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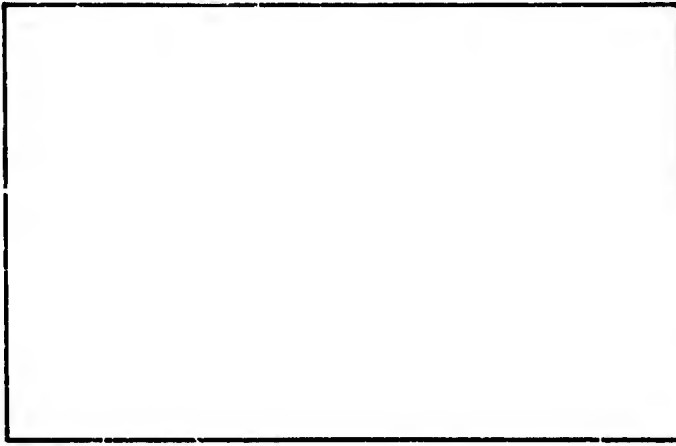
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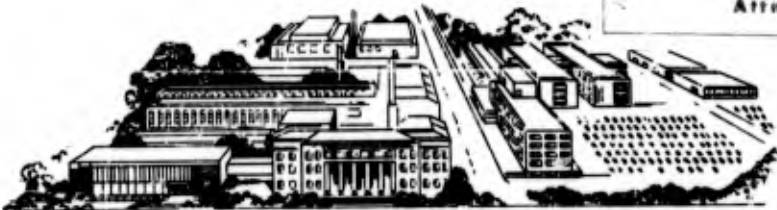


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TECHNICAL REPORT

on

**FURTHER STUDIES ON RHENIUM
ALLOYING EFFECTS IN MOLYBDENUM,
TUNGSTEN, AND CHROMIUM**

to

**Department of the Navy
Office of Naval Research
Contract Nonr-1512(00)**

by

W. D. Klopp, F. C. Holden, and R. I. Jaffee

July 12, '960

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FURTHER STUDIES ON RHENIUM ALLOYING EFFECTS IN MOLYBDENUM, TUNGSTEN, AND CHROMIUM

by

W. D. Klopp, F. C. Holden, and R. I. Jaffee

Further studies on molybdenum-rhenium alloys indicate that the improved fabricability is associated with redistribution of the grain-boundary oxide as a complex rhenium-molybdate. The tolerance for oxygen in Mo-35Re is several hundred ppm, but small increases in carbon or nitrogen render the alloy less fabricable. The contribution of valence electrons from rhenium to the molybdenum lattice is believed to be associated with the reduced interstitial solubility. The improved ductilities of Mo-35Re and W-30Re are associated with lower interstitial content, enhanced capacity for slip at low temperatures, and associated with low critical stresses for deformation by twinning, which appears to be a function of rhenium content alone. Rhenium also significantly lowers the ductile-to-brittle transition temperature of chromium to below -196 C in bending.

INTRODUCTION

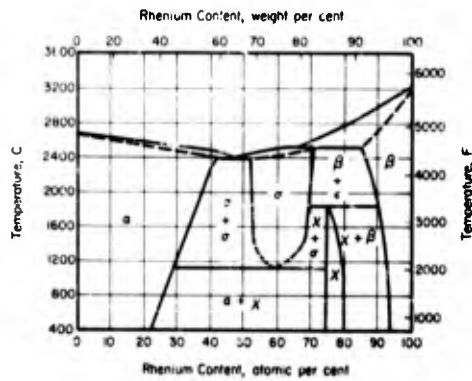
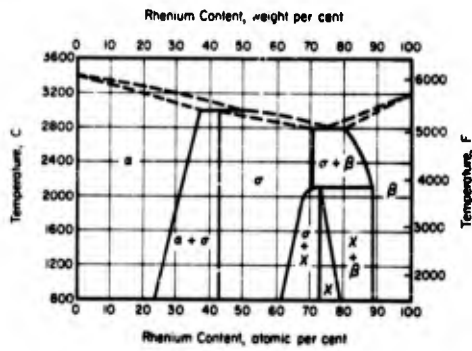
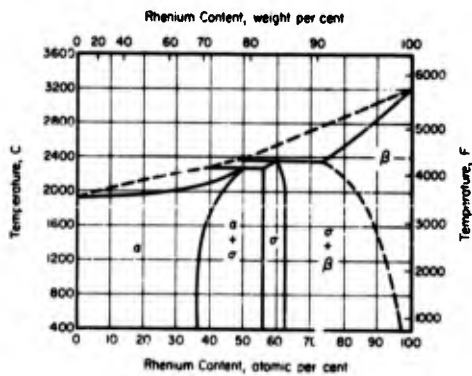
Recent studies have shown that rhenium significantly improves both the fabricability and low-temperature ductility of molybdenum and tungsten. This was observed first by Geach and Hughes^{(1)*}, who reported that a Mo-35Re** alloy could be cold rolled to a reduction of 90 per cent, a considerable improvement over the limited fabricabilities of the components. Similarly, these workers found that a W-35Re alloy could be fabricated easily at a few hundred degrees centigrade.

Savitskii and Tylkina⁽²⁾ also examined the fabricability of molybdenum-rhenium alloy, but could not confirm the findings of Geach and Hughes. They found that the ductility of Mo-10Re in compression was better than that of unalloyed molybdenum, but the ductility decreased progressively with increasing rhenium contents up to 60 per cent rhenium.

The remarkable effects of rhenium on the fabricability and ductility of molybdenum and tungsten later were confirmed by Jaffee, Sims, and Harwood.⁽³⁾ Optimum compositions were found at about Mo-35Re and W-30Re. These alloys are more fabricable, and have higher strengths and better ductilities than unalloyed molybdenum and tungsten. Deformation at low temperatures occurs initially by mechanical twinning, rather than by slip. Evidence for reduced interstitial solubility in the alloy was found, which resulted in absence of the yield point and enhanced capacity for slip at low temperature. The ability of these alloys to be warm worked was postulated to be a result of

*References are listed on page 31.

**All compositions are given in atomic per cent unless noted otherwise.

a. Molybdenum-Rhenium System ⁽¹⁶⁾b. Tungsten-Rhenium System ⁽¹⁷⁾c. Chromium-Rhenium System ⁽¹⁸⁾

C-3476

FIGURE 1. CONSTITUTION DIAGRAMS FOR MOLYBDENUM-, TUNGSTEN-, AND CHROMIUM-RHENIUM SYSTEMS

(1) formation of an oxide phase which does not wet the grain boundaries, and (2) a reduced solubility for oxygen in the alloys.

No information on the fabricability or mechanical properties of chromium-rhenium alloys has been reported in the literature.

The constitution diagrams of the systems molybdenum-rhenium⁽⁴⁻⁶⁾, tungsten-rhenium^(7,8), and chromium-rhenium⁽⁹⁾ have been established, as shown in Figure 1. All three systems are similar, being characterized by rather extensive solubilities for rhenium in the Group VIA elements, intermediate brittle sigma phases with the formula Re_3X_2 , and restricted solubilities of the Group VIA elements in rhenium. The chi phase observed in both the molybdenum-rhenium and tungsten-rhenium systems was not found by Savitskii, et al.,⁽⁹⁾ in the chromium-rhenium system.

The present work extends the investigations of Jaffee, et al.⁽³⁾ Included are studies of the mechanical properties of alloys of the Group VIA metals with rhenium, the effects of impurities, and further studies of the mechanisms by which rhenium improves the mechanical properties of these elements.

EXPERIMENTAL PROCEDURES

The starting materials for this investigation included rhenium, molybdenum, and tungsten in powder and granular form, and iodide-refined chromium crystals. The types, sources, and major impurities in these materials are given in Table 1.

TABLE 1. SOURCES AND TYPICAL ANALYSES OF STARTING MATERIALS

Material	Supplier	Analysis, ppm						
		O	N	C	Fe	Al	Si	Ni
Rhenium	Chase Brass	6	<5	--	50	100	70	--
Molybdenum granules ^(a)	Battelle	160	2	20-30	10	--	--	--
Molybdenum powder	Fansteel	1020	--	--	--	--	--	--
Tungsten sheet	Fansteel	--	--	--	--	--	--	--
Tungsten powder (Type 425)	Fansteel	--	--	--	--	--	--	--
Chromium crystals (high iron)	Chromalloy	10	<2	20	200	0.5	--	10

(a) From vacuum-melted molybdenum ingots.

Alloys were consolidated into 35- to 75-gram ingots by inert-electrode arc melting on a water-cooled copper hearth. Generally, each ingot was melted three times, although certain alloys were given additional melts in attempts to remove impurities and thereby improve fabricability. Powdered materials were prepared for arc melting by blending and compacting.

Molybdenum-wound tube furnaces with tank hydrogen atmospheres were employed to preheat alloys for fabrication and for most of the annealing treatments. Some of the annealing treatments were made in vacuum furnaces, employing tantalum heaters.

RESULTS AND DISCUSSION

Molybdenum-Rhenium Alloys

Fabrication

The fabricability of sintered and arc-cast binary molybdenum-rhenium alloys was investigated previously by Jaffee, et al. (3) Powder-metallurgy bars containing up to 20 per cent rhenium can be warm rolled at 1250 C after hydrogen sintering; arc-cast alloys containing 20 to 37.5 per cent rhenium can be warm rolled at 1000 C. Room-temperature fabricability is restricted to a region near the composition Mo-35Re.

The effects of oxygen, nitrogen, and carbon on the fabricability of molybdenum-rhenium alloys were evaluated in the present work. High-oxygen alloys were prepared by arc melting blended compacts of high-oxygen molybdenum and rhenium powder. The ingots were analyzed, and their fabricability was evaluated by forging and/or rolling. Unfabricable ingots were remelted to reduce the oxygen level by boiling off molybdenum and rhenium oxides, and the evaluation was repeated. A high-nitrogen alloy was prepared by melting a low-oxygen Mo-35Re button in a partial atmosphere of equal parts of nitrogen and argon; this was followed by remelting under 20 cm argon pressure. Carbon was added in the form of Mo₂C to a Mo-35Re ingot by arc melting.

The effects of these additions on the fabricability of molybdenum-rhenium alloys are tabulated in Table 2 and illustrated in Figure 2.

