V	As-cast	449	443	445	436	436

TABLE XXXI

INTERSTITIAL ANALYSES OF ALLOY NO. 6 (Cb-9.8W-1.6Hf) BEFORE AND AFTER EXPOSURE IN VACUUM CREEP-RUPTURE EQUIPMENT

Test Conditions

Temperature: 2000°F
Time: 150 hours
Initial Pressure: 8×10^{-7} Torr
Final Pressure: 5.8×10^{-10} Torr
Specimen: 0.250-inch diameter

	Analysis (ppm)			
	C	O	H	N
Before Exposure	50	63	1	66
After Exposure	45	66	2	38

TABLE XXXII

CREEP-RUPTURE DATA AT 2000°F FOR Cb-W-Hf TERNARY ALLOYS

Alloy No.	Composition (Wt.%)	Stress (psi)	Time to Specified Elong.(hr) 1%	2%	5%	10%	Rupture Life(hr)	Total Elong.(%)
6	Cb-9.8W-1.6Hf	12,500 12,500	3.2 6.4	7.0 11.4	13.0 20.0	17.6 26.6	23.3 36.7	44.7 54.0
7	Cb-10.6W-30.8Hf	12,500 20,000	6.0 4.0	30.0 12.4	74.0 34.6	126.0 51.0	300.6 92.3	57.6 41.0
22	Cb-12.1W-35.5Hf	20,000	12.5	18.0	29.0	44.0	71.4	46.0
30	Cb-14.2W-28.8Hf	20,000	10.0	25.0	68.0	107.0	199.0	51.7
21	Cb-14.4W-35.9Hf	20,000	22.0	35.0	67.0	100.0	132.0	36.0

TABLE XXXIII

CREEP-RUPTURE DATA AT 2000°F FOR ALLOYS OF NOMINALLY Cb-15W-35Hf WITH ADDITIONS OF RHENIUM, TITANIUM, CARBON AND NITROGEN

Alloy No.	Composition (Wt.%)	Stress (psi)	Time to Specified Elong. (hr.)				Rupture Life(hr)	Total Elong(%)
			1%	2%	5%	10%		
21	Cb-[illegible].4W-35.9Hf	20,000	22.0	35.0	67.0	100.0	132.0	36.0
23	Cb-15.1W-34.8Hf-1.9Re	20,000	16.0	43.0	88.0	135.0	198.4	28.8
24	Cb-16.9W-33.2Hf-6.3Ti	20,000	0.8	1.1	2.0	2.9	5.3	51.5
25	Cb-16.7W-35.2Hf-11.0Ti	20,000	0.13	0.15	0.18	0.27	0.4	44.2
27	Cb-15.5W-36.0Hf-6.6Ti -0.048N-0.052C	20,000	0.7	0.9	1.6	2.6	3.9	54.0
29	Cb-15.0W-35.6Hf-6.4Ti -0.11C	20,000	0.4	0.8	1.6	2.3	3.8	51.2
6	Cb-9.8W-1.6Hf	12,500	6.4	11.4	20	26.6	36.7	54.0
27	Cb-15.5W-36.0Hf-6.6Ti -0.048N-0.052C	12,500 12,500(1)	1.0 0.25	2.6 1.0	6.2 3.0	12.0 5.6	15.6 13.5	43.2 81.0
29	Cb-15.0W-35.6Hf-6.4Ti -0.11C	12,500 12,500(1)	1.5 0.65	2.5 1.2	4.8 2.7	7.8 4.4	13.6 8.9	61.8 74.6

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(1) Specimen in stress-relieved condition; i.e., 1 hour at 2200°F

TABLE XXXIV

WEIGHT GAIN, METAL LOSS, OXYGEN CONTAMINATION, AND TOTAL PENETRATION DATA FOR Cb-W-Ta ALLOYS OXIDIZED IN AIR FOR 2 and 20 HOURS AT 2200°F

Alloy No.	Composition (Wt. Percent)
1	Cb-10.3W-15.6Ta
2	Cb-9.8W-28.3Ta
3	Cb-25.1W-15.8Ta
4	Cb-24.6W-31.6Ta
5	Cb-16.9W-23.8Ta

	Weight Gain (mg/cm^2)		Metal Loss (mils/radius)		Contamination (mils/radius)		Total Penetration (mils/radius)	
Alloy No.	2 hrs.	20 hrs.	2 hrs.	20 hrs.	2 hrs.	20 hrs.	2 hrs.	20 hrs.
1	32	142	3.5	15.5	≥ 128	≥ 116	≥ 131	≥ 131
2	24	109	3.0	10.0	≥ 130	≥ 123	≥ 133	≥ 133
3	26	140	8.5	41.0	≥ 117	≥ 84	≥ 125	≥ 125
4	84	398	45.5	86.0	≥ 80	≥ 39	≥ 125	≥ 125
5	33	168	3.5	20.5	≥ 96	≥ 79	≥ 99	≥ 99

Notes: Specimens were cylindrical.

