NASA TECHNICAL NOTE

NASA TN D-3531

NASA TN D-3531

B065268

AMPTIAC

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

EFFECT OF ALLOYING ON GRAIN REFINEMENT OF ELECTRON-BEAM-MELTED TUNGSTEN

by Walter R. Witzke

Lewis Research Center

Cleveland, Ohio

20020328 114

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1966

NASA TN D-3531

EFFECT OF ALLOYING ON GRAIN REFINEMENT OF ELECTRON-BEAM-MELTED TUNGSTEN

By Walter R. Witzke

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – Price $1.00

EFFECT OF ALLOYING ON GRAIN REFINEMENT OF ELECTRON-BEAM-MELTED TUNGSTEN

by Walter R. Witzke

Lewis Research Center

SUMMARY

Ingot structures resulting from electron-beam melting of tungsten consist mainly of columnar grains extending the length of the ingot. In order to examine the grain refining capabilities of various elemental and refractory compound additions, small ingots of tungsten containing these additions were prepared by electron-beam melting. Measurements on transverse ingot sections from each melt indicated that all the additions decreased the average grain diameter of the columnar grains typical of electron-beam melted tungsten and that grain refining effectiveness varied with the concentration of the solutes. Losses of the additions during melting were in excess of 90 percent in many cases.

The most potent grain refiner was boron. A nominal addition of 0.5 weight percent decreased the average grain diameter of the columnar grains from 0.48 to 0.008 centimeter. The effectiveness of the elemental additions decreased in the following order: boron, yttrium, carbon, hafnium, zirconium, molybdenum, columbium, rhenium, and tantalum. The losses of these elements during melting also decreased in approximately the same order. The elemental additions were generally more effective grain refiners than the refractory compounds. The elements with the smallest distribution coefficients were the most effective grain refiners.

INTRODUCTION

The importance of grain size in metals as a means for influencing the workability and mechanical properties is well known. For improved properties the usual aim is toward finer grained materials.

The requirements for materials with improved properties for high temperature applications have stimulated considerable interest in tungsten and its alloys. Fine-

grained tungsten is not unusual and is readily prepared by powder metallurgy techniques. However, the consolidation of tungsten by melting, particularly electron-beam melting, results in ingot grains that are relatively large and columnar. Since large grain size is often associated with brittleness and lack of toughness, considerable improvement in mechanical properties and workability might be expected from a refinement of the grain size of electron-beam-melted tungsten.

Methods for controlling the as-cast grain size are discussed in some detail in the literature (refs. 1 to 3). Grain size refinement during solidification generally depends on how effectively the nucleation and growth rates in the ingot can be controlled through cooling rate, mechanical vibration, and alloying.

The promotion of grain refinement by means of alloying occurs as a result of (1) the increased nucleation caused by the addition of finely divided particles of an element or compound to the liquid metal and/or (2) the inhibition of grain growth by an element in solution. To act most effectively as a nucleus, a substance must be solid at the melting temperature of the bulk liquid, have a density similar to the base metal, and be wet by the liquid. Considering both the high melting point and high density of tungsten, the number of substances that might fulfill the requirements of a nucleating agent for refining the grain size of tungsten is quite limited.

However, the restriction of grain growth by alloying offers another means for grain size control in tungsten. Through use of a solute which with tungsten has a small distribution coefficient (ratio of solute concentration in the solid to that in the liquid in equilibrium with it), a concentration gradient is established in the melt at the solid-liquid interface that retards the growth of preexisting grains. Besides inhibiting grain growth, a concentration gradient may establish liquid regions where the actual temperature is less than the liquidus temperature. Under certain conditions, this constitutional supercooling can result in the formation of additional nuclei. Thus, solutes that can restrict grain growth or induce nucleation of new grains by constitutional supercooling might be expected to satisfactorily refine the grain size of electron-beam-melted tungsten.

The purpose of this study was to examine the effectiveness of various alloying elements and refractory compounds in decreasing the grain size of electron-beam-melted tungsten. The additions included potential alloying elements in tungsten, substances with high melting points, and elements with a wide range of distribution coefficients in tungsten.

The experimental work consisted of electron-beam melting each alloy twice and determining the characteristics of ingot slices removed after each melt. Data are presented for each alloy regarding grain size, retention of addition, hardness, and interstitial content.

TABLE I. - ANALYSIS OF TUNGSTEN POWDER

Element	Impurity level, ppm
Carbon	10
Oxygen	240
Aluminum	<10
Calcium	<10
Chromium	<10
Copper	<10
Iron	<10
Magnesium	<10
Manganese	<10
Molybdenum	30
Nickel	<10
Silicon	<10
Tin	<10

TABLE II. - MELTING POINTS OF ALLOY COMPOUNDS AND ELEMENTS ADDED

Alloy element or compound	Melting point[a]		Estimated equilibrium distribution coefficient[b]
	^{o}F	^{o}C	
Tungsten	6170	3410	------
Carbon[c]	6740	3727	0.0071
Rhenium	5755	3180	.56
Tantalum	5425	2996	------
Molybdenum	4730	2610	.71
Columbium	4474	2468	.51
Hafnium	4032	2222	.017
Boron	~3690	~2030	.0091
Zirconium	3366	1852	.089
Yttrium	2748	1509	<.01
Hafnium carbide	7050	3887	------
Tantalum carbide	6872	3800	------
Thorium oxide	5970	3299	------
Hafnium boride	5882	3250	------
Tantalum boride[d]	5430	3000	------
Zirconium oxide	4919	2715	------
Aluminum oxide	3659	2015	------

[a]Refs. 11 and 12; Manufacturers data sheet.

[b]Based on data from refs. 7 to 9.

[c]Sublimes.

[d]Decomposes.

EXPERIMENTAL PROCEDURE

Materials

The tungsten starting material for this study was commercial powder with a Fisher average particle size of 4.6 microns. The supplier's analysis of the powder is given in table I.

