NASA TECHNICAL MEMORANDUM

NASA TM X-52134

NASA TM X-52134

GPO PRICE $ ________

CFSTI PRICE(S) $ ________

Hard copy (HC) $1.00

Microfiche (MF) .50

ff 653 July 65

FACILITY FORM 602

N65-34250 (ACCESSION NUMBER)

(THRU)

22 (PAGES)

1 (CODE)

TMX-52134 (NASA CR OR TMX OR AD NUMBER)

17 (CATEGORY)

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Lewis Research Center
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TECHNICAL PREPRINT prepared for Fourth Symposium on Refractory Metals sponsored by the Refractory Metals Committee of the Institute of Metals Division of AIME, French Lick, Indiana, October 3-5, 1965

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION · WASHINGTON, D.C. · 1965

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E-3150

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INTRODUCTION

Recent studies have shown that the high-temperature strength of tungsten can be significantly increased by alloying; however, the lack of ductility in these materials at ambient temperatures remains a deterrent to their future use. Various approaches have been investigated in order to alleviate the ductility problem, including purification and alloying.

Consolidation by electron-beam (EB) melting has been shown to improve the purity with respect to trace metallics as compared to arc-melting or powder metallurgy techniques. The EB-melted unalloyed tungsten, however, does not possess improved low-temperature ductility (1) except in the form of fine wire (2).

The extraordinary effects of high rhenium additions (in the range 22 to 39 atom percent) in promoting low-temperature ductility in tungsten, molybdenum, and chromium are well known (3, 4), although a satisfactory description of the mechanism of this effect has not yet evolved. The observation of a significant decrease in hardness (8 to 10 percent) on adding about 5 percent rhenium to tungsten has prompted several studies to determine if improved ductility could be achieved in these less costly, dilute tungsten-rhenium alloys. Pugh et al.(5) have demonstrated that this is indeed the case with fine wire of doped tungsten made by powder metallurgy techniques. In a previous study, the authors (6) observed room temperature bend ductility in worked sheet fabrication from EB-melted tungsten alloys containing 2.1 and 6.6 percent rhenium.

In view of the desirability of improving the low-temperature ductility of tungsten, the previous limited study by the authors on tungsten-rhenium alloys was extended. The purpose of the present study was to determine the extent of the ductility improvement and to characterize the effects of composition and melting method on the ductility and other properties of the alloys (7).

EXPERIMENTAL PROCEDURES

Materials

The starting materials for this study consisted of -325-mesh commercially pure (undoped) tungsten powder and -200-mesh commercially pure rhenium powder. Electrodes were compacted from the blended powders, sintered at 4100° F, and consolidated either by triple EB-melting or by arc-melting. The ingots were $2\frac{1}{2}$ in. in diameter and ranged from about 4 to 8 in. in length.

The compositions selected for study included eight EB-melted and five arc-melted dilute alloys containing from 1.00 to 9.05 percent rhenium. In addition, an EB-melted W-24.0 Re alloy and an arc-melted commercial W-25.6 Re alloy were included in this study for comparison with the dilute alloys. All alloys were within the single-phase tungsten-rich region of the tungsten-rhenium phase diagram (7). Analyses of the alloys are given in Table 1.

Fabrication

The ingots were machined into billets measuring about 2 in. in diameter by 4 in. long and were canned in 3/8-in. wall molybdenum. The billets were extruded in a hydraulic extrusion press at temperatures ranging from 3200° to 4200° F. Fourteen billets were obtained from the nine EB-melted alloys. Nine of these were extruded into sheet bar, while the other five EB billets and all five arc-melted billets were extruded to rounds. The reduction ratios were 6:1 or 8:1. The extrusions were fabricated to 0.03- to 0.05-in. sheets and 0.35-in. rod by rolling and swaging in the temperature range 1750° to 2700° F.

Evaluation

Bend test specimens measured 0.3 by 0.9 in. or 0.5 by 2 in. Most of the specimens were electropolished in a 2 percent aqueous solution of NaOH to remove 3 to 5 mils of metal per side before bend testing. Heat treating of the specimens prior to bend testing was conducted in an induction-heated hydrogen atmosphere tube furnace (1800° to 3200° F) or a resistance-heated vacuum furnace (3400° to 4200° F). Bend tests were performed at a crosshead speed of 1 in./min over a bend radius of 4 times the specimen thickness.