Poor fabricability was observed at 1200 C to 1250 C for molybdenum alloys containing up to 20 per cent rhenium, even at very low oxygen contents. At the 30 per cent rhenium level, ingots containing 102 ppm oxygen can be warm rolled, and at 35 per cent rhenium, the tolerance is at least 250 ppm oxygen. For fabrication of Mo-35Re at room temperature, the upper limit of oxygen is between 60 and 110 ppm.

The hot-working tolerance of the Mo-35Re alloy is much less for nitrogen and carbon than for oxygen. The ingot containing 60 ppm nitrogen cracked at a reduction of about 5 per cent on forging at 1400 C. Similarly, ingots containing 18 to 70 ppm carbon cracked when forging at 1400 C was attempted. Metallographic examination of the fractured alloy containing carbon revealed a continuous second phase (probably carbide) outlining the grain boundaries, which resulted in extensive intergranular cracking.

TABLE 2. FABRICATION OF MOLYBDENUM-RHENIUM ALLOYS WITH VARIOUS OXYGEN, NITROGEN, AND CARBON LEVELS

Nominal Composition, at. %	Impurity Content, ppm			Forgeability at 1400 C	Fabricability by Rolling		Condition
	O	N	C		Temperature, C	Reduction, per cent	
<u>Alloys Containing Oxygen</u>							
100 Mo	(50) ^(a)	--	--	--	20 1250	10 15	Cracked Cracked
Mo-20Re	28	--	--	--	1250	24	Cracked
Mo-25Re	88 355	-- --	-- --	-- --	1250 1200	45 18	Cracked Cracked
Mo-30Re	102 344	-- --	-- --	-- --	1200 1200	59 32	Good Cracked
Mo-35Re	50 60 110 105 140 250 370 549	-- -- -- -- -- -- -- --	-- -- -- -- -- -- -- --	-- -- -- Good -- -- -- -- --	20 20 20 1250 1250 1250 1200 1250	95 95 56 ~80 95 95 17 95	Good Good Cracked Good Good Good Cracked Good
<u>Alloy Containing Nitrogen</u>							
Mo-35Re	--	60	--	Cracked	--	--	--
<u>Alloys Containing Carbon</u>							
Mo-35Re	--	--	70 (35) ^(b) (18) ^(b)	Cracked Cracked Cracked	-- -- --	-- -- --	-- -- --

(a) Typical oxygen content.

(b) Estimated carbon content.

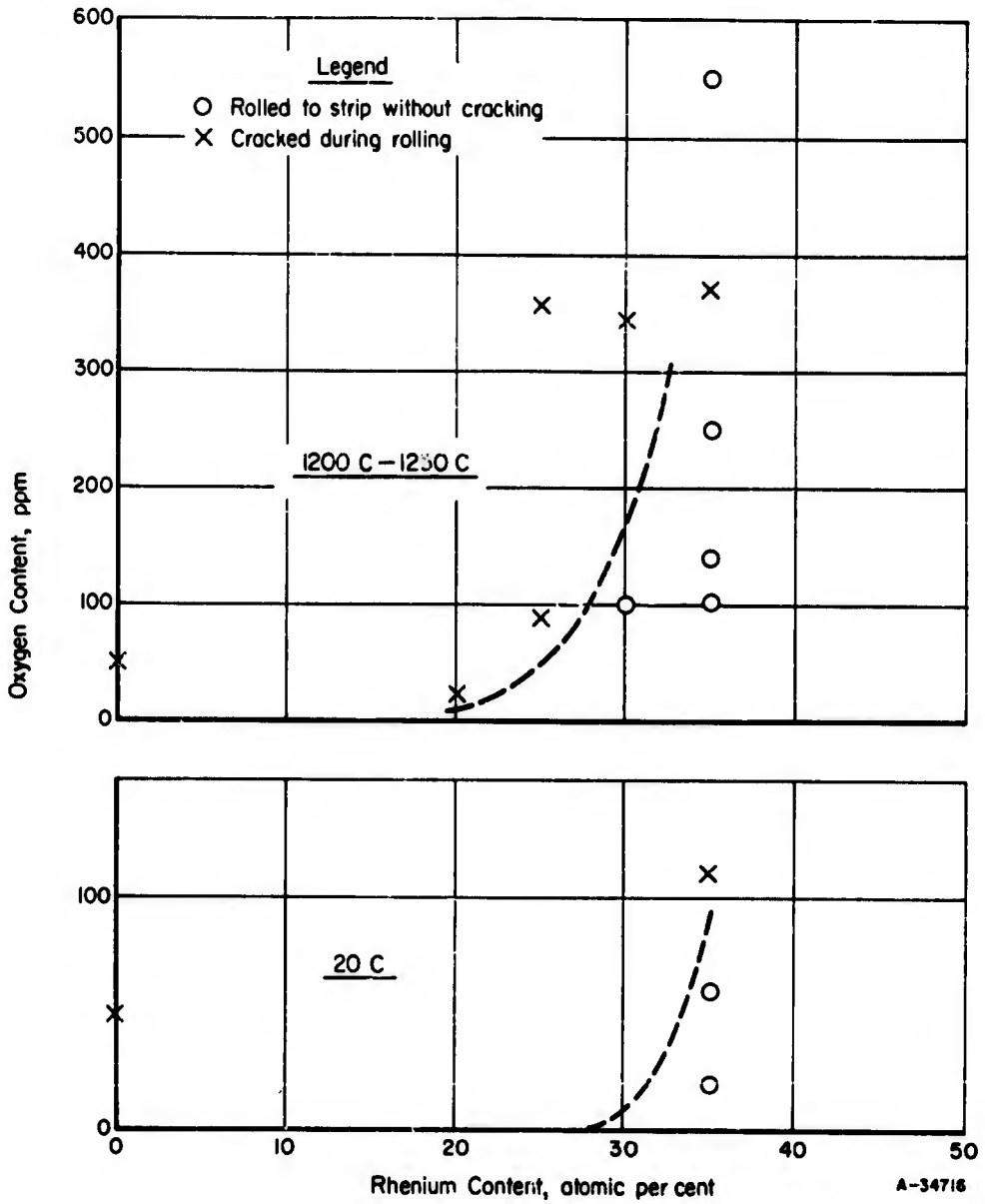


FIGURE 2. EFFECTS OF OXYGEN CONTENT ON THE FABRICABILITY OF MOLYBDENUM-RHENIUM ALLOYS AT ROOM AND ELEVATED TEMPERATURES

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Several molybdenum-rhenium-0.5 wt % titanium alloys were prepared by arc melting to provide material for mechanical-property tests. The titanium additions were made either by adding iodide-refined titanium metal to the melting stock or by using commercial Mo-0.5 wt % Ti sheet as melting stock. In general, the fabrication characteristics of these alloys were similar to those of binary molybdenum-rhenium alloys, although the investigation of the ternary alloys was not extensive.

Bend Ductility

Because rhenium has a pronounced effect on the ductility of molybdenum when added at the 35 per cent level, it is of interest to examine the ductility of molybdenum as a function of both rhenium content and bending temperature. Bend data are presented in Figure 3 for molybdenum and molybdenum-rhenium alloys in the recrystallized and wrought conditions. The bend ductility is expressed as the ratio of the smallest bend radius at which no fracture occurred to the thickness of the bend sample. For the recrystallized condition, unalloyed molybdenum exhibits a sharp transition from brittle to ductile behavior over the temperature range 20 to 94 C. Additions of rhenium significantly improve the bend ductility, and the transition temperature is decreased with increasing rhenium content. The recrystallized Mo-35Re alloy showed no transition to brittle behavior at temperatures as low as -254 C. This alloy was bent over a 3T radius in liquid hydrogen (-254 C); aside from some microcracks on the outer surface, no evidence of failure could be observed.

Mechanical twinning was observed metallographically in the bend samples containing 20 to 35 per cent rhenium. The amount of twinning increased both with rhenium content and with decreasing test temperature.

The bend properties of wrought molybdenum and molybdenum-rhenium alloys also are shown in Figure 3. The transition temperatures for molybdenum and Mo-25Re are appreciably lower in the wrought than in the recrystallized condition, whereas that for Mo-35Re is higher for the wrought condition. This apparently anomalous behavior is explained by the fact that rhenium promotes twinning as an initial deformation mechanism, but for large amounts of deformation, slip becomes predominant. Thus, the recrystallized Mo-35Re alloy can deform sufficiently by mechanical twinning to be ductile at -254 C, but the worked Mo-35Re must deform by slip. The latter thus exhibits a more normal ductility transition behavior than does the recrystallized material. This behavior is consistent with tensile data, to be discussed later, which indicate that the yield strength, i. e., the critical twinning stress, does not change appreciably with temperature over the temperature range -196 C to 400 C.

Tensile and Creep Properties

Tensile properties of alloys containing 10 to 37.5 per cent rhenium were determined at -196 C, adding to data obtained earlier at room temperature. Extensive data also were obtained on the Mo-35Re alloy at temperatures of -196 C to 1204 C in various conditions of cold or hot work. These results are given in Table 3.

