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The Rhenium Effect in Sintered Tungsten-Molybdenum-Base Alloys

by

W. H. Lenz

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THE RHENIUM EFFECT IN SINTERED TUNGSTEN-MOLYBDENUM-BASE ALLOYS

W. H. Lenz and R. E. Riley

ABSTRACT

A brittleness test developed at the Los Alamos Scientific Laboratory (LASL) made it possible to quantitatively measure the limited ductility of sintered tungsten-base alloys. Subsequently, numerous sintered tungsten-molybdenum-rhenium compositions were evaluated to establish alloys which combined room-temperature ductility with a melting point above 2900°C. Ductility trends of the alloys were related to sintering temperature, molybdenum and rhenium content, and ThO_2 additive. The fusion temperatures of 18 alloys were determined.

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1. INTRODUCTION

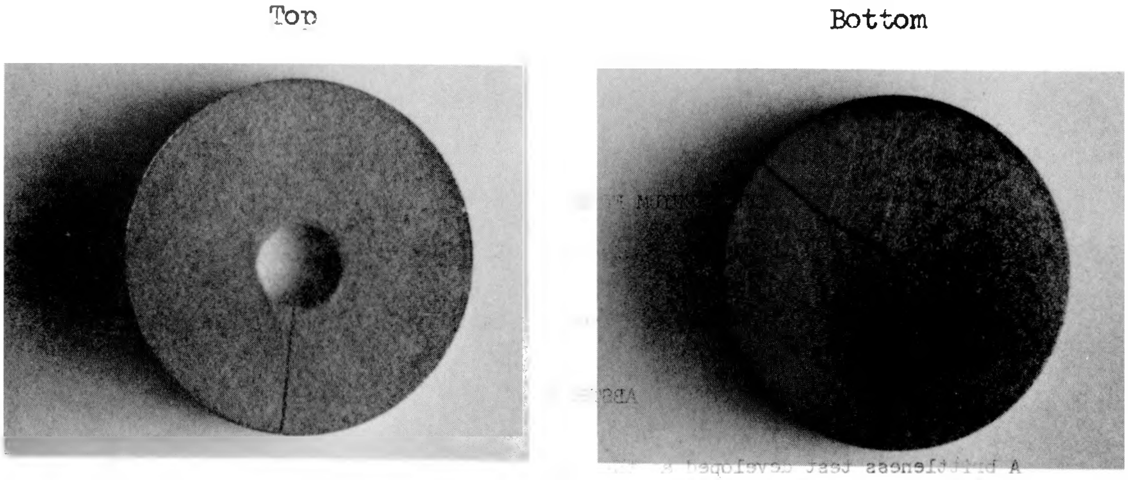
The Los Alamos Scientific Laboratory (LASL) has been concerned with the application of refractory materials at extremely high temperatures for many years. Tungsten, with the highest melting point of all metals, is subject to room-temperature brittleness particularly after high-temperature exposure. Tantalum was eliminated because of its incompatibility with hydrogen at moderate temperatures. The metals with the next highest melting points are osmium and rhenium. Both of these materials are scarce and expensive, and osmium is very brittle. Molybdenum is more ductile than tungsten; however, it melts at 2610°C, which is lower than the 2900°C minimum arbitrarily chosen for this investigation. Therefore, it appeared that the alloy systems most suitable for meeting the minimal melting point requirement and improving the ductility over that of pure tungsten were the W-Re and W-Mo-Re systems.

Most refractory metal properties are usually cited in the wrought condition; however, the powder metallurgy approach is indispensible in some cases. Therefore, the properties in the sintered condition may be important and critical. No previous attempts to establish ranges of room-temperature ductility in sintered tungsten-base alloys were known and melting-point data for tungsten, molybdenum and rhenium were meager. It was our intention to find sintered alloys based on the W-Mo-Re system that combined room-temperature ductility (or plasticity) with melting points in excess of 2900°C. In doing this, the rhenium content was to be as low as possible.

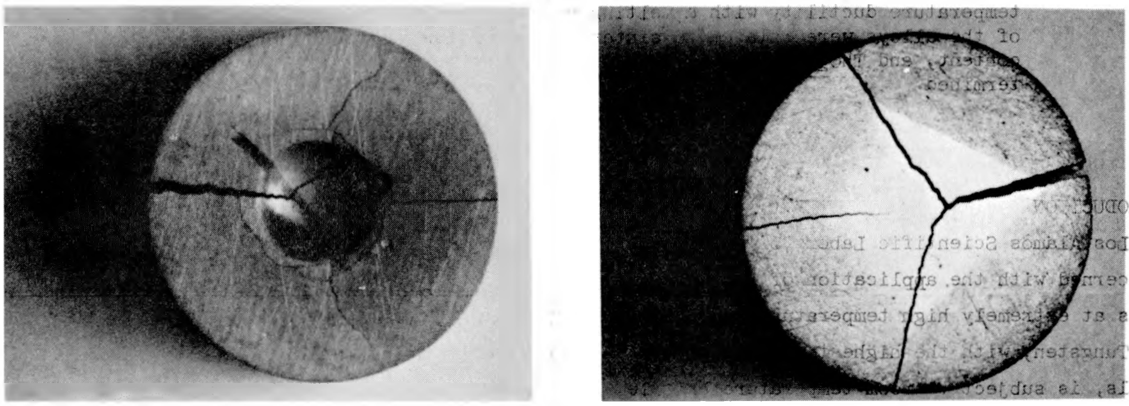
Part of the work of this report has been published.[1] Consolidation techniques in this field are well known and were presented in earlier reports on tungsten-base alloys and cermets.[2] Under certain conditions, the Kirkendall effect will cause inferior sintering in W-Mo-Re alloys formed from elemental powders. These problems are discussed in an associated report.[3]

2. THE DUCTILITY TEST

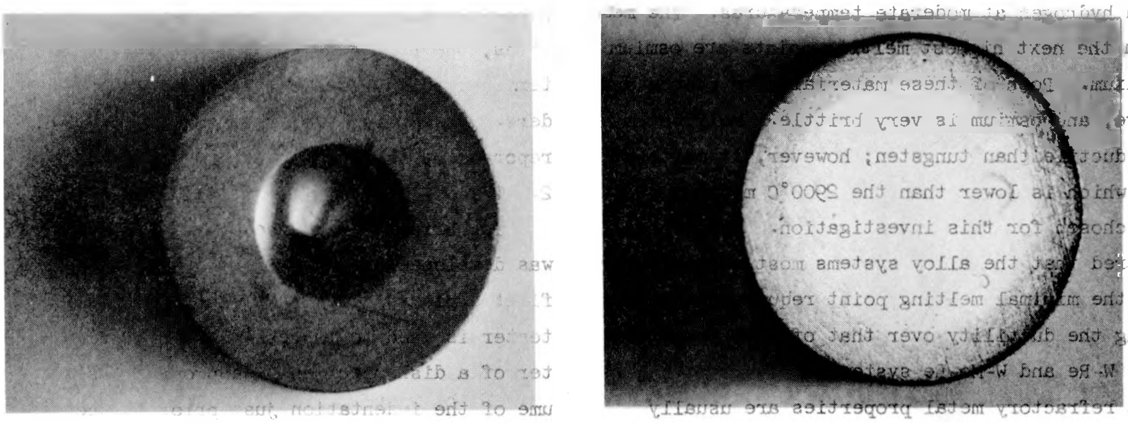
The Brinell brittleness test[4] used in this work was developed about the time that W-Re alloys were first explored at LASL. Briefly, a Brinell hardness tester is used to impress a 10-mm ball into the center of a disk specimen of appropriate size. The volume of the indentation just prior to specimen failure is used as a measure of the ductility. Since this volume is very nearly proportional to the indentation diameter, d, taken to the fourth power, the value, d^4, where d is measured in millimeters, is called the ductility number. Figure 1 shows the appearance of three different alloy specimens at widely differing ductility levels.



