3.2 Development of Mo-Re Alloys — M.A. Sokolov and E.K. Ohriner (Oak Ridge National Laboratory)

OBJECTIVE

Mo-Re alloys are attractive in high-temperature reactor applications due to their good thermal properties and high strength at elevated temperatures. The objective of this research is to evaluate Mo-Re alloys that are expected to be tolerant to irradiation and viable for use in high temperature reactor environments. This work is also expected to add to the scientific understanding of Re-bearing refractory alloys.

SUMMARY

Most previous work on Mo-Re alloys focused on 5-13 or 41-47wt% Re, leaving large gaps in the understanding of the influence of Re in improving properties of Mo and W alloys. Previous studies on these alloys focused on tensile and smooth bar bend tests, whereas fracture toughness data are needed to evaluate suitability for structural applications. The scarce existing fracture toughness data shows poor toughness for up to 5 wt% Re and very high toughness for 41-47 wt% Re, with no data for intermediate Re contents. Preparation of Mo-15 wt.% Re and Mo-25 wt.% Re alloys is in progress. The materials are prepared by vacuum arc remelting (VAR) of pure molybdenum with a Mo-Re master alloy.

PROGRESS AND STATUS

Introduction

Nearly 40 years ago, studies found that molybdenum alloyed with rhenium resulted in improved ductility and fabricability over unalloyed Mo. This “rhenium effect” [1-6] has been observed in group VI-A refractory metals (W and Mo especially) and results in improved strength, creep resistance, and low temperature ductility. Early studies suggested the improved low-temperature ductility was associated with enhancement of mechanical twinning [2,6]. Alternative explanations include solid solution softening (decreased resistance to dislocation glide), and reduction of oxygen content along grain boundaries, due to increased interstitial oxygen solubility [7].

Dilute Mo-Re alloys (<18 wt% Re) have been studied and reported to have maximum tensile ductility at 11-13 wt% Re in room temperature tests [8-9]. However, in a subsequent critical review of the data, Wadsworth et al. [7] found that many of these claims were not conclusive due to inadequately controlled C and O impurity levels. As a result, the improved performance of Mo-Re with Re contents from 10-30 wt% Re alloys is largely unproven. However, more concentrated Mo-Re alloys (with 40-50 wt% Re) are used extensively in industries ranging from medicine to defense. In particular, two alloys (with 41 and 47.5 wt% Re) have been commercially available since the 1960’s. These alloys are more expensive and dense than unalloyed Mo, but possess better ductility, strength, thermal properties, and fabricability.

A major concern for Mo-based alloys is their low fracture toughness even at temperatures above the ductile-to-brittle transition temperature. The limited available data for Mo and Mo alloys [10-11] suggest that the unirradiated fracture toughness of Mo alloys containing < 5% solute additions is less than 30 MPa√m up to at least 450ºC, with a typical value at 230ºC of ~20 MPa√m. Additions of 1 to 2 volume percent of dispersed oxide particles or Re solute produces a slight increase in the fracture toughness and a shift in the DBTT to lower

temperatures, although the effect on fracture toughness is small. Fracture toughness for concentrated Mo-Re alloys has been measured only recently by Sokolov for Mo-41Re and Mo-47.5Re over a range of temperatures [12]. It was shown that the fracture toughness values for the Mo-41Re and Mo-47.5Re are a factor of 5-10 higher than TZM (Mo with Zr and Ti additions) and Mo-5Re alloys. This drastic improvement over unalloyed Mo and dilute Mo alloys creates further incentive for investigating the Re effect in Mo and W alloys.

Another key factor in assessing potential materials for reactor applications is the material performance under neutron irradiation. Studies of the effects of neutron irradiation at high fluence on Mo–Re alloys (~20×10^{21} n/m^2, E>0.1 MeV) at temperatures of 373 to 800°C report dramatically decreased ductility following irradiation [13-14], leading to the belief that the minimum operating temperature for Mo-Re alloys to avoid low temperature radiation embrittlement is ~830ºC. However, in a very recent study by Busby et al. [15], Mo-41Re and Mo-47.5Re were irradiated at even higher temperatures to investigate the suitability of Mo-Re alloys for high temperature reactor applications. Instead of improving ductility with increasing irradiation temperature, a relatively low maximum in ductility was observed for Mo-41Re around 950ºC which rapidly degrades at even higher temperatures. The ductility of Mo-47.5Re reaches a maximum after irradiation at only 800ºC. Further, the fracture surfaces were found to be increasing intergranular with increasing temperature, indicating that a different embrittlement mechanism is responsible.

