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TUNGSTEN-NICKEL-COPPER TERNARY ALLOYS FOR HIGH-TEMPERATURE APPLICATIONS

by Ruluff D. McIntyre
Lewis Research Center
Cleveland, Ohio

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SUMMARY

Ternary tungsten-nickel-copper alloys were investigated to develop a fabricable alloy which could be sintered at low temperatures and used at temperatures above 3000° F. In this study, an effort was made to relate mechanical properties to composition over a range of 1/2 to 10 total weight percent nickel and copper in tungsten. The result was a tungsten - 0.3-percent-nickel - 0.2-percent-copper ternary alloy that exhibited strength and ductility comparable to wrought, recrystallized powder-metallurgy and arc-cast tungsten at temperatures in the vicinity of 3000° to 4000° F, while retaining its capacity for sintering at temperatures as low as 2200° F. Elongation values were comparable to values normally shown for recrystallized tungsten over the temperature interval 3000° to 4000° F. Heat treatment of this alloy following sintering increased the elongation before fracture at 3000° F from 4.0 to 20.0 percent with little loss of strength. In the heat-treated condition, the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy could be rolled to a 50-percent reduction in thickness at temperatures of approximately 3000° F. The rolled tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy 4 T bend transition temperature compared favorably to that of conventional, unalloyed, worked tungsten sheet material. It is felt that an alloy such as this might be used to prepare tungsten composite materials strengthened by ultrafine dispersoids or strong fibers. Two other alloy compositions investigated, tungsten - 1.5 percent nickel - 1 percent copper and tungsten - 6 percent nickel - 4 percent copper, lost almost all their useful strength and elongation at 2500° F. Both of these alloys, however, could be rolled at temperatures near 2000° F in the as-sintered condition. Rolling the tungsten - 6-percent-nickel - 4-percent-copper alloy to a 50-percent reduction in thickness imparted to it a strength comparable to wrought, recrystallized tungsten at 1000° F and increased the elongation from 2.0 to 26.0 percent relative to the as-sintered material.

INTRODUCTION

Tungsten can play a significant role in materials applications at temperatures above 3000° F because of its high melting point (approximately 6170° F). Although much effort today is concerned with the development of arc- and electron-beam-melted tungsten, powder-metallurgy tungsten continues to be of major interest. High sintering and mechanical working temperatures, however, make powder-metallurgy tungsten difficult to process into useful hardware. Special techniques for sintering tungsten at low temperatures usually result in materials which have poor mechanical properties above 2000° F. Much work has been done on low-temperature sintering of powder-metallurgy tungsten through the addition of relatively low-melting, metallic additives. This work has involved chiefly heavy alloy ternary materials like tungsten, nickel, and iron (ref. 1) and tungsten, nickel, and copper (ref. 2) or binary tungsten alloys containing additions of nickel, cobalt, or iron (refs. 3 and 4). Recent work (ref. 5) has shown that other metallic additives such as ruthenium, palladium, platinum, and rhodium will also promote the sintering of tungsten at relatively low temperatures. The composition and temperature ranges of interest in these prior investigations involved total alloying additions varying from 1/10 to 20 weight percent and sintering temperatures varying from 1800° to 2500° F. Virtually all mechanical property data acquired on these systems were obtained at room temperature or at slightly elevated temperatures of approximately 400° F (ref. 6). One study (ref. 1) has shown that heavy alloy materials like tungsten, nickel, and iron possess some useful strength at temperatures as high as 2000° F. None of the preceding investigations explored the possibility of combining low-temperature sintering with high-temperature strength through the selection of a suitable alloy system.

This investigation was conducted to develop a powder-metallurgy tungsten alloy with two important qualities: It should have useful strength at temperatures over 3000° F, and it should have the capability for accelerated sintering at significantly lower temperatures and shorter times than currently possible with conventional pure tungsten. It was felt that these objectives might be accomplished by using tungsten containing copper and nickel in quantities sufficiently small to permit both of these constituents to enter into solid solution with tungsten at high temperatures subsequent to accelerating the sintering at very low temperatures. If this were possible, a product that has strength at high temperatures subsequent to sintering at very low temperatures might be created. An effort was made to relate the observed structures to mechanical properties obtained over a composition range from 1/2 to 10 total weight percent nickel and copper added to tungsten.

Pressed compacts of three alloy compositions were sintered at temperatures which varied from 2200° to 2500° F. Heat treatment of as-sintered compacts was performed to improve high-temperature mechanical properties. A few samples of each alloy were

TABLE I. - MATERIALS INVESTIGATED

Powder	Method of preparation	Chemical analysis		Average particle size[a], μ	Source
		Element	Concentration, weight percent		
Tungsten	Hydrogen reduction of oxides	Molybdenum	0.002	1.2	General Electric Co., Lamp Metals and Components Department, Cleveland, Ohio
		Aluminum	.001		
		Calcium	.001		
		Copper	.001		
		Tungsten	Balance		
Nickel	Reduction from carbonyl	Oxygen	0.07	2.5	Charles Hardy, Inc., New York, New York
		Carbon	.05		
		Iron	.002		
		Nickel (minimum)	99.8		
Copper	Electrolysis	Copper (minimum)	99.0	3.1	The Glidden Co., Hammond, Indiana

[a]By a sub-sieve sizer.

evaluated for fabricability by rolling, and specimens representing each composition were tested in tension at various temperatures ranging up to 4000° F in the as-sintered, heat-treated, or worked condition. Ultimate tensile strength and percent elongation were related to the microstructural characteristics of the alloy compositions investigated.

MATERIALS AND PROCEDURE

Materials

The present investigation explored the high-temperature tensile properties of ternary composite alloys of tungsten with 0.5, 2.5, and 10 total weight percent nickel and copper in the ratio 3 nickel to 2 copper. This particular ratio was selected because prior work (ref. 2) demonstrated that an optimum in low-temperature mechanical properties appeared to be associated with a ratio of 3 nickel to 2 copper in the tungsten-nickel-copper ternary system. It was felt, therefore, that this ratio of nickel to copper would constitute a good starting point in the exploration of high-temperature properties. The specific alloys tested were, in weight percentages, tungsten - 0.3 nickel - 0.2 copper, tungsten - 1.5 nickel - 1 copper, and tungsten - 6 nickel - 4 copper. The atomic percentages were tungsten - 0.9 nickel - 0.6 copper, tungsten - 4.5 nickel - 3 copper, and tungsten - 15 nickel - 10 copper, respectively. The materials used in this investigation are described in table I.