Figure 4 shows the strength properties of molybdenum-rhenium alloys at -196 C compared with the room-temperature properties reported by Jaffee, et al. (3) Higher strengths and lower ductilities were obtained at the lower temperature. A sharp drop

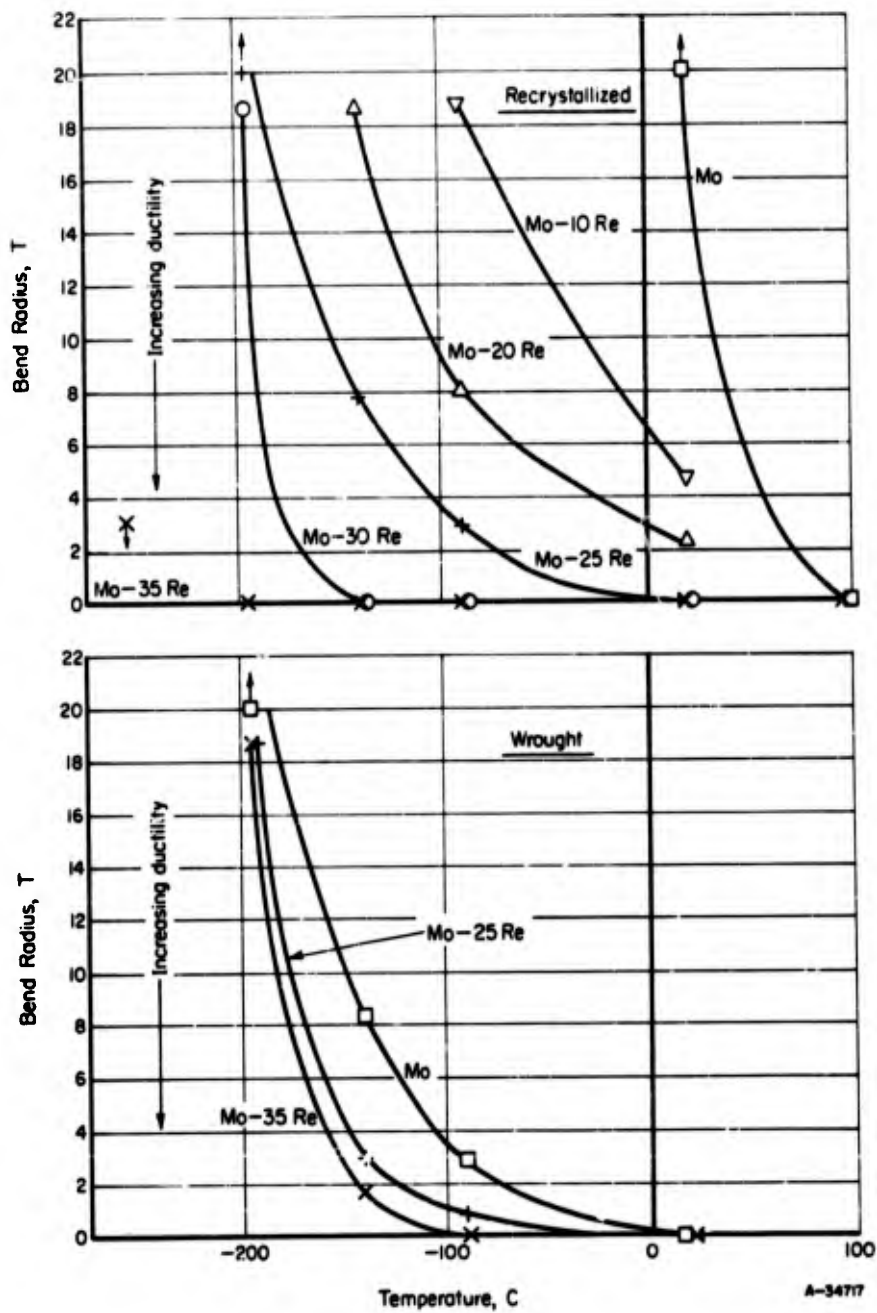


FIGURE 3. BEND DUCTILITIES OF MOLYBDENUM AND MOLYBDENUM-RHENIUM ALLOYS VERSUS TEMPERATURE

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TABLE 3. TENSILE PROPERTIES OF MOLYBDENUM-RHENIUM ALLOYS

Composition, at. %	Condition ^(a)	Test Temperature, C	Yield Strength at			Ultimate Strength, 1000 psi	Ductility	
			Indicered Offset, 1000 psi				Elongation, %	Reduction in Area, %
			0.01%	0.1%	0.2%			
100Mo ^(b)	Rx	20			65.2	81.2	29	21.5
	Rx	225			30.2	53.5	50	71.5
	Rx	450			26.0	43.0	48	81.5
	Rx	975			19.0	34.5	41	97.5
	Rx	1100			16.0	24.9	72	97
Mo-10Re	Rx	-196				136.0	<1	<1
	Rx	-196				139.0	<1	<1
	Rx	20	48	53		68	4	6
Mo-20Re	Rx	-196		126.0		145.0	<1	2
	Rx	20	74	78		92	5	8
Mo-30Re	Rx	-196		122.0	131.0	165.0	2	3
	Rx	20	89	93		129	12	47
Mo-35Re	HCW; A 1-1850	-196		50.1	56.1	187.3	13.3	52
	CW 95%	20	105.0	216.0	251.0	257.3	<1	
	CW; A 2-1600	20	153.0	163.0	163.0	176.0	2	
	HCW 60%	20	122.0	173.0	183.0	191.5	4	8
	HCW; A 1/4-1800	20			126.0	130.0	0.6	4
	HCW; A 1/4-1800	20		110.0	116.5	144.0	7.7	
	HCW; A 1-1800	20	68.3	84.0	87.0	192.2	20.0	
	HCW; A 1-1850	20		57.4	55.0	130.8	27.4	76.0
	HCW; A 1-1850	200		53.6	50.5	92.5	16.0	66.3
	HCW; A 1-1850	400		55.7	52.6	76.2	20.0	70.5
	HCW 60%	982			57.2	80.1	10.0	
	HCW 60%	1204			12.5	48.5	17.5	
	HCW; A 1-1850	-196		87.3	99.6	210.6	15.4	13
	HCW; A 1-1850	20		82.5	88.2	142.4	19.1	51
	HCW; A 1-1850	200		67.3	70.0	107.2	17.7	44.9
HCW; A 1-1850	400		64.3	58.5	95.1	24.0	61.8	
Mo-37.5Re	Rx	-196				210.0	1	<1
	Rx	-196		185.0	200.0	216.0	1	1
Mo-35Re-0.5Ti ^(c)	HCW 60%	20	135.5	162.8	168.2	177.0	10.0	22.4
	HCW 60%	982			71.7	87.2	10.9	16.0
Mo-35Re-0.5Ti ^(d)	HCW 60%	20	147.5	168.0	171.0	176.2	8.0	25.6
	HCW 60%	982			66.3	98.6	18.0	17.9

(a) HCW - hot-cold worked at 1000 to 1250 C

Rx - recrystallized

A 1-1850 - annealed 1 hour at 1850 C.

(b) Data from Reference 10.

(c) Prepared with iodide-refined titanium; titanium content is given in weight per cent.

(d) Prepared with molybdenum-0.5 wt % titanium sheet.

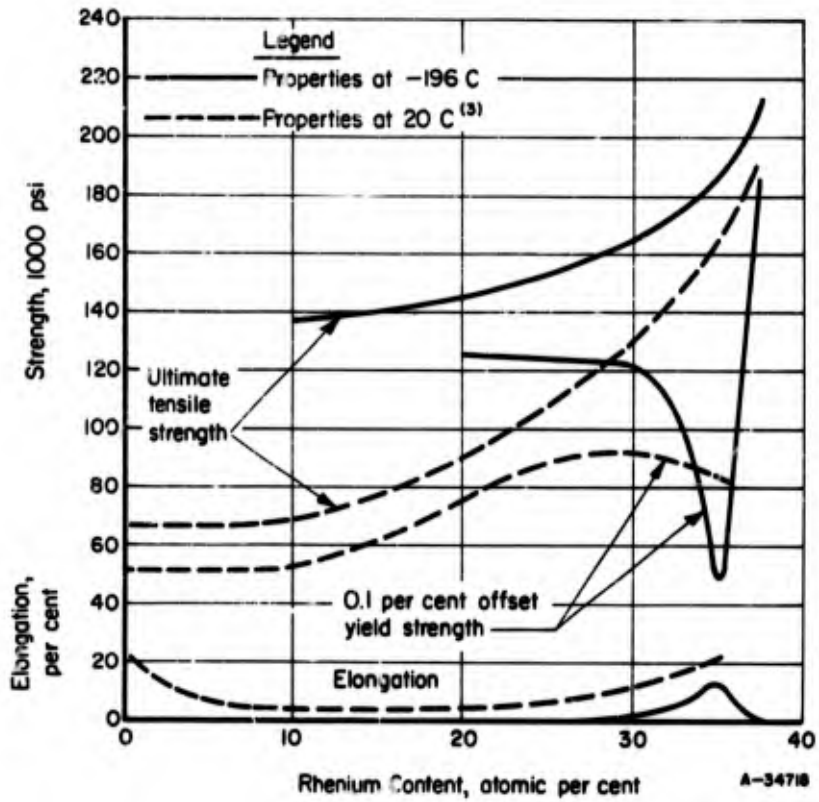


FIGURE 4. TENSILE PROPERTIES OF MOLYBDENUM-RHENIUM ALLOYS

in the yield strength and a corresponding increase in elongation are observed at the 35 per cent rhenium level at both temperatures. This behavior is associated with the onset of twinning, which is particularly heavy at the 35 per cent rhenium level. This alloy deforms initially by twinning, but as deformation increases, slip becomes the predominant mechanism, accounting for the absence of a discontinuity in the curve of ultimate tensile strength versus temperature.

The effects of test temperature (over the range -196 C to 400 C) and oxygen content on the mechanical properties of Mo-35Re alloys are shown in Figure 5. To provide materials with differing oxygen contents for these experiments, ingots were arc melted from molybdenum powder (1020 ppm oxygen) and from granular molybdenum (160 ppm oxygen). These alloys analyzed 18 and <10 ppm oxygen, respectively, after testing, indicating substantial reductions in oxygen content during processing. Figure 5 shows that the ultimate strength of the Mo-35Re alloy decreases rapidly from -196 C to 400 C, but the yield strength and ductility both remain approximately constant. This is interpreted as indicating that the stress for initiating twinning is not affected much by temperature over the range -196 C to 400 C. The increase in oxygen content from <10 to 18 ppm increases the strength of the Mo-35Re alloy by about 10 to 20 per cent.

Rhenium additions increase the tensile strength of molybdenum by solid-solution strengthening, since no second phases are formed up to about 40 per cent rhenium. It is therefore of interest to determine whether titanium, which strengthens molybdenum by forming a fine dispersion, also is effective in molybdenum-rhenium, and whether the two strengthening mechanisms are additive. Mo-35Re-0.5 wt % Ti materials were prepared using either high-purity iodide titanium or commercial Mo-0.5 wt % Ti melting stock as described earlier. Tensile properties of these alloys are given in Table 3 and are compared with Mo-35Re (in the 60 per cent hot-cold-worked condition) in Figure 6. It is seen that Mo-35Re has higher yield and ultimate strengths than the titanium-containing alloys at room temperature, but at 980 C, the titanium-containing alloys are stronger. Solid-solution strengthening by rhenium is more effective at room temperature, whereas at elevated temperatures, the two strengthening mechanisms are additive.

