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AUTHOR(S): M. A. Merrigan and L. B. Lundberg

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AN INITIAL EVALUATION OF MOLYBDENUM-RHENIUM ALLOY FOR REACTOR HEAT PIPES

M. A. Merrigan and L. B. Lundberg

Los Alamos National Laboratory
Los Alamos, New Mexico

ABSTRACT

Molybdenum-rhenium alloys containing less than 15% Re have been investigated for space nuclear power system applications. A ductile-brittle transition temperature of less than 135 K has been demonstrated for recrystallized Mo-13 wt% Re alloy. Thermophysical properties have been measured over the temperature range from ambient to 1500 K and the elastic modulus determined to be 289 GPa. Thermal conductivity of the alloy at temperature has been demonstrated as comparable to pure molybdenum. Fabricability of the material has been demonstrated and an investigation of weld characteristics initiated. Optimization of alloy composition for the planned application is continuing.

INTRODUCTION

Alloy choices for high temperature heat pipes planned for use in uranium-oxide-fueled space nuclear reactor designs have been limited to molybdenum, tungsten, and their alloys by availability and compatibility considerations. Molybdenum has been the material of choice for heat pipe reactors at temperatures near 1500 K. High density and poor fabricability limit the use of tungsten for space power heat pipes except where necessary to meet extreme temperature requirements.

The principal disadvantage of molybdenum in this application is the high ductile-brittle transition temperature (DBTT), which is normally above room temperature for recrystallized material. This is of concern in the reactor heat pipe application, to some extent because of fabrication problems, but primarily because of the possibility of damage to the system from dynamic loading during launch and orbital transfer. System temperatures during transfer from low Earth orbit to geosynchronous orbit may be as low as 200 K. Interest exists, therefore, in the development of refractory alloys that are uranium oxide fuel and alkali metal compatible and display low DBTT in the recrystallized condition.

BACKGROUND

Alloying of molybdenum with rhenium in the interest of improving low temperature ductility and lowering the ductile-brittle transition temperature (DBTT) has been the subject of a number of prior investigations (1-4). A review of these earlier investigations (5) indicated that a ductility peak could be expected between 9 and 14 wt% Re, in agreement with models explaining the softening on the basis of alloy electron concentration (3).

The pronounced peak in room temperature elongation indicated in Fig. 1, reproduced from Ref. 5, for low rhenium content alloys has led to questions of possible secondary causes in material processing differences between investigators. Extreme material purity has been suggested as an explanation for the high ductility displayed by some electron beam (EB) melted materials. Similar considerations apply to the variation of DBTT with rhenium content indicated in Fig. 2 (also reproduced from Ref. 5). The present investigation has been directed to an attempt to duplicate the high ductility and low DBTT evidenced by low rhenium content alloys in prior investigations with production sized lots of material. Plans are to produce round bar, tubing, and wire of low rhenium content alloys and demonstrate their fabricability, weldability, compatibility, and general applicability to high-temperature space nuclear power systems.

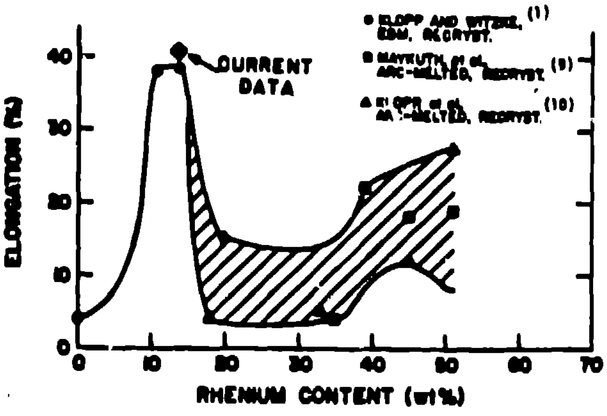

Fig. 1. Effect of rhenium content on room temperature ductility.

