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EXPLORATORY STUDY OF MECHANICAL PROPERTIES AND HEAT TREATMENT OF MOLYBDENUM-HAFNIUM-CARBON ALLOYS

by Peter L. Raffo

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ABSTRACT

A preliminary study was made of the structure and properties of Mo-Hf-C alloys. The compositions of the alloys ranged from 0. 09 to 1. 83 atomic percent Hf and 0. 29 to 1. 07 atomic percent C. The mechanical properties of these alloys were measured in the as-swaged, recrystallized, solution-treated, and solution-treated and aged conditions at room temperature and 1500° to 3000° F (1088 to 1922 K). The mechanical properties were compared with data on other molybdenum alloys from the literature, and two commercial molybdenum alloys that were evaluated during this program. The Mo-Hf-C alloys show a strength advantage over the other alloys in creep-rupture tests at 2400° F (1588 K) and short-time tensile tests at 3000° F (1922 K).

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SUMMARY

An exploratory study was made of the mechanical properties of nine molybdenum-hafnium-carbon alloys to determine whether potentially useful materials existed in this alloy system. The alloys contained 0.09 to 1.83 atomic percent hafnium and 0.29 to 1.07 atomic percent carbon. The alloys were evaluated in the as-swaged, recrystallized, solution-treated, and solution-treated and aged conditions. Tensile strengths greater than 70 ksi (483 MN/m^2) were found for as-swaged alloys at 2400° F (1588 K). However, the molybdenum-hafnium-carbon alloys showed their biggest strength advantage over previous molybdenum alloys in stress-rupture tests at 2400° F (1588 K) and short-time tensile tests at 3000° F (1922 K). The molybdenum-hafnium-carbon alloys are heat treatable. Tensile strengths of 74.9 ksi (516 MN/m^2) at 2400° F (1588 K) were observed in the solution-treated condition. A prestrain of 4 percent at 300° F (422 K) increased this to 79.5 ksi (598 MN/m^2) which was the highest strength observed in this investigation at 2400° F. The recrystallization temperature of the molybdenum-hafnium-carbon alloys varied from 2670° to 3300° F (1740 to 2088 K) increasing with increasing hafnium and carbon content. It was concluded that molybdenum-hafnium-carbon alloys offer considerable promise as useful materials.

INTRODUCTION

Significant advances have been made in the development of molybdenum (Mo) base alloys since the early work of Semchyshen and others (refs. 1 to 4). These and later studies resulted in the identification of a series of useful carbide strengthened molybdenum base alloys containing various amounts of titanium (Ti), zirconium (Zr), and columbium (Cb) with carbon (C) (refs. 4 to 7). Three commercial molybdenum alloys have arisen from these developments. These are a Mo - 0.5-percent-Ti - 0.03-percent-C alloy (Mo - 1/2 Ti), a Mo - 0.5-percent-Ti - 0.08-percent-Zr - 0.03-percent-C (Mo-TZM) alloy, and a Mo - 1.25-percent-Ti - 0.15-percent-Zr - 0.12-percent-C (M0-TZC) alloy (all compositions in weight percent). The strengths of these alloys have proved to be highly dependent on heat treatment (refs. 6 to 9). This is evident in tests both on solution-treated alloys (refs. 6 and 7) and on alloys where the solution treatment was employed as a portion of the processing cycle (refs. 8 and 9).

Each of the previously mentioned alloys contains a group IVA metal (either titanium or zirconium or both) and carbon. The carbides of Ti and Zr have relatively high thermodynamic stabilities (ref. 10), a necessary requisite to their use as strengthened dispersed phases. Of the group IV carbides, hafnium carbide (HfC) has the highest free energy of formation and, thus, might be expected to be the most stable as a dispersed phase at high temperatures. Experimenters at Lewis Research Center have shown that tungsten-hafnium-carbon (W-Hf-C) alloys exhibit outstanding strength at temperatures above 3000° F (1922 K) (refs. 11 and 12). The high-temperature stability of the HfC precipitate in tungsten base alloys suggested that similar molybdenum-base alloys might have attractive strength properties.

In this report, some preliminary results are presented on the strength and ductility of nine experimental Mo-Hf-C alloys. The object was to determine the potential advantage to using hafnium as an alloying element in place of titanium or zirconium. Hafnium contents of the alloys ranged from 0.09 to 1.83 atomic percent, and the carbon contents from 0.24 to 1.11 atomic percent. Tensile tests at room temperature, 1800°, 2400°, and 3000° F (298, 1255, 1588, and 1922 K) were performed on the alloys in various structural conditions. In addition, stress rupture tests at 2400° and 3000° F (1588 and 1922 K) were performed on materials in the as-swaged condition.

MATERIALS AND EXPERIMENTAL PROCEDURES

Table I lists the compositions, grain size, hardness, and other data on the nine alloys in this program. (Hereinafter all compositions are in atomic percent.) These analyses were obtained on the finished swaged rod. The carbon to hafnium ratios ranged from 0.58 to 2.67. A listing of a composition parameter X_c is also given in table I. This parameter is defined as either the hafnium or carbon content, whichever is smaller. It is equivalent to the maximum amount of stoichiometric hafnium carbide that may be formed in a given alloy. Even though the major carbide phase in some of the dilute alloys was a carbide of molybdenum rather than hafnium, the parameter X_c still represents the potential for forming HfC, which is believed to be the strengthening phase. The use of X_c was particularly convenient in graphically presenting the data and was used extensively.

TABLE I. - COMPOSITION, CHEMICAL ANALYSES AND OTHER CHARACTERISTICS OF Mo-Hf-C ALLOYS

Alloy	Analyzed composition, at. %	Carbon to hafnium ratio	Composition parameter,[a] X_c	As-cast grain size, μm	Vicker's hardness number[b]			One-hour recrystallization temperature[c]	
					As-cast	As-extruded	As-swaged	^{o}F	K
MHC-20	Mo-0.09Hf-0.24C	2.67	0.09	375	179	195	289	2670	1735
MHC-21	Mo-0.18Hf-0.42C	2.33	.18	191	183	187	322	2840	1830
MHC-22	Mo-0.37Hf-0.29C	.78	.29	380	194	233	322	3000	1922
MHC-23	Mo-0.39Hf-0.65C	1.67	.39	326	210	210	342	2770	1792
MHC-26	Mo-0.37Hf-0.89C	2.41	.37	163	209	268	330	2950	1894
MHC-24	Mo-0.58Hf-0.77C	1.33	.58	152	219	253	319	3170	2015
MHC-25	Mo-0.96Hf-0.82C	.85	.82	146	253	235	325	3150	2005
MHC-27	Mo-0.98Hf-1.11C	1.13	.98	139	247	238	363	3300	2090
MHC-28	Mo-1.83Hf-1.07C	.58	1.07	104	276	274	351	3120	1990

[a] The composition parameter is the hafnium or carbon content, whichever is smaller, and is equivalent to the maximum mol % of stoichiometric hafnium carbide which can be formed in a given alloy.

[b] 10 kg loads.

[c] The recrystallization temperature is defined as the temperature for two-thirds of the drop in hardness from the as-swaged to the fully recrystallized values.

Consolidation and Fabrication

Elemental molybdenum, hafnium, and carbon powders were blended, hydrostatically pressed into 1-inch (2.54-cm) diameter electrodes and vacuum sintered at 2800° F (1810 K). The alloys were then melted in a consumable-arc melting furnace (see ref. 11 for a description) into 2-inch (5.08-cm) diameter ingots in vacuum.

Three of the nine ingots were ground smooth and extruded bare, and the other six ingots were zirconia sprayed and inserted into 3-inch (7.62-cm) diameter molybdenum cans. After extrusion, the extruded alloy then separated easily from the canning material at the zirconia-molybdenum interface. The extrusion temperature was 3500° F (2200 K), and the reduction ratio was 8 to 1 for all the alloys.

The alloys were swaged from 0.75- to 0.40-inch (1.91- to 1.02-cm) diameter at 2500° F (1644 K) and finally to 0.25-inch (0.64-cm) diameter at 2100° F (1422 K). This gave a total reduction of 89 percent from the extrusion. A chemical analysis for hafnium and carbon was then performed on the swaged rod.

Annealing

Annealing at temperatures below 3000° F (1922 K) was performed by induction heating in hydrogen using a tungsten susceptor. Above 3000° F (1922 K) a tungsten-element resistance furnace was employed at a pressure of less than 5×10^{-5} torr. At 3500° F (2200 K), and above, annealing treatments were conducted in an atmosphere of argon with 0.3-percent methane in order to prevent decarburization (ref. 8). For solution treatments on tensile specimens at 4000° F (2477 K), another induction furnace with a tungsten susceptor was employed with an atmosphere of argon-methane. The furnace was equipped to quench the specimens in helium after the heat treatment.

Mechanical Testing

Tensile specimens were centerless ground from the swaged rod according to the configuration shown in figure 1. Specimens for room-temperature tests were electropolished prior to the testing, but specimens were left in the as-ground condition for tests above 1500° F (1088 K). The details of the tensile testing procedure are given in references 11 and 13. Tensile tests were performed at a pressure of less than 5×10^{-5} torr in the temperature range 1500° to 3000° F (1088 to 1922 K) and at a strain rate of 0.05 per minute. The equipment used for creep-rupture testing is also described in reference 11. Creep-rupture tests were performed at 2400° and 3000° F (1588 and 1922 K) at a pressure of less than 5×10^{-5} torr.

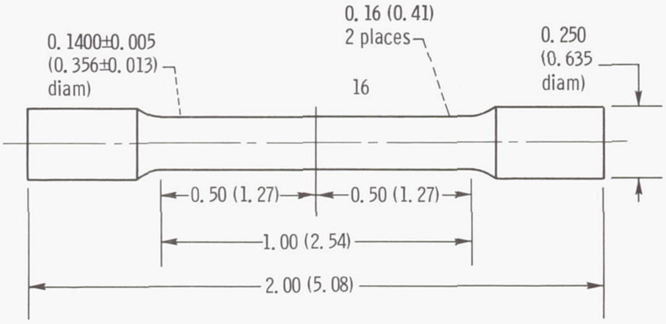


Figure 1. - Button head tensile specimen (All dimensions are in inches (cm)).

Phase Separation and Metallography

The carbide phase in selected alloys was extracted electrolytically in a 7-percent solution of hydrochloric acid in ethyl alcohol (ref. 6). The extracted residue was washed thoroughly with alcohol and identified by X-ray diffraction using copper $K\alpha$ radiation with a nickel filter.

Light metallography was performed on specimens electropolished in a 12.5-percent solution of sulfuric acid in methyl alcohol and etched electrolytically in a 10-percent aqueous solution of ammonium persulfate. Platinum-shadowed carbon surface replicas were also prepared from selected specimens.

Thin foils were prepared for transmission electron microscopy from 0.125-inch (0.318-cm) diameter disks which were spark machined from the reduced section of selected tensile specimen. These disks were mounted on a brass block and ground on emery paper to a thickness of 0.1 to 0.5 millimeter. The disks were then thinned electrolytically in a solution of 12.5-percent sulfuric acid in methanol at 10 to 15 volts in a fixture designed by Schoone and Fishione (ref. 14). The foils were subsequently examined at 100 kilovolts.

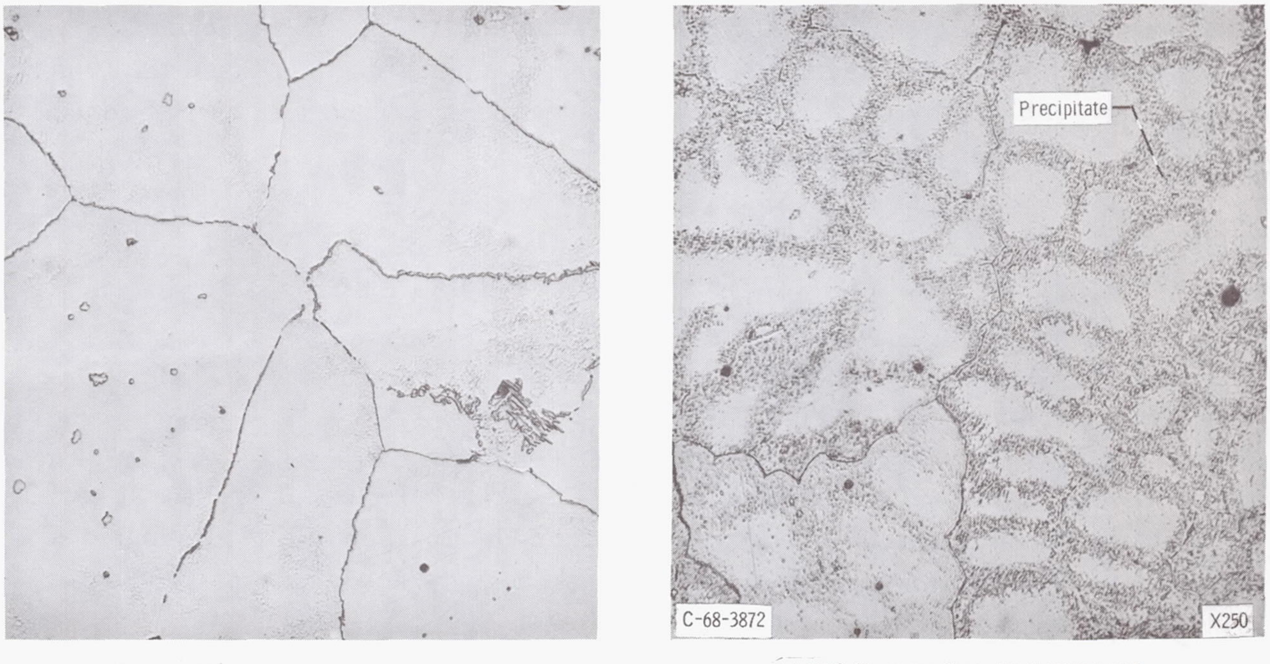
RESULTS AND DISCUSSION

The results and discussion are divided into two sections. First, the microstructure and annealing behavior of the nine alloys are presented. The purpose of this section is to report on the type of microstructures and precipitate distribution that are present in the Mo-Hf-C alloys. This will serve as a background to the mechanical-property data presented in the second section. The purpose of the mechanical-properties section is to present the high-temperature tensile and creep-rupture strength of these alloys and of two commercial alloys for comparison. The section is concluded by a brief correlation of the properties with the microstructure.

Microstructure and Annealing Behavior

As-cast metallography. - Figure 2 shows typical as-cast microstructures for three of the nine alloys studied. The more dilute alloys (MHC-21 and 23) contained an intergranular carbide phase and additional globular precipitates within the grains. At the higher alloying level in MHC-27 (fig. 2(c)), less massive carbide was present at the grain boundaries although the grains were delineated by a region of fine precipitate (see fig. 2(c)). These precipitate particles were very closely spaced and appeared as a heavily etched region rather than discrete particles.

(a) MHC-21; composition. Mo-0.18Hf-0.42C.



(b) MHC-23; composition, Mo-0.39Hf-0.65C.

(c) MHC-27; composition Mo-0.98Hf-1.11C.

Figure 2. - Typical as-cast microstructures.

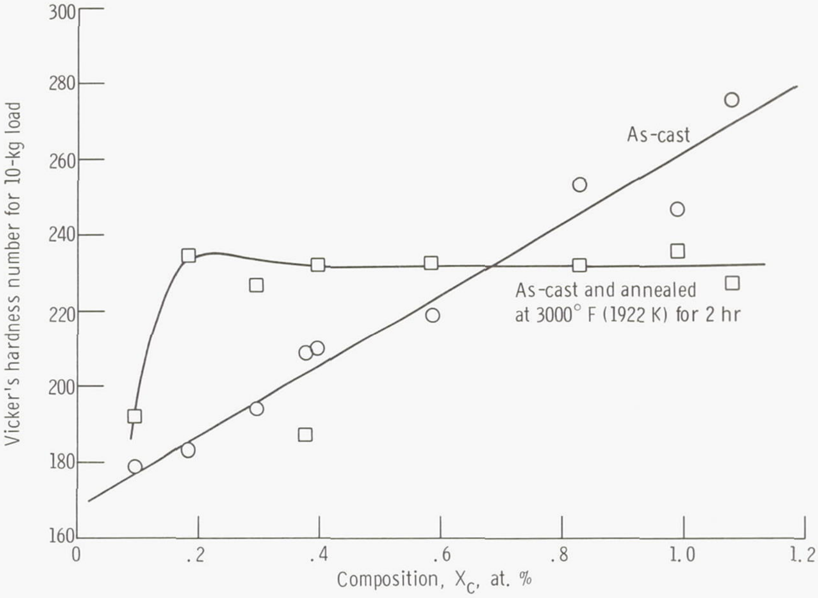
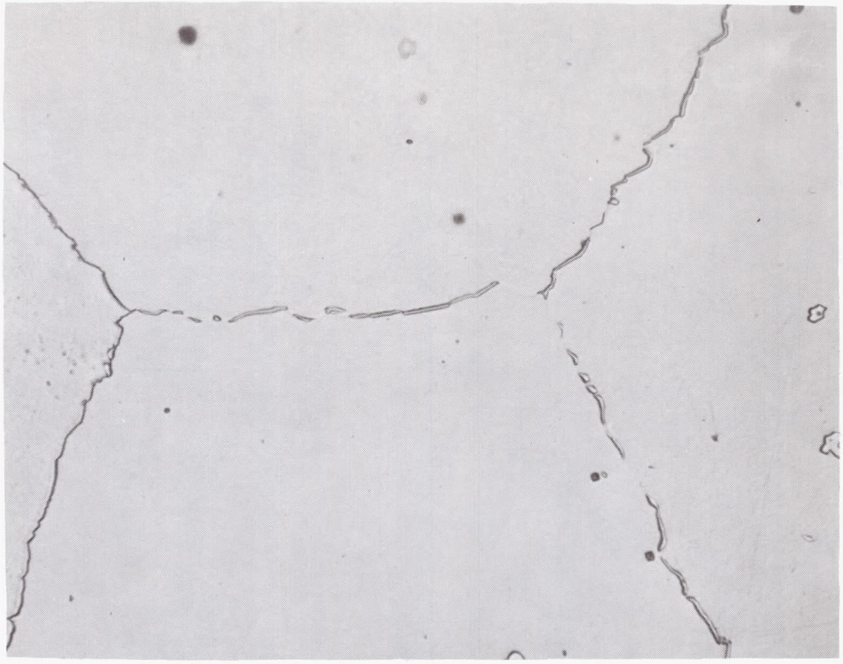


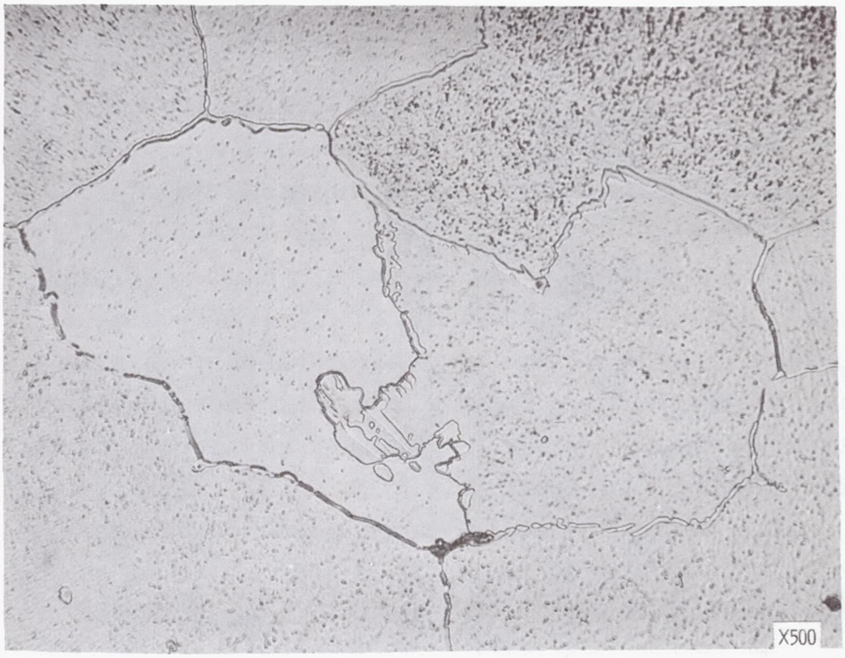
Figure 3. - Effect of annealing on room-temperature hardness of as-cast alloys.