Spec. A, 585-kg load, 2.15 mm indentation, ductility No. 21



Spec. B, 1310-kg load, 3.15 mm indentation, ductility No. 97



Spec. C, 3000-kg load, 4.30 mm indentation, ductility No. 344

Fig. 1. Appearance of tungsten-molybdenum-rhenium disks of different ductility levels after the brittleness test. 5X.

The Brinell test was first evaluated on sintered tantalum and W-Re alloys where a wide range of ductility was available. With the sintered W-Re alloys, only a slight ductility effect was noted below 15 at. % rhenium (Fig. 2), but there was a pronounced improvement at 20 at. % rhenium with a peak in ductility occurring at about 25 at. % rhenium. The curve represents the average ductility values of tungsten with 0, 10, 15, 20, 25, and 28 at. % rhenium. Two or more tests were made for each composition after sintering for 3 h in dry hydrogen at 1700°C, plus 1 h in vacuum at 1900°C. Bend tests performed elsewhere on wrought W-Re alloys showed a similar trend of ductility with composition.[5]

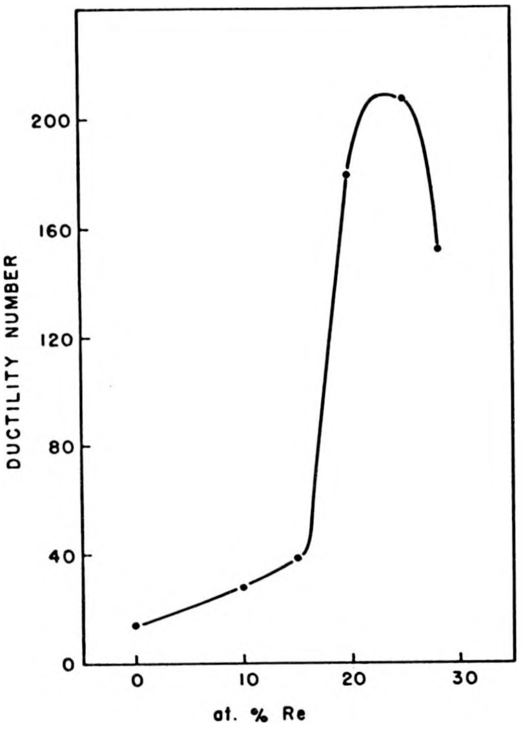


Fig. 2. Ductility of sintered W-Re alloys determined by the Brinell test.

3. INVESTIGATION OF W-Mo ALLOYS CONTAINING RHENIUM

3.1 Preliminary Compositions

Initially, W-Mo alloys of 20, 40, 60, and 80 at. % molybdenum were investigated. Rhenium additions were made to the 40-60 and 60-40 at. % tungsten-molybdenum powder blends. The actual compositions in weight and atomic percent are shown in Table I. Also presented in Table I are the sintered densities and ductility values after the 1700°C sintering treatment.

TABLE I

COMPOSITION, DENSITY, AND DUCTILITY DATA ON W-Mo AND W-Mo-Re ALLOYS

Alloy Composition[a]								
Atomic %			Weight %			% of Theor Density[b]	No. Disks Tested	Average Ductility Number
W	Mo	Re	W	Mo	Re			
80.0	20.0		88.3	11.7		91.7	2	13
60.0	40.0		74.0	26.0		93.4	3	17
55.6	36.8	7.6	66.7	23.4	9.9	89.0	5	175
53.1	35.4	11.6	63.0	22.1	14.9	87.8	2	209
50.7	33.7	15.7	59.2	20.8	20.0	86.4	3	243
40.0	60.0		55.8	44.2		95.6	3	92
37.4	55.8	6.7	50.3	39.8	9.9	91.7	5	179
35.9	53.8	10.3	47.5	37.6	14.9	89.9	3	259
34.5	51.4	14.1	44.7	35.3	20.0	88.3	3	291
20.0	80.0		32.1	67.9		96.6	5	206

[a] The 60-40 and 40-60 wt% tun-sten-molybdenum ratios were maintained in the two series containing 10, 15, and 20 wt% rhenium.

[b] Compacted at 100 tsi, 0.410-in. die and sintered 3 h at 1700°C in hydrogen.

For the compositions without rhenium, there was a considerable increase in room-temperature ductility as the composition changed from tungsten-rich to molybdenum-rich, especially above 60 at. % molybdenum. The rhenium additions show a marked increase in ductility with increasing rhenium content over that of the base compositions investigated. Furthermore, rhenium additions of 15 at. % and less were quite effective in W-Mo alloys, where they were nearly ineffective with the tungsten alone (Fig. 2).

3.2 W-Mo Alloys with 0, 7, 12, and 17 at. % Rhenium

In view of the above promising results, new alloy powder was blended to cover the entire tungsten-molybdenum range at 10 at. % intervals. We realized that the rhenium content should be expressed as atomic percent to maintain an equitable relationship over a broad range of compositions. Therefore, additions of 7, 12, and 17 at. % rhenium (roughly comparable to the 6.7 to 15.7 at. % rhenium additions of Table I) were made to certain of the tungsten-molybdenum-base compositions. The 0.410-in.-diam disks were compacted at 100 tsi. Sintering of the various compositions was similar to the previous experiment, except that most of the compositions were also given an additional sintering treatment at 1950°C for 2 h in vacuum to ensure better diffusion in the higher Re alloys. The composition, density, and average ductility of these alloys are presented in Table II.