TABLE II. - FABRICATION OF TUNGSTEN-NICKEL-COPPER SPECIMENS

(a) Sintering and heat treatment

Alloy	Temperature, $^{\circ}F$	Time, min	Atmosphere	Grain diameter, mm	Density g/cc
Sintering					
Tungsten - 0.3 nickel - 0.2 copper	2200	10	Hydrogen	0.004	18.4
Tungsten - 1.5 nickel - 1 copper	2200	120	Vacuum	.03	18.1
Tungsten - 6 nickel - 4 copper	2500	30	Hydrogen	.03	17.1
Heat treatment					
Tungsten - 0.3 nickel - 0.2 copper	2500	30	Vacuum	0.01	18.4
Tungsten - 0.3 nickel - 0.2 copper	2900	60	Vacuum	.02	18.4
Tungsten - 1.5 nickel - 1 copper	2900	60	Vacuum	.09	18.1

(b) Rolling

Alloy	Approximate temperature, $^{\circ}F$	Total reduction in area, percent	Density, g/cc
Tungsten - 0.3 nickel - 0.2 copper	3000	50	18.9
Tungsten - 1.5 nickel - 1 copper	2000	10	18.2
Tungsten - 6 nickel - 4 copper	2000	50	17.1

Specimen Fabrication

Powders were blended by rolling in glass jars for 1/2 hour after the addition of a 1-percent-by-weight paraffin binder. The paraffin was dissolved in benzene prior to mixing. Sheet bars weighing 100 grams were hydraulically pressed in a single-action die from the blended powders at 12.5 tons per square inch into compacts measuring approximately 6 by 1 by 0.10 inch.

Some of the important processing conditions related to sintering, heat treatment, and rolling are shown in table II.

Sintering times varied from 10 minutes to 2 hours, and temperatures ranged from 2200° to 2500° F. The tungsten - 6-percent-nickel - 4-percent-copper alloy was sintered for 1/2 hour at 2500° F in hydrogen (dew point, -67° F); the tungsten - 1.5-percent-nickel - 1-percent-copper alloy for 2 hours at 2200° F in a vacuum of 5.0×10^{-5} torr; and the tungsten - 0.3-percent nickel - 0.2-percent-copper alloy for 10 minutes at 2200° F in hydrogen. Samples of the tungsten - 0.3-percent-nickel -

0.2-percent-copper alloy were reheated (heattreated) at 2500° F for 1/2 hour in a vacuum of 5.0×10^{-5} torr. Samples of both tungsten - 0.3-percent-nickel - 0.2-percent-copper and tungsten - 1.5-percent-nickel - 1-percent-copper alloys were heattreated at 2900° F for 1 hour in a vacuum of 5.0×10^{-5} torr.

In order to acquire some idea as to fabricability, a few samples of each alloy were reduced by rolling. The as-sintered tungsten - 6-percent-nickel - 4-percent-copper and tungsten - 1.5-percent-nickel - 1-percent-copper alloys were rolled to 50-percent and 10-percent reductions in thickness, respectively, at approximately 2000° F. The heat-treated tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy was reduced 50 percent in thickness by rolling at approximately 3000° F using a rolling schedule similar to that used at the Lewis Research Center for rolling unalloyed tungsten.

Mechanical Property Testing

Elevated-temperature tensile properties were investigated by using a tensile testing machine with a crosshead speed of 0.01 inch per minute. Elongation results were obtained from crosshead motion. Test specimens had a 1-inch gage length and a 0.01-square-inch cross-sectional area. Tests were conducted in an evacuated chamber (5.0×10^{-5} torr) equipped with a tantalum sleeve heater (ref. 7). Temperatures were measured with a tungsten - tungsten-26-percent-rhenium thermocouple or a platinum - platinum-13-percent-rhodium thermocouple and are estimated accurate to ±20° F. The 4 T bend transition temperature of the heat-treated and rolled tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy was determined in air at a crosshead speed of 1 inch per minute.

Metallographic Studies

In order to study grain size and void shape and distribution, microstructures were studied at various magnifications. An etch composed of five parts ammonium hydroxide plus one part hydrogen peroxide was used for the tungsten-nickel-copper phase, while Murakami's etchant (10 parts potassium hydroxide, 10 parts potassium ferricyanide, and 100 parts water) or boiling hydrogen peroxide was used for the tungsten grains. Grain size was determined by counting the number of grain-boundary intercepts of a straight line of given length drawn across photographs of representative microstructures and computing an approximate average grain diameter in millimeters (ref. 8). At least three separate determinations were made for each microstructure, and these determinations were averaged to give a typical value.

To obtain some insight into the effect of heat treatment on the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy fractures at 3000° F, electron microfracto-

TABLE III. - ALLOY TENSILE DATA

Composition, weight percent	Condition	Test temperature, °F	Ultimate tensile strength, psi	Elongation, percent
Tungsten - 0.3 nickel - 0.2 copper	Heat-treated[a]	77	23 000	9.0
	Rolled	77	77 300	12.0
	Sintered	2000	24 200	3.0
	Sintered	2500	14 000	4.0
	Sintered	3000	10 000	4.0
	Heat-treated[a]	3000	9 000	20.0
	Sintered	3500	8 000	52.0
	Sintered	4000	4 500	75.0
Tungsten - 1.5 nickel - 1 copper	Sintered	1000	31 500	22.0
	Sintered	2000	20 000	28.0
	Sintered	2500	3 500	10.0
	Sintered	3000	0	0
	Rolled	(b)	(b)	(b)
Tungsten - 6 nickel - 4 copper	Sintered	1000	27 600	2.0
	Sintered	2000	10 000	1.0
	Sintered	2500	900	1.0
	Rolled	1000	46 000	26.0
	Rolled	2000	9 000	1.5
	Rolled	2500	1 000	1.0

[a]At 2500° F for 1/2 hr.

[b]Specimens not tested; under conditions of rolling, which were not optimized, not more than 10-percent reduction in area was achieved without encountering severe edge cracking.

graphs of the tensile-tested specimens were obtained at a magnification of 19 000 by using a cellulose acetate replication technique.

RESULTS

Mechanical Properties

Tensile properties. - Utlimate tensile strength data as related to temperature for the compositions studied appear in figure 1 and table III. The scatter band in figure 1 presents a range of reported ultimate tensile strengths for worked, recrystallized tungsten made from powder-metallurgy, arc-cast, or electron-beam-melted starting materials over the temperature interval 2000° to 4000° F (refs. 9 to 11). The strength values for the

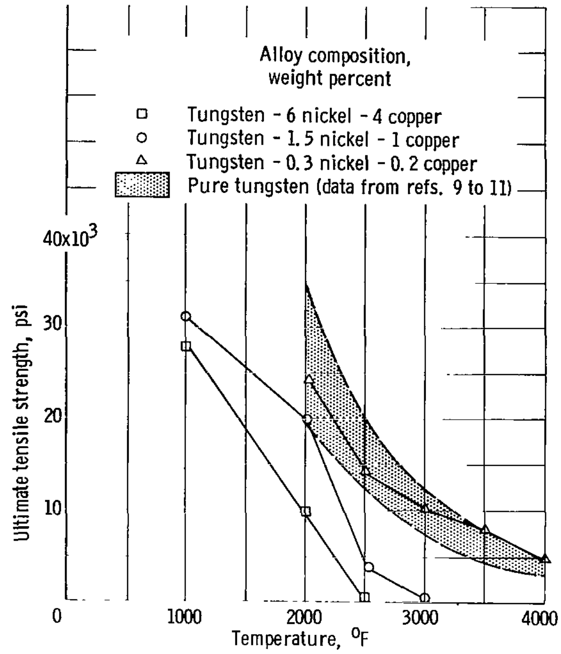


Figure 1. - Ultimate tensile strength of tungsten-nickel-copper alloys as function of test temperature.