Hardness measurements were made on the as-cast specimens before and after annealing at 3000° F (1922 K) for 2 hours. The results are plotted in figure 3 against X_c. The as-cast hardness data showed a linear increase with X_c. At values of X_c less than about 0.7, the 3000° F (1922 K) anneal increased the hardness of the alloy over that of the as-cast condition. Phases chemically extracted from the as-cast ingots of these dilute alloys were almost exclusively Mo_2C. It is believed that the hardening at low hafnium contents may be a result of a conversion of some of the large Mo_2C particles to a fine HfC precipitate. The precipitation observed on aging the as-cast structure is illustrated for alloy MHC-21 in figure 4. A similar carbide conversion has been found to occur in Mo-Ti-Zr-C alloys (refs. 6 and 7). At composition levels above $X_c > 0.7$, the hardness of the as-cast specimens decreased on annealing. The phase extraction revealed HfC as the only carbide phase present. Thus, this softening may be a result of an overaging reaction of the HfC already present.

Microstructure of wrought and recrystallized alloys. - Figures 5 and 6 show light micrographs of three typical as-extruded and as-swaged alloys. The alloy MHC-21 was fully recrystallized in the extruded condition (fig. 5(a)) while the other two alloys were in a partially recrystallized condition (figs. 5(b) and (c)). Only the most dilute alloys, MHC-20 and MHC-21 had a fully recrystallized microstructure after extrusion. The remainder of the alloys had microstructures typical of those seen in figures 5(b) and (c).



(a) As-cast condition.



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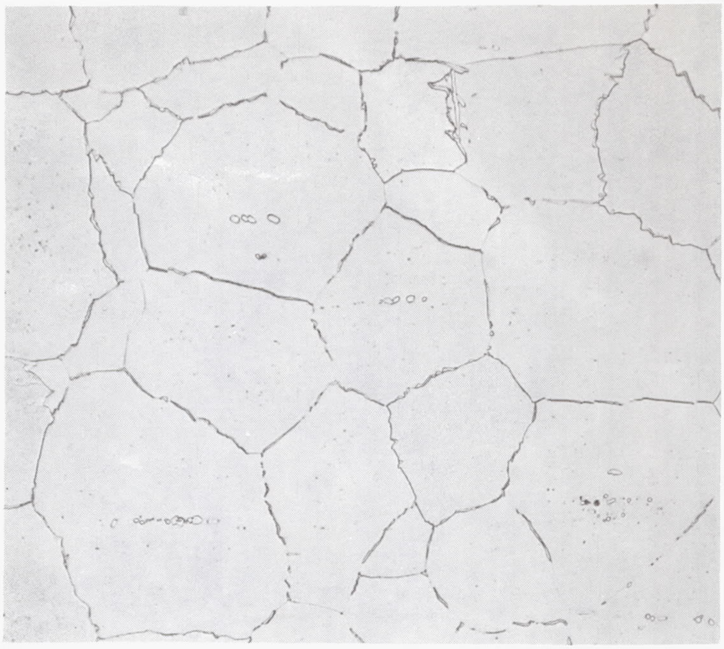
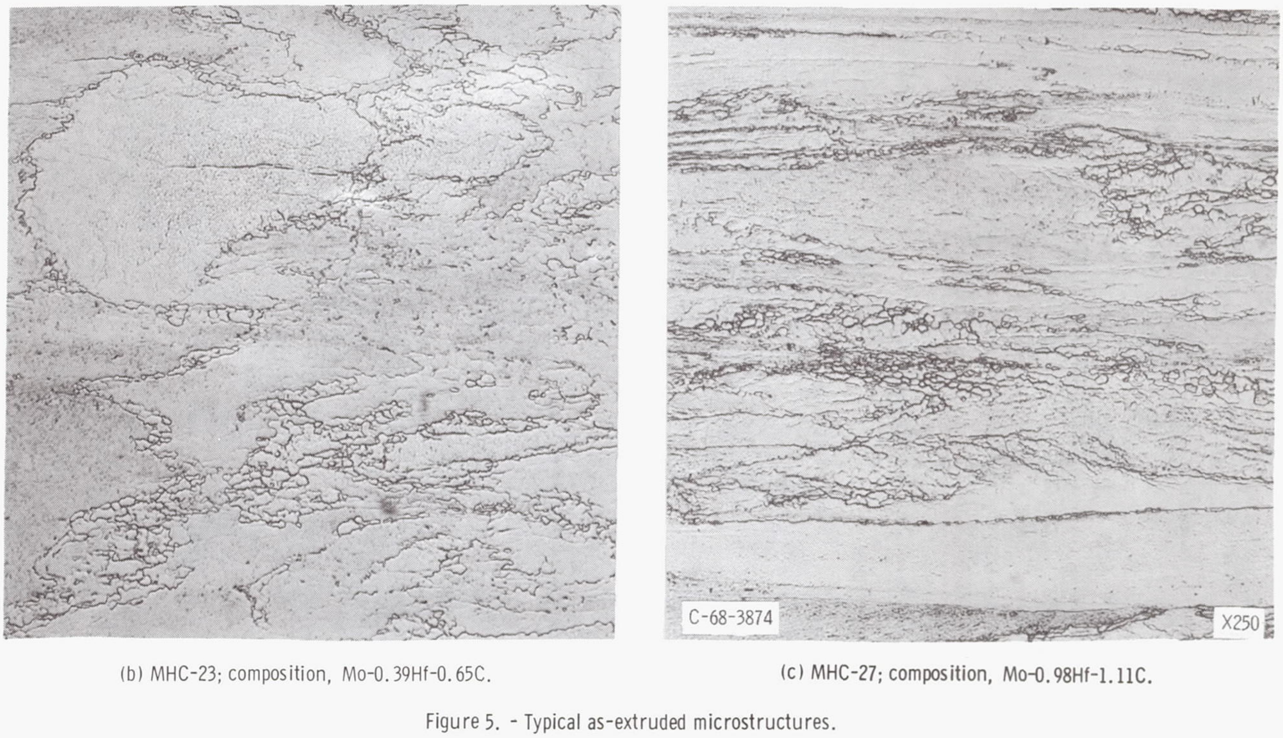
(b) As-cast and annealed at 3000° F (1922 K) for 2 hours.

Figure 4. - Influence of aging on microstructure of MHC-21 (Mo-0.18Hf-0.42C).



(a) MHC-21; composition, Mo-0.18Hf-0.42C.

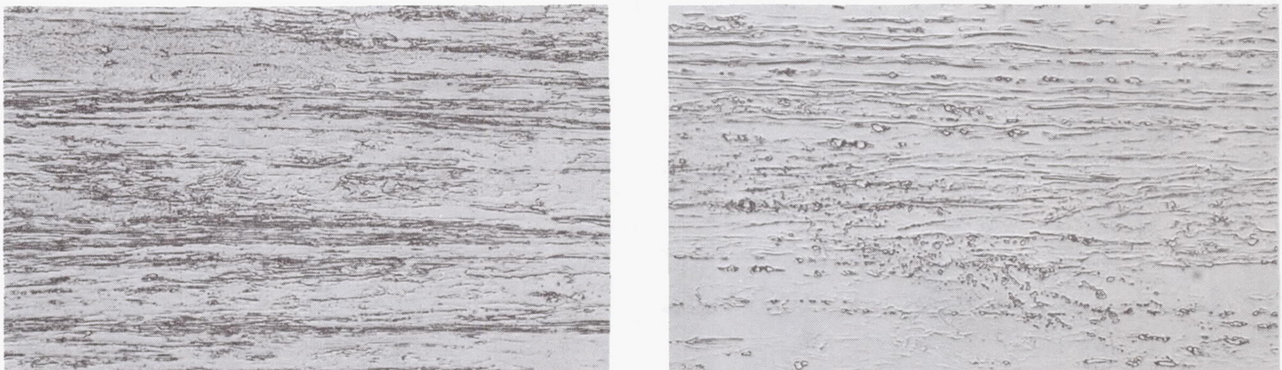


(b) MHC-23; composition, Mo-0.39Hf-0.65C.

(c) MHC-27; composition, Mo-0.98Hf-1.11C.

Figure 5. - Typical as-extruded microstructures.

(a) MHC-21; composition, Mo-0.18Hf-0.42C.



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(b) MHC-23; composition, Mo-0.39Hf-0.65C.

(c) MHC-27; composition, Mo-0.98Hf-1.11C.

Figure 6. - Typical as-swaged microstructure.

The as-swaged microstructures reflected the differences in the as-extruded microstructures. This is shown in figures 6(a) to (c). The alloy MHC-21 had a relatively coarse structure (fig. 6(a)) compared with the other rather fine fibrous structures seen in alloys MHC-23 and MHC-27.

The microstructure of one alloy, MHC-25 (Mo-0.96Hf-0.82C), was studied in more detail using electron microscopy. Studies were made in both the as-swaged and fully recrystallized (3500° F (2200 K) for 1 hr) condition. Figure 7 is a micrograph of a replica of the wrought microstructure. The worked grains exist as long fibers oriented in the swaging direction. The HfC particles were distributed uniformly throughout the cross section and had an average diameter of 0.12 micrometer.

Figure 8 is a replica micrograph of the particle distribution after recrystallization of this alloy for 1 hour at 3500° F (2200 K). The average particle diameter has increased to 0.3 micrometer. The light microstructure of this alloy showed that after recrystallization, the grains were still alined in the working direction. This was characteristic of the majority of the alloys.

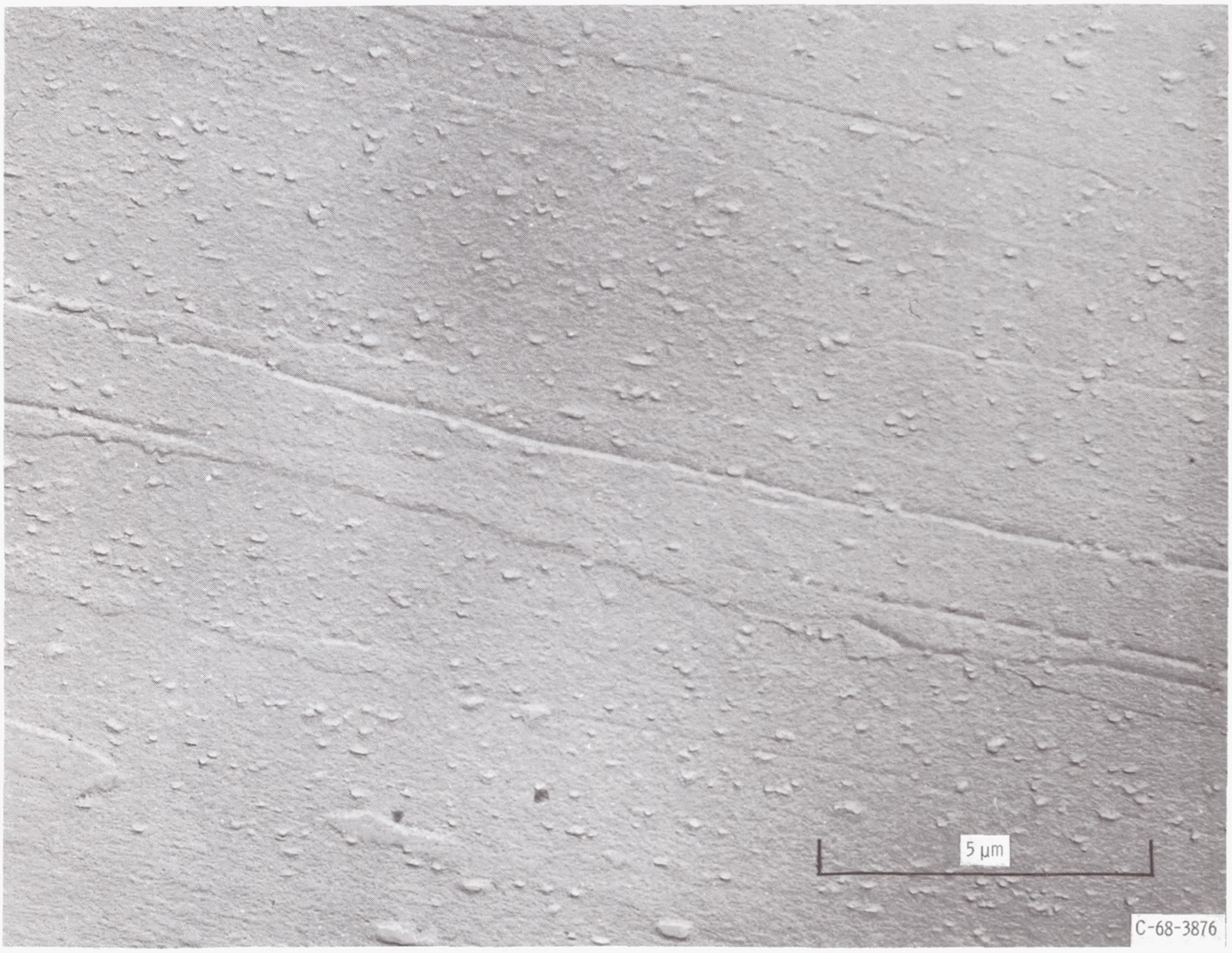


Figure 7. - MHC-25; composition, Mo-0.96Hf-0.82C; as-swaged microstructure; carbon replica.

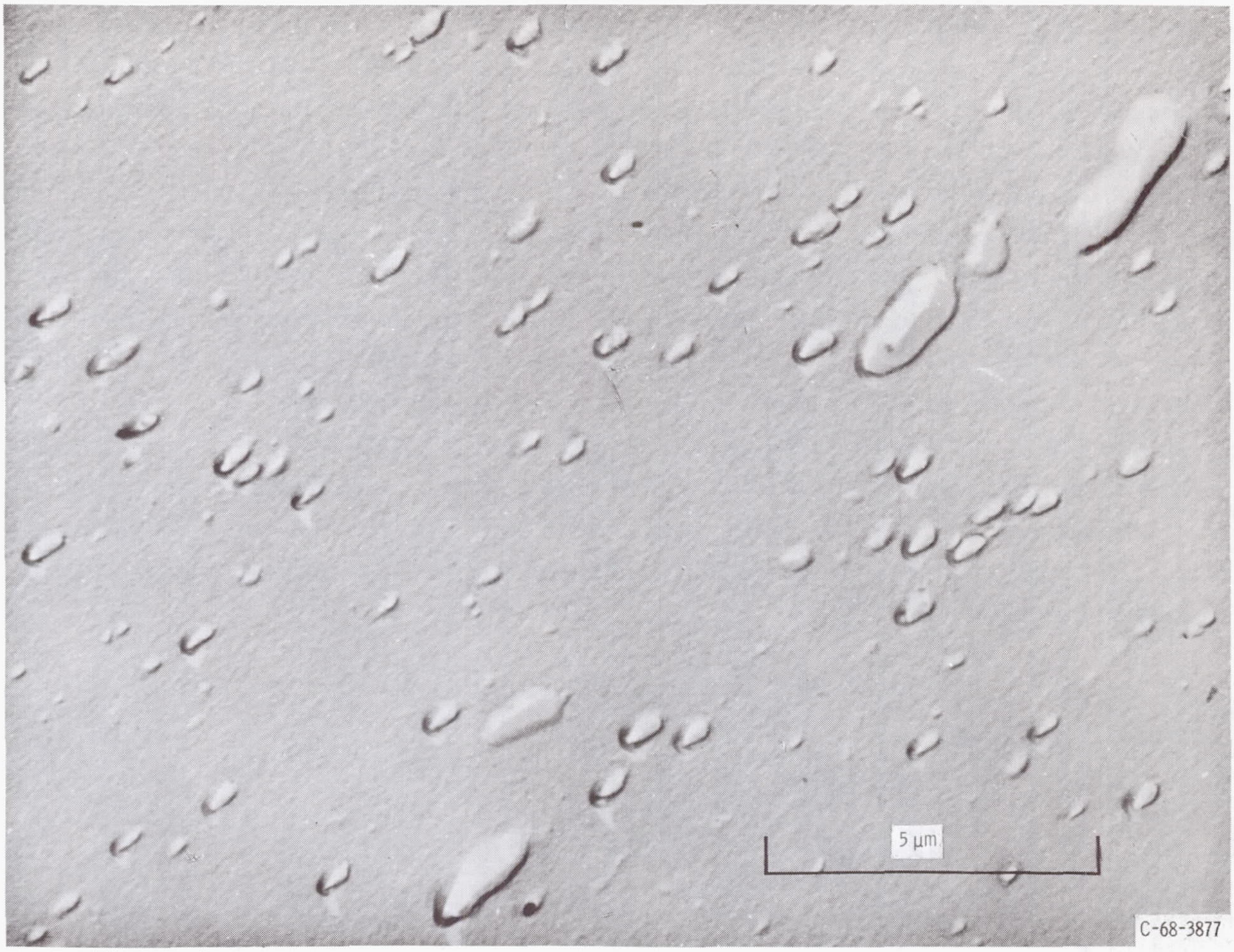


Figure 8. - MHC-25; composition, Mo-0.96Hf-0.82C; recrystallized at 3500° F (2200 K) for 1 hour; carbon replica.