Sheet and/or rod tensile specimens were machined from each alloy to study the high-temperature tensile and creep properties.

Sheet specimens had a 0.25-in.-wide by 1-in.-long reduced section, while rod specimens were machined with a 0.16-in.-diameter by 1.03-in.-long reduced section.

Tensile tests at 3000° and 3500° F were conducted in an Instron Universal Testing Machine equipped with a water-cooled stainless-steel vacuum unit (1×10^{-5} torr) and a tantalum sleeve heater. Crosshead speed was 0.05-in./min.

Step-load creep tests were conducted at 3500° F in a conventional beam-load unit equipped with a vacuum shell and tantalum heater similar to that used for tensile testing. Specimen extensions were measured from loading rod movement.

RESULTS AND DISCUSSION

Ductile-Brittle Bend Transition Behavior

Effects of composition. - The bend transition temperatures determined for the EB-melted and arc-melted alloys as rolled and after annealing at 3000° and 3600° F are summarized in Figures 1 to 3. A more extensive compilation of these data is given elsewhere (8).

It is apparent that dilute rhenium alloying effects a significant improvement in low-temperature ductility, particularly in the worked condition. The alloys prepared by EB-melting were outstanding in this respect. The EB-melted W-1.85 percent Re alloy showed a transition temperature of -75° F as rolled, a 310° F improvement over unalloyed tungsten (1). The low transition temperature in the worked condition is particularly significant, since it suggests that damage during handling can be reduced and that some slow forming operations on this material could be conducted at ambient temperatures.

Outstanding ductility was also exhibited by the as rolled EB-melted W-9.05 Re alloy, with a transition temperature of -100° F.

The intermediate alloys, containing 2.47 to 6.51 percent Re were slightly less ductile, with transition temperatures ranging between 25° and -25° F. It is believed that the ductility of these as rolled alloys is significantly affected by cleaning and rolling conditions and resulting structures, as will be discussed in more detail in a later section. The very low transition temperatures of -75° and -100° F may represent the best ductilities obtainable in this composition range, while the higher transition temperatures are likely associated with less than optimum structures or cleaning procedures.

In comparison to the EB-melted alloys, the arc-melted alloys were less ductile, with transition temperatures ranging between 50° and 280° F. This compares with a transition temperature of 215° F for unalloyed arc-melted tungsten (9). Considerable scatter was also observed in the transition temperatures for the as rolled arc-melted alloys.

The high-rhenium alloys showed excellent ductility in the as rolled condition, as expected. The bend transition temperature of the EB-melted W-24.0 Re alloy, $<-275^{\circ}$ F, was lower than that of the worked (as received) arc-melted W-25.6 Re alloy, -150° F.

Rhenium alloying is also effective in improving the ductility of fully recrystallized materials, as shown in Figures 2 and 3.

These data indicate that, for materials annealed at 3000° F, rhenium progressively improves the ductility, which is similar to the behavior observed for the as rolled alloys (Fig. 1). After annealing at 3600° F, minima in the transition temperature-composition curves were observed at about 2 percent rhenium for the EB-melted alloys and about 4 percent rhenium for the arc-melted alloys. At slightly higher rhenium levels the transition temperatures for the EB-melted alloys are higher than those for unalloyed tungsten. The recrystallized arc-melted alloys have slightly lower transition temperatures than the EB-melted alloys.

The high-rhenium alloys, which deform initially by twinning in the recrystallized condition, were only slightly more ductile than the dilute alloys (which deform entirely by slip) after annealing at 3600° F. Their transition temperatures were 350° and 375° F compared to minima of 375° and 425° F for the dilute alloys.

Purity and grain size appear responsible for the differences in ductility between the EB-melted and arc-melted alloys. In the worked condition the better ductility of the EB-melted alloys is attributed to their higher purities. Although the analytical data in Table 1 indicate little difference in either interstitial or metallic impurity contents between the EB-melted and arc-melted alloys (with the exception of iron), it has been shown earlier (1) that unalloyed EB-melted tungsten is lower in metallic impurities than arc-melted tungsten. Further, the grain sizes of the EB-melted alloys after annealing at 3600° F were larger than those of the arc-melted alloys, indicating higher grain growth rates and strongly suggesting higher purity.

In the annealed condition, the finer grain size of the arc-melted alloys apparently contributes to their slightly better ductilities at 3600° F. As evidenced by the differences in ductility between EB-melted materials annealed at 3000° and 3600° F, the ductility of the W-Re alloys appears to be affected by grain size, or at least annealing temperature, to a greater extent than unalloyed tungsten.