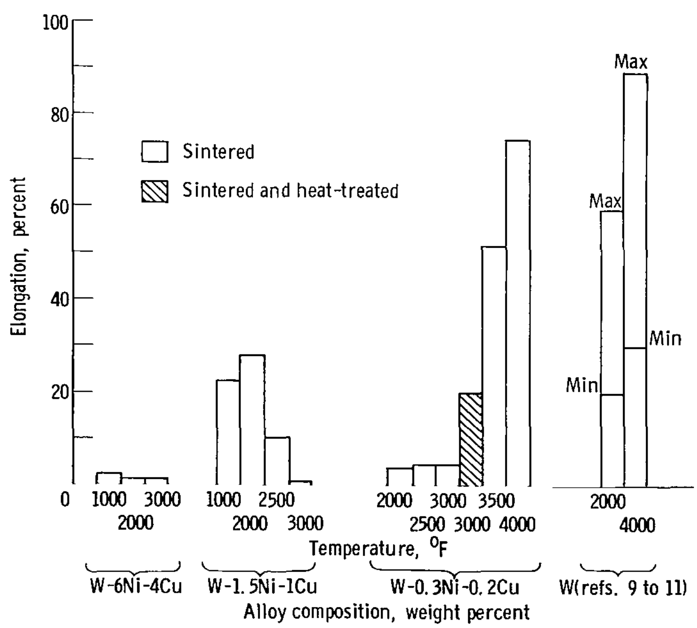


Figure 2. - Elongation of sintered or sintered and heat-treated tungsten-nickel-copper alloys at various temperatures.

tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy fall within the scatter band over the entire temperature interval and appear to lie close to the maximum reported strength values for temperatures over 3000° F. Comparison of the data of table III and figure 1 with reference to the tungsten - 1.5-percent-nickel - 1-percent-copper and tungsten - 6-percent-nickel - 4-percent-copper alloys reveals that the former alloy had higher strength for the temperature interval from 1000° to 2500° F. The tungsten - 6-percent-nickel - 4-percent-copper alloy showed a linear decrease in tensile strength as temperatures rose from 1000° to 2500° F and had no practical strength at 2500° F. The tungsten - 1.5-percent-nickel - 1-percent-copper alloy had no strength at 3000° F.

Elongation properties. - Elongation appears plotted against test temperatures in figure 2. The as-sintered tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy displayed similar elongation values in the 2000° to 3000° F range. A very pronounced increase in ductility was noted for testing temperatures above 3000° F. The effect of the 2500° F heat treatment of this alloy composition was to increase the elongation from 4.0 to 20.0 percent at 3000° F with little loss in strength (table III). The 4 T bend transition temperature of the heat-treated and rolled tungsten - 0.3-percent-nickel -

0.2-percent-copper alloy was found to be 275°±25° F. Specimens could be bent around a 4 T radius at temperatures of 300° F and higher. At temperatures of 250° F and below, however, the alloy broke in a brittle manner. Included in figure 2 is the spread in elongation values of worked, recrystallized tungsten at 2000° and 4000° F. For the temperature range beyond 3000° F the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy showed elongation values comparable to recrystallized tungsten. The elongation values for the tungsten - 1.5-percent-nickel - 1-percent-copper alloy decreased significantly above 2000° F, in correspondence with the progressive decrease in ultimate tensile strength (fig. 1). The as-sintered tungsten - 6-percent-nickel - 4-percent-copper alloy had low elongation values during the entire testing interval.

Effects of composition. - Figure 3 relates ultimate tensile strength and percent elongation data to alloy composition for testing temperatures ranging from 1000° to 4000° F. Figure 3(a) shows that at 2000° F the two-phase composite alloy materials have ultimate tensile strength values that are approximately a linear function of the weight percent tungsten present over the total range of composition investigated. At 2500° F the relation between strength and percent tungsten seems to be approximately exponential. It appears from figure 3(b) that the elongation values at 2000° and 2500° F were greater for the tungsten - 1.5-percent-nickel - 1-percent-copper alloy than for either the tungsten - 0.3-percent-nickel - 0.2-percent-copper or the tungsten - 6-percent-nickel - 4-percent-copper composition.

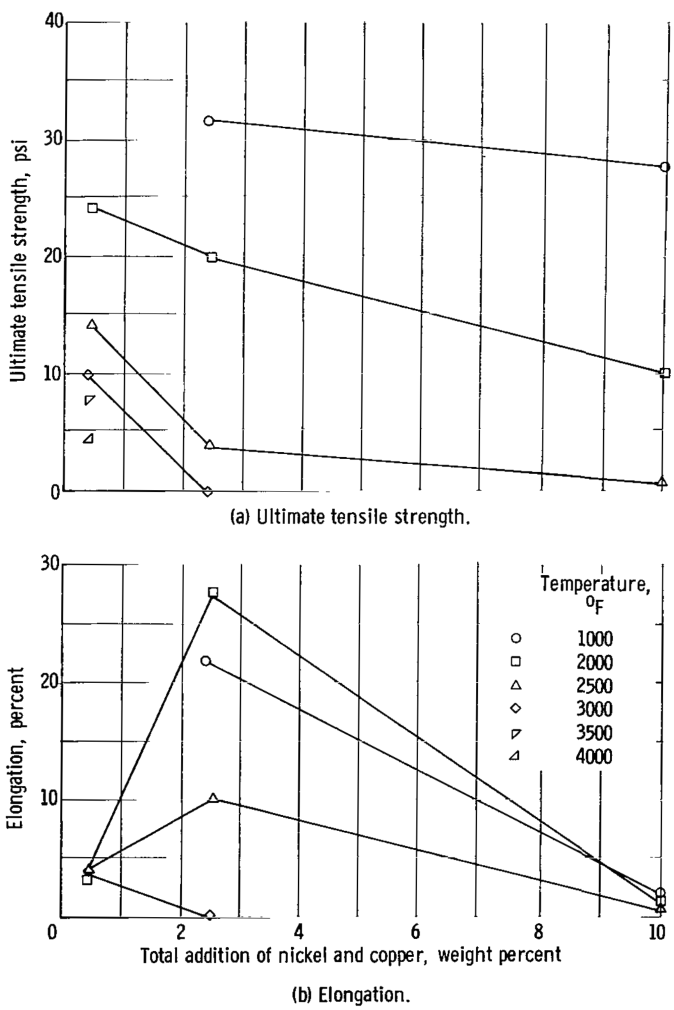
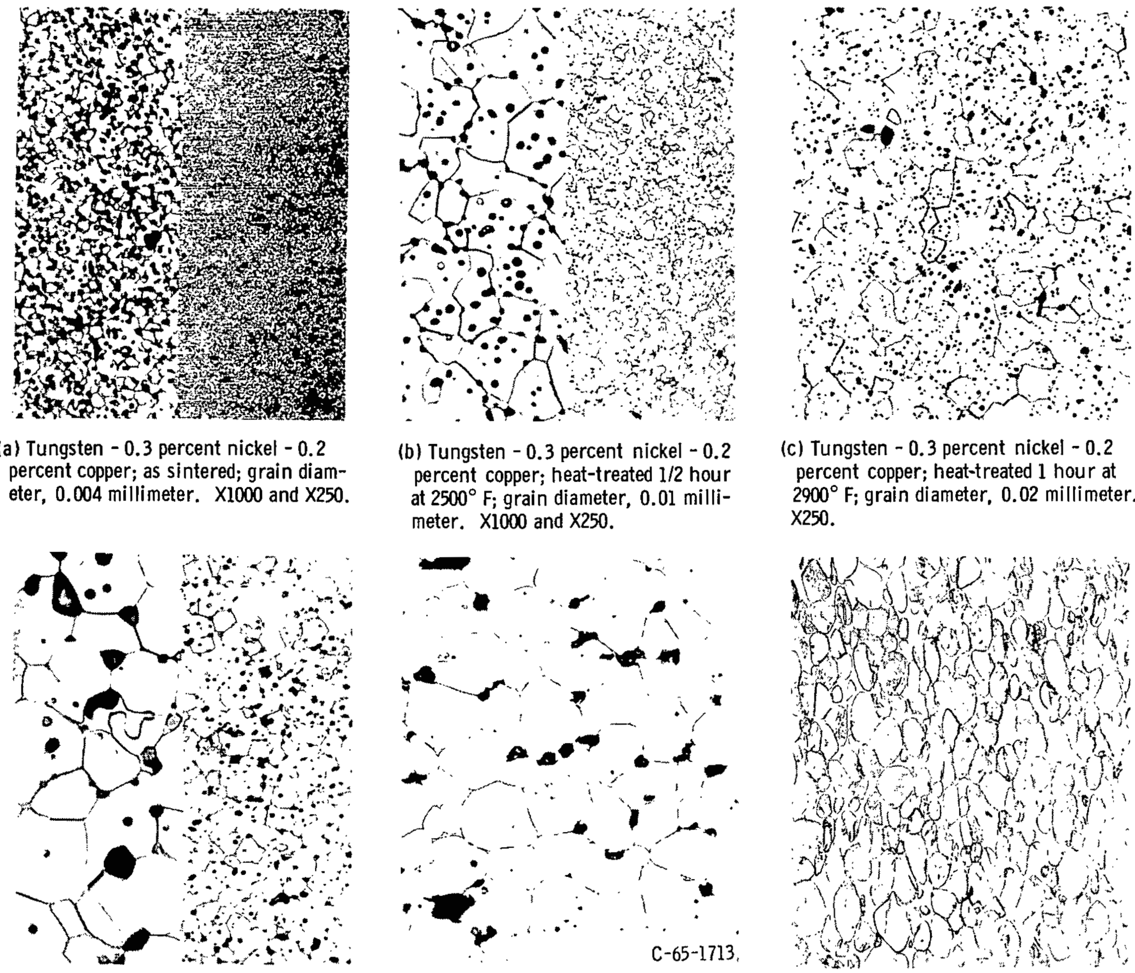


