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MECHANICAL PROPERTIES OF ARC-MELTED TUNGSTEN-RHENIUM-HAFNIUM-CARBON ALLOYS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ABSTRACT

A study was conducted on the effect of 4 atomic percent rhenium on the mechanical properties of hafnium carbide strengthened tungsten-base alloys. The high temperature strengthening from HfC and improved low temperature bend ductility from the rhenium addition could be combined without detrimental interaction. Maximum strength alloys contained 0.3 to 0.4 mol percent hafnium carbide. The highest tensile strength observed at 3500° F (1927° C) was 75.4 ksi (520 MN/m^2) in the solution annealed and aged condition, while the mean 4t bend transition temperature noted was 200° F (93° C) for as-rolled sheet.

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SUMMARY

The properties of arc-melted W-Re-Hf-C alloys were evaluated to determine whether or not the previously observed high-temperature strengthening effects of HfC in tungsten could be combined with the low-temperature ductilizing effect of dilute rhenium additions to tungsten. The general conclusion from this study is that these two effects can be combined without detrimental interaction. The optimum alloy, W-4Re-0.35Hf-0.35C (atomic percent), designated tungsten-RHC, has a tensile strength of 60 to 70 ksi at 3500° F (1927° C) and bend ductile-brittle transition temperatures of 200° and 540° F (93° and 282° C) in the as-rolled and solution-annealed conditions, respectively.

The strength increment associated with HfC particles is proportional to the square root of the mol percent HfC and decreases with increasing HfC particle size, in accord with recent dispersion strengthening theory.

Growth of the HfC particles is fairly rapid above 3500° F (1927° C), limiting this type of alloy to short time use at these temperatures. Calculations indicate that, at lower temperatures, particle stability and high strengths should be maintained for hundreds to thousands of hours.

INTRODUCTION

Over the past few years, a continuing study has been conducted at the NASA-Lewis Research Center to develop tungsten-base alloys combining improved ductility at low temperatures with high strength at elevated temperatures (refs. 1 to 3). Studies of tungsten-rhenium alloys by the authors of reference 3 and by Pugh et al. (ref. 4) indicated that rhenium is effective in lowering the ductile-brittle transition temperature of tungsten in dilute concentrations. This ductility improvement at rhenium levels near 4 percent is associated with the solution softening effect, a low-temperature phenomenon

resulting from a decrease in the Peierls stress in body-centered-cubic metals on dilute alloying (ref. 5).

More recently, Friedman and Dickinson (ref. 6), Raffo and Klopp (ref. 2), and Rubenstein (ref. 7) showed that hafnium carbide (HfC) is a very effective precipitate strengthener for tungsten at elevated temperatures. Alloys containing 0.3 to 0.4 mol[1] percent HfC exhibited up to a seven-fold improvement in the short-time tensile strength of tungsten at 3500° F (1927° C), as compared to a maximum fourfold improvement by solid-solution alloying with hafnium.

The objective of the present study was to determine if the high-temperature strengthening effect of HfC and the low-temperature ductility improvement effect of rhenium could be simultaneously achieved in an arc-melted alloy without detrimental interaction. Based on previous work (ref. 3), a constant rhenium level of 4 atom percent was selected to give maximum ductility improvement in both the worked and recrystallized conditions. The amounts of hafnium and carbon were varied from about 0.01 to 1.0 atom percent. The high temperature strength characteristics in tensile and creep testing and the low temperature bend ductile-brittle transition temperatures were determined as functions of composition and heat treatment. These were supplemented by recrystallization and particle coarsening studies and by extensive transmission electron microscopy examinations.

EXPERIMENTAL PROCEDURE

Composition of the 15 alloys in this investigation are given in table I. The analyzed hafnium contents ranged from 0.22 to 0.76 atomic percent, carbon from 0.009 to 0.98 atomic percent, and rhenium from 3.1 to 4.4 atomic percent. Mol percent HfC was taken as equal to the hafnium or carbon content, whichever was lower. The major impurities determined were oxygen (4 to 18 ppm), nitrogen (1 to 20 ppm), and iron (3 to 5 ppm).

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[1]Mol percent is defined as the number of moles of any component times 100 and divided by the sum of the number of moles of all components. In the above alloys the maximum mol percent HfC present is taken as equal to the atomic percent of Hf or C present, whichever is the smaller.

Melting

The alloys were prepared by consumable vacuum arc melting of pressed and sintered electrodes. High purity powders of elemental tungsten, rhenium, hafnium, and carbon were blended and hydrostatically pressed at 30 to 70 ksi (207 to 483 MN/m^2) into 10-pound (4.5-kg) electrodes with about a 1.25-inch (3.17-cm) diameter. Excess graphite was added to provide for carbon losses that occurred during sintering and melting. The electrodes were sintered in vacuum at 4000° F (2204° C) prior to melting into a 2.5-inch (6.35-cm) diameter water-cooled copper crucible. The arc melting was conducted using direct current with electrode negative at a chamber pressure of less than 10^{-4} torr (10^{-2} N/m^2).

Fabrication

The alloys were fabricated into rod and sheet by extrusion and subsequent swaging or rolling. The ingots were initially machined into billets 2.25 inches (5.71 cm) in diameter and canned in sintered powder metallurgy molybdenum with a nominal outside diameter of 3 inches (7.6 cm). The canned billets were heated in hydrogen to 4000° F (2204° C) and then extruded to rod at a reduction ratio of 8:1 in a conventional hydraulic press. All 15 alloys were satisfactorily extruded in this manner.

Swaging of the extruded alloys was conducted with the molybdenum cladding intact and at a preheat temperature of 3200° to 3300° F (1759° to 1815° C). Reductions of 10 to 15 percent per pass were taken to a total reduction in area of about 83 percent and a diameter of 0.360 inch. The molybdenum cladding was removed in the process of grinding the swaged bars into buttonhead-type tensile specimens.

Portions of the extruded alloy rod were rolled to 0.040-inch (0.102-cm) thick sheet. Starting temperatures of 3100° to 3300° F (1704° to 1815° C) were used in rolling to a thickness of about 0.250 inch (0.635 cm) at which stage the molybdenum cladding was chemically removed. Following conditioning of the surface, the material was reduced to final thickness at a temperature 200° F (111° C) lower than the initial rolling furnace temperatures.

Testing

Tensile and creep tests were performed on specimens having a 1-inch (2.5-cm) gage length and reduced diameter ranging from 0.11 to 0.14 inch (0.28 to 0.36 cm). Tensile testing was carried out in a vacuum chamber at a pressure below 10^{-5} torr

(10^{-3} N/m^2) and at temperatures ranging from 2000° to 4500° F $(1093^o$ to 2482° C). A constant crosshead speed of 0.05 inch per minute $(2.1 \times 10^{-5}$ m/sec) was used. Constant-load creep-rupture and step-load creep tests were conducted under vacuum $(10^{-6}$ torr $(10^{-4} \text{ N/m}^2))$ and at 3500° F $(1927^o$ C) in a conventional beam-loaded machine. Strain measurements were made from loading rod movement or movement of extension rods connecting the specimen buttonheads to a linear variable differential transformer. Both methods of strain measurement gave essentially the same results. Test temperatures were measured by tungsten/tungsten-26 percent rhenium thermocouples attached to the reduced section of the specimen.

Longitudinal sheet specimens (1 by 0.3 in. (2.5 by 0.8 cm)) were bend tested following grinding and electropolishing to remove about 0.010 inch (0.025 cm) of material. The bend ductile-brittle transition temperature is defined here as the lowest temperature at which a sheet specimen could 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 1 inch per minute.

Annealing was conducted in an induction-heated hydrogen-atmosphere furnace for temperatures up to 3200° F $(1759^o$ C) while annealing treatments requiring temperatures from 3200° to 5000° F $(1759^o$ to 2759° C) were conducted in a resistance-heated vacuum furnace at a pressure of 10^{-5} torr (10^{-3} N/m^2).

Thin films for electron transmission microscopy were prepared from disks about 0.12 inch (0.3 cm) in diameter and 0.01-inch (0.03-cm) 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 NaOH solution until the center spot was just pierced.

Electron photomicrographs of selected areas of the thin films were used in conjunction with a Zeiss particle size analyzer to determine the median particle diameters of the carbide phase.

RESULTS AND DISCUSSION

High Temperature Tensile Properties

Tensile data for the W-Re-Hf-C alloys at 2500° to 4000° F $(1371^o$ to 2204° C) are given in table II and are shown in figure 1.

The strengths of these alloys at elevated temperatures are seen, first, to be exceptionally high and, second, to depend on the amount of HfC precipitate in the alloy. At 3500° F $(1927^o$ C) in the swaged condition, the highest tensile strength observed was 66.5 ksi (459 MN/m^2) for alloy A235, which contained an estimated 0.25 m/o HfC. The

(a) As-swaged condition.

(b) Recrystallized condition.
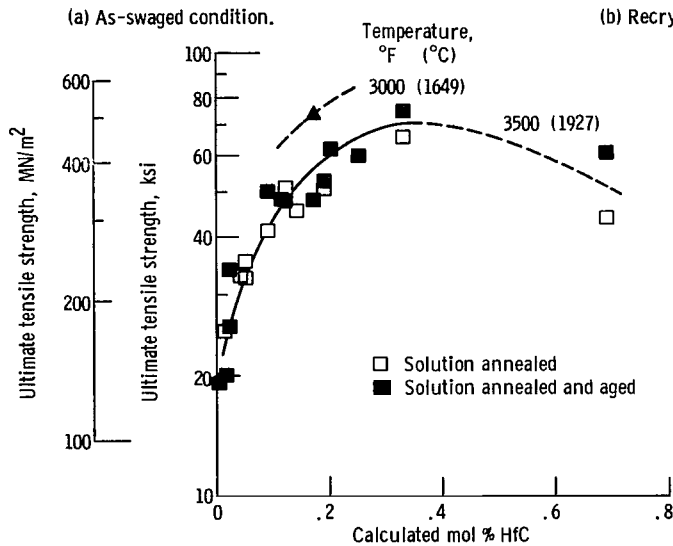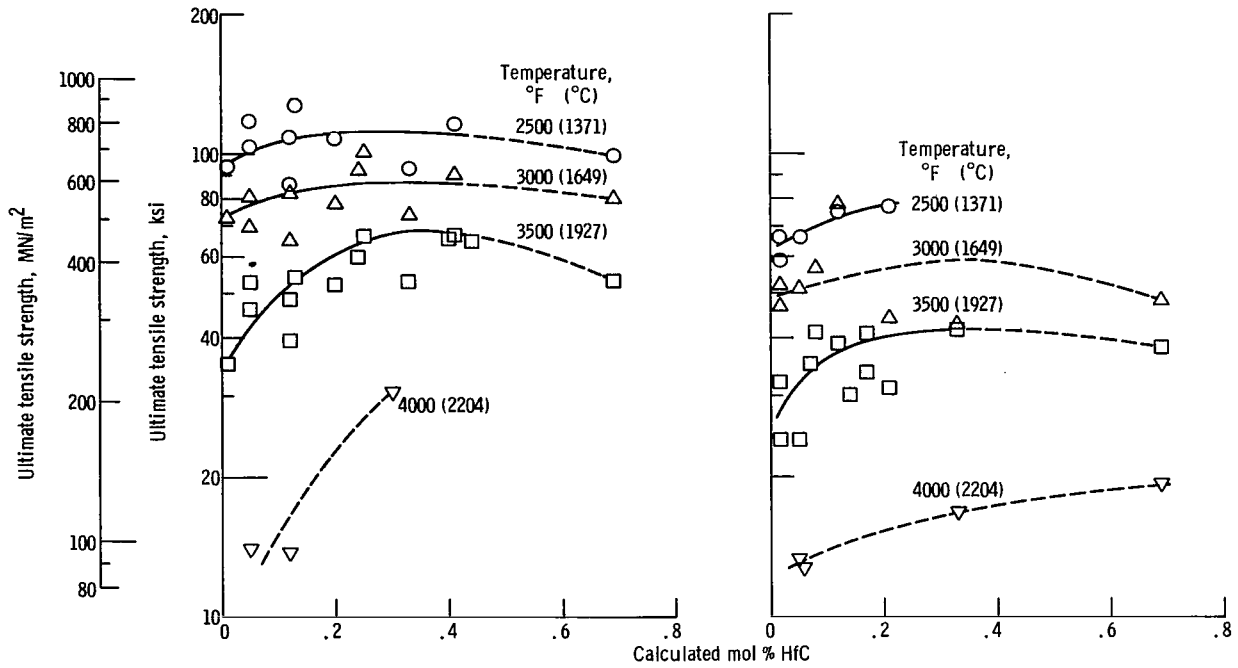
(c) Solution annealed and solution annealed and aged conditions.