Figure 3 shows the effect of the additional sintering treatment at 1950°C over that of the 1700°C sinter for the W-Mo binary alloys, which resulted in grain growth and lower ductility. Although consid-

TABLE II

DENSITY AND DUCTILITY OF SINTERED W-Mo ALLOYS

WITH 0, 7, 12, AND 17 AT. % RHENIUM

Composition, at. %			% of Theor Density		Av Ductility Value	
W-Mo Base						
W	Mo	Re	Sint[a] 1700°C	Sint[b] 1950°C	Sint[a] 1700°C	Sint[b] 1950°C
100	0	0	91.3	94.7		5
90	10	0	93.2	95.0	7	5
80	20	0	91.8	93.3	10	7
70	30	0	93.8	94.8	7	10
60	40	0	93.5	94.3	12	10
50	50	0	95.7	93.6	40	20
40	60	0	95.6	95.3	90	30
30	70	0	97.0	95.0	95	48
20	80	0	96.6	96.1	215	115
10	90	0	96.1	96.7	220	145
0	100	0	95.1	97.2	685	260
100	0	7	90.8	95.1		30
70	30	7	89.9	91.4		75
50	50	7	91.0	91.0		156
0	100	7	92.5	93.4		570
100	0	12	90.8	94.5	94	57
90	10	12	89.6	92.6	124	78
70	30	12	88.7	89.4	177	215
50	50	12	88.8	89.2	220	197
30	70	12	89.8	89.8	285	320[c]
10	90	12	90.2	90.4		500
0	100	12	91.6	92.7		590[c]
100	0	17	89.5	94.0		132
70	30	17	87.6	88.8		250
50	50	17	87.8	88.2		285[c]
30	70	17	88.4	88.1		410[c]
0	100	17	88.0	88.8		550[c]

[a] Condition A: Sintered 3 h at 1700°C in H_2.

[b] Condition B: Same as Condition A plus 2 h at 1950°C in vacuum.

[c] One or more specimens survived full 3000-kg load.

erable scatter was encountered on the molybdenum-rich side of the W-Mo binary alloys, the average values produced a smooth curve. It is again evident that the ductilizing effect of molybdenum additions is very weak in the tungsten-rich region, but becomes much stronger above 50 at. % molybdenum.

Figure 3 also shows the effect of rhenium additions on the ductility of selected tungsten-molybdenum-base compositions. The ductility curve of the 12 at. % rhenium compositions, after the 1700°C sinter, agrees with the ductility values of similar compositions previously listed in Table I. The additional 1950°C sintering treatment lowered ductility by approximately 50 points for the tungsten-rich 12 at. % rhenium alloys, but not for those rich in molybdenum.

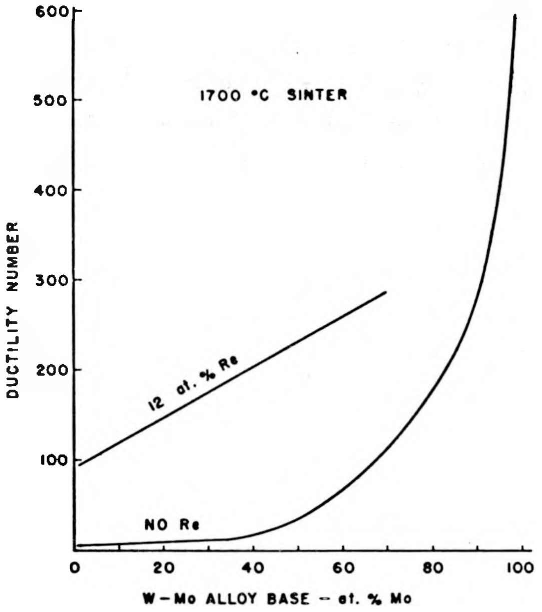


Fig. 3a. 1700°C sinter.

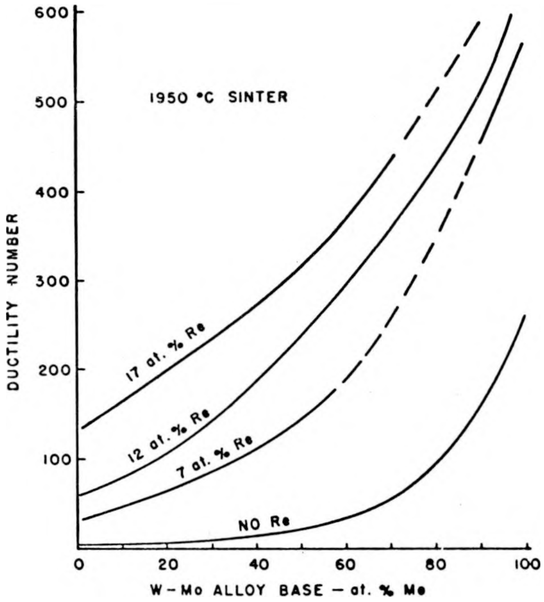


Fig. 3b. 1950°C sinter.

Fig. 3. Ductility of various tungsten-molybdenum-base alloys for two sintering treatments.

In general, the tungsten-molybdenum-rhenium curves of Fig. 3 show this trend for the 1950°C treatment, tending to sweep upward in the molybdenum-rich region. Thus, the combined effect of increasing rhenium and molybdenum is to resist grain-growth and grain-size embrittlement. In this region, the ductility values of the 17 at. % rhenium curve may actually be higher than shown, because the molybdenum-rich specimens did not break at maximum load. At all rhenium levels, however, the ductility improvement over the tungsten- or tungsten-molybdenum base compositions is substantial.

3.3 Sintering W-Mo-Re Alloys Above 1950°C

Based on these results and from the viewpoint of higher sintering temperatures, it appeared that the tungsten-rich region with 20-30 at. % molybdenum should be explored further, and that the effect of low rhenium contents on the 50-70 at. % Mo alloys should be determined. New powder mixtures were made for the compositions involved and all of the disks were presintered at 1700°C for 3 h in hydrogen. After the ductility for the 1700°C treatment was determined, the remainder of the specimens were sintered at 2340°C for 0.5 h in vacuum.

The ductility-test results on specimens given these treatments are shown in Table III. The average values for ductility of these samples were plotted in Fig. 4. In every case, the 7 and 12 at. % rhenium alloys show only about half as much ductility for the samples sintered additionally at 2340°C as compared with identical specimens given just the 1700°C sintering treatment. The 17 at. % rhenium curves, however, again represent minimum values because most of the specimens did not fail under full test load. Also, there was greater resistance to embrittlement for the 2340°C treatment than with the 7 and 12 at. % Re alloys.

TABLE III

DUCTILITY OF VARIOUS W-Mo-Re ALLOYS AFTER SINTERING AT 1700 AND 2340°C

Composition: Ratio At. % W	Composition: Ratio At. % Mo	At. % Re Added	Av Ductility Number (d^4) 1700°C: No. of Tests	1700°C: d^4	2340°C[b]: No. of Tests	2340°C[b]: d^4
80	20	12	2	157	2	80
70	30	12	2	155	2	100
70	30	17	2 1	235 156[c]	2 2	230[d] 99[c]
50	50	7	3	180	3	93
50	50	12	3	230	3	155
50	50	17	2 1	310[d] 178[c]	2 2	296[d] 135[c]
30	70	7	3	311	3	137

[a] 3 h at 1700°C in dry H_2.

[b] Same as [a] plus 1/2 h at 2340°C in vacuum.

[c] Specimens reduced to 0.320-in diam to ensure failure below 3000-kg load limit.

[d] One or both specimens survived the 3000-kg maximum load.

The above experiment was partially repeated using a different set of powders. The compositions ranged from 20 to 50 at. % molybdenum in 10% increments with 0, 7, and 12 at. % rhenium. The powders used were 1.7-μm tungsten, 3.7-μm molybdenum, and 1.35-μm Fisher average particle size (APS) and all specimens were pressed at 60 tsi. The essential sintering and ductility test data are presented in Table IV. Figure 5 shows that the usual trends were realized and that the ductility values for the rhenium-containing alloys are similar to those of Fig. 4 for the same compositions.

