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$ZrTiO_4$ secondary phase effects on ductility and toughness of molybdenum alloys

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ABSTRACT

Molybdenum materials are widely used in electronics and high-temperature applications because of their high strength and recrystallization temperature, good electrical and thermal conductivity. However, molybdenum brittleness, low ductility, and fracture toughness have been limiting its applications. In this work, a new Mo-ZT (Mo-$ZrTiO_4$) alloy was designed containing various amounts of the $ZrTiO_4$ secondary phase, ranging from 0.5 wt% to 3 wt%. The Mo-ZT alloy with 2.5 wt% $ZrTiO_4$ has the ultimate tensile strength above 1,000 MPa(rolled) and 25% elongation (annealed), which is higher than previously reported molybdenum alloys. Compared with the Mo-1ZT alloy, the elongation is increased by 166% with 2.5 wt% $ZrTiO_4$ addition. This offers novel insights for improving alloys' ductility.

1. Introduction

Molybdenum alloys have high-temperature strength and high recrystallization temperature, along with high electrical and thermal conductivity. Molybdenum is suitable for high temperature and electronic materials, targets, etc. [1]. However, molybdenum is brittle and difficult to process, which have been the main reasons restricting its development and applications.

The research of molybdenum alloys mainly focuses on the improvement of strength, ignoring the influence of ductility on processing and application. Studies have shown that adding TiC or ZrC to Mo can increase room temperature tensile strength [2]. Japan have reported that adding a small amount of carbides (0.2–1 wt%, TiC, ZrC, HfC) to Mo, dispersion strengthened molybdenum, reduced the alloy's ductile-to-brittle transition temperature, and improved the alloy's room temperature and high-temperature strength, along with recrystallization temperature [3,4]. First-principles calculations revealed that adding TiC (1 1 1) to Mo (1 1 0) in Mo-TiC can increase the bonding strength and toughness/ductility of the Mo (1 1 0) [5]. Currently, multi-component secondary phases can effectively improve the strength of molybdenum alloys, but the elongation does not exceed 10%. Therefore, further alloy design could improve the plastic toughness of molybdenum materials, so exploring strengthening mechanisms has an important research significance and value.

Our team has confirmed that $ZrTiO_4$ has a strong bonding with the molybdenum matrix. The interface electron density of $ZrTiO_4$ reached 6.5×10^5 e/nm^3, which is much higher than TiC, ZrC, TiO_2, ZrO_2, and La_2O_3 ($\sim 1.5 \times 10^5$ e/nm^3). The interface is not prone to fracture and can absorb more energy in the deformation process, resulting in higher ductility and toughness [6]. The Mo-ZT alloy with multiple components was designed and prepared. The structure and mechanical properties of the alloy were studied, and the reasons for the alloy toughness improvement were explored.

2. Materials and methods

Table 1 shows six molybdenum alloys with different compositions. The $ZrTiO_4$ content was varied from 0.5 wt% to 3 wt%. The starting materials included high-purity molybdenum powder (Jinduicheng Molybdenum Co., Ltd.) and $ZrTiO_4$.

The preparation process includes $ZrTiO_4$ powder was prepared by the nano-coprecipitation method. According to the composition listed in

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Table 1
Designed composition of the Mo-ZT alloy system (wt.%).

Sample	Mo-0.5ZT	Mo-1ZT	Mo-1.5ZT	Mo-2ZT	Mo-2.5ZT	Mo-3ZT
$ZrTiO_4$, wt.%	0.5	1	1.5	2	2.5	3
Mo, wt.%	99.5	99	98.5	98	97.5	97

Table 1, the molybdenum powder was mixed with ultrasonically dispersed $ZrTiO_4$. After the mixture became uniform, the solution dried in a vacuum oven at 80 °C for 4 h. After cooling to room temperature in the furnace, the alloy powder was pressed at 180 MPa for 10 min with a cold isostatic press and then sintered at 1780 °C in hydrogen. The sintered samples were hot-rolled, warm rolled and cold rolled to 0.5 mm plate, respectively. At last, some samples were annealed at 900 °C for 2 h.