The creep-rupture properties of Mo-35Re in various conditions are compared with those of recrystallized molybdenum and Mo-0.5 wt % Ti in Table 4. Mo-35Re alloy is seen to be significantly stronger in creep than either of the other two materials at 982 C (1800 F), but at 1093 C (2000 F) the Mo-0.5 wt % Ti alloy is the most creep-resistant of the three materials. The dispersion-strengthening mechanism thus becomes more effective at higher temperatures than solid-solution strengthening.

Mechanism Studies

The mechanisms by which rhenium improves the fabricability and ductility of molybdenum were discussed in the earlier work by Jaffee, et al. (3) Three major mechanisms were postulated:

- (1) Rhenium forms a complex grain-boundary oxide with molybdenum, postulated to be ReMoO_4 . This oxide has a high surface tension and is relatively nonwetting (compared with MoO_2), thereby reducing intergranular cracking during hot fabrication.

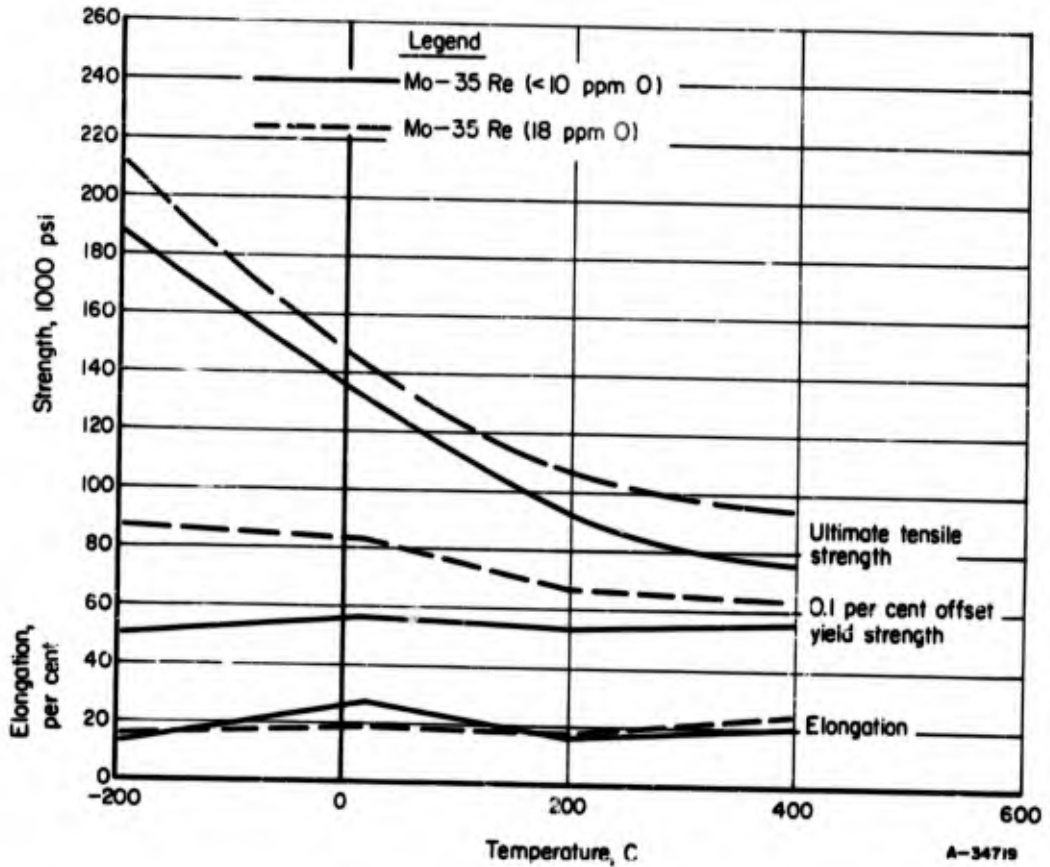


FIGURE 5. TENSILE PROPERTIES OF ANNEALED Mo-35Re PREPARED FROM GRANULES (<10 ppm O) AND FROM POWDER (18 ppm O)

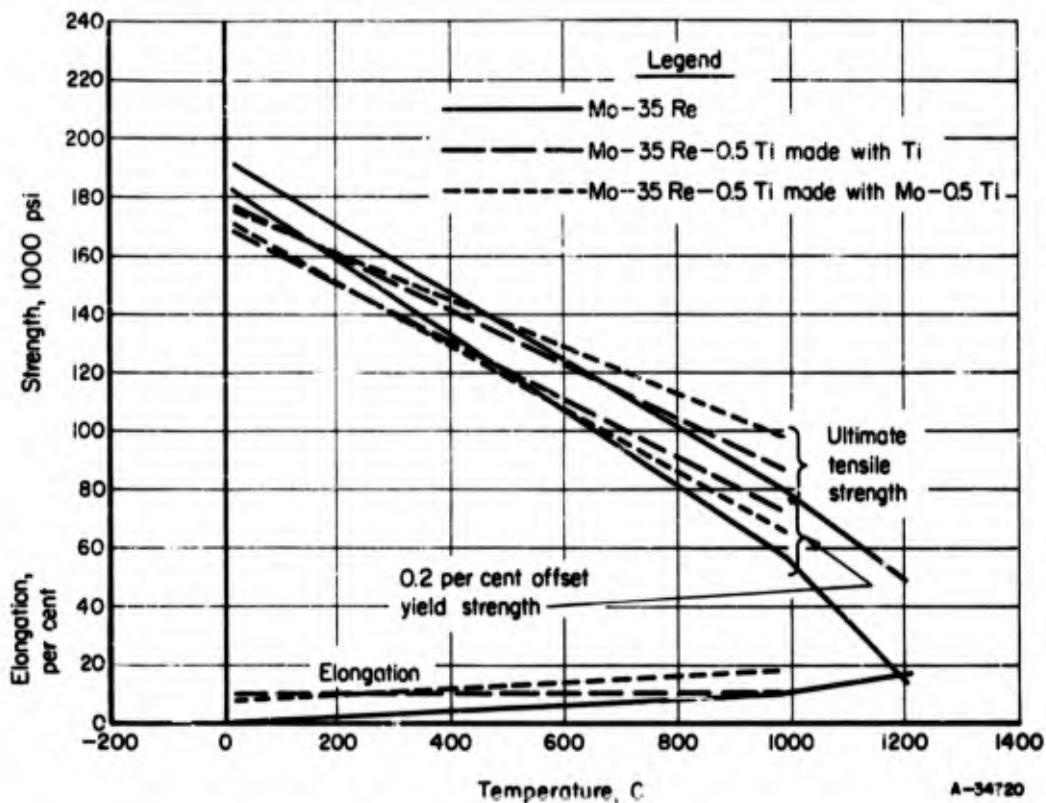


FIGURE 6. TENSILE PROPERTIES OF Mo-35Re AND Mo-35Re-0.5Ti IN THE HOT-COLD-WORKED CONDITION

TABLE 4. CREEP-RUPTURE DATA FOR Mo, Mo-0.5Ti^(a), and Mo-35Re

Composition, at. %	Condition ^(b)	Stress, 1000 psi	Rupture Time, hours	Minimum Creep Rate, %/hour	Elongation, %	Reduction in Area, %
<u>982 C (1800 F)</u>						
100Mo	A 1-1180	12.0	93.3	0.28	75.2	93.2
		15.0	5.5	7.0	54.4	94.5
		20.0	0.5	--	48.8	95.7
Mo-0.5Ti ^(a)	A 1-1340	27.5	>328.7	0.014	22.4	--
		29.0	82.3	0.32	63.2	89.4
		31.0	3.9	5.8	45.6	89.7
		35.0	0.35	--	50.5	92.3
Mo-35Re	HCW; A 1-1500	40.0	20.5	1.4	40.0	25.0
	HCW 60%	40.0	47.1	0.8	56.6	30.2
	HCW 95%	40.0	6.4	3.2	38.2	--
	HCW + CW 60%	40.0	72.8	0.5	44.5	--
	CW 95%	25.0	>165 ^(c)	0.00034	(9.4)	--
<u>1093 C (2000 F)</u>						
100Mo	A 1-1180	12.0	5.3	3.0	41.3	63.0
		17.5	0.15	--	60.1	83.1
Mo-0.5Ti ^(b)	A 1-1340	18.0	>280 ^(c)	0.023	(12.6)	--
		20.0	221.1	0.11	32.8	88.2
		25.0	4.4	6.0	51.7	86.7
		30.0	0.3	--	48.3	89.7
Mo-35Re	HCW 95%	20.0	55.9	0.07	119.0	--

(a) Titanium content is given in weight per cent.

(b) HCW - hot-cold worked at 1000 or 1250 C

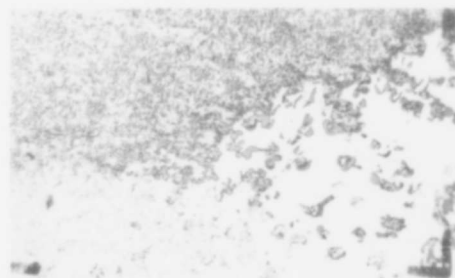
A 1-1180 - annealed 1 hour at 1180 C.

(c) Test discontinued.

- (2) Rhenium improves the fabricability and low-temperature ductility of molybdenum by reducing the interstitial solubility and eliminates the yield-point effect promoted by interstitials in solution. The reduction of interstitial solubilities is indicated by a lowering of the cast hardness by about 20 points Vickers as 5 per cent rhenium is added (see Figure 15). The reduction is in accord with the recent theory by D. A. Robins⁽¹¹⁾, which predicts a lowering of the interstitial solubilities in Group VIA metals as higher group metals are added because of the tendency to maintain a maximum of six bonding electrons. Additions of rhenium with seven electrons reduces the solubilities of interstitials because of their tendency to ionize and contribute electrons to the alloy. Oxygen is also eliminated during arc melting of molybdenum-rhenium alloys because of the high volatility of Re_2O_7 .
- (3) Rhenium promotes mechanical twinning at ambient and lower temperatures, for which the critical shear stress is lower than that required for slip. The ease with which Mo-35Re twins also might be associated with local ordering in the alloy, the reduction of interstitial segregation and polygonization by rhenium, or a change in the cleavage system from (100), characteristic of molybdenum, to (110). Studies were conducted to clarify which of these mechanisms might be operative.

