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INTRODUCTION

Tungsten appears to be one of the most important metallic materials being considered for structural use in aerospace applications at temperatures above 2500° F. It has been shown previously by a number of investigators that the high temperature tensile and creep strength of tungsten can be substantially increased by alloying (1-6). Both solid solution and dispersion strengthening were found to be effective. The purpose of the present study was to extend the authors' previous work on various tungsten alloy systems (1). The main conclusions from the earlier study were (a) the tensile and creep strength of arc melted tungsten at 2500° to 3500° F were increased, in decreasing order of effectiveness, by hafnium, tantalum, columbium, and rhenium and (b) the additions of carbon to a nominally W-1 atom percent columbium alloy resulted in a further increase in strength over that of the W-Cb binary alloy due to stabilization of the cold worked structure by carbide precipitates.

The present study was aimed at exploring the W-Hf system in more detail and examining the properties of several ternary alloys containing the above mentioned alloy additions. The mechanisms by which the various substitutional alloying elements strengthened tungsten were also considered.

An investigation of the effect of carbon additions on the high temperature strength of tungsten and tungsten alloys was conducted.

The alloy systems studied fell into two groups: solid solution strengthened alloys (W-Hf, W-Ta-Re, W-Ta-Hf, W-Re-Hf, and W-Cb-Hf) and carbide strengthened alloys (W-C, W-Cb-C, W-Ta-C, W-Ta-Re-C, and W-Hf-C). High temperature tensile tests in the temperature range of 2500° to 4000° F and step load creep tests at 3500° F were performed on swaged and recrystallized rod from these alloys. The results from this study are reported in greater detail in reference 7.

EXPERIMENTAL PROCEDURE

The alloys were prepared by consumable arc melting of pressed and sintered electrodes made from high purity elemental tungsten and alloy addition powders. The majority of the alloys were melted onto a tungsten pad attached to a retractable water-cooled copper stool. As the ingot was formed, it was retracted so that melting occurred near the top of the mold and consequently with a greater exposure to the vacuum than is possible with conventional deep mold techniques. The alloys were canned in molybdenum and fabricated by extrusion and swaging. The extrusion billets were induction heated in hydrogen and rapidly transferred to a conventional hydraulic press where they were extruded at reduction ratios of either six or eight to one at 3600° to 4300° F. The extrusions were then cut and swaged at 2300° to 3300° F with the molybdenum can intact. The swaged rod was ground into tensile specimens having a 1-in. gauge length and a 0.16-in. gauge diameter. Tensile tests were conducted in vacuum at a crosshead speed of 0.05 in./min. Step load creep tests were performed at 3500° F by applying a series of loads to a single specimen and measuring the minimum (steady state) creep rate as a function of stress. Further details on the experimental techniques may be found elsewhere (1, 7, 8).

RESULTS AND DISCUSSION

Consolidation And Fabrication

As mentioned in the section EXPERIMENTAL PROCEDURE, the majority of the alloys in this study were melted by a retractable stool technique that allowed the melting to take place in better vacuum than did the previous deep mold techniques employed in references 1 and 8. A comparison is made in table I of the metallic and interstitial impurity analyses of a lot of retractable stool melted tungsten with similiar data on five lots of deep mold melted tungsten from reference 8. It is seen that the retractable stool melted tungsten has a lower concentration of metallic impurities, while the interstitial impurities tend to be on the low side of the range indicated for the deep mold melted materials. The retractable stool melted ingot was particularly lower in aluminum, iron, and silicon. The extruded bar was rolled to sheet from retractable stool melted tungsten and annealed for 1 hr at various temperatures. After a 2200° F anneal, it was found to be 30 percent recrystallized. In contrast, deep mold melted material with the same amount of warm working recrystallized to this extent in the temperature range of 2600° to 2900° F (8). The lower recrystallization temperature of the retractable stool melted tungsten is believed to reflect its higher purity.

All of the alloys were fabricated after canning in molybdenum. Although no quantatative data are available on the relative extrudability of canned and uncanned alloys, it was found previously that the uncanned carbide strengthened alloys could only be extruded at 4800° F (1). In the present work, canned alloys of this type could be easily extruded at 4000° F. In addition, after a carbide strengthened alloy was extruded, cracking and center bursts during secondary fabrication were avoided by swaging with the can intact. Extrusion temperatures for the majority of the alloys were on the order of 4000° F.

