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COMPOSITION EFFECTS ON MECHANICAL PROPERTIES OF TUNGSTEN-RHENIUM-HAFNIUM-CARBON ALLOYS

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16. Abstract

The mechanical properties of rod and sheet fabricated from arc melted W-4Re-Hf-C alloys containing up to about 0.8 mol percent hafnium carbide (HfC) were evaluated in the as-worked condition. DBTT's of electropolished bend and tensile specimens were independent of HfC content in this range but dependent on excess Hf or C above that required for stoichiometric HfC. Low-temperature ductility was a maximum at Hf contents slightly in excess of stoichiometric. Variations in high-temperature strength were also dependent on excess Hf and C. Maximum creep strengthening also occurred at Hf contents in excess of stoichiometric. Analysis of extracted second-phase particles indicated that creep strength was reduced by increasing WC content in the HfC particles.

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COMPOSITION EFFECTS ON MECHANICAL PROPERTIES OF TUNGSTEN-RHENIUM-HAFNIUM-CARBON ALLOYS

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SUMMARY

Arc melted tungsten - 4 percent rhenium - hafnium - carbon (W-4Re-Hf-C) alloys containing up to about 0.8 mol percent HfC were fabricated into rod and sheet for evaluation of compositional effects on mechanical properties in the as-worked condition. The bend and tensile ductile-brittle transition temperatures (DBTT) of electropolished bend and tensile specimens were strongly dependent on composition. The low-temperature ductility of the worked alloys was determined to be independent of calculated HfC content in the range studied but dependent on the excess Hf or C above stoichiometric HfC. The lowest DBTT was found at Hf contents slightly in excess of stoichiometric. Tensile and creep strengths appeared to be highest at about 0.35 mol percent HfC. Strength variations at 0.2 to 0.5 mol percent HfC were also dependent on excess Hf and C. Maximum creep strengthening occurred also where the Hf content was slightly in excess of stoichiometric.

Lattice parameter measurements and emission spectroscopy analysis of extracted second-phase particles indicated that the particles consist of hafnium carbide with a minor amount of tungsten carbide in solid solution. Creep strength was reduced by increasing tungsten carbide content in the particles.

INTRODUCTION

Interest in tungsten (W) alloys for aerospace and nuclear applications has prompted investigations to improve the strength and workability of this highest melting metal.

Previous studies (refs. 1 and 2) have shown that the high-temperature strength of tungsten can be increased up to eightfold by the presence of hafnium carbide (HfC) precipitates and that low-temperature ductility could be improved by moderate additions of rhenium (Re). Subsequently, additions of 4 atom percent Re to the W-Hf-C alloys have

been shown to improve the strength-ductility properties of the ternary alloys (refs. 3 and 4). The purpose of this continued study of the W-Re-Hf-C alloys has been to examine the effects of Hf and C in excess of stoichiometric HfC on mechanical properties.

The present report provides additional data on as-worked W-Re-Hf-C alloys and describes the effect of excess hafnium and carbon on bend, tensile, and creep properties. A correlation between carbide particle composition and high temperature creep behavior is presented. Limited experiments involving in-process solution annealing treatments at various stages of fabrication are discussed in the appendix.

EXPERIMENTAL PROCEDURE

Materials

The tungsten alloys used in this study contained from 3.1 to 4.4 atom percent (at. %) rhenium, 0.20 to 0.76 at. % hafnium, and 0.01 to 1.35 at. % carbon. Oxygen and nitrogen impurities ranged from 6 to 12 ppm and 1 to 4 ppm, respectively. Mol percent (mol %) HfC was assumed to be equal to the at. % Hf or C, whichever was lower. Hafnium contents were determined by an ion exchange and colorometric procedure with an estimated precision of ±5 percent. Carbon determinations were made by a combustion chromatographic procedure (Leco) and are also considered to have a precision of about ±5 percent.

The alloy materials were prepared by thorough blending of the metal and graphite powders, hydropressing, and sintering into electrode shapes and vacuum arc melting into 5.8-centimeter (cm) (2.3-in.) diameter ingots weighing about 4500 grams (g) (10 lb). Billets machined from these ingots were canned in powder metallurgy molybdenum and extruded at 2200° C (4000° F) with a reduction ratio of 8. The extruded rod was further fabricated at 1760° C (3200° F) by rolling or swaging with 88 to 94 percent reduction in area.

A limited study of thermomechanical processing as opposed to the standard fabrication procedure is discussed in the appendix.

Evaluation

Mechanical tests. - Bend tests were performed in order to determine ductile-brittle transition temperature (DBTT) on approximately 0.076-cm (0.030-in.) thick longitudinal sheet specimens measuring 2.5 by 0.8 cm (1.0 by 0.3 in.). The specimens were electropolished to remove a minimum of 0.008 cm (0.003 in.) of material from each side before bending. The bend DBTT is defined here as the lowest temperature at which a

sheet specimen can be bent through 90° over a bend radius four times the specimen thickness without failure. Three-point loading was used with a ram speed of 2.5 cm/min (1 in./min).

Tensile and creep specimens had a 2.5-cm (1-in.) gage length and a reduced diameter of 0.28 to 0.36 cm (0.11 to 0.14 in.). Tensile tests were performed at 1930° C (3500° F) in a vacuum chamber below 10^{-3} newton per square meter $(N/m^2)(10^{-5}$ torr). Tensile tests were also conducted at lower temperatures ranging from 90° to 700° C (200° to 1300° F); air or argon was the environment for these tests. A constant crosshead speed of 0.13 cm/min (0.05 in./min) was used.

Constant load creep rupture tests were carried out at 1930° C (3500° F) under vacuum of 10^{-4} N/m^2 (10^{-6} torr) in a conventional beam-loaded machine. Strain measurements were determined from the movement of tungsten extension rods connecting the specimen buttonheads to a linear variable differential transformer. Test temperature was measured by a W/W-26Re thermocouple attached to the reduced section of the specimen.

Microstructural studies. - Thin films for transmission electron microscopy were prepared from disks about 0.03-cm (0.01-in.) thick removed from the transverse cross section of each material. The center of each disk was reduced in thickness by jet electropolishing. The entire disk was then reduced in thickness by electropolishing in a 2 percent sodium hydroxide solution until the center spot was just pierced. Electron micrographs of selected areas of the thin films were used in conjunction with a Zeiss particle size analyzer to determine the median particle diameter (or longest dimension) of the carbide phase.

The second-phase particles were extracted from the matrix by electroetching in an aqueous 2 percent sodium hydroxide solution at 3 volts. The carbide particles were isolated by centrifuging and by thorough hot water rinsing to remove the sodium tungstate. X-ray diffraction analysis provided lattice parameter measurements of the carbide particles. Emission spectrographic analysis of the extracted particles gave a quantitative measure of metallics present with a precision of ±10 percent.

RESULTS AND DISCUSSION

Low-Temperature Ductility

The effect of alloy composition on the low-temperature ductility of HfC-strengthened tungsten alloys was studied by determining the DBTT in bending (for sheet) or in tension (for bars) on as-worked electropolished materials.

Bend test results are presented in table I. The variation in Re content ranging from 3.1 to 4.4 at.% in these alloys is neglected in the following analysis because these dif-

ferences would be expected to change the DBTT values by only about 15° C (25° F) (ref. 2). The effect of the calculated HfC content on the bend ductility of as-rolled W-Re-Hf-C sheet is difficult to ascertain in figure 1 because of the scattered data. There appears to be no significant dependence of bend ductility on HfC content over the composition range investigated in these W-4Re-Hf-C alloys.