Recrystallization behavior. - Specimens from the swaged rod from each of the alloys were annealed for 1 hour at 2000° to 4000° F (1366 to 2477 K) in 250 F° (394 K) increments. The specimens were examined for evidence of recrystallization and/or carbide solution. Figure 9 shows the variation of hardness with annealing temperature for two of the alloys. The general shapes of the curves are typical of the other alloys also. In each alloy, annealing at 2000° F (1366 K) produced a decrease in hardness from that in the as-swaged condition. Annealing at 2250° F (1505 K), however, increased the hardness above that of the as-swaged value, presumably due to a precipitation reaction. After this maximum in the curve, the hardness decreased continuously for the dilute alloy, MHC-21. The more concentrated alloy, MHC-27, had another maximum in the hardness temperature curve at 3000° F (1922 K). The maximum in hardness at 2250° F (1505 K) was found in all of the alloys, but the secondary maximum at 3000° F (1922 K) was found only in some of the more concentrated alloys. The recrystallization temperature T_r was taken

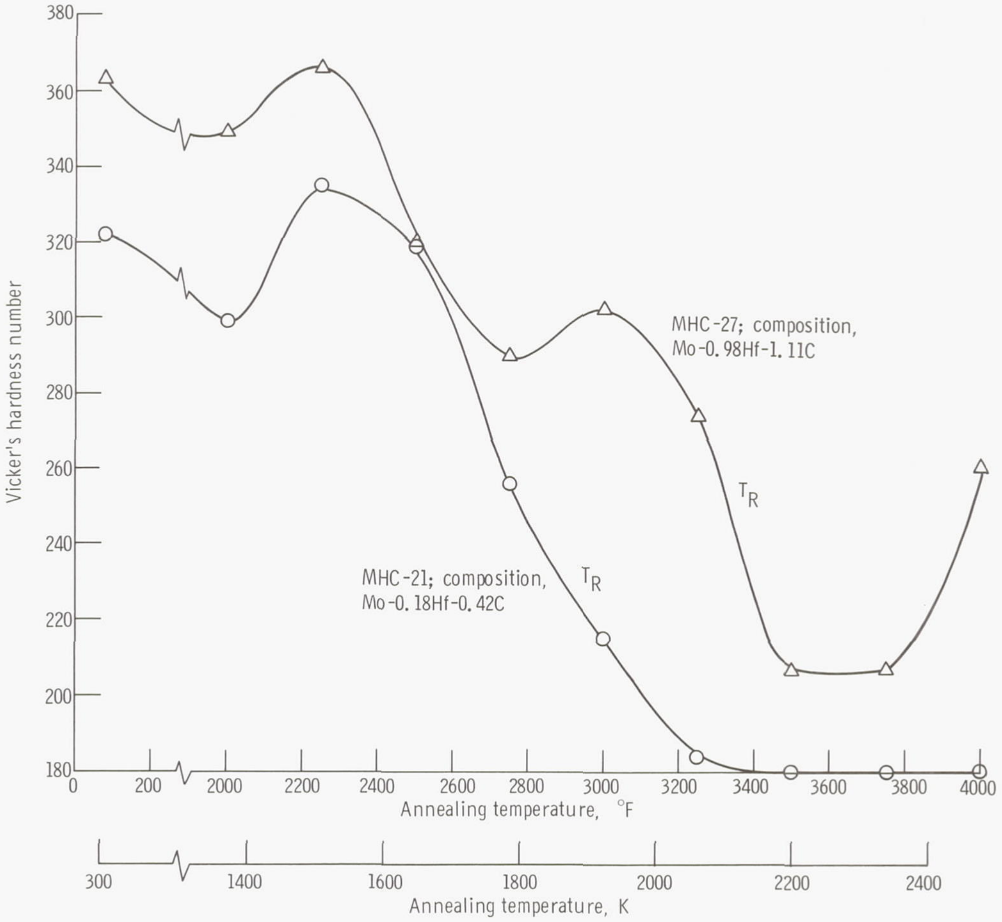


Figure 9. - Typical recrystallization curves for molybdenum-hafnium-carbon alloys.

as the temperature for a two-third decrease in hardness from the as-swaged to the fully recrystallized value. The value of T_r is indicated on figure 9 for the two alloys shown. Values of T_r for the remainder of the alloys are given in table I. The recrystallization temperature ranged from 2670° to 3300° F (1735 to 2090 K) and, in general, increased with increasing X_c.

Figure 9 shows that the hardness of MHC-27 after recrystallization begins to increase again above 3750° F (2338 K). This can be taken as evidence for carbides dissolving into solid solution and subsequently reprecipitating on cooling. Similar behavior is typical of other molybdenum alloys (refs. 6 and 7). There is some confusion in the literature as to how the solubility of carbon in molybdenum is affected by a group IV solute. Chang (ref. 6) has stated that titanium and zirconium increase the solubility of carbon in molybdenum and that this is a prime factor in rendering them heat-treatable. However, Chang used as a basis of comparison the determination of the carbon solubility in unalloyed molybdenum of Few and Manning (ref. 15) which is now known to be a low estimate (refs.

16 and 17). Perkins (refs. 8 and 9) noted that a Mo-Cb-Ti-Zr-0.56 percent C alloy underwent exaggerated grain growth at temperatures of approximately 3750° F (2338 K). He interpreted this as indicating complete carbide solubility. In the present study, exaggerated grain growth was also observed to occur on annealing above the recrystallization temperature. The temperature range where this occurred was dependent only on the carbon content as shown in figure 10. Also included in figure 10 are the more recent determinations of the solubility of carbon in unalloyed molybdenum according to Gebhardt, et al., (ref. 16) and Rudman (ref. 17). The temperature range in which exaggerated grain growth occurred in seen, generally, to closely approximate the carbon solubility line drawn through Gebhardt's and Rudman's data. This strongly suggests that the solubility of carbon in molybdenum is not affected by hafnium in the composition range of 0.09 to 1.83 percent hafnium. The temperature range for exaggerated grain growth mentioned by Perkins can also be shown to bracket the solubility curve in figure 10, which implies that all the Group IVA solutes used in current molybdenum alloys have

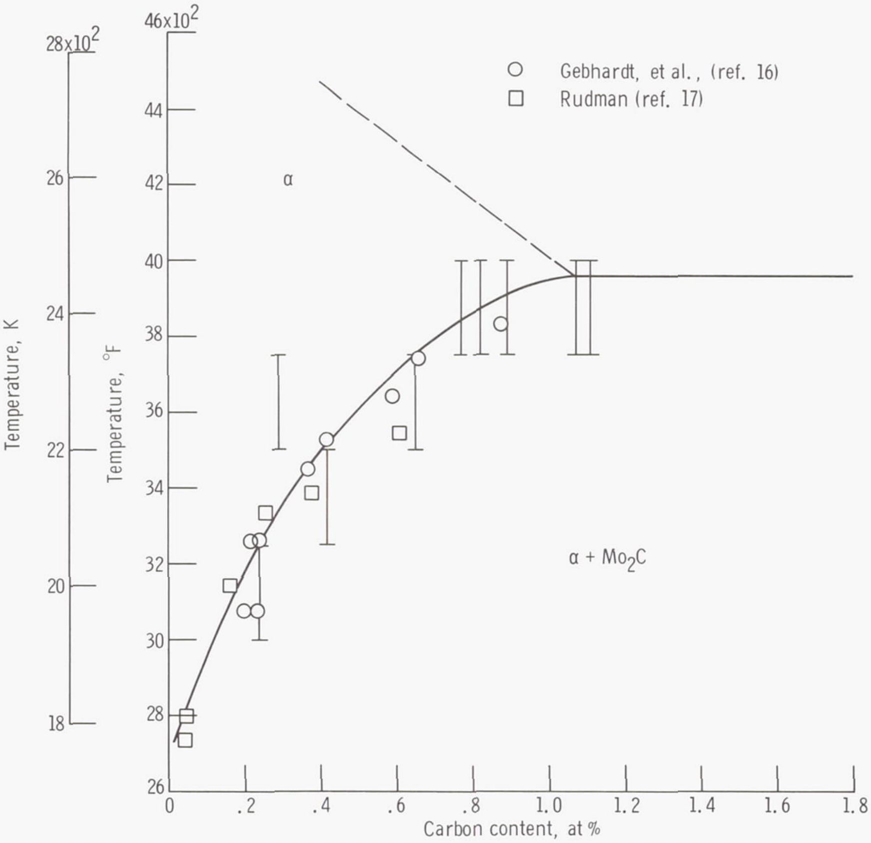


Figure 10. - Molybdenum-carbon phase diagram according to Gebhardt, et al., (ref. 16) and Rudman (ref. 17). Error bars give temperature range where exaggerated grain growth was observed in present work.

little, if any, effect on the carbon solubility. This is consistent with the minor effect of dilute hafnium additions on the solubility of carbon in columbium noted recently by Taylor and Doyle (ref. 18).

The preceding discussion is not meant to be a determination of the equilibrium solubility of carbon in Mo-Hf alloys. However, the observance of exaggerated grain growth in the region of the Mo-C solvus strongly suggests that the Mo-C phase diagram may be employed in order to predict solution-treating temperatures for molybdenum alloys containing small concentrations of a group IV or group V solute.

Age-hardening characteristics. - A limited study of the age-hardening characteristics of alloy MHC-24 (Mo-0.58Hf-0.77C) was performed. The study consisted of solution treating a series of 1/4-inch (0.635-cm) diameter by 1/4-inch (0.635-cm) long cylinders at 4000° F (2477 K) for 30 minutes and helium quenching. The specimens were then aged for 1 hour at 2250° to 3000° F (1505 to 1922 K) in hydrogen and for times up to 4 hours at 2750° F (1783 K). The Vicker's hardness number (VHN) hardness in the solution-treated condition was 228. The 1-hour anneal produced a peak hardness of approximately 285 VHN at approximately 2800° F (1810 K). The isothermal aging characteristics at 2750° F (1783 K) are shown in figure 11. A peak VHN of approximately 295 was developed after 2 hours.

Light metallography was performed on all the samples. Figure 12(a) shows the microstructure of the as-solution-treated material. It is apparent that a full retention

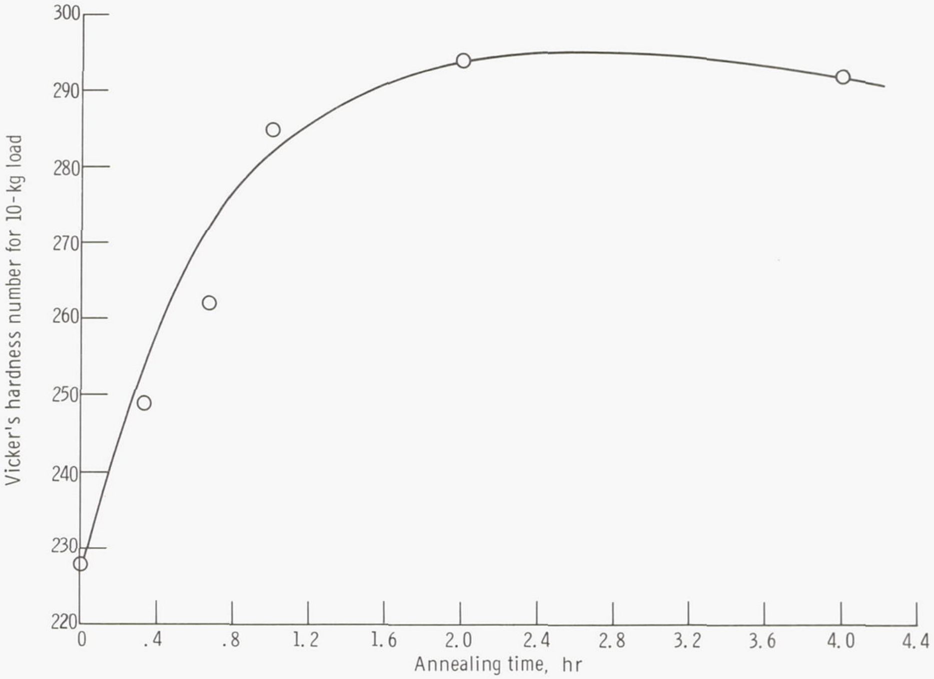
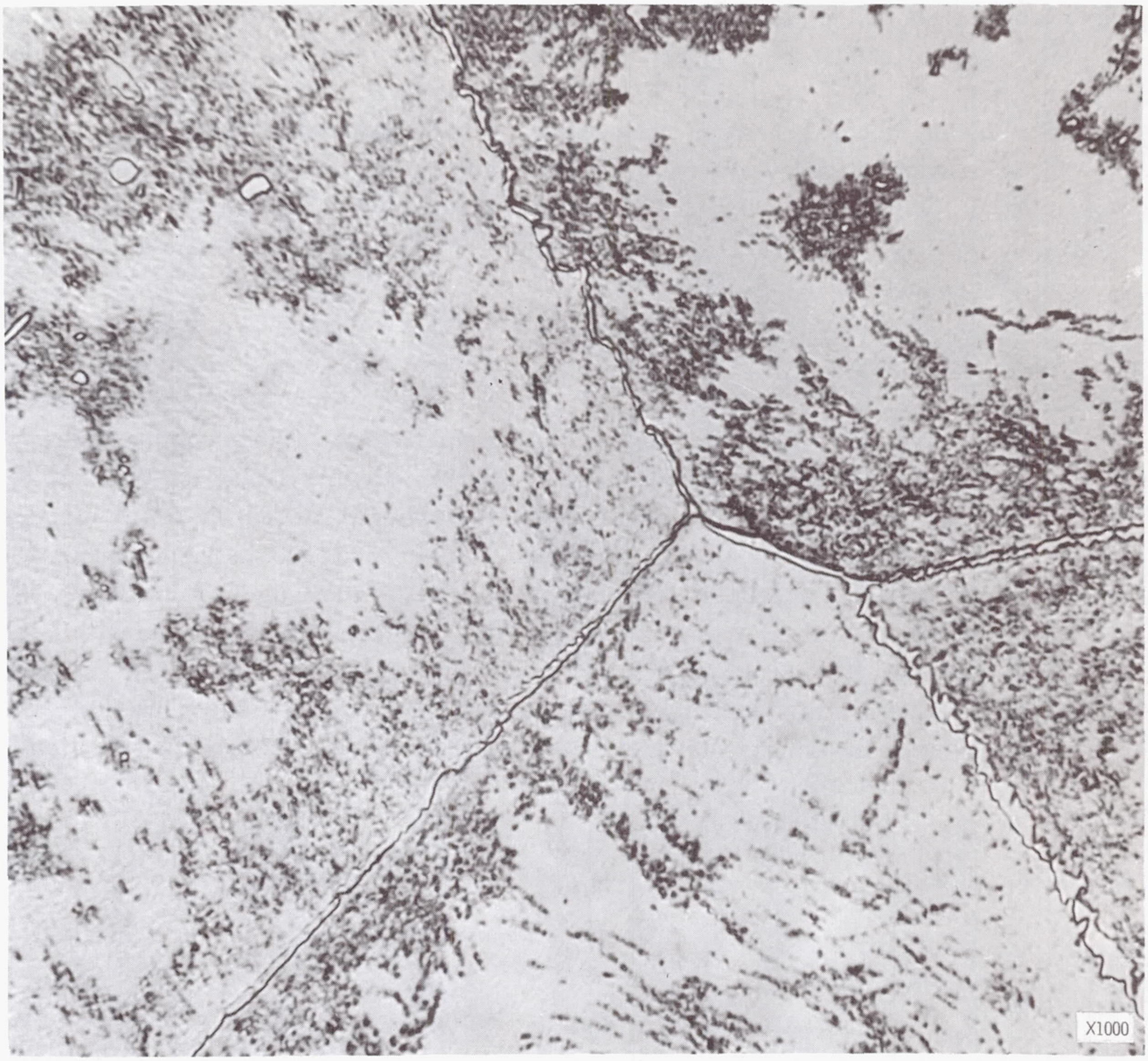


Figure 11. - Age hardening curve for MHC-24 (Mo-0.58Hf-0.77C). Annealed at 2750° F (1783 K) after solution treatment at 4000° F (2477 K).



