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Mechanical properties of ternary molybdenum–rhenium alloys at room temperature and 1700 K

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Molybdenum–rhenium alloys have a lower ductile-to-brittle transition temperature than molybdenum, which is advantageous in applications requiring improved room temperature ductility or impact toughness. However, at high temperatures rhenium strengthens molybdenum only slightly. This work screens the effect of alloying additions of Ti, Nb, Ta, and Hf on the room temperature ductility and high temperature strength of Mo–26 at.% Re (Mo–40.5 wt.% Re). Hafnium is found to be a particularly effective high temperature strengthener.

Keywords: Refractory alloys; Mechanical strength; Fracture; High temperature

The nozzles in wind tunnels operating at high Mach numbers (e.g. Mach number 6 or greater) must survive extreme conditions of temperature, stress and thermal shock [1]. The duration time of a wind tunnel run is a major factor dictating the mode of operation of the nozzle [1]. For example, the Arnold Engineering Development Center (AEDC) T9 wind tunnel at White Oak, MD, operates with a heat sink nozzle. In tunnels that operate with inert gases such as nitrogen, refractory metals are a logical nozzle materials choice. The AEDC T9 wind tunnel uses the body-centered cubic Nb-based refractory alloy C-103 (Nb–5.3Ta–2.0Ti, at.%; Nb–10Ta–1Ti, wt.%). However, the combination of mechanical and thermal stress in the T9 nozzle exceeds the yield stress of C-103 in a thin layer adjacent to the hot gas. This results in local yielding (i.e. plastic deformation) in this portion of the nozzle. Repeated operation results in compounded deformation and eventually requires replacement of the nozzle when its dimensions go out of tolerance. In case of an upgrade of the T9 wind tunnel to higher Mach numbers, the C-103 alloy may not work at all. One solution to this problem is to replace the C-103 alloy with a material having improved high temperature strength. A possible choice is rhenium. Pure rhenium exhibits a hexagonal close-packed crystal structure, is ductile at room temperature and, because of its high melting point of 3453 K (3180 °C), maintains high strength at elevated temperatures. At 1643 K (1370 °C) its yield stress can be as high as 210 MPa [2], which is much higher than the corresponding value for C-103, ~75 MPa [3]. Its major disadvantage is its high price, which, at the time of writing, is on the order of \$5000 kg^{-1}.

Instead of pure Re, Mo and its alloys may also be considered as nozzle materials. However, the room temperature ductility of Mo is marginal, i.e. depending on the types and concentrations of residual impurities such as oxygen and carbon, it may or may not be ductile [4]. Alloying with substantial amounts of Re (e.g. 26.4 at.% Re (41 wt.%) or 31.8 at.% Re (47.5 wt.%)) improves the room temperature ductility and reduces the ductile-to-brittle transition temperature [5–7]. However, the ultimate tensile strength (UTS) of Mo–31.8 at.% Re at 1700 K, ~160 MPa, is significantly lower than the corresponding value of ~300 MPa for Re [8].

If the high temperature strength of Mo–Re alloys could be further improved, the Mo–Re system might become a lower-cost alternative for pure Re. With densities of 10.3 and 21.0 Mg m^{-3} for Mo and Re, respectively, it is readily seen that the cost of the Re contained in a given volume of Mo–26.4 at.% Re is only about one-quarter of the cost of the same volume of pure Re. In the present work we explore the possibility of improving the high temperature strength of Mo–Re by ternary alloying additions. To this end, we screen

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the effect of the ternary alloying elements Ti, Nb, Ta and Hf on the mechanical properties of Mo–26.4 at.% Re. The Ti, Nb and Ta concentrations were chosen to be 5 at.%, which will be seen to be within the solid solubility limit for these elements. The Hf concentration was varied between 0 and 5 at.%. Small concentrations of Zr (0.1 at.%) were typically added in order to reduce the concentration of dissolved oxygen.

Alloy buttons with masses on the order of 30 g were arc-melted from elemental starting materials with a purity of 99.9 wt.% or better in a partial pressure of argon. Each button was flipped over and re-melted five or six times in order to improve its chemical homogeneity. The buttons were subsequently annealed for 1 h at 1873 K in vacuum ($\sim 1 \times 10^{-3}$ Pa). The carbon and oxygen concentrations of a cast and annealed Mo–26 at.% Re alloy were measured by combustion and inert gas fusion analysis, respectively. The carbon concentration was 70 wppm (600 appm) and the oxygen concentration 160 wppm (1000 appm). Alloys that contain the strong oxide formers Zr or Hf are likely to exhibit even higher oxygen concentrations. Average grain sizes were estimated from optical micrographs of polished metallographic sections that were etched with Murakami's etch. The average grain size was defined as the mean lineal intercept length between grain boundaries. Because of inhomogeneities in the grain sizes within each button, the average grain sizes are only a rough estimate.