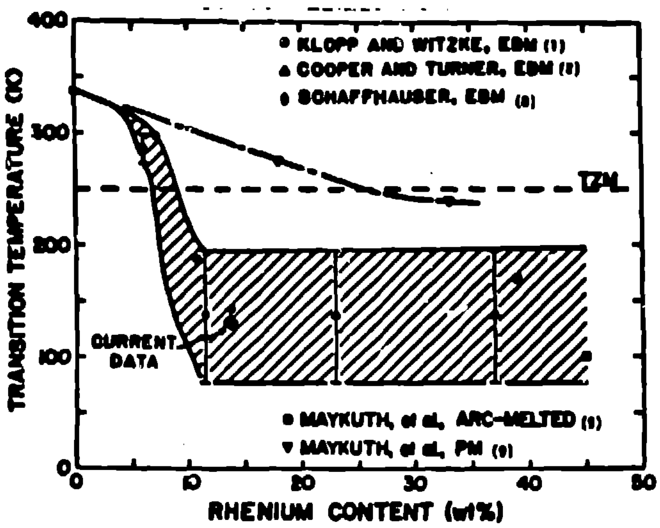

Fig. 2. Ductile-brittle transition for recrystallized molybdenum-rhenium alloys.

FABRICATION DEVELOPMENT

Primary Alloy Production

Production of an initial lot of molybdenum-rhenium alloy was undertaken using arc cast molybdenum bar stock and high purity rhenium sheet stock as starter materials. These molybdenum and rhenium materials were surplus from prior Los Alamos Laboratory programs. The molybdenum bar material had been obtained from Climax Molybdenum Corporation (Melt No. C10007). Typical chemistry of this material is given in Table I. The molybdenum had been stress relieved at 1325 K and was in 5% recrystallized condition. The rhenium plate used in the alloy production had been purified by electron beam melting. Chemistry for the refined material is given in Table II.

Initial plans were to have the molybdenum and rhenium materials electron beam melted at Oak Ridge National Laboratory (ORNL) to produce an alloy of 13 wt% Re. However, because of schedule conflicts in the use of the electron beam melter at ORNL the materials were transferred to Cabot Corporation in Kokomo, Indiana. Plans were to produce 100-mm-diam ingots by double melting from electrodes prepared from the Los Alamos starter materials by Thermoelectron Corporation. The electrodes were fabricated by tungsten-inert-gas (TIG) arc welding the rhenium plate to the surface of the molybdenum bar. Attempts to electron beam melt the resulting electrodes at Cabot Corporation failed due to insufficient cooling capacity in their melter. As an alternative the electrodes were transferred to ORNL and vacuum-arc-melted for initial consolidation. The resulting ingots were prepared for extrusion by Metals Division of Thermoelectron Corporation and extruded at ORNL. The material was reduced from 102-mm diam to 50-mm diam in the extrusion process. The extrusion was conducted at a temperature of about 1920 K and high rate. Chemical analysis of the resulting extrusion indicated high-carbon levels, leading to renewed interest in electron beam melting of the material for purification. The extrusions were therefore shipped to the Rocky Flats Plant operated by Rockwell International for the Department of Energy for remelting by electron beam. Both extrusions were first EB melted and cast as 50-mm diam ingot. Part of the material was then remelted by EB and cast as 100-mm-diam ingot. A total of 16 kg of the double melted material was produced and used for the investigations of EB melted Mo-13% Re properties described herein.

TABLE I
CHEMICAL COMPOSITION OF MOLYBDENUM BAR STOCK
(Climelt (R) molybdenum 75 mm-diam wrought bar)
(Melt No. C10007)

Element		wt%
C		0.009
O		0.0002
H	<*	0.0001
N	<	0.0001
Fe		0.001
Ni	<	0.001
Si	<	0.001
Mo		major

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* indicates less than the stated detection limit.

TABLE II
CHEMICAL ANALYSIS OF RHENIUM PLATE

Element	wt ppm
Re	Major
O	15
C	< 5
N	12
Li	< 15
B	< 15
Na	< 50
Si	60
P	< 150
Ti	< 15
V	< 15
Cr	< 15
Mn	< 5
Fe	50
Co	< 15
Zn	< 150
Zr	< 150
Nb	< 1600
Sn	< 15
Ba	< 2
Bi	< 15
Mo	< 150

A second sample of low rhenium content alloy was procured from the Metallwerk-Plansee Corporation, Austria. This material which was produced by powder metallurgical techniques has a measured rhenium content of 14.5 wt%. Preparation of the material involved mechanical mixing of molybdenum and rhenium powders, cold pressing, and sintering in hydrogen. The material was furnished as 15.4-mm-diam, 0.89-mm-thick tubing.