Solid Solution Strengthened Alloys

Figure 1 illustrates the effect of hafnium on the strength of tungsten at 2500° to 3500° F in the recrystallized condition and 3000° and 4000° F in the as-swaged condition. The alloys tested at 4000° F recrystallized during heating to the test temperature and thus may be considered to have been tested in the recrystallized condition. Considerable strengthening was achieved with the hafnium additions. The tensile strength of a recrystallized W-1.7 percent Hf alloy* was nearly three times that of unalloyed tungsten in the temperature range of 2500° to 4000° F. The as-swaged tensile strengths of these alloys also increased with hafnium content, reaching a value of 81,000 psi at 3000° F at the 1.7 percent Hf level. At 3500° F, the as-swaged tensile strength is similiar to that of the recrystallized material, suggesting that the recrystallization temperature for these materials is below 3500° F.

A summary of the influence of binary alloy additions on the tensile strength of recrystallized tungsten is presented in figure 2. Included are data from references 1 and 9 in addition to the new results obtained on the W-Hf alloys in the present study. The curves drawn through the points are least-square fits of the data according to the relationship

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* All compositions in atom percent.

$$a_1\sigma_u^2 + a_2\sigma_u + a_3 = c$$

where σ_u is the ultimate tensile strength, c is the composition in atom percent, and a_1, a_2, and a_3 are constants. No great importance should be attached to the functional form of this equation as it was chosen primarily for convenience in calculating slopes of the curves and imterpolation.

At 2500° to 3500° F, hafnium has the greatest strengthening effect in tungsten. Columbium, tantalum, and rhenium are less effective. At 2500° F, the columbium and rhenium points fall on the same curve. Data for binary W-Ta alloys at 3500° F fell on a curve approximately 1000 psi above the curve for W-Cb alloys in figure 2(c). The W-Ta data are not given for clarity, and reference 1 may be consulted for details. Data at 4000° F was available only for hafnium and rhenium alloys (not shown), and the same order of effectiveness was seen. Plots of the creep strength at 3500° F versus alloy content (not shown) also indicated the same order of effectiveness in that hafnium additions produced the largest increase in strength and rhenium the least. For example, the stress at a minimum creep rate of 10^{-6} $\sec^{-1}$ was 10,000 psi for the W-1.7 percent Hf alloy and 4150 psi for a W-Re alloy of the same composition. These data are detailed elsewhere (7).

Figure 3 illustrates the effect of temperature on the tensile strength of worked ternary solid solution alloys. Of particular interest is the strength of the W-2.60 percent Ta-4.20 percent Re alloy. This alloy had a strength at 3500° F in the swaged condition of 38,900 psi and a value of 19,100 psi in the recrystallized condition. Subsequent metallographic examination revealed that the alloy had retained a cold worked structure after tensile testing at 3500° F. This increased stability of the cold worked structure at 3500° F was peculiar to the W-Ta-Re alloys. Other ternary solid solution alloys did not exhibit this retention of cold work to as high temperatures and the strengths at 3500° F were nearly identical in the recrystallized and swaged conditions. In the recrystallized condition, the binary W-1.7 percent Hf alloy was stronger than any of the ternary alloys tested. Additional data on these ternary alloys may be found in reference 7.

It is generally believed that each solute in a ternary solid solution alloy should contribute the same increment of strength in the ternary as it does in a binary alloy (10). To test this for arc melted tungsten alloys, the increments of strength were calculated from the binary alloy data in figure 2 for the individual solutes in the W-Cb-Hf, W-Ta-Hf, W-Ta-Re, and W-Re-Hf ternary alloys. The increments of strength were then added to the average strength for unalloyed tungsten at the temperature of interest. Figure 4 compares the calculated and experimentally determined strengths for alloys annealed for 1 hr at 3600° F. The agreement with the assumption of additive strengthening is good, especially considering that no corrections were made for variations in grain size or interstitial content among the alloys.

A quantitative measure of the effectiveness of a given solid solution strengthener is the slope of the strength-composition curve. These slopes at 1 percent solute were calculated from the curves in figure 2. Previous studies on are melted tungsten alloys revealed a qualitative dependence of the strengthening effectiveness on the difference in atom size between tungsten and the alloy addition (1). A more quantitative correlation was attempted here by plotting the slopes of the strength-composition curves against the percentage difference in atom size between tungsten and the alloy addition. The straigth line log-log correlation shown in figure 5 illustrates the atom size effect on the elevated temperature strength of tungsten alloys.