Representative microstructures of selected alloys after bending are shown in Figure 4. Figure 4(a) illustrates crack propagation in a worked W-2.47 Re specimen bent to fracture just below the transition temperature. A crack has encountered a plane of weakness in the sheet and temporarily changed its direction of propagation from transverse to longitudinal. This behavior produces the fibrous- or laminated-type of fracture characteristic also of worked unalloyed tungsten.

In Figure 4(b), a transverse crack in a fully recrystallized specimen of W-2.78 Re is propagating partly intergranularly and partly transgranularly. Fractographic studies have indicated that the mode of crack propagation is about 50 percent transgranular in these alloys (10). This is in contrast to unalloyed recrystallized tungsten, which fractures almost entirely intergranularly.

The structure of a recrystallized specimen of W-24.0 Re adjacent to the fracture is shown in Figure 4(c). This specimen exhibits profuse twinning, characteristic of the high-rhenium alloys

Effects of fabrication variables. - The effects of rolling temperature, in-process anneals, salt-bath cleaning, pack rolling, and specimen size on the ductile-brittle transition temperature in the as rolled condition were evaluated.

Rolling temperatures between 1750° and 2600° F were studied on the EB-melted alloys containing 2.47, 4.47, 4.70, and 6.51 percent Re. Rolling at 2200° F may increase the transition temperature slightly as compared to rolling at 2000° F or lower The W-4.70 Re alloy, however, had a much higher transition temperature after rolling at 2600° F (175° F) than after rolling at 2000° F (-75° F). There was no discernible microstructural difference between the two sheets. This observation is in accord with previous studies on unalloyed tungsten (11), which indicated that lower transition temperatures were associated with lower final rolling temperatures.

The effects of in-process stress-relief anneals of 1/2 hr at 2200° F were investigated on the EB-melted W-2.74 Re alloy. These data, which were obtained on 0.03- by 0.5- by 2.0-in. specimens indicated no detectable effect of in-process stress-relief annealing, although the scatter in the data for the straight-rolled materials would mask any stress-relieving effect of 50° F or less on the transition temperature.

The effects of frequent salt-bath cleaning during rolling may be significant. The EB-melted alloys containing 1.85, 4.70, 9.05, and 24.0 percent rhenium were cleaned and conditioned three times during rolling, while the alloys containing 2.47, 2.78, 4.47, and 6.51 percent rhenium were conditioned once during rolling and cleaned only after final rolling. All four of the frequently cleaned alloys exhibited exceptionally low bend transition temperatures in the as rolled condition. These ranged from -75° to -100° F for the dilute alloys to less than -275° F for the W-24.0 percent rhenium alloy. In comparison, the alloys which were conditioned only once during rolling had transition temperatures between +25° and -25° F. Thus, the maintenance of a clean surface during rolling, which likely reduces subsurface contamination, appears to be quite beneficial to the subsequent ductility.

It is also noted that the transition temperatures were generally best in the as rolled condition and tended to increase slightly on stress-relief annealing after final rolling, possibly from dissolution of surface impurities during annealing.

Pack rolling was briefly evaluated on the W-1.85 Re alloy in order to reduce possible lamination associated with light reductions during final rolling and resultant inhomogeneous residual stress distributions through the sheet. Pack rolling of a single W-Re alloy sheet at 1800° F from 0.06 to 0.03 in. thick between 0.06-in. molybdenum sheets produced an alloy sheet which was free from detectable laminations. However, the pack-rolled sheet exhibited a transition temperature of 175° F as rolled, compared with -75° F for the straight-rolled sheet. Thus, although pack rolling should effect a more uniform residual stress distribution through the sheet, it appeared to raise rather than lower the ductile-brittle transition temperature under the conditions investigated.

The effects of specimen size and surface preparation were evaluated on sheet of W-2.78 Re. The bend transition temperatures for electropolished specimens measuring 0.5- by 2.0-in. ranged from approximately 50° to -50° F after rolling at temperatures from 2000° to 2600° F. After annealing at 3600° F, the bend transition temperatures ranged from 400° to 500° F. These transition temperatures are almost identical with those determined for 0.3- by 0.9-in. specimens, 0° F as rolled and 450° F after a 3600° F anneal. These data indicate no detectable effect of specimen width and length in the ranges investigated.