3.4 Metallography

The effect of rhenium on the ductility of tungsten and molybdenum appears to originate at the atomic structural level (perhaps affecting both lattice and grain boundary conditions) so it is not surprising that metallography does little to explain the various ductility relationships in the alloys with the exception of embrittlement accompanying grain growth. All of the described binary and ternary alloys consist of a single phase when adequately sintered. With the nominal 2-μm powders used for this work, some larger particles such as 20-μm were sometimes present. The sintering treatments below 2340°C often homogenized the W-Mo binary alloys, but usually yielded finer grains and some undissolved rhenium in the ternary alloys. Sintering at higher temperatures, to ensure complete solution of the rhenium, promoted grain growth and usually lowered the ductility; thus, the grain-size effect usually overcame the ductilizing effect of previously undissolved rhenium. A decrease in density usually accompanied an increase in rhenium content regardless of the sintering conditions.[3]

Metallographic structure typical of the alloys so far presented in this report are shown in Fig. 6. The progress of solid solution formation and grain growth with increasing sintering temperature is evident in both the binary and ternary alloys. The use of finer powders would hasten the diffusion process,

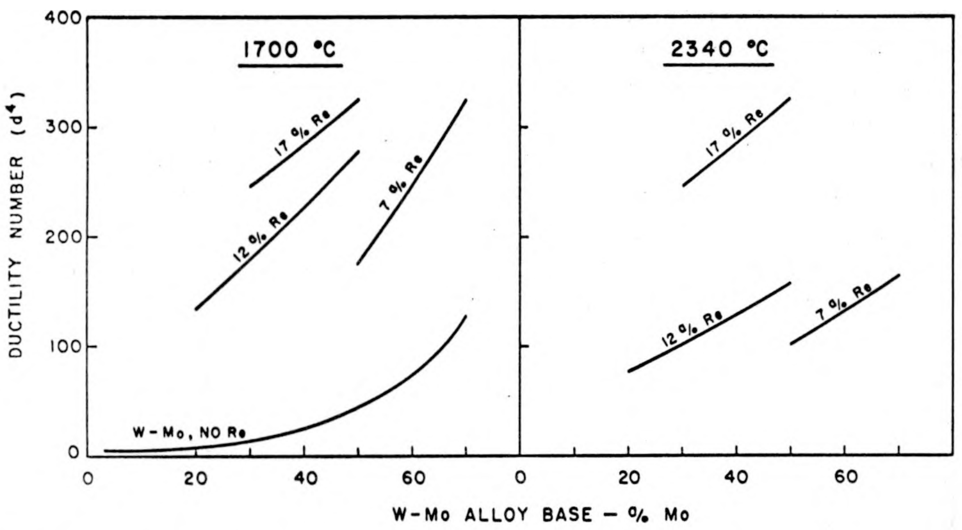


Fig. 4. Effect of sintering temperature on several W-Mo alloys with various rhenium contents.

TABLE IV

ADDITIONAL DUCTILITY DATA
ON VARIOUS W-Mo-Re ALLOYS

Composition, At. %		Av Ductility[a]	
W-Mo Ratio	Re	3 h, H_2 1700°C	1/2 h, Vac 2340°C
80-20	0	17	9
	7	127	17
	12	143	42
70-30	0	21	10
	7	136	25
	12	186	54
60-40	0	66	15
	7	172	41
	12	256	120
50-50	0	127	15
	7	414	94
	12	367	195

[a] Three or more tests for each value.

but might be worse from the standpoint of oxygen pickup on the higher surface area of the powders.

4. ATTEMPTS TO IMPROVE THE RHENIUM EFFECT

While most of this work covers the ductilizing effect of rhenium, other factors also influence ductility. The effect of rhenium on the ductility of tungsten and molybdenum has been attributed to the fact that the rhenium has more free electrons than the tungsten and molybdenum atoms.[6] This theory made us think that the same results might be accomplished with other metals of Group VII and VIII elements. Most of these metals can be eliminated for various reasons, i.e., high vapor pressure (manganese), insolubility in tungsten and molybdenum (iron group and most of both Groups VII and VIII), extreme scarcity (technetium, rhenium, iridium), or by prior knowledge regarding negative effects (iron group, platinum, palladium, ruthenium).

4.1 Ruthenium and Osmium Additions

Some of the platinum group metals of Group VIII show theoretical promise, but these are nuclearly more undesirable than rhenium. However, it was decided to try ruthenium because it is nuclearly more compatible than rhenium, and osmium because it was known to be soluble in tungsten; furthermore, both of these metals have relatively high melting points. Also, the effect in a tungsten-molybdenum-rhenium base might be better than in tungsten or molybdenum.

The effects of ruthenium and osmium were evaluated by adding approximately 1.5 at. % of these elements to a 70-30 at. % ratio W-Mo alloy containing 12 at. % rhenium. The sintering treatments and properties of these disks, which were limited in number, are shown in Table V.

The ruthenium addition increased the density and hardness as sintered, but embrittled the alloy. The osmium addition increased the hardness, but otherwise appeared neutral; i.e., it did not change the measured ductility values as compared with the alloy containing no osmium. There is no metallographic

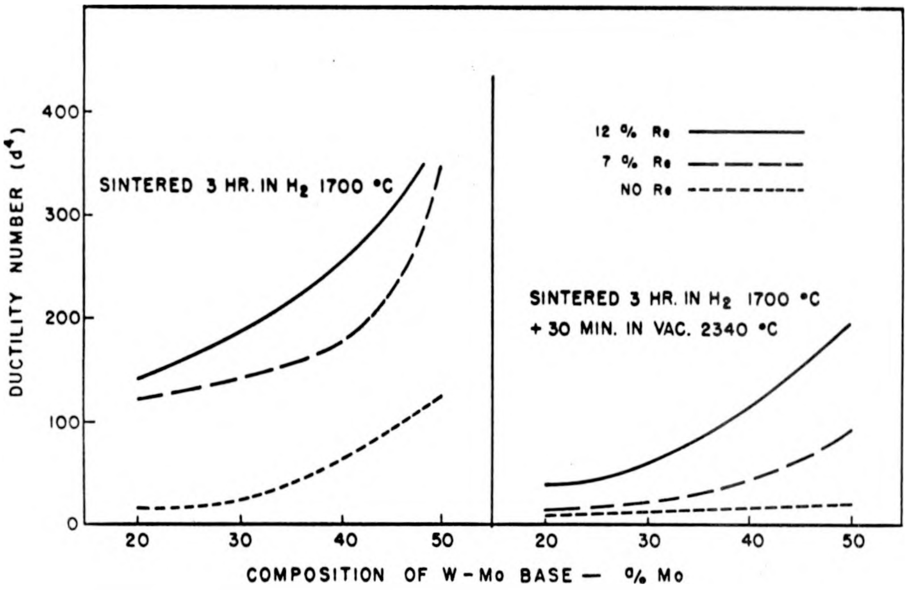


Fig. 5. Effect of sintering temperature on alloys of Table IV.

explanation for the embrittlement by the ruthenium, since both the ruthenium and osmium appear to have gone into solid solution. Of the two, should additional work be justified, osmium seems more favorable for further trials, but it has very undesirable nuclear properties.

