Int. Journal of Refractory Metals & Hard Materials 27 (2009) 173–176

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals & Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Microstructure and strengthening mechanisms of molybdenum alloy wires doped with lanthanum oxide particles

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ARTICLE INFO

Article history:
Received 2 April 2008
Accepted 25 June 2008

Keywords:
Molybdenum alloy wire
Lanthanum oxide particle
Strengthening mechanism

ABSTRACT

Lanthanum oxide doped molybdenum alloy wires with different diameters were prepared by using the powder metallurgy method and press working technology. The strength were experimentally determined and related to the microstructures. The effects of the oxides mass fractions and wires diameter on the microstructures and on the mechanical properties of the molybdenum alloy wires were quantitatively investigated. Results showed that the microstructure of the doped molybdenum alloy wires will be refined with increasing the oxides mass fractions and reducing wire diameter, resulting in the increase in the yield strength. The quantitative relationships between the yield strengths and the volume fraction of lanthanum oxide particles and the subgrain sizes were presented. Calculations show that the lanthanum oxide particles strengthening effect, fine substructural strengthening effect and dislocation strengthening effect are the main strengthening mechanisms of the lanthanum oxide doped molybdenum alloy wires.

1. Introduction

Pure molybdenum wire have been used as structural materials in many applications, such as coiling mandrels, filament support wires, foil seals, reflectors for halogen lamps, electronic polar wires for line cut machining and so on. A problem with these pure wires is intergranular fracture. A well-known solution for this problem is to add some dopants (such as rare earth oxides) before the working process. The effect of dopants is to produce bundles of elongated but interwoven grains at high temperature. So the oxide doped molybdenum alloy (ODMA) wire is an important product because it possesses superior strength and recrystallization temperature to their pure counterparts [1–4].

Although the microstructural analysis and mechanical properties testing of ODMA material have been reported recently, few works have been focused on the strengthening mechanism of ODMA wires [5,6]. In this paper, 0.9 wt% and 2.5 wt% mass fractions lanthanum oxide doped molybdenum alloy wires with different diameter of 0.28–1.5 mm were prepared and the effects of mass fractions of the oxides and wires diameter on the microstructures and the strength of the molybdenum alloy wires were investigated. In addition, the contribution of different strengthening mechanisms of the wires were also discussed on the basis of current results and of data reported in literature.

2. Experimental Procedures

The molybdenum alloy with different mass fraction (0.9 wt% and 2.5 wt%) lanthanum oxide(La_2O_3) was prepared by proprietary powder metallurgical processing. The rare earth lanthanum oxide was added to molybdenum oxide as aqueous solutions of $La(NO_3)_3$. The doped oxide powders were reduced into Mo-La_2O_3 powder in dry hydrogen. The Mo-La_2O_3 powder was cold isostatically pressed into a 17 mm diameter cylindrical compact, and then sintered at 1850 °C for 4 h in flowing dry hydrogen. Finally, the cylindrical compact was thermomechanically processed and drawn into the molybdenum alloy wires with the diameter of 0.28 mm–1.5 mm. The wires were carefully heat treatment at 1200 °C in a dry hydrogen atmosphere for 0.5 h. Heat treatment of the wire samples was performed in dry hydrogen using radiative heating in tungsten tube furnace.

The microstructure of all samples was observed by transmission electron microscopy with maximum accelerating voltage of 300 kV. The wire was tested in tension using a constant-strain, screw-driven tensile machine. The strain rate used for all tests was 0.25 mm per minute. Tensile tests were conducted at room temperature and the yield strength was determined by an offset method at 0.2% plastic strain according to ASTM standard E8M-93.