Data were also obtained on W-2.78 Re specimens in the unpolished condition. These specimens were cut from a sheet which had been salt-bath cleaned only after final rolling. The edges were lightly deburred with emery paper prior to testing. The transition temperature as rolled was 50° F, compared to 0° F for electropolish specimens from the same sheet. This indicates that electropolishing decreases the bend transition temperature by about 50° F.

A substantial increase in bend transition temperature occurred on stress-relief annealing the as cleaned material at 1800° and 2000° F. The transition temperatures of 550° and 650° F compare with values of 75° and -25° F, respectively, for similar sheet which was electropolished to remove about 3 mils per side after annealing at the same temperatures. It appears likely that surface impurities diffused into the specimen during annealing and produced a shallow case which was prone to cracking. This case can be removed by electropolishing. It is evident that care must be exercised in the stress-relief annealing of the sheet, preferably by removing the surface layer after annealing, such as by electropolishing.

High-Temperature Tensile Properties

Tensile properties were studied on both EB-melted and arc-melted materials at 3000° and 3500° F after annealing for 1 hr at 3600° F. The strength data are shown in Figure 5.

Rhenium is a moderate strengthener for tungsten at these temperatures, being less effective than additions such as hafnium, tantalum, or columbium (6). The strength increases with increasing rhenium content to at least 9 percent, typical of a substitutional addition having an extensive solubility range. The improvement at 3500° F is about 130 percent for EB-melted alloys, as illustrated in Figure 5. The EB-melted alloys are 2000 to 3000 psi weaker than the arc-melted alloys at 3500° F, reflecting the larger grain sizes and higher purities.

The high-rhenium alloys exhibit several unusual deformation characteristics at elevated temperatures. The elongations of the EB-melted W-24.0 Re alloy and the arc-melted W-25.6 Re alloy at 3500° F were 110 and 119 percent, higher than those of the dilute alloys (31 to 106 percent).

A second significant observation is low work hardening in the high-rhenium alloys at 3500° F. Unalloyed tungsten and the dilute W-Re alloys exhibit normal stress-strain curves, while the W-24.0 Re alloy exhibits a sharp decrease in stress (about 8 percent) immediately after yielding, with no evidence of subsequent work hardening.

These observations, together with the fact that the alloy compositions are close to the solubility limit for rhenium in tungsten, suggest that this behavior may be related to a strain-induced structural change in the alloy.

A more complete study of the unusual behavior of these alloys, however, was beyond the scope of the present study.

High-Temperature Creep Behavior

The creep behavior of EB-melted and arc-melted tungsten-rhenium alloys was studied by step-load creep tests at 3500° F.

The strength at a steady creep rate of 10^{-6} sec^{-1} was interpolated from stress-creep rate plots and shown in Figure 6 as a function of rhenium content. This creep rate corresponds approximately to a rupture life of 50 hr. Additions of rhenium up to 6 to 8 percent are seen to increase the creep strength of tungsten by about 70 percent, or approximately half the increase observed in short-time tensile testing. However, the high-rhenium alloys, containing 24.0 and 25.6 percent rhenium, are considerably weaker than the dilute alloys, having approximately the same strength as unalloyed tungsten at 3500° F. This is in contrast to the behavior during short-time tensile testing, where the high-rhenium alloys had almost the same strength as the dilute alloys, both being considerably stronger than unalloyed tungsten. This behavior suggests that dislocation climb, assumed to control the creep rate at this temperature, is more rapid in these alloys than in the stronger dilute tungsten-rhenium alloys.

CONCLUSIONS

The major conclusions from this study are as follows:

1. Sheet fabricated from electron-beam-melted (EB-melted) tungsten alloys containing 1.85 to 9.05 percent rhenium exhibit ductile-brittle bend transition temperatures in the worked condition as low as -75° to -100° F, compared to +200 F for unalloyed tungsten (electropolished). Sheet fabricated from similar

arc-melted alloys was less ductile, with bend transition temperatures of 50° to 280° F. This difference suggests that the improved ductility may be related, in part, to the higher purity achieved by EB melting.

2. Important fabrication variables include cleanliness during rolling and rolling temperature. The best ductilities were obtained on sheet cleaned several times during rolling at temperatures of 1750° to 2400° F. Stress-relief annealing during or after rolling had little effect on ductility.