The alloy addition powders included boron, carbon (graphite), columbium, hafnium, molybdenum, rhenium, tantalum, yttrium, zirconium, and the compounds aluminum oxide, thorium oxide, zirconium oxide, hafnium boride, tantalum boride, hafnium carbide, and tantalum carbide. Table II lists the additions along with their melting points and estimated distribution coefficients in tungsten. These powders were of commercial high purity and generally were -325 mesh size.

The tungsten and alloying powders were blended and hydrostatically pressed into bars about $1\frac{1}{4}$ inches in diameter and weighing 5 pounds. Prior to melting, the bars were sintered in vacuum (10^{-4} torr) for 3 hours at 3400° F.

Melting

The bars were melted at a pressure of approximately 10^{-5} torr in a 150-kilowatt electron-beam furnace, which is described in reference 4. Each alloy was melted twice. The first melt, considered a consolidation melt, involved horizontal feeding of the sintered bar into an electron beam projected from a distant electron gun. The bar was drip-melted onto a layer of tungsten chips on a retractable pad in a $1\frac{1}{2}$-inch-diameter water-cooled copper crucible. The distant electron gun is a water-cooled copper structure containing a tungsten wire filament which emits electrons on heating. The electron stream is accelerated toward the crucible by the high voltage (10 kV) imposed on the gun and is focused by means of electromagnetic coils. The distant gun is more suited for the initial melting than a close electron gun since the distant gun, positioned about 20 inches from the crucible, is less sensitive to the gas bursts and resultant molten metal splattering that occur when sintered bars are initially melted. The tungsten ingot resulting from the first melt has an irregular surface and generally is remelted.

The second melt was made by feeding the ingot vertically through a close electron gun and drip-melting into a $1\frac{1}{2}$-inch-diameter crucible. The close gun was positioned 1 to 2 inches above the crucible and employed electrostatic focusing. Second melts usually involved little or no splattering or gas eruptions, most of the high vapor pressure additions having been removed in the first melt. Surface quality of the final ingots was im-

proved over that of the single-melt ingots but was not as good as that of larger diameter ingots prepared for other studies.

Sampling and Examination

A disk, approximately 1/4-inch thick, was cut from each ingot after each of the two melts for grain size and hardness determinations and chemical analysis. The disks were cut at least 1/4 inch from the top of the ingot to avoid the grain structure and possible compositional variations in the material last to solidify. After the faces had been ground parallel, the disk was electropolished in a 2 percent sodium hydroxide solution. Vickers hardness measurements (10-kg load) were averaged from the edge to the center of the disk. The macrostructure was revealed by electroetching or etching with Murakami's reagent. Grain diameter measurements were made on the etched transverse cross sections by the line intercept method (ref. 5). The microstructures of the metallographic specimens were examined after etching with boiling 3 percent hydrogen peroxide.

Chemical analyses were made on portions of the disks after grain size measurements. Gravimetric and X-ray fluorescence methods were employed for the determination of most of the addition elements. A Kjeldahl microanalysis for nitrogen and a wet chemical analysis for boron were carried out by an independent laboratory. Carbon was determined by the induction-combustion conductometric method, and oxygen by vacuum fusion.

RESULTS AND DISCUSSION

The results of grain size and hardness measurements on unalloyed tungsten and the 20 alloys studied are given in table III (p. 13). This table also includes the solute concentrations and the carbon, oxygen, and nitrogen analysis after each melt. The concentrations of carbon, oxygen, and nitrogen, except where large intentional additions of carbon were made, were essentially at the same level as in the unalloyed tungsten. Therefore, no effect on the grain refinement would be expected from these interstitials.

Ingot Grain Structure

Grain formation was influenced significantly by the method of heat extraction from the ingot and by the melting rate. The grain structure typical of the central portion of electron-beam-melted tungsten and tungsten alloy ingots is shown in figure 1. At the bottom of the ingot the first grains to form on the starter pad were small. As ingot formation proceeded, some of the grains in the first layer grew upward and continued to

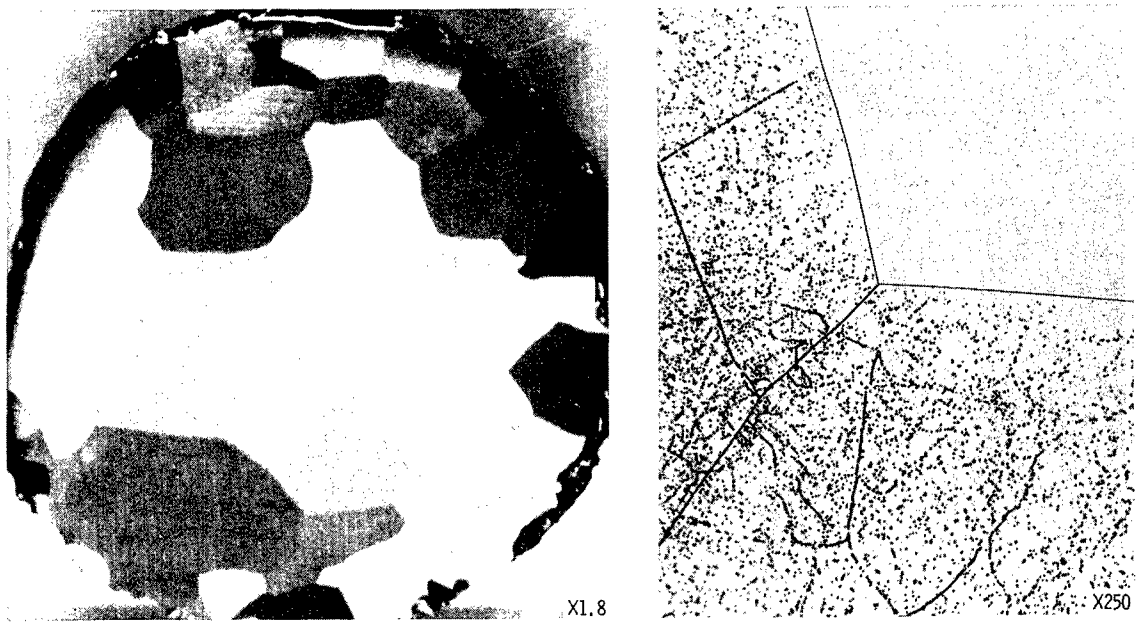
C-66-1707

Figure 1. - Typical longitudinal macrostructure of central section of double electron-beam-melted tungsten ingot. Murakami etchant. X1.9.