For the mechanical testing, cylindrical compression specimens with typical heights and diameters of 5 and 3 mm, respectively, were electro-discharge machined (EDM'd) from the buttons. Miniature tensile specimens with a gage cross-section of $\sim 1.2 \times 0.7$ mm and a gage length of 5 mm were EDM'd and ground with 320 grit SiC paper to remove EDM damage. Room temperature tensile and compression tests were performed at a strain rate of $1 \times 10^{-3}\ s^{-1}$, and engineering stresses and strains were evaluated. Several three-point bend tests on ground specimens with a square cross-section of $\sim 2 \times 2$ mm, a span of 10 mm and a crosshead velocity of 1 mm min^{-1} were also performed. Compression tests at 1700 K (1427 °C) were conducted in flowing argon in a gas-tight furnace equipped with SiC rams and $MoSi_2$ heating elements.

In order to interpret the mechanical property results it is desirable to know whether the ternary alloying additions are in solid solution, or whether second phases are present. Scanning electron microscope (SEM) examination of Mo–26Re–5Ti–0.1Zr (at.%) did not reveal any second phases, indicating that the solubility of Ti in Mo–26 at.% Re at 1873 K is 5 at.% or more. While SEM examination of Mo–26Re–1Hf did not reveal second phases, some of the grain boundaries in Mo–26Re–1.5Hf and most of the grain boundaries in Mo–26Re–2Hf were decorated with a ternary Mo–Re–Hf phase (Fig. 1a). Energy-dispersive spectroscopy in an SEM showed its composition to be consistent with a phase in the ternary phase diagram [9] with the approximate composition Mo_3HfRe_4. Mo–26Re–5Hf–0.1Zr contained, in addition to the phase on the grain boundaries, many second phase particles within its grains (Fig. 1b). These particles had the same composition as the grain boundary phase, $\sim Mo_3HfRe_4$. The

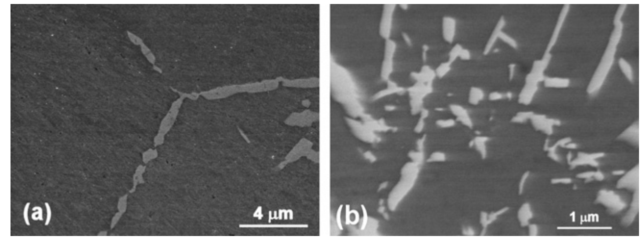

Figure 1. SEM micrographs of Mo–Hf–Re precipitates in (a) Mo–26Re–2Hf, at.% and (b) Mo–26Re–5Hf–0.1Zr, at.%.

matrix between the precipitates exhibited small variations in back-scattered electron contrast corresponding to compositional changes on the order of 1 or 2 at.%; these were not further investigated in this study. The main finding is that, consistent with the ternary phase diagram, the solubility limit for Hf in the Mo–26Re phase is on the order of 2 at.%. The solubility limits for all the ternary alloys examined are summarized in Table 1.

Figure 2 shows a room temperature compression curve. Almost all of the alloys tested in compression at room temperature showed instantaneous load drops accompanied by audible clicks. Binary Mo–Re is well known to exhibit twinning and therefore the load drops observed in the ternary alloys are attributed to twinning. The twinning made the evaluation of a 0.2% yield stress of questionable value. Instead, the stress at 1% plastic strain was evaluated. This stress is not as sensitive to the load drops as the 0.2% yield strength. Table 2 summarizes the results of the room temperature compression tests, as well as approximate grain sizes. With the exception of the 5 at.% Hf alloy, the room temperature strengthening due to ternary alloying additions is modest.

Hot-worked and recrystallized Mo–26.4 at.% Re exhibits a uniform elongation of ~20% at 373 K, with a yield strength and ultimate tensile strength of 700 and 910 MPa, respectively [10]. At room temperature in tension, ~80% of the Mo–Re–X alloys examined here fractured in a brittle matter, i.e. they failed without noticeable plastic deformation. Figure 3 shows the stress–strain curves for alloys that exhibited some ductility. It is seen that the room temperature yield strength of Mo–26 at.% Re is lower than that of hot-worked and recrystallized Mo–26.4 at.% Re, that it exhibits twinning and that its ductility is not very reproducible. Likely reasons for these differences are (i) the relatively large grain size of the cast Mo–26 at.% Re, i.e. a lack of Hall–Petch strengthening; (ii) its relatively high oxygen concentra-

Table 1. Solubility x_{max} of ternary alloying additions X in Mo–26Re–xX, at.%

Ternary alloying addition	Temperature (K)	x_{max} (at.%)	Reference
Nb	1973	74	Villars [9]
Ta	2373	74	Villars [9]
Zr	1623	3	Villars [9]
Hf	1873	2	Villars [9]; this work
Ti	1873	>5	This work