Differences in atom size may contribute to the elevated temperature strength by causing solute atoms to bind themselves to edge dislocation jogs in screw dislocations, resulting in a general decrease in dislocation mobility (12). In addition, differences in atom size may result in vacancies being bound to solute atoms so that the self-diffusion rate of the solvent is decreased with a subsequent decrease in the rate of dislocation climb (12).

Carbide Strengthened Alloys

The elevated temperature tensile strength of several carbon-containing alloys is illustrated in figure 6. Included are alloys in the W-C, W-Cb-C, W-Ta-C, and W-Hf-C systems. With the exception of W-0.75 percent Cb-0.24 percent C, the data shown in figure 6 were obtained on alloys in the as-swaged condition.

At 3000° F, the strengths of the alloys in the swaged condition varied from 62,000 to 88,000 psi, the latter being the strength of the W-0.20 percent Hf-0.26 percent C alloy. All the alloys retained a worked structure after testing at this temperature. At 3500° F, the strengths of the alloys showed wide variations. For example, the strength of a W-0.93 percent C alloy was only slightly higher than that of unalloyed tungsten (~ 10,000 psi). The W-Ta-C, W-Ta-Re-C, and W-Cb-C had strengths in the range of 16,000 to 26,000 psi and were recrystallized after testing. In contrast, the tensile strength of the W-0.20 percent Hf-0.26 percent C alloy was 62,500 psi and is, to these authors' knowledge, the highest strength yet reported for a metallic material at 3500° F. Subsequent metallographic examination revealed that the alloy had retained a wrought structure after the 3500° exposure. Recrystallizing the alloy (4 hr at 4200° F) resulted in a strength at 3500° F of 36,500 psi, which was still significantly higher than any of the other carbon containing alloys tested. The alloy had a 1-hr recrystallization temperature (50 percent recrystallized) of 4200° F.

The reason for the superior strength of the W-Hf-C alloys was revealed by metallographic analysis of these materials. In the W-C, W-Cb-C, W-Ta-C, and W-Ta-Re-C alloys, the carbides were relatively coarse and tended to be aligned in the working direction. In contrast, the carbides in the W-Hf-C composition were so fine that they could not be resolved at magnifications up to 1000×. An electron micrograph of the carbide structure of this alloy is shown in figure 7. A fine intragranular dispersion of particles, believed to be carbides, is seen in the micrograph. The carbide particle size ranged from approximately 0.05 to 0.2 μ, and no dependence of particle size on annealing temperature in the range of 3600° to 4200° F was observed. The excellent retention of cold work in this alloy was probably a result of this fine carbide particle size.

Limited studies were conducted on the compositions of the carbide phase in several of these carbide strengthened alloys. Particles extracted from a W-0.51 percent Cb-0.29 percent C alloy were identified by X-ray diffraction as W_2C. The position of the lines was shifted slightly, indicating a slight expansion of the W_2C lattice, possibly by dissolved columbium. Similar results were noted on a similiar alloy in reference 1. Identification of the carbides in the other alloys could not be made due to experimental difficulties in extracting the particles from the matrix. The similiar morphology of the carbides in the W-C, W-Cb-C, and W-Ta-C alloys, however, suggested that these were primarily W_2C also. The carbides in the W-Hf-C alloys had consistently finer particle sizes and were of a different morphology. It is believed that these carbides are HfC or complex tungsten-hafnium carbide. Hafnium carbide has been identified in tungsten-hafnium-carbon alloys by electron diffraction by a previous investigator (13).

Comparison of the Relative Strengthening Effect of Carbon and Boron in Tungsten

Elevated temperature tensile data have been obtained on both the W-C and W-B (14) systems. A portion of the data on the W-C system was previously shown in figure 6. Carbon has been shown to exist as an interstitial in tungsten (15), while it has been proposed that boron may exist simultaneously as a substitutional and an interstitial (16). A comparison of the strength data on alloys from both systems was made to determine the effect of this type of solid solution on the elevated temperature strength.