Figure 1. - Tensile strength of W-4Re-Hf-C alloys.

strength is about eightfold higher than the 8 ksi (55 MN/m^2) for unalloyed tungsten at this temperature (ref. 8). In the recrystallized condition, the strengths were lower due to the absence of a worked structure and probably to the presence of larger HfC particles. The highest strength at 3500° F (1927° C) in the recrystallized condition was 42.1 ksi (290 MN/m^2) for A219, which contained 0.33 m/o HfC.

Highest strengths, however, were observed for specimens which had been solution annealed for 0.25 hour at 4600° to 5000° F (2538° to 2760° C) and subsequently aged for 1 hour at 2000° to 3000° F (1093° to 1649° C). The highest strength at 3500° F (1927° C) for the solution annealed and aged condition was 75.4 ksi (520 MN/m^2), exhibited by A219, with a HfC content of 0.33 m/o. This is over nine times the strength of unalloyed tungsten and is the highest strength reported for a metallic material at this temperature.

The strengthening effect of 4 a/o rhenium (added to W-Hf-C) is very similar to that observed in binary W-Re alloys. The strengths of the quaternary W-4Re-Hf-C alloys were slightly higher than those of ternary W-Hf-C alloys, consistent with the average 7100 psi tensile strength increment at 3500° F (1927° C) due to rhenium in a binary W-4 Re alloy (ref. 3). It is concluded that rhenium exerts its normal solid solution strengthening effect in W-Re-Hf-C alloy and does not detract from the strengthening increment due to HfC.

In order to better determine the relation between composition and strength and to assist in defining the optimum HfC level, the strength data for solution treated materials were analyzed to determine the strengthening contributions from each constituent. As shown earlier by Raffo and Klopp (ref. 2), the observed strengths of ternary solid solution tungsten-base alloys, including W-Re-Hf, agree well with those calculated from the strengthening increments in binary solid solution alloys. Accordingly, the strengthening increments due to HfC were calculated by subtracting the strength of unalloyed tungsten and the strengthening increments due to rhenium and free hafnium from the observed alloy strengths. No allowance was made for excess carbon since earlier work (ref. 2) showed that carbon per se has no significant strengthening effect on tungsten at high temperatures.

Least-squares analysis of the strength data for solution annealed specimens (with and without aging prior to test) of both W-Hf-C (ref. 7) and W-Re-Hf-C containing 0.04 to 0.40 mol percent HfC indicated that the HfC strengthening increment could be plotted parabolically, that is, against the 0.5 power of mol percent HfC. It was found necessary to subtract 0.013 from the atom percent carbon before calculating the mol percent HfC in order for the strength plots to pass through the origin when no HfC was present. It is possible that this correction represents the amount of carbon in solid solution during testing at this temperature.

The HfC strength increment data are shown in figure 2. The experimental data show a high degree of scatter around the least squares line, probably indicating that the
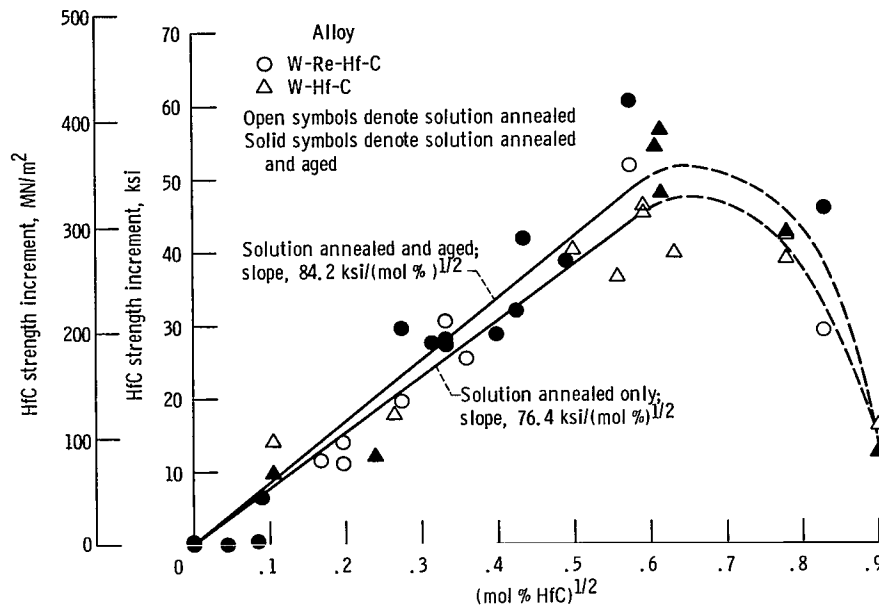
Figure 2. - Hafnium carbide tensile strength increment in W-Re-Hf-C and W-Hf-C alloys at 3500° F (1927° C). (Alloys were solution annealed at 4600° to 5000° F (2538° to 2760° C) before testing.)

strengthening increment is due not only to the amount of HfC but also to its size and distribution. The highest strengths were observed in the range of 0.57 to 0.62 $m/o^{1/2}$ HfC, equivalent to approximately 0.35 m/o HfC. At higher HfC levels, the strengthening increment decreases rapidly, and is quite low at HfC levels above 0.8 m/o. Aging the solution annealed specimens for 1 hour at 2000° to 3000° F (1093° to 1649° C) increased the strengthening rate of HfC at 3500° F (1927° C) from 76.4 to 84.2 ksi/(mol %)$^{1/2}$, presumably by increasing the number of precipitation nuclei and thus reducing the interparticle spacing.

The observation of an optimum level of HfC for maximum strengthening is believed related to the solubility of carbon in a tungsten-rhenium-hafnium matrix and the effect of this relation on the particle size distribution. Apparently, at carbon levels above the optimum, a portion of the HfC remains undissolved throughout extrusion, secondary working, and heat treating. This undissolved HfC could serve as precipitation nuclei during subsequent heat treatment and reduce the effective amount of fine particles.

However, even at lower carbon levels, the expectation of a completely supersaturated solution following solution annealing was generally not realized. The cooling rates following solutioning must be extremely rapid to retain HfC in solution. Even a cooling time of 1 minute from the solutioning temperatures to black heat was shown by metallographic examination to be too slow to prevent HfC precipitation.

Typical electron micrographs of W-Re-Hf-C alloys after tensile testing are shown
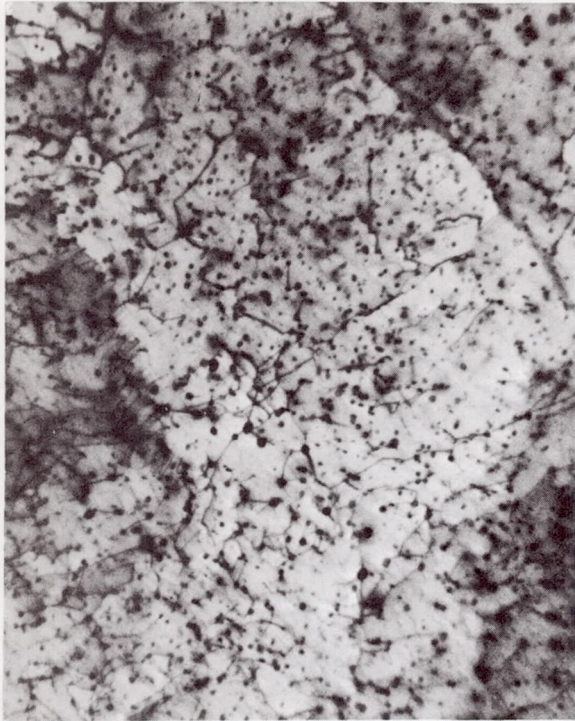
(a) Alloy A234 (W-4.0 Re-0.23 Hf-0.30C), after tensile testing at 3500° F (1927° C) in swaged condition
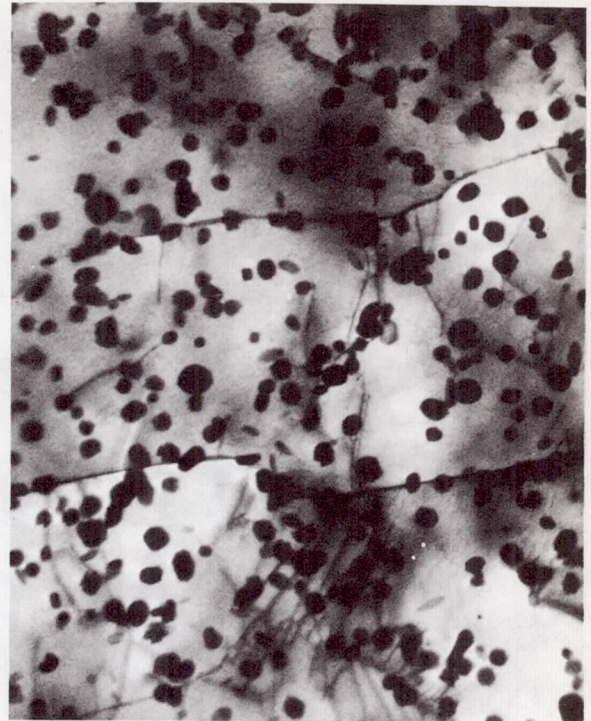
(b) Alloy A219 (W-3.7 Re-0.33 Hf-0.67C), annealed 1 hour at 3800° F (2093° C), and tensile tested at 3500° F (1927° C).
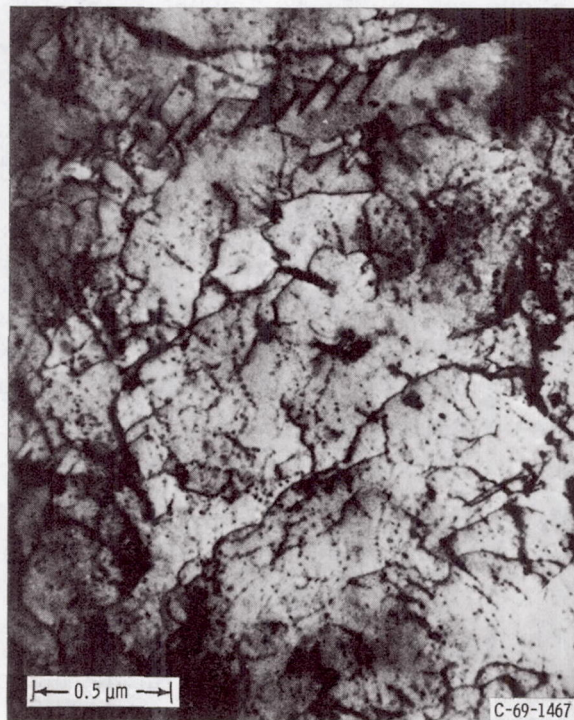
(c) Alloy A235 (W-3.9 Re-0.35 Hf-0.25C), solution annealed 15 minutes at 4600° F (2558° C), aged 1 hour at 2500° F (1371° C), and tensile tested at 3500° F (1927° C).

Figure 3. - Transmission electron micrographs after tensile testing.

in figure 3. The swaged and tensile tested structure in figure 3 shows numerous fine globular particles associated with both individual dislocations and subgrain boundaries. Figure 3(b) shows the structure of a specimen annealed for 1 hour at 3800° F (2093° C) and tensile tested at 3500° F (1927° C). The HfC particles are considerably larger than in the as-swaged structure, reflecting coarsening during the annealing treatment. Many of the particles are located at grain and subgrain boundaries. The structure of a solution annealed and aged specimen after tensile testing at 3500° F (1927° C) is shown in figure 3(c). Complete solutioning was achieved in this sample, evidenced by absence of large HfC particles in the electromicrographs. The fine HfC particles are mostly lined up indicating nucleation on dislocations.

From these and other microstructures examined after tensile testing it is apparent that the high strengths of the worked and of the solution annealed materials are associated with the presence of very fine carbide particles that retard the movement of dislocations and sub-boundaries. The particles coarsened by recrystallization annealing are less effective in pinning dislocations, resulting in reduced strength for the recrystallized materials.

