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TECHNICAL REPORT

on

**THE EFFECT OF RHENIUM ON THE
FABRICABILITY AND DUCTILITY OF
MOLYBDENUM AND TUNGSTEN**

to

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

by

R. I. Jaffee and C. T. Sims

April 1, 1958

**BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio**

Battelle Memorial Institute

5 0 5 K I N G A V E N U E C O L U M B U S I . O H I O

April 16, 1958

Dr. J. J. Harwood
Head, Metallurgy Branch
Department of the Navy
Office of Naval Research
Washington 25, D. C.

Dear Dr. Harwood:

Enclosed are ten copies of our Technical Report, "The Effect of Rhenium on the Fabricability and Ductility of Molybdenum and Tungsten", by R. I. Jaffee and C. T. Sims, covering some aspects of the work being conducted under Contract Nonr-1512(00). Copies also have been sent to those on the enclosed distribution list.

Yours very truly,

Robert I. Jaffee

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THE EFFECT OF RHENIUM ON THE FABRICABILITY AND DUCTILITY OF MOLYBDENUM AND TUNGSTEN

by

R. I. Jaffee and C. T. Sims

The favorable effects of rhenium on the hot workability of molybdenum have been found to result from the redistribution of oxygen as a complex oxide or molybdate at rhenium contents over about 25 atomic per cent rhenium. The low-temperature ductility of the Mo-25 to 35 Re alloy is much better than that of molybdenum alone as a result of mechanical twinning and reduction of dislocation locking. The effects of rhenium on tungsten have been found to be similar, although the improvement in low-temperature ductility is less marked.

INTRODUCTION

Rhenium has aroused much interest in recent years. The preparation of the metal in ductile form and its mechanical and physical properties were described by C. T. Sims and co-workers^{(1, 2)*} as part of an extensive research program carried out at Battelle Memorial Institute during the past 7 years. Another group, led by G. A. Geach at the Associated Electrical Industries Laboratory at Aldermaston, England, also conducted detailed studies on the metal, including a study of the deformation mechanism.⁽³⁾ Pure rhenium metal is of considerable interest for electrical and electronic applications, but its use is hampered by its working characteristics. It cannot be hot worked, and the rate of work hardening at room temperature is so great that frequent annealing is required.

A remarkable effect of rhenium on molybdenum and tungsten was reported at the Second Plansee Seminar, held in June, 1955, at which time G. A. Geach and J. E. Hughes⁽⁴⁾ reported that molybdenum alloyed with 35 at. %** rhenium (50 wt %) could be directly rolled in the as-cast condition to reductions of 90 per cent without cracking. The primary mode of deformation was noted to be coarse twinning. Tungsten-rhenium alloys containing 35% rhenium exhibited similar workability at several hundred degrees C. The alloys maintained their hardness very well to 800 C, indicating they they would have good high-temperature properties.

E. M. Savitskii and M. A. Tylkina⁽⁵⁾ also investigated the working of molybdenum-rhenium alloys. They found that the plasticity of the Mo-10Re alloy in static compression at room temperature was greater than that of molybdenum. However, alloy contents beyond about 10% were found to cause the plasticity to decrease progressively to zero at 60% rhenium. Thus, the extraordinary workability found by Geach and Hughes was not observed by these workers.

*References are listed at the end of the report.

**Atomic per cent is used throughout report, unless specifically noted otherwise.

The constitution of the molybdenum-rhenium system according to Dickinson and Richardson⁽⁶⁾ is shown in Figure 1. It is seen that the molybdenum-rich solid-solution field is extensive, and somewhat dependent upon temperature. It is succeeded by a sigma phase corresponding to Re_3Mo_2 and isomorphous with other sigma phases. This diagram agreed with the previous work of Greenfield and Beck⁽⁷⁾ on the intermediate phases in the molybdenum-rhenium and tungsten-rhenium systems. Greenfield and Beck found sigma between 48 and 67% rhenium. The second intermediate phase, with an alpha-manganese structure, was found at about 79% rhenium. Knapton⁽⁸⁾ also noted sigma phase in these alloys. An early report of a face-centered cubic phase at 15% rhenium by McHargue and Maynor⁽⁹⁾ has not been confirmed by other investigators.

Early work on the tungsten-rhenium system by Becker and Moers⁽¹⁰⁾ indicated a maximum melting point of 3010 C at about 62% rhenium, a composition corresponding to Re_3W_2 . This compound formed a 2890 C eutectic at 50% rhenium with tungsten, and a 2820 C eutectic at 67% rhenium with rhenium. Greenfield and Beck⁽⁷⁾ found the same phases in the tungsten-rhenium system as in the molybdenum-rhenium system, namely, a sigma phase from 37-58% rhenium and an alpha-manganese structure at 27% molybdenum.

The present study was initiated for the purpose of checking the extraordinary workability of molybdenum-rhenium and tungsten-rhenium alloys found by Geach and Hughes, to determine mechanical properties at room and elevated temperatures, and to determine, if possible, the reasons for the unique effects of rhenium on the hot and cold ductility of molybdenum and tungsten.

MATERIALS

The rhenium metal used in the investigation was obtained from the Chase Brass and Copper Company in the form of cold-rolled strips. The metal was prepared by powder-metallurgy methods from rhenium powder made by hydrogen reduction of ammonium perrhenate. A quantitative spectrographic analysis of the rhenium is given below:

	<u>Wt %</u>
Fe	0.005
Al	0.010
Si	0.007
Mg	0.005
Mo	0.005

A vacuum-fusion analysis revealed that rhenium of the type used contained 6 ppm oxygen, 6 ppm hydrogen, and less than 5 ppm nitrogen. ⁽¹⁾

The molybdenum used was hydrogen-reduced molybdenum powder further purified by vacuum arc melting with an inert tungsten electrode. The product contained about 5 ppm oxygen, 2 ppm nitrogen, 10 ppm iron, and 20 to 30 ppm carbon.

The tungsten powder used for powder-metallurgy work was Type 425 high-purity grade obtained from Fansteel Metallurgical Corporation. It was not purified further.

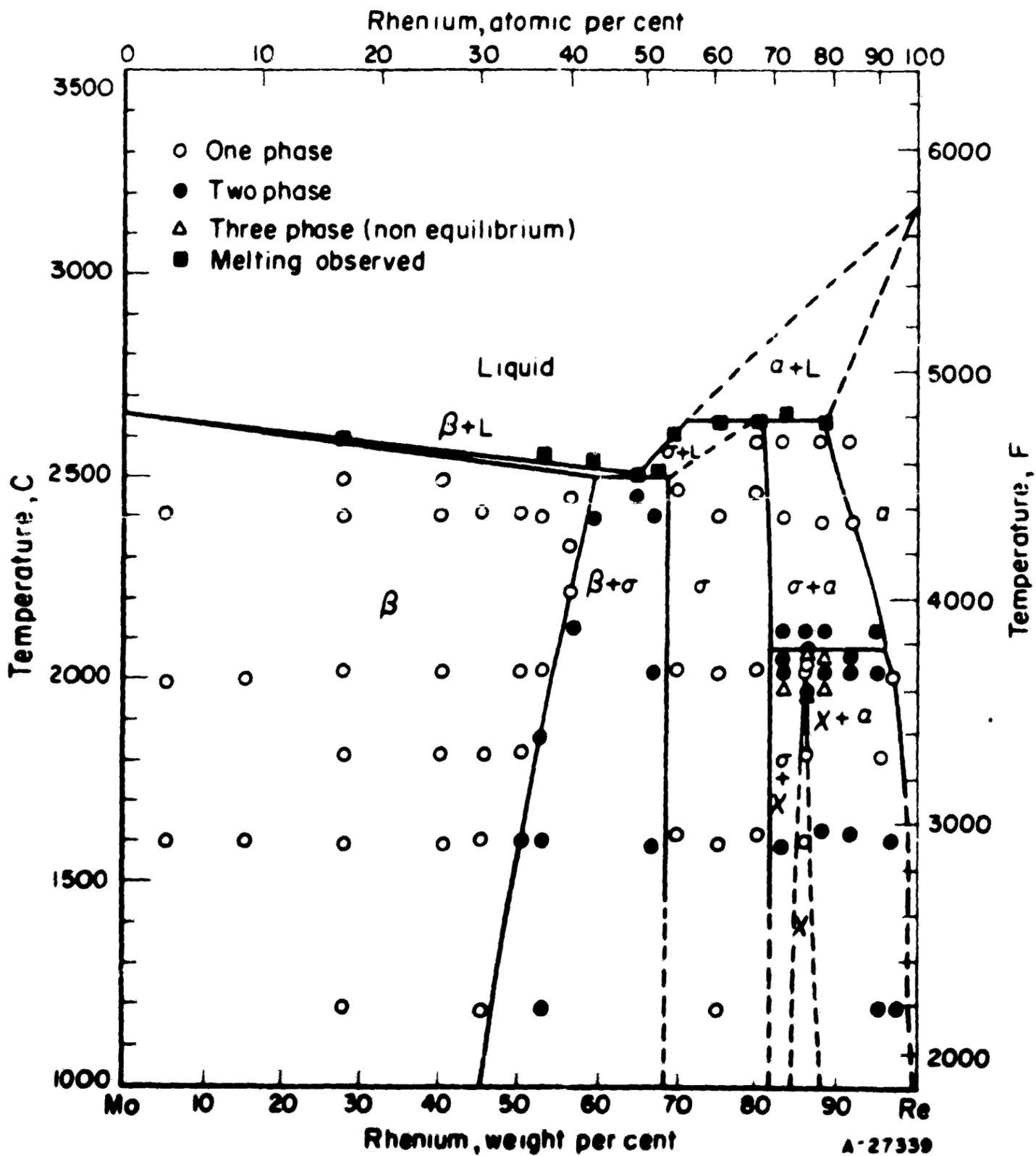


FIGURE 1. MOLYBDENUM-RHENIUM PHASE DIAGRAM

Dickinson and Richardson (6)

The tungsten for arc melting was about 100-mesh granular prepared by crushing 5-mil Fansteel sheet that had been recrystallized in hydrogen.

MOLYBDENUM-RHENIUM ALLOYS

Preparation of Alloys

Most of the molybdenum-rhenium alloys studied were prepared as 10-gram buttons by arc melting the charge in a water-cooled copper-hearth crucible at about 275 amperes. An inert tungsten electrode was used under argon at a pressure of 10 cm of Hg. The ingots were inverted three or four times and remelted for homogenization. Weight losses were low enough that the nominal analysis was accurate to better than 1 per cent. The buttons were large grained and bright in appearance and about half as high as their diameter. A small amount of oxygen contamination occurred in melting; vacuum-fusion analyses gave 36 ppm for a molybdenum button and 50 ppm for a Mo-35Re button.

Powder metallurgy was used as an alternative method of preparing the alloys. The rhenium powder used was of the ammonium perrhenate-reduced type used in previous studies.⁽¹⁾ It was found difficult to attain high sintered densities in alloys containing more than about 10% rhenium. Pressing was done dry. No improvement resulted from adding 0.5 per cent stearic acid to the blended powders. The densities of molybdenum-rhenium alloys after presintering and sintering are listed in Table 1. Pressing was done at 30 tons per square inch in a steel die with a 0.25 x 0.25 x 6-inch cavity. The die could be dismantled to remove the pressed bar. The pressed bar was presintered in a vacuum furnace for 1-1/2 hours at 1200 C and then sintered in tank hydrogen in a resistance sintering bottle described previously.⁽¹¹⁾ Density, in per cent of ideal, decreased progressively with increasing rhenium contents. Despite this, powder-metallurgy bars with up to about 20% rhenium have been fabricated.

TABLE 1. DENSITIES OF SINTERED MOLYBDENUM-RHENIUM ALLOYS

Bar Size: 0.25 x 0.25 x 6 inches
Pressing Pressure: 30 Tons per Square Inch

Rhenium, atomic per cent	Presintered 1 Hr at 1200 C		Sintered 1 Hr at 90 Per Cent Melting Point	
	G/CC	Per Cent Ideal	G/CC	Per Cent Ideal
0	6.16	61	9.58	94
10	7.72	64	10.3	85
20	7.75	57	11.2	82
30	8.09	54	12.1	80
35	8.3	53	12.0	76
40	8.11	50	12.8	79

The work of Geach and Hughes⁽⁴⁾ on the workability of cast molybdenum-rhenium-alloy buttons was confirmed by a series of tests on 10-gram buttons rolled at 5 per cent reduction per pass at room temperature, 500 C, and 1250 C. The ability of the buttons to be reduced without signs of major edge or surface cracking was used as an indication of workability. Table 2 gives the results on the amount of reduction before cracking. Figure 2 shows the appearance of the buttons after rolling at room temperature and at 500 C. At room temperature, the workability of molybdenum was slightly increased by the addition of 25 and 30% rhenium, but the 35% rhenium button could be rolled 95 per cent to 0.020-inch thicknesses without cracking. This great increase in room-temperature workability is confined to the range close to 35% rhenium, since, at 40% rhenium, workability is severely reduced again.

