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Oxidation of Mo-41Re at Low Oxygen Pressures: 2000 Status Report

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ABSTRACT

Rhenium generally improves the properties of molybdenum, and, therefore, there is interest in use of Mo-Re alloys in space system applications. Both Mo and Re have relatively low solubilities for oxygen but readily form oxide scales when exposed to oxidizing environments above ~350°C. Studies are being conducted on Mo-41Re to determine the rate of oxidation, type of scale formation, and effects on mechanical properties as a function of temperature and partial pressure of oxygen. Thus far, weight gains associated with formation of MoO_2 have been found for $P_{O_2} < 10^{-3}$ Pa (torr) in vacuum, and weight losses associated with evaporation of MoO_3 above 10^{-3} Pa. However, no significant changes in tensile properties were measured.

1. INTRODUCTION

Alloys of Mo-Re have the potential for structural use in space systems because of their excellent high temperature strength and corrosion resistance to liquid alkali metals. Although Re does not affect the already good corrosion resistance of unalloyed Mo, the addition of Re does enhance strength, ductility, and fabricability, especially, with respect to welding. In general, refractory metals and alloys all have significant high temperature strength, but they do not have satisfactory oxidation resistance at temperatures above 300-400°C. Some refractory metals (Nb, Ta, e.g.) have relatively high oxygen solubilities, and they often readily embrittle due to internal oxidation.[1,2] However, Mo, Re, and W have low oxygen solubilities and form surface oxide scales at the onset of oxidation, even at relatively low oxygen partial pressures. However, there are few quantitative data on oxidation rate as a function of pressure and temperature and the subsequent effect on mechanical properties under these conditions.

2. EXPERIMENTAL

Mo-41Re (wt%) tensile samples were stamped from arc cast sheet material that was fabricated at ORNL. The subsized tensile samples are the SS-3 design used for measuring tensile properties after irradiation. These tensile specimens have a 1.5 mm X 7.6 mm long gage section and are ~0.5 mm thick. Prior to oxidation the samples were annealed for 2 h at 1400°C in vacuum. Oxidation tests at low oxygen partial pressure in vacuum were conducted by first evacuating the system to a low base pressure (~10^{-6} Pa) and then, while the system is still being pumped, opening a micrometering valve to admit either pure oxygen or argon containing a known concentration of oxygen until the desired pressure is achieved. Tests were also conducted in argon (~5 vppm oxygen) at 1 atmosphere. After evacuating the system, the vacuum valve was closed and the test system pressurized to 1 atmosphere. Excess pressure was relieved through an oil bubbler.

Weight changes were measured after oxidation and selected samples were characterized metallographically and for changes in tensile properties.

3. RESULTS

3.1 Weight Changes

Results from exposure to pure oxygen at reduced oxygen pressures are shown in Fig. 1. At 10^{-3} - 10^{-4} Pa (10^{-5} - 10^{-6} torr) small weight gains were observed after 500 h that generally increased with temperature. However at 10^{-2} Pa (10^{-4} torr) weight losses were measured that became significantly larger at 800-900°C. In Fig. 2, the weight change rate after 500 h exposures is shown as a function of Po_2. Weight gains were measured at all temperatures below ~1 x 10^{-5} Pa (10^{-3} torr), but as was indicated in Fig. 1 weight losses occurred at higher pressures.