The degradation of concentrated Mo-Re alloys at temperatures above 800ºC is likely due to radiation-induced precipitation (RIP). Radiation-induced precipitation of both σ and χ phases has been reported in several studies [16-19] and could be the result of radiation-induced segregation (RIS). Predictions of RIS in Mo-Re [20] indicate that Re will become enriched at defect sinks such as grain boundaries and dislocations (network or dislocation loops). For concentrated alloys, only a small amount of local Re enrichment is required to enter a regime where precipitation will occur. Precipitation could also result from radiation-induced transmutation [21]. Both ^{185}Re and ^{187}Re have large (n,γ) thermal energy cross-sections which lead to significant transmutation of Re to Os, although the rates of transmutation will depend on the neutron energy spectrum. Osmium has a lower solubility limit in Mo than Re and could form Mo_3Os at relatively low doses in a high-Re alloy, leading to embrittlement. Mo-Re-Os precipitates may also be possible.

Thus, while the recent work by Busby et al. indicates that highly concentrated alloys such as Mo-41Re and Mo-47.5Re may not be suitable for high temperature reactor environments, the very high fracture toughness values measured by Sokolov provides motivation to continue to look at Mo-Re alloys. Reducing the Re content from the commercially available Mo-41Re and Mo-47.5Re to more moderate 15 and 25wt% Re may considerably improve the alloys performance under irradiation while retaining good ductility and fracture toughness. In addition, this study could provide fundamental information on the impact of Re content and C and O concentrations in Mo and W alloys, filling a key gap in understanding the “Re-effect”. For example, while Mo alloys are not of interest to fusion energy programs due to issues with waste disposal, W-Re alloys don’t have this problem and are of interest because of their lower sputtering rates by the plasma relative to other candidate materials for this application. As a result, an improved understanding of the “Re effect” applied to W-Re alloys could also allow this class of materials to be utilized for fusion reactor applications.

Alloy Preparation

Preparation of Mo-15 wt.% Re and Mo-25 wt.% Re alloys is in progress. The materials were prepared by vacuum arc remelting (VAR) of pure molybdenum with a Mo-Re master alloy of either 41% or 52% Re. The materials are alloyed to contain about 80 ppm carbon in the melted product. The master alloy was prepared by electron beam melting of sintered powder compacts. The electrode assembly within the VAR furnace is shown in Figure 1. The Mo-15% Re following melting is shown in Figure 2 along with the remaining unmelted portion of the electrode. It is planned to extrude the melted ingots to sheet bar during August 2011 and hot roll to sheet material for testing.

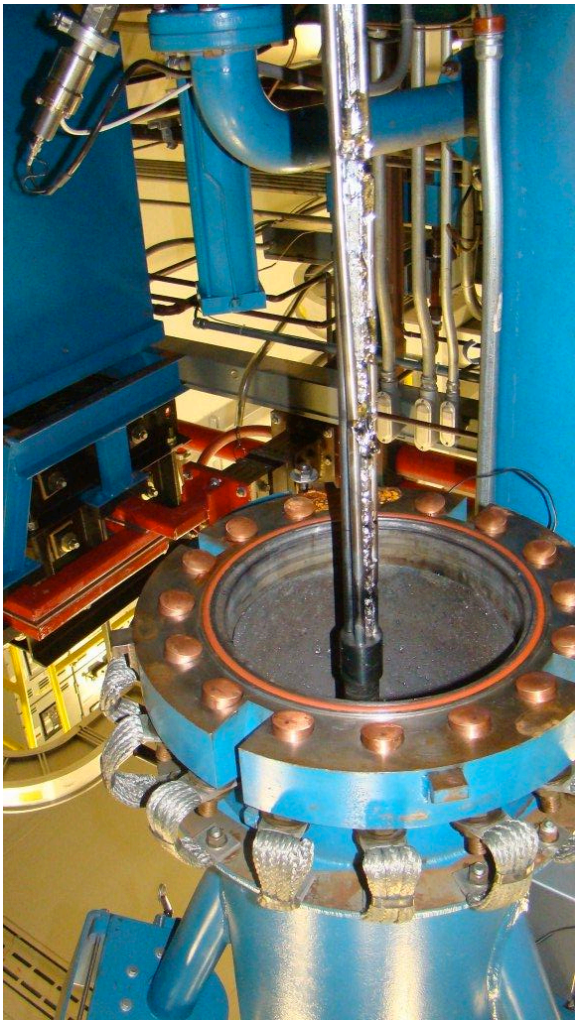

Figure 1. Electrode assembly for Mo-25% Re alloy consisting of Mo rods and EB melted Mo-Re master alloy bars.

Figure 2. Vacuum arc remelted ingot of Mo-15% Re alloy on molybdenum pad with remaining unmelted portion of the electrode consisting of Mo rods and EB melted Mo-Re master alloy bars.

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