(a) Solution treated at 4000° F (2477 K) for 30 minutes.

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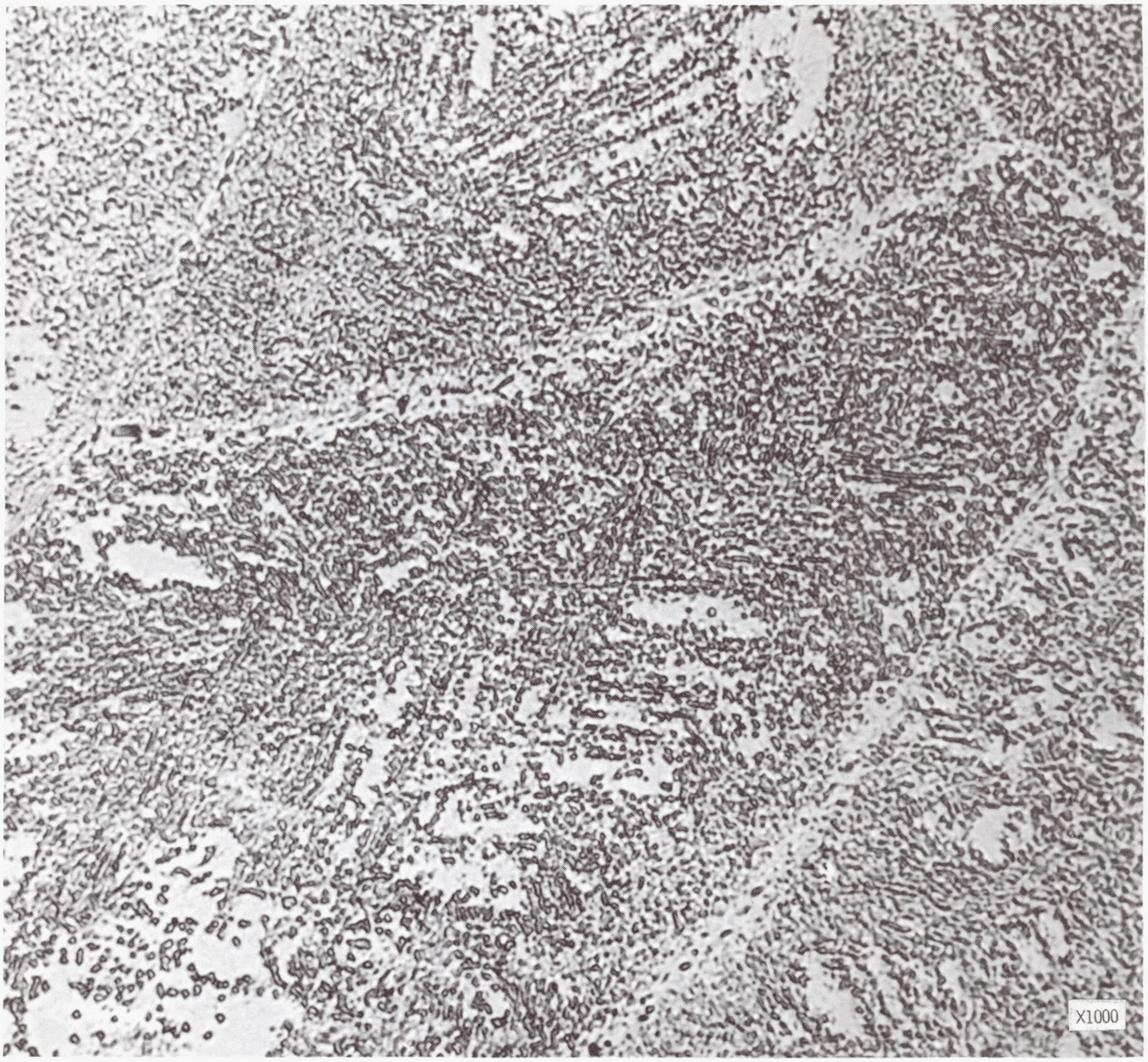
Figure 12. - Microstructures of MHC-24 (Mo-0.58Hf-0.77C).

of the carbide phase in solid solution was not realized. Rapid precipitation on cooling from the solution temperature is characteristic of molybdenum alloys (refs. 6 and 9). The carbide in figure 12(a) is present as an almost continuous grain-boundary phase and as a fine intragranular phase. On aging for 2 hours at 2750° F (1783 K), the structure in figure 12(b) resulted. The intragranular carbide phase is now widely dispersed, while the grain-boundary phase has disappeared.

Transmission electron microscopy (TEM) was also performed on the specimens pictured in figure 12. The foil taken from the solution-treated specimen showed some



(b) Solution treated and aged at 2750° F (1783 K) for 2 hours.

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Figure 12. - Concluded.

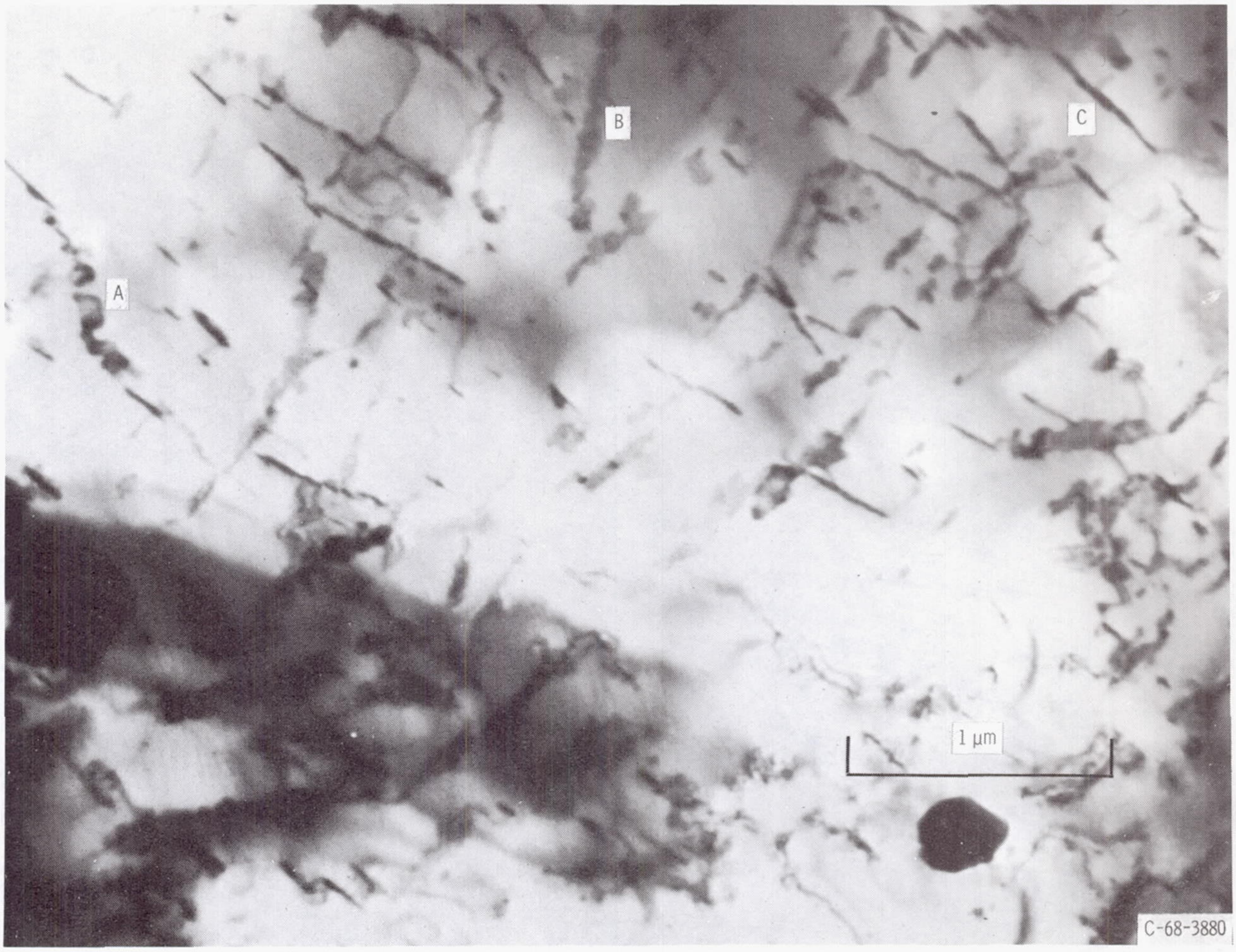


Figure 13. - MHC-24 (Mo-0.58Hf-0.77C) solution annealed at 4000° F (2477 K) for 30 minutes and aged at 2750° F (1783 K) for 2 hours. Transmission electron micrograph.

widely spaced particles with an average diameter of 0.5 micrometer and some precipitation on widely spaced dislocations. Figure 13 is a TEM micrograph from the specimen annealed for 2 hours at 2750^{0} F (1783 K). This gave peak hardness as shown in figure 11. The precipitation of HfC occurred both on dislocations (points A and B) and in the dislocation-free matrix (point C; fig. 13). The matrix precipitates intersected the foil on the $\{001\}$ trace and, thus, apparently lie on $\{001\}$ planes. This general precipitation behavior is in agreement with the work of Ryan and Martin (ref. 19). They also noted that the carbide initially precipitates coherently in the matrix. No evidence of coherency was seen in the specimen studied in this investigation.

Tensile Properties of Mo-Hf-C Alloys

The purpose of this section is to evaluate the strength of the nine alloys as a function of temperature and structural condition. The data are listed in tables II to VI. Tensile tests were performed on the nine Mo-Hf-C alloys in the as-swaged and recrystallized conditions at room temperature, 1800°, 2400°, and 3000° F (298, 1255, 1588, and 1922 K). In addition, tests were performed at 2400° F (1588 K) for all the alloys in the solution-treated condition. Five of the alloys were also solution treated and aged at various temperatures and tensile tested at 2400° F (1588 K). One alloy, MHC-24 (Mo-0.58Hf-0.77C) was chosen for more complete evaluation of the strength in the solution-treated condition. Tests were performed on this alloy in the temperature range 1500° to 3000° F (1088 to 1922 K).

Swaged and recrystallized conditions. - Tensile data in the as-swaged and recrystallized condition at room temperature, 1800°, 2400°, and 3000° F (1255, 1588, and 1922 K) are listed in tables II and III and are plotted against X_C in figures 14 and 15. The highest strength alloy in the as-swaged condition was MHC-27 (Mo-0.98Hf-1.11C). At 2400° F (1588 K), a temperature at which Mo alloys are frequently considered for use, the tensile strength of the alloy was 76.3 ksi (526 MN/m^2). Several other Mo-Hf-C alloys had 2400° F (1588 K) tensile strengths approaching 70 ksi (483 MN/m^2). In general, the range of strengths of 60 to 76 ksi (414 to 524 MN/m^2) at 2400° F (1588 K) compares favorably with other current high-strength molybdenum alloys. Molybdenum alloys containing titanium, zirconium, columbium, and carbon have been produced with tensile strengths greater than 80 ksi (552 MN/m^2) at 2400° F (1588 K) (refs. 8 and 9). However, special processing procedures are required to attain this strength as will be discussed in a later section. For example, the irregular variation of strength with composition indicated in figures 14 and 15 is believed to be a result of processing effects.

Room-temperature tensile data are listed in tables II and III. Elongations of 1 to 16 percent and 4 to 38 percent were obtained in the as-swaged and recrystallized conditions, respectively. These are consistent with room-temperature ductilities that have been measured on other molybdenum alloys (refs. 5 to 9). Only one alloy, MHC-26 (Mo-0.37Hf-0.89C) had poor ductility in both structural conditions. This may have resulted from its high carbon to hafnium ratio of 2.41. We can conclude from the data, however, that all the alloys have a tensile ductile-brittle transition temperature below room temperature in the recrystallized condition, and most have a similarly low ductile-brittle transition temperature in the as-swaged condition.

Solution-treated and aged conditions. - The strength in the solution-treated and aged conditions are listed in tables IV and V and are plotted in figures 16 to 18. The maximum strength level attained in the solution-treated condition was 74.9 ksi (516 MN/m^2) for alloy MHC-25. This compares with the value of 66.8 ksi (461 MN/m^2) measured in the

TABLE II. - TENSILE PROPERTIES OF AS-SWAGED ALLOYS

Alloy	Analyzed composition, at. %	0.2-percent offset yield stress		Ultimate tensile strength		Elongation, percent	Reduction in area, percent
		ksi	MN/m^2	ksi	MN/m^2		
Room temperature							
MHC-20	Mo-0.09Hf-0.24C	115	791	121	836	12	33
MHC-21	Mo-0.18Hf-0.42C	121	834	---	---	4	3
MHC-22	Mo-0.37Hf-0.29C	134	925	143	982	10	33
MHC-23	Mo-0.39Hf-0.65C	139	960	151	1040	12	31
MHC-26	Mo-0.37Hf-0.89C	130	898	---	---	1	2
MHC-24	Mo-0.58Hf-0.77C	130	899	---	---	4	4
MHC-25	Mo-0.96Hf-0.82C	145	997	195	1350	8	8
MHC-27	Mo-0.98Hf-1.11C	155	1070	175	1210	12	32
MHC-28	Mo-1.83Hf-1.07C	132	910	148	1020	16	42
1800° F (1255 K)							
MHC-20	Mo-0.09Hf-0.24C	68.3	471	70.8	488	11	80
MHC-21	Mo-0.18Hf-0.42C	85.2	587	86.8	598	10	68
MHC-22	Mo-0.37Hf-0.29C	94.1	649	95.4	658	10	87
MHC-23	Mo-0.39Hf-0.65C	87.7	605	92.5	638	10	70
MHC-26	Mo-0.37Hf-0.89C	81.8	563	84.5	583	10	67
MHC-24	Mo-0.58Hf-0.77C	81.4	561	82.7	570	10	77
MHC-25	Mo-0.96Hf-0.82C	84.8	585	86.7	598	14	74
MHC-27	Mo-0.98Hf-1.11C	94.2	651	102.8	709	12	63
MHC-28	Mo-1.83Hf-1.07C	85.7	591	92.0	634	10	49
2400° F (1588 K)							
MHC-20	Mo-0.09Hf-0.24C	57.3	395	59.8	412	14	87
MHC-21	Mo-0.18Hf-0.42C	68.9	475	71.4	492	12	59
MHC-22	Mo-0.37Hf-0.29C	65.2	450	67.9	468	16	61
MHC-23	Mo-0.39Hf-0.65C	67.7	467	70.7	487	18	57
MHC-26	Mo-0.37Hf-0.89C	61.5	424	66.5	459	18	58
MHC-24	Mo-0.58Hf-0.77C	61.7	425	63.5	438	16	66
MHC-25	Mo-0.96Hf-0.82C	64.2	443	66.8	461	14	67
MHC-27	Mo-0.98Hf-1.11C	73.6	507	76.3	526	18	62
MHC-28	Mo-1.83Hf-1.07C	56.10	387	59.3	409	28	63
3000° F (1922 K)							
MHC-20	Mo-0.09Hf-0.24C	6.57	45	8.27	57.0	55	98
MHC-21	Mo-0.18Hf-0.42C	24.9	165	25.6	177	22	98
MHC-22	Mo-0.37Hf-0.29C	22.8	157	24.3	168	22	98
MHC-23	Mo-0.39Hf-0.65C	19.5	134	21.2	147	20	88
MHC-26	Mo-0.37Hf-0.89C	18.2	125	19.5	134	32	53
MHC-24	Mo-0.58Hf-0.77C	27.0	186	29.0	200	26	83
MHC-25	Mo-0.96Hf-0.82C	27.3	188	29.1	201	25	76
MHC-27	Mo-0.98Hf-1.11C	24.5	169	28.5	197	26	98
MHC-28	Mo-1.83Hf-1.07C	22.1	152	24.7	163	54	53

TABLE III. - TENSILE PROPERTIES OF RECRYSTALLIZED ALLOYS

Alloy	Analyzed composition, at. %	0.2-percent offset yield strength		Ultimate tensile strength		Elongation, percent	Reduction in area, percent
		ksi	MN/m^2	ksi	MN/m^2		
Room temperature							
MHC-20	Mo-0.09Hf-0.24C	[a]50.1	345	75.0	517	28	[b]25
MHC-21	Mo-0.18Hf-0.42C	[a]54.4	381	80.1	552	38	[b]49
MHC-22	Mo-0.37Hf-0.29C	[a]55.7	384	83.2	574	34	[c]48
MHC-23	Mo-0.39Hf-0.65C	[a]60.6	418	86.9	599	35	[b]44
MHC-26	Mo-0.37Hf-0.89C	[a]57.4	396	---	---	4	[c]3
MHC-24	Mo-0.58Hf-0.77C	[a]57.1	393	88.5	611	34	[c]37
MHC-25	Mo-0.96Hf-0.82C	[a]56.2	386	90.4	623	27	[c]37
MHC-27	Mo-0.98Hf-1.11C	[a]61.7	425	95.9	661	28	[c]33
MHC-28	Mo-1.83Hf-1.07C	53.8	371	106.	727	20	[c]20
1800° F (1255 K)							
MHC-20	Mo-0.09Hf-0.24C	17.4	120	30.9	213	45	98
MHC-21	Mo-0.18Hf-0.42C	22.0	152	36.7	253	36	83
MHC-22	Mo-0.37Hf-0.29C	25.7	177	39.3	271	30	86
MHC-23	Mo-0.39Hf-0.65C	23.8	164	37.1	256	37	98
MHC-26	Mo-0.37Hf-0.89C	23.3	161	39.6	273	33	77
MHC-24	Mo-0.58Hf-0.77C	25.8	178	40.3	278	30	83
MHC-25	Mo-0.96Hf-0.82C	38.4	265	54.8	378	16	84
MHC-27	Mo-0.98Hf-1.11C	30.9	213	47.8	330	22	98
MHC-28	Mo-1.83Hf-1.07C	30.8	330	53.0	365	26	76
2400° F (1588 K)							
MHC-20	Mo-0.09Hf-0.24C	14.9	103	24.10	166	53	98
MHC-21	Mo-0.18Hf-0.42C	17.9	133	33.6	231	48	78
MHC-22	Mo-0.37Hf-0.29C	23.0	159	39.6	273	26	76
MHC-23	Mo-0.39Hf-0.65C	22.6	156	35.3	243	37	85
MHC-26	Mo-0.37Hf-0.89C	19.8	137	30.4	210	45	82
MHC-24	Mo-0.58Hf-0.77C	20.7	143	29.7	205	32	83
MHC-25	Mo-0.96Hf-0.82C	28.1	194	46.4	320	24	79
MHC-27	Mo-0.98Hf-1.11C	24.10	166	42.2	291	28	98
MHC-28	Mo-1.83Hf-1.07C	25.9	179	35.2	243	43	82
3000° F (1922 K)							
MHC-20	Mo-0.09Hf-0.24C	7.83	54	10.50	72	65	98
MHC-21	Mo-0.18Hf-0.42C	8.82	61	13.70	95	65	98
MHC-22	Mo-0.37Hf-0.29C	12.50	86	19.60	135	43	79
MHC-23	Mo-0.39Hf-0.65C	10.1	70	15.10	104	59	98
MHC-26	Mo-0.37Hf-0.89C	12.2	84	15.20	105	65	90
MHC-24	Mo-0.58Hf-0.77C	12.8	88	15.60	108	49	98
MHC-25	Mo-0.96Hf-0.82C	14.5	100	15.40	106	39	93
MHC-27	Mo-0.98Hf-1.11C	15.6	108	20.40	141	30	98
MHC-28	Mo-1.83Hf-1.07C	17.5	121	19.70	136	63	78

[a] Lower yield stress.