Figure 3. - Elevated-temperature properties of as-sintered alloys as function of percentage of nickel and copper.

Effects of rolling. - The tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy was rolled to a 50-percent reduction in thickness at temperatures close to 3000° F, in the heat-treated condition. Table III shows that the ultimate tensile strength of 77 300 pounds per square inch for the heat-treated and rolled material was much greater than the 23 000 pounds per square inch



(a) Tungsten - 0.3 percent nickel - 0.2 percent copper; as sintered; grain diameter, 0.004 millimeter. X1000 and X250.

(b) Tungsten - 0.3 percent nickel - 0.2 percent copper; heat-treated 1/2 hour at 2500° F; grain diameter, 0.01 millimeter. X1000 and X250.

(c) Tungsten - 0.3 percent nickel - 0.2 percent copper; heat-treated 1 hour at 2900° F; grain diameter, 0.02 millimeter. X250.

(d) Tungsten - 1.5 percent nickel - 1 percent copper; as sintered; grain diameter, 0.03 millimeter. X1000 and X250.

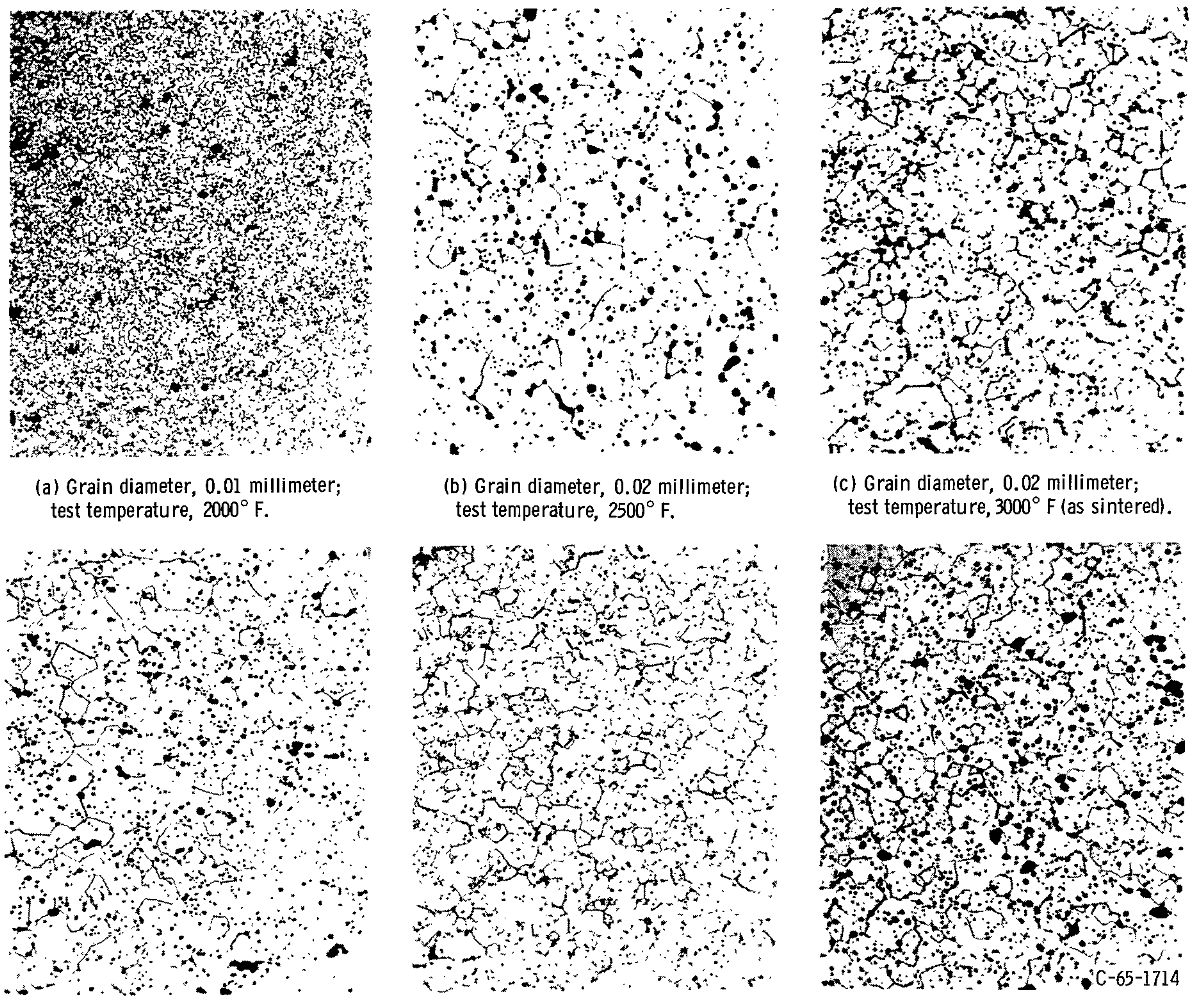
(e) Tungsten - 1.5 percent nickel - 1 percent copper; heat-treated 1 hour at 2900° F, grain diameter, 0.09 millimeter. X250.