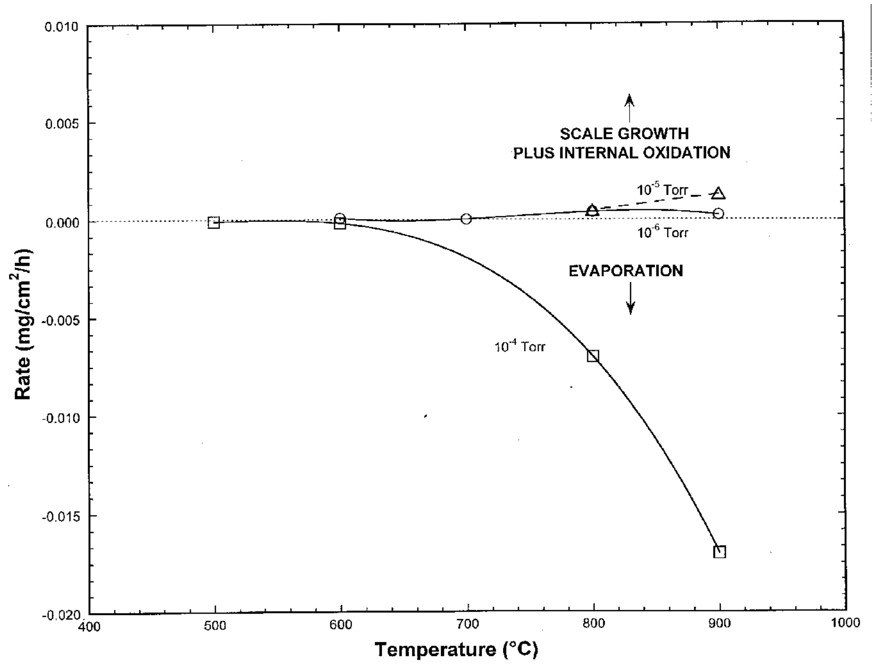

Fig. 1. Plot of weight change rate (500 h) versus temperature at several partial pressures of oxygen.

Results in argon (1 atm) are shown in Fig. 2 and Fig. 3. In contrast with the results in vacuum, weight gains were measured at the higher temperatures and only at 600°C was a weight loss measured.

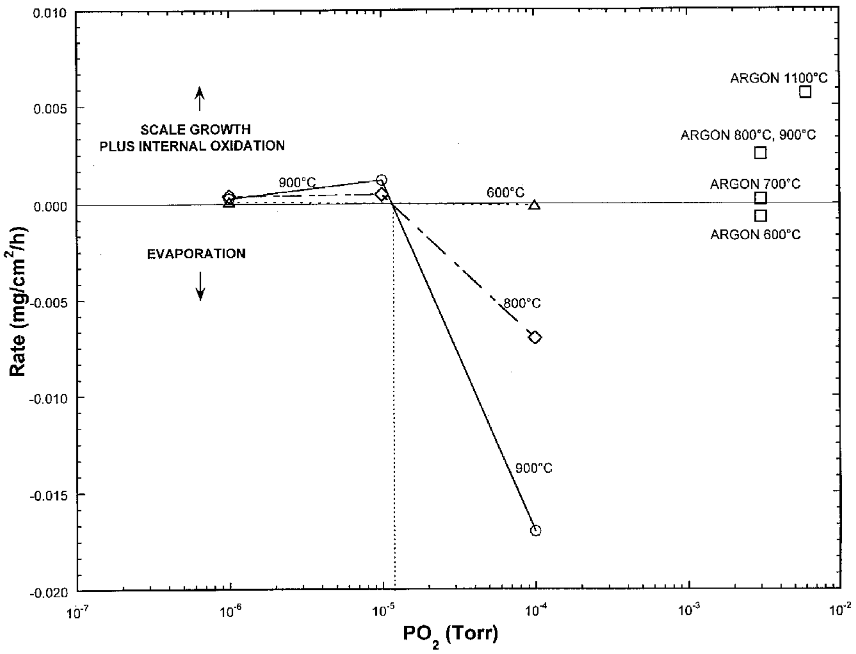

Fig. 2. Weight change rate (500 h) versus oxygen partial pressure at temperatures from 600-900°C.

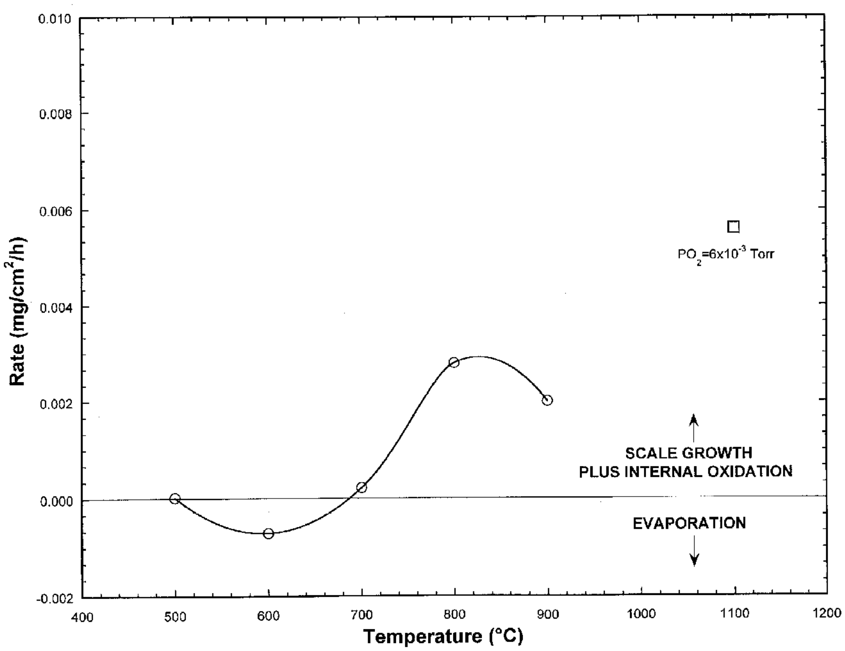

Fig. 3. Weight change rate (500 h) versus temperature in argon containing 5 wppm oxygen (10 wppm for test at 1100°C).