TABLE 2. EFFECT OF RHENIUM ON WORKABILITY OF AS-CAST MOLYBDENUM-RHENIUM ALLOYS AT ROOM AND ELEVATED TEMPERATURES

Rhenium, atomic per cent	Per Cent Reduction Before Cracking		
	Room Temperature	500 C	1250 C
0	10	--	10-15
5	--	14	15
15	--	20	22
25	18	>94	32, >95
30	19	>93	>95
35	>95	>94	>94
40	18	>93	>93
50	10	10	10

At rolling temperatures of 500 C or 1250 C, the range of workability was greatly extended for alloys containing 25 to 40% rhenium. One button of the Mo-25Re alloy did not exhibit good workability at 1250 C, but a second button rolled very well to 95 per cent without cracking. It is probable that the 25% rhenium composition is close to the lower limit for good as-cast hot workability. The reason for the difference in behavior of the two buttons might have been that the unworkable button contained more oxygen than the other.

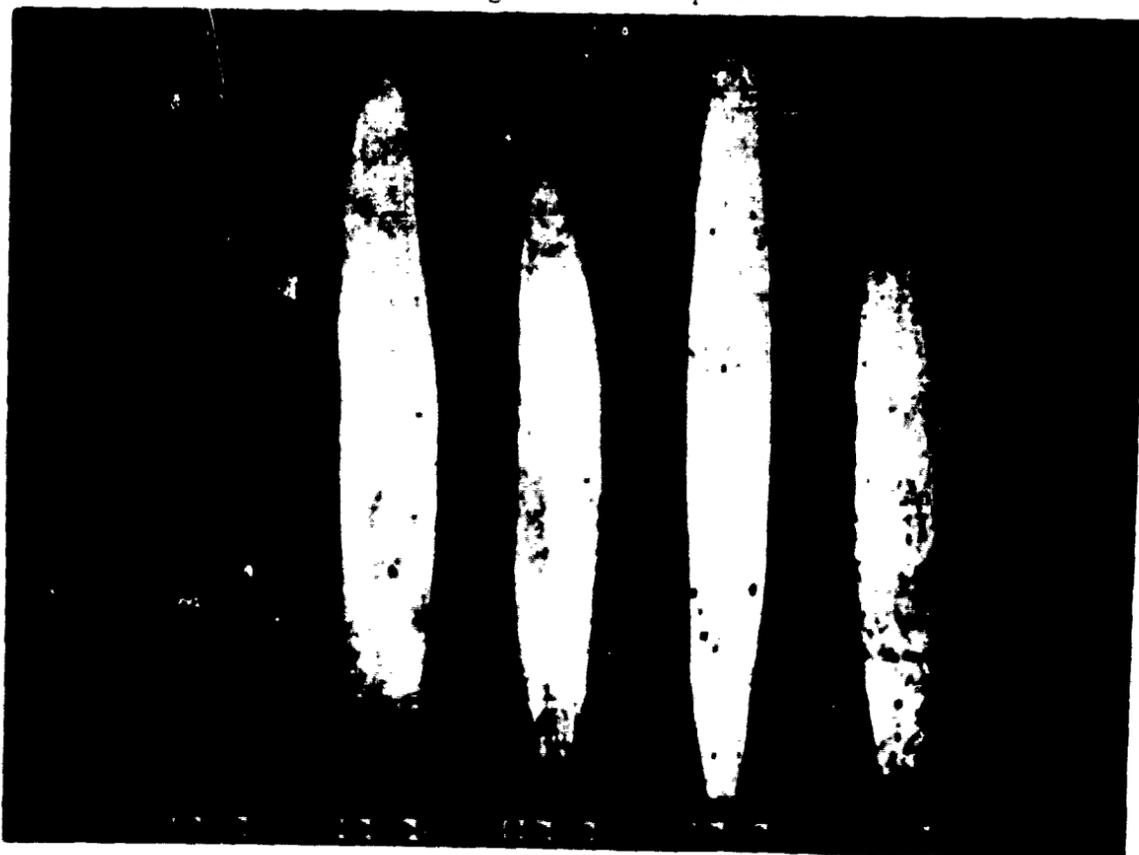
Vacuum-fusion analyses of arc-melted alloys gave values of 36 to 50 ppm oxygen. This amount of oxygen is extremely high to expect workability in cast molybdenum, unless extrusion or some method of lateral restraint were used in fabrication. The fact that the molybdenum-rhenium alloys rolled so well indicates a high tolerance for oxygen with the maintenance of direct workability. It was of interest, therefore, to determine the limits of oxygen permissible in Mo-35Re before hot or cold workability was lost. To achieve the high oxygen contents, compacts were made of blended rhenium and molybdenum powder and arc melted into buttons. The surface oxides would be expected to result in oxygen contents of up to about 1000 ppm. The buttons were rolled at 1250 C or room temperature. If they could not be fabricated under these conditions, they were remelted and re-rolled. Remelting resulted in a reduction of the oxygen content. Buttons that were rolled successfully were analyzed for oxygen. The results are given in Table 3. Apparently at least 100 ppm oxygen can be tolerated and good cold workability be maintained; the oxygen tolerance for good hot-working characteristics is at



1/2X

N30215

a. Rolling at Room Temperature



1/2X

N30966

N33233

N30966

N33233

N30966

b. Rolling at 500°C

FIGURE 2. APPEARANCE OF MOLYBDENUM-RHENIUM ALLOY BUTTONS AFTER ROLLING

least 250 ppm oxygen. A limit was not set at oxygen contents greater than 250 ppm because conflicting results were obtained in hot rolling buttons containing 370 and 540 ppm oxygen.

TABLE 3. ROLLING OF HIGH-OXYGEN Mo-35Re BUTTONS

Rolling Temperature, C	Oxygen Content, ppm	Per Cent Reduction Before Cracking
Room	110	56
	60	95 (no cracking)
	50	95 (no cracking)
1250	540	95 (no cracking)
	370	17
	250	92 (no cracking)
	140	95 (no cracking)

The strength and ductility values of the Mo-35Re alloy after a variety of fabrication and annealing histories are listed below:

Fabrication History	Ultimate Tensile Strength, psi	Elongation, per cent
Cold rolled 95 per cent to 0.020-inch strip	257,000	Less than 1
Above material annealed 2 hours at 1600 C	177,000	2
Hot rolled at 1250 C to 0.020-inch strip	192,000	20
Hot rolled at 1400 C, annealed, and cold rolled 60 per cent	247,000	2
Above material annealed 1 hour at 1700 C	140,000	22

Despite the fact that the Mo-35Re alloy could be directly cold rolled in the as-cast condition, cold rolling of the cast alloy is not recommended as a method of fabrication. Material cold rolled to strip was found to have low ductility, and the ductility could not be restored by annealing. When fabrication was conducted at conventional working temperatures for molybdenum alloys, or if the amount of cold work between recrystallization anneals was kept to about 60 per cent reduction, good ductility was obtained. Also, the structure of recrystallized material so processed is clean and equiaxed, whereas the strip cold rolled 95 per cent exhibited a dispersion of a second phase that could not be eliminated by high-temperature annealing.

Structure

Molybdenum-rhenium alloys containing up to 40% rhenium are predominantly single-phase body-centered cubic solid-solution alloys. Small amounts of sigma phase are present at 35% rhenium, and these increase in amount at 40%. X-ray diffraction measurements of the lattice constants of as-cast alloys homogenized 72 hours at 1000 C and water quenched are listed in Table 4. Rhenium decreases the lattice constant of molybdenum linearly up to 35% rhenium, as would be expected from the atomic sizes for the metals. Careful examination of the diffraction patterns did not show evidence of any superlattice lines.

TABLE 4. LATTICE CONSTANTS OF MOLYBDENUM-RHENIUM ALLOYS

Composition, atomic per cent	Type of Lattice	Lattice Constants, A
Mo	BCC (Mo)	$a = 3.1466(a)$
5.4 Re	BCC (Mo)	$a = 3.1443 \pm 0.0006$
18.1 Re	BCC (Mo)	$a = 3.1366$
31.4 Re	BCC (Mo)	$a = 3.1269$

(a) Barrett, C. S., Structure of Metals, McGraw-Hill Book Company, New York (1952).

Because of the unusual tolerance of the molybdenum-rhenium alloys for oxygen, it was of interest to determine the distribution and form of the oxygen-bearing phase. Figures 3 and 4 are photomicrographs of molybdenum and the Mo-35Re alloy with high oxygen content resulting from arc melting powder compacts. In cast molybdenum, the oxygen-containing phase, actually a eutectic between molybdenum and MoO_2 , is located primarily at the grain boundaries. There, it has a low dihedral angle with the grain boundary, indicating good wetting. In the cast 35% rhenium alloy, most of the oxygen-bearing phase occurs as globules within the grains themselves. The oxide phase at the grain boundaries occurs as discrete inclusions that make large dihedral angles with the grain boundaries. Two possibilities present themselves to explain the difference in disposition of oxygen: either the surface tension of the MoO_2 -Mo eutectic has been greatly increased by the rhenium, or a new phase has formed. On the basis of the available evidence, it appears most probable that a new phase has formed.

The section of Mo-35Re alloy containing high oxygen (Figure 4) was etched in Murakami's reagent, leaving the grain-boundary phase in relief. The sample was coated with a thin plastic film, which, on stripping, carried off the grain-boundary material. A diffraction pattern was obtained from this phase; the d values are listed in Table 5. This phase was not MoO_2 , so a new phase must have formed. The crystal structure of the new phase is not known yet.

Attempts were made to synthesize a complex oxide of rhenium and molybdenum. ReO_3 and MoO_3 were compacted in a weight ratio of 1:1, the ratio of the two metals in the Mo-35Re alloy. The specimen was heated in air and observed. At about 650 C, MoO_3 crystals began forming on the surface of the specimen.



500X

N35147

FIGURE 3. MOLYBDENUM-POWDER COMPACT, ARC MELTED



500X

N33949

FIGURE 4. Mo-35Re POWDER COMPACT, ARC MELTED

TABLE 5. X-RAY DIFFRACTION PATTERN OF PARTICLES EXTRACTED FROM ARC MELT OF Mo-35Re POWDER

Iron Radiation With MnO₂ Filter

θ	$\text{Sin}^2\theta$	I(a)	d, A	θ	$\text{Sin}^2\theta$	I(a)	d, A
10.40	0.0326	MF	5.37	41.20	0.4425	M	1.47
11.10	0.0371	MS	5.03	42.30	0.4529	VVF	1.44(β)
15.35	0.0701	F	3.66(β)	43.25	0.4695	F	1.41($\beta+$)
16.25	0.0783	M	3.46	44.50	0.4913	MF	1.38
16.85	0.0840	VS	3.34	45.20	0.5035	S	1.36
17.45	0.0899	VF	3.23	46.55	0.5270	F	1.33
18.05	0.0960	MF	3.13	47.85	0.5497	M+	1.31
19.55	0.1120	VVF	2.89	48.55	0.5618	MF	1.29
20.25	0.1198	MS	2.80	49.90	0.5851	M	1.27
20.95	0.1278	VVF	2.71	51.15	0.6065	M-	1.24
23.15	0.1546	MS	2.46	51.85	0.6184	F	1.23
24.90	0.1773	F	2.30($\beta+$)	53.25	0.6252	M	1.21
26.65	0.2012	MF	2.16	54.55	0.6636	F	1.19
27.45	0.2125	S	2.10	55.60	0.6808	MS	1.17
28.20	0.2233	VVF	2.05(β)	59.00	0.7347	MS	1.13
29.10	0.2365	M	1.99	62.15	0.7818	S	1.09
30.75	0.2607	VVF	1.89(β)	66.30	0.8384	M	1.06
31.40	0.2715	MS	1.86	67.25	0.8505	M+	1.05
32.85	0.2942	M	1.79	69.25	0.8745	MS	1.04
34.30	0.3176	S	1.72	71.25	0.8967	MF	1.02
35.00	0.3290	M	1.69	74.80	0.9313	F	1.00
36.70	0.3572	VVF	1.62(β)	77.50	0.9532	M	0.991(α_1)
37.75	0.3580	VF	1.58	78.10		MF	0.991(α_2)
38.45	0.3867	MF	1.56	79.20	0.9649	M	0.985(α_2)
39.80	0.4097	F	1.51(β)	79.95		MF	0.985(α_2)

(a) Visually estimated intensities:

- VS = very strong
- S = strong
- MS = medium strong
- M = medium
- MF = medium faint
- F = faint
- VF = very faint
- VVF = very, very faint

The compact was heated to a maximum temperature of 770 C. A portion of the center of the compact was studied by X-ray diffraction. The major phase was MoO_3 , and there were some very faint diffraction lines corresponding to ReO_3 . In addition, there were several faint unidentified lines that correspond to the pattern of the grain-boundary material removed from the high-oxygen Mo-35Re specimen grain boundaries. Therefore it appears possible that the oxygen-bearing phase in the workable molybdenum-rhenium alloys is a complex oxide of molybdenum and rhenium. Less probable is the thesis that the lines were from a decomposition product of ReO_3 , since this phase decreased in intensity but the MoO_3 remained strong.