Figure 8 shows the effect of boron and carbon on the ultimate tensile strength of tungsten at 2500° and 3500° F. Carbon additions up to at least 0.3 atom percent decreased the strength. In contrast, boron produced a rapid initial increase in strength followed by a leveling off at higher boron contents. The some trends were observed at 3000° and 4000° F. It is believed that these differences between the W-C and W-B alloys reflect the previously mentioned differences in the type of solid solution formed. The initial strengthening by boron additions has been examined previously by the present authors who concluded that the magnitude of the intial slope of the strength-composition curve fit well with the concept of a simultaneous interstitial-substitutional solid solution with the balance tending toward substitutional (14). In contrast, carbon additions apparently weaken by promoting an increase in the self-diffusion rate of tungsten. This behavior has been previously noted for carbon additions to gamma iron (17,18). The increase in the self-diffusion rate results in a more rapid rate of dislocation climb which subsequently lowers the elevated temperature strength.

Low Temperature Tensile Properties of Binary Tungsten-Carbon Alloys

The low temperature tensile properties (400° to 800° F) of the binary tungsten-carbon alloys were studied to more fully characterize the materials. Figure 9 illustrates the low temperature yield strength and percent elongation as a function of temperature. The yield strength increased continuously with increasing carbon content in the temperature range of 400° to 800° F. A measurable amount of ductility was observed at 400° F for the W-C alloys and the extrapolation of the elongation-temperature curve intersected the temperature axis (the nil-ductility temperature) at a temperature from 150° to 200° F lower than that for unalloyed tungsten. These results are in sharp contrast to a previous investigation on the influence of carbon where it was shown that carbon added by carburization of the surface and subsequent diffusion annealing produced a significant increase in the ductile-brittle transition temperature of tungsten (19). In this previous study, the major portion of the carbide precipitate was present at the grain boundaries, while the carbide was mainly stringered in the working direction in the present study and only a small amount was present in the grain boundaries. It is apparent that the low temperature ductility of such a tungsten-carbon alloy depends strongly upon the distribution of the second phase.

CONCLUSIONS

1. The most effective solid solution strengthener in tungsten in the temperature range of 2500° to 4000° F is hafnium. Tantalum and columbium are less effective, while rhenium is the least effective. The same order holds in creep as in short time tensile tests.

2. The relative solid solution strengthening effects could be correlated with the difference in atom size between tungsten and the solute atom.

3. The strengths of ternary solid solution alloys could be represented as the sum of the individual strengthening effects found in the binary alloys at 2500° to 3500° F. Tungsten-tantalum-rhenium alloys showed greatly enhanced resistance to recrystallization at 3500° F.

4. Carbon additions to W-Cb, W-Ta, W-Ta-Re and W-Hf alloys produced various degrees of strengthening. The greatest strengthening was found in the W-Hf-C system. The strongest alloy, W-0.20 percent Hf-0.26 percent

C (-0.017 wt percent carbon) had strengths of 88,200 and 62,500 psi at 3000° and 3500° F, respectively, The differences in strength between the various carbide strengthened alloys were related to the differences in carbide particle size. The particle size in the W-Hf-C alloys was the finest, being on the order of 0.05 to 0.20 μ.

5. Carbon additions to unalloyed tungsten at 2500° to 4000° F produced a minimum in the strength-composition curve. This behavior may be caused by an increase in the self-diffusion rate of tungsten by carbon. The nil-ductility temperature of arc melted tungsten was lowered by additions of carbon in the range 0.12 to 0.93 percent.

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TABLE 1. - COMPARISON OF CHEMICAL ANALYSES OF DEEP MOLD AND RETRACTABLE STOOL ARC MELTED UNALLOYED TUNGSTEN

ANALYSES		
Element	Retractable stool	Deep mold (Average of 5 lots)
C	4	4 to 9
N	5	8 to 13
O	2	2 to 6
Al	< 1	2 to 20
Ca	< 1	< 10
Cr	1	< 5 to 7
Cu	5	1 to 5
Fe	3	5 to 60
Mn	< 1	< 1
Mo	5	15
Na	< 1	< 10 to 20
Ni	< 1	2 to 10
Si	< 1	5 to 15
Sn	< 1	< 5
K	< 1	< 10 to 10