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doi:10.1016/j.ijrmhm.2008.06.007

3. Results

Fig. 1a–c and Fig. 1d–f show the bright field transmission electron micrograph of heat-treated molybdenum alloy wires doped with 0.9wt% and 2.5wt% lanthanum oxide, respectively, both in different diameters of 1.5, 0.6, and 0.28 mm. All the micrographs show that the molybdenum alloy wires have fibrous grain structure. Fiber widths of less than 0.5 μm in the 1.5 mm diameter wire and less than 100 nm in 0.28 mm diameter wire were noted, respectively. Comparisons indicated that molybdenum alloy wires doped with 2.5wt% lanthanum oxide have finer grain size than the wires doped with 0.9wt% lanthanum oxide. Fig. 1 also shows that the thinner wire have finer grain size, which is applicable to the two doped wires. These results indicated that the grain size of lanthanum oxide doped molybdenum alloy wires would become finer with both the increase of the oxides mass fractions and the reduction of molybdenum alloy wire diameter.

The mechanical properties testing results are presented in Fig. 2, from which one can find that the yield strength of the doped molybdenum alloy wires is also remarkably dependent on the dopant density and wire size. In other words, the more is the doped oxides and the thinner is the wire size, the larger is the yield strength. Especially, the yield strength intensely increased by about 30% when reducing the size from 1.5 mm down to 0.28 mm.

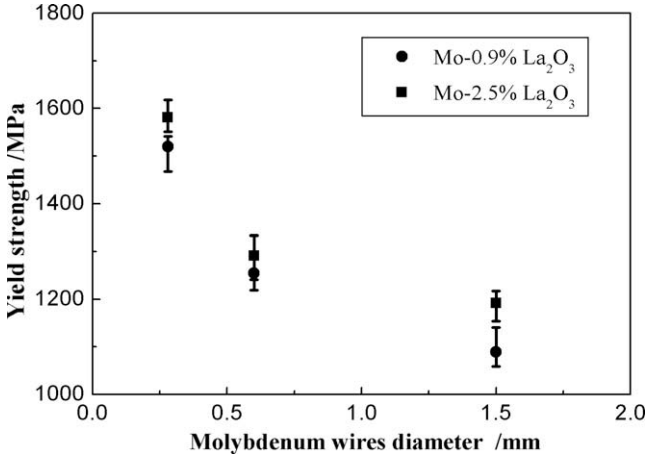

Fig. 2. The yield strength of the molybdenum alloy wires with different mass fractions of lanthanum oxide and different diameter.

4. Discussion

The microstructural analysis shows that the molybdenum alloy wires had fine fibrous grain substructure and fine lanthanum oxide particles. Besides, extensive dislocations can be easily observed, as typically shown in the Fig. 3. These dislocations, induced in the thermomechanical processing and wire drawing, will also contribute much to the strength of the wires. Mainly, the strengthening contributions of the molybdenum alloy wires include three components: particle strengthening, substructural strengthening and dislocation strengthening. This means that the yield strength of the molybdenum alloy wire is the addition of matrix intrinsic strength, substructural strengthening term, particle strengthening term and dislocation strengthening term, i.e.,

$$\sigma_Y = \sigma_M + \sigma_P + \sigma_S + \sigma_D \quad (1)$$

where σ_M is the matrix intrinsic strength of the material (very large grained molybdenum) in the absence of any other strengthening mechanisms and has been evaluated to 417 MPa [7], σ_P is the strength contributed by fine lanthanum oxide particles and can be explained in the terms of the Orowan model, σ_S is the strength related directly to scale of the substructure and can be formulated by Hall–Petch relation, and σ_D is the strength come from retained dislocations and can be formulated by Taylor relation.

4.1. Particle strengthening mechanisms

As showed in Fig. 3a, the fine lanthanum oxide particles were well-distributed within the grains and were spherical in shape, while many of the dislocations were tangled with these particles. So the lanthanum oxide particles are the obstacles to the moving dislocation. When the dislocations pass by these lanthanum oxide particles, they tend to bend like bow between particles and leave