The available data were further analyzed to try to ascertain the effects of Hf and C in excess of that required to form stoichiometric HfC in tungsten base alloys. Let us first consider the influence of C and Hf separately on unalloyed tungsten. Previously unpublished bend results determined by Raffo at Lewis are presented in table II and figure 2. Compared to unalloyed tungsten (ref. 5) these data indicate a rapid rise in bend transition temperature as the C content in tungsten is increased; however, additions of Hf cause an initial lowering of the DBTT followed by a gradual increase. The initial drop in DBTT by Hf additions may be the result of this reactive metal combining with interstitial impurities in the tungsten. Thus, the presence of uncombined or excess Hf or C can be expected to have a considerable influence on ductility.

This is examined further in figure 3 where excess solutes measured as the difference between total C and total Hf contents is plotted against bend DBTT for W-Hf-C and W-4Re-Hf-C alloys. The shaded areas show the general trend of the data and its similarity to the superimposed curves for W-C and W-Hf alloys. The data scatter within the bands may represent the effects of fabrication differences. This plot indicates that bend ductility tends to improve as stoichiometry is approached, with a possible minimum in DBTT at a slight excess of Hf.

Tensile tests at low temperatures were conducted, and the ductile-brittle transition temperatures observed (based on at least a 5% reduction in area for ductile behavior) are recorded in table III. In figure 4 the various tungsten alloys are noted to yield similar trends in tensile ductility with excess solute as were observed with the bend data. The tensile DBTTs increase directly with the amount of excess C present in the tungsten alloy, and a minimum in DBTT is projected in the region of a slight excess of Hf.

High-Temperature Tensile Strength

It is well known that the high-temperature strength of refractory metals is greatly influenced by the presence of second-phase particles such as carbides (ref. 6). But the presence of an excess of a second-phase component such as Hf or C and its effect on alloy strength has not been examined previously.

The tensile properties of swaged W-4Re-Hf-C alloys tested at 1930° C (3500° F) are presented in table IV. In figure 5 the ultimate tensile strength is plotted against the calculated HfC content. As with the bend data in figure 1, the data show considerable scatter, especially for the alloys containing an excess of C. Tensile data in references

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1 and 3 had previously indicated a strength maximum in the region of 0.3 to 0.4 mol % HfC. Using the data for alloys from the 0.2 to 0.5 mol % region, figure 6 was constructed to determine the possible effect on strength of the C or Hf in excess of the calculated stoichiometric HfC. This plot suggests that there is a correlation between excess solute and high-temperature (1930° C) tensile strength. Peak strengthening occurs at or near the calculated stoichiometric HfC composition and decreases rapidly with excess of either C or Hf. (No explanation is presently available for the unusually high strength shown for alloy A272, which contained 4.1% Re, 0.28% Hf, and 0.39% C.) The scattered data in figure 5 appear to be reasonably explained by the presence of excess C or Hf.

High-Temperature Creep Properties

The W-4Re-Hf-C alloys were further evaluated by creep-rupture testing each material at 1930° C (3500° F) under a stress of 103 MN/m^2 (15 ksi). The results of these tests are presented in table V. As shown in figure 7, a maximum in rupture life occurs at about 0.35 mol % HfC. In this plot, as with the previous tensile results, the data are shown in a wide scatter band.

An examination of creep data for compositions ranging from 0.2 to 0.5 mol % HfC was made with respect to excess solute. Figure 8 shows the effect of excess C and Hf on the minimum creep rate of these alloys. This plot indicates the lowest value of minimum creep rate (and therefore the highest creep strength) occurs in alloys with Hf contents slightly in excess of stoichiometric.

Unalloyed tungsten tested at 1930° C (3500° F) and extrapolated to the same stress used here would have a minimum creep rate of about 10^{-2} reciprocal second (sec^{-1}) and a rupture life approaching 1 minute (ref. 7). Solid solution strengthening by rhenium and hafnium, in quantity, can be appreciable (ref. 5) but the major strengthening in the W-4Re-Hf-C alloys studied here is due to the second phase particles. The variations in creep properties observed in figure 8, however, are indicated as related to excess amounts of hafnium or carbon after satisfying stoichiometric HfC combinations.

A small excess of solute, for example Hf, would not be expected to change these creep parameters greatly through solid solution strengthening. Changes in the size or distribution of the second-phase particle were considered more likely to account for the observed strengths and therefore a closer study was made of the carbide particles in these W-4Re-Hf-C alloys.

Carbide Particle Examination

Second-phase particles are the primary strengtheners in the W-4Re-Hf-C alloys. These particles promote strengthening by restricting the mobility of dislocations through the matrix material. A major portion of the second-phase particles in the alloys investigated here were formed during solidification of the melt and during fabrication. In figure 9 transmission electron microscopy of a swaged alloy illustrates the fine substructure and maze of dislocations resulting from the presence of small (10 to 100 nm; 100 to 1000 Å), well distributed particles in the matrix during working.

Following creep rupture testing of these tungsten alloys, transmission electron micrographs of the test sections near the fracture zone were examined. The morphological features of the particles are not readily discernible. The particles in figure 10(a) are three dimensional, but the contrast in the particles in figure 10(b) suggest a platelet character or the presence of dislocation helices in the particle. Similarly shaped particles were observed also in untested swaged material. No apparent relation was detected between particle shape and alloy composition or creep-rupture properties.

The particle sizes (longest dimension) of the specimens examined ranged from 10 to 500 nm (100 to 5000 Å). The median particle sizes determined after creep-rupture testing are given in table V.

Second-phase particles were extracted from the unstressed button heads of selected W-4Re-Hf-C creep specimens by chemical dissolution of the matrices. Lattice parameter measurements and emission spectrographic analyses of these particles are presented in table V. The lattice parameter values of the extracted carbide particles ranged from 0.4567 to 0.4615 nm (4.567 to 4.615 Å). Pearson (ref. 8) indicates that HfC has a cubic sodium chloride (NaCl) type of structure and gives the lattice parameter a_o of $HfC_{0.97}$ as 0.46395 nm (4.6395 Å). Assuming that the extracted particles are composed primarily of Hf and C, the difference in lattice parameters would reflect lack of stoichiometry or the presence of dissolved impurities, or both.

The lattice parameter of HfC has been reported by Ramqvist (ref. 9) to vary with carbon content and shows a maximum at carbon to hafnium ratio of about 0.90. Ramqvist has attributed the presence of this maximum to two opposing forces, geometrical and bonding, that affect the carbide lattice. Other carbides, such as titanium carbide and zirconium carbide, also show similar maximums in lattice parameter at carbon to metal ratios less than stoichiometric. Also the melting points of these carbides show maximums at roughly the same carbon to metal ratios as noted for lattice parameter.

The influence of tungsten carbide (WC) additions on the lattice parameter of HfC has been studied by Nowotny et al. (ref. 10), who indicate a linear decrease in a_o for the single-phase region wherein up to 30 mol% WC can be dissolved in HfC. Emission spectroscopy analyses of the extracted particles, given in table V, reveal tungsten concentrations (based on metal content only) ranging from 2.3 to 25.4 at. %. Essentially

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no rhenium was detected in the particles, and the zirconium found was in proportion to that in the hafnium powder used in the alloy preparation. Accepting the tungsten values as equivalent to the mol % WC in the particles, figure 11 shows fair agreement between the extracted particle data and the HfC-WC results of Nowotny et al. These results indicate that the second-phase particles in the W-4Re-Hf-C alloys are a solid solution of hafnium and tungsten carbides. The complexity of the carbide particles in the alloys examined here may explain why the strength maximum appears to shift from stoichiometric.