E-3132

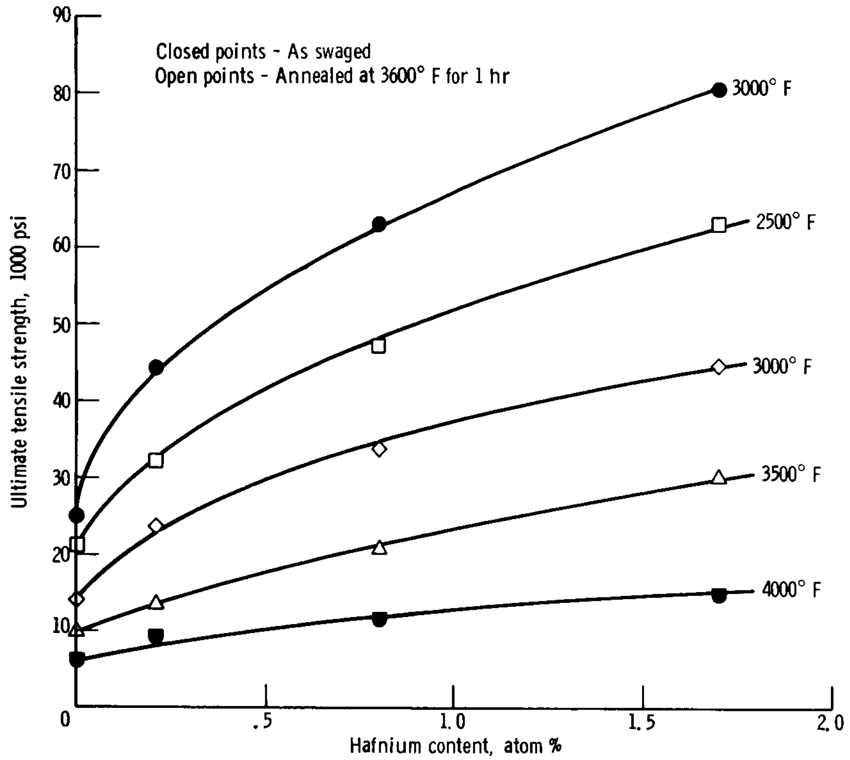
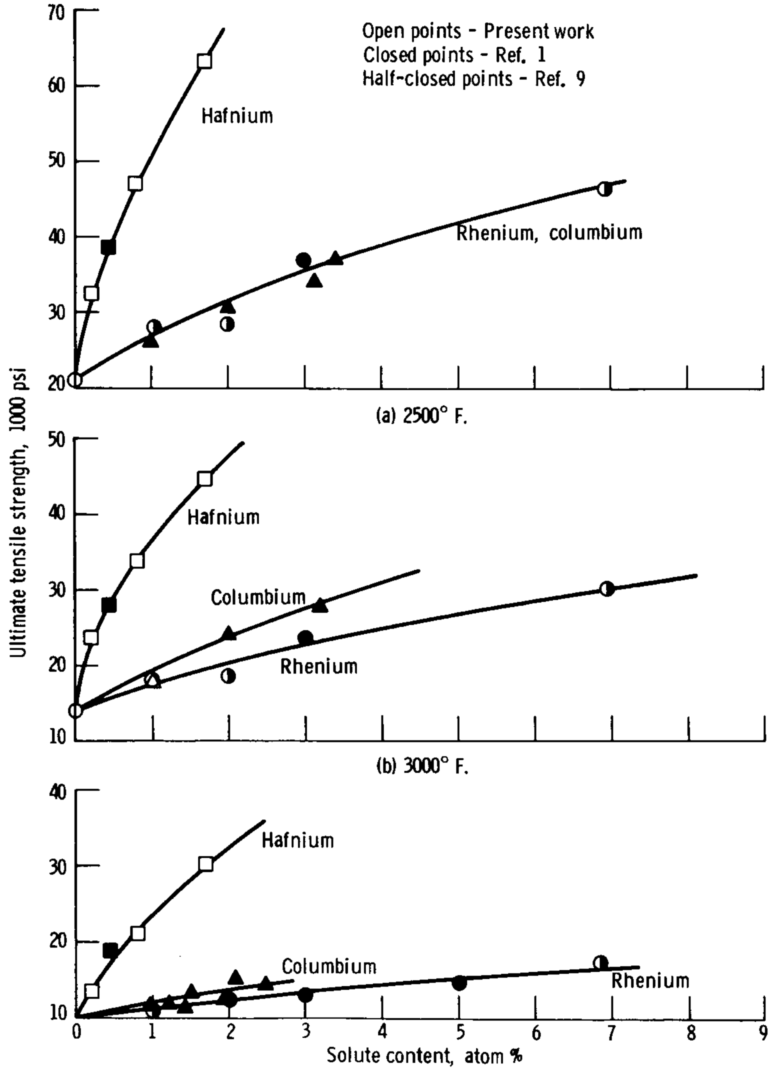


Figure 1. - Effect of hafnium on the 2500° to 4000° F tensile strength of recrystallized tungsten.