C-66-1708

Figure 2. - Longitudinal grain structure of second-melt ingot whose initial composition was tungsten-0.5 weight percent boron. Murakami's etchant. X2.4.

(a) First melt.



(b) Second melt.

C-66-1709

Figure 3. - Transverse cross section and microstructure of unalloyed tungsten after first and second electron-beam melts.

grow the entire length of the ingot. Because the orientation of the elongated grains in electron-beam-melted tungsten ingots has been shown to be completely random (ref. 4), it is difficult to explain the preferential growth of one grain over another. Even the tungsten-boron ingot that represented the best grain refinement in this report displayed an elongated grain structure (fig. 2).

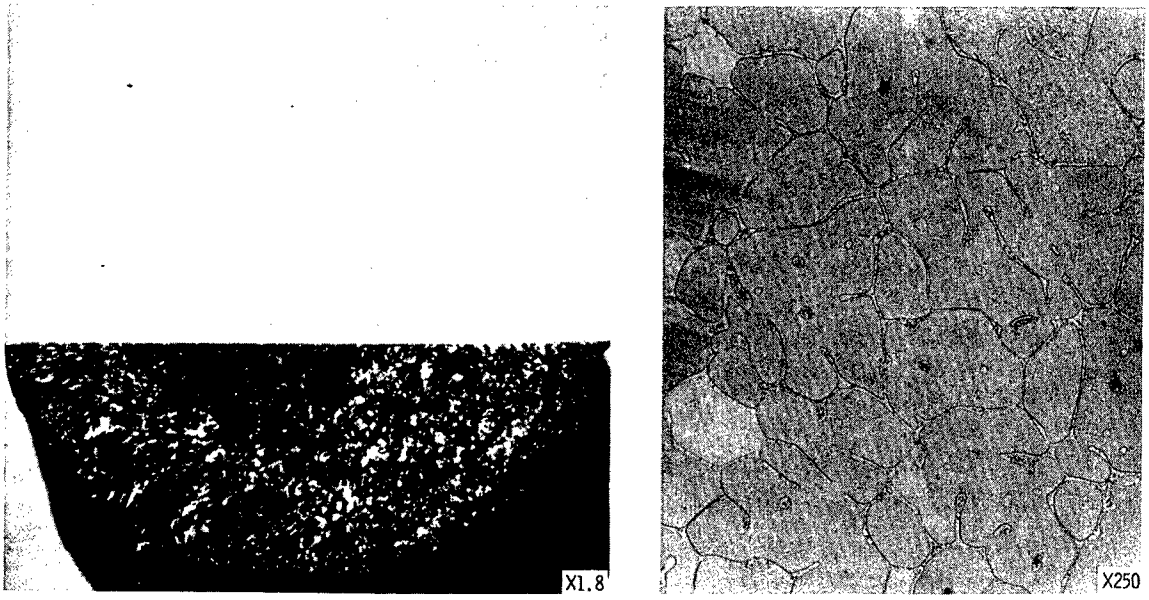
The elongated grain structure in the central portion of the ingots indicates that cooling was primarily by conduction through the retractable starter piece attached to the ingot base. Cooling from the crucible side walls limited the outer edges of the molten pool at the ingot top, but the solidified ingot shrank from the crucible walls and thus passed heat to the water-cooled crucible primarily by radiation. For this reason retractable-mold electron-beam-melted tungsten does not develop grains that grow radially from the outer edge to the ingot axis as is the case with conventional deep-mold arc-melted tungsten. The slow melting rates (up to 25 lb/hr) used in electron-beam melting are not conducive to small grain formation. Higher rates are precluded by power interruptions which are designed to protect the electrical equipment from overcurrent conditions that result when excessive vaporization of the melt materials occurs and high gas pressures exist at the gun. The combination of slow melting rate with almost unidirectional cooling of the ingot is largely responsible for the growth of the long axial grains in electron-beam-melted tungsten ingots.

The grain size of the ingots appears to have been primarily determined when the first layer was nucleated. No evidence was found for new grains forming among the elongated grains and, therefore, the influence of the additions was measured as a function of the average grain diameter in the transverse cross section of the ingots.