The microstructure, fracture, and dislocations configuration were characterized by scanning electron microscopy (SEM) and an transmission electron microscopy (TEM). The microhardness of the samples was tested by the 401MVD digital micro Vickers hardness tester with a 200 g load for 15 s. Tensile tests were carried out using Instron 8801 fatigue tester with a tensile speed of 0.5 mm/min. Metal sheet tensile samples were prepared according to the ASTM E8 standard.

3. Results and discussion

3.1. Secondary $ZrTiO_4$ nanophase morphology

Prepared $ZrTiO_4$ 20–40 nm powder has good morphology and dispersibility in Fig. 1(a). The structure is a single crystal with high strength. X-ray diffraction (XRD) analysis in Fig. 1(b) shows that the powders reduced for a different time under argon atmosphere and in air consist of $ZrTiO_4$ single phase. The powder reduced in the air has higher diffraction peak intensity and crystallinity. The morphology of the main components of molybdenum powder is shown in Fig. 2(c). Molybdenum powder particles are 1–5 μm in diameter and are nearly spherical. Large and small particles are agglomerated. $ZrTiO_4$ as a nano-alloying additive phase can significantly strengthen and toughen molybdenum alloys.

3.2. Mo-ZT alloys tensile properties

The mechanical tensile properties of Mo-ZT molybdenum alloys prepared with different secondary phase amounts were tested, and the results are presented in Fig. 2(a). The tensile strength of rolled alloy with different $ZrTiO_4$ content varies slightly and is greater than 1000 MPa. The Mo-3$ZrTiO_4$ alloy has the highest strength (1078 MPa) and elongation. The Mo-2.5ZT alloy has the lowest strength of 1028 MPa. The properties of the annealed samples with different compositions as showed in Fig. 2(b).

The Mo-ZT alloy hardness is shown in Fig. 2(e), where the rolled

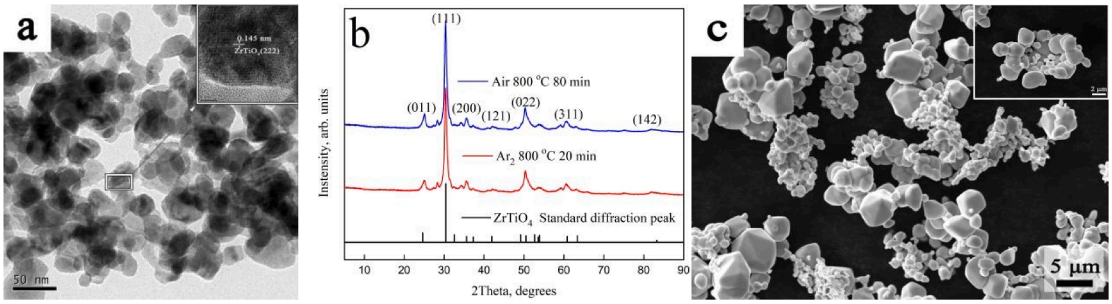

Fig. 1. Mo-ZT raw materials: (a) morphology of the $ZrTiO_4$ powder prepared by chemical co-precipitation; (b) XRD phase analysis of the $ZrTiO_4$ powder; (c) pure molybdenum powder.