Chemistry

Chemical analysis of the cast ingot indicated a rhenium content of 13.8 wt% and an impurity content as given in Table III. The chemical analysis of the Mo-14.5 Re tubing made by Plansee from powder metallurgically produced stock is also listed in Table III.

TABLE III
CHEMICAL COMPOSITION OF
MOLYBDENUM-RHENIUM

Element	EB Ingot No. 1 As received	Plansee Tube As received
Re	13.8 wt%	14.5 wt%
O	100	25 ppm
C	40	< 5*
N	19	20
H		5
Li		< 25
B		< 25
Na		< 240
Si	70	< 300
S		< 20
P		< 20
Ti		< 20
V		< 70
Cr		< 10
Mn		2
Fe	30	< 25
Co		< 25
Zn		< 700
Zr		< 70
Nb		< 700
Sn		< 70
Ba		< 70
W		< 2400
Bi		< 240

Metallography of the EB cast material did not disclose preferential attack of the grain boundaries in etching, suggesting that the contaminants were distributed throughout the material. The ingot was prepared for extrusion by machining approximately 2 mm from the outer surface and wrapping in pure molybdenum foil. Preheating consisted of 30 min at 1920 K. The ingot was reduced to 3.6 cm diam in the extrusion, an area reduction of 8.13 to 1. Initial extrusion pressure was 950 tons and final was 550. The extruded bar was reheated to 1275 K and straightened in a hydraulic press.

A 50-cm length of the bar was separated and gun drilled for use in fabrication of a test heat pipe. Samples of the material as extruded were taken at this time. The remainder of the material was annealed at 1645 K for 1 hr and swaged to 1.85 cm diam. A part of this rod was annealed a second time and swaged to 0.762 cm diam. Strips for bend tests were machined from this 0.762 cm material as were 0.635 cm diam tensile specimens. Samples taken from the 1.85-cm bar were used for thermal conductivity measurements and for weld samples.

Mechanical Properties Studies

Bend Tests. The bend test specimens were subjected to 4-T bend tests at 215 K. The results corroborated the low temperature ductility indicated by the tensile specimens. Bend angles of 35° and 45° were observed for recrystallized material and 70° for wrought material.

Uniaxial Tensile Tests. Uniaxial tensile tests were performed on both the Mo-13.8 Re melted stock and the Mo-14.5 Re PM tubing. Subsize, ASTM tensile specimens were prepared from the 0.762 cm diam swaged rod taken from the first ingot of Mo-13.8 Re material and tensile tested in wrought condition at room temperature and in recrystallized condition at room temperature, 200 K, 135 K, and 75 K with an Instron test machine at a strain rate of about 7 x 10^{-4} s^{-1}. The tensile test specimens displayed upper and lower yield point behavior as indicated in the room temperature stress strain curve seen in Fig. 3. This yield point behavior was observed at temperatures to as low as 135 K for the recrystallized samples, and was detectable in the wrought sample at room temperature. As can be seen from the test results seen in Table IV, the recrystallized samples exhibited the highest total plastic elongation, 41%, at room temperature, and the ductility did not disappear until the temperature was reduced below 200 K. Our current estimate of the DBTT for the set of recrystallized samples is 150 K.