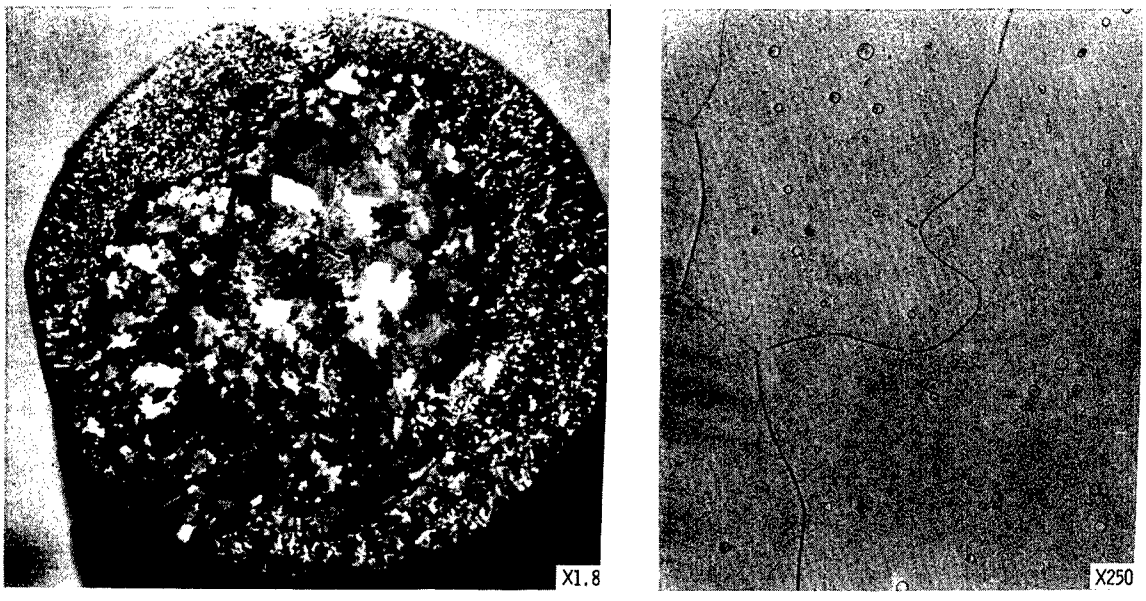
Grain Refinement by Elemental Alloying

In order to provide baseline grain size data, an unalloyed tungsten ingot was electron-beam melted. A longitudinal section of this ingot (fig. 1) illustrates the typical columnar grain growth in electron-beam melted ingots. The average ingot grain diameter determined for the transverse cross section was 0.48 centimeter for the first melt and 1.1 centimeters for the remelt (fig. 3). The increase in grain size on remelting is attributed to additional purification through vaporization of impurities that retard grain growth or augment nucleation. The microstructures in figure 3 show the etch pits and subgrain structure also typical of electron-beam-melted unalloyed tungsten.

The smallest grain size observed for the tungsten alloys was 0.008 centimeter for the nominal tungsten - 0.5 percent-boron alloy after one melt. The analyzed boron content after melting was 0.055 percent, approximately 10 percent of the original boron content. On remelting, the grain size increased to 0.031 centimeter and the boron content



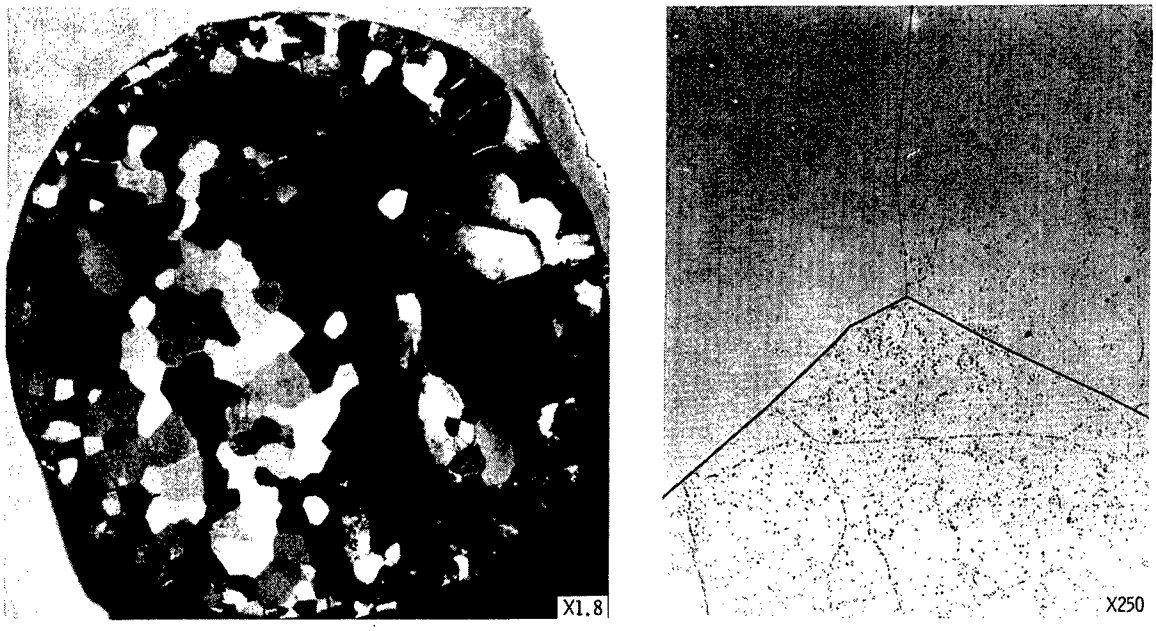
(a) First melt, 553 parts per million boron remaining.