The tungsten alloy composition could also be expected to affect the equilibrium composition of the second phase particles. Figure 12 is a plot of the WC content of the particles as a function of excess solute in the tungsten alloy. The WC content was determined from lattice parameter measurements based on the relation found by Nowotny et al. (ref. 10). These data indicate a high sensitivity of WC content to a small excess of Hf and a slight change in WC content with excess carbon content. The change in dependence occurs at nil excess solute in the alloy and about 15 mol % WC in the particles.

Relating Creep Strength to Particle Composition

Having shown the effect of excess solute in the W-4Re-Hf-C alloys on the amount of WC in the second-phase particles (fig. 12) and on creep behavior (fig. 8), a correlation between the latter two parameters should be possible. In figure 13 the minimum creep rates are plotted as a function of the WC content of the extracted carbide particles. This indicates that the minimum creep rate will increase directly with the amount of WC in the particles. In other terms, the creep strength of the swaged W-4Re-Hf-C alloys is inversely proportional to the amount of WC in the particles that serve to strengthen the matrix. From this relation one can project that the minimum creep rate for swaged W-4Re-Hf-C alloys containing 0.3 to 0.4 (calculated) mol % HfC particles with no WC present may be as low as 6×10^{-9} sec^{-1} when tested at 1930° C (3500° F) and a load stress of 103 MN/m^2 (15 ksi).

Re-examination of figure 8 in light of the particle examination suggests that HfC particle strengthening can show a maximum under nonstoichiometric conditions. This may indicate that HfC is more stable at carbon to hafnium ratios near 0.9 as suggested by melting point and lattice parameter data, but consideration has not been given here to the potential influence of the tungsten matrix. The presence of WC in solid solution with HfC can account for the loss in strength when excess C is present in the alloy. The decreased strengthening for alloys containing excess Hf greater than 0.05 at. % requires further study. The excess Hf may weaken by increasing the rates of particle coarsening (ref. 3).

It is recognized that the treatments of size, spacing, and morphology of the carbide particles have been inadequate to examine their effects on the mechanical properties of these alloys. However, the large differences in the high-temperature strength and the low-temperature ductility that result from small compositional differences in these tungsten alloys make it mandatory that the alloy content first be properly controlled. For maximum strengthening at high temperatures the optimum composition indicated for W-4Re-Hf-C alloys would be about 0.35 mol % HfC with a slight excess of Hf.

SUMMARY OF RESULTS

Studies were made of the effects of alloy composition on the mechanical behavior of as-worked tungsten - 4 percent rhenium - hafnium - carbon (W-4Re-Hf-C) alloys containing up to about 0.8 mol percent HfC. Extracted second-phase particles were analyzed and related to alloy composition and creep strength. The following observations were made:

1. While strengthening is attributed to hafnium carbide (HfC) particles, the presence of excess hafnium or carbon (above the calculated amounts for stoichiometric HfC) in swaged W-4Re-Hf-C alloys generally causes reduction of the high-temperature (1930° C) tensile strength; maximum creep strength is, however, indicated for alloys with a slight (about 0.05 to 0.1 at. %) excess of hafnium. Particle strengthening is reduced by tungsten carbide in solid solution with HfC for alloy compositions with an excess of carbon.

2. The low-temperature ductility of worked W-4Re-Hf-C alloys appears to be far more dependent on the amount of excess C or Hf present than on the HfC particle content in the range studied. Bend and tensile ductility decrease as excess carbon is increased. Maximum ductility occurs at hafnium contents slightly in excess of stoichiometric.

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APPENDIX - THERMOMECHANICAL PROCESSING

Thermomechanical processing is used to improve alloy strengthening through formation of a finely divided and evenly dispersed second-phase material in addition to providing a worked microstructure. Recent application of thermomechanical processing to Mo-Hf-C alloys (ref. 11) with resultant increases in strength prompted a study of the potential of applying similar processing to W-4Re-Hf-C alloys. Therefore, a limited investigation was made to examine the mechanical properties of tungsten alloys prepared with in-process solution anneals and to determine the best stage of fabrication to include solution annealing. Figure 14 shows the schedules followed in processing the arc-melted W-4Re-Hf-C alloy billets to swaged rod.

Schedule I is similar to the standard procedure for fabrication except for the additional step of solution annealing before swaging. The extruded rod normally can be successfully swaged at 1700° to 1810° C (3100° to 3300° F) in its retained molybdenum extrusion can. However, after solution annealing and recanning in molybdenum, the rod cracked after several swaging passes. As experienced for cast structures and shown by the later results for schedules II and III, fabrication of the fully recrystallized or solution annealed alloy requires larger reductions and/or higher working temperatures than ordinarily used in swaging.

The schedule II material was solution annealed before canning and extruding. Both extruding and swaging operations were successful.

Schedule III, which involved extrusion at the solution annealing temperature (similar to that used for the molybdenum alloys in ref. 11), required a tungsten can to accommodate the higher temperature. Following solution annealing and successful extrusion, the unalloyed tungsten can was removed from the alloy by grinding. Although the alloy was recanned in molybdenum tubing, several swaging attempts resulted in fracture after only a few passes. Since the extruded alloy had a fully recrystallized microstructure, additional working was attempted by extrusion as indicated by schedule IIIA. The ground alloy rod was canned in tungsten, solution annealed at 2650° C (4800° F), and followed by immediate extrusion at 2200° C (4000° F) at a reduction ratio of 8. The successful resulting extrusion had a fully worked structure. Because of its small diameter, swaging was not attempted, and the rod was tested in the double-extruded condition.

Limited mechanical property data for the schedule II and IIIA fabricated materials have been included in table VI. The bend and tensile ductilities at low temperatures of the schedule II material are comparable with those observed for standard process alloys of similar composition. Tensile testing of a single specimen of schedule IIIA material at 260° C (500° F) resulted in a reduction in area of 1 percent and would indicate a ductility similar to or less than that of standard process alloys.

The strengths of the thermomechanically processed alloys at high temperatures, as reflected by tensile and creep-rupture data, would appear to be comparatively good for

schedule IIIA but only fair for schedule II material. But when examined on the basis of excess Hf content, these materials are very comparable with the standard process alloys.

This limited investigation discloses no advantage of thermomechanical processing over the standard procedure of alloy fabrication. The lack of advantage in high-temperature strength and low-temperature ductility and the additional problems involved in thermomechanical processing of W-4Re-Hf-C alloys all indicate the desirability for processing these tungsten alloys without a solution annealing treatment.

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TABLE I. - DUCTILE-BRITTLE TRANSITION TEMPERATURES FOR WORKED

AND ELECTROPOLISHED W-4Re-Hf-C ALLOY SHEET MATERIALS

Alloy	Rhenium content, at. %	Hafnium content, at. %	Posttest carbon content, at. %	Calculated hafnium carbide content, mol %	Excess solute, at. %		Ductile-brittle transition temperature for 4t bend	
					Hafnium	Carbon	°C	°F
A201	4.4	0.44	[a]0.01	[a]0.01	[a]0.43	----	95	[b]200
A226	3.9	.44	.05	.05	.39	----	80	[b]175
A202	3.6	.76	[a].05	[a].05	[a].71	----	135	[b]275
A224	3.8	.22	.10	.10	.12	----	65	[b]150
A211	3.6	.27	.11	.11	.16	----	-30	[b]-25
A210	3.9	.25	.13	.13	.12	----	80	[b]175
A216	3.1	.30	.20	.20	.10	----	95	[b]200
A234	4.0	.24	.43	.24	-----	0.19	175	[b]350
A263	4.0	.26	.25	.25	.01	----	150	300
A272	4.1	.28	.41	.28	-----	.13	150	300
A235	3.9	.35	.30	.30	.05	----	120	[b]250
A270	3.5	.31	.90	.31	-----	.59	370	700
A219	3.7	.33	[a].67	.33	-----	[a].34	>205	[b]>400
A271	4.1	.34	1.03	.34	-----	.69	355	675
A278	4.1	.36	.55	.36	-----	.19	135	275
A261	4.0	.39	.38	.38	.01	----	80	175
A265	↑	.54	.38	.38	.16	----	105	225
A264		.39	.45	.39	-----	.06	-80	175
A246	↓	.40	.45	.40	-----	.05	230	450
A245	3.9	.41	.50	.41	-----	.09	205	400
A242	3.8	.42	.57	.42	-----	.15	175	350
A236	3.9	.44	.46	.44	-----	.02	40	[b]100
A247	3.1	.50	.48	.48	.02	----	220	425
A253	4.1	.69	.55	.55	.14	----	95	200
A217	3.8	.69	1.35	.69	-----	.66	205	[b]400

[a] Estimated values.