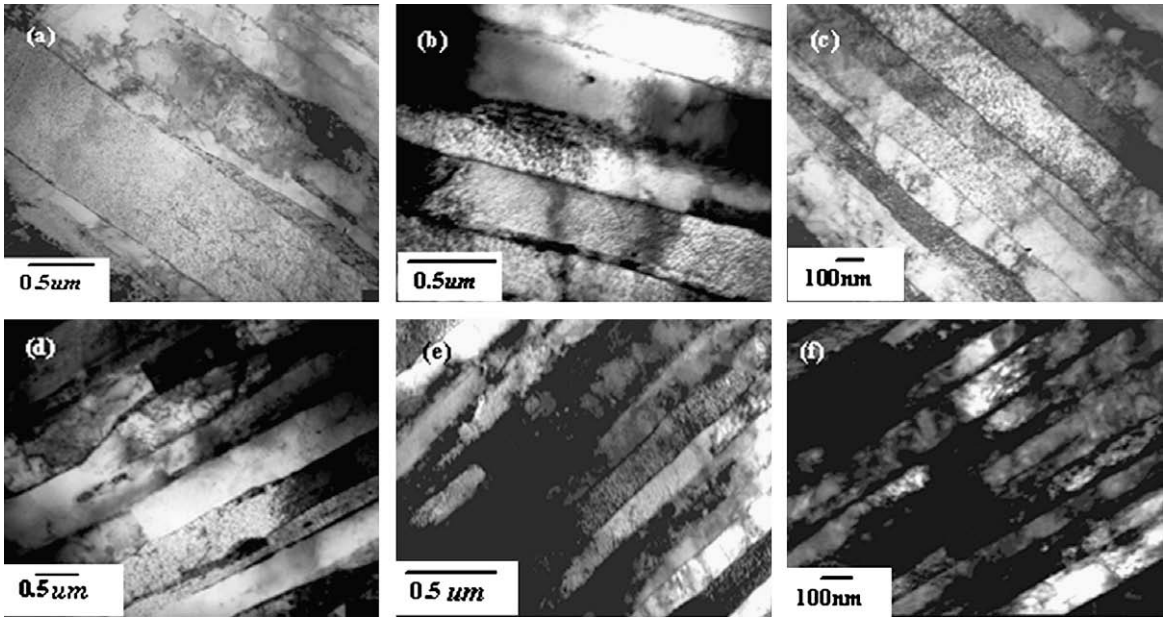

Fig. 1. Transmission electron micrographs of heat-treated lanthanum oxide doped molybdenum alloy wires (a) doped 0.9% La_2O_3, 1.5mm diameter, (b) doped 0.9% La_2O_3, 0.6mm diameter, (c) doped 0.9% La_2O_3, 0.28mm diameter, (d) doped 2.5% La_2O_3, 1.5mm diameter, (e) doped 2.5% La_2O_3, 0.6mm diameter, (f) doped 2.5% La_2O_3, 0.28mm diameter.

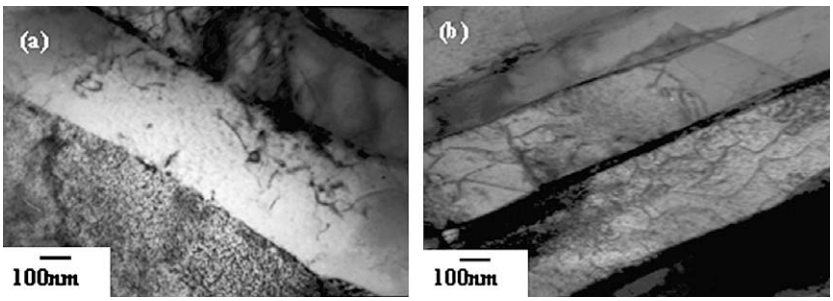

Fig. 3. Transmission electron micrographs of dislocations and lanthanum oxide particles in lanthanum oxide doped molybdenum alloy wire (a) doped 0.9% La_2O_3, 0.6mm diameter, (b) doped 2.5% La_2O_3, 0.6mm diameter.