Further attempts at forming the complex oxide by heating MoO_3 - ReO_3 mixtures were unsuccessful. One mixture heated to 850 C, at which temperature part of the mixture was molten (MoO_3 melts at 795 C), exhibited only MoO_3 upon X-ray diffraction analysis. A 1:1 mixture of ReO_2 and MoO_2 was heated to 900 C, and X-ray diffraction gave MoO_2 and orthorhombic ReO_2 ⁽¹²⁾, rather than the phase extracted from the Mo-35Re alloy.

The molybdenum-rhenium alloys exhibiting good low-temperature ductility undergo extensive mechanical twinning, which will be discussed further in the next section. The twinning system is not known, though there is no reason to believe that it is different from the (112)[111] characteristic of other body-centered cubic metals. Cahn found such deformation twins in molybdenum deformed in compression by impact at liquid-oxygen temperature.⁽¹³⁾ However, before concluding that the structural indications thought to be twins actually were twins, it was necessary to determine that they were not martensite plates formed by strain transformation at low temperature. To determine this, filings were taken from a Mo-35Re alloy at room temperature and at -196 C. Debye-Scherrer powder patterns were then examined to see whether there were any indications of a face-centered cubic or hexagonal close-packed martensite-transformation product. The patterns were somewhat fuzzy, as a result of the cold work, but there were no indications of a new martensitic phase being formed.

Low-Temperature Mechanical Behavior

The hardnesses of as-cast molybdenum-rhenium alloys are shown in Figure 5. Shown along the bottom of the graph are the phase ranges at 1600 C found by Dickinson and Richardson.⁽⁶⁾ It is seen that there is an initial region up to 5% rhenium where there is no hardening, and may even be softening. Beyond this, the variation of hardness with composition up to 36% rhenium is the normal variation expected for solid solutions. From 30 to 36% rhenium, the hardness is substantially constant. As more sigma phase appears, the hardness increases very rapidly to about 1550 Vickers for all sigma.

The tensile properties of rolled and recrystallized molybdenum-rhenium alloys with up to 35% rhenium are shown in Figure 6. The speed of testing was maintained at 0.005 inch per minute throughout the test. The molybdenum and the Mo-10Re and Mo-20Re alloys were prepared by powder metallurgy, and the Mo-30Re and Mo-35Re alloys were arc melted. The alloys up to 30% rhenium were rod rolled at 1400 C to 0.15-inch-square wire and recrystallized by heating for 1 hour at 1400 C to 1800 C, depending on the alloy content. The Mo-35Re alloy was rolled at 1250 C and recrystallized by annealing 1 hour at 1800 C. Up to 20% rhenium increases the strength and decreases the ductility of molybdenum in a normal manner for solid-solution alloys. The initial 10% rhenium does not increase the strength, which agrees with the hardness data, but the strength increases significantly at 20% rhenium. The tensile strength and the ductility

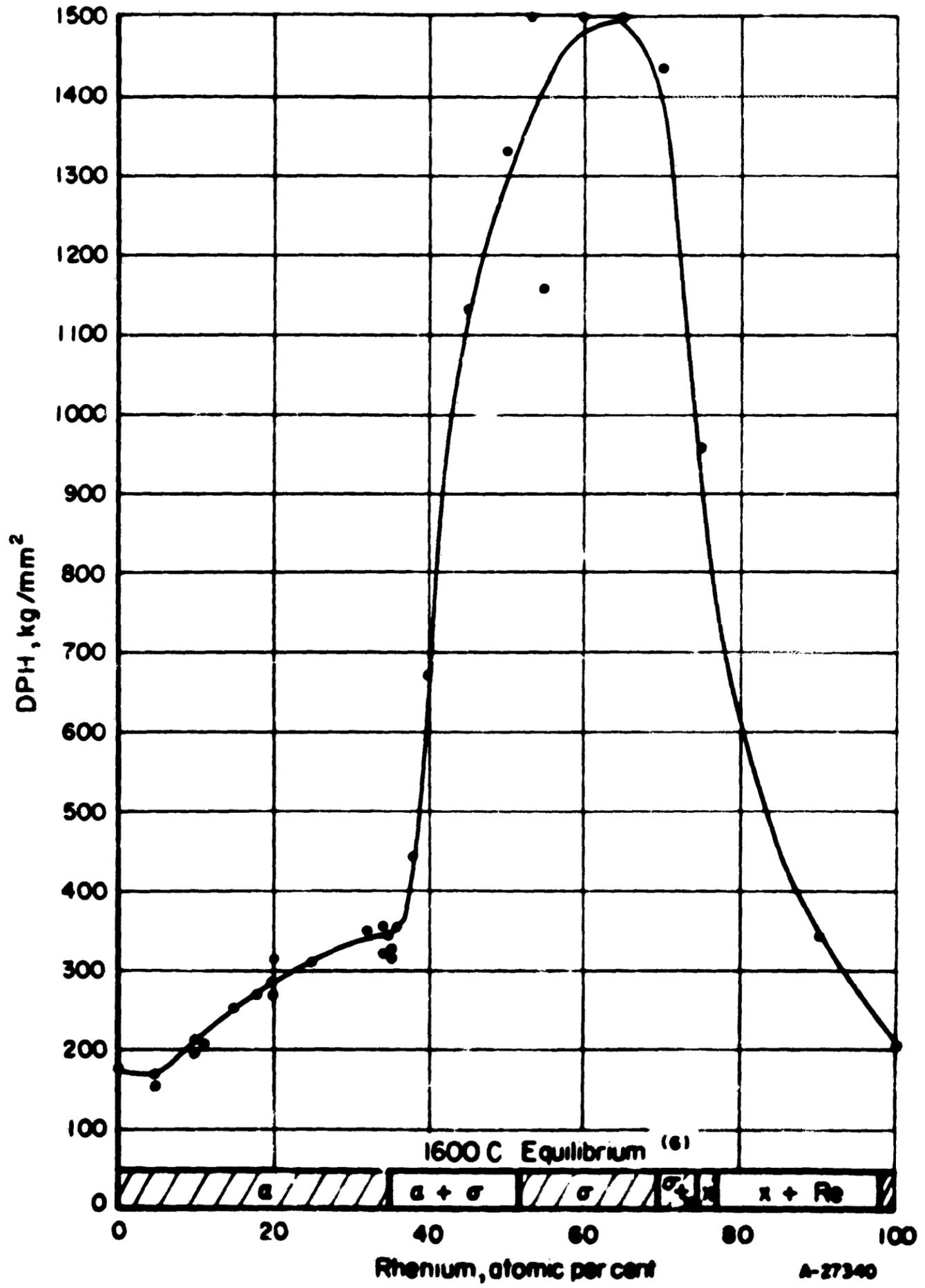


FIGURE 5. HARDNESS OF AS-CAST MOLYBDENUM-RHENIUM ALLOYS

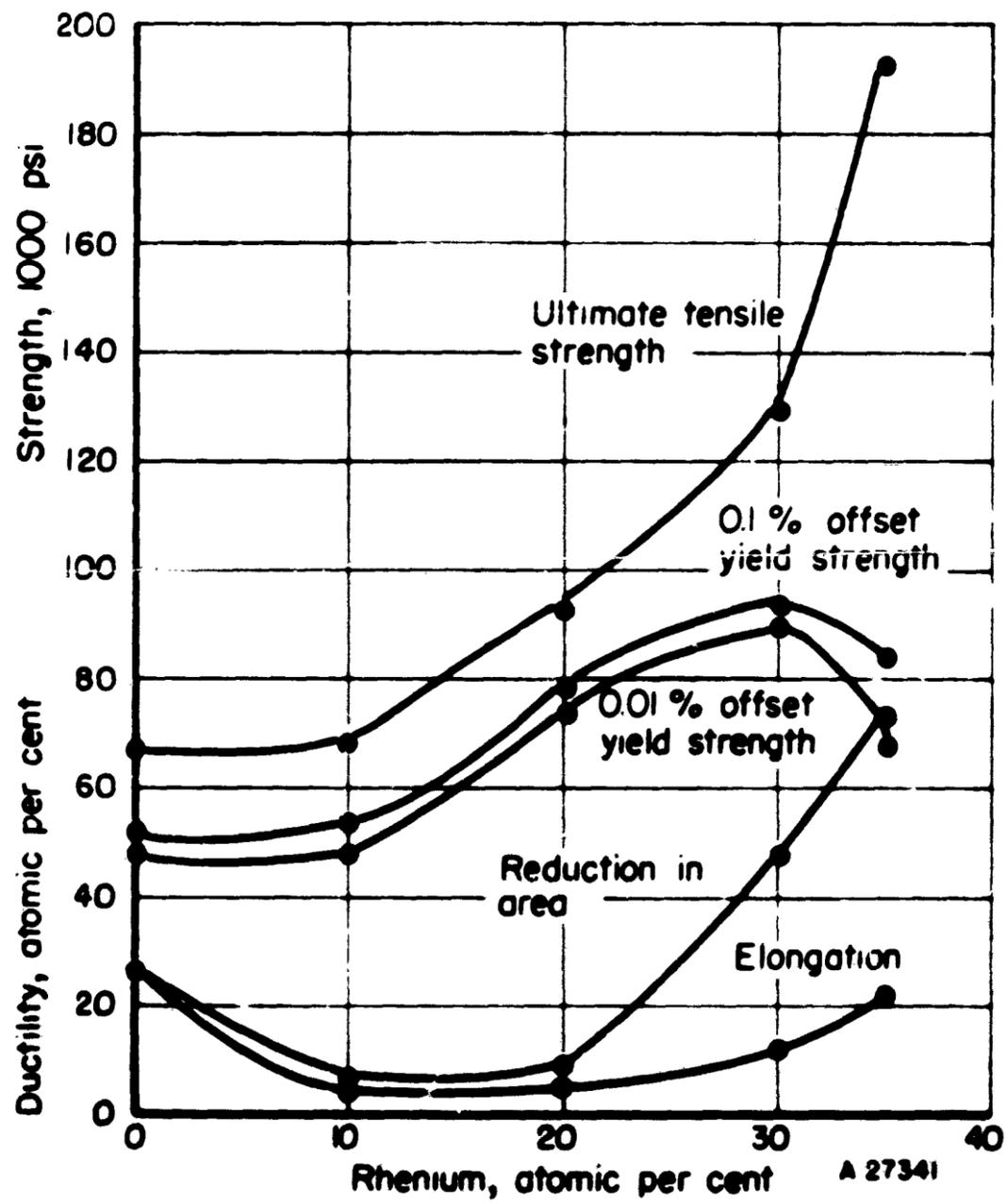


FIGURE 6. ROOM-TEMPERATURE TENSILE PROPERTIES OF MOLYBDENUM-RHENIUM ALLOYS

then increase at an accelerating rate up through 35% rhenium. The yield strength levels off at 30% rhenium, and actually decreases at 35% rhenium. It is apparent that a deformation mechanism other than slip is initiating plastic deformation at lower stresses at 30 and 35% rhenium.

The microstructures of the tensile fractures of the molybdenum and the Mo-20Re, Mo-30Re, and Mo-35Re alloys shown in Figure 7 indicate the difference in mechanical behavior below 20% rhenium and above 30% rhenium. The high-rhenium alloys exhibit mechanical twinning, whereas the low-rhenium alloys do not. Twinning also was noted to result in audible clicks or a "cry" when a rod of Mo-35Re was bent.