(f) Tungsten - 6 percent nickel - 4 percent copper; as sintered; grain diameter, 0.03 millimeter. X250.

Figure 4. - Transverse microstructures of various as-sintered and heat-treated alloys. (Reduced 50 percent in printing.)

for the heat-treated alloy alone at room temperature. The elongation for the heat-treated and rolled alloy at room temperature was 12 percent, which can be compared to 9 percent for the heat-treated material before rolling.

Both the tungsten - 1.5-percent-nickel - 1-percent-copper and the tungsten - 6-percent-nickel - 4-percent-copper alloys could be rolled at temperatures near 2000° F in the as-sintered condition. The tungsten - 1.5-percent-nickel - 1-percent-copper alloy, however, could be reduced only 10 percent in thickness before developing severe edge cracks. A 50-percent reduction in thickness gave the tungsten - 6-percent-nickel - 4-percent-copper alloy a strength comparable to wrought, recrystallized tungsten at 1000° F, and it increased the elongation from 2.0 to 26.0 percent relative to the as-sintered material at this temperature (table III, p. 6).



(a) Grain diameter, 0.01 millimeter; test temperature, 2000° F.

(b) Grain diameter, 0.02 millimeter; test temperature, 2500° F.

(c) Grain diameter, 0.02 millimeter; test temperature, 3000° F (as sintered).

(d) Grain diameter, 0.02 millimeter; test temperature, 3000° F; heat-treated at 2500° F.

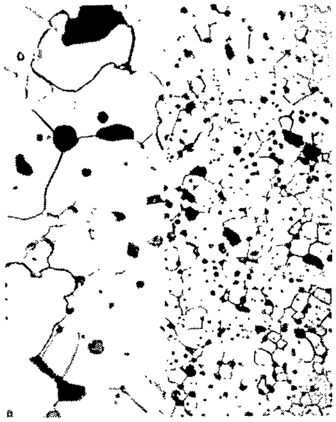
(e) Grain diameter, 0.02 millimeter; test temperature, 3500° F.

(f) Grain diameter, 0.02 millimeter; test temperature, 4000° F.

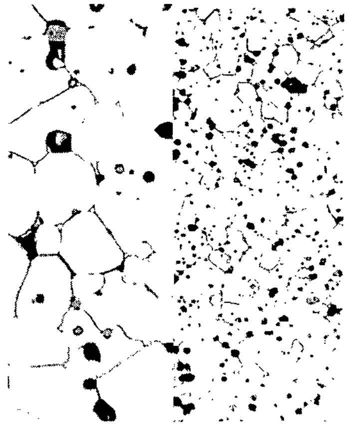
Figure 5. - Transverse microstructures of tungsten - 0.3 percent-nickel - 0.2-percent-copper alloy after tensile testing at temperatures from 2000° to 4000° F. X250. (Reduced 50 percent in printing.)

Microstructure

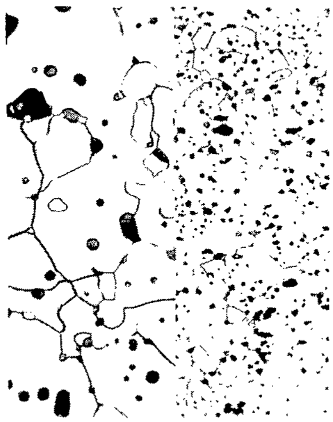
As-sintered. - The sintered microstructures are shown in figures 4(a), 4(d), and 4(f). For the sintered condition the grain diameter varied from 0.004 millimeter for the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy to 0.03 millimeter for the other two alloys. There was no perceptible grain-boundary film for the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy. The tungsten - 1.5-percent nickel - 1-percent-copper alloy showed a discontinuous grain-boundary film surrounding the tungsten grains, while the tungsten - 6-percent-nickel - 4-percent-copper alloy showed



(a) Grain diameter, 0.03 millimeter; test temperature, 1000° F.



(b) Grain diameter, 0.03 millimeter; test temperature, 2000° F.



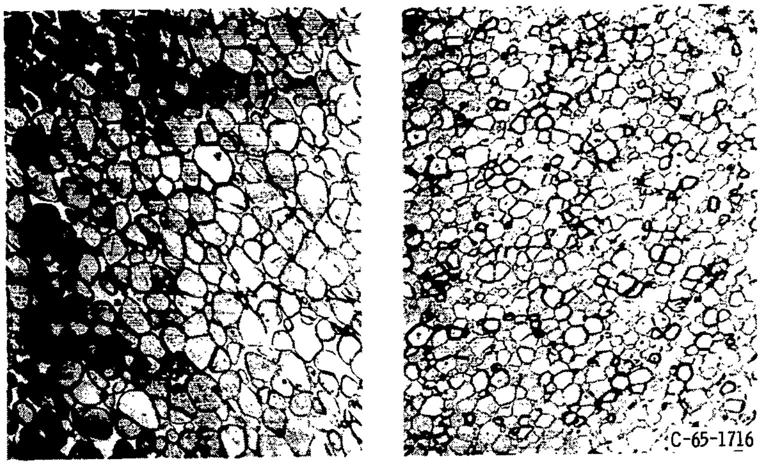
(c) Grain diameter, 0.03 millimeter; test temperature, 2500° F.

(d) Grain diameter, 0.03 millimeter; test temperature, 3000° F.

Figure 6. - Transverse microstructures of tungsten - 1.5-percent-nickel - 1-percent-copper alloy after tensile testing at temperatures from 1000° to 3000° F. X1000 and X250. (Reduced 50 percent in printing.)

a completely continuous grain-boundary film. The amount of porosity shown in figure 4 does not necessarily represent the porosity of the samples, but it does represent, at least in part, porosity which was exaggerated because of etching effects.

Heat-treated. - As-sintered and heat-treated microstructures appear in figures 4(b), 4(c), and 4(e). Heat treatment affected the grain sizes and the void shapes and distributions for the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloys as well as for the tungsten - 1.5-percent-nickel - 1-percent-copper alloys. Heat treatment of the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy at 2500° and 2900° F increased the grain diameter from 0.004 to 0.01 and 0.02 millimeter, respectively. At the same time, the void shape became progressively rounder and the distribution of voids became less concentrated at grain boundaries. Heat treatment of the tungsten - 1.5-percent-



(a) Grain diameter, 0.04 millimeter; as sintered.

(b) Grain diameter, 0.01 millimeter; rolled 50 percent RH.

Figure 7. - Transverse microstructures of tungsten - 6-percent-nickel - 4-percent-copper alloy after tensile testing at 1000° F. X250. (Reduced 50 percent in printing.)

nickel - 1-percent-copper alloy at 2900° F increased the grain diameter from 0.03 to 0.09 millimeter and lowered the residual porosity within the grain interiors. Considerable void growth occurred at grain-boundary junctions. A discontinuous grain-boundary film is clearly indicated for the tunsten - 1.5-percent-nickel - 1-percent-copper alloy following the 2900° F heat treatment.