[b] Recrystallized at 3250° F (2060 K) for 1 hour.

[c] Recrystallized at 3500° F (2200 K) for 1 hour..

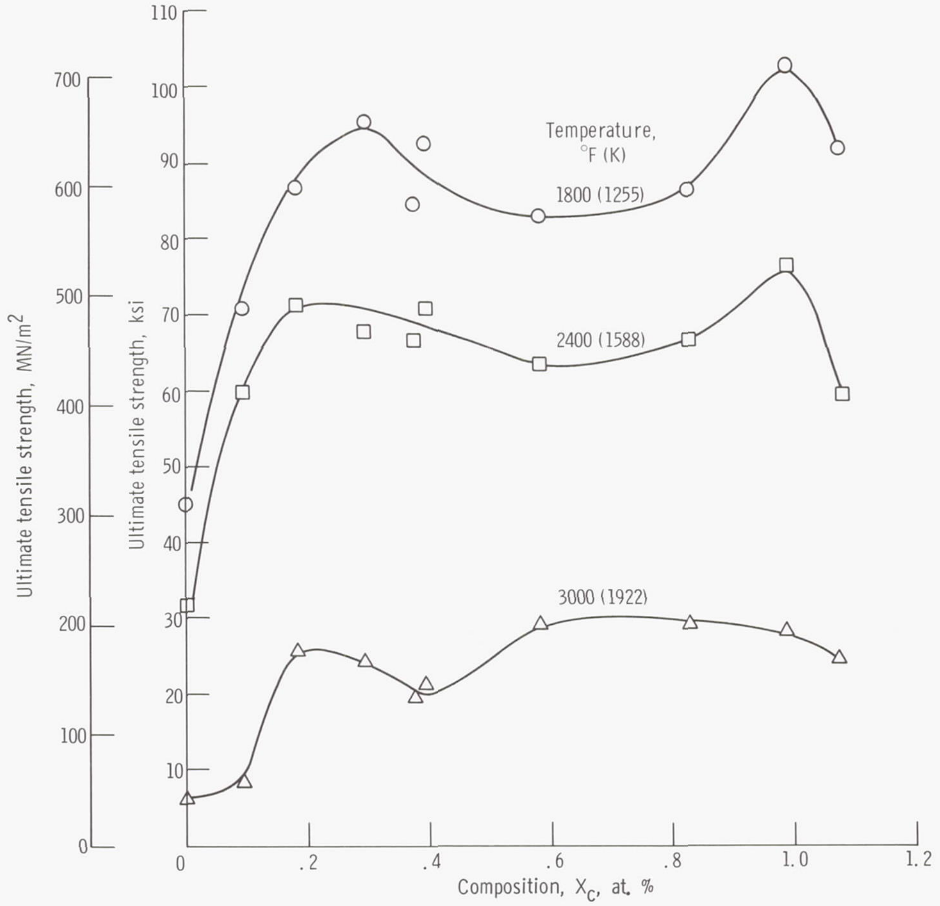


Figure 14. - As-swaged tensile properties as function of X_C and temperature.

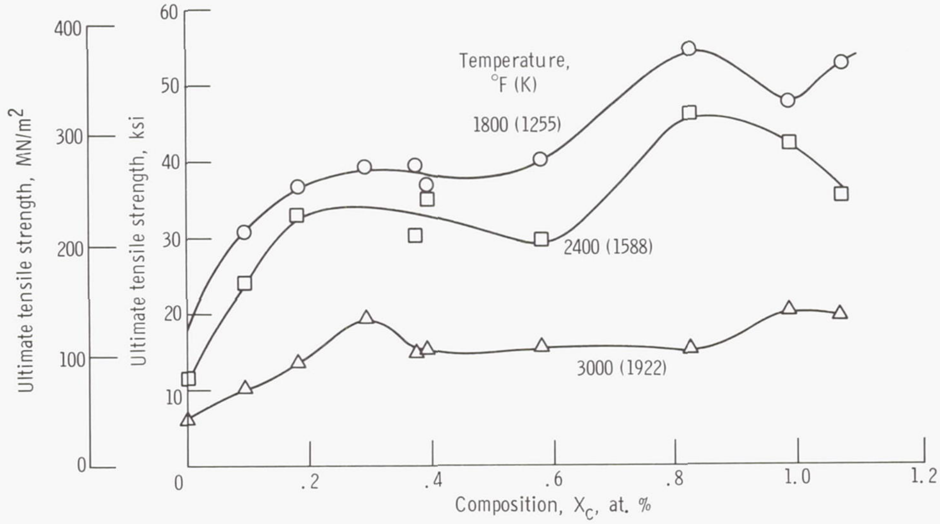


Figure 15. - Recrystallized tensile properties as function of composition parameter.

TABLE IV. - TENSILE PROPERTIES OF ALLOYS ANNEALED AT 4000^{o}

(2477 K) FOR 1 HOUR AND HELIUM QUENCHED

Alloy	Analyzed composition, at. %	Test temperature		0.2-percent offset yield strength		Ultimate tensile strength		Elongation, percent	Reduction in area, percent
		^{o}F	K	ksi	MN/m^{2}	ksi	MN/m^{2}		
MHC-20	Mo-0.09Hf-0.24C	2400	1588	18.40	127	26.30	181	6	80
MHC-21	Mo-0.18Hf-0.42C			26.20	181	37.90	261	24	84
MHC-22	Mo-0.37Hf-0.29C			37.00	255	50.90	351	14	80
MHC-23	Mo-0.39Hf-0.65C			37.50	259	49.90	341	16	77
MHC-26	Mo-0.37Hf-0.89C	1500	1088	44.70	308	60.00	414	14	49
		1800	1255	44.50	306	59.00	407	16	68
		2100	1422	45.10	311	61.90	427	16	72
		2400	1588	41.80	288	62.80	433	16	69
		2400	1588	43.80	302	62.70	432	20	70
		2700	1755	39.60	273	54.50	376	18	32
		3000	1922	34.80	240	40.90	282	6	8
MHC-24	Mo-0.58Hf-0.77C	2400	1588	43.10	297	74.90	516	16	69
MHC-25	Mo-0.96Hf-0.82C			37.80	260	53.04	366	16	69
MHC-27	Mo-0.98Hf-1.11C			41.10	283	71.00	489	18	57
MHC-28	Mo-1.83Hf-1.07C			45.30	312	71.50	493	16	71

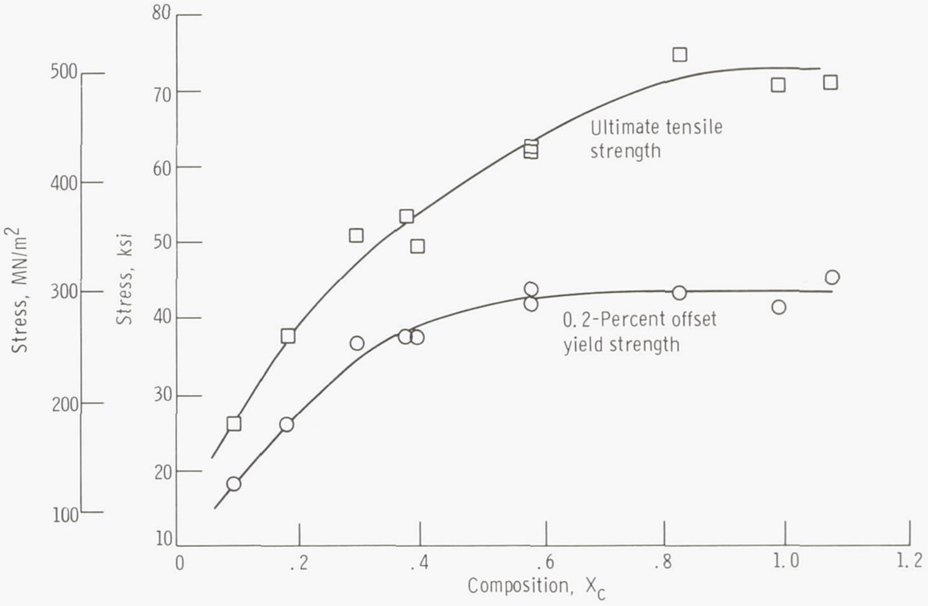


Figure 16. - Tensile properties at 2400° F (1588 K) after 30-minute anneal at 4000° F (2477 K) and quench.

TABLE V. - INFLUENCE OF AGING TEMPERATURE ON 2400° F (1588 K) ALLOY STRENGTH

Alloy	Analyzed composition, at. %	One-hour-aging temperature		0.2-percent offset yield strength		Ultimate tensile strength		Elongation, percent	Reduction in area, percent
		°F	K	ksi	MN/m^2	ksi	MN/m^2		
MHC-21	Mo-0.18Hf-0.42C	2250	1505	23.30	161	37.10	256	24	64
		2500	1644	24.50	169	36.60	252	22	81
		2750	1783	24.30	167	33.00	228	18	84
		3000	1922	21.70	150	21.20	187	26	83
MHC-22	Mo-0.37Hf-0.29C	2250	1505	35.60	254	52.40	361	14	69
		2500	1644	32.50	224	51.80	357	14	58
		2750	1783	35.60	245	43.70	301	16	58
		3000	1922	33.10	228	36.20	250	16	59
MHC-23	Mo-0.39Hf-0.65C	2250	1505	34.00	234	50.40	348	18	71
		2500	1644	36.00	248	49.70	343	16	73
		2750	1783	39.00	269	49.10	339	18	68
		3000	1922	32.90	227	36.40	251	20	83
MHC-26	Mo-0.37Hf-0.89C	2250	1505	37.00	255	49.70	343	16	74
		2500	1644	37.80	261	51.50	355	16	62
		2750	1783	40.00	276	49.50	342	16	58
		3000	1922	35.61	245	37.60	259	16	57
MHC-24	Mo-0.58Hf-0.77C	2250	1505	---	---	62.50	431	18	68
		2500	1644	41.50	286	60.50	417	20	65
		2750	1783	41.70	288	53.80	371	16	47
		3000	1922	41.70	288	46.70	322	15	79
MHC-25	Mo-0.96Hf-0.82	2250	1505	43.40	299	73.60	507	22	68
		2500	1644	45.10	311	72.50	500	20	77
		2750	1783	44.00	303	51.80	357	28	82
		3000	1922	34.90	241	41.40	285	26	79

as-swaged condition for that alloy at 2400° F (1588 K). In the solution-treated condition (fig. 11) at 2400° F (1588 K), the yield and tensile strength increased continuously with increasing X_c. This is in contrast to the discontinuous changes in strength observed for the as-swaged and recrystallized alloys (figs. 14 and 15). The data in figure 16 support the contention made previously that the nature of the curves in figures 14 and 15 is due to intrinsic processing differences. The solution treatment erases all traces of prior processing history.

One of the alloys, MHC-24, was tested in the solution-treated condition over a range of temperatures 1500° to 3000° F (1088 to 1922 K). These data are plotted in figure 17 along with the strengths measured on this alloy in the as-swaged and recrystallized conditions. In figure 17, at 2400° F (1588 K) and below, the strength in the as-swaged con-

TABLE VI. - TENSILE STRENGTH OF MHC-25 (Mo-0.96Hf-0.82C)

AT 2400° F (1588 K) AFTER SOLUTION

TREATMENT AND PRESTRAINING

Condition	0.2-percent yield stress		Ultimate tensile strength		Elongation, percent	Reduction in area, percent
	ksi	MN/m^2	ksi	MN/m^2		
A; solution treated for 30 min at 4000° F (2477 K)	43.1	297	74.5	514	16	69
B; treatment A plus 4-percent prestrain at 300° F (422 K)	62.2	427	79.2	546	14	53
C; treatment B plus aging treatment for 2 hr at 1800° F (1255 K)	64.0	441	79.5	548	14	48

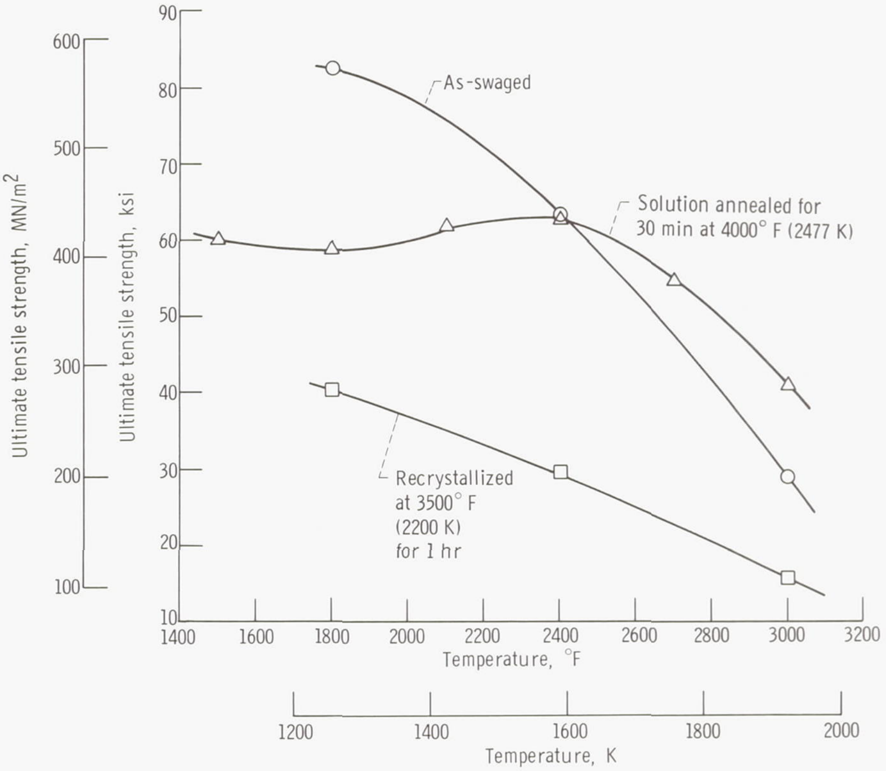


Figure 17. - Effect of temperature on tensile strength of MHC-24 (Mo-0.581 Hf-0.77C) in three conditions.

dition is highest, but, above 2400° F (1588 K), the strength of the solution-treated alloys is highest. The strength in the solution-treated condition for MHC-24 at 3000° F (1922 K) of 40.9 ksi (282 MN/m^2) represents the highest strength observed for a molybdenum alloy at this temperature. At all temperatures, the strength of the recrystallized alloy is well below that for the other two conditions.