3.2 Microstructural Changes

The surface and grain structure of Mo-41Re after annealing 2 h at 1400°C followed by exposure to argon (5 O_2 -15N_2) for 100 h at 900°C is shown in Fig. 4. Under these conditions the sample picked-up ~200 wppm oxygen and there was little change observed microstructurally. However, after longer times a surface layer and a subsurface, duplex reaction zone developed as shown in Fig. 5. X-ray and microprobe analyses identified the outer layer as MoO_2, but the reaction zone beneath the MoO_2 was fine-structured and difficult to analyze precisely. Microprobe analysis of a sample exposed at 1100°C indicated the reaction zone beneath the MoO_2 contained several different compositions of Mo, Re, and O (Fig. 6 and Table 1). It is likely that this region also contains MoO_2 since it was very hard (~1375 DPH), together with Mo-Re alloy. In one analysis (Position 3), the Re content was above that in the base alloy, an indication that some depletion of Mo occurred due to formation of MoO_2. It must be remembered, however, that the analyses are dependent on which phases and how much of each are included in the microprobe spot size. In Fig. 7, a plot of weight change versus time is shown along with the depths of the outer and inner reaction zones. Note that the growth of the outer and inner reaction zones occur at approximately the same rates at 900°C.

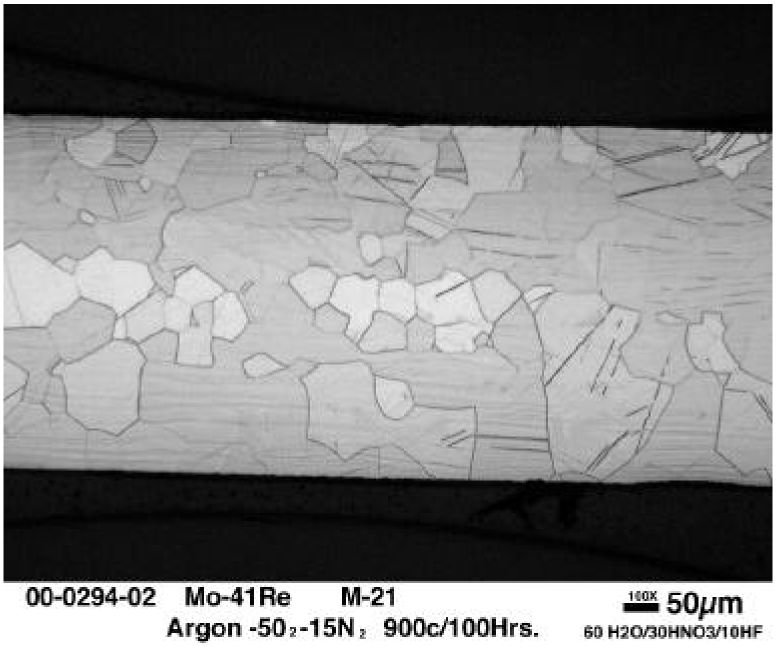

Fig. 4. Mo-41Re sample after oxidation in argon-5 wppm O_2 for 100 h at 900°C.