[b] From ref. 3.

TABLE II. - DUCTILE-BRITTLE TRANSITION TEMPERATURES FOR WORKED

AND ELECTROPOLISHED TUNGSTEN ALLOY SHEET MATERIALS

Alloy	Rhenium content, at. %	Hafnium content, at. %	Posttest carbon content, at. %	Calculated hafnium carbide content, mol %	Excess solute, at. %		Ductile-brittle transition temperature for 4t bend	
					Hafnium	Carbon	°C	°F
W-C alloys								
A142	---	----	0.12	----	----	0.12	190	375
A141	---	----	.33	----	----	.33	290	550
W-Hf alloys								
A149	----	0.19	----	----	0.19	----	40	100
A88	----	.44	----	----	.44	----	95	200
A133	----	.80	----	----	.80	----	220	425
W-Hf-C alloys								
A220	----	0.61	0.16	0.16	0.45	----	205	400
A231	----	.91	.19	.19	----	----	165	325
A221	----	.20	.26	.20	----	0.06	150	300
A229	----	.22	.20	.20	.02	----	120	250
A194	----	.23	.21	.21	.02	----	190	375
A222	----	.31	.61	.31	----	.30	315	600
A218	----	.31	.87	.31	----	.56	>315	>600
A191	----	.91	.94	.91	----	.03	175	350

TABLE III. - DUCTILE-BRITTLE TRANSITION TEMPERATURES OF SWAGED

AND ELECTROPOLISHED TUNGSTEN ALLOYS

Alloy	Rhenium content, at. %	Hafnium content, at. %	Posttest carbon content, at. %	Calculated hafnium carbide content, mol %	Excess solute, at. %		Ductile-brittle transition temperature for 4t bend	
					Hafnium	Carbon	°C	°F
W-C alloys								
A142	---	----	0.12	----	----	0.12	260	500
W-Hf alloys								
A149	---	0.19	----	----	0.19	----	140	280
W-Hf-C alloys								
A197	---	0.19	0.01	0.01	0.18	----	205	400
A192	---	.44	.18	.18	.26	----	195	380
A231	---	.19	.19	.19	----	----	270	500
A229	---	.22	.20	.20	.02	----	320	610
W-4Re-Hf-C alloys								
A204	4.7	0.20	0.01	0.01	0.19	----	235	455
A159	4.9	.36	.01	.01	.35	----	210	410
A224	3.8	.22	.05	.05	.17	----	140	285
A202	3.6	.76	.05	.05	.71	----	345	650
A212	3.6	.27	.12	.12	.15	----	250	480
A226	3.9	.44	.12	.12	.32	----	100	215
A272	4.1	.28	.39	.28	----	0.11	345	650
A269	4.1	.35	.31	.31	.04	----	345	650
A270	3.5	.31	1.00	.31	----	.69	640	1180
A265	4.0	.39	.33	.33	.06	----	250	400
A260	4.1	.39	.33	.33	.06	----	215	415
A278	4.1	.36	.60	.36	----	.24	320	605

TABLE IV. - TENSILE PROPERTIES OF SWAGED W-4Re-Hf-C ALLOYS AT 1930° C (3500° F)

Alloy	Calculated hafnium carbide content, mol %	Posttest carbon content, at. %	Excess solute, at. %		Ultimate tensile strength		Yield strength (0.2% offset)		Elongation, percent	Reduction in area, percent
			Hafnium	Carbon	MN/m²	ksi	MN/m²	ksi		
[a]A216	[b]0.20	[b]0.20	[b]0.10	-----	361	52.4	322	46.8	21	85
[a]A234	.24	[b].30	-----	[b]0.06	411	59.7	264	38.3	14	78
A263	.26	.46	-----	.20	407	59.0	383	55.5	18	90
A272	.28	.35	-----	.07	528	76.6	503	72.9	11	31
A272	.28	.39	-----	.11	538	78.1	492	71.4	14	92
A270	.31	.86	-----	.55	293	42.5	279	40.4	17	83
A261	.31	.31	.08	-----	381	55.3	364	52.8	21	84
[a]A235	.31	.31	.04	-----	458	66.5	413	59.9	20	76
[a]A219	.33	.67	-----	.34	367	53.3	305	44.2	16	77
[a]A246	.34	.34	.06	-----	452	65.6	426	61.8	22	88
A278	.36	.53	-----	.17	349	50.6	307	44.5	7	81
A264	.39	.45	-----	.06	426	61.8	399	57.9	17	89
A265	.39	.39	.15	-----	383	55.6	362	52.5	22	88
[a]A245	.41	.46	-----	.05	457	66.3	429	62.2	16	80
[a]A236	.44	[b].47	-----	[b].03	445	64.6	381	55.3	20	88
A253	.55	.55	.14	-----	319	46.2	289	41.9	24	79

[a]From ref. 3.
[b]Estimated.