The observed strengths and microstructures resulted in the selection of an optimum composition, W-4 Re-0. 35 Hf-0. 35 C, which has been designated as tungsten-RHC.
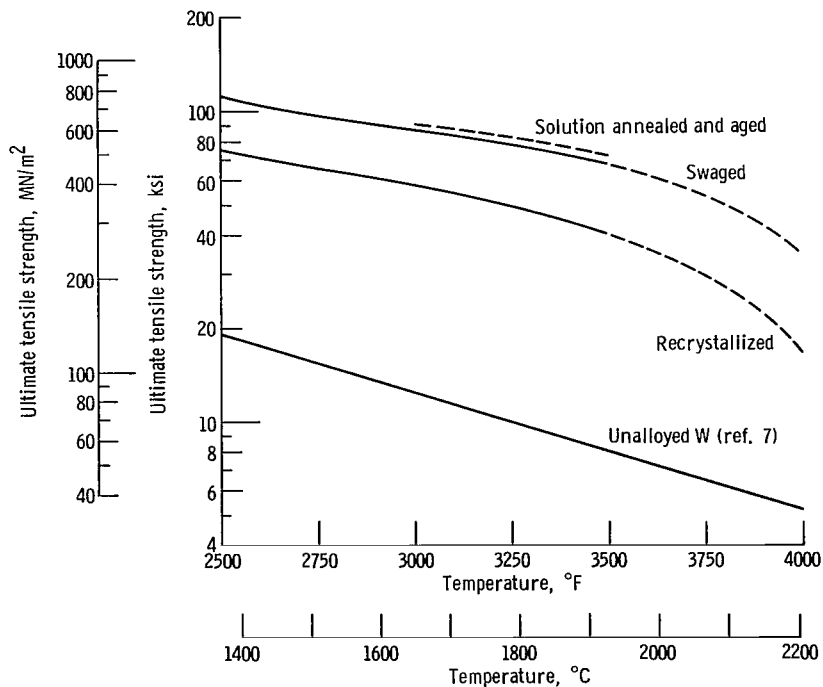
Figure 4. - Tensile strength of optimum alloy composition W-4Re-0.35Hf-0.35C (taken from fig. 1), compared with strength of unalloyed tungsten at 2500° to 4000° F (1371° to 2214° C).

Figure 4 shows the ultimate tensile strength of tungsten-RHC as a function of temperature as determined from the plots in figure 1. These strengths represent average experimental strength values for the optimum composition and differ from the highest strengths observed. For example, in the solution annealed condition at 3500° F, A219, W-3.7 Re-0.33 Hf-0.67C, exhibited a strength of 75.4 ksi (520 MN/m^2), somewhat higher than the average value of 70 ksi (483 MN/m^2) shown in figure 4.

Some caution must be employed in use of nominal or initial composition data to project strength value for these alloys since compositional changes can occur during processing or use that will, in turn, affect the strength properties. In particular, significant carbon losses (up to 50% in 100 hr at 3500° F (1927° C)) occur during vacuum annealing treatments and during high temperature testing at pressures in the range of 10^{-6} torr. These carbon losses result from reaction of carbon from the alloy with trace oxygen in the atmosphere to form CO.

Creep Properties

Creep properties of the W-Re-Hf-C alloys in the as-swaged, recrystallized, and solution annealed conditions were evaluated at 3500° F (1927° C) both by single-load creep-rupture tests and by step-load creep tests. Rupture lives in the single-load tests ranged from 0.72 to 128.0 hours. Data from these tests are presented in tables III and IV.

Representative creep data at 3500° F for one of the stronger alloys, A219, W-3.7 Re-0.33 Hf-0.67C, are plotted in figure 5. Although the strength increase over unalloyed tungsten is not as great in creep as in short time tensile tests, this alloy exhibits an approximate three-fold strength increase in the recrystallized condition and a five-fold to sixfold increase in the solution annealed condition.
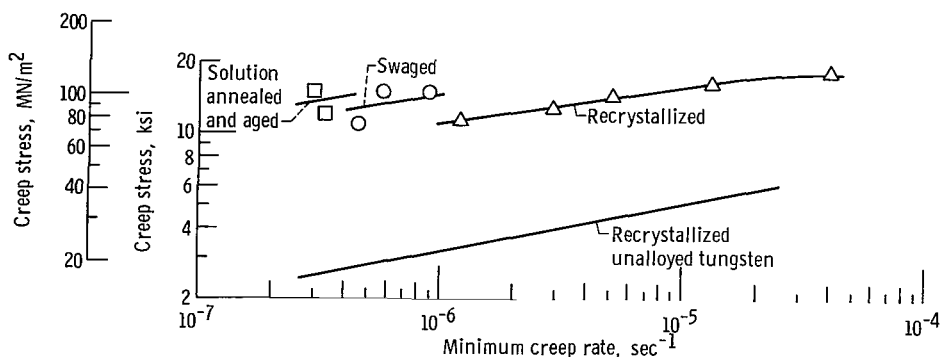
Figure 5. - Creep rates for alloy A219 (W-3.7Re-0.33Hf-0.67C) at 3500° F (1927° C) in as-swaged, recrystallized, and solution-annealed conditions. Unalloyed tungsten is included for comparison.

(a) Swaged.

(b) Recrystallized.

(c) Solution annealed and aged.
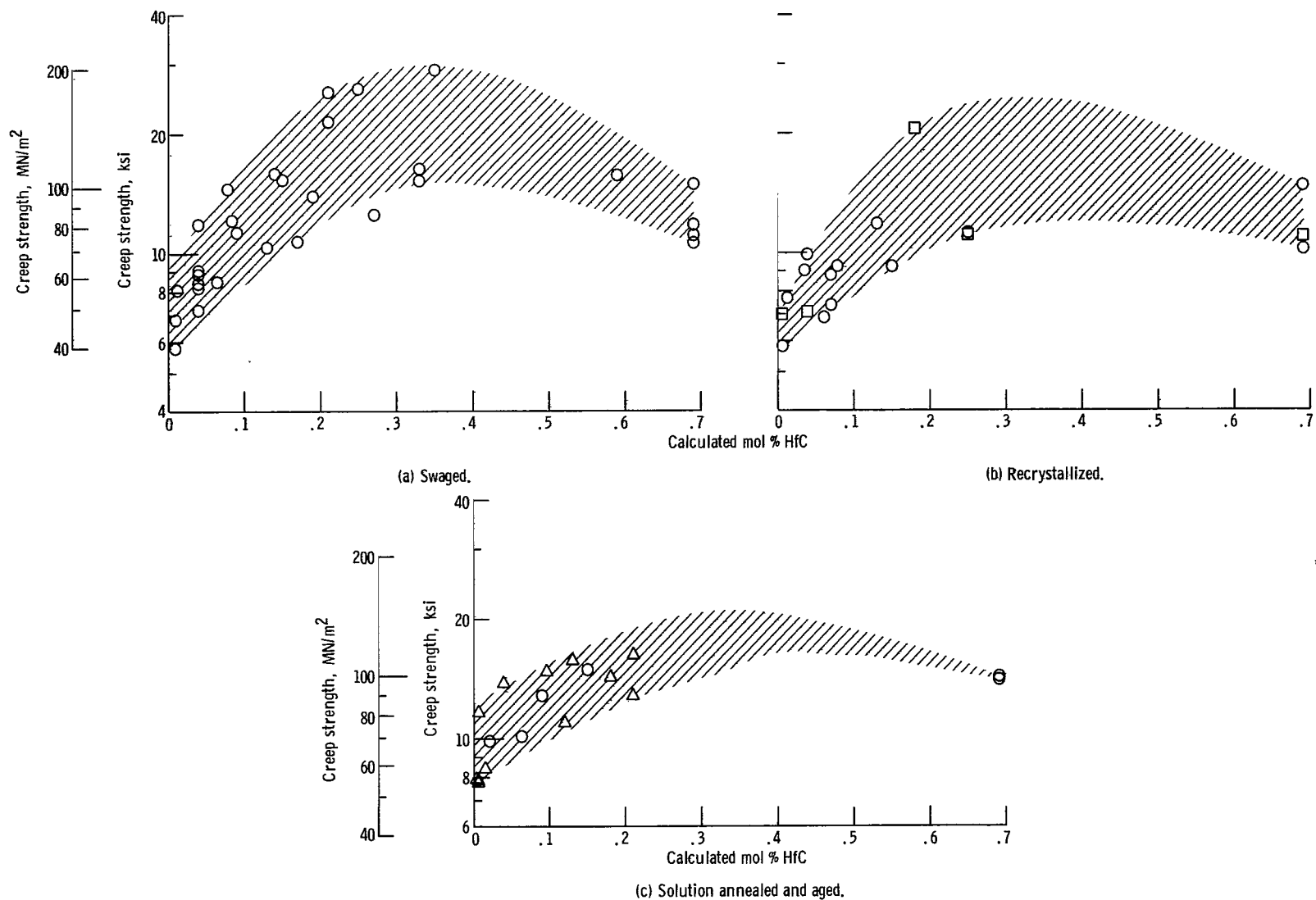
Figure 6. - Creep strength range of W-4Re-Hf-C alloys at 3500° F (1927° C) and minimum creep rate of 10^{-6} reciprocal second.

In order to assess the strengthening effects of HfC in creep, the creep strength values at a creep rate of 10^{-6} sec^{-1} were determined from each step-load creep test and from each creep-rupture test and plotted against the calculated mol percent HfC. These data are shown in figure 6. Due to the scatter in strength values, the data points were enclosed within projection bands to represent the range of creep strengths resulting from differences in microstructure. Substantial strengthening was noted for all three conditions with the swaged materials showing the highest strengths. The creep plot for the swaged materials indicates maximum strengthening between 0.3 and 0.4 m/o HfC, as was observed in the tensile data.

In order to investigate the temperature dependence of creep strength for W-Re-Hf-C alloys, an alloy of near optimum composition (A246, W-4.0 Re-0.40 Hf-0.48C) was prepared and creep tested in the swaged condition in 500° F $(278^{\circ}$ C) increments over the range 2000° to 4000° F $(1093^{\circ}$ to 2204° C). These results are compared with creep data
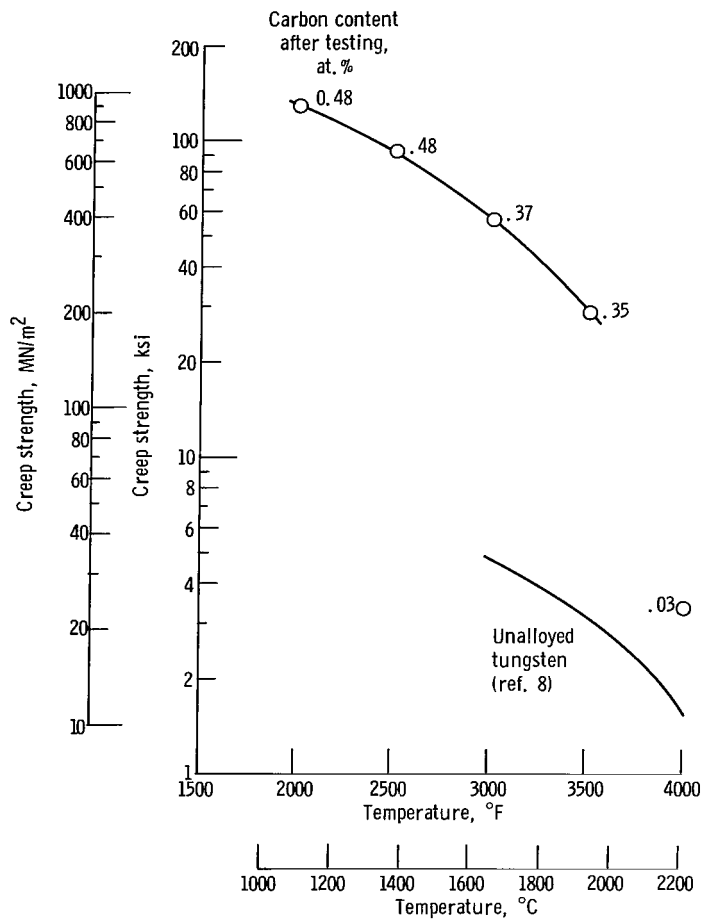
Figure 7. - Creep strength of alloy A246 (W-4.0Re-0.40Hf-0.48C) in swaged condition, at minimum creep rate of 10^{-6} reciprocal second compared with strength of unalloyed tungsten.

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for unalloyed tungsten in figure 7. Note that in this near optimum composition, the strength improvement in the swaged condition is ninefold at 3500° F (1927° C). The carbon content after testing is shown with each strength data point; note that creep testing at 4000° F (2204° C) resulted in loss of most of the carbon originally present.