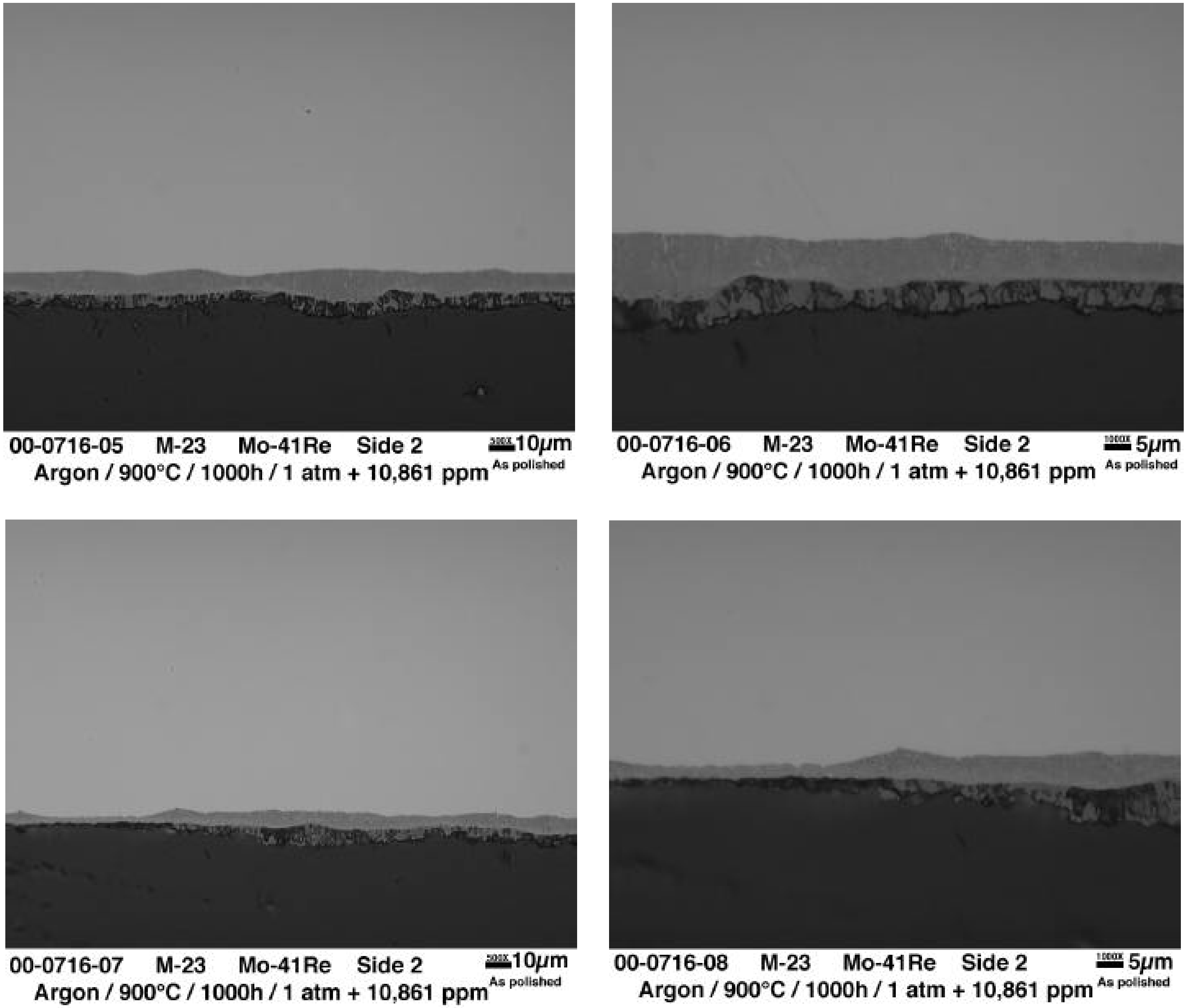

Fig. 5. Duplex reaction layers on Mo-41Re after oxidation.

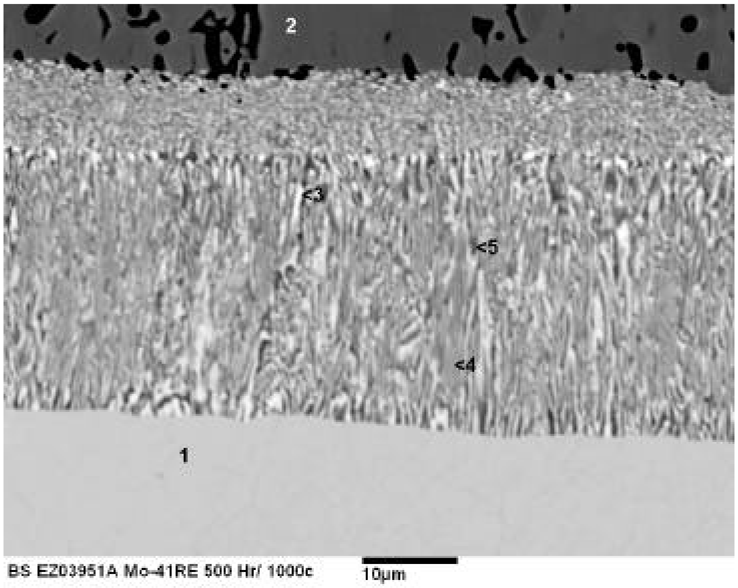

Fig. 6. Reaction zone in Mo-41Re exposed to argon-10 wppm oxygen for 500 h at 1100°C.