To investigate the process of deformation in the Mo-35Re alloy, an interrupted flow study was conducted. A recrystallized Mo-35Re strip was prepared for testing by polishing the surfaces to a metallographic finish. Then this strip was intermittently strained, and repolished and etched to eliminate the slip markings from the surface. The initial 1 per cent strain required a true stress at 88,700 psi. The structure after repolishing and etching is shown in Figure 8. The direction of testing was parallel to the stringers of sigma phase, and it can be seen that twins have formed in many grains around the 45 degree maximum-shear-stress direction. No twins are present parallel to the stress direction. Figure 9 is a photomicrograph of the same area after 14 per cent strain (144,000-psi true stress). More grains now exhibit twins, as the resolved shear stress along the twinning plane has increased to the critical shear stress for twinning. Some grains have become oriented such that no twinning occurred at all. The widths of the twins have increased considerably, and they have become segmented as slip and cross twinning have occurred.

Flow curves for recrystallized molybdenum and Mo-20Re, Mo-30Re, and Mo-35Re alloys are shown in Figure 10. The initial flow stress for the Mo-35Re alloy is lower than those of the Mo-20Re and the Mo-30Re alloys only up to about 0.1 per cent strain; beyond 4 per cent strain, the flow stresses of the Mo-30Re and the Mo-35Re alloys are about the same.

The effects of temperature and strain rate on the tensile properties of the Mo-35Re alloy in the vicinity of room temperature were investigated in order to study their effects on flow stress, ductility, and the extent of twinning. Table 6 gives the tensile properties obtained at -50 C, room temperature, and 250 C at testing speeds of 0.005 per minute and 0.1 per minute. Testing was done using a Baldwin-Southwark hydraulic machine, which, although not particularly "hard", is capable of indicating yield-point behavior. Figure 11 shows the tensile fractures. Decreasing the temperature to -50 C and increasing the strain rate increases the amount of twinning, and increasing the temperature to 250 C reduces twinning. Also, at the lower strain rate, there was more tendency toward intergranular fracture. All of the specimens fractured at 0.005 inch per minute exhibited grain-boundary separations away from the fracture. None of the specimens tested at 0.1 inch per minute exhibited such separations.



100X

N45831

a. Mo



100X

N45833

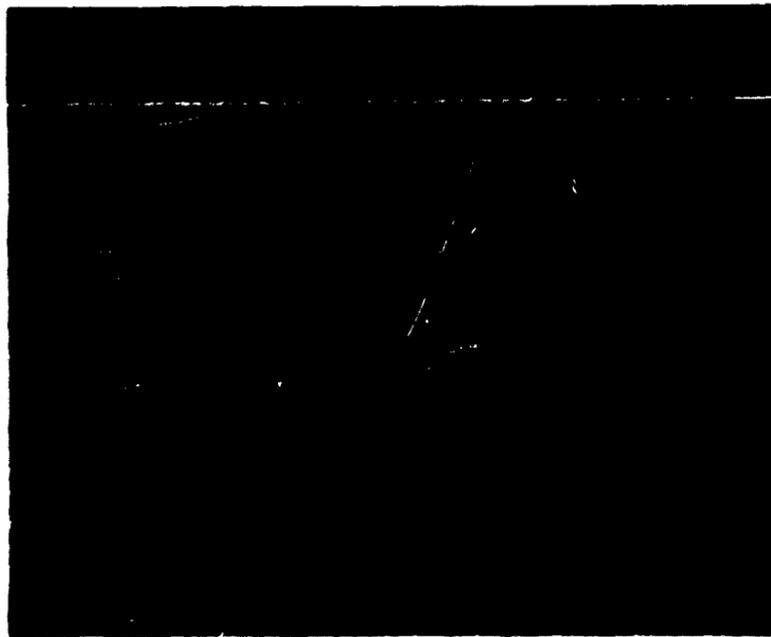
b. Mo-20Re



100X

N45834

c. Mo-30Re

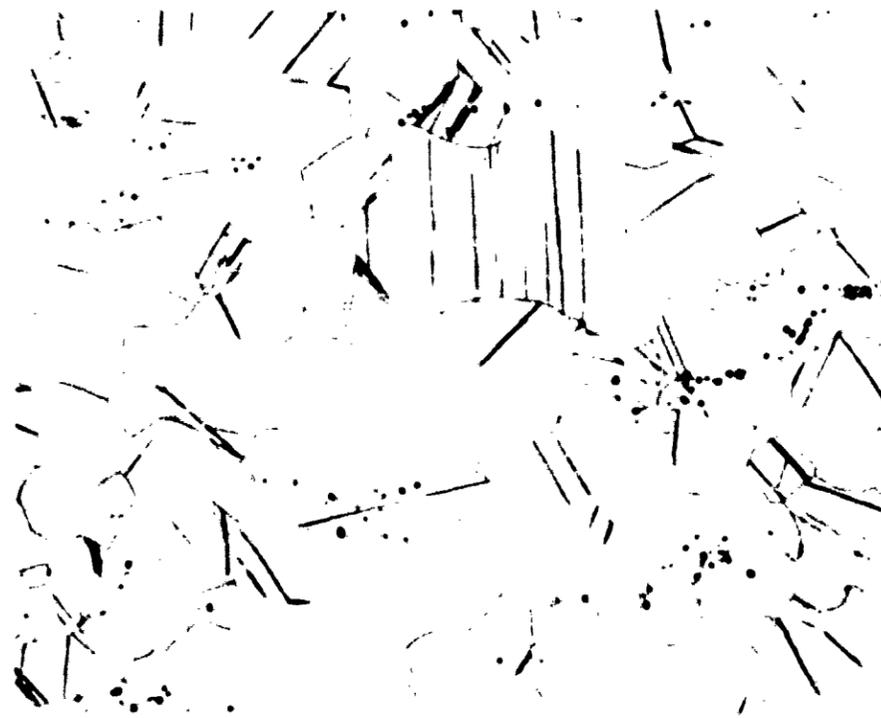


100X

N46612

d. Mo-35Re

FIGURE 7. EFFECT OF RHENIUM ON TENSILE FRACTURE OF MOLYBDENUM AT ROOM TEMPERATURE



100X

N42247

FIGURE 8. Mo-35Re ALLOY STRAINED 1 PER CENT AT 88,700-PSI TRUE STRESS



100X

N42265

FIGURE 9. Mo-35Re ALLOY STRAINED 14 PER CENT AT 144,000-PSI TRUE STRESS

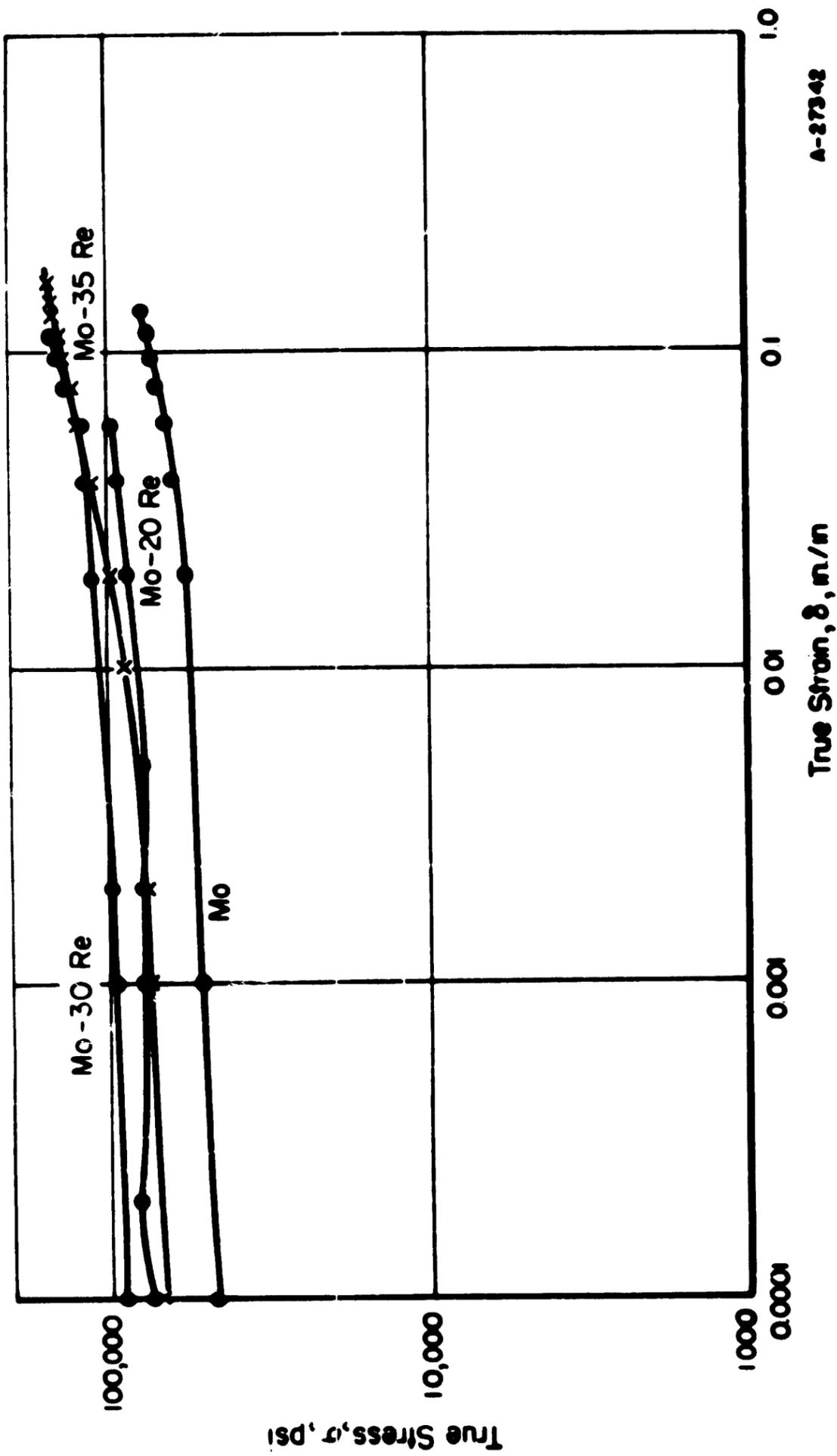


FIGURE 10. FLOW CURVES FOR Mo-Re ALLOYS

A-27342

TABLE 6. EFFECT OF STRAIN RATE AND TEMPERATURE ON Mo-35Re ALLOY

	0.005 In. /Min			0.1 In. /Min		
	-50 C	RT	250 C	-50 C	RT	250 C
Ultimate Tensile Strength, 1000 psi	134	135	113	152	141	99
Yield Strength (0.1 Per Cent Offset), 1000 psi	85	103	70	79.5	90	58
Yield Strength (0.2 Per Cent Offset), 1000 psi	88.5	105.5	73.5	89.5	95	60
Elongation, per cent in 3/4 inch	11	24	20	15	25	17
Reduction in Area, per cent	43	38	54	35	36	60

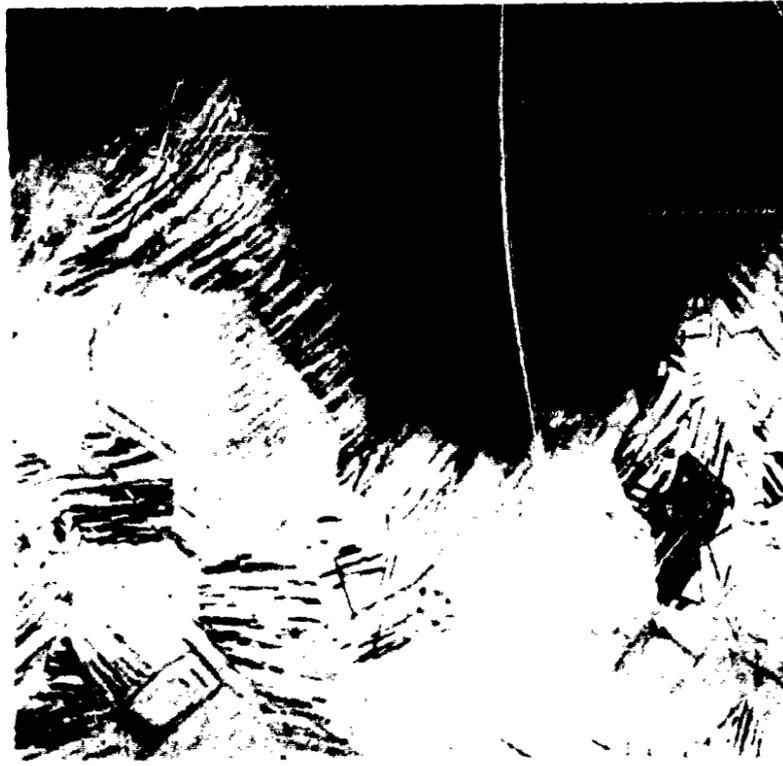
The yield strength increases rather sharply with decreasing temperature from 250 C to room temperature. This usually signifies the onset of the ductile-to-brittle transition in molybdenum alloys. However, from room temperature to -50 C, the yield strength decreases significantly. At the higher strain rate, flow is initiated at still lower stresses. The tests at lower temperature and higher strain rate were accompanied by increased twinning and maintenance of ductility. In deformation by slip alone, these factors usually cause brittleness, because the increased flow stresses required exceed the fracture stress. Figure 12 illustrates the serrated stress-strain curve obtained in these tests. It is believed that twinning occurs in the flat regions of the curve, and slip occurs in the steep portions.