The substructure of a solution annealed and aged creep specimen of alloy A212, W-3.6 Re-0.27 Hf-0.12C, after creep testing for 28.2 hours at 3500° F (1927° C), is shown in figure 8. The HfC particles are larger than those observed in a tensile specimen of a similar alloy A235 which had been heat treated identically (fig. 3(c)). The
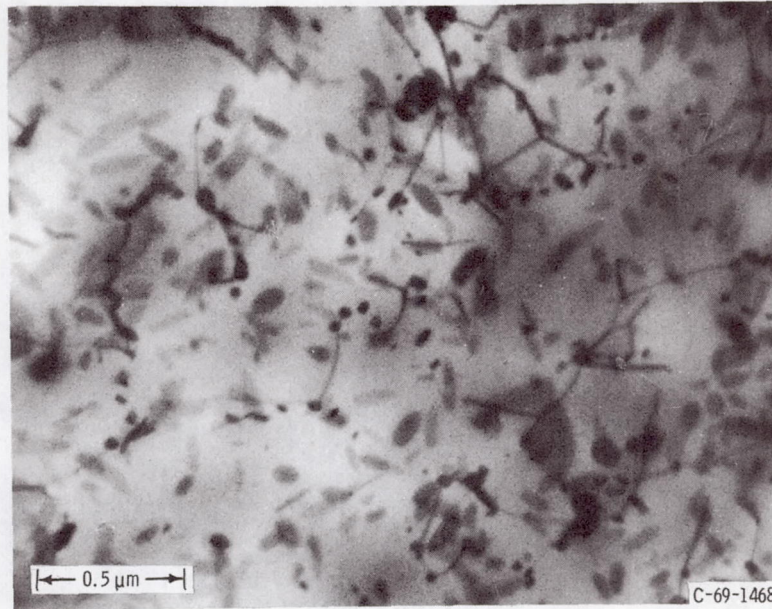
Figure 8. - Transmission electron micrograph of alloy A212 (W-3.6 Re-0.27 Hf 0.12C), solution annealed 15 minutes at 4600° F (2537° C), aged 1 hour at 2500° F (1371° C), and creep tested 28.2 hours at 3500° F (1927° C).

larger size of the HfC particles in the creep specimen is believed to reflect particle growth during creep testing. These larger particles, however, are still capable of pinning dislocations. Some of the particles are alined, indicating nucleation on dislocations during early creep straining.

Correlation of Creep Strength with Particle Size

The effect of HfC particle size on the creep strength increment was also investigated. For this purpose, the creep strength increment due to HfC was determined by subtracting the creep strength increments due to tungsten, rhenium, and free hafnium

from the observed strength at a creep rate of 10^{-6} sec^{-1}, in much the same manner as the tensile strength increments due to HfC were calculated. This strength increment was compensated for composition by dividing by (m/o HfC)$^{1/2}$ and plotted against the median particle diameter determined metallographically after testing. Data for alloys containing from 0.03 to 0.33 m/o HfC are shown in figure 9. It is seen that a line of slope -1 fairly correlated these data.
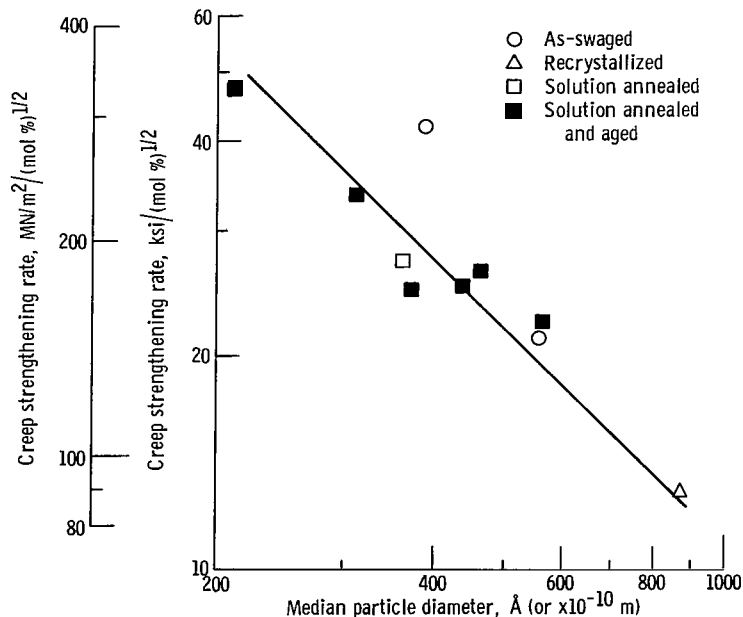
Figure 9. - Dependence of creep strengthening rate on hafnium carbide particle size.

The observed relations between the HfC strength increment and the amount and size of the HfC particles are in accord with recent theories on particle strengthening and suggest that plastic flow occurs primarily by dislocations bowing between the particles. It was first derived by Orowan (ref. 9) and later discussed in detail by Ansell (ref. 10) that

$$\tau_{ys} = \frac{\mu_m b}{L} + \tau_s \tag{1}$$

where

τ_{ys} shear yield strength of particle strengthened material

μ_m matrix shear modulus

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b   Burgers vector

L   planar interparticle spacing

τ_s matrix shear strength

This relation is based on dislocations bowing between the particles as opposed to cross-slipping around the particles or particle shearing.

Recent discussions on particle strengthening have been concerned with the method for calculating the interparticle spacing, L. Westmacott et al. (ref. 11) have shown that both the planar and volumetric approaches yield relations in which the interparticle spacing L varies directly with the particle diameter d and inversely with the square root of the volume fraction of dispersed particles f. The planar relation given by Westmacott et al. is expressed as

$$L = \left(\frac{\pi}{6}\right)^{1/2} \frac{d}{f^{1/2}} \tag{2}$$

Combining relations (1) and (2) gives

$$\tau_{ys} = \mu_m b \left(\frac{6}{\pi}\right)^{1/2} \frac{f^{1/2}}{d} + \tau_s \tag{3}$$

The first term on the right hand side of this relation represents the particle strengthening increment, which is seen to be directly proportional to $f^{1/2}$ and inversely proportional to d. Since m/o HfC is directly related to f, the experimental observations in the present work are in qualitative agreement with equation (3).

It is further possible to formulate an empirical relation similar in form to equation (3) to express the creep strength of HfC-strengthened tungsten and W-Re based on the data presented earlier in figure 9. This relation is

$$\sigma_c = a \frac{f^{1/2}}{d} + \sigma_{c(m)} \tag{4}$$

where

σ_c alloy creep strength at 3500° F (1927° C) and a creep rate of 10^{-6} sec^{-1}

a   empirically determined constant

$\sigma_{c(m)}$ matrix creep strength

From figure 9, the constant a is calculated as 10 900 (ksi)(Å)(m/o HfC)$^{-1/2}$.

Low Temperature Ductility Properties

The low temperature ductility properties of W-Re-Hf-C alloys were studied by determining the bend ductile-brittle transition temperatures of sheet specimens of each alloy in several conditions. The results of these tests are presented in table V. Analysis of the data indicates that the structural condition as affected by heat treatment has a large effect on the transition temperature as would be expected. However, there is no consistent relation between transition temperature and amount of hafnium carbide.

The average ductile-brittle transition temperatures for the quaternary W-Re-Hf-C alloys are compared to those for ternary W-Hf-C alloys (unpublished work, L. S. Rubenstein, Lewis Research Center) and unalloyed tungsten (ref. 8) in figure 10. Alloy-
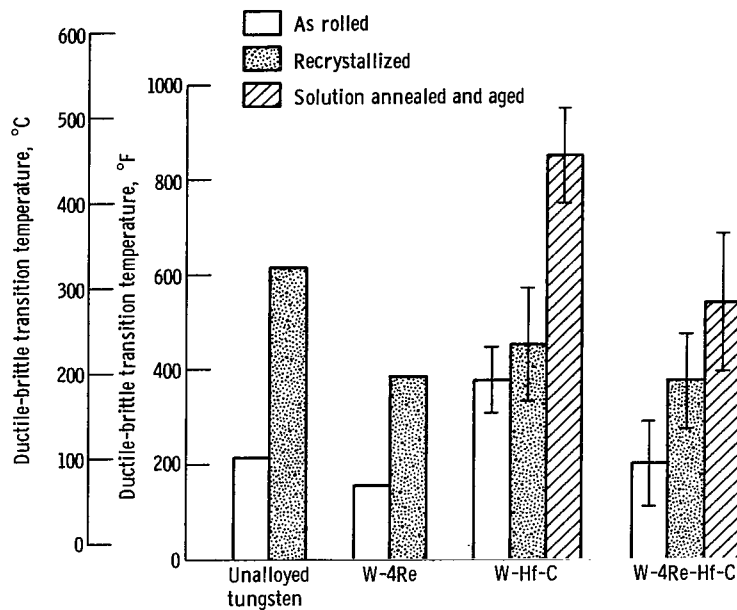
Figure 10. - Ductile-brittle transition temperatures for arc-melted tungsten, W-4Re, W-Hf-C, and W-4Re-Hf-C. Average values are shown for tungsten and W-4Re, while median values and average differences from median are shown for W-Hf-C and W-4Re-Hf-C.

ing of tungsten with HfC increases the ductile-brittle transition temperature by $150°$ to $200°$ F ($83°$ to $111°$ C) in the as-rolled and solution annealed conditions but decreases it moderately in the recrystallized condition. The addition of about 4 a/o rhenium to W-Hf-C effects a decrease in the transition temperature in all three structural conditions, as expected from prior work on dilute W-Re alloys (ref. 3). The improvement relative to W-Hf-C ranges from $75°$ F ($42°$ C) in the worked condition to $310°$ F ($172°$ C)

in the solution annealed condition, similar to the improvement in W-4Re relative to un-alloyed tungsten.

Recrystallization Behavior

Data on the recrystallization behavior of the fifteen W-Re-Hf-C alloys are presented in table VI and figure 11. The addition of hafnium and carbon increases the 1-hour re-crystallization temperature (100% recrystallized) from 3000° F (1649° C) for W-4Re
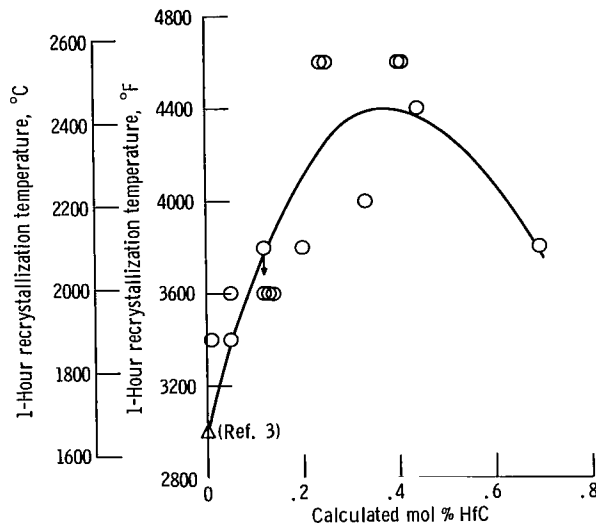
Figure 11. - One-hour recrystallization temperature of W-4Re-Hf-C alloys as function of hafnium carbide content.

(ref. 3) to as high as 4600° F (2538° C) for four of the near optimum alloys. Apparently the worked structure is stabilized by the fine hafnium carbide particles up to the temperature at which the carbide dissolves in the W-4Re matrix.

The optimum amount of HfC for retention of the worked structure is in the range of 0.25 to 0.50 mol percent C, with larger amounts causing a decrease in the recrystallization temperature.

The microstructure of alloy A234 after annealing at each of several temperatures is shown in figure 12. The microstructure after annealing at 3600° F (1982° C) shows only traces of recrystallization. After 4000° F (2204° C) the structure is partially recrystallized but many worked areas remain. Following annealing at 4400° F (2427° C) the microstructure consists primarily of recrystallized grains. The large temperature
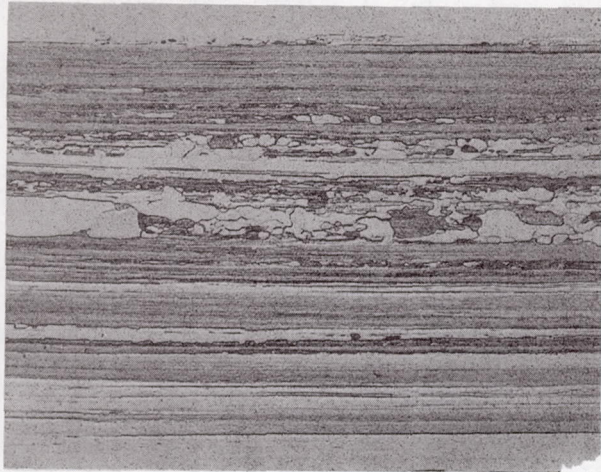
(a) Temperature, 3600° F (1982° C).
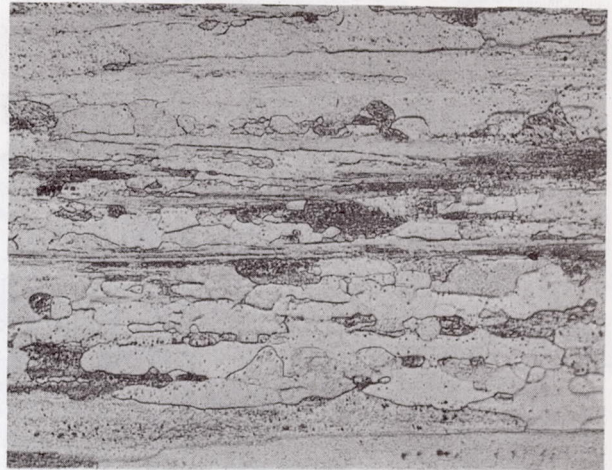
(b) Temperature, 4000° F (2204° C).
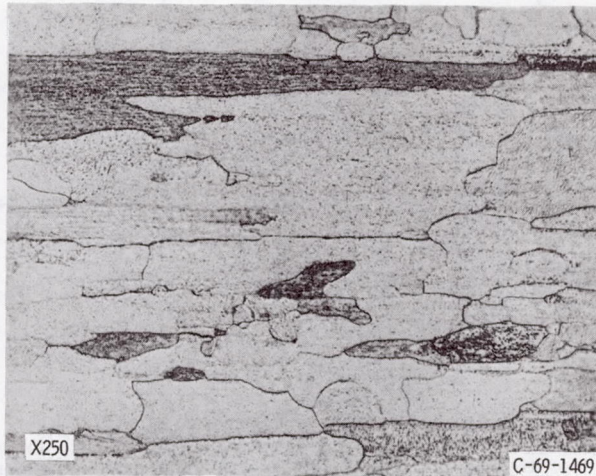
(c) Temperature, 4400° F (2427° C).