Table 1. Microprobe results of Mo-41Re sample after oxidation in argon-10 wppm oxygen for 500 h at 1100°C

	Element Wt %				At. % - Normalized		
Quantity #	Mo	Re	O	Total	Mo	Re	O
Position 1 (base metal)							
1	60.1	41.5	0.0	101.6	73.8	26.2	0.0
2	60.0	41.4	0.0	101.4	73.7	26.3	0.0
3	60.3	40.8	0.0	101.1	74.2	25.8	0.0
Position 2 (outer layer)							
4	74.7	0.6	26.7	102.1	31.7	0.1	68.1
5	74.7	0.5	26.6	101.8	31.9	0.1	68.0
6	74.5	0.4	26.7	101.6	31.7	0.1	68.2
Position 3 (inner oxidation region)							
7	44.1	52.7	7.4	104.1	38.1	23.5	38.4
8	39.8	54.1	8.1	102.0	34.2	23.9	41.9
9	34.9	61.2	6.8	102.8	32.6	29.4	38.0
10	48.6	44.7	8.8	102.0	39.1	18.5	42.4
11	43.4	52.0	4.2	99.6	45.7	28.2	26.2
Position 4 (inner oxidation region)							
12	46.6	41.6	13.7	101.9	31.0	14.3	54.8
13	53.3	36.3	14.7	104.3	33.3	11.7	55.0
14	50.2	40.5	11.4	102.1	36.1	15.0	48.9
15	51.5	38.5	13.3	103.2	34.1	13.1	52.7
Position 5 (inner oxidation region)							
16	62.4	17.7	21.2	101.3	31.4	4.6	64.0
17	58.2	24.3	21.5	104.0	29.1	6.3	64.6
18	63.9	17.3	22.5	103.7	30.8	4.3	64.9
19	56.6	28.5	19.6	104.7	30.0	7.8	62.2

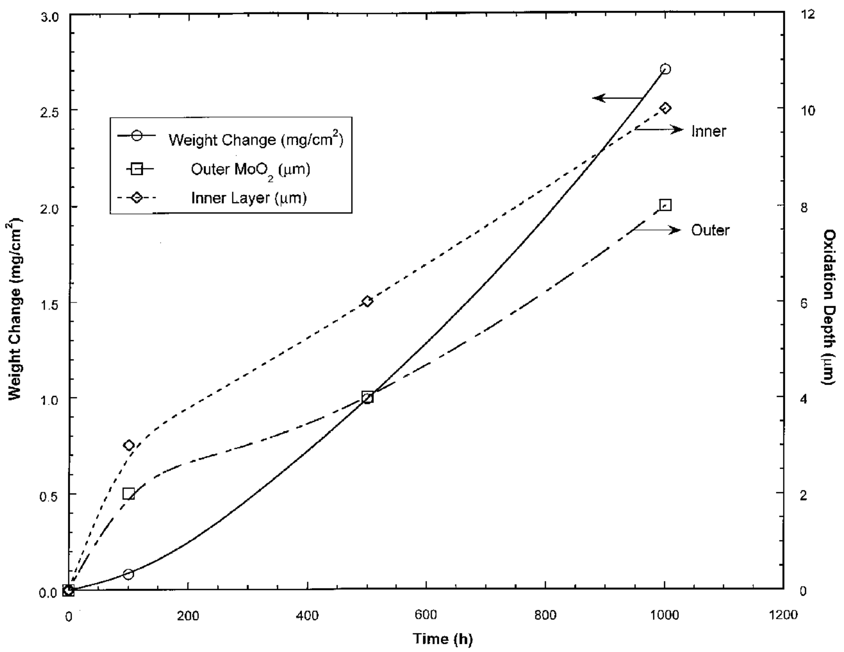

Fig. 7. Growth of reaction zone during oxidation in argon at 900°C.