Total Penetration = Metal Loss + Contamination.

Specimens were completely penetrated in all tests.

TABLE XXXV

WEIGHT GAIN, METAL LOSS, OXYGEN CONTAMINATION, AND TOTAL PENETRATION DATA FOR Cb-W-Ta ALLOYS OXIDIZED IN AIR FOR 20 HOURS AT 2000°F

Alloy No.	Composition (Wt. Percent)
1	Cb-10.5W-15.6Ta
2	Cb-9.8-28.3Ta
3	Cb-25.1W-15.8Ta
4	Cb-24.6W-31.6Ta
5	Cb-16.9W-25.8Ta

Alloy No.	Weight Gain (mg/cm^2)	Metal Loss (mils/side)	Contamination (mils/side)	Total Penetration (mils/side)
1	120	20	≥ 30	≥ 50
2	115	18	≥ 30	≥ 48
3	95	17	≥ 32	≥ 49
4	302	≥ 54	-	≥ 54
5	162	8	≥ 42	≥ 50

Notes: Specimens were rectangular.
Total Penetration = Metal Loss + Contamination.
Specimens were completely penetrated in all tests.
Specimen of Alloy No. 4 was completely oxidized.

TABLE XXXVI

WEIGHT GAIN, METAL LOSS, OXYGEN CONTAMINATION, AND TOTAL PENETRATION DATA FOR Cb-W-Hf ALLOYS OXIDIZED IN AIR FOR 2 AND 20 HOURS AT 2200°F

Alloy No.	Composition (Wt. Percent)
6	Cb-9.8W-1.6Hf
7	Cb-10.6W-30.8Hf
8	Cb-24.1W-4.4Hf
9	Cb-23.0W-26.5Hf
10	Cb-14.7W-18.7Hf

Alloy No.	Weight Gain (mg/cm^2)		Metal Loss (mils/side)		Contamination(mils/side)		Total Penetration (mils/side)	
	2 hrs.	20 hrs.	2 hrs.	20 hrs.	2 hrs.	20 hrs.	2 hrs.	20 hrs.
6	69	322	7.5	46	≥ 124	≥ 85	≥ 131	≥ 131
7	33	122	3	11	9	31	12	42
8	39	232	6	46	≥ 119	≥ 79	≥ 125	≥ 125
9	28	73	2	6	6	13	8	19
10	31	127	1	13	14	≥ 36	15	≥ 49

Notes: Specimens of Alloys No. 6 and 8 were cylindrical; therefore, oxidation measurements are mils/radius.

Specimens of Alloys No. 7, 9, and 10 were rectangular.

Total Penetration = Metal loss plus contamination.

TABLE XXXVI (continued)

WEIGHT GAIN, METAL LOSS, OXYGEN CONTAMINATION, AND TOTAL PENETRATION DATA FOR Cb-W-Hf ALLOYS OXIDIZED IN AIR FOR 2 AND 20 HOURS AT 2200°F

Alloy No.	Composition (Wt. Percent)	Alloy No.	Composition (Wt. Percent)
12	Cb-6.5W-26.3Hf	30	Cb-14.2W-28.8Hf
13	Cb-4.0W-34.4Hf	31	Cb-15.1W-34.1Hf
14	Cb-8.5W-28.6Hf	32	Cb-20.2W-21.6Hf

Alloy No.	Weight Gain (mg/cm^2)		Metal Loss (mils/side)		Contamination (mils/side)		Total Penetration(mils/side)	
	2 hrs.	20 hrs.	2 hrs.	20 hrs.	2 hrs.	20 hrs.	2 hrs.	20 hrs.
12	39	240	4	22	14	24	18	46
13	53	248	3	12	16	26	19	40
14	39	204	3	14	14	28	17	42
30	28	77	4	8	10	28	14	36
31	30	78	2	2	8	22	10	24
32	29	94	5	3	9	27	14	30

Notes: Specimens were rectangular.
Total Penetration = Metal Loss + Contamination

TABLE XXXVII

WEIGHT GAIN, METAL LOSS, OXYGEN CONTAMINATION, AND TOTAL PENETRATION DATA FOR Cb-W-Hf ALLOYS OXIDIZED IN AIR FOR 20 HOURS AT 2000°F

Alloy No.	Composition (Wt. Percent)
6	Cb-9.8W-1.6Hf
7	Cb-10.6W-30.8Hf
8	Cb-24.1W-4.4Hf
9	Cb-23.0W-26.5Hf
10	Cb-14.7W-18.7Hf

Alloy No.	Weight Gain (mg/cm^2)	Metal Loss (mils/side)	Contamination (mils/side)	Total Penetration (mils/side)
6	251	29	≥ 25	≥ 54
7	171	3	≥ 48	≥ 51
8	132	5	≥ 46	≥ 51
9	48	2	13	15
10	73	5	≥ 44	≥ 49

Notes: Specimens were rectangular.