The temperature region over which twinning occurs is lower with lower rhenium contents. In the Mo-25Re Alloy, profuse twins were observed deformed at -196 C and -140 C, a few twins were observed at -90 C, and none at room temperature. For pure molybdenum, Cahn⁽¹³⁾ observed twins only in material deformed in compression at impact speeds at -196 C.

The transition from ductile to brittle behavior was investigated by subjecting hot-cold-worked and recrystallized 0.020-inch strip of Mo-35Re alloy to bend tests. The bend ductility at temperature was determined using a Vee die with a 75-degree included angle. The specimen was placed across the Vee span. Ten punches with progressively sharper radii, from 0.375 inch to "sharp", were impressed in the specimen until cracking or fracture occurred. The bend ductility is expressed by the minimum bend radius, designated as a multiple of the specimen thickness over which the strip could be bent successfully. The results of these tests are shown in Figure 13. The recrystallized alloy could be bent through a sharp bend radius (zero T) at temperatures down to -196 C. The hot-cold-worked specimen had been rolled 60 per cent at 1250 C, after recrystallization, and was brittle at -196 C but ductile at -140 C. Thus, the recrystallized condition is shown to be the most ductile condition for the Mo-35Re alloy. The usual behavior for molybdenum, which has been confirmed, is to have lower ductile-to-brittle transition temperature when hot-cold worked than when recrystallized. The transition for the recrystallized Mo-35Re alloy is below -196 C.



100X N46613
a. -50 C, 0.005 In./Min



100X N46609
b. -50 C, 0.1 In./Min



100X N46608
c. RT, 0.1 In./Min



100X N46610
d. 250 C, 0.1 In./Min

FIGURE 11. EFFECT OF TEMPERATURE AND STRAIN RATE ON TENSILE FRACTURE OF Mo-35Re ALLOY

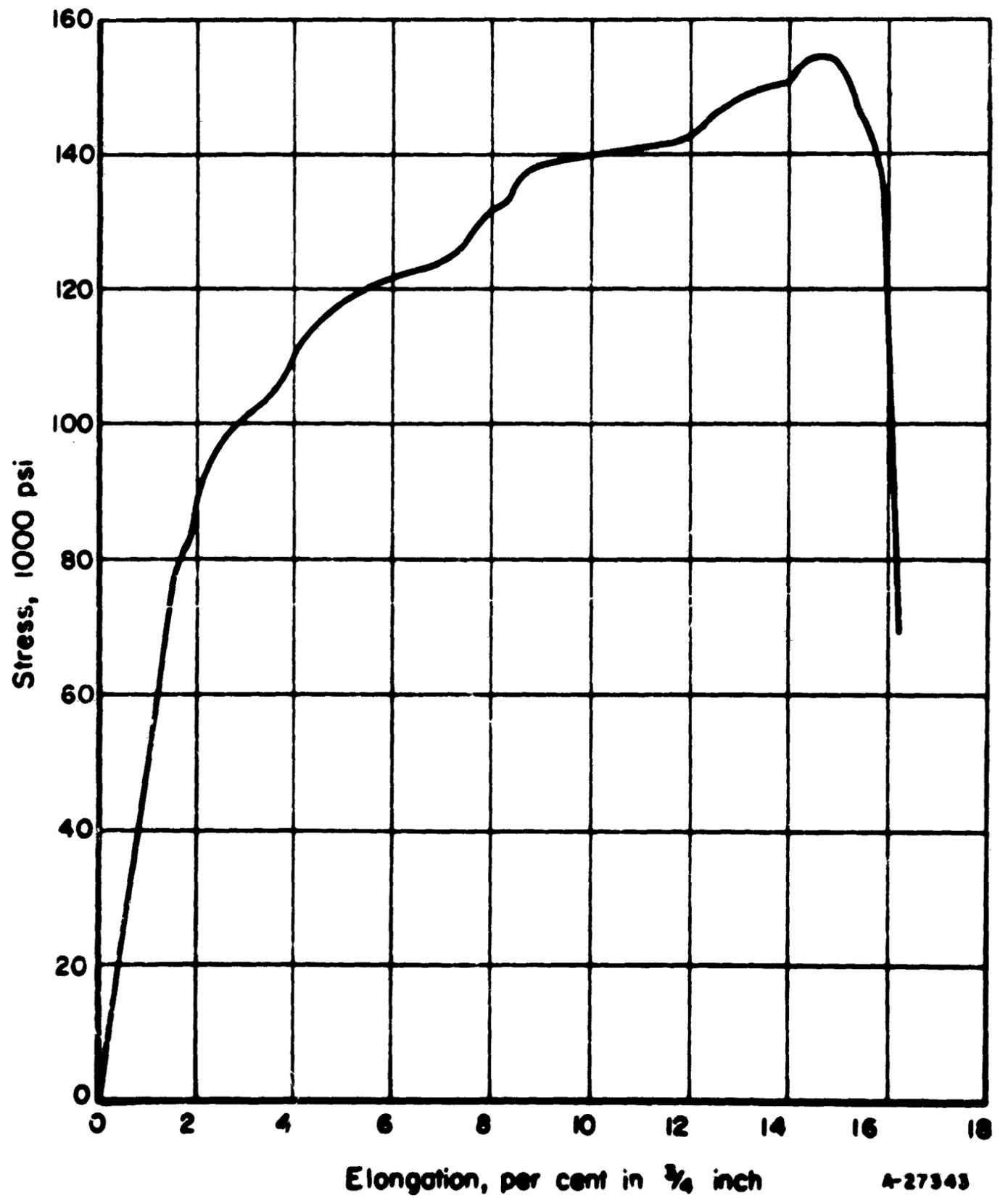


FIGURE 12. STRESS-STRAIN CURVE OF Mo-35Re ALLOY AT -50 C

Strain rate: 0.1 inch per minute.

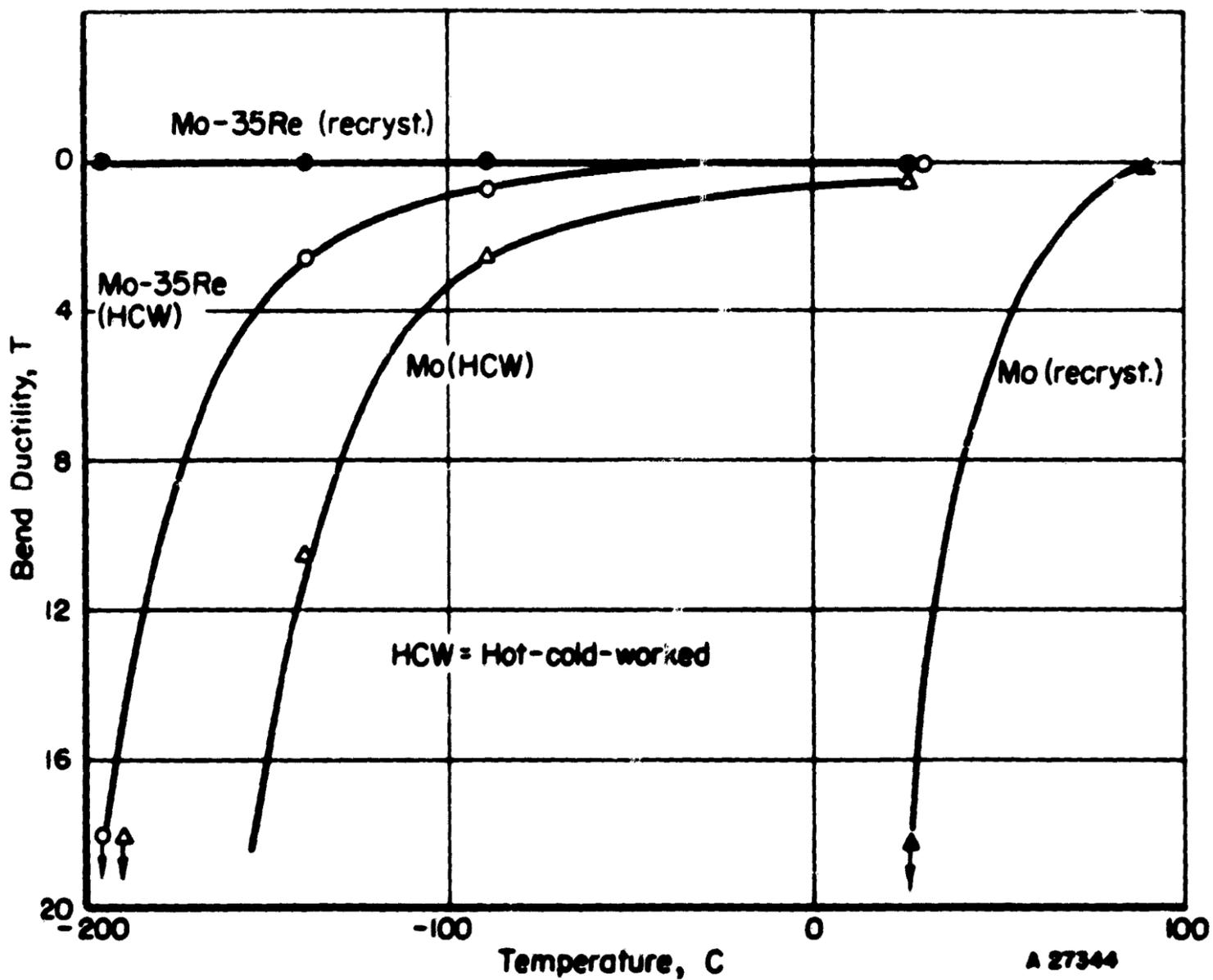


FIGURE 13. BEND-TRANSITION CURVES FOR MOLYBDENUM AND THE Mo-35Re ALLOY IN THE RECRYSTALLIZED AND HOT-COLD-WORKED CONDITIONS

The Mo-35Re alloy also has a low ductile-to-brittle transition temperature in the as-cast condition. The alloy is extremely difficult to fracture by hammering as-cast material at temperatures down to -196°C . When as-cast metal is broken up under these conditions, the fracture generally is composed of shear and cleavage, in contrast to the predominantly intercrystalline fracture of as-cast molybdenum. Figure 14 shows sections of a button that was refrigerated at -196°C and fractured by a sharp blow. The upper section shows cleavage with patches of shear fracture. The lower section shows a cleavage fracture along steps or twins, terminated at a grain boundary; the fracture in the adjacent grain is very fragmented, indicating a shear-type ductile failure.

As a result of its good as-cast ductility, the Mo-35Re alloy is ductile in the welded condition. Welds also have been made in molybdenum sheet using Mo-35Re alloy as filler metal. Bend tests on such welds generally fail in a brittle manner in the heat-affected zone of the recrystallized base metal. Where deformation is confined to the alloy weld metal, ductile bend behavior is observed, as illustrated in Figure 15.

In these welds, 0.062-inch molybdenum sheets were assembled with a 1/16-inch gap over a copper back-up bar, and welded in a helium-atmosphere chamber using a Mo-35Re wire as a consumable electrode at 90 to 120-ampere current.