After tensile testing. - The effect of the thermal treatments necessarily associated with elevated-temperature tensile testing helped to influence the concentration and distribution of the ternary phase. Evidence of this may be seen in figures 5 to 7. In addition, these microstructures show the effect of the thermal treatments on such parameters as grain size, void shape, and void distribution, as modified by the presence or absence of the ternary phase as well as its concentration. As mentioned previously regarding the sintered microstructures, the amount of porosity shown in figures 5 to 7 is not necessarily the amount of porosity found in the samples, but represents, at least in part, porosity which was exaggerated because of etching effects. Comparisons of relative amounts of porosity would still be valid, however, since etching would be expected to affect specimens in approximately the same way. As-sintered and heat-treated microstructures for the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy after tensile testing at temperatures from 2000° to 4000° F appear in figure 5. The grain diameter increased from 0.004 millimeter for the as-sintered condition to 0.01 millimeter during testing at 2000° F. The higher temperatures associated with tensile testing as-sintered material at 3500° and 4000° F did not result in additional grain growth beyond the 0.02-millimeter grain diameter obtained for 2500° F testing. There were, however, significant differences in void shape and distribution at 3500° F and in void shape at 4000° F. The microstructures showed fewer voids with irregular surfaces at the higher testing temperatures as well as more grain boundaries relatively free of interconnected porosity.

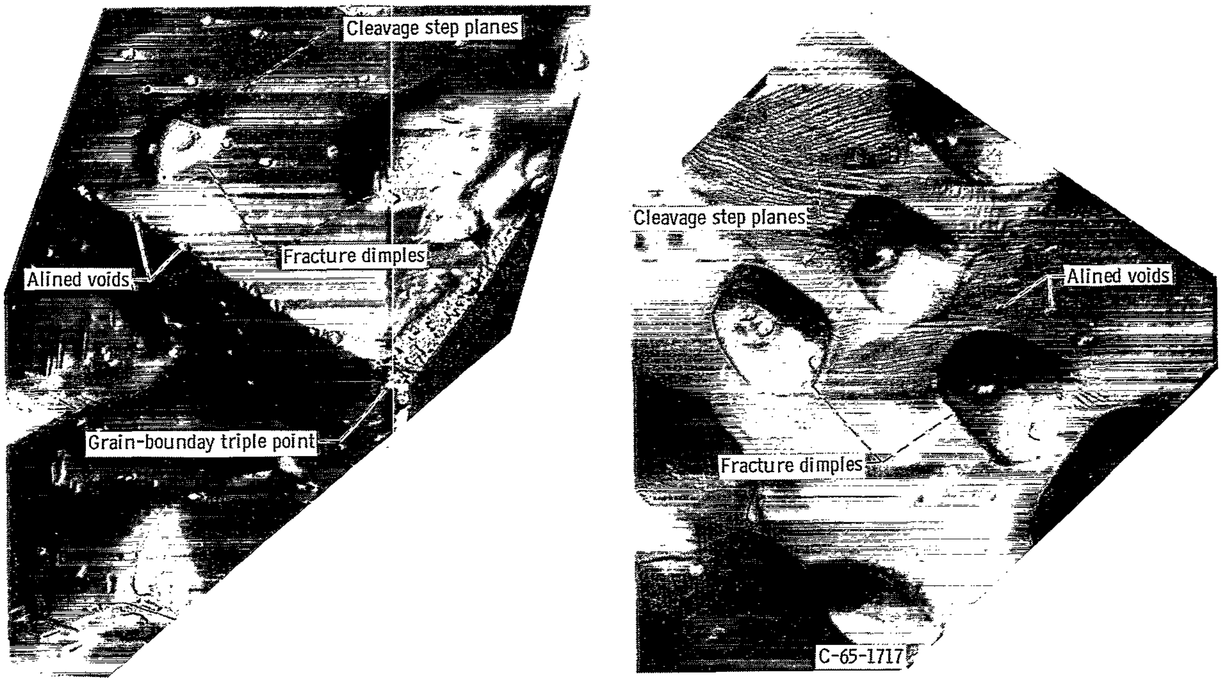
It appears that heat treatment prior to testing at 3000° F resulted in a microstructure similar to the microstructures obtained for the as-sintered specimens following the testing at 3500° and 4000° F. The sintered, heat-treated specimen following 3000° F tensile testing possessed a much rounder void shape; grain boundaries and grain-boundary junctions contained relatively fewer voids, especially those having sharp, irregular internal crevices. The increased ductility at 3000° F for the 2500° F heat-treated specimen was not connected with a difference in grain diameter between the as-sintered and the heat-treated specimens because both showed the same grain size.

Figure 6 shows the microstructures for tungsten - 1.5-percent-nickel - 1-percent-copper alloys in the as-sintered condition following tensile testing at temperatures from 1000° to 3000° F. No change in grain diameter occurred for this testing interval. There was, however, a progressive change in grain shape, void shape, and distribution of the ternary boundary phase as the testing temperature was raised. The grains and voids became gradually rounder and voids appeared to coalesce to make larger voids. The grain-boundary phase distribution changed from relatively isolated pockets (fig. 6(a)) to an almost continuous grain-boundary film (fig. 6(d)) as the testing temperature rose from 1000° to 3000° F.

Figure 7 shows a microstructure of the tungsten - 6-percent-nickel - 4-percent-copper alloy in the sintered and in the sintered and rolled conditions after tensile testing at 1000° F. Figure 7(b) reveals that the 50-percent reduction in thickness at 2000° F decreased the grain size. Only a few void areas were opened by the rolling operation, and these areas did not appear to be continuous from grain to grain along the grain boundaries. The 1000° F testing temperature did not completely remove signs of prior cold work.

Electron Microfractographs

Specimens of the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy, after tensile testing at 3000° F, appear in figure 8. The specimen shown in figure 8(a) did not receive a heat treatment prior to testing. The sample shown in figure 8(b) was reheated to 2500° F for 1/2 hour before testing. Both electron microfractographs reveal approximately symmetrical fracture dimples about 2 microns across the base, and small alined voids 0.25 micron in diameter separated by a distance of 1 micron. The lower right corner of figure 8(a) shows an example of grain-boundary sliding at a boundary triple point. There are significant differences in the number of dimples, the uniformity of their distribution, and the extent of development during testing for the heat-



(a) Not reheated prior to testing.

(b) Reheated to 2500° F for 1/2 hr before testing.

Figure 8. - Electron microfractographs of sintered tungsten - 0.3 percent-nickel - 0.2 percent-copper alloy after tensile testing at 3000° F in vacuum (5.0×10^{-5} torr). Cellulose acetate replication technique. X19 000. (Reduced 60 percent in printing.)

treated specimen and the as-sintered sample (compare figs 8(a) and (b). Both microfractographs show cleavage step planes about 0.05 micron (500 Å) long, but the degree of complexity of the interactions of these step planes is much greater for the heat-treated specimen.