Total Penetration = Metal Loss + Contamination.

TABLE XXXVII (continued)

WEIGHT GAIN, METAL LOSS, OXYGEN CONTAMINATION, AND TOTAL PENETRATION DATA FOR Cb-W-Hf ALLOYS OXIDIZED IN AIR FOR 20 HOURS at 2000°F

Alloy No.	Composition (Wt. Percent)	Alloy No.	Composition (Wt. Percent)
11	Cb-4.9W-34.9Hf	30	Cb-14.2W-28.8Hf
12	Cb-6.3W-26.3Hf	31	Cb-15.1W-34.1Hf
13	Cb-4.0W-34.4Hf	32	Cb-20.2W-21.6Hf
14	Cb-8.3W-28.6Hf		

Alloy No.	Weight Gain (mg/cm^2)	Metal Loss (mils/side)	Contamination (mils/side)	Total Penetration (mils/side)
11	263	≥ 52	—	≥ 52
12	257	≥ 49	—	≥ 49
13	290	≥ 56	—	≥ 56
14	267	≥ 52	—	≥ 52
30	51	3	≥ 49	≥ 52
31	54	2	15	17
32	66	9	≥ 44	≥ 53

Notes: Specimens were rectangular.

Total Penetration = Metal Loss + Contamination .

Specimens of alloys No. 11, 12, 13 and 14 were completely oxidized.

TABLE XXXVIII

WEIGHT GAIN, METAL LOSS, OXYGEN CONTAMINATION, AND TOTAL PENETRATION DATA FOR Cb-W-Hf ALLOYS OXIDIZED IN AIR FOR 20 AND 65 HOURS AT 2000°F

Alloy No.	Composition (Wt. Percent)
21	Cb-14.4W-35.9Hf
22	Cb-12.1W-35.5Hf

Alloy No.	Weight Gain (mg/cm^2)		Metal Loss (mils/side)		Contamination (mils/side)		Total Penetration (mils/side)	
	20 hrs.	65 hrs.	20 hrs.	65 hrs.	20 hrs.	65 hrs.	20 hrs.	65 hrs.
21	58	100	2	3	16	27	18	30
22	59	110	1	2	19	32	20	34

Notes: Specimens were rectangular.
Total Penetration = Metal Loss + Contamination.

TABLE XXXIX

X-RAY DATA FROM SURFACE OF ALLOY NO. 9 (Cb-25.0W-26.5Hf) FOLLOWING INCREMENTAL REMOVAL OF OXIDATION PRODUCTS. SPECIMEN OXIDIZED 20 HOURS AT 2200°F

As Oxidized			1 mil Removed			4 mils Removed		
d(Å)	Relative Intensity	Possible Identification(1)	d(Å)	Relative Intensity	Possible Identification(1)	d(Å)	Relative Intensity	Possible Identification(1)
3.74	100	A	3.75	100	A	3.75	100	A
3.65	27	A	3.65	27	A	3.62	56	A
3.53	52	A	3.53	40	A	3.55	51	A
3.38	27	A	3.38	20	A	3.21	25	A
2.96	50	B	2.96	38	B	2.96	55	B
2.88	35	-	2.88	20	-	2.88	30	-
2.85	30	A	2.86	19	A			
2.75	40	A	2.75	20	A	2.74	27	A
2.72	39	A	2.73	25	A			
2.64	43	-	2.64	28	-			
2.33	22	A	2.33	14	A			
1.91	37	A	1.91	52	A	1.91	80	A
1.68	30	A	1.68	25	A	1.69	40	A
1.58	25	A	1.58	21	A	1.58	19	A

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(1) A: Cb_2O_5 type

B: $Cb_2O_5 \cdot 6Hf\ O_2$ isostructural with $Cb_2O_5 \cdot 6Zr\ O_2$

TABLE XXXIX (continued)

X-RAY DATA FROM SURFACE OF ALLOY NO. 9 (Cb-23.0W-26.5Hf) FOLLOWING INCREMENTAL REMOVAL OF OXIDATION PRODUCTS. SPECIMEN OXIDIZED 20 HOURS AT 2200°F