3.3 Tensile Properties Changes

Tensile properties of selected Mo-41Re samples were measured after oxidation either at room temperature or at the oxidation temperature. Variations in yield and ultimate tensile strength were generally within one standard deviation after test, but the samples tested at room temperature and 650°C were slightly weaker after oxidation compared with an unoxidized sample as shown in Table 2. Note that this did not occur at 900°C and the tensile data did not show any significant variation after oxidation. Elongation, a measure of the material's ductility, was relatively unchanged at each temperature. After oxidation that produced a weight increase of >1%, room temperature tensile properties were not significantly different from samples showing either a small weight increase or decrease. At 900°C, the same type of behavior was found for a weight decrease of 1.5%. Thus, weight changes that result in relatively thin layers of MoO_2 or small losses due to evaporation of MoO_3 do not appear to significantly affect the tensile properties of Mo-41Re.

Table 2. Tensile properties of Mo-41Re after oxidation

Sample number	wppm	Tensile test temperature (°C)	YS (MPa)	UTS (MPa)	Uniform (%) elongation	Total (%) elongation
M93	−	RT	689	656	14	19
M32	−322	RT	584	688	13	15
M21	+322	RT	564	734	13	14
M22	+310	RT	586	776	14	17
M23	+10,861	RT	506	668	13	17
M25	+3,883	RT	557	719	13	18
M94	−	650	339	517	15	28
M13	+147	650	266	480	22	30
M14	+167	650	258	468	20	26
M16	+4,614	650	267	465	20	26
M8	+217	850	464	505	19	26
M9	+311	850	343	511	19	33
M7	+500	850	350	538	19	34
M11	−	900	320	449	13	36
M6	+159	900	339	457	17	36
M5	+221	900	348	446	13	36
M3	−1.5%	900	318	415	14	35

4. Discussion

In vacuum, weight changes in Mo-41Re are a function of temperature and pressure. At 10^{-3} and 10^{-4} Pa (10^{-5}, 10^{-6} torr), the rate of weight increase was positive but very low to 900°C. Above 10^{-3} Pa the weight change became negative. On the other hand, the thickness of the MoO_2 layer is primarily a function of pressure. After exposure for 200 h at 10^{-4} Pa and 850°C, the specimen had a weight gain and a 1.5 µm thick MoO_2 layer. But after exposure for 100 h at 3×10^{-3} Pa at 900°C, the specimen showed a weight loss but a 10 µm MoO_2 layer. In argon, weight changes were almost always gains even though the oxygen partial pressure was higher, and, at 900°C the growth of the oxide regions paralleled the weight increase. Weight changes are the net of the increase in MoO_2 minus evaporation of MoO_3, so it is difficult to determine whether oxidation is actually slowed in argon compared with vacuum or if evaporation is occurring. Nevertheless, it is very encouraging that relatively small amounts of weight increase due to oxide formation have relatively little effect on the mechanical properties of Mo-41Re. This seems to support the hypothesis that without internal oxidation, embrittlement is less likely.

5. Summary

Studies were conducted to examine the oxidation behavior of Mo-41Re at reduced oxygen pressures ($10^{-3} - 10^{-6}$ torr range) as might occur in vacuum or argon environments that could be encountered during fabrication and testing of space system components. In vacuum, weight change rates were low below ~600°C ($10^{-4} - 10^{-5}$ mg/cm^2/h). In general, low temperatures/pressures result in weight gains due to growth of MoO_2 at the surface. Although weight gains generally increase with temperature, if the pressure of oxygen reaches a sufficient level, oxidation of MoO_2 to MoO_3 occurs which leads to weight losses from evaporation of MoO_3 in the dynamic environment. Contrarily, in flowing argon (1 atm), weight increases continued to occur even at high temperatures/pressures. Significant weight changes, either gains or losses and in vacuum or argon, were characterized by formation of an external layer of MoO_2 and a complex, hard, internal oxidation zone that consisted of several phases containing some combination of Mo, Re, and oxygen. Oxidation exposure generally resulted in no systematic change in tensile strength and ductility with growth of the oxidation zone.

Thus far the data indicate that dynamic vacuum environments containing oxygen partial pressures $\leq 10^{-4}$ Pa (10^{-6} torr) would be required to limit Mo-41Re to small weight gains from oxidation at temperatures to 900°C. If an argon environment is required, oxygen levels of 5-10 ppm are sufficient to cause a significant oxidation rate of this alloy at temperatures $\geq$800°C. However, the effect of oxidation is either growth of a surface oxide, MoO_2, or evaporation of MoO_3. These effects should be considered with respect to any changes in properties required for a particular application, e.g., emittance or strength of thin sections.

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