loops around the particles, as shown in Fig. 3b. According to well-known Orowan–Ashby equation [8] the increase in yield strength due to hard lanthanum oxide particles strengthening is represented as follows:

$$\sigma_P = \sigma_{OR} = \frac{m\mu b}{(1.18)\cdot 2\pi\cdot\phi\cdot\left(\sqrt{\frac{\pi}{6f}}-1\right)}\ln\left(\frac{\phi}{2b}\right) \quad (2)$$

where m is the Taylor factor, μ is the shear modulus, b is the Burgers vector, ϕ is the particle size and f is the volume fraction of oxide particles. Although previous investigations (see, e.g., [9,10]) have shown that the lanthanum oxide particles would deform together with the Mo matrix and the particle shape would somewhat change during heat treatment, it is simply assumed here that the molybdenum alloy wires doped with lanthanum oxide may have almost same particle size and particle volume fraction with the molybdenum alloy bars prepared by the same doping method and doped with same mass fraction lanthanum oxide. We have quantitatively assessed the increase in yield strength due to the presence of oxide particle in the molybdenum bars doped with the lanthanum oxide, and the results show that the particle size, volume fraction and yield strength contributed by oxide particles is 103 nm, 1.16% and 114.31 MPa for the molybdenum alloy doped with 0.9% La_2O_3, and is 206 nm, 2.88% and 113.38 MPa for molybdenum alloy doped with 2.5% La_2O_3 [7], respectively. Here, we noted that the molybdenum alloy doped with higher mass fraction lanthanum oxide has almost the same strength contributed by lanthanum oxide particles with lower mass fraction lanthanum oxide doped alloy. This can be possibly explained by the aggregation of particles at high volume fraction. According to formula (2), the increased strengthening effect caused by more density of particle will be sacrificed by the enlarged particle size that is resulted from the particle aggregation.

Besides, the presence of oxide particles is helpful to refine the microstructural size during working. For example, dynamic recovery during wire drawing should be somewhat inhibited if oxide particles are present. Therefore for a given drawing stain, a molybdenum alloy wire containing dispersed oxide particles possesses surely finer substructures than that without oxide particles doped.

4.2. Substructural strengthening mechanisms

Substructural strengthening can be directly estimated using the Hall–Petch relation, which relates the yield stress enhancement to subgrain size d. The increase in strength cause by reduction of subgrain size can be given by $k/d^{1/2}$, where k is the Hall–Petch slope and an analogously constant value of 121 MPa $\mu m^{0.5}$ was suggested in lanthanum oxide doped molybdenum alloy [7], d is the subgrain size and can be determined by the TEM analysis, and then the strength contributed by substructure can be computed as shown in Table 1.

The contribution of the substructural on the strength is about 154–336 MPa for the range of wire diameter studied here, which seems to be somewhat larger than the contribution of the oxide particles. While as discussed above, the part of substructural strengthening term contains also the attribution from the oxide particles through the substructure size refined by them.

4.3. Dislocation strengthening mechanisms

During the thermomechanical processing and wire drawing of the molybdenum alloy wires, large numbers of dislocations will be induced to accommodate the lattice stretch. These dislocations do not contribute to plastic strain but they act as obstacles to the motion of other statistically stored dislocations and hence contribute to the work hardening of the wires. Additional, In the case of lanthanum oxide particle doped molybdenum alloy wires, the incompatibility in deformation between the plastically deforming matrix and the essentially rigid oxide particles leads to the creation of strong strain gradients in the metallic matrix. Thus, for a given application of plastic flow, a finer microstructure should lead to a greater strain gradient in the alloy, which, in turn, should also result in a greater density of dislocations.

When a plastic crystal is deformed, dislocations are generated, move, and are stored, this storage causes the material to work-harden. The dislocations that are mutually trapped are referred to as statistically stored dislocations [11] and the dislocations that are stored due to incompatibility in deformation are called geometrically necessary dislocations [12]. Considering these effects, the total dislocation density ρ_T in molybdenum alloy wires doped with lanthanum oxide can be written as:

$$\rho_T = \rho_G + \rho_S \quad (3)$$

where ρ_G is the geometrically necessary dislocation density and ρ_S is the statistically stored dislocation density in molybdenum alloy wires.

According to Taylor relation, the contribution to the yield strength due to the presence of dislocations in the matrix may be given by: [13]

$$\sigma_D = \alpha b\mu\sqrt{\rho_T} \quad (4)$$

where α is dislocation strengthening coefficients and are taken to be 1.5 in subsequent calculations [14], μ is the shear modulus of the matrix material, and b is Berges vector. Then the increase in yield strength due to dislocations can be calculated as shown in Table 1 according to the total dislocation density measured by an intercept method.