The influence of aging on the 2400° F (1588 K) strength of solution-treated alloys is given in table VII, and data for alloys MHC-21, 24, and 25 are plotted in figure 18. The specimens were aged for 1 hour in hydrogen at 2250°, 2500°, 2750°, and 3000° F (1505, 1644, 1783, and 1922 K) following the 4000° F (2477 K) solution anneal. In general, aging had relatively little beneficial effect in the 2400° F (1588 K) tensile strength. As seen in

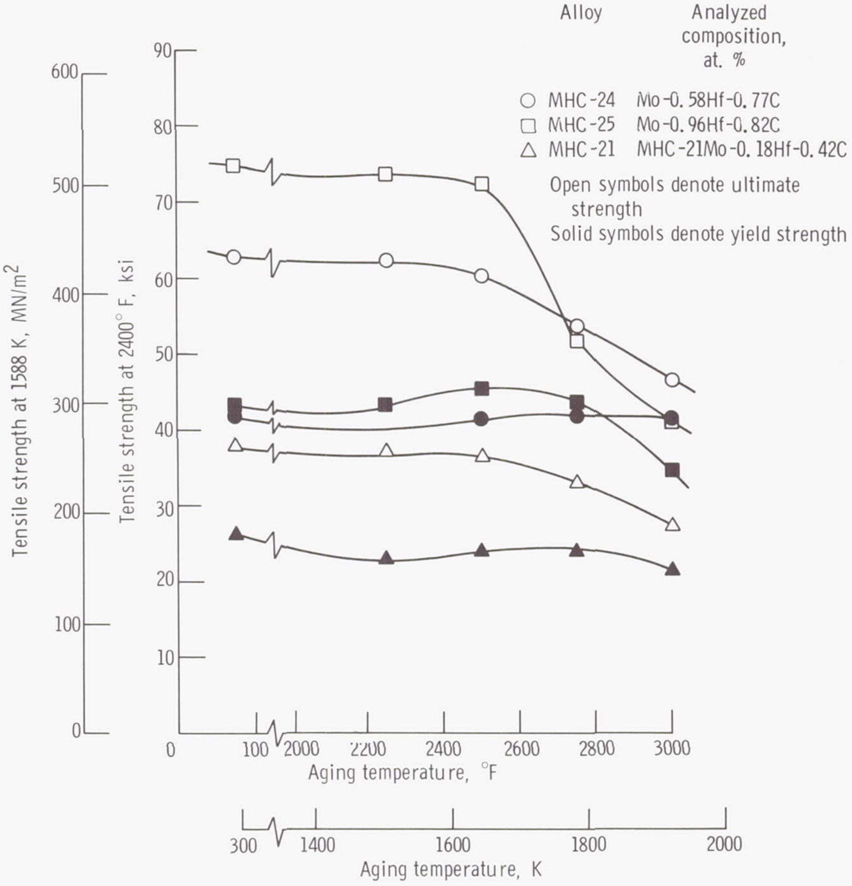


Figure 18. - Influence of aging temperature on 2400° F (1588 K) strength of two alloys.

figure 18, the yield strength passes through a slight maximum with increasing aging temperature. This was typical of all the alloys with the exception of MHC-22 (Mo-0.37Hf-0.29C) (see table V). The tensile strength, however, decreases slightly on aging at 2250° and 2500° F (1505 and 1644 K), and decreases very sharply at higher aging temperatures. The difference between the yield and ultimate stress also decreases sharply at the higher aging temperatures, indicating a lowering of the work-hardening rate.

Additional experiments were performed on alloy MHC-25 (Mo-0.96Hf-0.82C) to determine whether a low-temperature prestrain would enhance the strength of the solution-treated alloy. Two specimens were solution treated and then prestrained 4 percent at 300° F (422 K). One of the prestrained specimens was subsequently aged for 2 hours at 1800° F (1255 K). The specimens were then tested at 2400° F (1588 K). The data are given in table VI and can be compared with the strength of alloy MHC-25 in the solution-

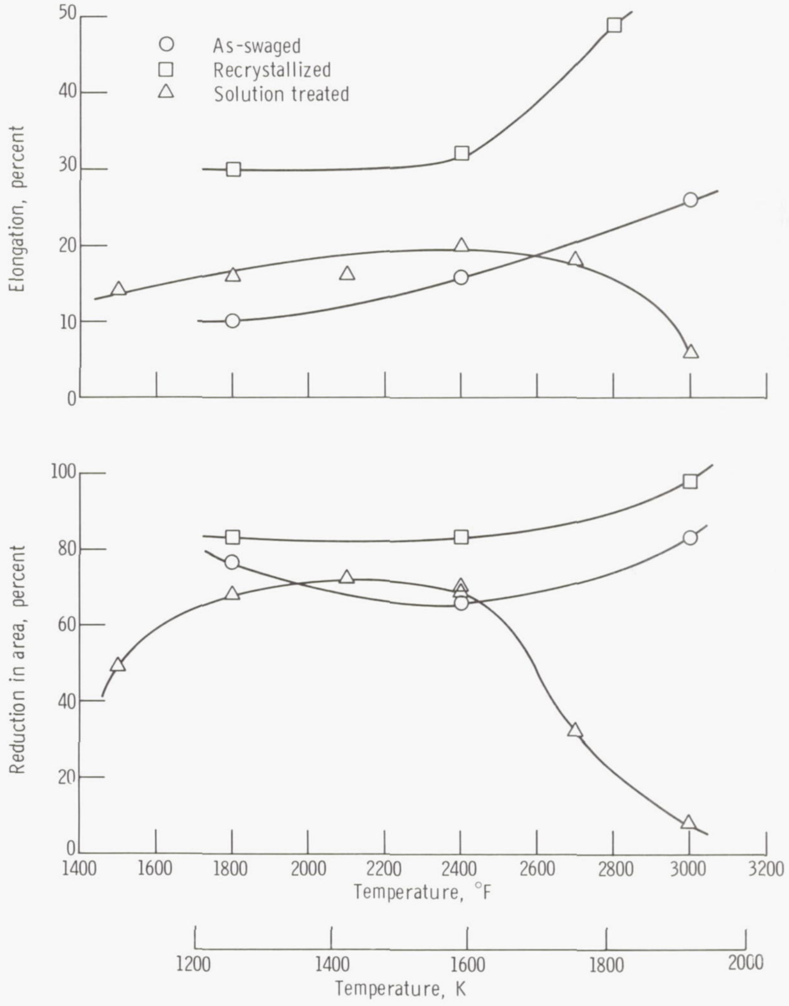
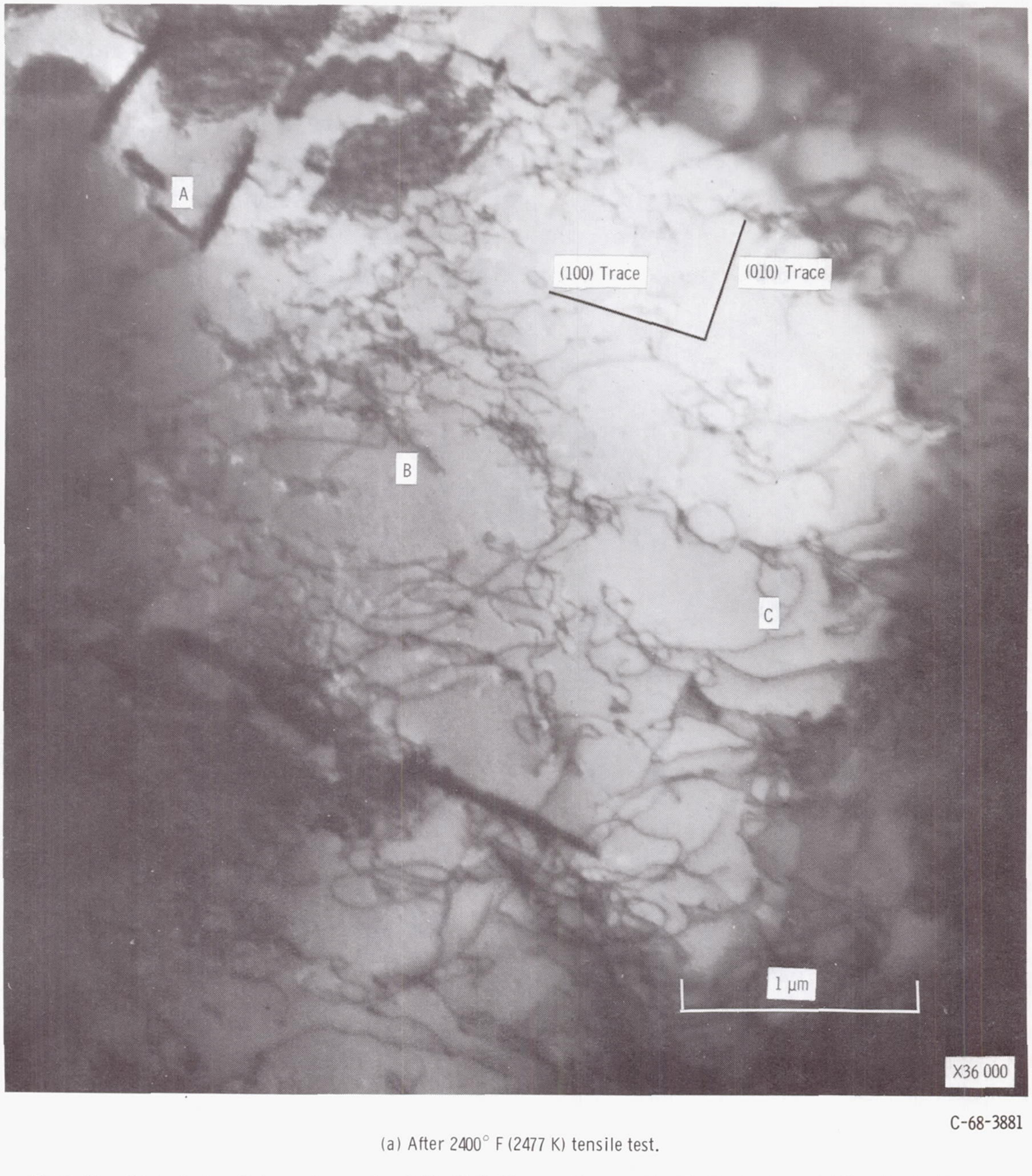


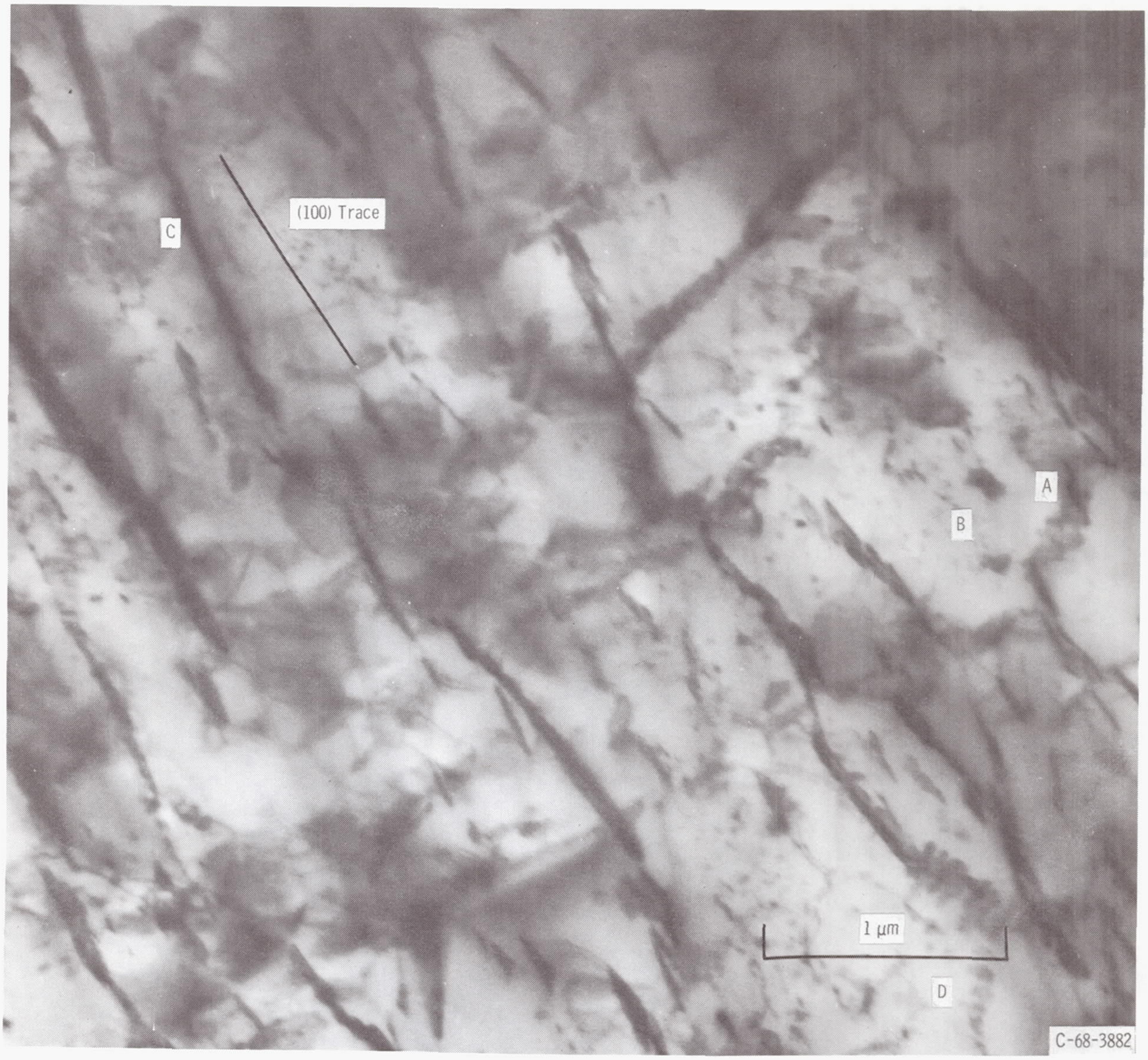
Figure 19. - Ductility of MHC-24 (Mo-0.58Hf-0.77C) as function of temperature in three conditions.



C-68-3881

(a) After 2400° F (2477 K) tensile test.

Figure 20. - Transmission electron micrographs of alloy MHC-24 (Mo-0.58Hf-0.77C). Solution treated at 4000° F (2477 K) 30 minutes prior to testing.



(b) After 3000° F (1922 K) tensile test.

Figure 20. - Concluded.

treated condition from table IV. The prestraining treatment has the greatest effect on the yield stress of the solution-treated alloy, raising it from 43.1 to 62.2 ksi (297 to 427 MN/m^2). Subsequent aging raised the yield stress still further to 64.0 ksi (441 MN/m^2). The tensile strength was less affected, and the maximum increase was noted in the prestrained and aged specimen from 74.5 to 79.5 ksi (514 to 548 MN/m^2). The second strength was the highest measured at 2400^{0} F (1588 K) in this study.

High-temperature ductility. - The high-temperature elongation and percent reduction in area for MHC-24 (Mo-0.58Hf-0.77C) is plotted against temperature in figure 19 in three structural conditions, as-swaged, recrystallized, and solution treated. In the as-swaged and recrystallized conditions, the ductility increased moderately with increasing temperature up to the maximum test temperature (3000° F (1922 K)). This contrasts with the ductility behavior of the solution-treated alloy. Above 2400° F (1588 K), the ductility of the solution-treated alloy begins to decrease. At 3000° F (1922 K) the reduction in area decreased from a maximum at 2400° F (1588 K) of 69 to 70 percent to 8 percent while the elongation at 3000° F (1922 K) was 6 percent.

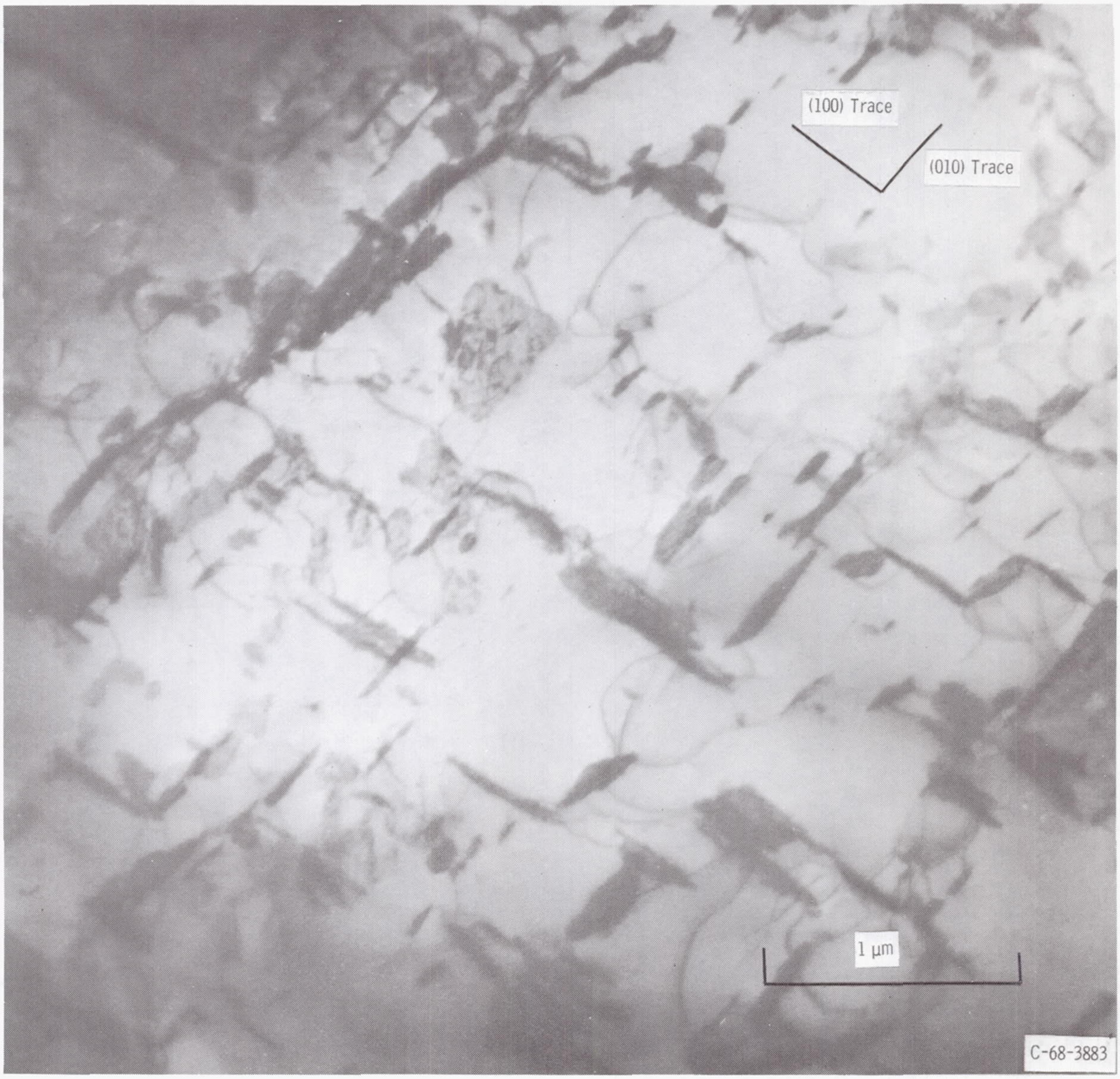


Figure 21. - Transmission electron micrograph of alloy MHC-24, (Mo-0.58Hf-0.77C). Solution treated at 4000° F (2744 K) for 30 minutes and aged for 1 hour at 3000° F (1922 K) prior to tensile testing at 2400° F (1588 K).