(a) 2500° F.

(b) 3000° F.

(c) 3500° F.

Figure 2. - Effect of alloying on the strength of arc melted tungsten at 2500° to 3500° F.

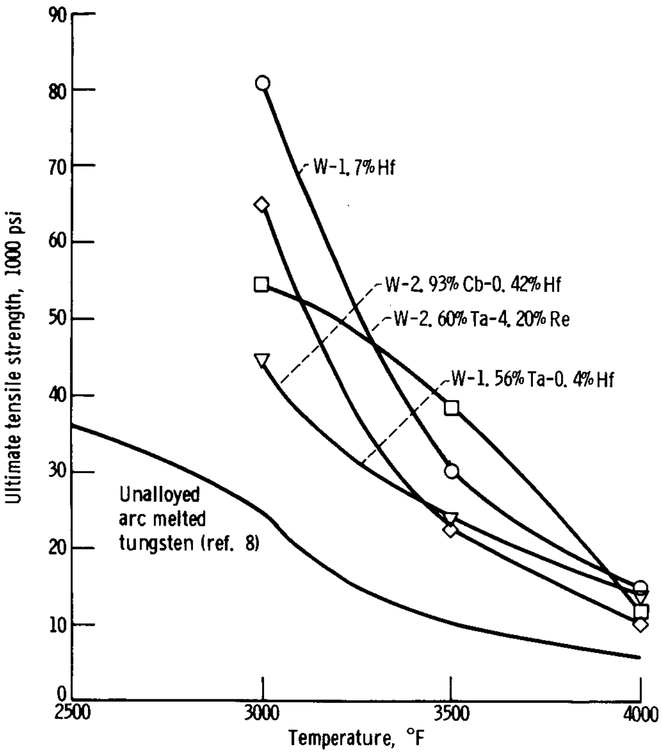


Figure 3. - Elevated temperature tensile strength of swaged solid solution strengthened alloys.

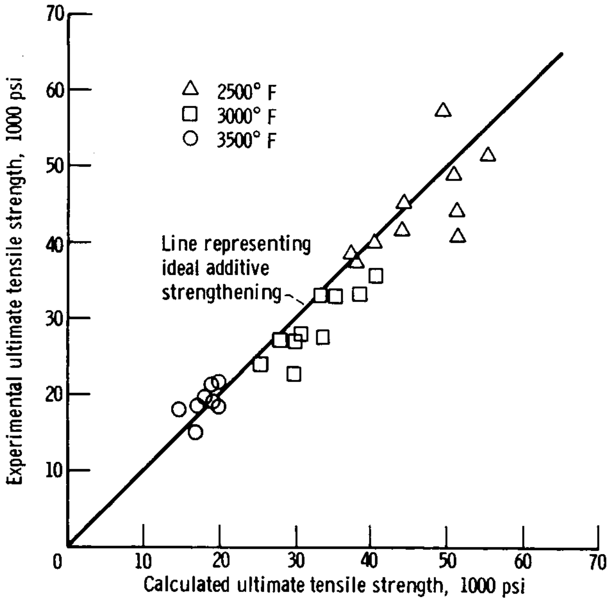


Figure 4. - Comparison of experimental tensile strengths with the values calculated by assuming that the strengthening effects are additive. Alloy systems include W-Ta-Re, W-Re-Hf, W-Ta-Hf, and W-Cb-Hf.

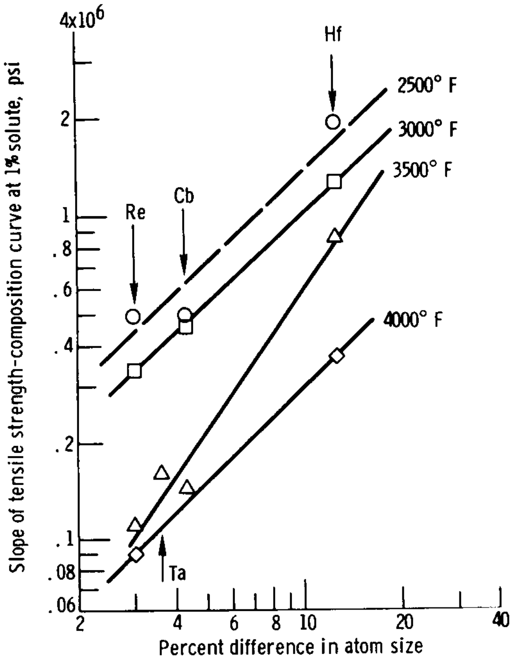


Figure 5. - Variation of rate of solid solution strengthening with percent difference in atom size between tungsten and solute.