Figure 12. - Microstructure of alloy A234 (W-4.0 Re-0.24 Hf-0.30C) after annealing for 1 hour at indicated temperatures.

span from onset to completion of recrystallization reflects the stability provided by the presence of the carbide particles.

The hardness response to annealing is shown in figure 13 for average carbon levels of 0.04 atom percent and 0.39 atom percent. The curve for an average carbon content of 0.04 atom percent shows a minimum at 3600° F (1982° C), indicating complete recrystallization. The hardness increase after annealing at higher temperatures is probably associated with solutioning and reprecipitation of hafnium carbide. The curve for an average carbon content of 0.39 atom percent shows only the normal hardness decrease associated with recrystallization.
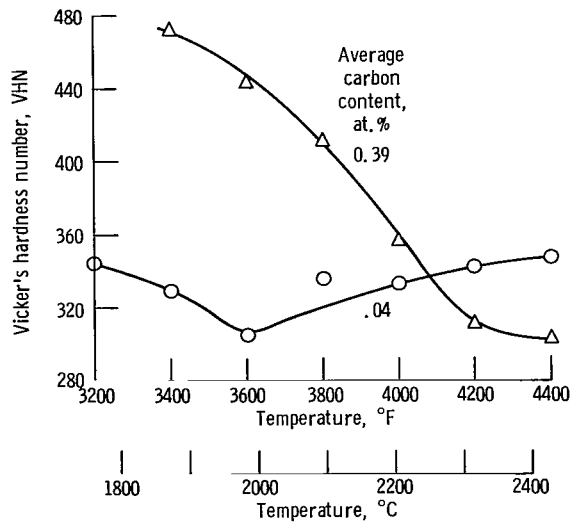
Figure 13. - Effects of annealing for 1 hour at various temperatures on hardness of swaged W-Re-Hf-C alloys with 0.04 atomic percent carbon (av of A201, A224, A202) and with 0.39 atomic percent carbon (av of A234, A236, A235).

Particle Growth

Since the strength of a precipitate strengthened material depends in part on the maintenance of a fine particle size, it is of interest to determine the growth rates for HfC in W-Re-HfC alloys.

Particle sizes were estimated from electron transmission micrographs of specimens of W-Re-Hf-C which had been creep tested at 3500° F (1927° C) or heat treated at temperatures from 3600° to 5000° F (1982° to 2760° C). These observations are presented in table VII, along with similar observations on ternary W-Hf-C alloys from unpublished work of Rubenstein (Lewis Research Center). These data indicate, as expected, that the sizes of the HfC particles tend to increase with increasing exposure time at temperatures approaching the solution temperature for HfC, assumed to be near the solvus line for carbon in tungsten.

The growth of precipitated particles in a binary system has recently been discussed by Ardell (ref. 12), who gives the equation for the rate of particle coarsening as

$$\bar{r}^3 - \bar{r}_0^3 = kt \tag{5}$$

where $\bar{r}$ is the average particle radius at time t, and $\bar{r}_0$ is the average particle radius at the onset of coarsening. The rate constant k is given by (ref. 12)

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$$k = \frac{8\gamma \, D c_e V_m^2}{9RT} \tag{6}$$

where γ is the interfacial free energy of the particle-matrix interface, D and c_e are the diffusion coefficient and the concentration, respectively, of the rate-limiting solute in the matrix in equilibrium with a particle of infinite size, V_m is the molar volume of the precipitate, R is the gas constant, and T is the absolute temperature.

Experimental values for the rate constant k were calculated for the present alloys from particle size measurements before and after heating, assuming the coarsening behavior in the present ternary and quaternary alloys to be similar to that for binary alloys. These cubic coarsening rates are given in table VII. For the solution annealed and aged W-Re-Hf-C alloys, $\bar{r}_o$ was negligible and assumed to be zero. In the case of W-Hf-C alloys, the initial conditions varied and actual measurements for the initial conditions were used for $\bar{r}_o$. It should be noted the magnitude of r_o has only a minor effect on the coarsening rate since r^3 is generally much larger than r_o^3.

A plot of the rate constant k against inverse absolute temperature is shown in figure 14. This line can be represented by the relation:

$$k = 1.2 \times 10^{-7} \, e^{-147\,000/RT} \tag{7}$$

The value of 147 000 cal/mol (6.15×10^5 J/mol) for the activation energy is similar to the value of 153 100 cal/mol (6.41×10^5 J/mol) observed by Andeline et al. (ref. 13) for self-diffusion in tungsten and quite different from the value of 40 400 cal/mol (1.69×10^5 J/mol) observed by Kovenskii for diffusion of carbon in tungsten (ref. 14). This similarity suggests that the observed value of 147 000 cal/mol (6.15×10^5 J/mol) represents the temperature dependency for hafnium diffusion in tungsten and that hafnium is the rate limiting solute.

By analogy with the behavior in binary systems, it can be inferred that the coarsening rate should be affected by the amount of excess hafnium or carbon. Analysis of the coarsening data did suggest that the coarsening rate tended to increase in the presence of excess hafnium and tended to decrease in the presence of excess carbon. Considerable scatter exists in these data, however, and it is not possible to draw a firm conclusion with regard to compositional effects on the coarsening rates.

An estimate of the stability of the hafnium carbide particles can be derived from equation (7). Figure 15 presents the calculated time for the hafnium carbide particles to grow to median diameters of 200, 500, and 1000 Å as a function of temperature. It is seen, for example, that at 3000° F (1649° C), good strength (assumed to go with particle sizes less than 500 Å) should be maintained for 10 000 hours, while at 4000° F (2204° C),
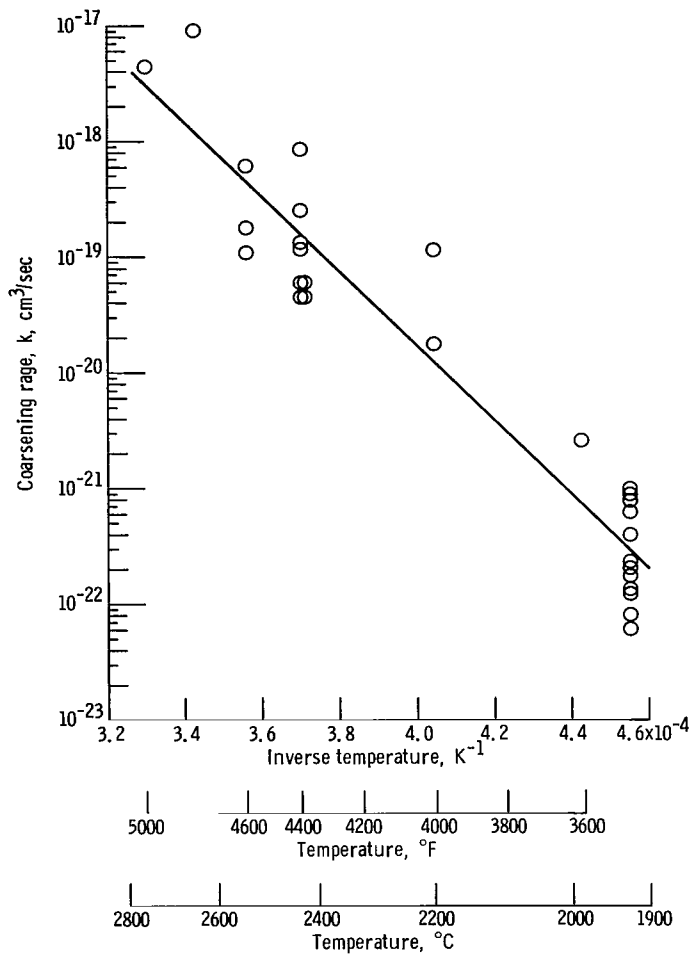
Figure 14. – Temperature dependence of hafnium carbide coarsening rate. Slope of plot corresponds to activation energy of 147 kilocalories per mol (6.15x10^5 joules per mol).
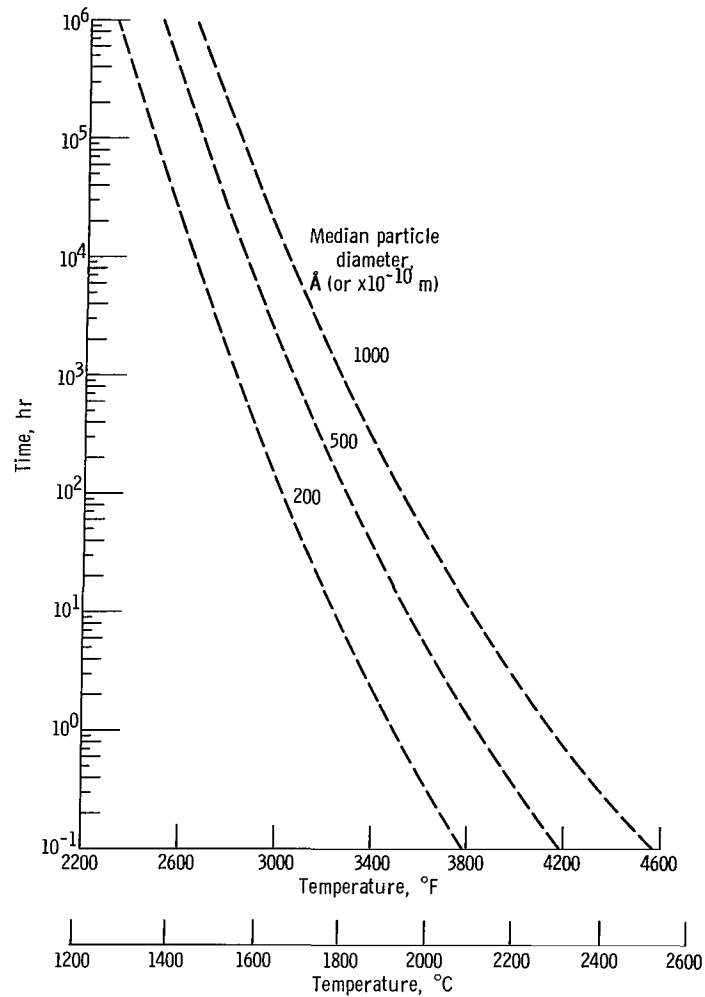
Figure 15. - Calculated time for hafnium carbide particles to grow from zero to indicated median particle diameter for various temperatures.

it is estimated that the particles will lose most of their strengthening effects in only several hours.

CONCLUSIONS

The following conclusions were made from the results of this study on tungsten-rhenium-hafnium-carbon alloys:

1. The high temperature strengthening effects of HfC and the low temperature ductility improvements associated with 4 atom percent rhenium can be incorporated in a single alloy without detrimental interaction. Rhenium decreases the low temperature

ductile-brittle transition temperature of W-Hf-C in bending, but does not reduce the high-temperature strengthening effects of HfC.

2. The optimum composition for high temperature strength is W-4Re-0.35 Hf-0.35C (atm.%), based on results from tensile and creep tests. This alloy, designated tungsten-RHC, shows in the swaged condition ninefold strength advantage over unalloyed tungsten in both short-time tensile and creep tests at 3500° F (1927° C); for example, 68 ksi against 8 ksi (469 mol/m^2 against 55 MN/m^2) in ultimate tensile strength and 29 ksi against 3.2 ksi (200 MN/m^2 against 22 MN/m^2) in creep strength at a minimum creep rate of 10^{-6} sec^{-1}.