The ductility in the solution-treated condition is also much lower than that in the recrystallized condition at all test temperatures investigated. Aging of the solution-treated alloy had little effect on restoring the ductility (see table V). The prestrain and aging treatment documented in table VI had little effect on the elongation of the solution-treated alloy, but the reduction in area decreased from 69 to 48 percent.

Microstructural aspects of strength of solution-treated alloys. - In this section some discussion is offered concerning the strength of the Mo-Hf-C alloys in the solution-treated and aged conditions. Chang (refs. 6 and 7) has shown that the strength of heat-treatable molybdenum alloys in the solution-treated condition is strongly influenced by the precipitation of carbides during straining. Such a process is a specific example of a general mechanism termed "dynamic strengthening" by Wilcox (ref. 20). The two main characteristics of an alloy undergoing precipitation during straining are a relatively large work-hardening rate and a peak in the flow stress-temperature curve (refs. 20 and 21). The peak in the flow stress-temperature curve is evident for alloy MHC-24 in figure 17. A more rapid work-hardening rate for alloys containing higher hafnium contents is seen in the plot in figure 16 where it is evident that the tensile strength increases more rapidly with X_c than does the yield strength.

Transmission electron microscopy was also employed to study the possibility of strain enhanced carbide precipitation. Figures 20(a) and (b) give views of the structure of a solution-treated specimen after straining at 2400° F (1588 K) and at 3000° F (1922 K), respectively. Figure 20(a) shows a few carbide platelets such as at point A, which appear to lie on $\{100\}$ planes. The dislocation density throughout the specimen was high as seen in the figure, and fine precipitation was evident as at point C where the dislocation line is somewhat discontinous.

Testing the solution-treated alloy at 3000° F (1922 K) produced an entirely different structure as seen in figure 20(b). Precipitation is much further advanced. A few platelets (point C) apparently lie on $\{100\}$ planes, but the majority of the carbides are precipitated on dislocations such as at points A and D. A fine precipitate is also present (point B).

Figure 21 shows a micrograph of a specimen which was first aged at 3000° F (1922 K) for 1 hour prior to testing at 2400° F (1588 K). The carbide platelets are in a regular array and few dislocations are present.

The micrographs confirm that precipitation on dislocations does take place during testing of the solution-treated alloys. The effect of the precipitation on strength is probably twofold. First, the actual precipitation immobilizes dislocations. Second, the immobilization requires that new dislocations be generated to allow the deformation to continue. This produces a rapid rate of dislocation multiplication and accounts for the dense network of dislocations seen in figure 20. The effect of aging prior to test on the 2400° F (1588 K) strength can be interpreted as a removal of the potential for strain enhanced precipitation and a subsequent lack of dislocation immobilization.

Creep Rupture Properties of Molybdenum-Hafnium-Carbon Alloys

Creep rupture tests were performed on the Mo-Hf-C alloys in the as-swaged condition at 2400° and 3000° F (1588 and 1922 K). The data are listed in table VII and plotted in figures 22 to 24. Each of the alloys was tested at 2400° F (1588 K) at a stress of 35 ksi (241 MN/m^2). Figure 22 shows the variation of the rupture life at this stress plotted against X_c. The variation is quite irregular as was previously indicated for the tensile properties at 2400° F (1588 K) in figure 14. The rupture lives for the alloys varied between 4.3 and 148.1 hours. Surprisingly, the highest value was measured on the relatively dilute alloy MHC-21 (Mo-0.18Hf-0.42C).

TABLE VII. - STRESS-RUPTURE DATA ON WROUGHT ALLOYS

Alloy	Analyzed composition, at. %	Temperature		Stress, σ		Rupture time, t_R, hr	Minimum creep rate, ϵ_s, sec^{-1}	Elongation, percent
		°F	K	ksi	MN/m^2			
MHC-20	Mo-0.09Hf-0.24C	2400	1588	35.0	241	18.1	3.67×10^{-7}	15
MHC-21	Mo-0.18Hf-0.42C	2400	1588	35.0	241	148.1	3.00×10^{-8}	10
		2400	1588	45.0	310	23.9	2.46×10^{-7}	14
		2400	1588	60.0	414	3.2	7.20×10^{-6}	16
		3000	1922	12.0	82	8	---------	41
MHC-22	Mo-0.37Hf-0.29C	2400	1588	35.0	241	18.5	2.47×10^{-6}	18
MHC-23	Mo-0.39Hf-0.65C	2400	1588	30.0	207	167.0	7.60×10^{-8}	20
				35.0	241	31.6	3.08×10^{-7}	19
				37.5	259	23.1	2.86×10^{-7}	19
				60.0	414	1.0	2.76×10^{-5}	18
MHC-26	Mo-0.37Hf-0.89C	2400	1588	25.0	172	105.8	4.69×10^{-8}	20
				30.0	207	37.6	2.58×10^{-7}	22
				35.0	241	21.3	7.53×10^{-7}	14
				45.0	310	4.3	---------	14
MHC-24	Mo-0.58Hf-0.77C	2400	1588	35.0	241	49.4	1.10×10^{-7}	22
		3000	1922	12.0	82	7.5	---------	--
MHC-25	Mo-0.96Hf-0.82C	2400	1588	35.0	241	6.7	1.10×10^{-6}	22
						10.8	6.80×10^{-7}	18
MHC-27	Mo-0.98Hf-1.11C	2400	1588	35.0	241	26.5	2.78×10^{-7}	24
						64.2	1.75×10^{-7}	18
MHC-28	Mo-1.83Hf-1.07C	2400	1588	35.0	241	4.3	7.30×10^{-6}	30
		3000	1942	12.0	82	7.6	---------	--

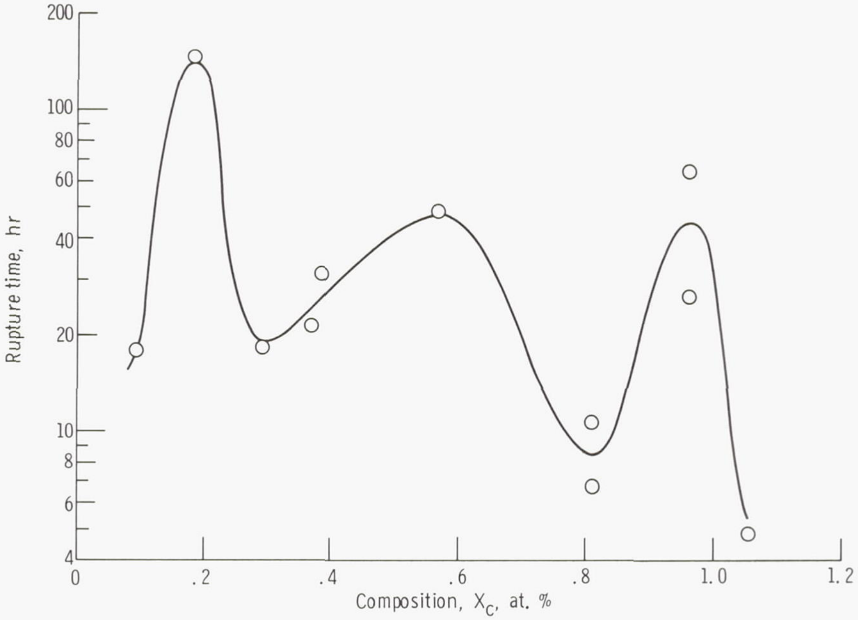


Figure 22. - Influence of composition on rupture life of molybdenum-hafnium carbon alloy at 2400° F (1588 K) and 35 ksi (241 MN/m^2).

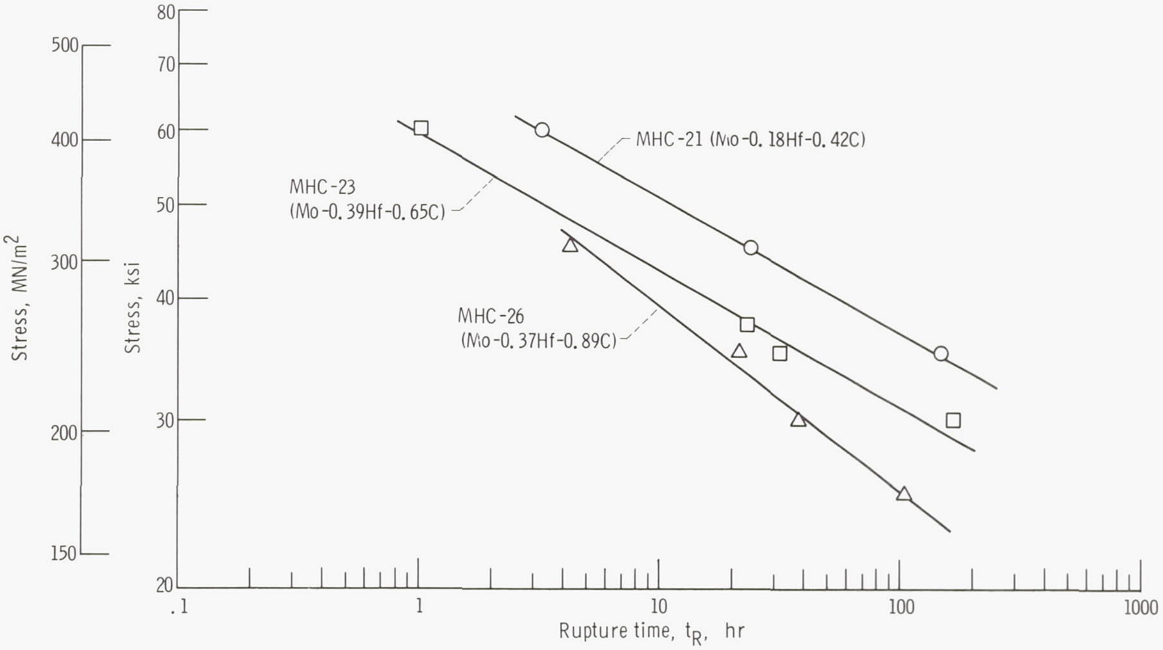


Figure 23. - Stress-rupture properties of wrought alloys at 2400° F (1588 K).

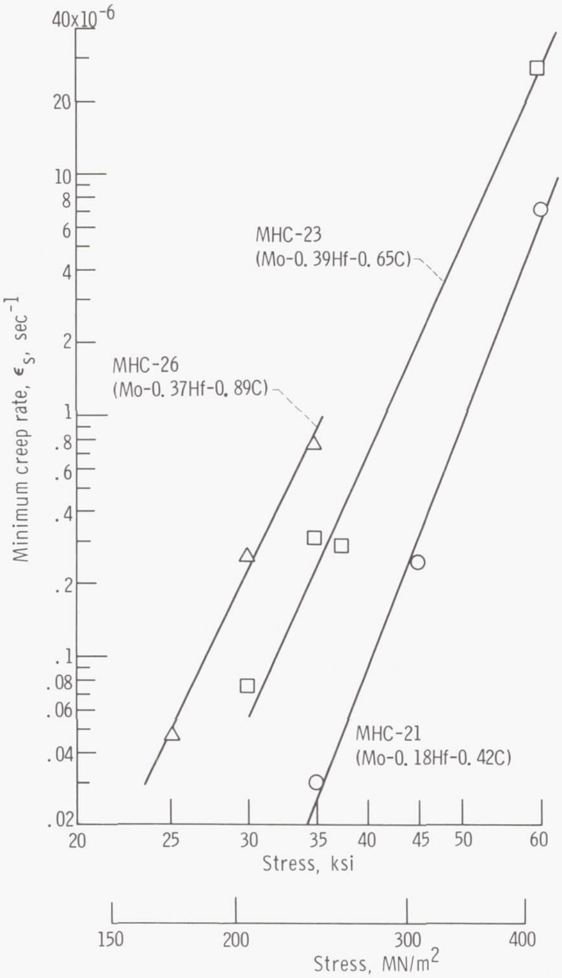
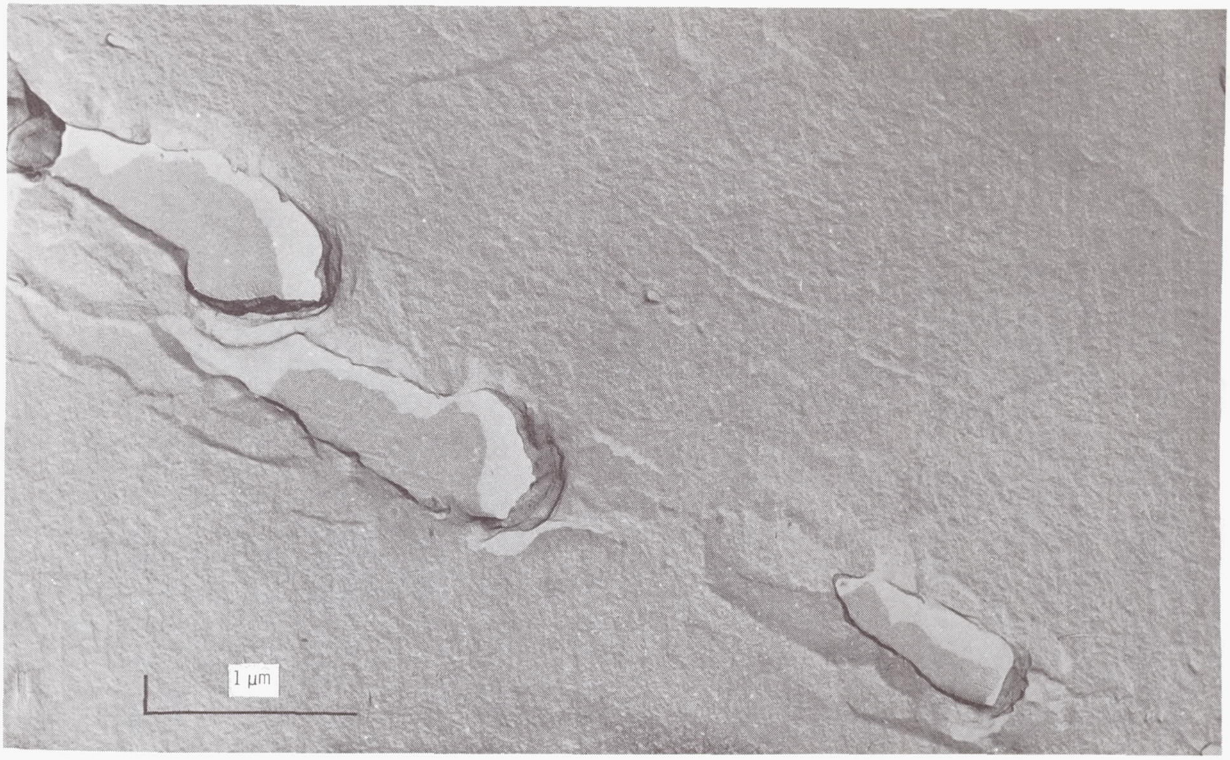


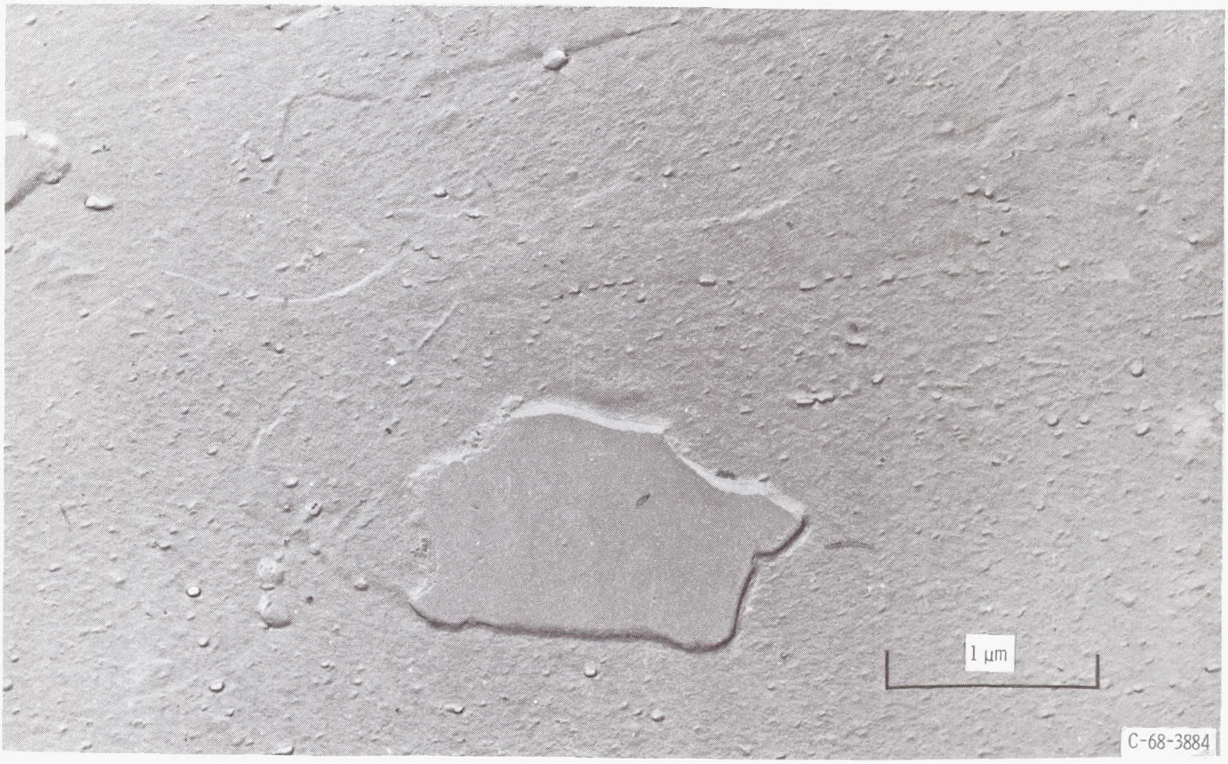
Figure 24. - Stress dependence of minimum creep rate at 2400° F (1588 F) for three alloys in wrought condition.