3. Annealing at 3600° F significantly increased the ductile-brittle bend transition temperatures of both EB-melted and arc-melted alloys. Transition temperatures of about 400° F were observed for alloys containing 2 to 4 percent rhenium. High-rhenium alloys containing 24.0 and 25.6 percent rhenium had transition temperatures of 350° to 375° F after similar annealing treatments.

4. Rhenium additions up to 9.05 percent strengthen tungsten at elevated temperatures in both short-time tensile and long-time creep. The alloys with 24.0 and 25.6 percent rhenium have similar tensile strengths to the 9.05 percent rhenium alloy, but in creep are considerably weaker, with strength approximating that of unalloyed tungsten.

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TABLE I. - ANALYSES OF MATERIALS

Rhenium content, wt %	Impurity content, ppm								Ingot hardness, VHN
	O	N	C	Al	Fe	Mo	Si	Ta	
Electron-beam-meter alloys									
1.85	10	<3	4	----	----	--	----	---	370
2.47	2	<5	5	----	----	--	----	---	326
2.78	5	<3	5	0.02	0.14	53	0.3	45	323
3.55	2	<3	3	----	----	--	----	---	322
4.47	3	<5	2	----	----	--	----	---	314
4.70	4	<3	4	.01	.2	77	.2	5	312
6.51	5	<5	8	----	----	--	----	---	297
9.05	1	<3	4	.1	.5	95	.2	2	314
24.0	8	<3	4	----	----	--	----	---	417
Arc-melted alloys									
1.00	3	5	3	0.06	1.6	31	0.3	100	366
1.96	2	5	4	----	----	--	----	---	345
3.04	2	9	2	.05	1.8	39	.2	24	353
5.06	3	46	7	.03	6.1	16	.2	81	313
6.82	12	<5	3	.1	1.2	48	.3	33	307
*25.6	28	29	44	<10	17	78	<20	---	---

*Supplier's analysis.

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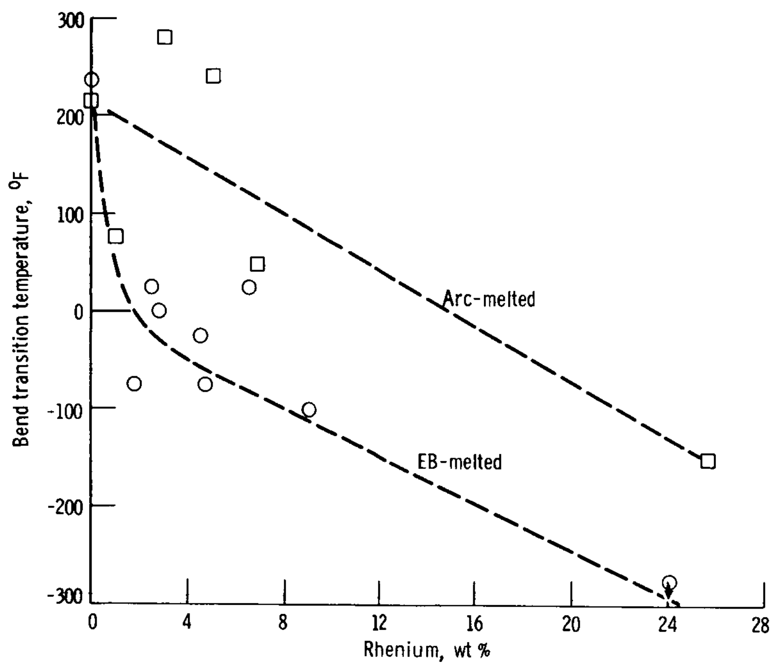

Figure 1. - Bend transition temperatures for as rolled tungsten-rhenium alloys.