3. Coarsening rates calculated for HfC indicate that particles can be expected to coarsen to 1000 Å or greater in about 3 hours at 4000° F (2204° C) or in 10 000 hours at 3000° F (1649° C). Since the alloy strength depends on substructural stabilization by fine HfC particles, decreased strength would be expected during these time-temperature exposures.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, May 1, 1969,
            129-03-02-02-22.

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TABLE I. - ANALYSIS OF MATERIALS

Alloy	Calculated hafnium carbide content, mol %	Composition, at. %			Impurity content[a], wt. %		
		Re	Hf	C	O	N	Fe
A201	0.009	4.4	0.44	0.009	0.0010	0.0002	0.0004
A224	.049	3.8	.22	.049	.0008	.0001	.0004
A202	.052	3.6	.76	.052	.0011	.0004	.0003
A212	.12	3.6	.27	.12	.0011	.0003	.0005
A226	.12	3.9	.44	.12	.0005	.0001	.0004
A210	.13	3.9	.25	.13	.0005	.0003	.0004
A211	.14	3.6	.27	.14	.0010	.0003	.0004
A216	.20	3.1	.30	.20	.0005	.0003	.0005
A234	.24	4.0	.24	.30	.0008	.0020	.0003
A235	.25	3.9	.35	.25	.0004	.0015	.0003
A219	.33	3.7	.33	.67	.0005	.0004	.0004
A246	.40	4.0	.40	.48	.0009	.0005	.0005
A245	.41	3.9	.41	.51	.0017	.0008	.0002
A236	.44	3.9	.44	.47	.0005	.0006	.0003
A217	.69	3.8	.69	.98	.0018	.0003	.0005

[a]Aluminum and silicon contents were analyzed as <0.001 and
<0.0002 weight percent, respectively for all alloys.

TABLE II. - TENSILE PROPERTIES OF W-Re-Hf-C ALLOYS AT 2500 to 4000° F (1371 to 2204° C)

Alloy condition	Heat treatment			Test temperature		Yield strength at 0.2 percent offset		Ultimate tensile strength		Elongation, percent	Reduction in area, percent	Post-test carbon content, at. % (a)	Median particle diameter, Å (or ×10⁻¹⁰ m)
	Time, hr	Temperature °F	°C	°F	°C	ksi	MN/m²	ksi	MN/m²				
A201 (W-4.4 Re-0.44 Hf-0.009C)													
As-swaged	----	-----	-----	2500	1371	70.0	482	94.4	650	16	87	(0.009)	-----
				3000	1649	60.0	413	72.7	501	25	99	(.009)	-----
				3500	1927	32.4	223	34.7	239	40	98	(.009)	-----
Heat treated	1	3800	2093	2500	1371	b30.8	b212	58.7	404	37	89	(0.015)	-----
				3000	1649	36.4	251	47.0	324	57	88	(.015)	-----
				3500	1927	20.4	141	23.8	164	60	95	.015	-----
	0.25	c4600	c2538	3500	1927	24.0	165	25.5	176	--	--	.02	-----
A224 (W-3.8 Re-0.22 Hf-0.049C)													
As-swaged	----	-----	-----	2500	1371	-----	----	104	713	10	87	(0.099)	-----
				3000	1649	60.7	418	81.4	561	12	89	(.049)	-----
				3500	1927	41.3	285	45.7	315	33	93	(.049)	-----
				3910	2154	10.1	69.6	14.1	97.1	52	90	(.049)	-----
Heat treated	1	3800	2093	2500	1371	b24.8	b171	65.9	454	16	89	(0.014)	-----
				3000	1649	32.9	227	51.7	356	16	63	(.014)	-----
				3500	1927	17.8	123	23.9	165	33	70	.914	-----
	0.25	e4600	c2538	3500	1927	15.6	107	19.6	135	--	--	.008	-----
B202 (W-3.6 Re-0.76 Hf-0.052C)													
As-swaged	----	-----	-----	2500	1371	63.5	438	119	816	12	81	(0.046)	----
				3000	1649	58.8	405	70.0	482	26	90	(.046)	----
				3500	1927	49.7	342	52.7	363	16	80	.046	----
Heat treated	1	3800	2093	2500	1371	b35.8	b247	66.2	456	80	87	(0.012)	
				3500	1927	25.3	174	31.7	218	55	92	.012	----
	0.25	c4600	c2538	3500	1927	31.2	215	34.1	235	--	--	.021	----
A212 (W-3.6 Re-0.27 Hf-0.12C)													
As-swaged	----	-----	-----	2500	1371	76.8	530	86.0	592	7	91	(0.12)	----
				3000	1649	48.7	336	64.6	445	14	92	(.12)	----
				3500	1927	28.6	197	39.6	273	18	94	(.12)	----
				4000	2204	11.3	77.9	13.8	95.1	--	97	(.12)	----
As-swaged	1	4400	2426	2500	1371	33.2	229	d75.2	d518	16	88	(0.12)	----
				3000	1649	40.8	281	78.4	540	12	54	(.12)	----
				3500	1927	34.4	237	39.0	269	--	69	.12	----
	0.25	4600	2538	3500	1927	36.1	249	40.7	281	9	36	0.089	----
		e4600	2538	3500	1927	45.1	311	50.4	347	9	17	(.089)	----
		c4600	2538	3500	1927	43.6	301	48.3	333	7	25	.12	----
		f4600	2538	3500	1927	43.3	298	47.6	328	8	23	(.12)	----
		4700	2593	3500	1927	29.4	203	33.1	228	16	35	.041	----
		4800	2649	3500	1927	31.9	220	35.4	244	18	39	.052	----
		5000	2760	3500	1927	28.4	196	32.6	225	12	39	(.052)	----

[a] Values in parentheses are estimated from measurements on similar specimens.
[b] Specimen yielded discontinuously.
[c] Plus one hour at 2500° F (1371° C).
[d] Discontinuous flow near ultimate.
[e] Plus one hour at 2000° F (1093° C).
[f] Plus one hour at 3000° F (1649° C).

Alloy condition	Heat treatment			Test temperature		Yield strength at 0.2 percent offset		Ultimate tensile strength		Elonga- tion, percent	Reduction in area, percent	Post- test carbon content, at. % (a)	Median particle diameter, Å (or ×10⁻¹⁰ m)
	Time, hr	Temperature °F	°C	°F	°C	ksi	MN/m²	ksi	MN/m²				
A226 (W-3.9 Re-0.44 Hf-0.12C)													
As-swaged	----	-----	-----	2500	1371	-----	-------	109	751	14	86	(0.089)	----
				3000	1649	66.0	455	82.4	568	14	94	(.089)	----
				3500	1927	44.4	306	48.5	334	18	94	.089	----
Heat treated	1	3800	2093	2500	1371	24.8	171	65.9	454	--	--	(0.049)	----
				3000	1649	32.3	223	50.6	349	29	89	.049	----
				3500	1927	18.9	130	24.8	171	50	95	(.049)	----
				4000	2204	11.3	77.9	13.4	92.3	84	82	(.049)	----
	0.25	4600	2538	3500	1927	21.1	145	24.9	172	--	--	0.012	----
A210 (W-3.9 Re-0.25 Hf-0.13C)													
As-swaged	----	-----	-----	2500	1371	117	806	127	872	13	79	0.15	----
				3500	1927	49.8	343	54.3	374	17	89	.15	----
Heat treated	1	3800	2093	3000	1649	b33.2	b229	57.3	395	20	87	0.083	----
				3500	1927	24.6	170	30.1	207	28	90	.14	----
				4000	2204	10.1	69.6	12.8	88.2	68	>98	.057	----
	0.25	4600	2538	3500	1927	41.3	285	45.3	312	13	36	0.14	----
	.25	c4600	c2538	3500	1927	43.2	298	47.9	330	8	22	.11	----
A217 (W-3.1 Re-0.30 Hf-0.20C)													
As-swaged	----	----	----	2500	1371	78.5	541	108	741	11	87	(0.20)	----
				3000	1649	60.6	418	77.8	536	17	88	(.20)	----
				3500	1927	46.8	322	52.4	361	21	85	(.20)	----
Heat treated	1	3800	2093	2500	1371	b52.4	b361	77.2	532	22	80	(0.21)	555
				3000	1649	-----	-----	44.4	306	45	94	(.21)	----
				3500	1927	26.3	181	32.0	220	31	94	.21	----
	0.25	4600	2538	3500	1927	45.0	310	50.8	350	6	9	0.12	----
		c4600	2538	3500	1927	16.8	116	20.4	141	--	--	.015	----
A234 (W-4.0 Re-0.24 Hf-0.30C)													
As-swaged	----	----	----	3000	1649	80.3	553	92.9	640	16	85	(0.30)	----
				3500	1927	38.3	264	59.7	411	14	78	(.30)	146
Heat treated	1	4000	2204	3500	1927	38.0	263	41.1	283	14	26	.084	146
		c4600	2538	3000	1649	b36.7	253	73.6	507	12	8	(.17)	<100
				3500	1927	44.6	307	47.8	329	8	9	.17	138
A235 (W-3.9 Re-0.35 Hf-0.25C)													
As-swaged	----	----	----	3000	1649	63.3	436	101	692	17	78	(0.25)	----
				3500	1927	59.9	413	66.5	458	20	76	(.25)	142
Heat treated	1	4000	2204	3500	1927	39.4	272	40.9	282	25	40	0.17	(g)
	.25	c4600	c2538	3500	1927	50.5	348	52.7	363	8	5	.19	<100
				3500	1927	55.9	385	62.3	429	12	4	.20	<100

a
Values in parentheses are estimated from measurements on similar specimens.

bSpecimen yielded discontinuously.

cPlus one hour at 2500° F (1371° C).

gA few large particles with estimated median diameter of 3440 Å plus fines on dislocations.

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TABLE II. - Concluded. TENSILE PROPERTIES OF W-Re-Hf-C ALLOYS AT 2500 to 4000° F (1371 to 2204° C)

Alloy condition	Heat treatment			Test temperature		Yield strength at 0.2 percent offset		Ultimate tensile strength		Elonga-tion, percent	Reduction in area, percent	Post test carbon content, at. % (a)	Median particle diameter, Å (or ×10⁻¹⁰ m)
	Time, hr	Temperature		°F	°C	ksi	MN/m²	ksi	MN/m²				
		°F	°C										
A219 (W-3.7 Re-0.33 Hf-0.67C)													
As-swaged	----	----	----	2500	1371	90.0	620	93.5	644	11	78	(0.67)	----
				3000	1649	62.2	429	74.2	511	11	79	(.67)	----
				3500	1927	44.2	305	53.3	367	16	77	(.67)	----
Heat treated	1	3800	2093	3000	1649	29.8	205	43.0	296	31	43	0.64	876
				3500	1927	39.6	273	42.1	290	--	--	(.65)	582
				4000	2204	14.5	100	16.8	116	25	72	.66	----
	0.25	4600	2538	3500	1927	53.3	367	66.5	458	14	49	0.54	h1950
		c4600	c2538	3500	1927	62.8	433	75.4	520	8	18	.50	----
A246 (W-4.0 Re-0.40 Hf-0.48C)													
As-swaged	----	----	----	3500	1927	61.8	426	65.6	452	22	88	0.34	----
A245 (W-3.9 Re-0.41 Hf-0.51C)													
As-swaged	----	----	----	2000	1093	118	814	128	883	16	73	(0.51)	----
				2500	1371	112	772	115	793	14	78	(.51)	----
				3000	1649	85.8	592	89.8	619	13	82	(.51)	----
				3500	1927	62.2	429	66.3	457	16	80	.46	----
				4000	2204	28.4	196	30.5	210	20	56	.30	----
				4500	2482	16.4	113	19.0	131	15	85	.42	----
Heat treated	1	4600	2538	3500	1927	33.6	232	35.1	242	20	77	0.07	----
	0.25	4700	2593	3500	1927	48.2	332	51.0	352	8	38	0.19	----
A236 (w-3.9 Re-0.44 Hf-0.47C)													
As-swaged	----	----	----	3500	1927	55.3	381	64.6	445	20	88	(0.47)	167
Heat treated	1	4000	2204	3500	1927	30.8	212	33.5	231	43	54	0.17	(i)
	0.25	4600	b2538	3500	1927	55.4	382	60.1	414	7	13	0.25	<100
A217 (W-3.8 Re-0.69 Hf-0.98C)													
As-swaged	----	----	----	2500	1371	88.4	609	99.5	696	15	74	(0.98	----
				3000	1649	63.6	438	79.8	550	15	70	(.98)	----
				3500	1927	48.8	336	53.0	365	21	89	(.98)	----
Heat treated	1	3800	2093	3000	1649	39.4	272	48.3	333	21	85	1.10	----
				3500	1927	33.3	230	38.3	264	29	95	1.27	----
				4000	2204	17.5	121	19.3	133	40	91	.96	----
	0.25	4600	2538	3500	1927	34.4	237	44.2	305	26	83	1.00	----
		c4600	c2538	3500	1927	45.7	315	60.9	420	25	80	.96	----

aValues in parentheses are estimated from measurements on similar specimens.
bSpecimen yielded discontinuously.
cPlus one hour at 2500° F (1371° C).
hPlus fines, less than 100 Å in diameter.