Three of the alloys were tested also at 12 ksi (82 MN/m^2) and 3000° F (1922 K). The results of these tests are given in table VII. The rupture lives varied between 0.8 and 7.6 hours. Insufficient tests were performed to document well the variation of the rupture life with composition.

Three of the alloys, MHC-21, 23, and 26, were chosen for more extensive determination of their 2400° F (1588 K) rupture strength. The variation of the rupture life with stress at 2400° F (1588 K) is given in figure 23, and the variation of the minimum creep rate is given in figure 24. The high creep-rupture strength of alloy MHC-21 is confirmed by the results at different stresses. A possible reason for the high strength of this relatively dilute alloy is shown in the electron micrographs in figure 25. Figure 25(a) shows the structure after tensile testing at 2400° F (1588 K), where a coarse-grain boundary carbide was observed with few intragranular particles. Figure 25(b) shows the same



(a) Tensile tested at 2400° F (1588 K) to failure.



(b) Rupture tested at 35 ksi (24/MN/m^2) and 2400° F (1588 K) to failure.

Figure 25. - MHC-21; composition, Mo-0.18Hf-0.42C; carbon replica.

TABLE VIII. - COMPOSITIONS OF MOLYBDENUM ALLOYS

Alloy designation	Composition	
	Weight percent	Atomic percent
TZM	[a]Mo-0.5Ti-0.096Zr-0.016C	[a]Mo-1.0Ti-0.1Zr-0.13C
TZC	[a]Mo-1.2Ti-0.17Zr-0.11C	[a]Mo-2.4Ti-0.18Zr-0.88C
Cb-TZM	[b]Mo-1.5Cb-0.5Ti-0.3Zr-0.07C	[b]Mo-1.55Cb-1.0Ti-0.32Zr-0.56C

[a] Analyzed composition of purchased TZM and TZC heats.

[b] Nominal composition (refs. 8 and 9).

TABLE IX. - TENSILE PROPERTIES OF COMMERCIAL WROUGHT MOLYBDENUM ALLOYS IN STRESS-RELIEVED CONDITION

Alloy	Temperature		0.2-percent yield stress		Ultimate tensile stress		Elongation, percent	Reduction in area, percent
	°F	K	ksi	MN/m^2	ksi	MN/m^2		
Mo-TZM	RT[a]	RT[a]	105.40	727	108.70	750	28	75
	1800	1255	59.90	413	60.80	419	18	>98
	2400	1588	46.30	319	47.80	330	18	>98
	3000	1922	7.60	52	10.30	71	75	>98
Mo-TZC	RT[a]	RT[a]	98.80	681	112.10	773	30	59
	1800	1255	56.90	389	59.50	410	20	84
	2400	1588	46.50	321	47.10	325	18	86
	3000	1922	21.80	150	22.20	153	35	>98

[a] Room temperature.

alloys after rupture testing at 35 ksi (241 MN/m^2). Here, extensive precipitation within the grains is noted in addition to the coarce particles observed in figure 25(a).

It was noted in a previous section that alloy MHC-21 was apparently solution treated during the extrusion process, accounting for its abnormally high tensile strength. The presence of the fine carbides in figure 25(b) suggests that this strength improvement results from precipitation during creep testing. The capability for this precipitation was provided by the in-process solution treatment.

Comparison of Tensile and Creep Properties of Molybdenum-Hafnium-Carbon Alloys With Those of Two Commercial Molybdenum Alloys

In addition to the Mo-Hf-C alloys tested in this program, one lot each of two commercial molybdenum alloys was purchased and evaluated for comparison purposes. The alloys are designated by the manufacturer as TZM and TZC. Their compositions are given in table VIII. The alloys were tested in the as-received (stress relieved) condition. Tensile tests were performed at 1800°, 2400°, and 3000° F (1255, 1588, and 1922 K), and creep-rupture tests were performed over a wide range of stresses at 2400° F (1588 K). The results of the tests are listed in tables IX and X.

TABLE X. - STRESS-RUPTURE PROPERTIES OF COMMERCIAL WROUGHT MOLYBDENUM ALLOYS IN STRESS-RELIEVED CONDITION

Alloy	Temperature		Stress		Rupture time, hr	Minimum creep rate, sec^{-1}	Elongation, percent
	°F	K	ksi	MN/m^2			
Mo-TZM	2400	1588	12.0	82	68.4	9.00×10^{-8}	43
			15.0	103	51.1	1.33×10^{-7}	28
			25.0	172	10.0	5.17×10^{-7}	22
			35.0	241	2.2	5.00×10^{-6}	26
			45.0	310	.05	1.12×10^{-5}	--
			50.0	345	.007	---------	16
Mo-TZC	2400	1588	20.0	138	111.2	1.83×10^{-7}	39
			25.0	172	33.7	8.33×10^{-7}	28
			30.0	207	9.9	1.08×10^{-6}	30
			35.0	241	2.2	4.33×10^{-6}	26
			40.0	276	.36	3.23×10^{-5}	20
	3000	1922	12.0	82	1.1	3.10×10^{-5}	79

Figure 26 compares the tensile strengths of Mo-TZM and Mo-TZC with the experimental Mo-Hf-C alloys. At 1800° and 2400° F (1255 and 1588 K), the strengths of both TZM and TZC are less than any of the Mo-Hf-C alloys, but at 3000° F (1922 K), they are within the scatter band for the Mo-Hf-C alloys. Room-temperature tensile properties for the two alloys are given in table IX. The elongation of TZM and TZC were 28 and 30 percent, respectively, and were more than twice as large as the ductilities for the Mo-Hf-C alloys (tables II and III). The rupture data on these alloys are compared in the next section.

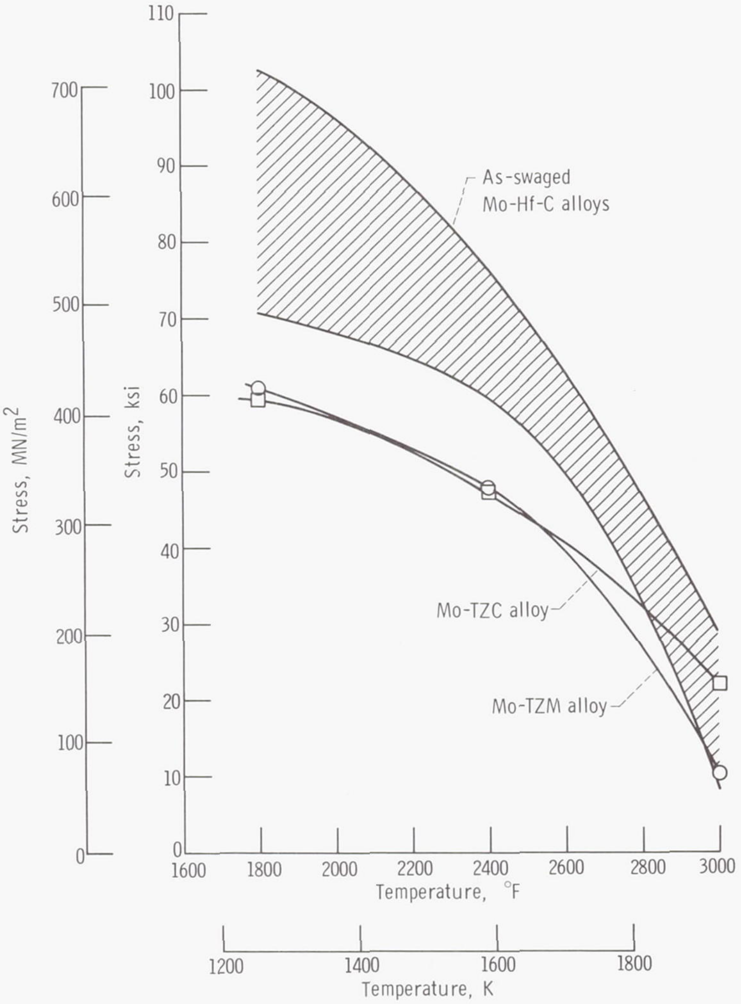
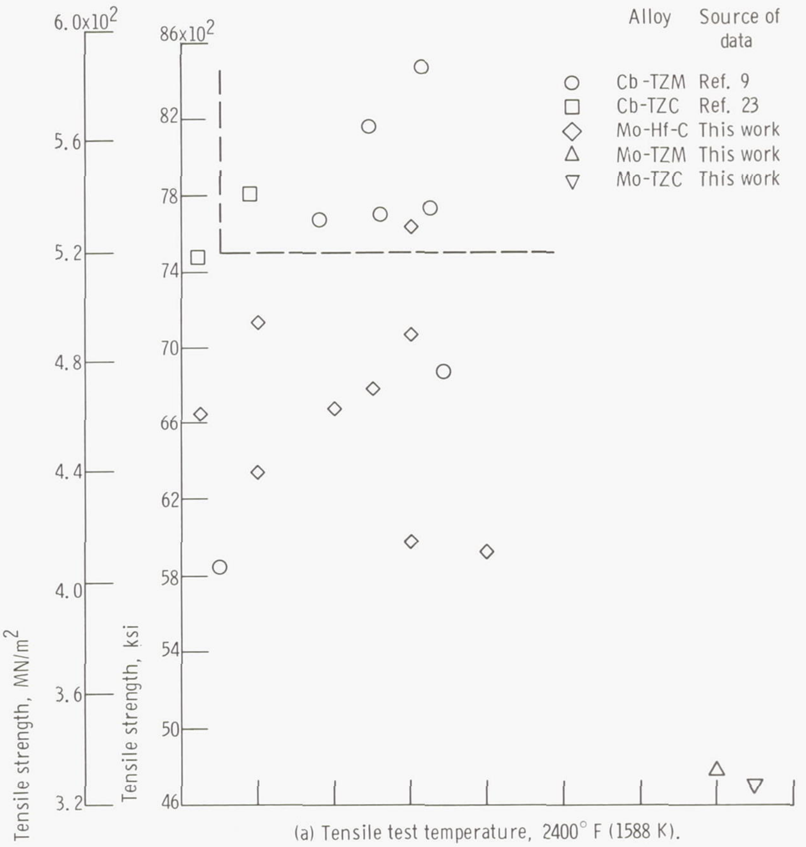
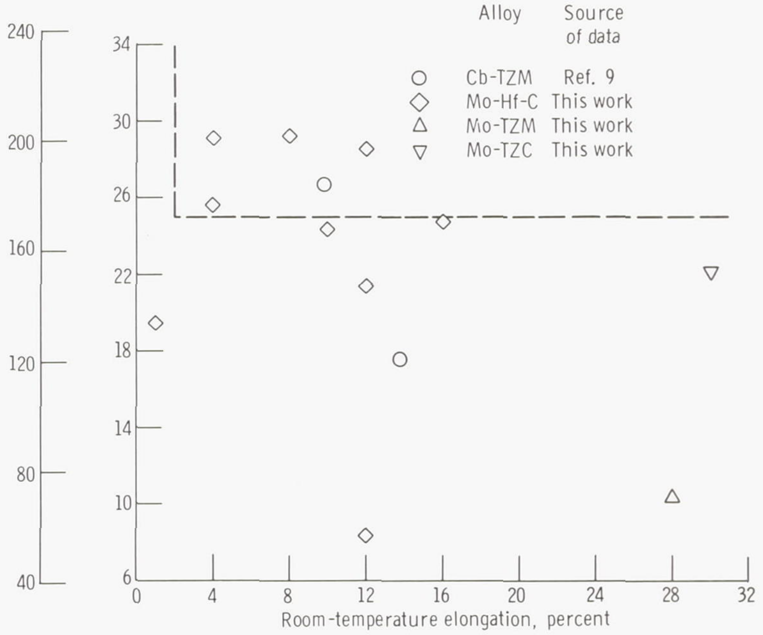


Figure 26. - Comparison of tensile strength of wrought molybdenum-hafnium-carbon alloys with commercial molybdenum alloys.



(a) Tensile test temperature, 2400° F (1588 K).



(b) Tensile test temperature, 3000° F (1922 K).

Figure 27. - Comparison of tensile strength and room-temperature ductility of selected alloys.

CONCLUDING REMARKS

In this final section, an attempt will be made to place our results on Mo-Hf-C alloys into proper perspective with previous work on other molybdenum alloys. A useful molybdenum alloy should have a good combination of both high-temperature strength and low-temperature ductility. Reasonable targets for high strength molybdenum alloys have been established by a panel of the Materials Advisory Board (MAB) (ref. 22). These targets are compared in figure 27 with data from this and other programs. Figure 27(a) is a plot of the 2400° F (1588 K) tensile strength against the room-temperature elongation in the as-swaged or stress-relieved condition. Figure 27(b) is an identical plot using the 3000° F (1922 K) tensile strength. The dashed lines in each figure join at the target properties set by the MAB panel.

The various data points for the TZC and Cb-TZM alloys in figure 27 represent different processing schedules for the same composition. The spread in properties of these alloys indicates the importance of a proper processing schedule for molybdenum alloys. Only one of the Mo-Hf-C alloys and the TZC and Cb-TZM have properties that exceeded the target properties at 2400° F (1588 K). This alloy was MHC-27 (Mo-0.98Hf-1.07C). At 3000° F (1922 K), the following Mo-Hf-C alloys had an attractive combination of

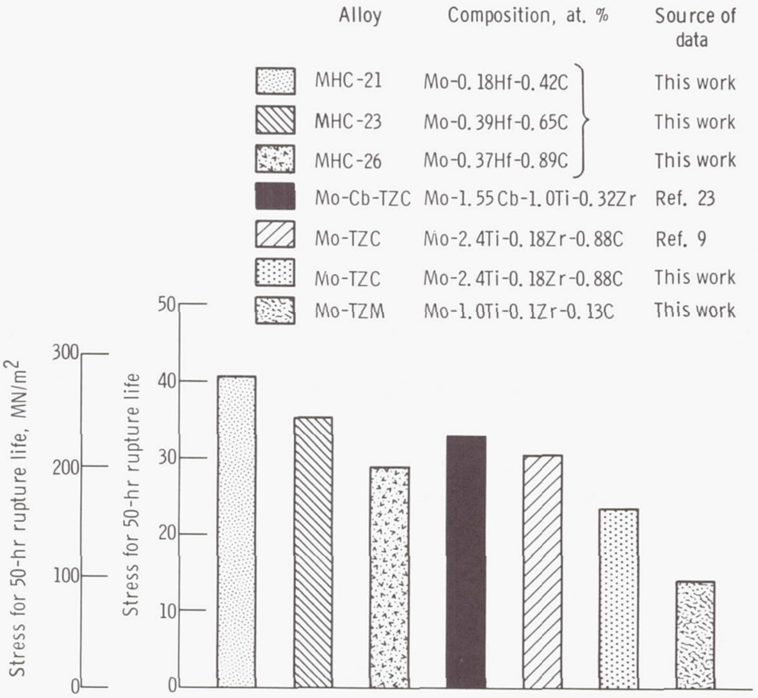


Figure 28. - 50-Hour rupture strength of various molybdenum alloys at 2400° F (1588 K) as-swaged or stress-relieved condition.

strength and ductility: MHC-21 (Mo-0.18Hf-0.42C); MHC-24 (Mo-0.58Hf-0.77C); MHC-25 (Mo-0.96Hf-0.82C); and MHC-27 (Mo-0.98Hf-1.07C).

The 2400° F (1588 K) stress-rupture strengths of three Mo-Hf-C alloys are compared in figure 28 with the published work on TZC and Cb-TZM as well as the data on the commercial alloys obtained in this program. The 50-hour rupture strength of 40.5 ksi (279 MN/m^2) obtained for MHC-21 (Mo-0.18Hf-0.42C) is superior to any of the other alloys tested. The rupture strength of MHC-23 (Mo-0.39Hf-0.65C) is also greater than that of Cb-TZC or TZC.

Thus, the main advantage of Mo-Hf-C alloys over previous alloys appears to lie in the long-time stress-rupture strength at 2400° F (1588 K) and the short-time tensile strength at 3000° F (1922 K). This high-temperature - long-time advantage may reflect the higher thermodynamic stability of HfC as compared with the carbides found in the other alloys. It is hoped that better short-time properties at 2400° F (1588 K) can be produced in these alloys.

CONCLUSION

A preliminary evaluation of the properties of Mo-Hf-C alloys yielded the following conclusions:

1. Potentially useful high-temperature materials are available in the molybdenum-hafnium-carbon system. For example, tensile strengths of greater than 70 ksi (483 MN/m^2) were found for as-swaged materials at 2400° F (1588 K). However, the molybdenum-hafnium-carbon alloys showed their biggest strength advantage over previous molybdenum alloys in stress-rupture tests at 2400° F (1588 K) and short-time tensile tests at 3000° F (1922 K).

2. The molybdenum-hafnium-carbon alloys are heat treatable. Tensile strengths of up to 74.9 ksi (516 MN/m^2) at 2400° F (1588 K) were observed in the solution-treated condition. A prestrain of 4 percent at 300° F (422 K) increased this to 79.5 ksi (548 MN/m^2), which was the highest strength observed in this program at 2400° F (1588 K).

3. The recrystallization temperature of the molybdenum-hafnium-carbon alloys varied from 2670° to 3300° F (1740 to 2088 K) increasing with increasing hafnium and carbon content.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 7, 1968,
129-03-02-08-22.

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