The contribution of the dislocation on the strength is about 442–700 MPa for the range of wire diameter studied here and it is evidently higher than the contribution of both the oxide particles and substructure. Summing the three parts together, the calculated

Table 1
The calculated strength contributed by substructure and dislocations

Materials	Wires diameter (mm)	Sub grain size (μm)	σ_S (MPa)	Dislocation density (m^{-2})	σ_D
Mo-0.9% La_2O_3	1.5	0.62	153.7	0.6×10^{14}	442.4
	0.6	0.34	207.5	0.9×10^{14}	541.9
	0.28	0.15	312.4	1.3×10^{14}	651.3
Mo-2.5% La_2O_3	1.5	0.58	158.9	0.7×10^{14}	477.9
	0.6	0.29	224.7	0.9×10^{14}	541.3
	0.28	0.13	335.6	1.5×10^{14}	699.6

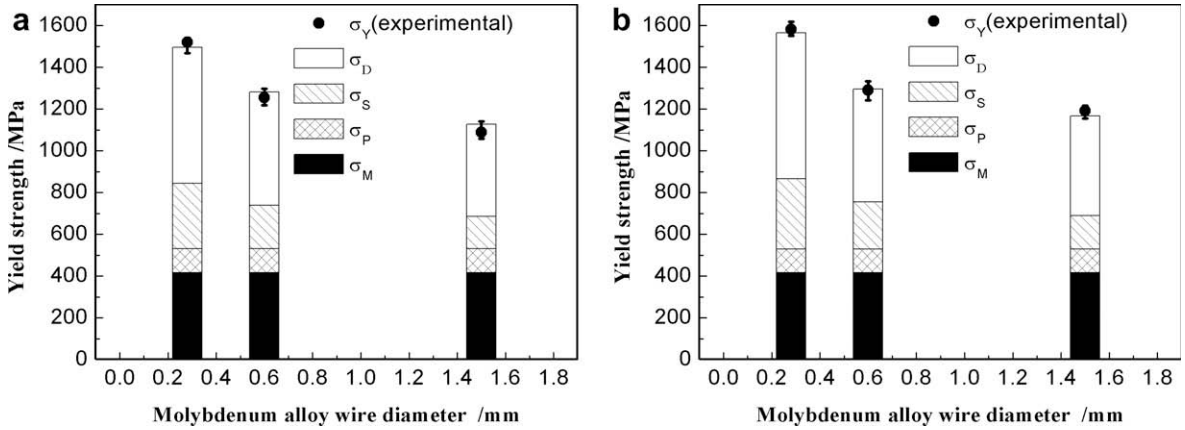

Fig. 4. The consist of calculated strength and the comparison of the theoretical strength and experimental strength of the molybdenum alloy wires doped with (a) 0.9wt% La_2O_3 and (b) 2.5wt% La_2O_3 particles.

yield strength of the studied molybdenum alloy wires are shown in the Fig. 4 to compare with the experimental results.

The good agreement between the calculations and measurements quantitatively shows that the main strengthening mechanisms of the lanthanum oxide doped molybdenum alloy wires are the dislocation strengthening effect, substructural strengthening effect and particle strengthening effect.

5. Conclusive remarks

The microstructural observations have shown that the subgrain size of lanthanum oxide doped molybdenum alloy wires would become finer with the increase of the oxides mass fractions and the reduction of molybdenum alloy wire diameter. The tensile strength of the lanthanum oxide doped molybdenum alloy wires increase with more oxides doped or finer wires diameter.

Calculations show that the main strengthening mechanisms in the lanthanum oxide doped molybdenum alloy wires are the particle strengthening, substructural strengthening, and dislocation strengthening. Especially, the dislocation strengthening is the most significant contribution, much more than that from both the particle strengthening and the substructural strengthening.

Acknowledgments

This study was supported by the National High Technology Research and Development Program of China (Grant NO. 2008AA031001) and the National Basic Research Program of China (Grant No. 2004CB619303). The authors also wish to express their special thanks for the supports from the State Key Laboratory for Mechanical Behavior of Materials and Jinduicheng Molybdenum Co. Ltd. of China.

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