Specimen necking like that seen in Fig. 4 resulting from plastic instability at failure was observed down to 200 K. Examination of the fracture surfaces of the broken tensile specimens indicated that the failure resulted primarily from transgranular cleavage with a minor amount of intergranular cleavage down to 200 K with an

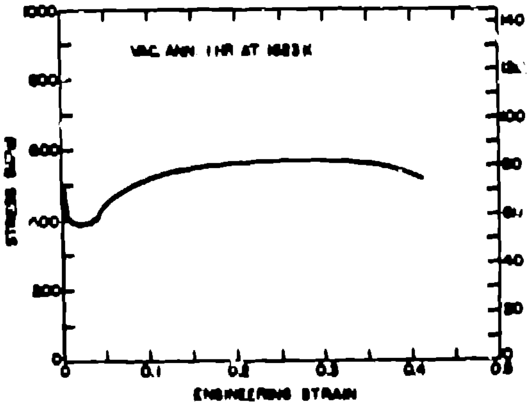

Fig. 3. Room temperature stress-strain behavior of recrystallized Mo-13 Re.

TABLE IV
TENSILE TEST RESULTS FOR Mo-13.8 Re SWAGED ROD

Sample Condition	Test Temperature (K)	Yield Strength (MPa) Upper	Yield Strength (MPa) Lower	Ultimate Strength (MPa)	Total Plastic Elongation (%)	Reduction of Area
As-swaged	300	720	710	783	32	65
Vacuum annealed 1 h at 1625 K	300	483	380	568	41	49
Vacuum annealed 1 h at 1625 K	200	643	510	725	28	33
Vacuum annealed 1 h at 1625 K	135	707	621	675	5	2
Vacuum annealed	75	Broke in threads prematurely				

increase in intergranular cleavage observed below this temperature. Intergranular cleavage was never found to be the dominant mode of failure in these specimens as is commonly seen in recrystallized molybdenum. A typical fracture surface is shown in Fig. 5.

An extensometer was attached to the tensile specimens tested at room temperature, and the elastic modulus of this alloy was determined from the two stress-strain curves obtained at room temperature to be 289 GPa. This value is lower than observed for pure molybdenum (320 GPa).

Plansee performed uniaxial tension tests on two specimens of the Mo-14.5 Re tubing that they fabricated from powder metal stock. Sections of tubing were used for the test specimens, which were held in serrated grips for the test. The tube diameter was supported with a steel plug. The results of their experiments on as-drawn and hydrogen annealed specimens are listed in Table V. It will be noted that the strength values for the tubing containing 14.5 wt% Re are comparable to those found for the bar stock containing 13.8 wt% Re. They also determined the DBTT and found that it was between 75 and 205 K for the as-drawn material and less than 210 K for the annealed material.

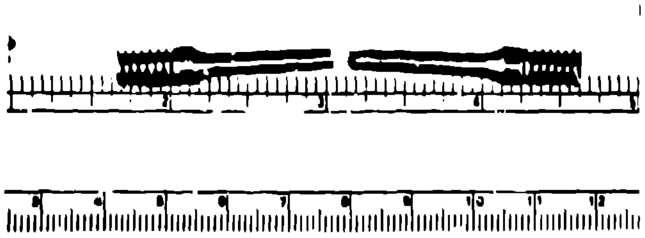

Fig. 4. Mo-13 Re tensile test specimen after failure.

Fig. 5. Fracture surface of Mo-13 Re tensile test specimen.

Ring Tension Tests. Twelve 2-mm long samples of the 15.9-mm diam by 0.89-mm wall thickness PM Mo-14.5 Re tubing were ring tension tested in an apparatus that applies hydraulic pressure to the inside of the tube. Strain gages were attached to the outside circumference of the rings so that stress-strain data could be obtained. The strain was not measured continuously so that only the Young's modulus and the 0.2% yield strength could be determined. Ring samples were tested in the as received condition and with five different heat treatments. The test results are included in Table V. The average Young's modulus measured for the ring samples is 316 ± 15 GPa, which is comparable to pure molybdenum and slightly greater than observed for the Mo-13.8 Re alloy.