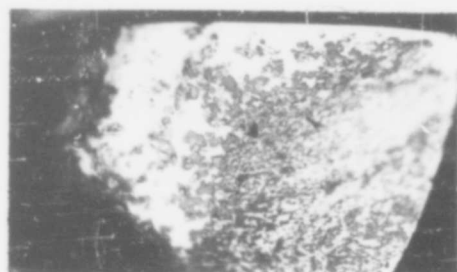
Oxide Studies. In previous work, attempts were made to identify the intergranular oxide in Mo-35Re by stripping the oxide from a heavily etched specimen onto a plastic film and studying by X-ray diffraction. Attempts were also made to synthesize the oxide. However, both attempts at identification were unsuccessful. In the present work, the oxide in a cast high-oxygen ingot of Mo-35Re was studied in situ with an electron-probe microanalyser. None of the oxide particles were large enough to absorb the entire electron beam, so that the analyses required a correction for the composition of the background matrix alloy. The results, although inconclusive, supported the postulated composition of ReMoO_4 . The rhenium content of the alloy was found to vary by as much as 15-20 per cent throughout the specimen, and was higher in grains with a higher population of oxide particles. The grain boundaries also were rich in rhenium, whereas the areas adjacent to the grain boundaries had a lower than average rhenium content. Efforts were made to compensate for the composition of the background alloy so that the oxide could be analyzed more accurately, but the variation in the alloy composition (on a microscopic scale) made this difficult. However, the important observation was made that the oxide is richer in rhenium than the matrix alloy, thus supporting the composition M_2ReO_4 .

Fractographic studies were conducted on molybdenum and molybdenum-rhenium alloys to investigate further the effects of rhenium on the distribution of the grain-boundary oxide. The internal grain surfaces of seven fractured ingots are shown in Figure 7. The alloys containing up to 10 per cent rhenium show large dark-gray globules of oxide, indicating an oxide with low surface tension. As the rhenium content is further increased, the amount of intergranular oxide decreases, probably as a result of a decrease in oxygen content by volatilization of Re_2O_7 during arc melting. At the 25 per cent rhenium level, deformation of the grains before grain-boundary failure is apparent, while at 30 per cent rhenium, the oxide particles are larger and more discrete, indicating an increase in the oxide surface tension as proposed earlier by Jaffee, et al.⁽³⁾



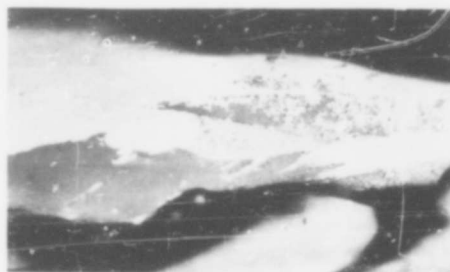
250X N33117

a. 100Mo



250X N33118

b. Mo-5Re



250X N33119

c. Mo-10Re



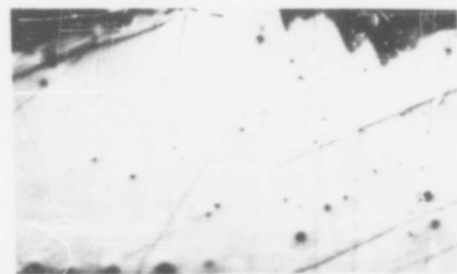
250X N33120

d. Mo-15Re



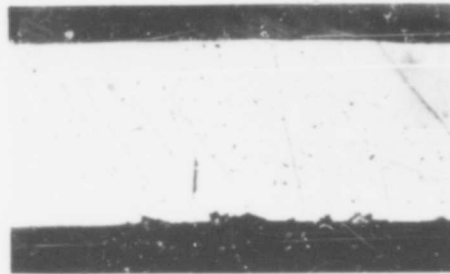
250X N33121

e. Mo-20Re



250X N33122

f. Mo-25Re



250X N33123

g. Mo-30Re

FIGURE 7. FRACTOGRAPHS OF CAST MOLYBDENUM AND MOLYBDENUM-RHENIUM ALLOYS ILLUSTRATING OXIDE DISTRIBUTION ON GRAIN SURFACES

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Twinning Studies. The observation that twinning occurs most readily in alloys with an atomic ratio of 2Mo:1Re led to the suggestion that twinning might be associated with ordering. A previous examination of diffraction patterns had revealed no indications of long-range ordering. (3) More recently, the electrical resistivity of Mo-35Re wire was measured.* The resistivity was found to vary linearly with temperature over the range 25 C to 350 C according to the relationship,

$$\rho \text{ (microhm-cm)} = 3.94 \times 10^{-2} T(\text{C}) + 20.23.$$

The linearity of this relationship indicates an absence of short-range ordering in Mo-35Re.

Twinning during tension loading was studied on Mo-35Re alloys over the temperature range -196 C to 400 C. The tensile properties obtained from this study are presented in Table 3. The stress-strain curves for low-oxygen Mo-35Re are shown in Figure 8. These curves show (1) apparent upper and lower yield points characteristic of body-centered cubic structures containing interstitial elements and (2) many flat steps and serrations, similar to discontinuous yielding in strain-aging alloys, occurring after the yield point and occasionally before the yield point. The drop in load at the apparent yield point was accompanied by an audible click, as were many of the other larger steps and serrations in the curves. This behavior suggested that the yield point behavior was caused by twinning rather than by dissolved interstitials.

A series of load-reload tests was conducted to study the possible yield-point phenomena further and, in particular, to determine whether this behavior is the result of dislocation locking by dissolved interstitials or is associated with a burst of twins. Interrupted tensile tests were conducted with immediate reloading, after holding for various times at room temperature, and after annealing 1 hour at 600 C. The load-elongation curves for these experiments are presented in Figure 9. In each case, the load-elongation curves continued in the same manner after reloading as before unloading. An apparent increase in flow stress after annealing at 600 C may be the result of sigma precipitation. Thus, it is concluded that the yield-point behavior and serrated stress-strain curves exhibited by the Mo-35Re alloy result from bursts of twins during plastic straining and are not associated with dislocation locking by interstitials. It is interesting to note that the load-elongation curves shown in Figure 8 contain many fine serrations at -196 C, resulting from heavy twinning, but as the test temperature is increased and the capacity for slip increases, the number of serrations decreases and the magnitude of the serration increases, suggesting that the twins form in bursts at higher temperature. Figure 10 illustrates the heavy twinning that occurred at -196 C compared with the relatively small amount of twinning at 400 C.

Attempts were made to prepare high-purity Mo-35Re by electron-beam melting to compare its tensile properties with those of normal arc-melted Mo-35Re. Three rods of this alloy were prepared by electron-beam melting and easily cold swaged to 0.11-inch-diameter rod, corresponding to a reduction in area of 50 per cent. Considerable quantities of sigma phase, however, were precipitated by annealing for 1 hour at 1850 C and water quenching, although this treatment results in a single-phase structure for normal arc-melted Mo-35Re. Thus, electron-beam-melted material suitable for tensile evaluation could not be obtained.

*Work performed at Battelle under Air Force Cambridge Research Center Contract No. AF 19(606)-1741, "Investigation of Rhenium for Electron-Tube Applications".