TABLE V. - CREEP RUPTURE PROPERTIES AND EXTRACTED CARBIDE PARTICLE ANALYSIS OF SWAGED W-4Re-Hf-C ALLOYS

Alloy	Rhenium content, at. %	Hafnium content, at. %	Posttest carbon content in reduced section, at. %	Calculated hafnium carbide content, mol %	Excess solute, at. % — Hafnium	Excess solute, at. % — Carbon	Min creep rate, sec⁻¹	Rupture life, hr	Total elongation, %	Median particle size (near fracture zone), Å	Median particle size (near fracture zone), nm	Lattice parameter a_0, nm	Lattice parameter a_0, Å	Fe	Hf	Mo	Re	W	Y	Zr	Tungsten content in extracted particles based on W/(W + Hf + Zr), at. %
A201	4.4	0.44	0.01	0.01	0.43	---	6.3×10^{-5}	1.32	66	---	---	---	---	---	---	---	---	---	---	---	---
A226	3.9	.44	.08	.08	.36	---	8.4×10^{-6}	4.18	53	---	---	---	---	---	---	---	---	---	---	---	---
[a]A235	3.9	.35	.21	.21	.14	---	8.0×10^{-8}	65.0	17	---	---	---	---	---	---	---	---	---	---	---	---
A278	4.1	.36	.22	.22	.14	---	2.1×10^{-7}	16.1	13	937	93.7	---	---	---	---	---	---	---	---	---	---
A260	4.1	.39	.25	.25	.14	---	3.3×10^{-7}	41.3	23	755	75.5	---	---	---	---	---	---	---	---	---	---
A263	4.0	.26	.27	.26	---	0.01	2.6×10^{-7}	[b]>14.7	>1	603	60.3	---	---	---	---	---	---	---	---	---	---
A272	4.1	.28	.27	.27	.01	---	3.4×10^{-8}	31.1	14	---	---	---	---	---	---	---	---	---	---	---	---
A270	3.5	.31	.76	.31	---	.45	4.0×10^{-6}	9.14	27	---	---	---	---	---	---	---	---	---	---	---	---
A270	3.5	.31	1.01	.31	---	.70	6.7×10^{-6}	[c]>.98	>4	---	---	0.4567	4.567	---	---	---	---	---	---	---	---
[a]A219	3.7	.33	.36	.33	---	.03	8.9×10^{-7}	17.8	24	---	---	.4579	4.579	0.6	59.2	0.2	[d]	16.4	0.4	3.6	20.7
[a]A219	3.7	.33	.58	.33	---	.25	5.7×10^{-7}	26.9	30	---	---	.4571	4.571	.3	49.6	.4	[e]	16.5	.4	3.1	23.8
A261	4.0	.39	.35	.35	.04	---	3.6×10^{-8}	66.5	12	1152	115.2	.4569	4.569	.3	57.1	.2	[e]	20.4	.4	2.7	25.4
A264	4.0	.39	.35	.35	.04	---	3.6×10^{-8}	81.8	12	971	97.1	.4608	4.608	4.6	74.7	4.0	[d]	1.8	1.8	1.0	2.3
A246	4.0	.40	.35	.35	.05	---	6.8×10^{-9}	95.8	15	2120	212.0	.3608	3.608	.6	64.4	.1	[d]	5.7	.4	2.3	7.9
A264	4.0	.39	.37	.37	.02	---	1.1×10^{-7}	48.5	15	1242	124.2	.4615	4.615	.6	76.7	(d)	[f]	7.5	2.2	2.7	8.6
A264	4.0	.39	.37	.37	.02	---	1.7×10^{-7}	38.2	22	777	77.7	.4601	4.601	1.0	50.0	>.1	[g]	3.7	.2	1.7	6.7
A264	4.0	.39	.43	.39	---	.04	1.8×10^{-7}	[b]>25.9	>7	937	93.7	---	---	---	---	---	---	---	---	---	---
A265	4.0	.54	.40	.40	.14	---	5.9×10^{-8}	56.3	15	737	73.7	---	---	---	---	---	---	---	---	---	---
A245	3.9	.41	.42	.41	---	.01	3.6×10^{-8}	[b]>37.1	>0	---	---	---	---	---	---	---	---	---	---	---	---
A253	4.1	.69	.45	.45	.24	---	4.4×10^{-7}	36.0	25	---	---	---	---	---	---	---	---	---	---	---	---
A253	4.1	.69	.50	.50	.19	---	9.2×10^{-7}	24.8	41	952	95.2	---	---	---	---	---	---	---	---	---	---

Creep-rupture test results at 1930°C (3500°F) and 103 MN/m² (15 ksi). Emission spectrographic analyses of extracted particles, at. % (based on Hf). Carbide particles extracted from creep specimen buttonheads.

[a] From ref. 3.
[b] Pullrod failure.
[c] Internal flaw.
[d] Not detected.
[e] Very weak.
[f] Faint trace.
[g] Weak.