11 mils Removed			18 mils Removed			37 mils Removed		
d(Å)	Relative Intensity	Possible Identification(1)	d(Å)	Relative Intensity	Possible Identification(1)	d(Å)	Relative Intensity	Possible Identification(1)
3.75	100	A	3.75	24	A			
3.59	40	A	3.59	40	A			
			3.43	30	A			
3.38	30	A	3.15	33	C			
2.96	80	B	2.96	43	B			
2.88	15	-						
2.85	17	A	2.84	29	A			
2.79	14	-						
2.73	9	A	2.58	30	C			
2.64	17	-	2.32	65	D	2.34	100	D
2.57	14	C						
2.24	85	-	2.25	100	-			
1.91	40	A						
1.68	36	A				1.66	35	D
1.58	22	A	1.58	24	A	1.35	55	D
1.29	28	-	1.29	24	-	1.17	12	D

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(1) A: Cb_2O_5 type
B: $Cb_2O_5 \cdot 6HfO_2$ isostructural with $Cb_2O_5 \cdot 6ZrO_2$
C: HfO_2
D: Cb-W-Hf solid solution

TABLE XI

WEIGHT GAIN, METAL LOSS, OXYGEN CONTAMINATION, AND TOTAL PENETRATION DATA FOR ALLOYS OF NOMINALLY Cb-15W-35Hf WITH ADDITIONS OF RHENIUM, TITANIUM, COBALT, ALUMINUM, VANADIUM, CARBON, AND NITROGEN OXIDIZED IN AIR AT 2000°F

Alloy No.	Composition (Wt. Percent)	Alloy No.	Composition (Wt. Percent)
21	Cb-14.4W-35.9Hf	25	Cb-16.7W-35.2Hf-11.0Ti
23	Cb-15.1 W-34.8Hf-1.9Re	27	Cb-15.5W-36.0Hf-6.6Ti-0.048N-0.052C
26	Cb-17.5W-33.5Hf-2.8Co	29	Cb-15.0W-35.6Hf-6.4Ti-0.11C
24	Cb-16.9W-33.2Hf-6.3Ti	28	Cb-15.7W-34.9Hf-5.5Ti-2.2Al-2.0V

Alloy No.	Weight Gain (mg/cm^2)				Metal Loss (mils/side)				Contamination (mils/side)				Total Penetration (mils/side)			
	4 (hrs)	20 (hrs)	65 (hrs)	100 (hrs)	4 (hrs)	20 (hrs)	65 (hrs)	100 (hrs)	4 (hrs)	20 (hrs)	65 (hrs)	100 (hrs)	4 (hrs)	20 (hrs)	65 (hrs)	100 (hrs)
21	-	58	100	-	-	2	3	-	-	16	27	-	-	18	30	-
23	-	90	123	-	-	6	11	-	-	14	23	-	-	20	34	-
26	-	62	112	-	-	3	20	-	-	6	8	-	-	9	28	-
24	-	42	82	-	-	3.5	9.5	-	-	9	12	-	-	12.5	21.5	-
25	-	57	116	-	-	7	12	-	-	6	7	-	-	13	19	-
27	21	53	99	134	0.5	3	7.5	10	6	8	11	12	6.5	11	18.5	22
29	21	57	94	116	1	3	5.5	10	7	10	17	17	8	13	22.2	27
28	17	46	116	155	0.5	1	5.5	19.5	3	5	7	5	3.5	6	12.5	24.5

Notes: Specimens were rectangular.

Total Penetration = Metal Loss + Contamination.

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13. ABSTRACT

This program was carried out for the development of a fabricable columbium-base alloy with improved oxidation resistance and good strength-properties at 2000°F and above for use as a blade material in gas turbine engines.

Nineteen electron beam melted ternary alloys from the Cb-W-Ta and Cb-W-Hf systems within the composition range 10-25 percent tungsten, 15-30 percent tantalum, 2-35 percent hafnium, were evaluated for fabricability, tensile and creep-rupture strength properties, and oxidation resistance. The composition Cb-15W-35Hf offered the best compromise in properties and was selected as the base for further alloying. A 1.9 percent addition of rhenium to this base did not enhance properties. Additions of 2.8 percent cobalt and nominally 5 and 10 percent titanium improved oxidation resistance but cobalt caused a pronounced depression in the solidus temperature and titanium reduced the creep-properties. Nominal additions of 1000 ppm carbon and 500 ppm carbon with 500 ppm nitrogen were not effective in restoring creep-rupture strength to the quaternary composition Cb-15W-35Hf-5Ti; an alloy containing approximately 2 percent each of aluminum and vanadium in this quaternary was the most oxidation resistant composition evaluated, but was not fabricated successfully.

The columbium alloys studied in this program did not meet the total property requisites placed upon a material for blade applications in gas turbine engines. Although the oxidation resistance and tensile properties shown by several of the Cb-W-Hf alloys were noteworthy, additional work would be required to achieve a better balance in properties for these materials.

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