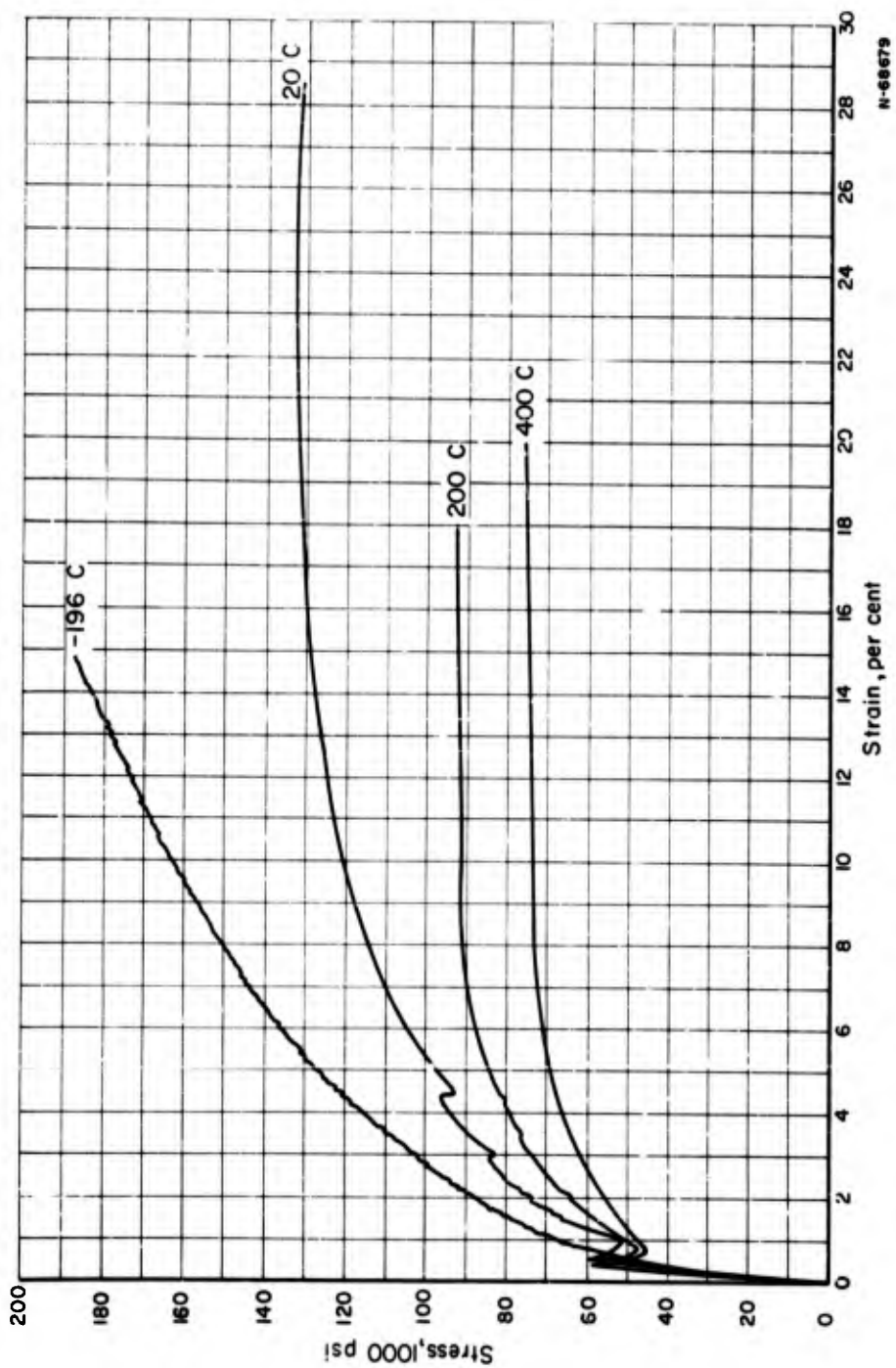


FIGURE 8. EFFECT OF TEMPERATURE ON THE STRESS-STRAIN CURVES FOR Mo-35Re (<10 ppm O) ALLOY

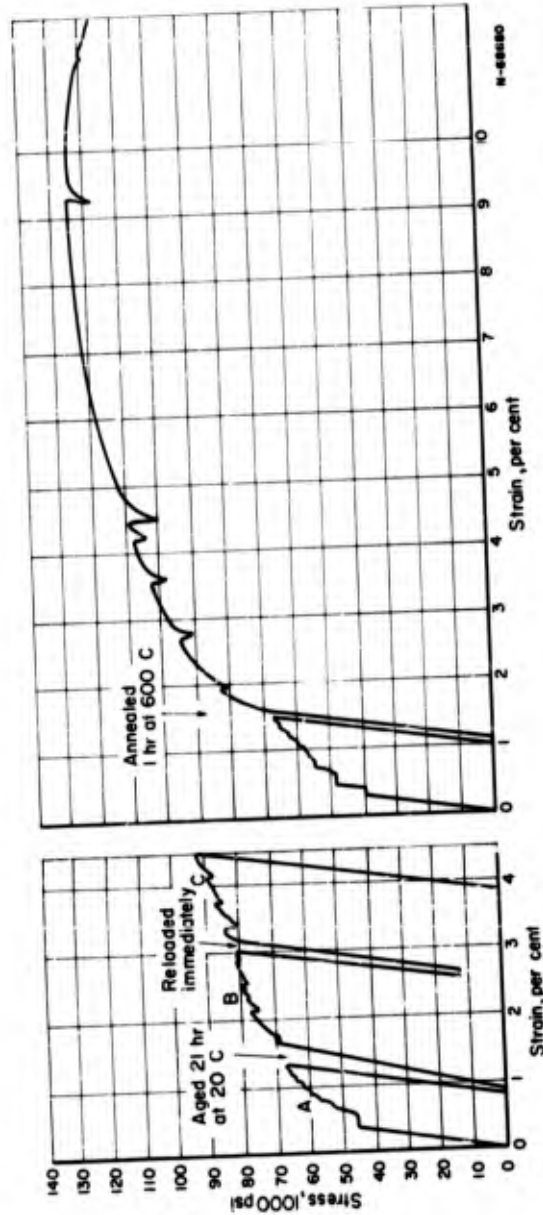


FIGURE 9. RESULTS OF LOAD-UNLOAD AGING EXPERIMENTS ON STRESS-STRAIN CURVES OF Mo-35Re (<10 ppm O) ALLOY TESTED AT 20 C



50X

N64038

a. Tested at -196 C



50X

N64040

b. Tested at 400 C

FIGURE 10. TENSILE FRACTURES IN Mo-35Re

Tungsten-Rhenium Alloys

Fabrication

Previous work⁽³⁾ had shown that arc-melted W-30Re could be flat rolled at 1000 C from ingot to strip, but that alloys containing 10, 20, 35, and 40 per cent rhenium were unfabricable. The fabricable range was studied further in the present work.

Alloys of tungsten containing 20, 22, 24, 26, and 28 per cent rhenium were consolidated by arc melting and fabricated by flat rolling at 1000 C. The W-20Re ingot fractured at a reduction of 56.4 per cent, confirming the previous results. However, the ingots containing 22, 24, 26, and 28 per cent rhenium all were rolled to sound strip at 1000 C. Thus the fabricable range for tungsten-rhenium alloys extends from 22 to 30 per cent rhenium at 1000 C.

Metallographic examination of the ingots after homogenization for 18 hours at 1600 C revealed that the 20, 22, and 24 per cent rhenium alloys were single phase, whereas the 26 and 28 per cent rhenium alloys contained small amounts of sigma phase. The solubility limit of rhenium in tungsten is thus placed at 25 per cent at 1600 C, in general agreement with the published phase diagram, Figure 1.

Bend Ductility

Bend properties over the range 25 C to 400 C were determined for the alloys containing 22 to 28 per cent rhenium after a recrystallization anneal of 1 hour at 1800 C followed by water quenching to reduce sigma precipitation. The bend ductilities of these alloys are plotted in Figure 11, which also includes data⁽³⁾ obtained previously on tungsten and W-30Re for comparison. The bend ductility is seen to improve with increasing rhenium content up to 28 per cent rhenium, falling off moderately at 30 per cent rhenium. In contrast with Mo-35Re, which is ductile to -254 C, the W-28Re alloy becomes increasingly less ductile with decreasing temperature below 200 C. Thus rhenium effects a lesser improvement in the ductility of tungsten as compared with molybdenum. This probably is associated with the lower solubility of rhenium in tungsten and a lesser enhancement of slip through interstitial solubility reduction.

The extent of twinning in tungsten-rhenium alloys was determined by metallographic examination of the alloys containing 20 to 28 per cent rhenium. No twinning was evident around hardness impressions in the homogenized W-20Re ingot, but twinning was observed, after bending, in the alloys containing 22 to 28 per cent rhenium. The amount of twinning increased with increasing rhenium content but decreased with increasing test temperature.

Tensile Properties

Two ingots of W-30Re were consolidated by arc melting, using commercial-purity tungsten wire and powder to provide materials with low and high oxygen content, respectively. These were forged at 1400 C and rod rolled and swaged at 1600 C to provide rod for tensile-property studies. The alloys were recrystallized by annealing for 1 hour at 1800 C and water quenched before being machined into tension test specimens.

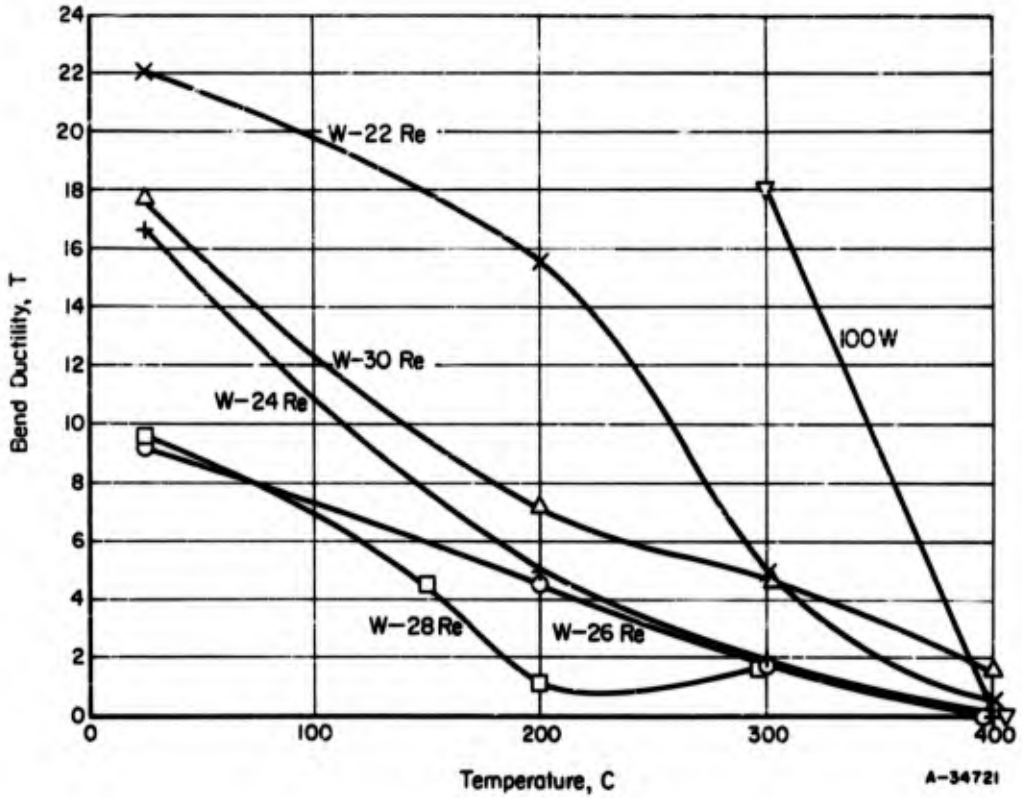


FIGURE 11. BEND DUCTILITIES OF RECRYSTALLIZED TUNGSTEN AND TUNGSTEN-RHENIUM ALLOYS VERSUS TEMPERATURE

One set of tensile samples from the low-oxygen ingot was also vacuum annealed at 2000 C for 1 hour before testing in an unsuccessful attempt to dissolve the small amount of sigma phase observed after annealing at 1800 C.

Tensile properties of these materials are given in Table 5. The properties of the low-oxygen W-30Re alloy also are plotted in Figure 12. The ultimate strength of W-30Re decreases normally with increasing temperature, but remains appreciably higher than that of Mo-35Re (Figure 5). Ductility decreases rapidly below 200 C, in agreement with the ductile-to-brittle transition range determined in the bend-ductility study. The lower strengths and ductilities for material annealed at 2000 C without quenching reflect the slightly larger amount of brittle sigma phase in this material as compared with the material quenched from 1800 C. Increasing the oxygen content from 42 ppm to 74 ppm reduced the ductility and ultimate strength, although the yield strength was not affected.

TABLE 5. TENSILE PROPERTIES OF W-30Re

Condition(a)	Test Temperature, C	Yield Strength at Indicated			Ductility	
		Offset, 1000 psi 0.1%	0.2%	Ultimate Strength, 1000 psi	Elongation, %	Reduction in Area, %
HCW; A 1-1800 WQ(b)	20	188.0	189.2	202.0	5.0	3.8
HCW; A 1-1800 WQ(b)	200	143.0	145.2	170.8	12.3	21.0
HCW; A 1-1800 WQ(b)	400	133.3	133.3	156.8	11.3	25.4
HCW; A 1-2000(b)	-196	192.5	215.0	219.5	0.6	1.0
HCW; A 1-2000(b)	20	158.3		158.3	0.5	6.9
HCW; A 1-2000(b)	400	137.9	132.7	158.4	6.1	22.6
HCW; A 1-1800 WQ(c)	20	182.6	184.3	185.0	1.1	1.8

(a) HCW - hot-cold-worked at 1400 to 1600 C

A 1-1800 - annealed 1 hour at 1800 C

WQ - water quenched after annealing.