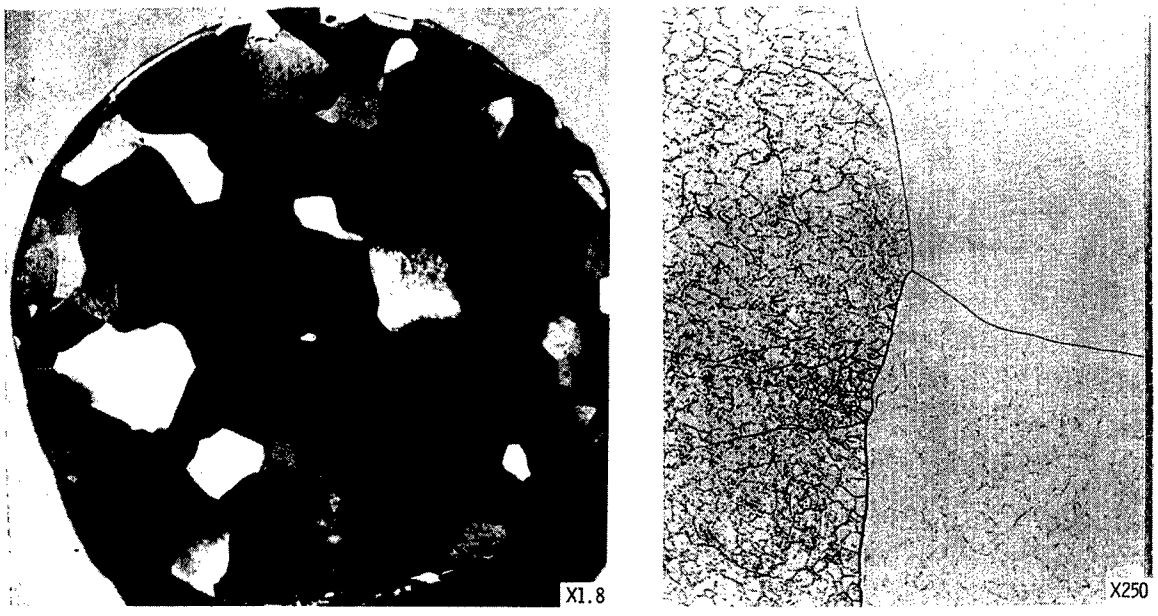
C-66-1710

(b) Second melt, 41 parts per million boron remaining.

Figure 4. - Transverse ingot cross section and microstructure of tungsten-0.5 weight percent boron after first and second electron-beam melts.



(a) First melt, 0.58 weight-percent molybdenum remaining.



(b) Second melt, 0.11 weight-percent molybdenum remaining. C-66-1711

Figure 5. - Transverse ingot cross section and microstructure of tungsten-2 weight percent molybdenum after first and second electron-beam melts.

decreased to 0.0041 percent. Figure 4 shows the ingot cross section and microstructures after the first and second melts. An intergranular and intragranular boride phase is apparent in both microstructures. These microstructures are similar to those observed in reference 6 in arc-melted tungsten-boron alloys of similar compositions. Two-phase microstructures were also noted in the melts containing additions of hafnium boride, tantalum boride, and tantalum carbide to be described in the section Grain Refinement by Compound Alloying.

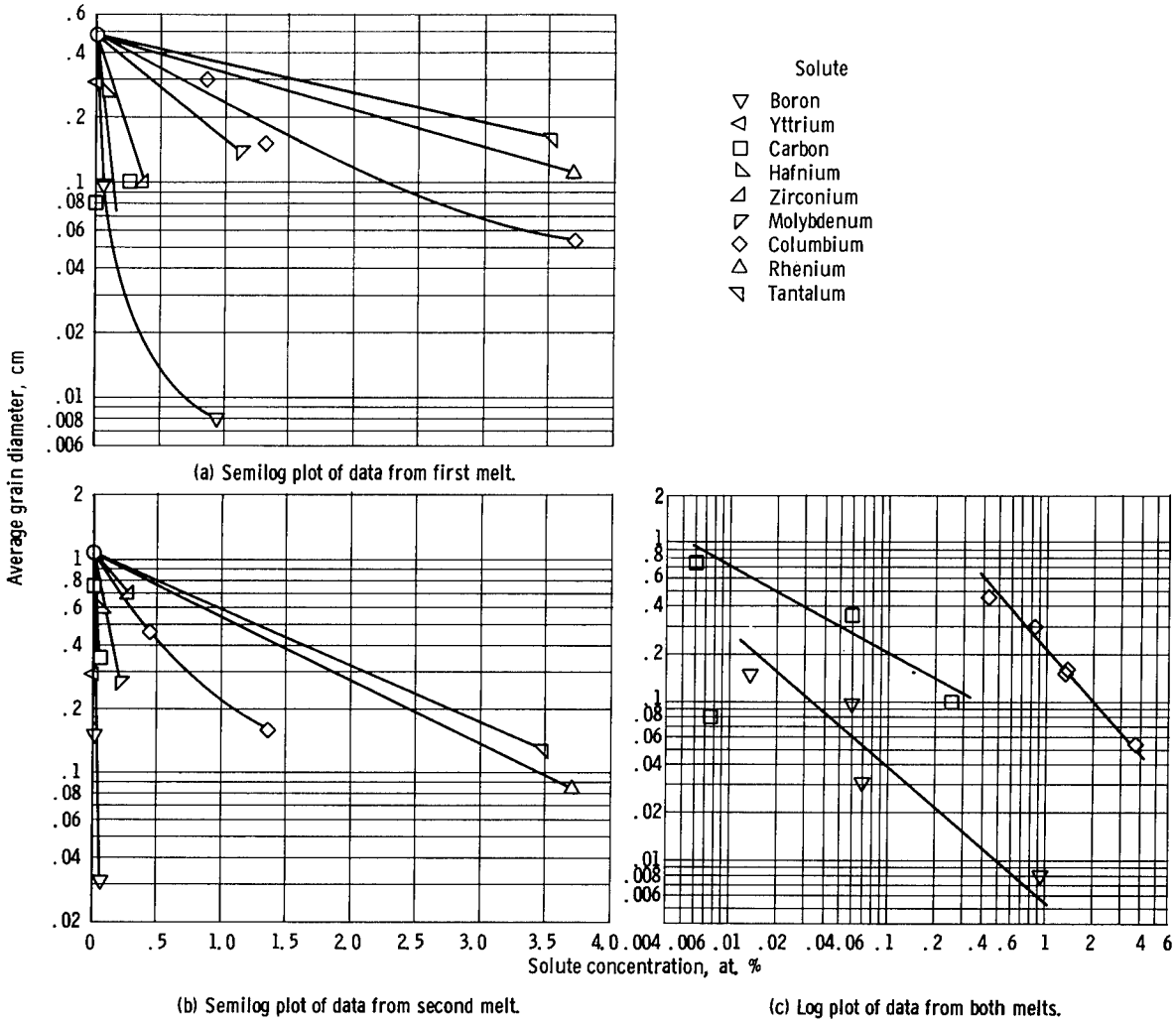
The tungsten-boron ingots prepared in this investigation were characterized by tears and laps. Frequent gas bursts produced by the boron evaporation caused power interruption and chilling of the molten pool at the top of the ingot with the resulting poor continuity apparent in the cross sections shown in figures 2 and 4. Tears were observed in all boron- and boride-containing ingots, especially at higher boron concentrations.