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TABLE VI. - MECHANICAL BEHAVIOR OF THERMOMECHANICALLY

PROCESSED W-4Re-Hf-C ALLOYS

	Schedule II	Schedule IIIA
Alloy composition, at. %	W-4. 1Re-0. 42Hf-0. 26C	W-3. 2Re-0. 30Hf-0. 24C
Ductility:		
Bend; DBTT, $^{\circ}$C ($^{\circ}$F)	80	175
Tensile; reduction in area at 260° C (500° F), %	5	1
Tensile properties at 1930° C (3500° F):		
0. 2 Percent yield strength, MN/m^2 (ksi)	278 (40. 3)	312 (45. 2)
Ultimate tensile strength, MN/m^2 (ksi)	343 (49. 7)	436 (63. 2)
Reduction in area, %	88	60
Elongation, %	35	20
Posttest carbon content, at. %	0. 22	0. 24
Creep properties at 1930° C (3500° F) and 103 MN/m^2		
(15 ksi):		
Minimum creep rate, sec^{-1}	$(2.6 - 7.6) \times 10^{-7}$	1.2×10^{-8}
Rupture life, hr	17. 3 - 28. 8	42. 7
Total elongation, %	15 - 19	6
Posttest carbon content, at. %	0. 25 - 0. 26	0. 22
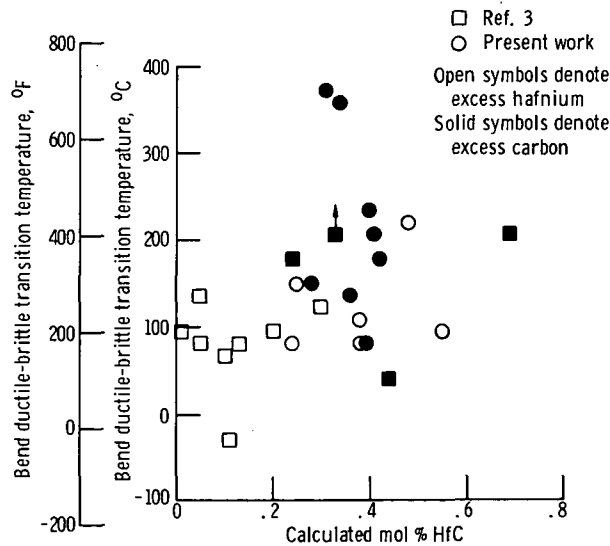
Figure 1. - Effect of hafnium carbide content in W-Re-Hf-C
alloys on bend ductility of electropolished as-worked sheet.
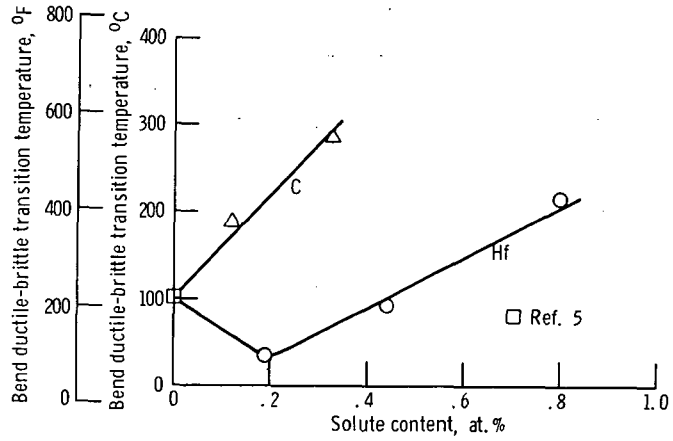
Figure 2. - Effect of carbon or hafnium additions on bend ductility of
as-worked tungsten sheet.
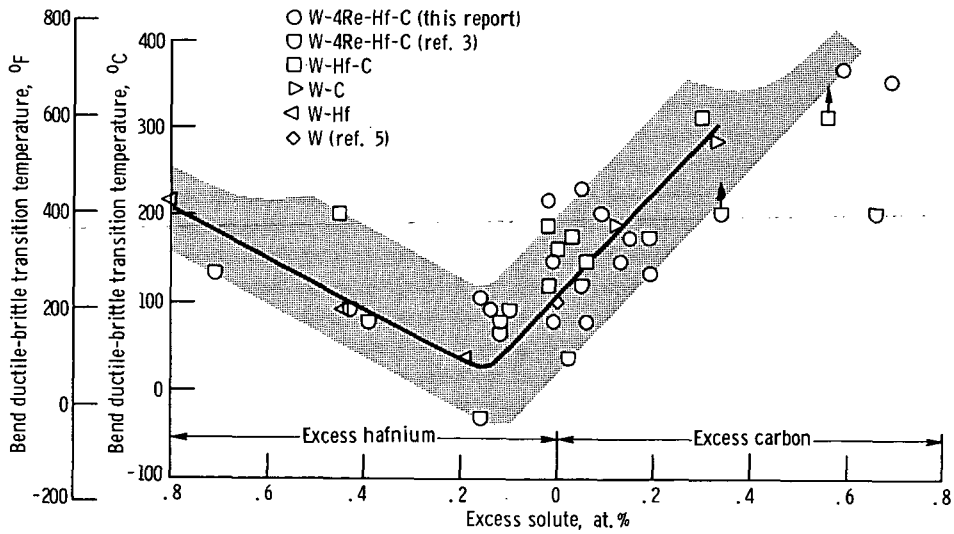
Figure 3. - Effect of excess carbon or hafnium on bend ductility of as-worked tungsten alloys.
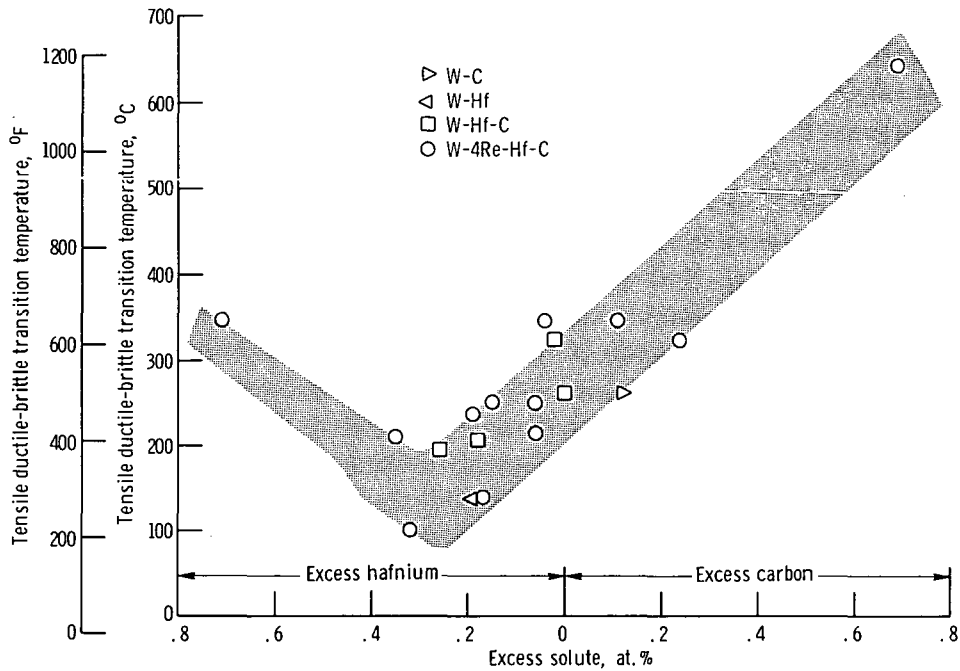
Figure 4. - Effect of excess carbon or hafnium on tensile ductile-brittle transition temperature at 5 percent reduction in area for as-worked tungsten alloys.
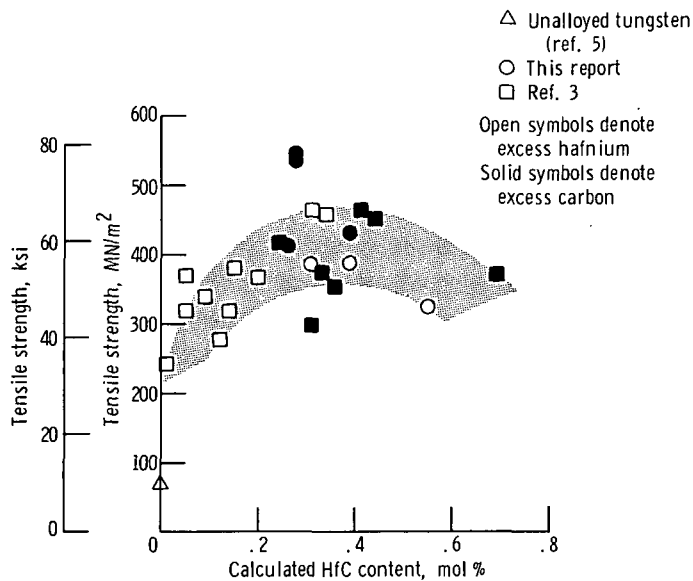
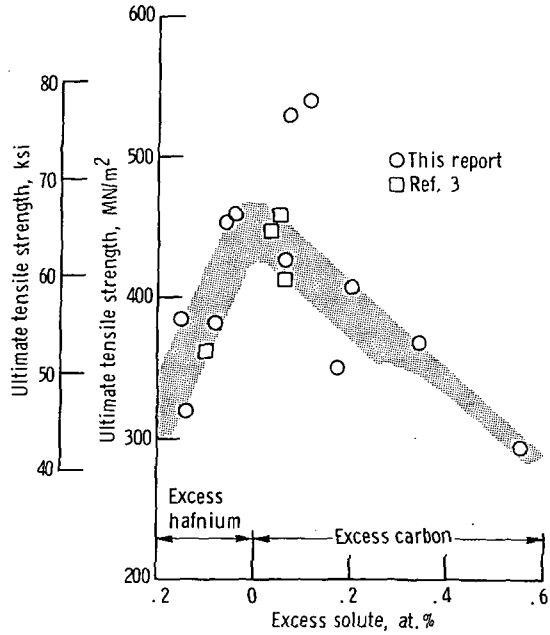Figure 5. - Effect of hafnium carbide content on ultimate tensile strength of swaged W-Re-Hf-C alloys at 1930^0 C $(3500^0$ F).

Figure 6. - Effect of excess hafnium or carbon over calculated stoichiometric hafnium carbide (HfC) on ultimate tensile strength of W-Re-Hf-C alloys with 0.2 to 0.5 mol % HfC at 1930° C (3500° F).
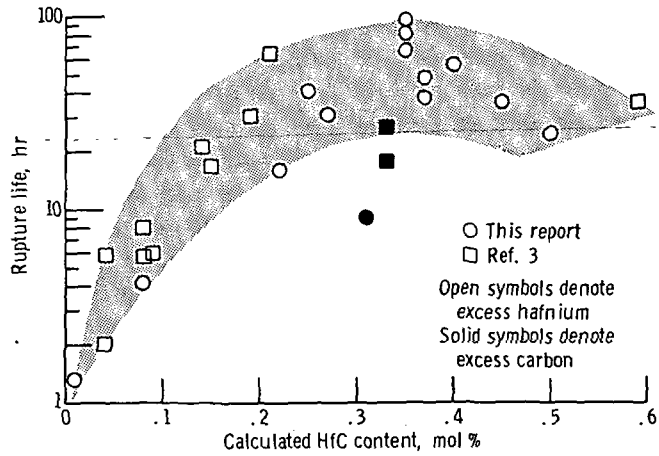
Figure 7. - Effect of hafnium carbide (HfC) content on rupture life of swaged W-4Re-Hf-C alloys at 1930° C (3500° F) and 103 MN/m² (15 ksi).