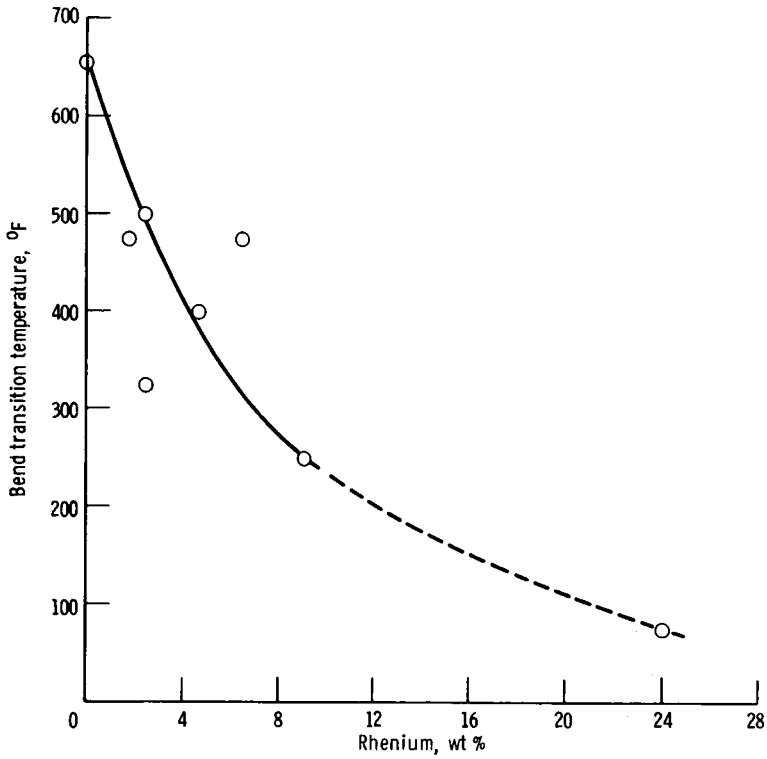

Figure 2. - Bend transition temperatures of EB-melted tungsten-rhenium alloys after annealing for 1 hr at 3000° F.

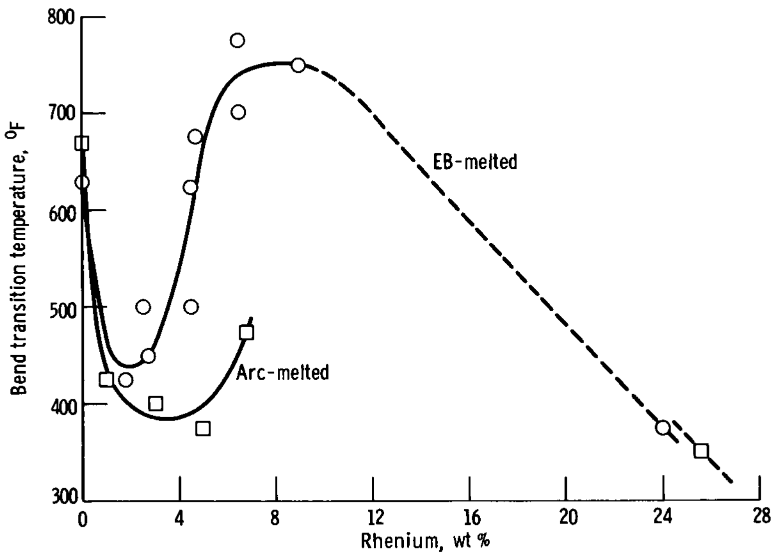

Figure 3. - Bend transition temperature of tungsten-rhenium alloys after annealing for 1 hr at 3600° F.

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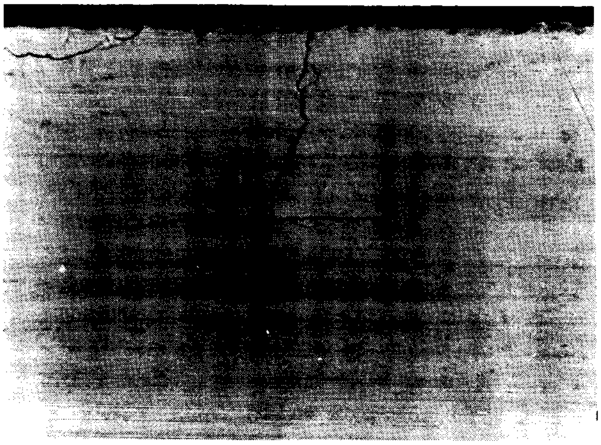
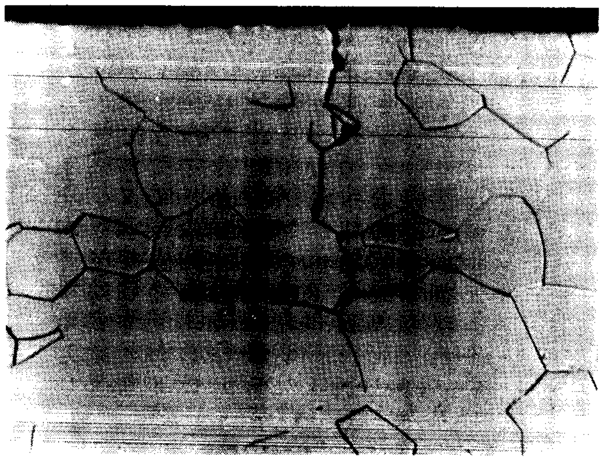


(a) W-2.47Re, rolled at 1750° F and annealed at 2200° F and bent to fracture at 25° F. Note that direction of crack propagation changed from transverse to longitudinal.