TABLE V
ROOM TEMPERATURE TENSILE TEST DATA FOR Mo-14.5 Re PM TUBING

Sample Condition	Test Type	0.2% Yield Strength (MPa)	Ultimate Strength (MPa)	Elongation (%)	Young's Modulus (GPa)
As-received	Ring	676	746	ND	295
		699	763	ND	324
		ND	715	ND	305
As-received	Tube tension	719	801	2.6	ND
1 h, H_2, 1475 K	Tube tension	355	595	23.4	ND
88.3 h, in vacuo 1400 K	Ring	367	537	ND	310
		374	538	ND	328
2 h, in vacuo, 1525 K	Ring	293	502	ND	352
		307	483	ND	328
2 h, in vacuo, 1645 K	Ring	310	525	ND	309
2 h, in vacuo, 1525 K	Ring	312	463	ND	323
+88.3 h, in vacuo, 1400 K		310	468	ND	300
2 h, in vacuo, 1645 K	Ring	231	460	ND	320
+88.3 h, in vacuo, 1400 K		254	410	ND	303

ND - not determined

Thermophysical Properties

A test sample of the swaged bar stock produced from the cast material was submitted to the Thermophysical Properties Research Laboratory of Purdue University for high temperature property measurements. The bulk density of the sample was determined from the geometry and mass to be 10.86 gm/cm^3. The thermal diffusivity was determined using the laser flash diffusivity method. The test apparatus employed a Korad K2 laser, a high vacuum bell jar system, a tantalum tube heater surrounding the sample, an infrared detector and appropriate instrumentation. A mini-computer-based digital data acquisition system capable of 40 µs data sampling was used.

Measured values for the diffusivity are given in Table VI for the temperature range from ambient to 1500 K. Temperature dependence of the diffusivity values is less than 3.2% over this temperature range with a gradual increase from 300 to 800 K and a decrease at higher temperature.

TABLE VI
MEASURED VALUES FOR DIFFUSIVITY

Temperature (K)	Diffusivity (cm^2 s^{-1})
296	0.278
396	0.278
482	0.290
574	0.292
687	0.295
789	0.296
875	0.295
973	0.292
1095	0.290
1226	0.290
1333	0.284
1485	0.280

Specific heat of the material was measured using a Perkin-Elmer Model DSC-2 Differential Scanning Calorimeter with sapphire as the reference material. The differential power required to heat the samples at the same rate was recorded and the specific heat of the sample determined from the mass of the sapphire standard and the sample, the differential power, and the known specific heat of sapphire. Measurements extended from room temperature to 950 K. Table VII presents the results. The measured values agree closely with values calculated from the mixing rule using reference values for pure molybdenum and rhenium. Mixing rule values were therefore used to extrapolate the specific heat to 1500 K.

Thermal conductivity for the molybdenum-rhenium sample was calculated from the density-specific heat-diffusivity product. The resulting values plotted in Fig. 6 show an increase with increasing temperature as expected for alloys. The thermal conductivity of pure molybdenum, is also indicated in the figure. The cross over point at which the alloy conductivity equals the conductivity of pure molybdenum is about 1500 K, the upper end of the measurement range. The value of 93.4 W/cm-K for the alloy at 1500 K is in reasonable agreement with values extrapolated from manufacturers data for higher rhenium content alloys.

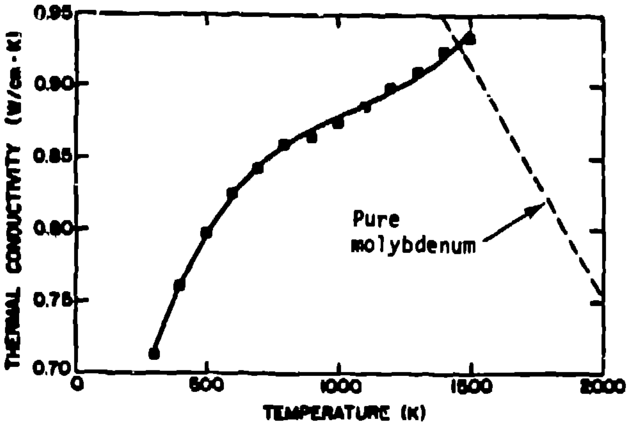

Fig. 6. Thermal conductivity of Mo-13 Re alloy.