Representative of many of the metallic alloying additions are the melts containing molybdenum (fig. 5). The first melt retained 29 percent of the original molybdenum addition and had a grain size of 0.14 centimeter. The second melt results indicated only 5 percent of the molybdenum addition retained and an average grain size of 0.27 centimeter. The microstructures are similar to those shown for unalloyed tungsten in figure 3.

The effectiveness of the elemental additions during the first and second melts is shown in figures 6(a) and (b). The solute content of the ingots in atom percent analyzed after each melt is plotted against the grain size. Based on the decrease in grain size from that of unalloyed electron-beam-melted tungsten to that of the alloyed tungsten, the following order of effectiveness in refining the grain size of electron-beam-melted tungsten is indicated: boron, yttrium, carbon, hafnium, zirconium, molybdenum, columbium, rhenium, and tantalum. Because a number of these elements have relatively low melting points and/or high vapor pressures, their poor retention makes it difficult to determine their effectiveness as a function of concentration. As an example, yttrium additions appear very potent since the second melt ingot grain size was unchanged from that of the first melt (0.29 cm) even though the actual yttrium contents analyzed after melting were below the level of detection.

Further comparisons can be made by plotting the experimentally determined ingot grain size against the analyzed solute content on a log-log graph as in figure 6(a). From the suggested straight line relation it is apparent that 0.03 to 0.04 atomic percent boron is required to reduce the average grain diameter of electron-beam-melted tungsten to 0.1 centimeter, whereas, to attain the same grain size, approximately 10 times as much carbon and 70 times as much columbium are required.

The magnitude of the equilibrium distribution coefficient should be related to the grain refining ability of a solute element in a solvent metal. The distribution coefficient, which is the ratio of solute concentration in the solid to that in the liquid as shown in a



(a) Semilog plot of data from first melt.

(b) Semilog plot of data from second melt.

(c) Log plot of data from both melts.

Figure 6. - Effect of solute concentration on grain size of electron-beam-melted tungsten.

phase diagram, should be greatly different from unity for effective grain refinement. Table II (p. 3) lists some of the distribution coefficients that have been estimated for the elemental additions to tungsten (refs. 7 to 9). The solute elements yielding the lowest distribution coefficients were those that produced the finest grain sizes.

Grain Refinement by Compound Alloying

The refractory compounds, as well as the elemental additions, reduced the grain size in electron-beam-melted tungsten. The effects of the compound additions on the grain size varied depending on the material and quantity retained. A comparison of the effectiveness of these additions along with the analyzed ingot compositions is presented in figure 7 and table III.

The oxide additions, thorium oxide and zirconium oxide, despite indications of complete loss during melting, reduced the ingot grain size in the first melt to about 0.15 centimeter. However, on remelting, the average grain sizes increased to 0.44 to 0.93 centimeter and approached that observed for unalloyed tungsten. Similar results were experienced with the aluminum oxide addition, which showed an analyzed retention of 7 to 13 percent of the added aluminum and a trace of oxygen. These data suggest that the use of these oxides will produce only limited grain size reduction in tungsten, particularly where more than one melt is required.

Additions of tantalum boride and hafnium boride were the least effective of the additions evaluated in promoting grain size reduction. This is in contrast to the results with elemental boron, which indicated that boron additions were highly effective.

Additions of tantalum carbide and hafnium carbide yielded a first-melt grain size of 0.21 to 0.29 centimeter that did not change significantly on remelting (0.26 to 0.35 cm). The reason for only a slight increase in grain diameter can probably be traced to retained metallic elements since the tantalum and hafnium concentrations decreased only a relatively small amount and the grain size showed a correspondingly slight increase.

Alloying Losses During Melting

Poor recovery of the grain refining additions was generally experienced, as can be noted from the analyzed contents in table III (p. 13). This was expected since vapor pressure curves of the various elements indicate that most would vaporize appreciably at the melting point of tungsten. Of the elements used, the one with the highest vapor pressure was boron, followed in decreasing order by yttrium, zirconium, molybdenum, carbon, columbium, hafnium, rhenium, and tantalum (ref. 10). Approximately the same order was noted with material losses in this investigation. Boron, yttrium, molybdenum, and carbon losses were greater than 90 percent; losses of hafnium, zirconium, and columbium were in the range 80 to 90 percent; and tantalum and rhenium lost 15 percent or less of their initial concentration.

Based on melting point (table II, p. 3) alone, the refractory compounds would be considered to have excellent potential for grain refining tungsten. However, heavy melting losses were experienced, notably with the oxides. Although congruent evaporation may account for the losses of zirconium oxide and thorium oxide, the large amount of metallics remaining compared to boron or carbon suggests that the other refractory compounds dissociated during melting and their components evaporated at different rates. In comparing the hafnium and hafnium carbide data, it can be noted that a greater percentage of the original hafnium was retained by adding it as a carbide rather than as an element.