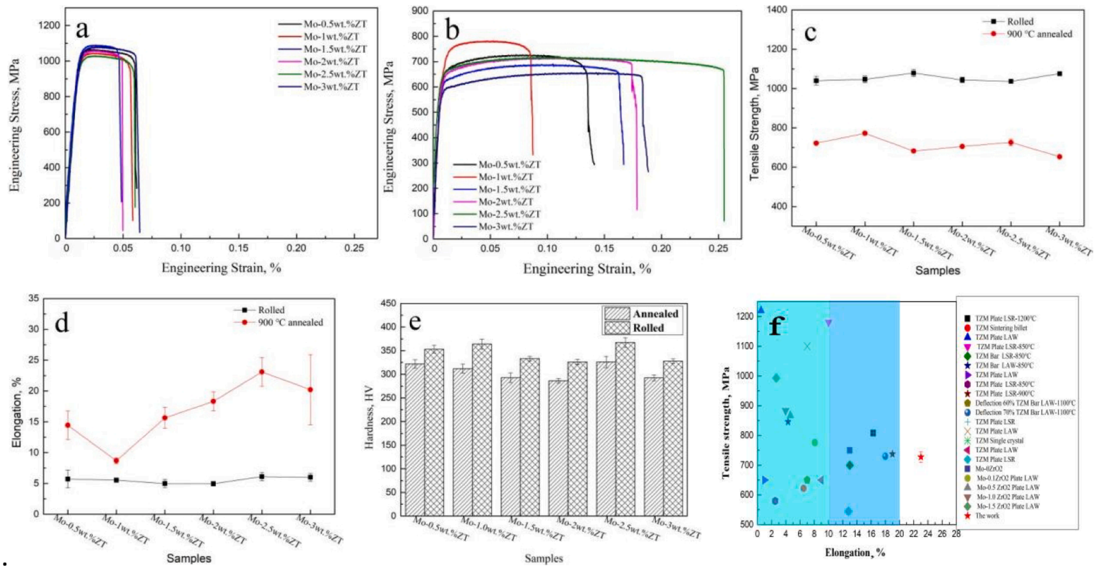

Fig. 2. Mechanical properties of Mo-ZT alloys with different composition: (a) as rolled; (b) annealed; (c) tensile strength changes with composition; (d) elongation changes with composition; (e) annealed and rolled alloys' hardness; (f), TZM and Mo-ZrO_2 alloys mechanical properties.

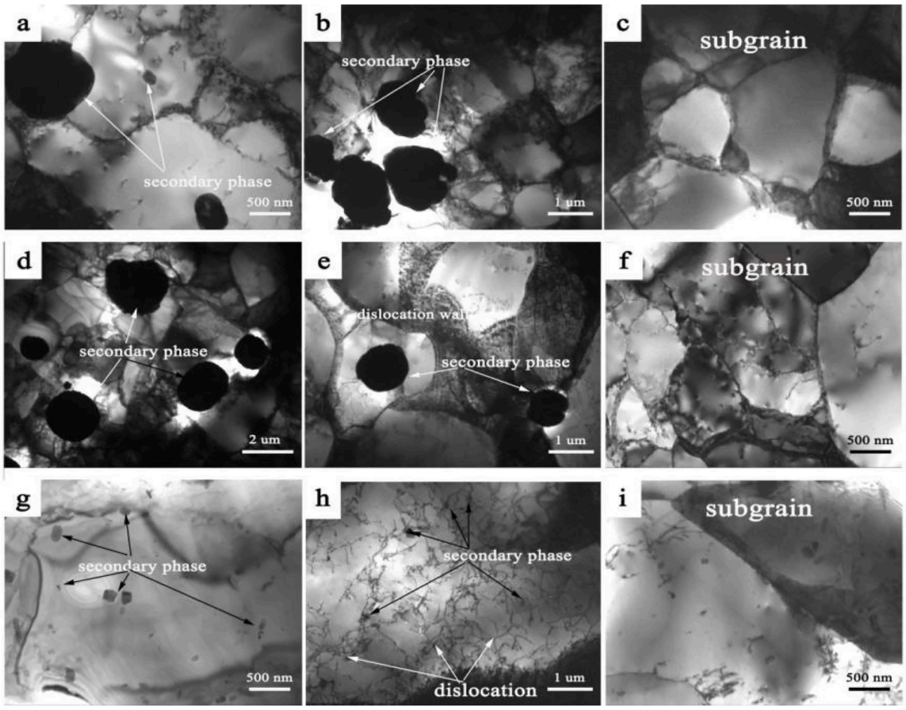

Fig. 3. TEM microstructure of annealed Mo-ZT alloys: (a, b, c) Mo-1ZT; (d, e, f) Mo-1.5ZT; (g, h, i) Mo-2.5ZT.