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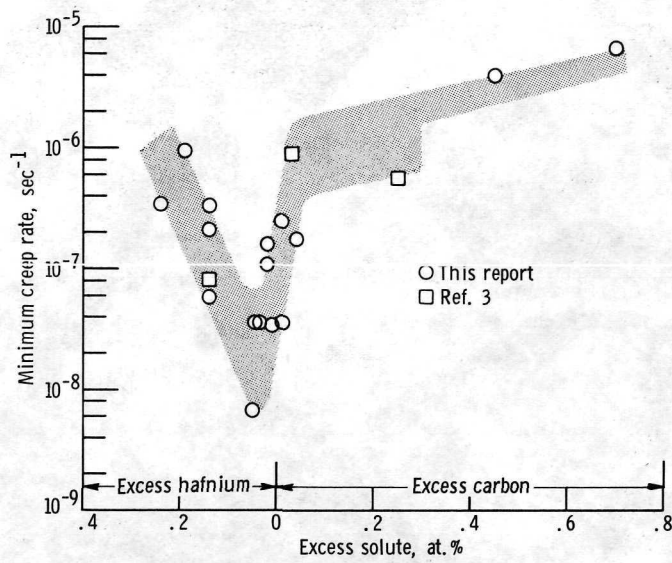
Figure 8. – Effect of excess carbon and hafnium on minimum creep rate at 1930^0 C (3500^0 F) and 103 MN/m^2 (15 ksi) for swaged W-4Re-Hf-C alloys containing 0.2 to 0.5 mol % hafnium carbide.
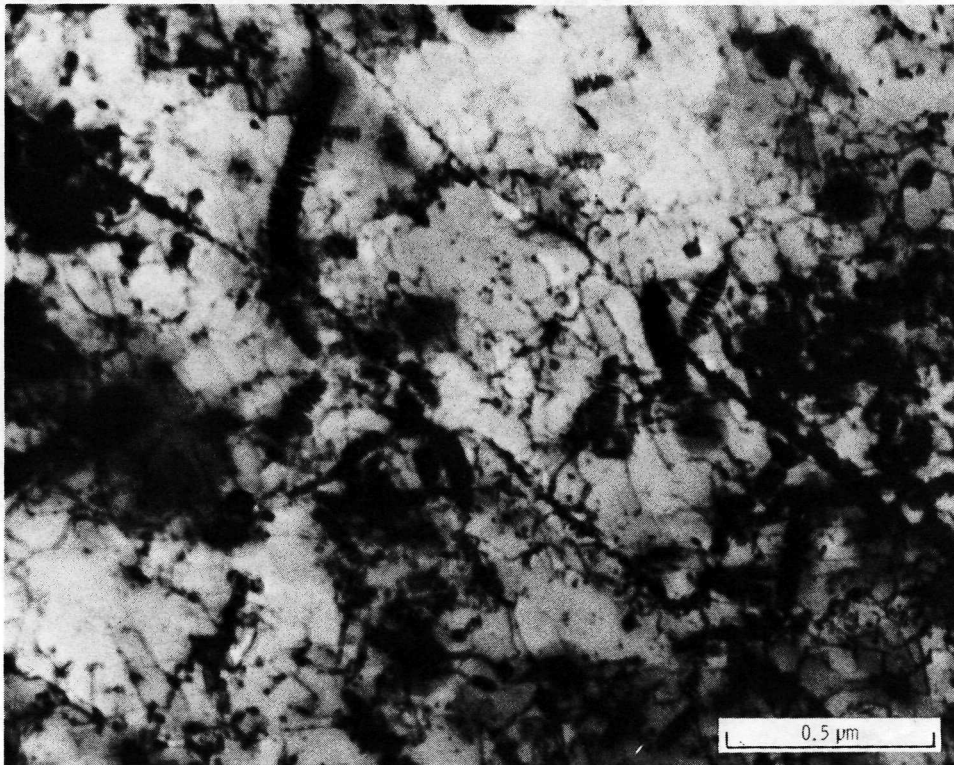
Figure 9. – Typical transmisssion electron micrograph of W-4Re-Hf-C alloys in swaged condition.

(a) Alloy A246 (W-4Re-0.40Hf-0.35C); life, 95.8 hours.

0.5 μm
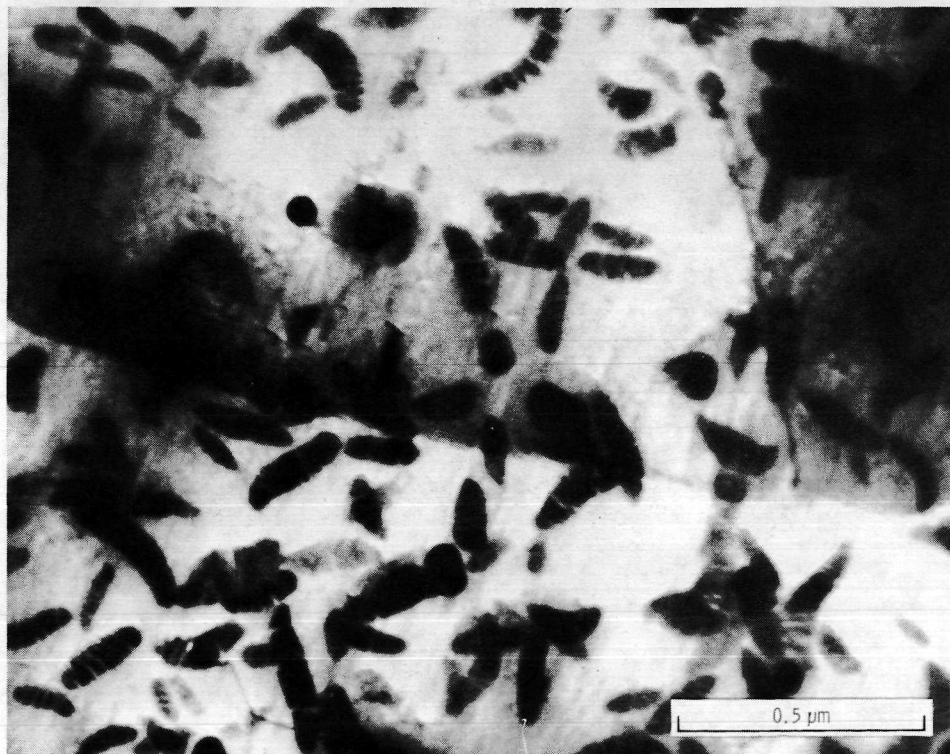
(b) Alloy A261 (W-4Re-0.39Hf-0.35C); life, 66.5 hours.

Figure 10. – Transmission electron micrographs after creep rupture testing at 1930° C (3500° F) and 103 MN/m² (15 ksi) in swaged condition.
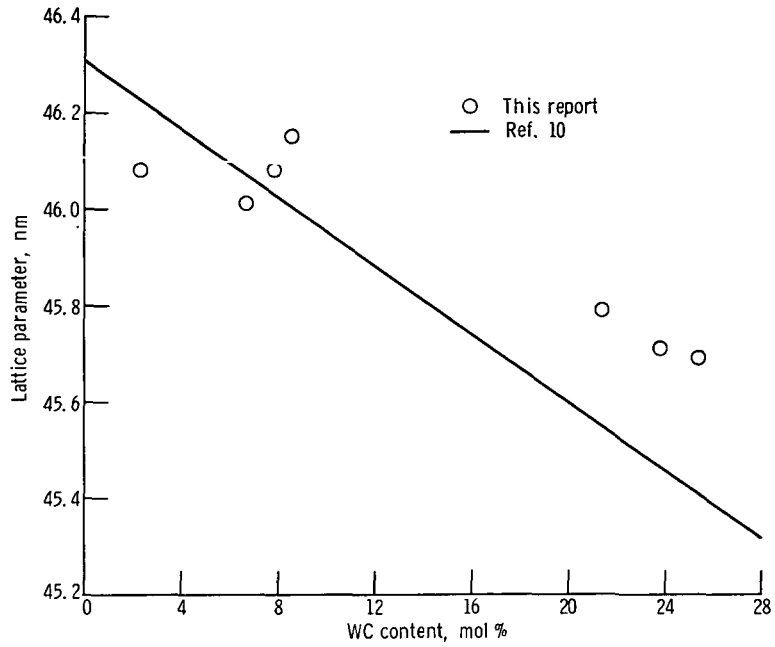
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Figure 11. – Lattice parameter as function of tungsten carbide content of extracted carbide particles from W-4Re-Hf-C creep specimens.
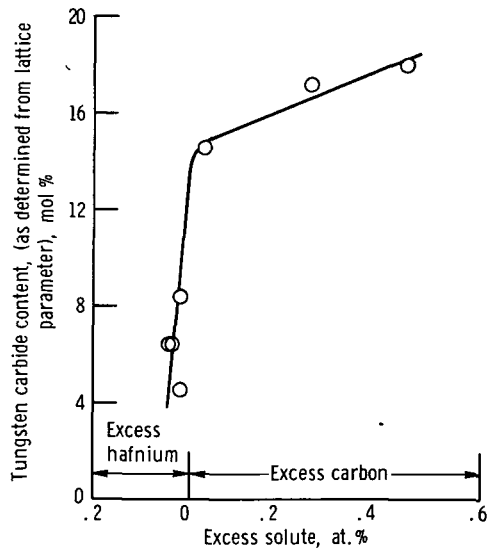