DISCUSSION

A tungsten alloy, tungsten - 0.3-percent-nickel - 0.2-percent-copper, has been produced which combines low-temperature sinterability, very-high-temperature strength, and fabricability at temperatures practical for processing. The use of accelerated sintering alloy systems for making tungsten structural materials could considerably reduce the problems associated with the conventional very-high-temperature equipment necessary for both sintering and heattreating tungsten. For example, such a material might have an important application in the making of massive tungsten parts such as rocket nozzles.

Tensile Strength at Grain Boundaries of As-Sintered Materials

It is believed that the microstructural behavior and the mechanical property results observed can be rationalized on the basis of the presence or absence of the ternary phase and the pattern of its distribution in the microstructure. As shown in figures 4 to 7, there was no perceptible grain-boundary film for the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy, while the tungsten - 1.5-percent-nickel - 1-percent-copper alloy showed a discontinuous grain-boundary film surrounding the tungsten grains and the tungsten - 6-percent-nickel - 4-percent-copper showed a completely continuous film. It should be recalled that the as-sintered tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy had tensile strengths (table III, p. 6) comparable, at temperatures ranging from 3000° to 4000° F, to tungsten made by conventional melting or powder techniques. Tensile strengths were as much as 24 200 pounds per square inch at 2000° F, 10 000 pounds per square inch at 3000° F, and 4500 pounds per square inch at 4000° F. Such high strengths are an indication that the grain boundaries of the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy behaved as if they were no different from ordinary tungsten grain boundaries under the test conditions. Figure 5 gave no evidence of a grain-boundary film.

While the presence of the boundary film in the tungsten - 1.5-percent-nickel - 1-percent-copper and tungsten - 6-percent-nickel - 4-percent-copper alloys produced interesting microstructural changes, figure 1 (p. 7) makes it clear that these alloys had no useful strength at temperatures of 2500° F and higher. This loss of strength appears to be associated with the presence of the grain-boundary phases during tensile testing (figs. 6 and 7, pp. 11 and 12). On the other hand, the strengths were considerable at the lower temperatures of 1000° and 2000° F, being as much as 46 000 pounds per square inch at 1000° F for the rolled tungsten - 6-percent-nickel - 4-percent-copper alloy (table III, p. 6).

Grain Size and Grain Shape as Related to the Grain-Boundary Phases

The presence or absence of the grain-boundary phase resulted in important differences in grain size and grain shape. For the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy, it is believed that an essentially uniform solute distribution around the grain boundaries of this alloy restrained grain growth and resulted in the stabilized grain sizes observed at tensile testing temperatures of 2500° F and shown in figure 5 (p. 10). When the phase was present either in a discontinuous or a continuous fashion in the tungsten - 1.5-percent-nickel - 1-percent-copper and tungsten - 6-percent-nickel - 4-percent-copper alloys, respectively, preferential diffusion of tungsten through the ternary boundary film could occur for a period of time sufficient to bring about an increase in grain size (ref. 12). Figure 4 (p. 9) shows these relations for the sintered condition alone and for the as-sintered and heat-treated condition. It is interesting that the 2900° F heat treatment of the tungsten - 1.5-percent-nickel - 1-percent-copper alloy resulted in a microstructure more nearly resembling that of the tungsten - 6-percent-nickel - 4-percent-copper alloy after sintering at 2500° F, but possessing a significantly greater grain size, for example, 0.09 compared to 0.03 millimeter. The larger grain size is probably related to the larger equilibrium grain size associated with the higher temperature. The two higher nickel and copper content materials displayed grains which tended to have rounded contours, probably because of preferential atom transport from regions of high curvature to regions of low curvature in order to minimize surface energy. The tungsten - 1.5-percent-nickel - 1-percent-copper and tungsten - 6-percent-nickel - 4-percent-copper alloys displayed the effects of the enlarged grain size and rounded grain shape most clearly because the boundary phase was physically evident for all the thermal treatments investigated, as indicated by figures 4, 6, and 7 (pp. 9, 11, and 12).

Strength and Ductility of Rolled Materials

The fact that samples of the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy could be rolled on the first attempt, without an optimized rolling schedule, to a 50-percent reduction in thickness at temperatures around 3000° F in the heat-treated condition demonstrates that this alloy is fabricable by rolling, an indication of ductility. The mechanical property results appearing in table III (p. 6) for the heat-treated and heat-treated and worked materials at room temperature compare favorably with published data (ref. 13) for unalloyed tungsten. The room-temperature tensile strength of 23 000 pounds per square inch for the sintered and heat-treated tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy can be compared to 18 000 pounds per square inch (ref. 13) for conventional sintered tungsten. While a direct comparison is not possible, the strength of 77 300 pounds per square inch for the heat-treated and worked alloy compares favorably with a range of values for conventional worked tungsten in the same condition (refs. 11 and 13 to 15). A range of elongation from 9 to 12 percent for the experimental alloy may be compared to values from zero to 0.2 percent for conventional unalloyed tungsten sheet (ref. 16). The experimental elongations are apparently indicative of the ability of the material to rupture by an internal tearing process, since the percent reductions in area were approximately zero. The 4 T bend transition temperature of 275° F for the rolled tungsten - 0.3-percent-nickel - 0.2-percent copper alloy appears to lie on the low side of the normal range of values for unalloyed, worked tungsten sheet, 175° to 700° F (refs. 14 and 17), which gives further evidence that the ductility of the sintered and heat-treated tungsten - 0.3-percent-nickel - 0.2-percent-copper is good.

Good rollability at low temperatures of the tungsten - 6-percent-nickel - 4-percent-copper alloy material was probably due to the better distribution of working stresses brought about by the larger amount of ductile, second-phase material distributed around essentially pure tungsten grains. A more uniform distribution of working stresses would tend to minimize local stress concentrations sufficiently large to initiate fracture. Figure 7(b) indicates that the bond between the ternary boundary phase and the tungsten grains was strong enough to withstand the considerable stresses necessary to deform tungsten at low temperatures.

Effects of Heat Treatment on Ductility of Tungsten - 0.3-Percent-Nickel - 0.2-Percent-Copper Alloy

As noted previously, heat treatment produced some significant effects on microstructure and ductility for the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy tested at 3000° F. A difference in uniformity, of defects in general and voids in particular, could lead to the differences (described on p. 13) in the types of microstructure observed in the electron microfractographs (fig. 8, p. 14). In these microfractographs, it can be seen that internal necking (fig. 8(b)) occurred in the heat-treated structure during tensile testing at 3000° F, as opposed to the brittle, cleavage fracture that can be seen in the as-sintered specimen (fig. 8(a)). Internal necking occurs in a tensile test when the pattern of distribution of voids or inclusions is sufficiently uniform to allow local regional constriction to occur in a regular fashion across the area of a specimen. This is similar to the manner in which a bundle of wires would deform when stressed in uniaxial tension. Fracture by this process is often referred to as ductile rupture and is characterized by residual fracture dimples or microscopic projections in the microstructure.

The heat-treated specimen (fig. 8(b)) displayed well-developed fracture dimples. It appears that considerably more effective surface energy was absorbed by the specimen during deformation by ductile rupture because of the greater surface area involved in the fracture process. Figure 8(a) shows that the as-sintered specimen apparently fractured by cleavage, the initial crack being produced by grain-boundary sliding at a triple point. Both microfractographs show cleavage step planes about 0.05 micron long, but the degree of complexity of interactions of these step planes was much greater for the heat-treated specimen and corresponded to the greater amount of surface area involved in ductile rupture. The fact that no ternary phase could be observed in the microfractographs may be considered to be additional evidence that the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy is a solid solution.