alloy hardness varies with the $ZrTiO_4$ content in the 325–367 HV range, while the annealed alloy hardness is in the 286–326 HV range. The Mo-2ZT alloy has the lowest hardness in both states, and Mo-2.5ZT is the highest. The plasticity of the molybdenum alloy has been greatly improved by the addition of the $ZrTiO_4$ secondary phase, as seen in Fig. 2(f). Mo-2.5ZT alloy has the best comprehensive performance in terms of strength, elongation, and hardness.

3.3. *Mo-ZT alloy plasticity-toughening mechanisms*

When the $ZrTiO_4$ content in the Mo-ZT alloy system is 0.5%, the secondary phase is in the form of a small number of nanoparticles. When $ZrTiO_4$ the content is 1%, the secondary phase mainly exists as micron particles. As the content continues to increase, the volume fraction of the secondary phase nano and micron particles begins to increase. When the content is 3%, the volume fraction of nanoparticles decreases and the volume fraction of micron particles continues to increase.

By comparing the TEM microstructure of the three alloys with different ductility, Mo-1ZT (8.5%), Mo-1.5ZT (16.3%), and Mo-2.5ZT (25.4%), the deformation resulted in the subgrains formation. The number of nanometer secondary phase particles in the Mo-1ZT alloy is less. $ZrTiO_4$ is mainly composed of micron particles in Fig. 3(a, b). Therefore, the dislocation movement cannot be uniformly hindered during the deformation process, and subgrains are easily formed in the grain in Fig. 3(b, c). Mo-1ZT alloy has more subgrains, with an average area of 0.73 μm^2. The number of micron particles increases in the Mo-1.5ZT alloy, and the number of nanometer secondary phase particles also increases slightly in Fig. 3(a, d). Therefore, it is easy to form larger subgrains in the grains during the deformation process in Fig. 3(e, f). The subgrain area of Mo-1.5ZT alloy increases to about 0.85 μm^2. The dislocation density for the deformed sample (at 25% elongation) is $1.5 \times 10^{10}/cm^2$ by TEM analysis.

On the contrary, the volume fraction of $ZrTiO_4$ nanoparticles in the Mo-2.5ZT alloy increases significantly in Fig. 3(g, h), which increases the difficulty of dislocation movement in the deformation process, inhibits dislocations movement in the long range, and makes dislocation distribution uniform in Fig. 3(h). Therefore, no small subgrains are formed in the alloy, and the subgrain area is about 3.4 μm^2. More plastic deformation energy is stored in the grain, which greatly improved the plasticity of the Mo-2.5ZT alloy without decreasing the room temperature strength. Compared with the Mo-1ZT alloy, the Mo-2.5ZT alloy elongation increases from 8.6% to 23%, which is a 166% overall increase.

4. Conclusions

In this paper, the Mo-ZT alloy strength increases with higher $ZrTiO_4$ secondary phase content, but the ductility reaches the maximum at 2.5 wt% $ZrTiO_4$ and the room temperature elongation is 25.4%. The number of secondary phase micro and nanoparticles increases with the $ZrTiO_4$ content in the Mo-ZT alloys. The main reason is that when the content of the micro-particles in the alloy reaches a certain value, the $ZrTiO_4$ starts to be dispersed and distributed in the nano-phase. The main mechanism of ductility improvement is nano-sized $ZrTiO_4$ particles with good interface bonding, which can inhibit the long-distance movement of dislocations during the deformation process of Mo-ZT molybdenum alloys. The dislocations are uniformly dispersed, so that small-sized subcrystals are not formed in the molybdenum matrix. The elongation is increased by 166% compared with the Mo-1ZT alloy.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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