4.2 Effect of Dispersed ThO_2

Another factor known to affect the ductility of refractory metals was the addition of a grain-growth inhibitor. Table VI shows the data on ductility of 70-30 at. % W-Mo base alloys with 7 and 12 at. % rhenium as affected by sintering temperature, atmosphere, and the addition of 1.5 or 3.0 wt% submicron ThO_2 ball-milled into the metal powders. Also shown is a 70-30 wt% W-Mo alloy with 20 at. % rhenium. In addition to the usual 1700 and 2340°C sintering treatments in dry H_2, samples from all five of these compositions were treated at 1700°C for 3 h in wet hydrogen to learn something about their response to increased oxygen content. It was assumed that some oxygen was added to the alloys from this atmosphere, which caused a trend toward even lower ductility than was obtained after the 2340°C sintering treatment in vacuum. Typical microstructures for these alloys are shown in Fig. 7.

If Table VI is viewed in its entirety, it will be seen that,

a. The ductility increases with the rhenium content following the initial dry-hydrogen sintering at 1700°C.

b. The ThO_2, by lowering the sintered density after the initial 1700°C stage, has a double effect in also reducing continuity of the alloy matrix, and ductility is thereby reduced.

c. At the 2340°C stage, higher rhenium tends to reduce the loss of ductility caused by grain growth.

d. By restricting grain growth, ThO_2 at 2340°C has a similar effect, especially evident with the 12 at. % rhenium alloy.

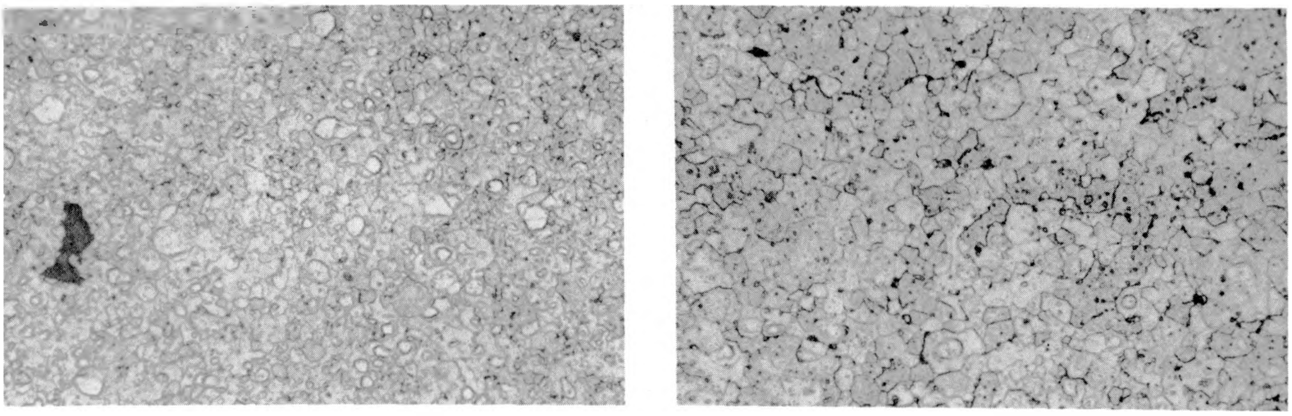
e. The higher rhenium content alloys and those with ThO_2 tend to retain more ductility after the wet-hydrogen treatment; and

f. At the 20 at. % rhenium level, it appears that the embrittling effects of high temperature (grain growth) and wet-hydrogen (oxidation) are overcome.

5. DISCUSSION OF THE RHENIUM EFFECT

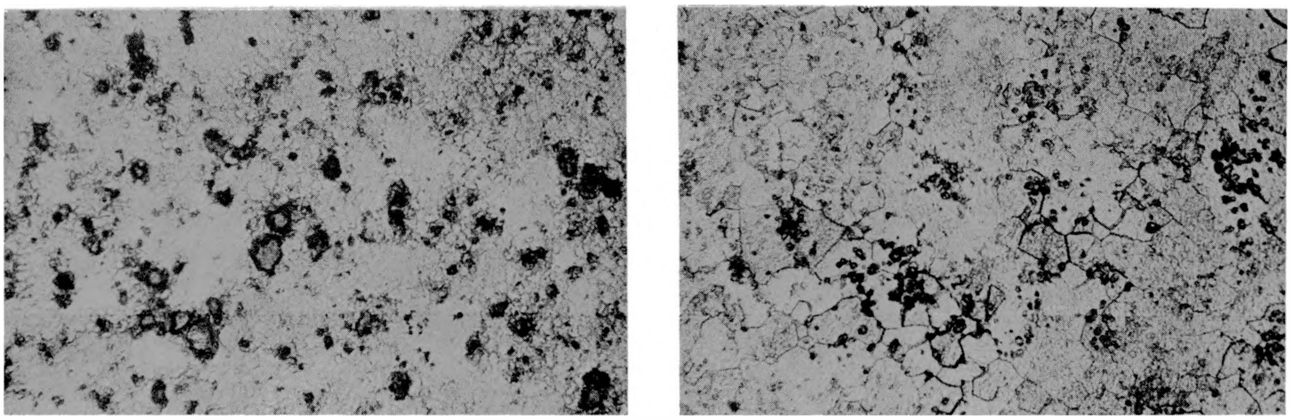
Although some highly impressive theories of the rhenium effect were advanced in recent years,[5,7] some of these explanations were contradictory and none were conclusive or above criticism. Still more recently, some of the same sources have agreed that the fundamental reasons for the rhenium effect are elusive, and that no good explanation exists.[8]

By avoiding the basic field of atoms and electrons, however, and by considering the properties of



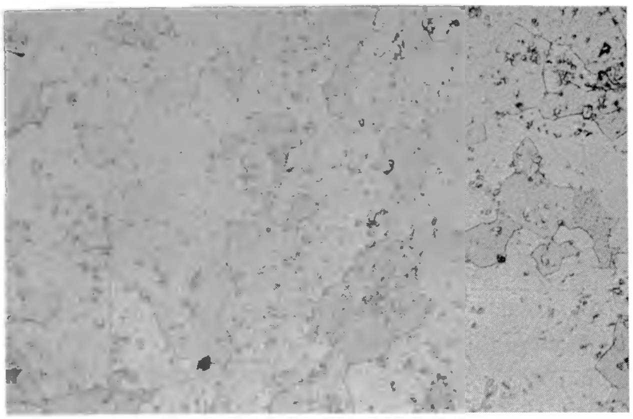
(a) 60-40 at. % W-Mo powder mixture sintered 3 h in H_2 at 1700°C. (250X).

(b) 60-40 at. % W-Mo powder mixture sintered same as (a) plus 2 h in vacuum at 1950°C. (250X).



(c) 50-50 at. % W-Mo with 12 at. % rhenium sintered 3 h in H_2 at 1700°C. (Dark areas rich in rhenium.) (250X).