Figure 12. – Effect of excess solute in W-4Re-Hf-C alloys on tungsten carbide content in second-phase particles based on reference 10.

Standard schedule

Billet → Can in molybdenum → Extrude at 2200^0 C (4000^0 F) → Swage

Schedule I

Billet → Can in molybdenum → Extrude at 2200^0 C (4000^0 F) → Solution anneal at 2650^0 C (4800^0 F) for 15 min; furnace cool → Swage

Schedule II

Billet → Solution anneal at 2650^0 C (4000^0 F) for 15 min; furnace cool → Can in molybdenum → Extrude at 2200^0 C (4000^0 F) → Swage

Schedule III

Billet → Can in tungsten → Solution anneal at 2650^0 C (4800^0 F) for 15 min and immediately extrude at 2650^0 C (4800^0 F) → Schedule III-A → Swage → Can in tungsten → Solution anneal at 2650^0 C (4800^0 F), immediately extrude at 2000^0 C (4000^0 F)

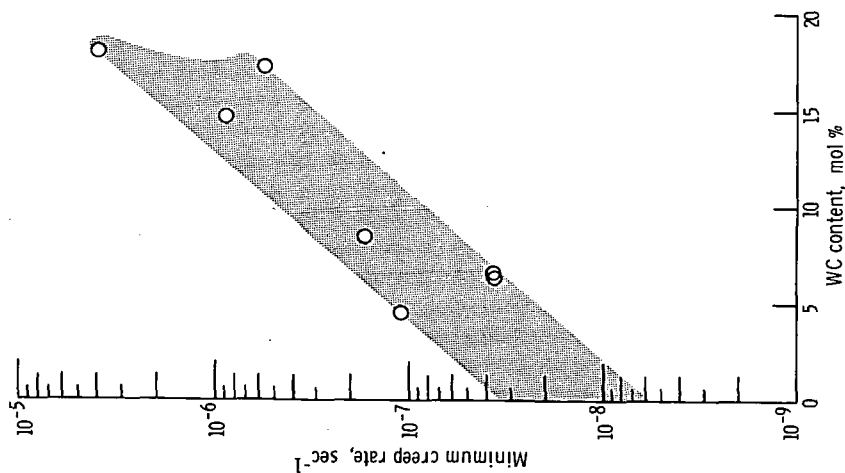Figure 14. – Thermomechanical processing schedules.

Figure 13. – Correlation of tungsten carbide (WC) content of extracted carbide particles (determined from lattice parameter measurements) with minimum creep rate at 1930^0 C (3500^0 F) and 103 MN/m^2 (15 ksi) for swaged W-4Re-Hf-C alloys containing 0.3 to 0.4 mol % hafnium carbide.
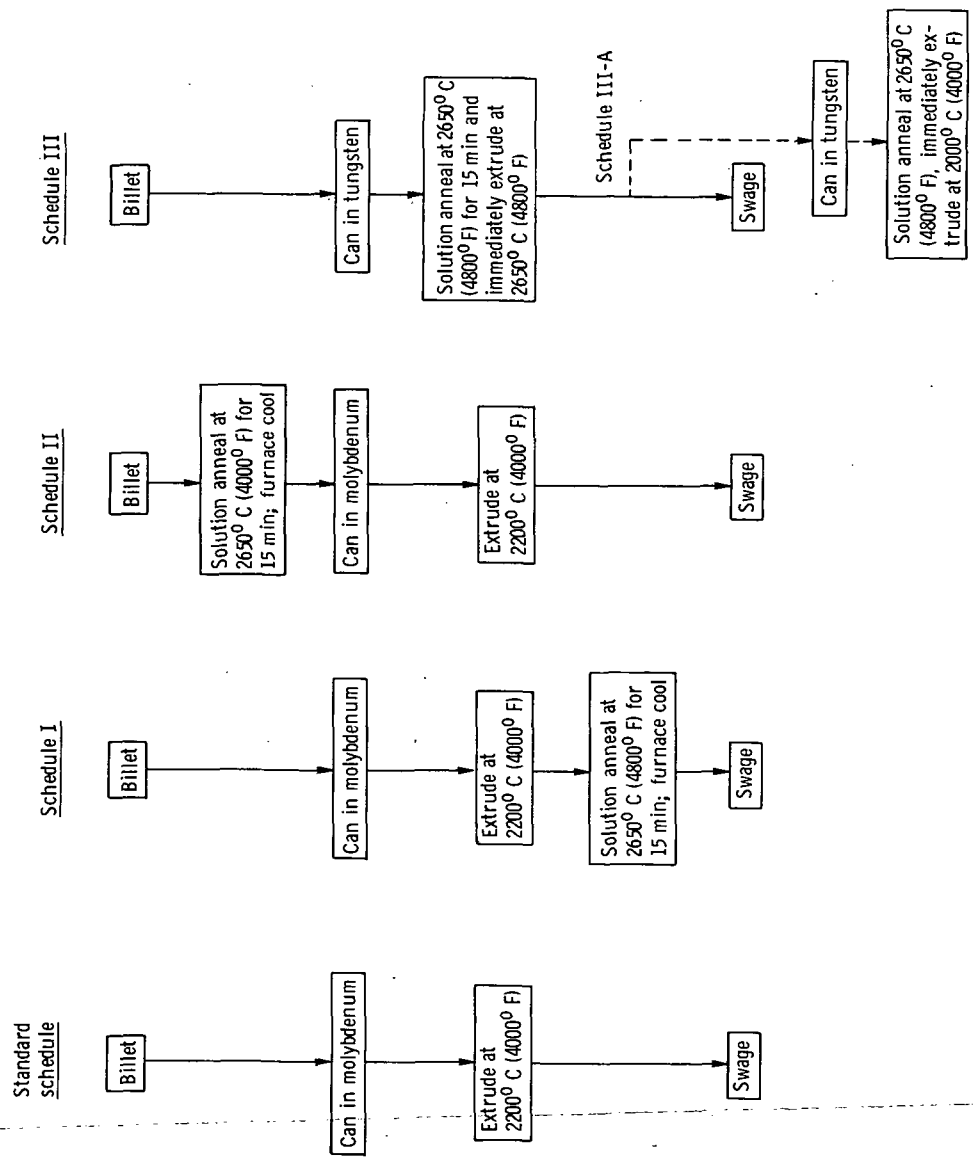
Minimum creep rate, sec^{-1}

WC content, mol %

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