CONCLUDING REMARKS

While it is generally accepted that tungsten can be sintered at low temperatures by utilizing certain additives such as iron, cobalt, and nickel, it has not been possible to combine low-temperature sintering behavior with elevated-temperature strength and ductility. The work presented in this report has provided an approach for practical utilization of tungsten systems displaying accelerated sintering behavior. The method employed in this study depends on selecting a third component which, in combination with the accelerating agent, decreases or eliminates the deleterious effect on mechanical properties of the accelerating agent. In practical terms, this will usually mean that the solubility of the accelerating agent in tungsten, or possibly other refractory metals, will be modified by an additional component so as to permit full and permanent solid solution of the accelerating agent at temperatures equal to or slightly higher than the sintering temperatures associated with a given two-component system.

Research into the tungsten - 0.3-percent-nickel - 0.2-percent-copper type alloy and similar alloys may facilitate the development of refractory metal materials suitable for high-temperature applications such as dispersion hardening and fiber reinforcement. For example, tungsten materials containing inert, insoluble dispersoids could possibly be prepared by powder-metallugy techniques at sintering temperatures sufficiently low to maintain ultrafine dispersions. This procedure would avoid the agglomeration and growth problems associated with the very high temperatures usually necessary for processing tungsten. Furthermore, the use of a tungsten alloy such as tungsten - 0.3 percent nickel - 0.2 percent copper for a matrix material in fiber composites could make possible very-high-temperature fiber composite materials, because the fibers could be incorporated into a very-high-temperature matrix at sufficiently low temperatures to avoid the loss of desirable fiber properties before the testing temperatures in question were reached. These possibilities are important ways such an alloy material might contribute to better engineering materials for conventional and space applications in addition to providing the inherent advantage of a fabricable, high-temperature tungsten base alloy which can be sintered at low temperatures.

SUMMARY OF RESULTS

From an investigation of tungsten-nickel-copper alloys for high-temperature applications the following results were obtained:

1. The tungsten - 0.3-percent-nickel - 0.2-percent-copper ternary alloy exhibited strength and ductility comparable to wrought, recrystallized powder-metallurgy or arc-cast tungsten at temperatures in the vicinity of 3000° to 4000° F, but did not sacrifice its capacity for sintering at temperatures as low as 2200° F.

2. The tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy showed elongation values comparable to values normally shown for recrystallized tungsten over the temperature interval from 3000° to 4000° F.

3. Heat treatment of the as-sintered tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy increased the elongation before fracture at 3000° F from 4.0 to 20.0 percent with little loss of strength.

4. In the heat-treated condition, the tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy could be rolled to a 50-percent reduction in thickness at temperatures close to 3000° F. The rolled tungsten - 0.3-percent-nickel - 0.2-percent-copper alloy 4 T bend transition temperature compared favorably with that of conventional unalloyed, worked tungsten sheet material.

5. The tungsten - 1.5-percent-nickel - 1-percent-copper and tungsten - 6-percent-nickel - 4-percent-copper alloys lost almost all their useful strength and elongation at 2500° F.

6. Both the tungsten - 1.5-percent-nickel - 1-percent-copper and tungsten - 6-percent-nickel - 4-percent-copper alloys could be rolled at temperatures of approximately 2000° F in the as-sintered condition.

7. Rolling the tungsten - 6-percent-nickel - 4-percent-copper alloy to a 50-percent reduction in thickness gave it a strength comparable to wrought, recrystallized tungsten at 1000° F and increased the elongation from 2.0 to 26.0 percent relative to the as-sintered material.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 30, 1965.

REFERENCES

1. Holtz, F. C.; and Van Thyne, R. J.: Development and Evaluation of High-Temperature Tungsten Alloys. Rept. No. ARF-2158-24, Armour Res. Foundation, Dec. 14, 1960.

2. Price, G. H. S.; Smithells, C. J.; and Williams, S. V.: Sintered Alloys: I - Copper-Nickel-Tungsten Alloys Sintered with a Liquid Phase Present. J. Inst. Metals, vol. 62, 1938, pp. 239-254; Discussion, pp. 254-264.

3. Vacek, J.: Über die Beeinflüssung des Sinterverhaltens von Wolfram. (Methods of Influencing the Sintering Behaviour of Tungsten.) Planseeber. Pulvermet., bd. 7, no. 1, 1959, pp. 6-17.

4. Holtz, F. C.; and Van Thyne, R. J.: Development and Evaluation of High-Temperature Tungsten Alloys. Rept. No. ARF-2158-12, Armour Res. Foundation, Nov. 12, 1959.

5. Prill, A. L.; Hayden, H. W.; and Brophy, J. H.: The Role of Phase Relationships in the Activated Sintering of Tungsten. Trans. AIME, vol. 230, June 1964, pp. 769-772.

6. Krock, Richard H.; and Shepard, Lawrence A.: Mechanical Behavior of the Two-Phase Composite, Tungsten-Nickel-Iron. Trans. AIME, vol. 227, Oct. 1963, pp. 1127-1134.

7. Sikora, Paul F.; and Hall, Robert W.: High-Temperature Tensile Properties of Wrought Sintered Tungsten. NASA TN D-79, 1959.

8. Hilliard, John E.: Estimating Grain Size by the Intercept Method. Metal Prog., vol. 85, no. 5, May 1964, pp. 99-102.

9. Taylor, J. L; and Boone, Donald H.: Tensile Properties of Tungsten from 2500° to 5400° F in Vacuum. ASM Trans., vol. 56, 1963, pp. 643-655.

10. Sikora, Paul F.; and Hall, Robert W.: Effect of Strain Rate on Mechanical Properties of Wrought Sintered Tungsten at Temperatures above 2500° F. NASA TN D-1094, 1961.

11. Pugh, J. W.: Tensile and Creep Properties of Tungsten at Elevated Temperatures. Proc. ASTM, vol. 57, 1957, pp. 906-916.

12. Mäkipirtte, Simo: On the Sintering of Tungsten-Nickel-Copper Heavy Metal. Powder Metallurgy, Intersci. Pub., 1961, pp. 97-111.

13. Lyman, Taylor, ed.: Metals Handbook. Vol. 1. ASM, 1961, p. 1226.

14. Anon.: Tungsten Sheet and Plate, Powder Metallurgy, Unalloyed. Product Data Sheet 1400-C, General Electric Co., Mar. 4, 1963.

15. Foyle, Fred A.; McDonald, Glen E.; and Saunders, Neal T.: Initial Investigation of Arc Melting and Extrusion of Tungsten. NASA TN D-269, 1960.

16. Sell, Heinz G.; Keith, George H.; Schnitzel, Randolph H.; and Cerulli, N. Francis: Physical Metallurgy of Tungsten and Tungsten Base Alloys. Rept. No. TR-60-37, Pt. IV, May 1963, p. 57.

17. Semchyshen, M.; and Perlmutter, I., eds.: Refractory Metals and Alloys. Vol. II. Intersci. Pub., Inc., 1963, p. 92.

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