(b) Made with tungsten wire. Alloy analyzed 42 ppm oxygen.

(c) Made with tungsten powder. Alloy analyzed 74 ppm oxygen.

Examination of the load-elongation curves for the W-30Re materials revealed fewer discontinuities than were observed for Mo-35Re (Figure 8), indicating less twinning in the tungsten alloy. Photomicrographs of the W-30Re tensile specimens also show less twinning, Figure 13, than do the corresponding Mo-35Re specimens, Figure 10.

Chromium-Rhenium Alloys

Constitution and Hardness

Because rhenium effects similar and significant improvements in the fabricability, ductility, and strength of both molybdenum and tungsten, it is of interest to investigate additions of rhenium to chromium, the third refractory Group VIA metal.

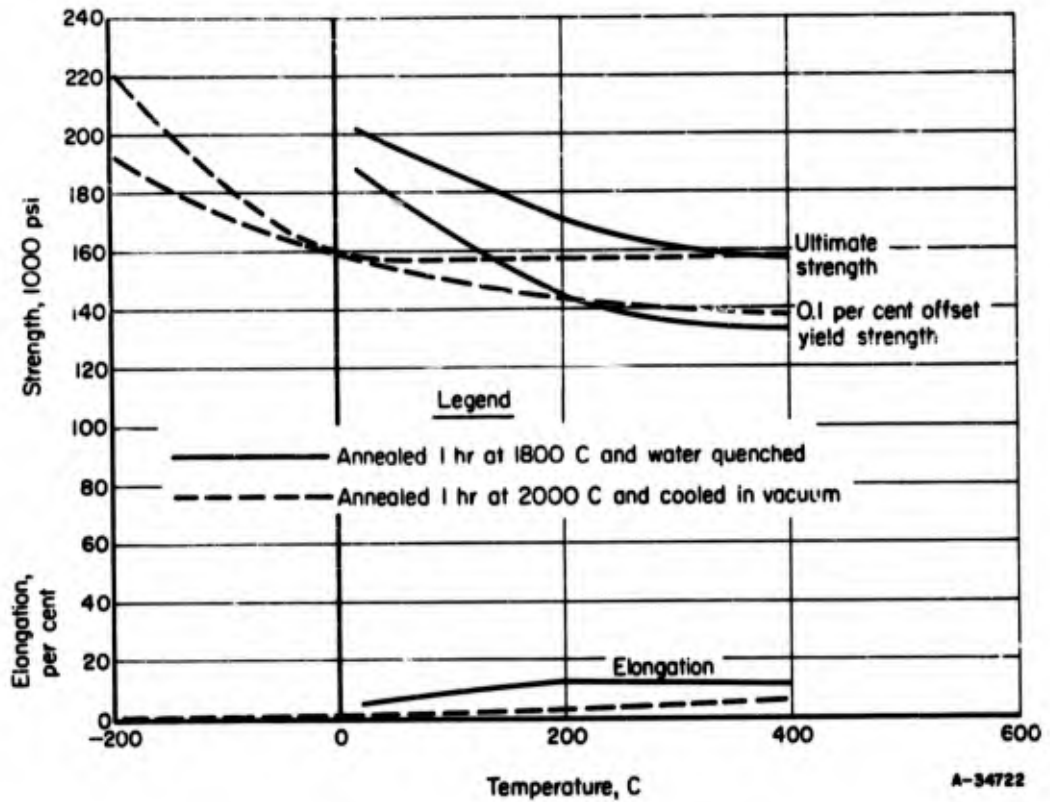
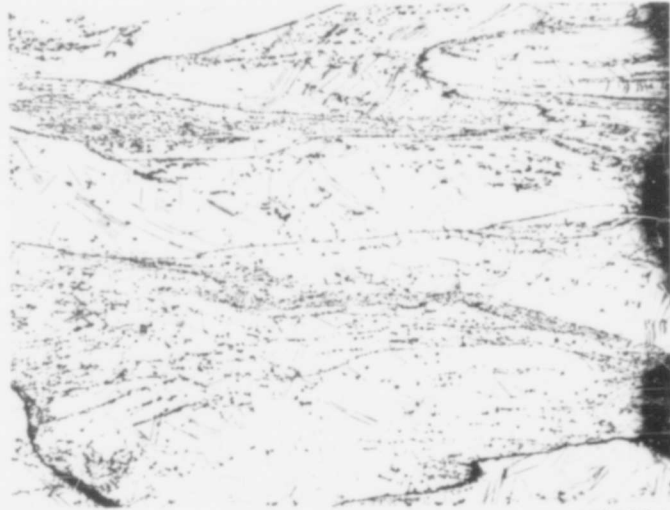


FIGURE 12. TENSILE PROPERTIES OF W-30Re AT -196 C to 400 C



100X

N64034

a. Tested at 20 C



100X

N64036

b. Tested at 400 C

FIGURE 13. TENSILE FRACTURES IN W-30Re

For this purpose, 30-gram ingots were arc melted from high-purity iodide chromium crystals and powder-metallurgy rhenium sheet. The nominal rhenium contents of the alloys were 20, 25, 30, 35, and 40 per cent. Check analyses indicated that chromium was lost during melting, and that the calculated analyses were 21.4, 35, 39, 44, and 54 per cent rhenium, respectively.

Metallographic studies of these alloys after homogenizing for 6 hours at 1500 C in hydrogen indicate that the solubility of rhenium in chromium lies between 35 and 39 per cent, in agreement with the diagram determined by Savitskii, et al. (9) Above the solubility limit, sigma phase is formed, as illustrated in Figure 14. Mechanical twinning is observed around hardness impressions in the alloys containing 35, 39, and 44 per cent rhenium, and is heaviest at 39 per cent rhenium (also shown in Figure 14).

The hardness values of homogenized chromium-rhenium alloys are compared in Figure 15 with the hardness values of molybdenum-rhenium and tungsten-rhenium alloys. All three are characterized by a moderate hardness increase with increasing rhenium content up to the solubility limit for rhenium in the base-metal matrix. The hardness then increases rapidly as sigma phase appears and increases in quantity.

Fabrication and Bend Ductility

Fabrication was attempted at 1000 C on the five chromium-base alloys containing 21.4 to 54 per cent rhenium, but all cracked after total reductions of 20 per cent or less. These failures are attributed to nitrogen contamination during the homogenization treatment in hydrogen.

An as-cast ingot of Cr-39Re, not homogenized, was successfully warm rolled 90.6 per cent total reduction at 1000 C to excellent strip. Hardness and bend ductility data for this material are presented in Table 6. The bend ductility is seen to be excellent at temperatures as low as at least -196 C, comparing favorably with the ductility of recrystallized Mo-35Re. In contrast, recrystallized high-purity chromium has a ductile-to-brittle bend transition temperature of about 200 C. (12) Thus, the improvements in fabricability and ductility effected by alloying with rhenium are common to all three Group VIA metals, molybdenum, tungsten, and chromium.

TABLE 6. HARDNESS AND BEND DUCTILITY OF Cr-39Re

Condition	Hardness, VHN	Temperature, C	Bend Ductility,
			T
Cast	348	20	1.9
Rolled 90.6 per cent at 1000 C	508	20	0
Rolled and vacuum annealed	342	20	0
1 hr at 1200 C		-196	<1.5
Rolled and hydrogen annealed	322	20	>11.7
1 hr at 1300 C			
Rolled and hydrogen annealed	1033	20	>11.7
1 hr at 1800 C			

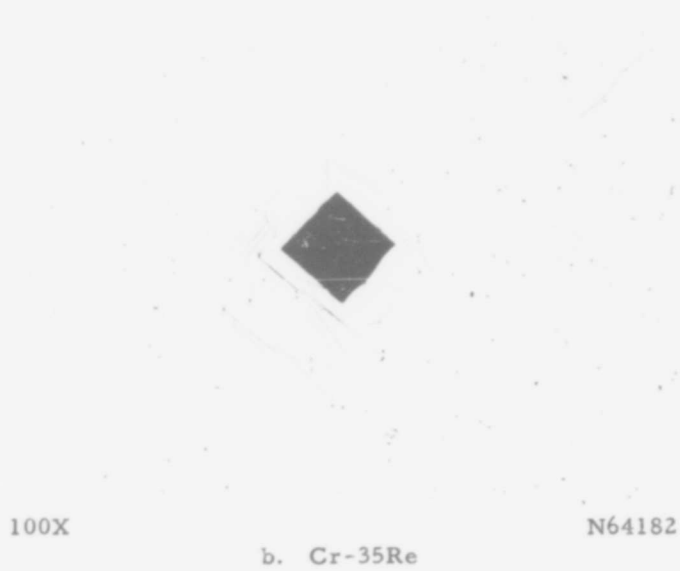
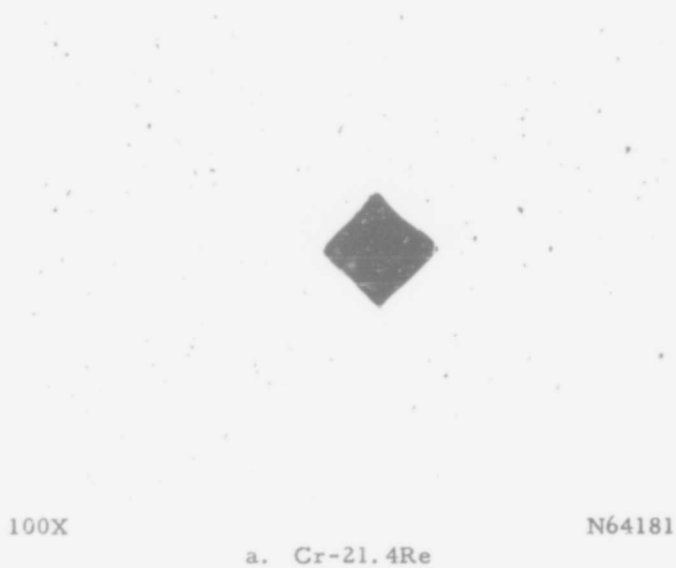