TABLE VII
SPECIFIC HEAT

Temperature (K)	Specific Heat (W s gm^{-1}K^{-1})
320	0.2406
325	0.2418
350	0.2443
375	0.2455
400	0.2468
425	0.2486
450	0.2503
475	0.2522
500	0.2535
525	0.2548
550	0.2563
575	0.2578
600	0.2595
625	0.2608
650	0.2617
675	0.2623
700	0.2636
725	0.2645
750	0.2652
775	0.2661
800	0.2672
825	0.2680
850	0.2689
875	0.2698
900	0.2708
925	0.2716
950	0.2725

DISCUSSION

The density of these alloys is lower than expected from a Vegard's law prediction; however, the values measured are close to those calculated from published lattice constants for molybdenum-rhenium alloys.^{6} The variation of density with rhenium content is illustrated in Fig. 7. By carefully examining this curve, one can detect a slight knee in the 10 to 15 wt% region with a trend toward a more rapid increase in density at the higher rhenium contents.

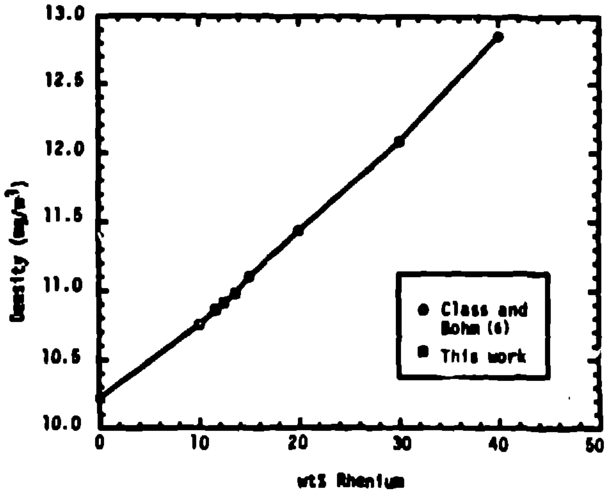

Fig. 7. Effect of rhenium content on the density of solid solution molybdenum-rhenium alloys.

The elastic modulus of the molybdenum rhenium alloys studied is lower than that published by Savitskii, et al.,^{7} for alloys containing 0 to 30 wt% Re. They report modulus values of 333 GPa at 5% Re, 353 GPa at 10% Re, and 383 GPa at 30% Re. The handbook value for pure molybdenum is 316 GPa. This observation suggests the need for some basic studies of the bonding found in the Mo-Re alloys in the solid solution regime. Modulus reduction in this composition regime may be a reflection of the general alloy softening reported by Stephens and Witzke^3 for low rhenium content molybdenum-rhenium alloys. The bonding of these alloys, as reflected by the Young's modulus, appears to be less than expected from a simple rule of mixtures. This may be an electronic effect similar to that hypothesized by Stephens and Witzke.^{3} A comparison of the strength data for the different samples tested in this study indicate a trend toward high ductility for annealed and recrystallized samples. Although the PM material appears to be somewhat less ductile, it shows good promise and with improved processing might be as ductile as the melted stock. All strength values are comparable for comparable heat treatments. Perhaps more significant for metal working concerns is the shape of the stress strain curve. The yield point phenomenon seen in the recrystallized material (Fig. 3) may lead to complications in metal forming operations. A close examination of the broken tensile specimen in Fig. 4 will reveal orange-peel in the necked region. Thermomechanical processing will probably have to be developed to avoid these difficulties.

The DBTT observed for these alloys is close to that previously estimated by Lundberg.[5] Further work is needed to determine the effects of impurities and strain rate on DBTT, but the results so far are very encouraging.

CONCLUSIONS

The results obtained to date indicate the suitability of Mo-13% Re alloy for use in space reactor heat pipe application. The low DBTT for the material in recrystallized condition is particularly promising. This alloy shows significant improvement in low temperature ductility over both pure molybdenum and TZM molybdenum alloy. Its low temperature strength is comparable to TZM. [illegible] thermal conductivity of the alloy at 1500 K [illegible] comparable to pure molybdenum.

Further investigations are needed to demonstrate fuel compatibility, high temperature creep resistance, radiation sensitivity and other critical properties. Further studies are needed to optimize the composition of this alloy for the current application.

ACKNOWLEDGEMENTS

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