(d) 50-50 at. % W-Mo with 12 at. % rhenium sintered same as (c) plus 1/2 h in vacuum at 2340°C. (250X).



(e) 50-50 at. % W-Mo with 12 at. % rhenium sintered same as (c) plus 10 min in H_2 at 2600°C. (250X).

Fig. 6. Effect of sintering treatment on microstructure of W-Mo and W-Mo-Re alloys. 250X.

tungsten crystals, the explanations have become clearer. During the past several years, it has been learned that small amounts of rhenium (under 7 at. %), which exhibited little or no ductilizing effect on most forms of tungsten, had a very powerful effect on fine tungsten wire where the grains (or crystals) became oriented, especially in conjunction with non-sag dope or dispersed ThO_2.[9,10] This would suggest that rhenium changed the properties of oriented tungsten crystals, and Garfinkle[11] has recently shown that this is the case.

The practical effects of rheniun in tungsten show that it would be a mistake to believe that a certain amount of rhenium contributes a certain degree of ductility to tungsten. This whole field of composition, orientation, and ductility is interrelated with the temperature factor. To properly ap-

TABLE V

EFFECT OF RUTHENIUM AND OSMIUM ADDITIONS ON THE PROPERTIES OF A 70-30 AT. % W-Mo ALLOY WITH 12 AT. % RHENIUM

Alloy No.	Addition (wt%)	Sintering		Brinell Brittleness Test		
		Maximum Temp, °C	% of Theor Dens	Hardness kg/d²	No. Tests	Average Ductility
217	None	1700[a]	83.5	140	3	169
		2340[b]	89.7	169	3	98
221	1 Ru[c]	1700[a]	86.4	185	3	37
		2340[b]	91.3	222	3	14
222	2 Os[c]	1700[a]	83.0	169	3	188
		2340[b]	89.7	207	3	89

[a] 3 h in H_2 at 1700°C.

[b] Same as [a] plus 1/2 h in vacuum at 2340°C.

[c] Approximately 1.5 at. %.

preciate these relationships, the critical role of temperature must be understood.

In common with many other metals, tungsten and molybdenum and their alloys posses what is known as a ductile/brittle transition temperature range. Several of the metals with very high melting points are brittle near or below room temperature. Schematically, the situation for tungsten, molybdenum, and their alloys with rhenium might be depicted approximately as shown in Fig. 8. Molybdenum, depending on its purity, has a transition temperature very near room temperature. A normal molybdenum sheet can be bent and formed readily at boiling-water temperature (100°C), whereas it may be brittle at room temperature (22°C) or in ice water (0°C).

Thus, in considering room-temperature ductility tests (including all in this report), the reservation should be made that these results could be different at a higher or lower temperature.

A ductile-brittle transition curve taken from the literature[12] and modified schematically is shown in Fig. 9. This represents the results of bend tests on a W-Re alloy sheet in the recrystallized condition. (The position and shape of the curve would be different for as-rolled or strain-annealed sheet.[12]) In Fig. 9, the arrows indicate in what direction the curve should be shifted by the various factors listed. These effects are not always independent; for example, purity will affect grain size.

From the above discussion, it should be evident that the rhenium effect, at least with dilute rhenium contents, is not a straightforward phenomenon. It should also be evident that the as-sintered form of W-Re alloys is in some ways the least favorable for obtaining ductility because purification by vacuum melting, or provision of fibrous or oriented grains, are not applicable. The one highly favorable aspect of an as-sintered structure, fine grain size, also tends to be removed by the necessity for high-temperature sintering or application.

The ductile-brittle transition temperatures of tungsten and molybdenum are apparently greatly affected by impurities, especially by oxygen.[13,14] Impurities in the grain boundaries are concentrated by grain growth, which is one explanation of brittleness increasing with grain size in tungsten and molybdenum. The function of rhenium additions is to remove these sensitivities and thereby lower the ductile-brittle transition temperature. However, at the lower rhenium contents, the bad effects of impurities are not completely overcome. Reproducibility of results is greatly dependent on close control of impurities in powders and sintering atmospheres as well as on alloy physical conditions (porosity, grain size, etc.). It becomes highly important to room-temperature ductility whether the ductile-brittle transition is at 50 or -50°C.

The data of this report did not always agree closely with the degree of ductility imparted by rhenium. While the trend of rhenium effects was consistent for a fixed set of conditions, different powders might affect the absolute results, and a given powder blend might behave differently for various sintering atmospheres. Assuming the sensitivities explained above, it is not surprising that the same powder sintered at 2340°C might end up differently for atmospheres of dry hydrogen, wet hydrogen, or vacuum.

6. MELTING POINTS OF W-Mo-Re ALLOYS

The melting temperatures of selected alloys from this investigation are shown in Table VII. Although the stated accuracy of the determinations was ± 50°C, an analysis of the results made by plotting the data with the accepted melting points of tungsten and molybdenum leads to a maximum spread nearer ± 35°C. The depression of the binary melting point by 12 at. % rhenium appears to be about 50°C at midsystem, increasing to a maximum of about 100°C at the tungsten end (Fig. 10).

Sintered cylinders about 3/8-in. diam by 5/8-in. long were used as melting-point specimens. A small hole, drilled in one end, extended beyond the cylinder midpoint. When the alloys were heated in a high

TABLE VI

EFFECT OF RHENIUM, ThO_2, AND WET H_2 ON A W-Mo BASE ALLOY

70-30 at. % W-Mo Base			Density Percent of Theor			Ductility (d^4)[b]		
			Cumulative Sintering[a]			Cumulative Sintering[a]		
Alloy No.	at. % Re	wt% ThO_2	Green	1700°C	2340°C	1700°C Dry H_2	2340°C Vac	1700°C Wet H_2
217	12		70.3	86.4	91.1	193	110	62
217-A	12	3	70.2	81.7	87.3	179	207	151
218	17		69.4	85.8	90.0	270[c]	232[c]	154
218A	17	1.5	69.6	83.6	88.9	255	232[c]	187
223	20		68.7	84.3	90.2	289[c]	232[c]	220[c]

[a] Sintering successively: 3 h at 1700°C in dry H_2
1/2 h at 2340°C in vacuum
3 h at 1700°C in wet H_2.

Fresh specimens tested after each sintering stage; density change during the last sinter was nil.

[b] d^4 values are averages of two or three specimens.

[c] One or more disks survived the 3000-kg load; value given is the minimum average.

frequency concentrator coil, the melting point was determined by optical pyrometer sighted on the bottom of the small hole, where the presence of liquid metal could instantly be observed.

The regularity of the results may be observed from both Table VII and from Fig. 10. A comparison of these results with those in Ref. 15 was made by plotting the LASL wt% compositions on a ternary diagram. The Russian work included seven alloys containing 10 and 20 wt% rhenium, which were also plotted on the diagram. Labelling the various points with the melting-point values permitted the sketching of isothermal lines for both sets of data. From this construction, not shown, it could be concluded that the Russian values were about 100°C lower than the Los Alamos values for the 10 wt% Re alloys and 200 to 200°C lower for the 20 wt% alloys.