FIGURE 14. MICROSTRUCTURES OF HOMOGENIZED CHROMIUM-RHENIUM ALLOYS

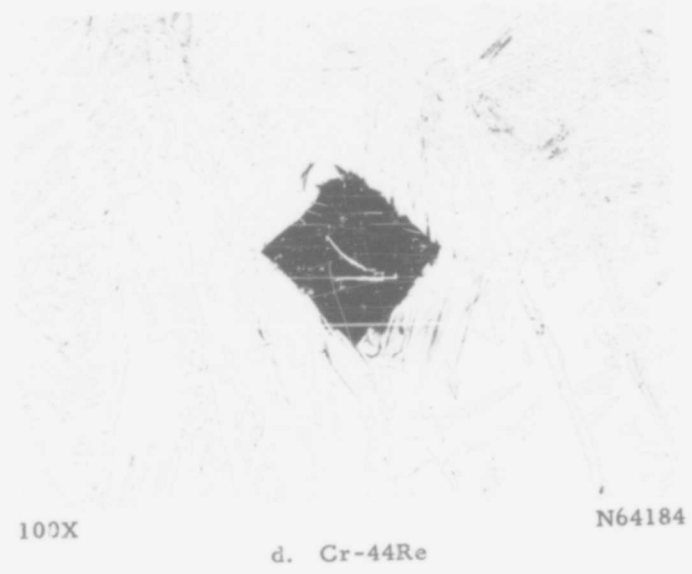
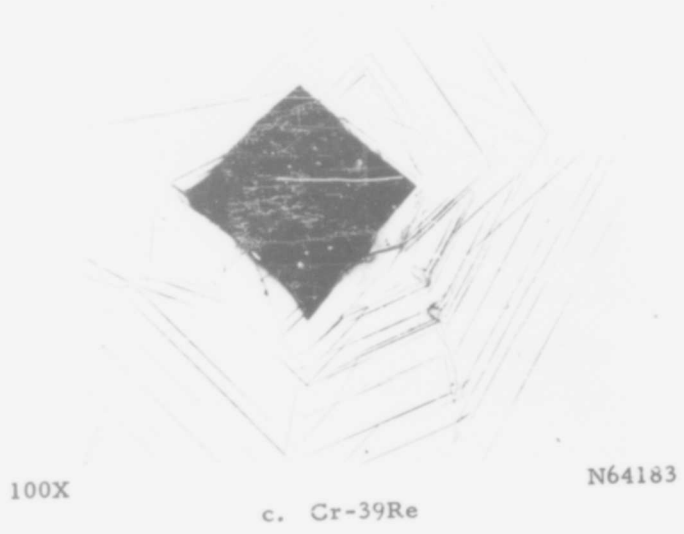


FIGURE 14. (CONTINUED)

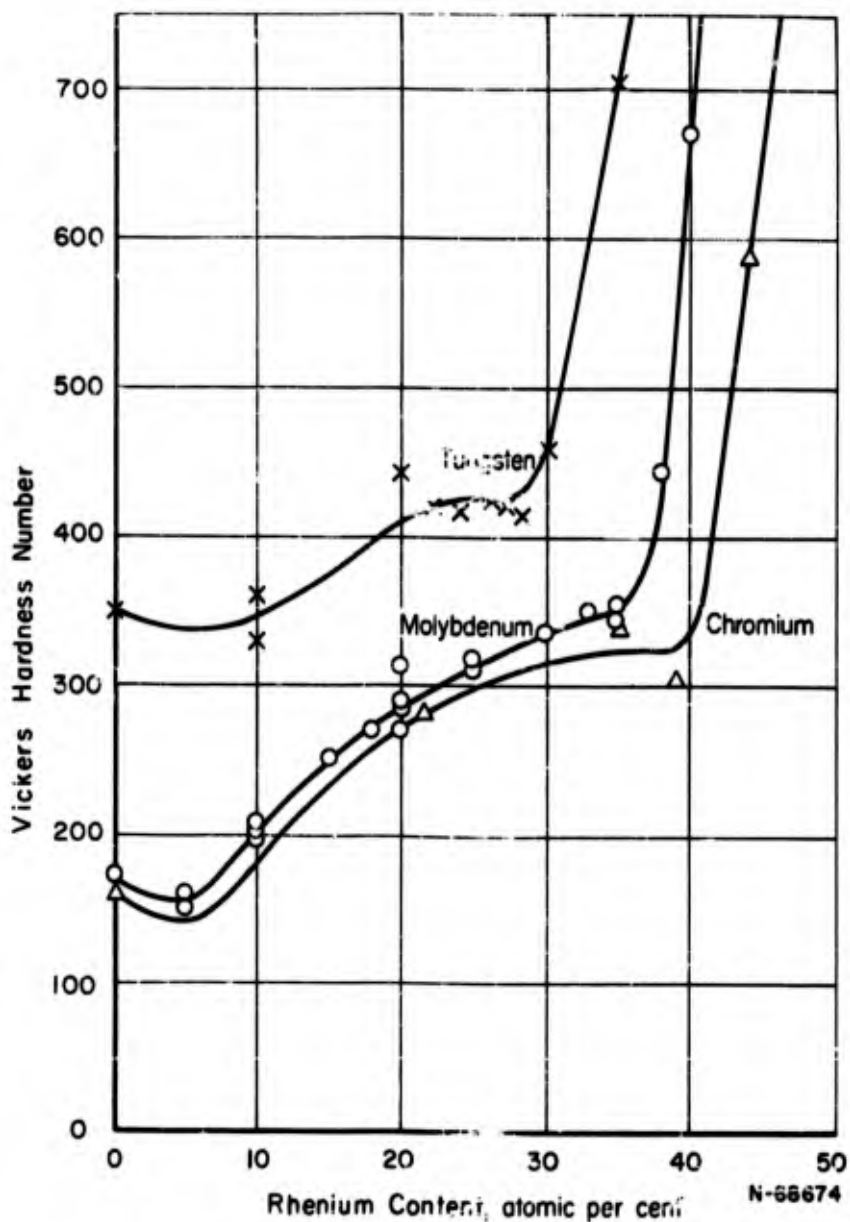


FIGURE 15. EFFECT OF RHENIUM ON THE AS-CAST HARDNESS OF CHROMIUM, MOLYBDENUM⁽³⁾, AND TUNGSTEN⁽³⁾

SUMMARY AND CONCLUSIONS

(1) The effect of rhenium in improving the hot working of molybdenum is restricted to alloys containing oxygen as an interstitial impurity. The maximum oxygen content for cold fabricability in Mo-35Re is between 60 and 110 ppm; the limit for fabricability at 1200 C to 1250 C is at least 250 ppm. In contrast, increasing the nitrogen content to 70 ppm or the carbon content to 18 ppm renders the alloy incapable of direct hot fabrication.

The composition ReMoO_4 suggested for the intergranular oxide in Mo-35Re is supported but not identified conclusively by electron microanalyses studies of the oxide in situ. The surface tension of the intergranular oxide in molybdenum is increased by rhenium additions, causing the oxide to agglomerate into round globules and thereby reducing its detrimental effects on fabricability.

The hot-working characteristics of molybdenum-rhenium alloys are also improved by a reduction in oxygen solubility as rhenium is added. The reduction in solubility is indicated by an initial hardness decrease on the addition of rhenium and is in agreement with the recent theory of Robins. (11)

(2) Twinning appears to be associated with rhenium content only, and occurs most profusely at the maximum rhenium solubility in molybdenum. No indications of long or short-range ordering have been found for Mo-35Re. The amount of twinning decreases with increasing temperature for a given composition. Twinning at room temperature is found for alloys containing 20 to 35 per cent rhenium.

Twinning effects appear during tensile testing as discontinuities in the stress-strain curves, resulting in serrations in the stress-strain curve similar to the discontinuities caused by interstitial locking. The yield-point behavior in these alloys is attributed to an audible burst of twins as the critical twinning stress is exceeded. Temperature has little effect on the critical twinning stress, i. e., the yield strength, over the range -196 C to 400 C.

(3) The bend ductility of recrystallized molybdenum improves with increasing rhenium content up to 35 per cent. The transition temperature for Mo-35Re is extremely low, below -254 C. Wrought molybdenum-rhenium alloys deform by slip rather than by twinning, and exhibit higher bend transition temperatures than do the recrystallized alloys.

(4) Molybdenum-rhenium alloys are considerably stronger than unalloyed molybdenum at -196 C to 1204 C. The ultimate strength increases with increasing rhenium content up to 35 per cent rhenium. The yield strength increases up to about 30 per cent rhenium and then dips sharply as twinning predominates as the initial deformation mechanism. Ductility also shows an increase at the 30 to 35 per cent rhenium level. Additions of 0.5 wt % titanium do not effect the room temperature properties significantly but improve the strength and creep resistance of Mo-35Re at elevated temperatures.

(5) Tungsten-rhenium alloys containing from 22 to 30 per cent rhenium can be warm rolled at 1000 C. The solubility limit for alloys quenched from 1800 C occurs at about 25 per cent rhenium.

(6) The bend ductility of tungsten-rhenium alloys is superior to that of tungsten but inferior to that of molybdenum-rhenium alloys. Recrystallized W-28Re, the most ductile alloy, has a brittle-to-ductile transition range of 150 C to 200 C. Twinning decreases in quantity with increasing temperature, and is observed at room temperature in alloys containing 22 to 30 per cent rhenium.

(7) The tensile strength of W-30Re decreases normally with increasing temperature, and is higher than that of Mo-30Re. Ductility increases as the temperature approaches 200 C, the transition range in bending. Twinning during tensile loading was apparent as discontinuities in the stress-strain curves, but was not as heavy as in Mo-35Re.

(8) The solubility of rhenium in chromium lies between 35 and 39 per cent, in agreement with the published diagram. Mechanical twinning at room temperature is observed at 35 to 44 per cent rhenium. A warm-rolled strip of Cr-39Re was bend ductile at -196 C after being annealed at 1200 C. Rhenium thus imparts similar improvements in fabricability and ductility to all three Group VIA metals, chromium, molybdenum, and tungsten.

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The information on which this report is based is contained in Battelle Laboratory Record Books Nos. 13976, pp 49-100; 15480, pp 1-100; 16499, pp 1-100; and 16942, pp 1-20.

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