High-Temperature Behavior

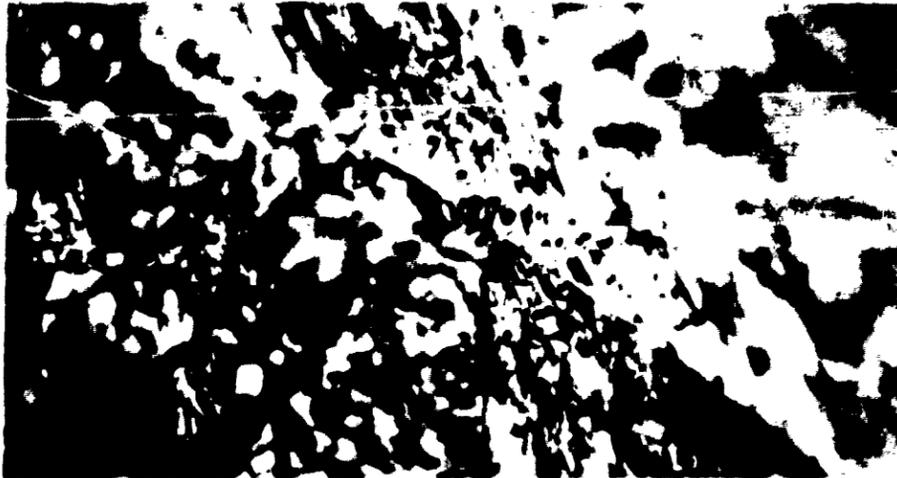
The recrystallization temperature for the Mo-35Re alloy is about 400°C higher than for molybdenum with a comparable amount of cold work. Figure 16 shows the effect on hardness of cold rolling an as-cast Mo-35Re alloy button to 60 per cent reduction in thickness and reheating 1 hour at temperatures from 1000°C to 2100°C . A slight softening occurs at 1000°C as a result of recovery without recrystallization. The twins start recrystallizing at 1200°C , and break up into very small equiaxed grains. This is accompanied by an increase in hardness. Recrystallization and softening in the areas subjected to slip start at about 1500°C and are complete at 1700°C . The very small equiaxed grains from the recrystallized twins do not become completely absorbed into the recrystallized, slipped grains until temperatures over 1800°C are reached; thereafter, considerable grain growth occurs. Figure 17 illustrates the sequence of recrystallization.

The results of a few tests conducted to determine the elevated-temperature strength properties are given in Table 7. An arc-melted Mo-35Re alloy button was rolled to 0.020-inch strip at 1250°C and recrystallized by heating 1 hour at 1800°C in hydrogen. Under comparable stress conditions recrystallized Mo-0.5Ti alloy is weaker than recrystallized Mo-35Re alloy at 982°C , but is of about the same strength at 1093°C . Thus, the molybdenum-rhenium alloy exhibits good recrystallization behavior and elevated-temperature strength, comparable to that of the Mo-0.5Ti alloy.



250X

N33115



250X

N33116

FIGURE 14. TWO FRACTURES PRODUCED AT -196 C IN A Mo-35 Re ALLOY



7.5X

N44512

FIGURE 15. RESULTS OF BEND TESTS OF MOLYBDENUM SHEETS HELIUM-ARC WELDED USING Mo-35Re FILLER METAL

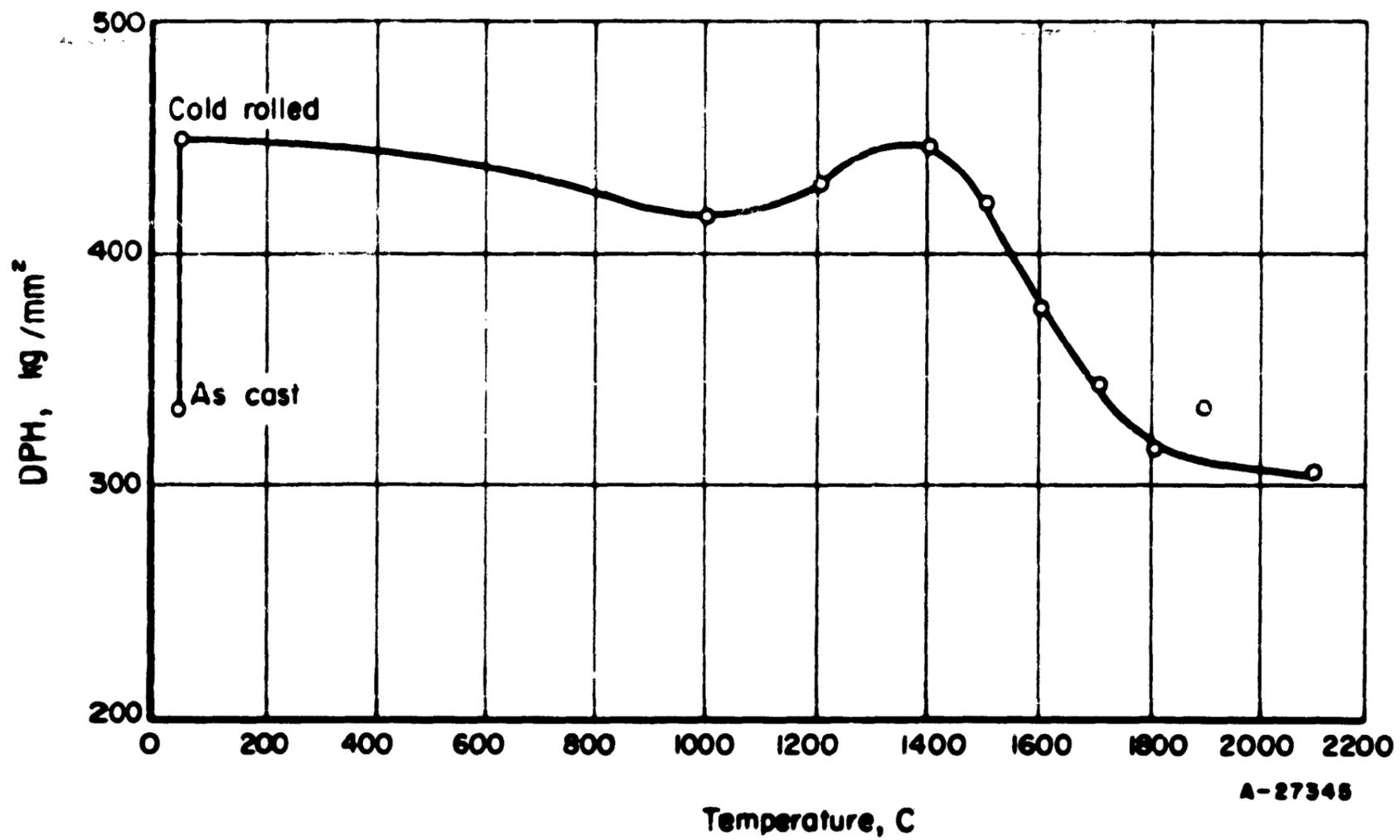


FIGURE 16. RECRYSTALLIZATION OF Mo-35Re ALLOY COLD ROLLED TO 60 PER CENT REDUCTION IN THICKNESS FROM THE AS-CAST CONDITION AND HEATED 1 HOUR AT TEMPERATURE

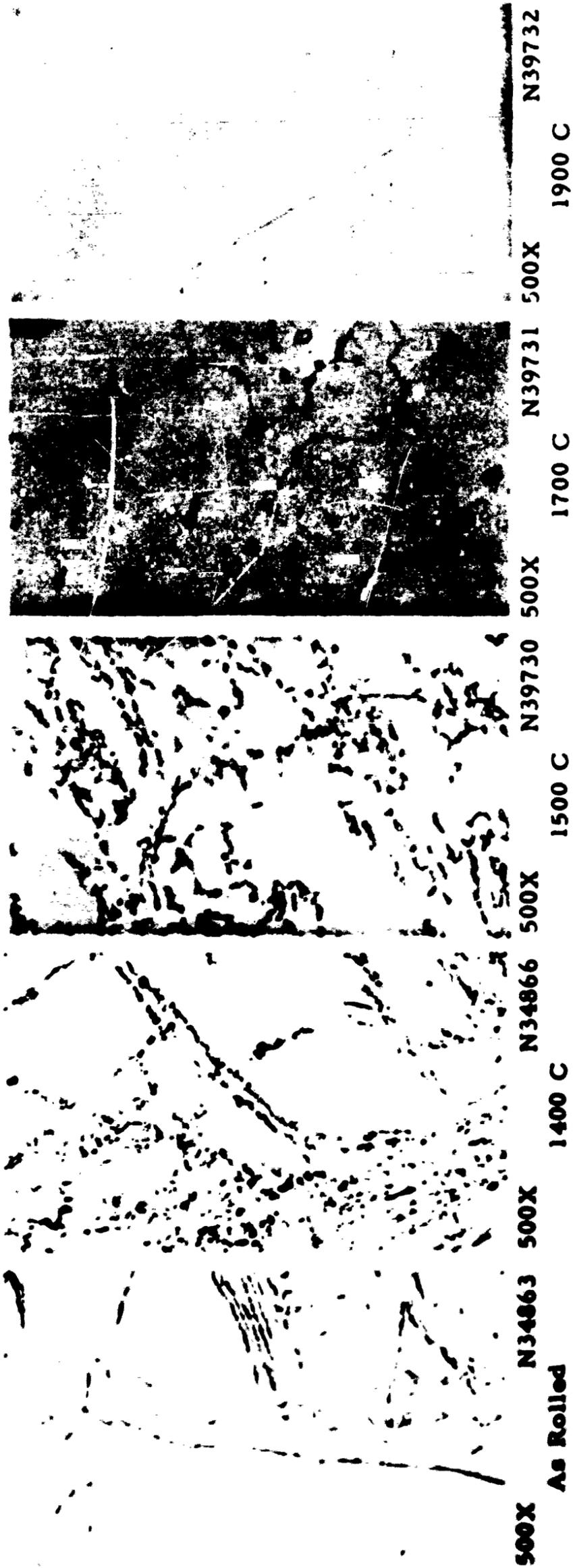


FIGURE 17. PHOTOMICROGRAPHS OF Mo-35 Re ALLOY AT VARIOUS STAGES OF RECRYSTALLIZATION

TABLE 7. ELEVATED-TEMPERATURE RUPTURE PROPERTIES OF Mo-35Re ALLOY, COMPARED WITH MOLYBDENUM AND Mo-0.5Ti ALLOY IN THE RECRYSTALLIZED CONDITION

Condition	Temperature, C	Stress, ksi	Rupture Time, hr		
			Mo-35Re	Mo ^(a)	Mo-0.5Ti ^(a)
Recrystallized	982	40	6.4	0.1	0.1
	1093	20	55.9	0.1	220

(a) Data from Summary Report on "Arc-Cast Molybdenum-Base Alloys" (Contract N8onr-78700) to Office of Naval Research by M. Semchyshen and R. Q. Barr, Climax Molybdenum Company, 1955.

TUNGSTEN-RHENIUM ALLOYS

Preparation of Alloys

Powder-metallurgy methods can be used in consolidating tungsten-rhenium alloys. A W-30Re bar was pressed at 10 tons per square inch to a 1/4 x 1/4 x 6-inch bar and presintered 1 hour at 1200 C. The density in this condition was 12.1 g/cc, about 61 per cent of ideal. The bar was then sintered in a hydrogen bell for 1 hour at 2500 C (black-body temperature); after this, its density was 17.3 g/cc, about 88 per cent of ideal. This bar was suitable for rod rolling to wire at 1600 C.

Most of the tungsten-rhenium alloys were studied in the form of arc-cast buttons. The tungsten used for this work was commercial 50-mil sheet recrystallized by heating in hydrogen at 1800 C and crushed to minus 100-mesh granules. Ten-gram buttons were arc melted under argon at a pressure of 20 cm of Hg on a water-cooled copper hearth at 300 to 325 amperes. The buttons were inverted three or four times to insure homogeneity.

Fabrication

Arc-cast buttons of tungsten-rhenium alloys containing 10, 20, 30, 35, and 40% rhenium were preheated in a hydrogen furnace at 1000 C and rolled, using 5 per cent reduction per pass, until cracking occurred. The appearance of the buttons and the amounts of reduction before cracking are shown in Figure 18. The W-30Re alloy rolled very well, but the other alloys cracked at early stages in the reduction. In subsequent tests, it was found that W-26Re and W-28Re alloy buttons could be rolled as well as W-30Re alloy at 1000 C. Lower rolling temperatures did not result in good rolling characteristics in the W-30Re alloy, as shown below:

<u>Rolling Temperature,</u> C	<u>Per Cent Reduction</u> <u>Before Cracking</u>
400	15.8
600	11.4
800	35.5
1000	86.4 (no cracks)

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1X

N39872

FIGURE 18. APPEARANCE OF W-Re ALLOY ARC-CAST
BUTTONS AFTER 1000 C ROLLING

Rolling temperatures higher than 1000 C work equally well for the W-30Re, and temperatures of the order of 1600 C are preferred for rod rolling.

Structure

The reason why alloys containing 35% rhenium or more could not be fabricated was apparent from their microstructure, which contained considerable sigma phase. The W-30Re alloy also has sigma phase present, but not enough to interfere with workability. The W-20Re alloy exhibit a clear, single-phase microstructure, and the W-26Re alloy had only a light scattering of sigma. Therefore, it is probable that the terminal solid solution of rhenium in tungsten is located at about 24 to 25% rhenium.

Low-Temperature Mechanical Behavior

The hardnesses of as-cast tungsten-rhenium alloys are shown in Figure 19. It is observed that hardness levels off as the terminal solid solution is approached, and then increases sharply as increasing amounts of sigma appear in the structure.