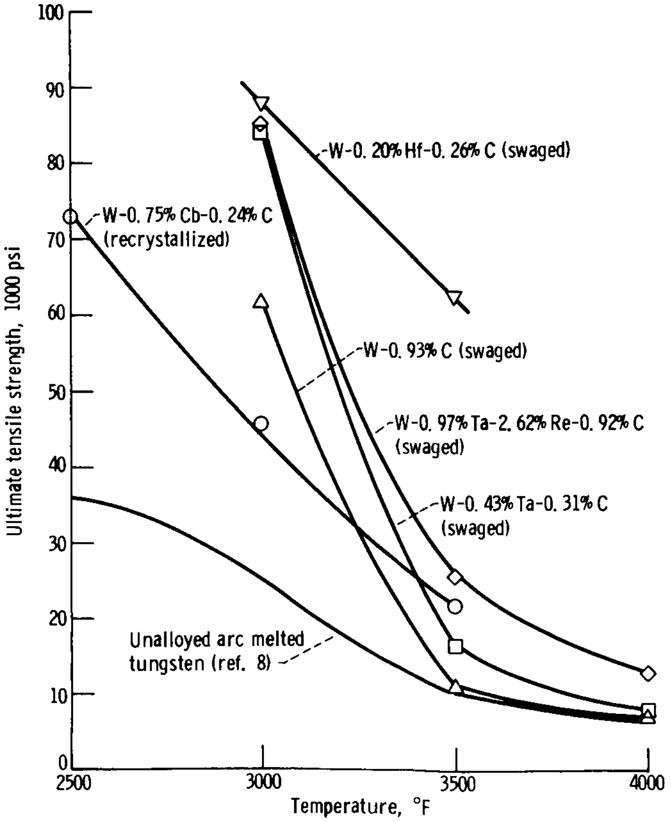


Figure 6. - Elevated temperature tensile strength of several carbide strengthened tungsten alloys.

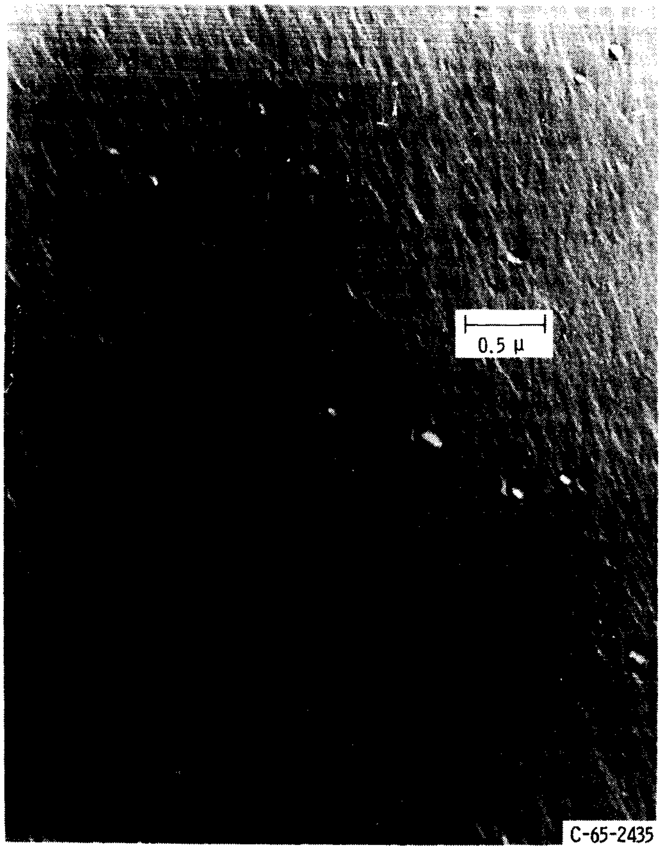


Figure 7. - Electron photomicrograph of a W-0.20% Hf-0.26% C alloy after annealing for 1 hr at 4200° F; 45,000X.