The method used by the Russian workers for determining melting point was not disclosed. Since the Los Alamos results with the binary W-Mo alloys were near accepted values, it appears that the melting points of the ternary alloys as determined at Los Alamos are to be preferred.

From Fig. 10, the alloys based on a W-Mo atomic ratio of 60-40 or greater, and containing up to 17 at. % rhenium, have a minimum melting point of 2950°C (values obtained from slight extrapolation of data plot). Some of the ternary alloys with melting temperatures in the 3050 to 3200°C range have appreciable room-temperature ductility compared to tungsten. This information, combined with the ductility data, permits comparisons to be made with the melting point and room-temperature ductility of sintered molybdenum. It appears that a gain of at least 350 to 400°C in the melting point can be obtained at the sintered molybdenum ductility level by using tungsten rich W-Mo-Re alloys containing up to 17 at. % rhenium.

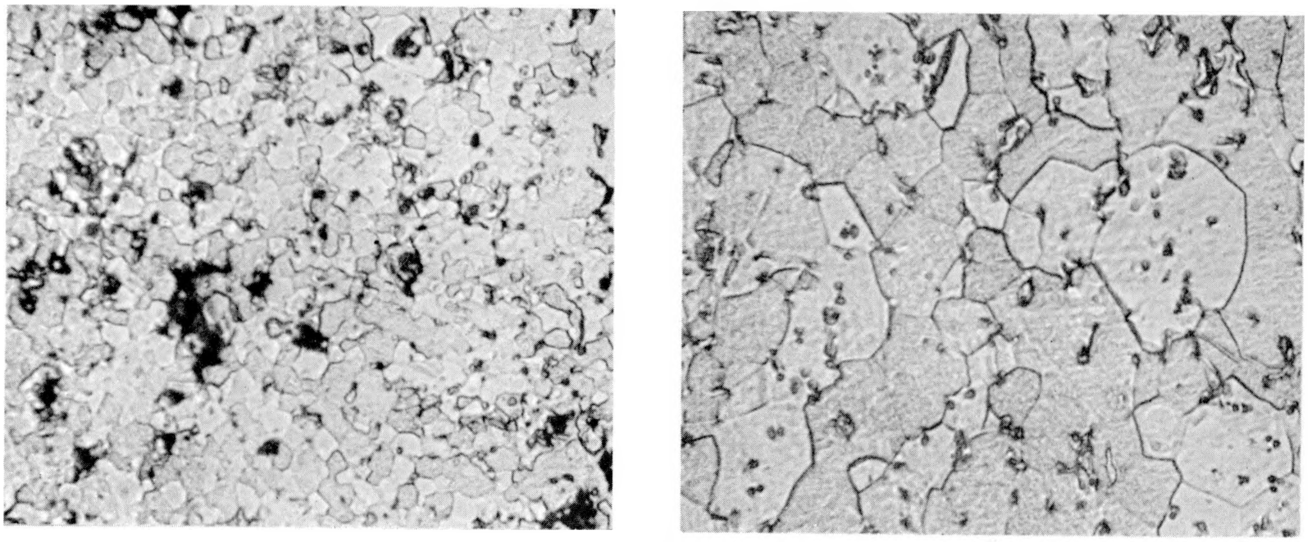
7. RESULTS AND CONCLUSIONS

The Brinell brittleness test appeared suitable for this work. Therefore, based on the data which resulted, certain conclusions and observations may be made. They are as follows:

a. The sintered W and Re binary alloys showed only a slight improvement in ductility with increasing rhenium up to 15 at. % rhenium over that of pure tungsten. However, there was a pronounced increase in ductility at the 20 at. % rhenium level with a peak ductility at about 25 at. % rhenium. The ductility started to drop off again at the 28 at. % rhenium level.

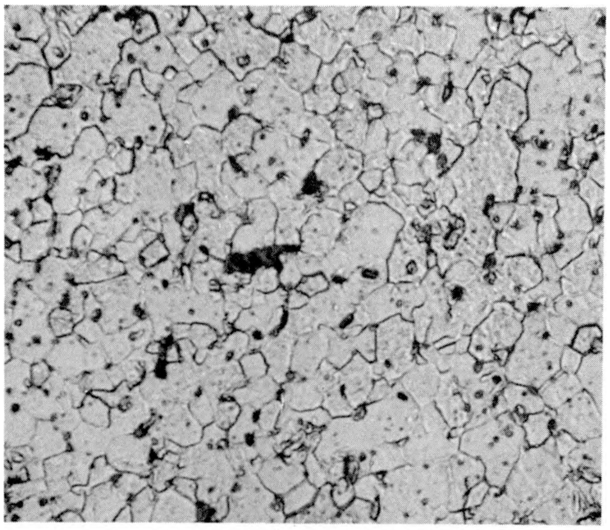
b. The sintered W-Mo binary alloys showed only a very slight improvement in ductility with increasing molybdenum content up to approximately 50 at. % molybdenum. Above this level, there was a sharp increase in ductility. Of course, this no longer becomes a tungsten-base alloy and the melting point becomes less than 2900°C.

c. In all cases, the W-Mo-Re alloys show a



(a) Alloy 218 sintered 1700°C, dry H_2. (Dark areas are rhenium rich).

(b) Same as (a) plus 2340°C vacuum sinter.



(c) Alloy 218-A, 1.5% ThO_2 sintered same as (b).

Fig. 7. Effect of ThO_2 on grain size of a W-Mo-Re alloy. 500X. (Table VI and text.)

marked improvement in ductility with increasing rhenium content regardless of the sintering condition.

d. Using the ductility values after the 1700°C sintering temperature as a base for comparison, there is a sharp drop in ductility in both the binary and ternary alloys. Up to and including the 12 at. % rhenium additions, the ductility dropped about 50% of the values obtained for the 1700°C sinter. At 17 at. % rhenium and greater, the effect was only slightly lower for the higher sintering temperatures. This lowering in the ductility with increasing sintering temperature has been associated with increasing grain growth. It was also noted that increasing rhenium content resulted in lowering the grain size of the sintered alloys.

e. A fine dispersion of ThO_2 in these ternary alloys restricted grain growth and helped to retain ductility up to about the 2350°C sintering temperature.

f. Ruthenium added to a ternary alloy resulted in increased sintered density and hardness, but embrittled the material. Osmium, on the other hand, also increased density and hardness, but did not change the measured ductility values as compared with the alloy containing no osmium.

g. The melting point data follows Vegard's law for the W-Mo alloys. The melting point of the ternary alloys are lowered as the rhenium content increases. As compared to tungsten, however, there are many alloy combinations that have melting points in excess of 2900°C and that still have considerable room-temperature ductility.