The tensile properties of a recrystallized W-30Re alloy strip at room temperature were determined, but the specimen failed at a punch mark at 167,000 psi with no measurable ductility. A stress-strain curve was plotted for this specimen, and indicated there had been about 0.25 per cent plastic strain before fracture. No evidence of yield-point behavior was observed. A room-temperature tensile test on a 0.040-inch recrystallized wire gave 194,000-psi ultimate strength, 4 per cent elongation in 1/2 inch, and 17 per cent reduction in area.⁽¹⁴⁾ These data show that the ductile-to-brittle transition in tension is above room temperature for recrystallized W-30Re alloy.

The ductile-to-brittle transition of the W-30Re alloy was investigated by bend testing strip specimens. The recrystallized-alloy strip used was prepared by rolling at 1600 C to 0.020-inch thickness and heating 1 hour at 1800 C in hydrogen. The wrought-alloy strip tested was prepared by rolling at 1000 C to 0.020-inch thickness.

Figure 20 shows the variation of minimum bend radius with temperature for both recrystallized and wrought W-30Re alloy, and for recrystallized and wrought tungsten strip, for comparison. The transition-temperature range for the recrystallized W-30Re alloy is not sharp, and extends from about 200 C to 300 C. However, even at 100 C, the recrystallized W-30Re alloy exhibits some bend ductility. In contrast, recrystallized tungsten has a sharp bend transition between 300 C and 325 C. The bend-transition temperature of wrought W-30Re alloy is below room temperature, significantly below the transition temperatures of wrought tungsten strip (175 to 200 C).

The W-30Re alloy is subject to mechanical twinning at room temperature. Figure 21a shows the alloy after it has been squeezed in a vise, and Figure 21b shows the twins formed around a hardness impression. Considerably less twinning occurs in tensile testing of W-30Re alloy. Only a few twins were found near the fracture end of a specimen tested at room temperature, and none were found in the fractures of the alloys tested at 800 C or higher.

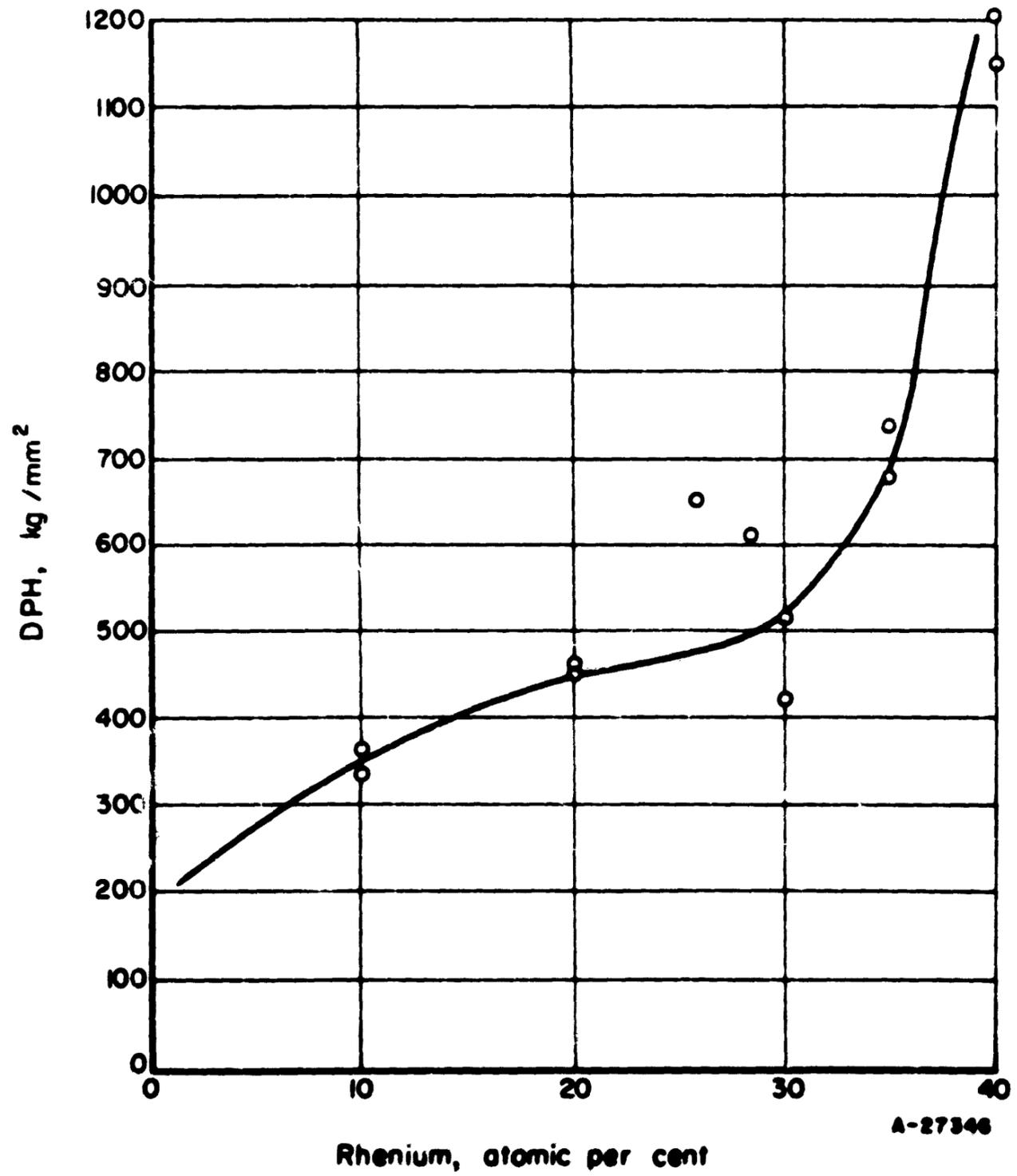


FIGURE 19. AS-CAST HARDNESS OF TUNGSTEN-RHENIUM ALLOYS

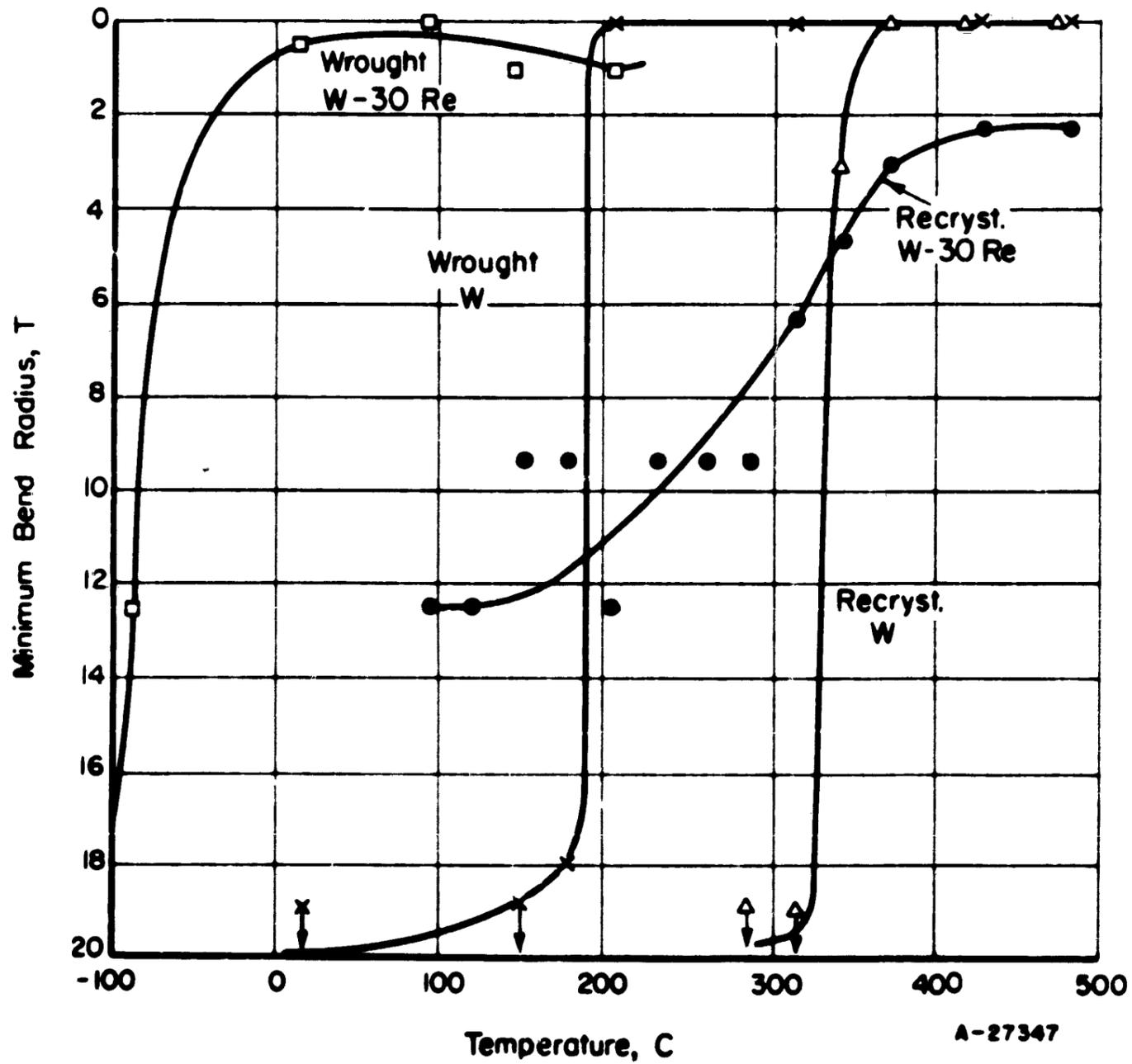


FIGURE 20. TRANSITION FROM DUCTILE TO BRITTLE BEND BEHAVIOR OF W-30Re ALLOY COMPARED WITH TUNGSTEN IN THE WROUGHT AND RECRYSTALLIZATION CONDITIONS



100X

N46493

a. Squeezed in a Vise



500X

N46496

b. Around a Hardness Impression

FIGURE 21. EXAMPLES OF MECHANICAL TWINNING IN W-30Re ALLOY

The elevated-temperature tensile properties of W-30Re alloy wire rolled at 1800 C and recrystallized by annealing in hydrogen 1 hour at 1800 C are shown in Figure 22.⁽¹⁴⁾ The ultimate strength decreases rapidly between room temperature and 500 C, whereas the ductility (reduction in area) increases. A strong dependence of strength on temperature is one of the conditions usually accompanying the onset of the brittle transition. Hence, the ductile-brittle transition in tension for recrystallized W-30Re alloy occurs at a temperature between room temperature and 500 C. The strength remains substantially constant from 500 to 900 C, is remarkably high at temperatures through 1700 C, just below the recrystallization-temperature range, and then decreases rapidly.

Recrystallization in the W-30Re alloy rolled to 90 per cent reduction in thickness at 1000 C from the as-cast button and also rolled 60 per cent at 1800 C after recrystallization is illustrated by softening curves for 1-hour reheats in hydrogen from these conditions, shown in Figure 23.⁽¹⁴⁾ It is seen that temperatures of 1800 C or above are required for appreciable softening. Microscopic examination revealed initial recrystallization at 1500 to 1600 C, and complete recrystallization at 1800 C. Grain growth was not apparent until 2200 C.

DISCUSSION

Rhenium has two major effects when alloyed with molybdenum and tungsten. The first effect is the redistribution of oxygen as a new phase with a high dihedral angle, probably a complex oxide or a molybdate (or tungstate) of rhenium. The second major effect, the improvement in low-temperature ductility, is a result of mechanical twinning, which permits plastic deformation at low stresses, thus avoiding increased locking of dislocations at low temperature and high strain rates.

Why are such large additions of rhenium required to accomplish these effects? For the oxygen-fixation effect, it appears that at least 25% rhenium is required before the new oxygen phase is stabilized. Thus, in a horizontal section, the ternary diagram of the molybdenum-rhenium-oxygen system is probably of the type shown in Figure 24. There is a point on the molybdenum-rhenium solid-solution field, at about 25% rhenium, where the three phases, alpha plus MoO₂ plus the complex oxide (assumed to be ReMoO₄), are in equilibrium. Molybdenum dioxide is the grain-boundary phase at lower rhenium contents, and typical low oxygen tolerance and lack of hot workability will be found. At higher rhenium contents, the nonwetting complex oxide phase will be present and good hot-working characteristics will be found. The hot workability, then, is limited only by the presence of excess amounts of sigma phase, which form at rhenium contents in excess of 40%. Although less work has been done with the tungsten-rhenium system, it appears probable that the situation is similar. However, because of the more limited alpha-tungsten phase field, the rhenium contents over which direct hot workability may be found probably are more restricted than in the case of molybdenum alloys.