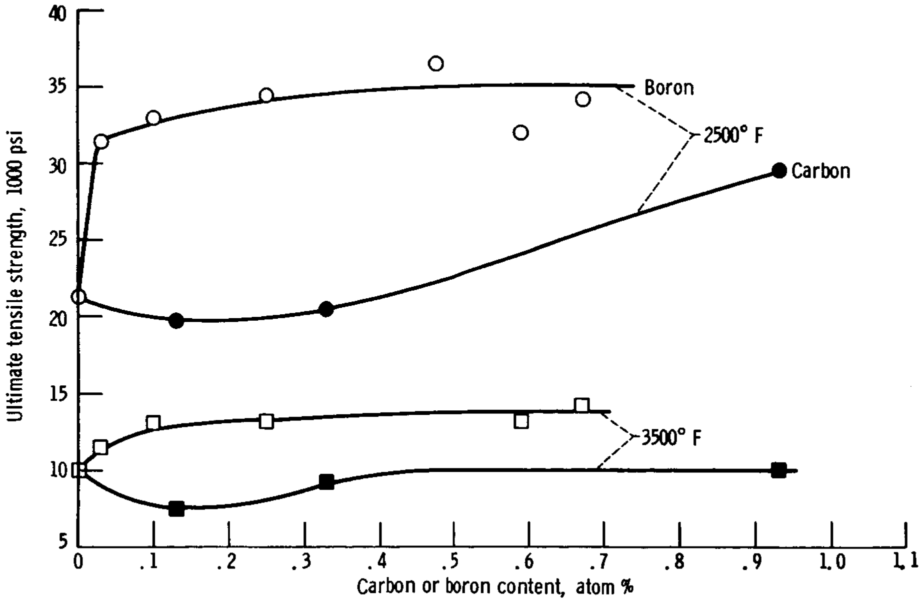


Figure 8. - Effect of carbon or boron on ultimate tensile strength of arc melted tungsten at 2500° F and 3500° F (W-B data from ref. 14).

E-3132

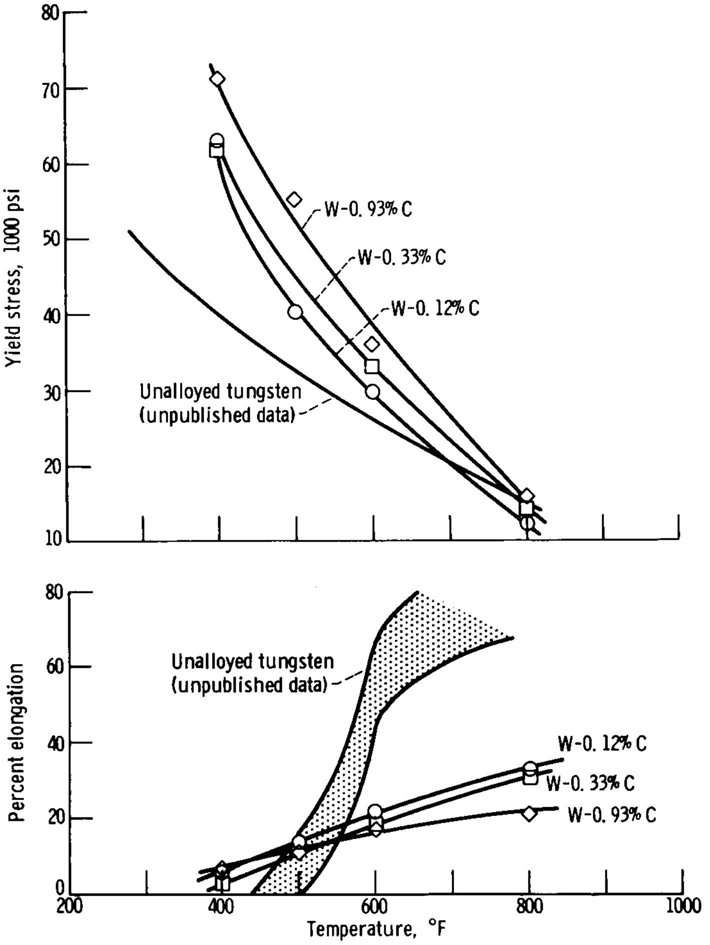


Figure 9. - Low temperature tensile behavior of recrystallized W-C alloys.