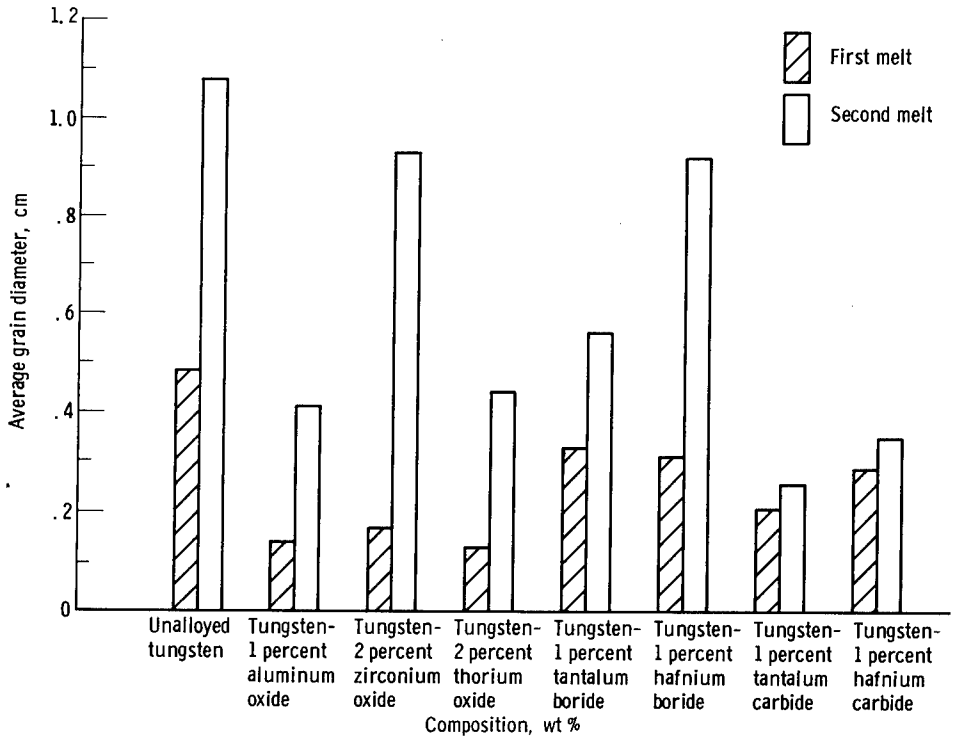


Figure 7. - Effect of refractory compounds on electron-beam-melted tungsten grain size. (See table III for analyzed composition after each melt.)

The Vickers hardness measurements shown in table III (p. 13) generally increase with increasing retained solute. The well-known softening effect of dilute rhenium additions to tungsten was also observed.

Practical Considerations

The results of this study indicate that grain refinement of electron-beam-melted tungsten can be accomplished to varying degrees through the use of elemental and refractory compound additions, depending on their concentrations. The most promising grain refiner was elemental boron. Its disadvantages were high boron losses during electron-beam melting and large laps and tears in the resultant ingot. However, these disadvantages were not noted in the arc melting of similar tungsten-boron alloys (ref. 6). The arc-melted products showed considerably smaller boron losses, good-quality fine-grained ingots, and generally improved mechanical properties (compared to unalloyed tungsten) in the fabricated condition. Therefore, under less drastic operating conditions than those experienced in the present electron-beam melting tests, boron additions in tungsten can result in a sound fine-grained ingot.

Carbon was also a potent grain refiner and is more suitable in electron-beam tungsten

TABLE III. - CHEMICAL ANALYSIS, GRAIN SIZE, AND HARDNESS OF ELECTRON-BEAM-MELTED TUNGSTEN ALLOYS

Nominal tungsten alloy composition, weight percent	Addition content						Average grain diameter, cm		Average Vicker's hardness[a]		Interstitial analyses, ppm					
	Calculated before melting		Analyzed after first melt		Analyzed after second melt		First melt	Second melt	First melt	Second melt	Carbon		Oxygen		Nitrogen (b)	
	Weight percent	Atomic percent (c)	Weight percent	Atomic percent (c)	Weight percent	Atomic percent (c)					First melt	Second melt	First melt	Second melt	First melt	Second melt
Unalloyed tungsten	-------	-----	------	-----	------	-----	0.48	1.1	344	373	1	7	3	3	ND <5	ND <5
Carbon, 0.005	[d]0.0026	[d]0.40	0.0005	0.008	0.0004	0.006	.08	.75	342	348	5	4	6	2	4	12
Carbon, 0.050	.05	.77	.017	.26	.0039	.060	.10	.35	386	377	168	39	4	6	18	11
Boron, 0.05	.05	.85	.0035	.060	.0008	.014	.098	.15	360	409	5	5	3	2	ND <5	ND <5
Boron, 0.5	.5	8.5	.055	.94	.0041	.070	.008	.031	433	376	5	7	5	6	ND <5	9
Hafnium, 0.5	.5	.52	.07	.07	.06	.06	.26	.59	378	364	5	7	4	3	10	18
Yttrium, 1.0	1.0	2.1	<.05	<.10	<.05	<.10	.29	.29	345	362	5	4	2	5	ND <5	ND <5
Zirconium, 1.0	1.0	2.0	.18	.36	.13	.26	.10	.69	354	354	6	10	3	1	14	16
Columbium, 2.0	2.0	4.0	.43	.85	.22	.44	.30	.46	357	377	7	5	3	2	ND <5	ND <5
Columbium, 2.0	2.0	4.0	.66	1.3	.69	1.4	.15	.16	363	380	6	7	3	3	ND <5	8
Columbium, 2.0	2.0	4.0	1.9	3.7	(e)	(e)	.054	(e)	401	(e)	5	(e)	4	(e)	1	(e)
Molybdenum, 2.0	2.0	3.8	.58	1.1	.11	.21	.14	.27	354	360	7	4	2	1	8	5
Rhenium, 4.0	4.0	4.0	3.8	3.7	3.7	3.7	.11	.085	322	317	8	6	2	2	7	13
Tantalum, 4.0	4.0	4.1	3.5	3.5	3.4	3.5	.16	.13	426	419	2	6	3	3	ND <5	ND <5
Aluminum oxide, 1.0	----	---	-----	-----	------	----	.14	.41	433	365	7	3	3	7	21	11
Aluminum[d]	.61	4.2	.042	.29	.080	.55	---	---	---	---	--	--	--	--	--	--
Oxygen[f]	.55	6.3	.0003	.003	.0007	.008	---	---	---	---	--	--	--	--	--	--
Zirconium oxide, 2.0	----	---	-----	----	-----	----	.17	.93	376	357	7	5	5	5	19	11
Zirconium[d]	1.8	3.7	<.03	<.06	<.03	<.06	---	---	---	---	--	--	--	--	--	--
Oxygen[f]	.64	7.4	.0005	.006	.0005	.006	---	---	---	---	--	--	--	--	--	--
Thorium oxide, 2.0	----	---	------	-----	------	-----	.13	.44	361	361	2	3	1	3	9	18
Thorium[d]	1.7	1.4	<.05	<.04	<.05	<.04	---	---	---	---	--	--	--	--	--	--
Oxygen[f]	.23	2.7	.0001	.001	.0003	.003	---	---	---	---	--	--	--	--	--	--
Tantalum boride, 1.0	----	----	------	-----	------	-----	.33	.56	401	370	5	3	3	3	9	7
Tantalum	.89	.90	.87	.89	.94	.96	---	---	---	---	--	--	--	--	--	--
Boron	.11	1.8	.0068	.12	.0006	.01	---	---	---	---	--	--	--	--	--	--
Hafnium boride, 1.0	---	----	-----	---	-----	---	.31	.92	376	363	4	5	3	3	18	12
Hafnium	.89	.92	.33	.34	.12	.12	---	---	---	---	--	--	--	--	--	--
Boron	.11	1.8	.022	.37	.0015	.026	---	---	---	---	--	--	--	--	--	--
Tantalum carbide, 1.0	---	----	----	---	-----	----	.21	.26	380	376	73	37	2	2	ND <5	8
Tantalum	.94	.95	.79	.80	.76	.77	---	---	---	---	--	--	--	--	--	--
Carbon	.06	.95	.0073	.11	.0037	.057	---	---	---	---	--	--	--	--	--	--
Hafnium carbide, 1.0	---	---	-----	---	-----	----	.28	.35	376	360	5	7	3	3	12	8
Hafnium	.94	.96	.83	.86	.74	.76	---	---	---	---	--	--	--	--	--	--
Carbon	.063	.96	.0005	.008	.0007	.011	---	---	---	---	--	--	--	--	--	--