The second question - why do molybdenum-rhenium alloys form mechanical twins more readily than molybdenum? - is more difficult to answer, and one can only speculate on possible reasons. There may be some significance to the fact that twinning occurs most readily at an atomic percentage of about 35, which corresponds to 2 atoms of

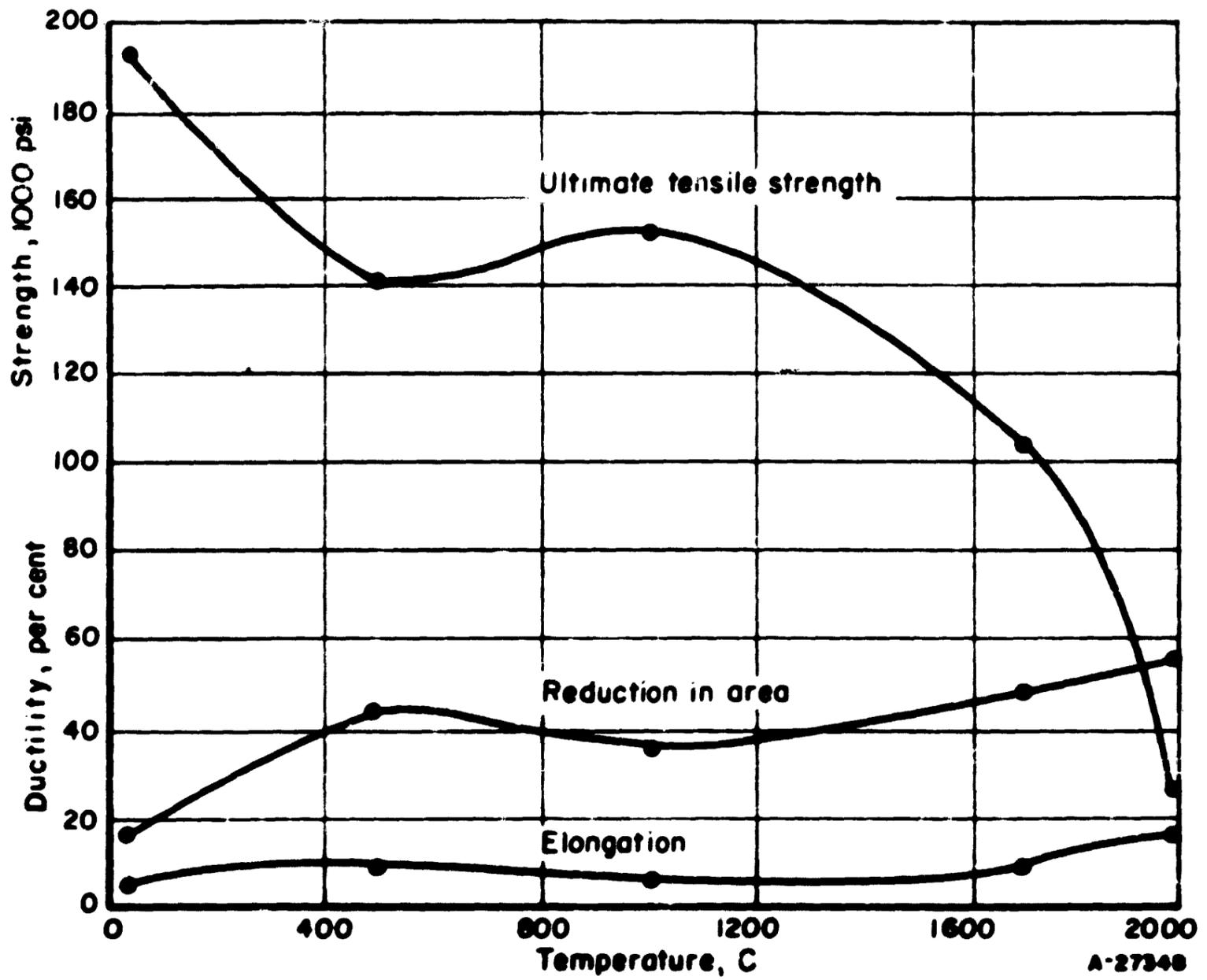


FIGURE 22. ELEVATED-TEMPERATURE TENSILE PROPERTIES OF W-30Re ALLOY WIRE

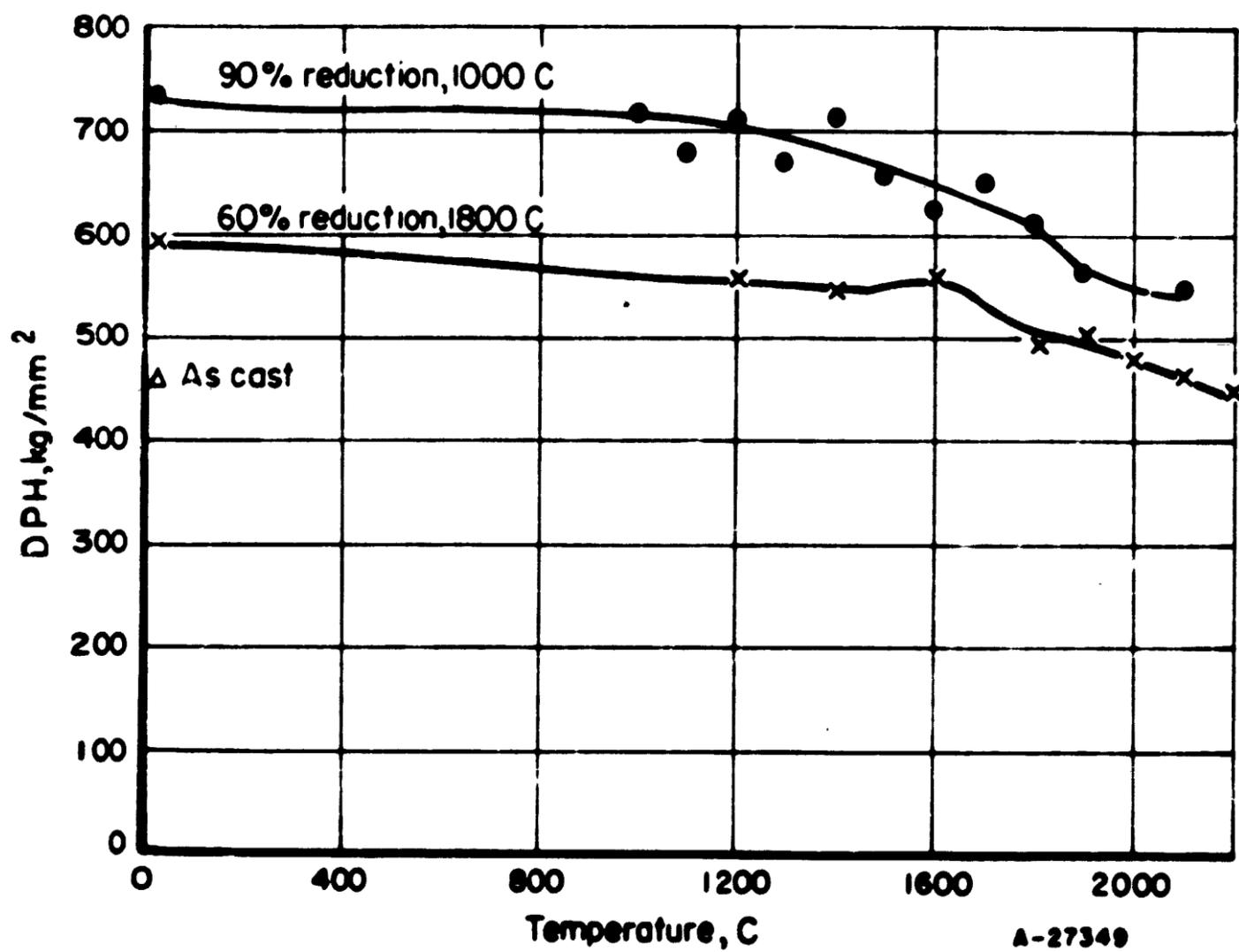


FIGURE 23. SOFTENING CURVES OF W-30Re ALLOY ROLLED AT 1000 C AND 1800 C

molybdenum for each atom of rhenium. If this atomic ratio is significant, the significance apparently has no connection with the formation of long-range order, because none was found by careful examination of the diffraction patterns.

Electrical-conductivity studies should be conducted to check the possibility of short-range order. The fact that the temperature at which molybdenum-rhenium alloys exhibit the twinlike structure increases with rhenium content appears very significant. This might suggest a low-temperature transformation centered about the composition Mo_2Re . Martensitic transformations might then be expected to occur at decreasing temperatures, as the composition departed from the ideal. However, this explanation is not feasible, since cold working at liquid-nitrogen temperatures did not produce measurable changes in the diffraction pattern.

Mechanical twinning would be expected to be promoted by large grain size and absence of polygonization. However, the grain-size effect would not be a factor in the molybdenum-rhenium case, since fine- and coarse-grained material twinned with equal facility. The presence of polygonization in molybdenum and its absence in molybdenum-rhenium is a reasonable possibility, and this should be checked in the future. An interaction between interstitial solutes and polygonization walls is even more likely, and it may be that rhenium prevents segregation of the dissolved interstitials at polygonization walls. This explanation certainly is one reason why iodide titanium, with about 0.02 to 0.05% total interstitial content, readily twins, whereas commercial titanium, with 0.15 to 0.25% interstitial content, does not.

The absence of delayed yielding and of yield-point phenomena with molybdenum-rhenium and tungsten-rhenium alloys is very significant. Such absence may be associated directly with twinning at shear stresses lower than those required to initiate slip. However, some slip is required in order to accommodate the distortions at the end of the twins. Also, considerable slip occurs in later stages of deformation. If the dislocations were pinned by impurity atoms, accommodation slip and secondary slip presumably would initiate low-temperature brittleness, but this was not found for molybdenum-rhenium at temperatures down to -196 . Therefore, it is probable that the dislocations are not pinned so strongly in the case of the molybdenum-rhenium as in ordinary molybdenum. This mechanism is supplementary to twinning for the low-temperature ductility of Mo-35Re alloy. Erickson and Low⁽¹⁵⁾ found that the deformation process in steel at low temperature is predominantly twinning, but the yield point still was observed when slip occurred.

The last possible explanation for mechanical twinning in molybdenum-rhenium is that the cleavage system changes from the (100) characteristic of molybdenum to (110). This would be similar to the behavior reported for tantalum by Barrett and Bakish⁽¹⁴⁾, who noted both twinning and cleavage on (110) in impact compression at -196 F.

In the case of tungsten-rhenium, the transition temperature from ductile-to-brittle behavior is lowered by 30% rhenium. However, the lowering is not so great as in the case of molybdenum-rhenium. There are two possible reasons for this. First, the alpha-phase field is more restricted in the case of tungsten-rhenium extending only to about 25% rhenium. If maximum twinning requires a Mo:Re atom ratio of 2:1, less twinning is possible for the tungsten alloys. Examination of tensile fractures revealed fewer twins for the tungsten alloys than in the case of the molybdenum alloys. However, the W-30Re alloy twinned profusely in compression, where the stresses are less likely to produce cracking. A second possible reason for the higher transition temperatures

in tungsten-rhenium is that the stresses for slip are so high that appreciable accommodation slip around the twins cannot occur until relatively high temperatures are reached.

The effects of rhenium on high-temperature strength appear normal. With a high content of a solid solution of rhenium, which is a refractory metal, major increases in the strength at elevated temperatures in the recrystallized condition can be expected. The increased recrystallization temperature also would be expected. The sequence of recrystallization with respect to the twins was rather unexpected, particularly the stability of the fine grains resulting from recrystallization of twins.

SUMMARY

(1) The results obtained by Geach and Hughes on the effects of rhenium in improving the working properties of molybdenum and tungsten have been confirmed.

(2) The ability of a molybdenum-rhenium alloy to be directly hot worked, even with high oxygen present, is the result of the formation of a new phase containing oxygen, which does not wet the grain boundaries so readily as the oxide of the base metal. The same mechanism probably holds also for the tungsten-rhenium alloy.

(3) The temperatures of transition from ductile to brittle behavior of both molybdenum and tungsten are lowered drastically by the presence of rhenium as a result of the ability of these alloys to deform at low stresses through mechanical twinning.

(4) Deformation by slip occurs at later stages, apparently with much less dislocation pinning than in the case of the parent metal. Yield-point behavior was not observed under conditions of testing.

(5) The elevated-temperature strengths and the recrystallization temperatures of molybdenum and tungsten are raised considerably by rhenium.

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