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TABLE III. - CREEP RUPTURE DATA AT 3500° F (1927° C)

Alloy condition	Heat treatment			Stress		Minimum creep rate, $\sec^{-1}$	Rupture time, hr	Post-test carbon content, at.% (a)	Estimated stress for $10^{-6}\ \sec^{-1}$ creep rate (b)		Median particle diameter, Å (or $\times 10^{-10}$ m)
	Time, hr	Temperature		ksi	MN/m²				ksi	MN/m²	
		°F	°C								
A201 (W-4.4 Re-0.44 Hf-0.009C)											
As-swaged	----	-----	-----	5.43	37.4	0.61×10^{-6}	93.0	0.008	5.8	40	----
				8.30	57.2	4.1	19.4	(.008)	6.8	47	----
Heat treated	1	4000	2204	9.95	68.6	10×10^{-6}	7.8	0.005	7.0	48	----
A224 (W-3.8 Re-0.22 Hf-0.049C)											
As-swaged	----	-----	-----	9.66	66.6	3.0×10^{-6}	15.6	(0.039)	8.2	57	----
				15.1	104	59	2.0	.039	8.4	58	----
Heat treated	1	3800	2093	10.0	68.9	10.5×10^{-6}	6.6	(0.039)	7.1	49	----
	.25	c4600	c2538	10.0	68.9	12	8.2	.015	8.4	58	----
		c4600	c2538	12.1	83.4	57	.72	.005	9.2	63	(d)
A202 (W-3.6 Re-0.76 Hf-0.052C)											
As-swaged	----	-----	-----	9.60	66.1	3.2×10^{-6}	16.5	(0.012)	8.1	56	----
Heat treated	0.25	c4600	c2538	7.65	52.7	0.77×10^{-6}	------	0.006	7.8	54	698
A212 (W-3.6 Re-0.27 Hf-0.12C)											
As-swaged	----	-----	-----	11.0	75.8	4.4×10^{-6}	16.1	(0.039)	8.9	61	----
				15.0	103	5.4	5.8	.039	11.8	81	----
A226 (W-3.9 Re-0.44 Hf-0.12C)											
As-swaged	----	-----	-----	7.06	48.6	0.84×10^{-6}	93.0	0.039	7.2	50	----
				8.59	59.2	.74	46.3	(.039)	9.0	62	----
				15.1	104	1.3	5.7	.078	14.5	100	----
(e)				15.0	103	49	1.9	.063	8.5	59	----
(f)				15.0	103	4.3	8.0	.083	12.1	83	----
(f)				15.0	103	7.2	5.9	.090	11.3	78	----
Heat treated	0.25	c4600	c2538	8.20	56.5	1.4×10^{-6}	12.8	0.006	8.0	55	725
A210 (W-3.9 Re-0.25 Hf-0.13C)											
As-swaged	----	-----	-----	11.5	79.2	2.1×10^{-6}	21.4	(0.13)	10.3	71	----
Heat treated	0.25	c4600	c2538	11.9	82.0	1.4	13.9	0.069	11.6	80	460

[a]Values in parentheses are estimated from measurements on similar specimens.

[b]Stress estimate calculated from creep rate and stress using n values of 6.9 for as-swaged or annealed specimens and 14.6 for solution annealed specimens.

[c]Indicated treatment plus 1 hour at 2500° F (1371° C).

[d]No particles visible.

[e]Prestrained at 3500° F (1927° C) and 6.94 ksi for 24 hours.

[f]Prestrained at 2500° F (1371° C) and 15.0 ksi for 24 hours.

TABLE III. – Concluded. *CREEP RUPTURE DATA AT 3500° F (1927° C)*

Alloy condition	Heat treatment			Stress		Minimum creep rate, $\sec^{-1}$	Rupture time, hr	Post-test carbon content, at.% (a)	Estimated stress for $10^{-6}\ \sec^{-1}$ creep rate (b)		Median particle diameter, Å (or $\times 10^{-10}$ m)
	Time, hr	Temperature °F	°C	ksi	MN/m²				ksi	MN/m²	
A216 (W-3.1 Re-0.30 Hf-0.20C)											
As-swaged	----	-----	-----	8.56	59.0	0.22×10^{-6}	61.4	(0.17)	10.7	74	----
				15.0	103	.66	21.0	.14	15.9	110	----
				15.1	104	1.8	30.3	.19	13.9	96	----
Heat treated	0.25	c4600	c2538	10.1	69.6	0.28×10^{-6}	28.0	0.12	11.0	76	----
	.25	c4600	c2538	15.0	103	.45	9.3	.13	15.8	109	----
A234 (W-4.0 Re-0.24 Hf-0.30C)											
As-swaged	----	-----	-----	14.8	102	0.80×10^{-6}	16.9	0.15	15.3	105	----
Heat treated	0.25	c4600	c2538	15.0	103	1.1×10^{-6}	5.0	0.096	14.9	103	310
A235 (W-3.9 Re-0.35 Hf-0.25C)											
As-swaged	----	-----	-----	14.9	103	0.080×10^{-6}	65.0	0.21	21.5	148	----
				24.9	172	.84	18.6	(.21)	25.6	176	----
Heat treated	1	4000	2204	14.9	103	0.11×10^{-6}	66.2	0.18	20.5	141	h823
	.25	c4600	c2538	14.8	102	1.44	14.9	.18	14.4	99	558
A219 (W-3.7 Re-0.33 Hf-0.67C)											
As-swaged	----	-----	-----	11.1	76.5	0.45×10^{-6}	128.0	0.27	12.5	86	----
				15.0	103	.57	26.9	.58	16.3	112	554
				15.0	103	.89	17.8	.36	15.2	105	----
Heat treated	1	3800	2093	10.8	74.4	0.83×10^{-6}	49.2	0.25	11.1	77	865
	.25	c4600	c2538	15.0	103	.29	20.9	.21	16.3	112	437
	.25	g2538	g2538	12.0	83	.33	25.8	(.21)	12.9	89	----
A246 (W-4.0 Re-0.40 Hf-0.48C)											
As-swaged	----	-----	-----	20.0	138	0.089×10^{-6}	18.9	0.25	26.0	179	----
A236 (W-3.9 Re-0.44 Hf-0.47C)											
Heat treated	0.25	c4600	c2538	14.8	102	2.9×10^{-6}	1.8	0.040	13.8	95	210
A217 (W-3.8 Re-0.69 Hf-0.98C)											
As swaged	----	-----	-----	10.1	69.6	0.70×10^{-6}	59.8	1.01	10.6	73	936
				11.5	79.2	1.3	-----	(.94)	11.1	77	----
				15.0	103	.73	36.0	.59	15.7	108	----
(f)				15.0	103	5.3	1.8	1.22	11.8	81	----
				25.0	172	36	1.7	1.16	14.9	103	----
Heat treated	1	3800	2093	10.0	68.9	0.53	75.8	(0.94)	11.0	76	1043

aValues in parentheses are estimated from measurements on similar specimens.

bStress estimate calculated from creep rate and stress using n values of 6.9 for as-swaged or annealed specimens and 14.6 for solution annealed specimens.

cIndicated treatment plus 1 hour at 2500° F (1371° C).

fPrestrained at 2500° F (1371° C) and 15.0 ksi for 24 hours.

gIndicated treatment plus 1 hour at 2000° F (1093° C).

hPlus fines (less than 100 Å).

TABLE IV. - STEP-LOAD CREEP DATA AT 3500° F (1927° C)

Heat treatment			Stress		Minimum creep rate, sec⁻¹	Post-test carbon content, at.% (a)	Estimated stress for 10^{-6} sec⁻¹ creep rate (b)		Slope, n	Median particle diameter, Å (or ×10⁻¹⁰ m)
Time, hr	Temperature °F	°C	ksi	MN/m²			ksi	MN/m²		
A201 (W-4.4 Re-0.44 Hf-0.009C)										
1	3800	2093	5.70	39.3	0.91×10^{-6}	-----	----	-----	----	---
			6.33	43.6	2.0	-----	----	-----	----	---
			6.96	48.0	3.6	-----	----	-----	----	---
			7.60	52.4	6.4	-----	----	-----	----	---
			8.44	58.2	16	-----	----	-----	----	---
			9.28	64.0	33	(0.005)	5.8	40	7.3	---
A202 (W-3.6 Re-0.76 Hf-0.052C)										
1	3800	2093	6.59	45.4	0.48×10^{-6}	-----	----	-----	----	---
			7.39	51.0	.82	-----	----	-----	----	---
			8.60	59.3	1.7	(0.012)	7.7	53	4.7	---
A212 (W-3.6 Re-0.27 Hf-0.12C)										
1	3800	2093	6.49	44.7	0.086×10^{-6}	-----	----	-----	----	---
			7.60	52.4	.19	-----	----	-----	----	---
			8.95	61.7	.83	-----	----	-----	----	---
			10.3	71.0	2.4	-----	----	-----	----	---
			11.4	78.6	5.2	-----	----	-----	----	---
			12.8	88.3	12	0.078	9.2	63	7.5	---
1	4400	2426	6.71	46.3	0.81×10^{-6}	-----	----	-----	----	---
			7.36	50.7	1.6	-----	----	-----	----	---
			8.19	56.5	3.1	-----	----	-----	----	---
			9.00	62.1	6.1	-----	----	-----	----	---
			9.99	68.9	12	(0.060)	6.9	48	6.7	---
0.25	c4600	c2538	9.28	64.0	0.30×10^{-6}	-----	----	-----	----	---
			10.2	70.3	1.3	-----	----	-----	----	---
			11.0	75.8	4.1	-----	----	-----	----	---
			12.4	85.5	17	0.064	10.1	70	14.1	369
A226 (W-3.9 Re-0.44 Hf-0.12C)										
1	3800	2093	7.55	52.1	0.33×10^{-6}	-----	----	-----	----	---
			8.21	56.6	.66	-----	----	-----	----	---
			9.10	62.7	1.4	-----	----	-----	----	---
			10.0	68.9	2.3	-----	----	-----	----	---
			11.1	76.7	5.1	0.070	8.8	61	7.0	---

[a] Values in parentheses are estimated from measurements on similar specimens.

[b] Stress estimated by graphical interpolation or extrapolation.

[c] Indicated treatment plus 1 hour at 2500° F (1371° C)

TABLE IV. - Continued. STEP-LOAD CREEP DATA AT 3500° F (1927° C)

| Heat treatment | | | Stress | | Minimum creep rate, sec^{-1} | Post-test carbon content, at.% (a) | Estimated stress for 10^{-6} sec^{-1} creep rate (b) | | Slope, n | Median particle diameter, Å (or ×10^{-10} m) |
Time, hr	Temperature °F	°C	ksi	MN/m^2			ksi	MN/m^2		
A210 (W-3.9 Re-0.25 Hf-0.13C)										
1	3800	2093	5.59	38.5	0.16×10^{-6}	-----	----	-----	----	---
			6.49	44.7	.45	-----	----	-----	----	---
			7.60	52.4	1.1	-----	----	-----	----	---
			8.28	57.1	2.2	-----	----	-----	----	---
			9.84	67.8	6.6	(0.069)	7.4	51	6.1	---
A216 (W-3.1 Re-0.30 Hf-0.20C)										
1	3800	2093	9.72	67.0	1.6×10^{-6}	-----	----	-----	----	---
			10.3	71.0	2.3	-----	----	-----	----	---
			10.9	75.2	4.4	-----	----	-----	----	---
			11.9	82.0	9.0	-----	----	-----	----	---
			13.2	91.0	22	(0.15)	9.2	63	8.7	---
0.25	4600	2538	12.5	86.2	0.5×10^{-6}	-----	----	-----	----	---
			14.1	97.2	8.8	-----	----	-----	----	---
			15.3	105	32	(0.090)	12.9	89	20.7	358
0.25	^{c}4600	^{c}2538	12.0	82.7	14×10^{-6}	-----	----	-----	----	---
			12.4	85.5	20	-----	----	-----	----	---
			13.1	90.3	44	0.021	9.9	68	13.2	---
A234 (W-4.0 Re-0.24 Hf-0.30C)										
1	4000	2204	8.03	55.4	0.13×10^{-6}	-----	----	-----	----	---
			8.76	60.4	.70	-----	----	-----	----	---
			9.49	65.4	2.7	-----	----	-----	----	---
			10.2	70.3	8.0	0.035	9.0	62	17.2	---
A235 (W-3.9 Re-0.35 Hf-0.25C)										
1	4000	2204	14.1	97.2	3.5×10^{-6}	0.13	11.8	83	----	---
A219 (W-3.7 Re-0.33 Hf-0.67C)										
1	3800	2093	11.4	78.6	1.2×10^{-6}	-----	----	-----	----	---
			12.9	88.9	2.9	-----	----	-----	----	---
			14.5	100	5.1	-----	----	-----	----	---
			16.4	113	13	-----	----	-----	----	---
			18.3	126	40	(0.25)	11.2	77	7.2	---

^{a}Values in parentheses are estimated from measurements on similar specimens.