Observations based on room-temperature data from the Brinell brittleness test, and from melting-point determinations, lead to the following conclusions:

h. Sintered W-Re alloys, containing up to 28 at. % rhenium show a strong ductility peak at 25 at.%

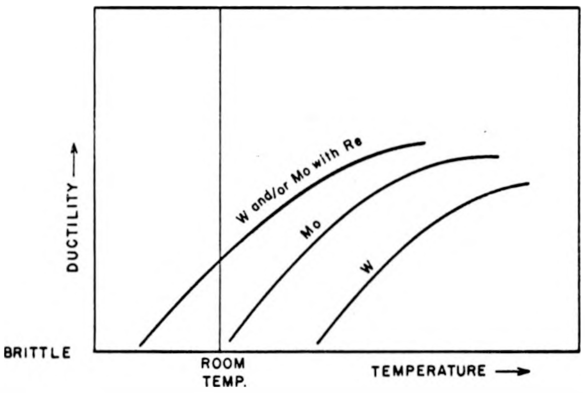


Fig. 8. Schematic relation of ductility and temperature for tungsten and molybdenum and their alloys with rhenium.

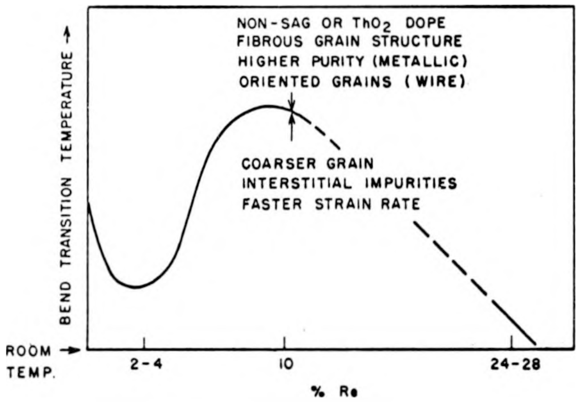


Fig. 9. Schematic of ductile/brittle transition temperature for tungsten-rhenium crystallized sheet (see text).

rhenium with only minor increase in ductility below 15 at. % rhenium.

i. When sintered at 1700°C, W-Mo alloys retained most of the brittleness of tungsten until the molybdenum content exceeded 40 at. %. Further additions of molybdenum raised the ductility at an increasingly rapid rate. The ductility gains in the molybdenum-rich region were greatly diminished, however, by each higher sintering temperature of 1950 and 2340°C (grain growth effect).

j. Rhenium additions of 7 at. % or greater to W-Mo alloys were more effective in improving ductility than the same additions to tungsten alone. Rhenium seems to activate the ternary lattice so that molybdenum also is effective in increasing ductility in the tungsten-rich region.

k. In W-Mo-Re alloys, the ductility was steadily greater with successive levels of 7, 12, and 17

TABLE VII

COMPOSITION AND MELTING TEMPERATURES OF SELECTED BINARY AND TERNARY W-Mo-Re ALLOYS

	Composition of Powders as Blended[a]						
Alloy No.	at. % W	at. % Mo	at. % Re	wt% W	wt% Mo	wt% Re	Melting Point, °C ±35°C
170	80.0	20.0		88.3	11.7		3275
171	60.0	40.0		74.0	26.0		3080
172	55.6	36.8	7.6	66.7	23.4	9.9	3050
174	50.7	33.7	15.7	59.2	20.8	20.0	2980
175	40.0	60.0		55.8	44.2		2915
176	37.4	55.8	6.7	50.3	39.8	9.9	2880
178	34.5	51.4	14.1	44.7	35.3	20.0	2830
179	20.0	80.0		32.1	67.9		2740
182	88.0		12.0	87.9		12.1	3315
184	90.0	10.0		94.5	5.5		3360
185	79.2	8.8	12.0	82.6	4.8	12.6	3220
186	70.0	30.0		81.7	18.3		3120
188	61.6	26.4	12.0	70.5	15.7	13.8	3115
190	50.0	50.0		65.7	34.3		2970
192	44.0	44.0	12.0	55.7	29.0	15.3	2950
194	30.0	70.0		45.1	54.9		2860
196	26.4	61.6	12.0	37.4	45.5	17.1	2850
198	10.0	90.0		17.6	82.4		2655

(Accepted melting points for tungsten and molybdenum are 3410 and 2610°C.)

[a] wt% is basis for blending; at. % values are calculated.

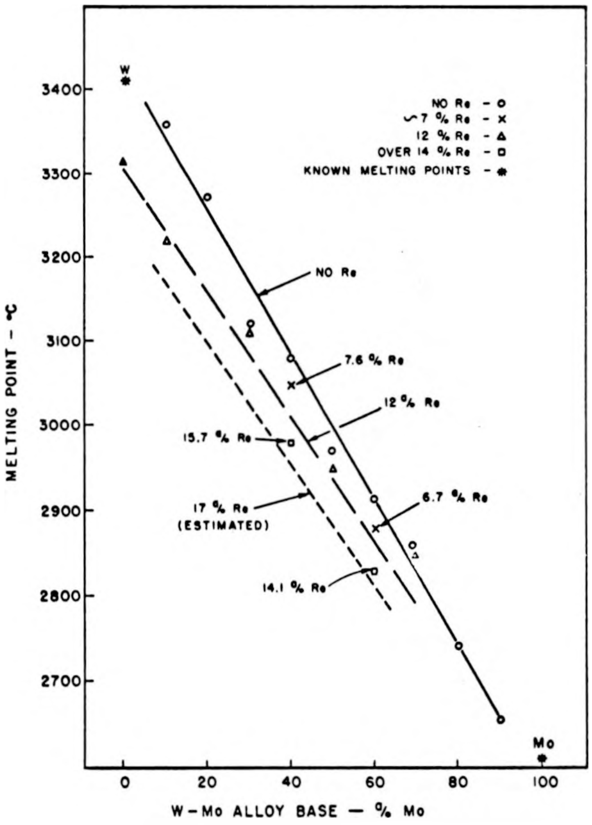


Fig. 10. Melting points of selected W-Mo and W-Mo-Re alloys.

at. % rhenium, and ductility also increased continuously with greater molybdenum content. The ductility levels attained by sintering at 1700°C tended to be reduced by sintering temperatures up to 2340°C, but this trend was partly or completely neutralized as the rhenium content increased to the 17 to 20 at. % level.

l. A 1700°C wet-hydrogen treatment, following the 2340°C sinter, caused a further reduction in ductility of certain W-Mo-Re alloys, ostensibly due to pick up of oxygen impurity. The presence of finely dispersed ThO_2 in duplicates of these alloys restricted grain growth and yielded higher ductility values for both the above treatments.

m. Addition of 1.5 at. % ruthenium to a W-Mo-Re alloy increased the hardness and lowered the ductility. Addition of 1.5 at. % osmium to the same ternary alloy did not lower the ductility, but increased the hardness.

n. The melting points of W-Mo alloys were in near agreement with linear proportions of accepted values for the melting points of tungsten and molybdenum. Melting points of the binary alloys were lowered in proportion to the rhenium addition with a maximum lowering of about 150°C at the tungsten-rich end for 17 at. % rhenium.

o. This report indicates that sintered W-Mo-Re alloys with 17 at. % rhenium, or less, may be selected to fit the following objectives:

(1) melting point in the range 2600 to 2950°C with room-temperature ductility well above that of sintered molybdenum,

(2) melting point 2950°C, or higher, with ductility at least equal to that of sintered molybdenum.

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