[a]10 Kilogram load.

[b]ND, not detected.

[c]Calculated from weight percent analysis.

[d]Sintered bar analysis.

[e]No second melt.

[f]Calculated from metal analysis in sintered bar.

melting than boron on the basis of ingot quality. Where little loss of the grain refiner is desired, the metals with high melting points should be used, but with an expected higher limit in minimum ingot grain size.

CONCLUSIONS

This report has shown that refinement of the ingot grain size in tungsten by alloying is possible even in the relatively slow electron-beam melting process; however, the excessive loss of solute during melting can limit the degree of refinement. The major conclusions from this report are

1. All the elemental solutes decreased the grain size relative to unalloyed tungsten during electron-beam melting. For each solute the effectiveness increased with concentration.

2. The most potent grain refiner was boron; other elemental solutes were effective in the following approximate decreasing order: yttrium, carbon, hafnium, zirconium, molybdenum, columbium, rhenium, and tantalum. The losses of these elements during melting were also in approximately the same decreasing order.

3. Refractory compounds tended to vaporize or decompose during electron-beam melting. The compounds which decomposed (carbides and borides) provided some grain size control depending on the residual concentrations of the constituent elements. The vaporized compounds (oxides) were effective in initial melts but not during remelting.

4. The solute elements with the lowest distribution coefficients in tungsten were the most effective grain refiners.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 19, 1966.

REFERENCES

1. Rutter, J. W.; and Chalmers, B.: A Prismatic Substructure Formed During Solidification of Metals. Canadian J. Phys., vol. 31, no. 1, Jan. 1953, pp. 15-39.

2. Tiller, W. A.: Grain Size Control During Ingot Solidification. J. Metals, vol. 11, no. 8, Aug. 1959, pp. 512-514.

3. Form, G. W.; and Wallace, J. F.: General Principles of the Solidification of Metals. Metal Castings, vol. 37, Apr. 1960, pp. 145-156.

4. Witzke, Walter R.; Sutherland, Earl C.; and Watson, Gordon K.: Preliminary Investigation of Melting, Extruding, and Mechanical Properties of Electron-Beam-Melted Tungsten. NASA TN D-1707, 1963.

5. Anon.: Standard Methods for Estimating the Average Grain Size of Metals. ASTM Standards, pt. 3, ASTM, 1961, pp. 638-648.

6. Raffo, P. L.; and Klopp, W. D.: The Influence of Dilute Boron Additions on the Physical and Mechanical Properties of Arc-Melted Tungsten-1 Percent Tantalum Alloy. NASA TN D-3247, Feb. 1966.

7. English, J. J.: Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum, and Tungsten. Rept. No. DMIC152, Defense Metals Info. Center, Apr. 28, 1961.

8. English, J. J.: Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum, and Tungsten. Rept. No. DMIC183 (Suppl.), Defense Metals Info. Center, Feb. 7, 1963.

9. Goldschmidt, H. J.; Catherall, E. A.; Ham, W. M.; and Oliver, D. A.: Investigation Into the Tungsten-Rich Regions of the Binary Systems Tungsten-Carbon, Tungsten-Boron, and Tungsten-Beryllium. Rept. No. ASD-TDR-62-25, Pt. II, B.S.A. Res. Centre, Kitts Green, Birmingham (Gt. Brit.), July 1963.

10. Darken, L. S.; and Gurry, R. W.: Physical Chemistry of Metals. McGraw-Hill Book Co., Inc., 1953. (Data taken from Leo Brewer, Rept. for Manhattan Proj., MDDC-438C, 1946.)

11. Lyman, Taylor, ed.: Metals Handbook. Vol. I. Properties and Selection of Metals. Eighth ed., ASM, 1961.

12. Hodgman Charles David, ed.: Handbook of Chemistry and Physics. Thirty-eighth ed., Chem. Rubber Pub. Co., 1956-1957.

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

TECHNICAL REPRINTS: Information derived from NASA activities and initially published in the form of journal articles.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546