^{b}Stress estimated by graphical interpolation or extrapolation.

^{c}Indicated treatment plus 1 hour at 2500° F (1371° C).

TABLE IV. - Concluded. STEP-LOAD CREEP DATA AT 3500° F (1927° C)

Heat treatment			Stress		Minimum creep rate, sec⁻¹	Post-test carbon content, at.% (a)	Estimated stress for 10^{-6} sec⁻¹ creep rate (b)		Slope, n	Median particle diameter, Å (or ×10^{-10} m)
Time, hr	Temperature °F	°C	ksi	MN/m²			ksi	MN/m²		
A246 (W-4.0 Re-0.40 Hf-0.48C)										
(d)	(d)	(d)	18.0	124	0.026×10^{-6}	-----	----	-----	----	---
			21.3	147	.065	-----	----	-----	----	---
			24.5	169	.22	-----	----	-----	----	---
			27.0	186	.57	-----	----	-----	----	---
			30.0	207	1.3	-----	----	-----	----	---
			33.0	228	4.2	0.35	29.0	200	----	387
1	4600	2537	10.0	68.9	0.89×10^{-6}	-----	----	-----	----	---
			12.0	82.7	18.00	-----	----	-----	----	---
			14.5	100	83.00	0.038	9.9	68.3	----	---
0.25	4700	2593	8.0	55.2	0.015×10^{-6}	-----	----	-----	----	---
			10.0	68.9	.017	-----	----	-----	----	---
			12.0	82.7	.042	-----	----	-----	----	---
			14.0	96.5	.092	-----	----	-----	----	---
			16.0	110	22.000	0.15	15.0	103	----	---
A217 (W-3.8 Re-0.69 Hf-0.98C)										
1	3800	2093	9.74	67.2	0.66×10^{-6}	-----	----	-----	----	---
			11.4	78.6	2.9	-----	----	-----	----	---
			13.6	93.8	8.9	-----	----	-----	----	---
			15.8	109	29	-----	----	-----	----	---
			18.3	126	150	(0.94)	10.2	70	8.3	---
1	3800	2093	13.7	94.5	0.70×10^{-6}	-----	----	-----	----	---
			15.0	103	1.1	0.73	14.7	101	5.0	---
0.25	4600	2538	13.9	95.8	0.82×10^{-6}	-----	----	-----	----	---
			15.3	105	2.7	-----	----	-----	----	---
			16.7	115	11	(0.94)	14.2	98	14.1	825
0.25	[c]4600	[c]2538	16.5	114	5.6×10^{-6}	-----	----	-----	----	---
			18.4	127	23	-----	----	-----	----	---
			18.8	130	32	(0.94)	14.5	100	13.4	---

[a]Values in parentheses are estimated from measurements on similar specimens.

[b]Stress estimated by graphical interpolation or extrapolation.

[c]Indicated treatment plus 1 hour at 2500° F (1371° C)

[d]As-swaged.

<div align="center">TABLE V. - DUCTILE-BRITTLE TRANSITION TEMPERATURES</div>

<div align="center">FOR W-Re-Hf-C ALLOYS</div>

Alloy condition	Heat treatment			Ductile-brittle transition temperature for 4T bend[a]		Post-test carbon content, at.% (b)
	Time, hr	Temperature °F	°C	°F	°C	
A201 (W-4.4 Re-0.44 Hf-0.009C)						
As-rolled	----	-----	-----	200	93	(0.009)
Heat treated	1	3800	2093	425	218	.017
	.25	[c]4600	[c]2538	850	454	.005
A224 (W-3.8 Re-0.22 Hf-0.049C)						
As-rolled	----	-----	-----	150	66	(0.049)
Heat treated	1	3800	2093	350	177	.998
	.25	[c]4600	[c]2538	550	288	.086
A202 (W-3.6 Re-0.76 Hf-0.052C)						
As-rolled	----	-----	-----	275	135	(0.052)
Heat treated	1	3800	2093	600	316	.028
	.25	[c]4600	[c]2538	750	399	.021
A226 (W-3.9 Re-0.44 Hf-0.12C)						
As-rolled	----	-----	-----	175	79	(0.12)
Heat treated	1	3800	2093	375	191	.10
	.25	[c]4600	[c]2538	500	260	.048
A210 (W-3.9 Re-0.25 Hf-0.13C)						
As-rolled	----	-----	-----	175	79	(0.13)
Heat treated	1	3800	2093	400	204	.15
	.25	[c]4600	[c]2538	550	288	.012
A211 (W-3.6 Re-0.27 Hf-0.14C)						
As-rolled	----	-----	-----	-25	-32	(0.14)
Heat treated	1	[d]3000	[d]1649	575	302	
	1	[d]3600	[d]1982	375	191	
	1	4000	2204	650	343	
	.25	4500	2482	400	204	
	.25	[c]4600	[c]2538	525	274	
	.25	4700	2593	350	177	
	.25	4800	2649	375	191	
	.25	4900	2704	<325	<163	
	.25	5000	2760	450	232	

[a]Bend radius equals four times specimen thickness.

[b]Values in parentheses are estimated from measurements on similar specimens.

[c]Indicated heat treatment plus 1 hour at 2500° F (1371° C).

[d]Microstructure was partially recrystallized after heat treating.

TABLE V. – Concluded. DUCTILE-BRITTLE TRANSITION TEMPERATURES

FOR W-Re-Hf-C ALLOYS

Alloy condition	Heat treatment			Ductile-brittle transition temperature for 4T bend[a]		Post-test carbon content, at.% (b)
	Time, hr	Temperature °F	°C	°F	°C	
A216 (W-3.1 Re-0.30 Hf-0.20C)						
As-rolled	----	-----	-----	200	93	(0.20)
Heat treated	1	3800	2093	300	149	.20
	1	4400	2427	>800	>427	(.20)
	.25	4600	2538	950	510	(.16)
	.25	[c]4600	[c]2538	>850	>454	.16
A234 (W-4.0 Re-0.24 Hf-0.30C)						
As-rolled	----	-----	-----	350	177	(0.30)
Heat treated	1	[d]3800	[d]2093	300	149	.30
	.25	[c]4600	[c]2538	625	329	.26
A235 (W-3.9 Re-0.35 Hf-0.25C)						
As-rolled	----	-----	-----	250	121	(0.25)
Heat treated	1	[d]3800	[d]2093	275	135	.25
	.25	[c]4600	[c]2538	700	371	.19
A219 (W-3.7 Re-0.33 Hf-0.67C)						
As-rolled	----	-----	-----	>400	>204	(0.67)
Heat treated	1	4400	2427	525	274	(.67)
	.25	4600	2538	600	316	(.52)
	.25	[c]4600	[c]2538	500	260	.52
A236 (W-3.9 Re-0.44 Hf-0.47C)						
As-rolled	----	-----	-----	100	38	(0.47)
Heat treated	1	[d]3800	[d]2093	250	121	.47
	.25	[c]4600	[c]2538	400	204	.38
A217 (W-3.8 Re-0.69 Hf-0.98C)						
As-rolled	----	-----	-----	400	204	(0.98)
Heat treated	1	3800	2093	250	121	1.23

[a]Bend radius equals four times specimen thickness.

[b]Values in parentheses are estimated from measurements on similar specimens.

[c]Indicated heat treatment plus 1 hour at 2500° F (1371° C).

[d]Microstructure was partially recrystallized after heat treating.

TABLE VI. - RECRYSTALLIZATION OF W-Re-Hf-C ALLOYS

Alloy	Estimated percent recrystallization and hardness (VHN, 10 kg-load) after 1-hour anneal at indicated temperature							1-Hour (100%) recrystallization temperature	
	3200° F (1760° C)	3400° F (1871° C)	3600° F (1982° C)	3800° F (2093° C)	4000° F (2204° C)	4200° F (2316° C)	4400° F (2427° C)	°F	°C
A201	1 (342)	100 (289)	(272)	(325)	(322)	(333)	(333)	3400	1871
A224	------	60 (405)	100 (348)	(334)	(326)	-------	--------	3600	1982
A202	3 (345)	100 (294)	(294)	(348)	(351)	(351)	(363)	3400	1871
A212	------	--------	--------	100 (376)	(373)	(383)	(376)	<3800	2093
A226	------	95 (417)	100 (353)	(362)	(335)	-------	--------	3600	1982
A210	0 (380)	7 (354)	100 (370)	(360)	(297)	(294)	--------	3600	1982
[a]A211	0 (373)	50 (319)	100 (322)	(309)	(380)	(322)	(327)	3600	1982
A216	0 (397)	10 (339)	10 (336)	100 (363)	(366)	(357)	(387)	3800	2093
A234	------	0 (478)	2 (450)	50 (380)	10 (363)	10 (342)	90 (317)	4600	2538
A235	------	0 (473)	0 (425)	0 (429)	10 (373)	20 (292)	85 (314)	4600	2538
A219	------	--------	--------	90 (433)	100 (397)	(376)	(360)	4000	2204
A246	------	0 (483)	(464)	12 (425)	12 (421)	(370)	90 (373)	4600	2538
A245	------	0 (473)	(468)	(433)	5 (429)	30 (373)	60 (348)	4600	2538
A236	------	0 (464)	1 (455)	60 (425)	35 (336)	20 (299)	100 (279)	4400	2427
A217	------	5 (366)	2 (383)	100 (401)	(348)	(306)	(317)	3800	2093

[a]0.04-inch (1.0 mm) sheet; other specimens were 0.25-inch (6.4 mm) rod.

TABLE VII. - COARSENING RATES FOR HAFNIUM CARBIDE

PARTICLES IN W-Re-Hf-C AND W-Hf-C ALLOYS

Alloy	Initial composition, at.%			Heat treatment time, hr	Median particle radius, Å		Coarsening rate, k, cm³/sec
	Re	Hf	C		Initial, r_o (a)	Final, r	
Heated at 3500° F (1927° C)							
A202	3.6	0.76	0.052	14.9	0	349	7.9×10^{-22}
A212	3.6	.27	.12	28.2		185	6.2×10^{-23}
A226	3.9	.44	.12	12.8		363	1.0×10^{-21}
A210	3.9	.25	.13	13.9		230	2.4×10^{-22}
A216	3.1	.30	.24	2.5		179	6.4×10^{-22}
A234	4.0	.24	.30	5.0		155	2.1×10^{-22}
A236	3.9	.44	.40	1.8		105	1.8×10^{-22}
A235	3.9	.35	.47	14.9		279	4.0×10^{-22}
A219	3.7	.33	.67	20.9		219	1.4×10^{-22}
A156	0	.26	.68	127.5	93	339	8.3×10^{-23}
A191	0	.91	.94	91.0	212	373	1.3×10^{-22}
A217	3.8	.69	.98	21.1	0	413	9.3×10^{-22}
Heated at 3600° F (1982° C)							
A191	0	0.91	0.94	1.0	286	322	2.7×10^{-21}
Heated at 4000° F (2204° C)							
A191	0	0.91	0.94	1.0	286	448	1.8×10^{-20}
				1.0	219	765	1.2×10^{-19}
Heated at 4400° F (2427° C)							
A193	0	0.48	0.50	1	298	630	6.2×10^{-20}
				1	298	805	1.4×10^{-19}
A156	0	.26	.68	1	93	555	4.7×10^{-20}
				1	93	555	4.7×10^{-20}
				1	93	610	6.3×10^{-20}
				1	93	745	1.2×10^{-19}
A191	0	.91	.94	7.5	360	2875	8.8×10^{-19}
				8.5	360	2010	2.6×10^{-19}
Heated at 4600° F (2538° C)							
A193	0	0.48	0.50	0.25	298	498	1.1×10^{-19}
				.25	298	570	1.8×10^{-19}
				.25	298	835	6.2×10^{-19}
Heated at 4800° F (2649° C)							
A193	0	0.48	0.50	0.25	298	2000	8.9×10^{-18}
Heated at 5000° F (2760° C)							
A191	0	0.91	0.94	0.33	286	1740	4.4×10^{-18}

[a]Initial particle radii were estimated as zero for solution annealed specimens.

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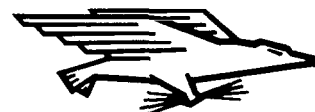
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