(b) W-2.78Re, annealed at 3600° F and bent to fracture at 400° F. Note transverse crack near final bend fracture.

(c) W-24.0Re, annealed at 3600° F and bent to fracture at 300° F. Note heavily twinned structure associated with cold deformation in bend area.

Figure 4. - Representative microstructures of EB-melted tungsten-rhenium alloys; X150. (Reduced 20 percent in printing.)

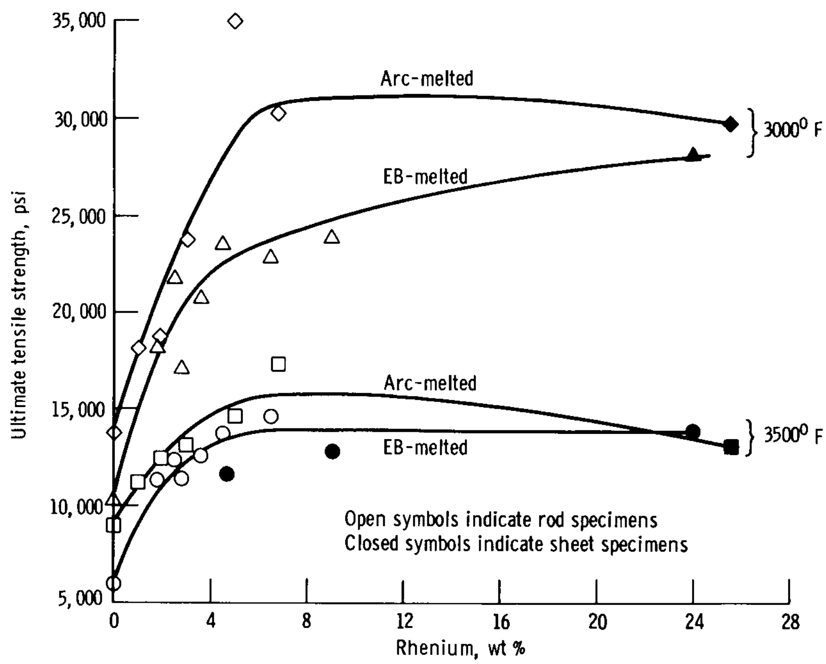


Figure 5. - Tensile strength of EB-melted and arc-melted tungsten and tungsten-rhenium alloys at 3000° and 3500° F, annealed for 1 hr at 3600° F prior to testing.

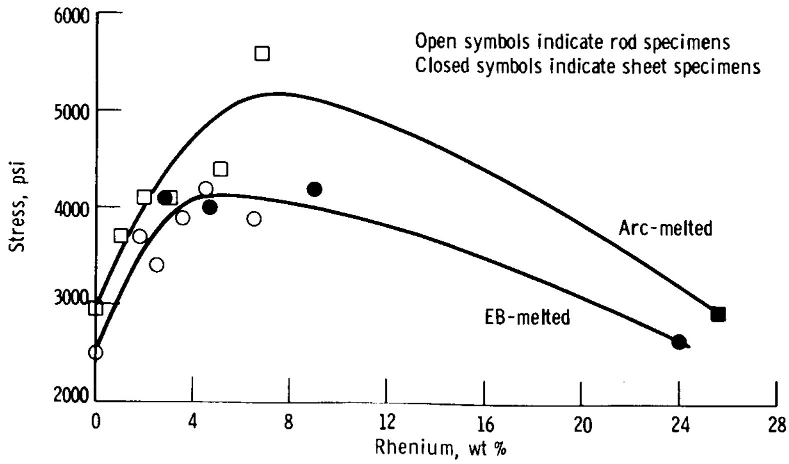


Figure 6. - Effect of rhenium on the 3500° F strength of tungsten-rhenium alloys at a steady creep rate of 10^{-6} sec^{-1} (corresponding approximately to a rupture life of 50 hr).