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The multi-scale microstructure and strengthening mechanisms of Mo-12Si-8.5BxZr (at.%) alloys

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ABSTRACT

Mo-12Si-8.5B alloys with different Zr contents (0 at.%, 1 at.%, 2 at.%, 3 at.%, 4 at.%) were manufactured via a mechanical alloying process followed by hot pressing sintering technology. The microstructure of Mo-12Si-8.5B alloy exhibited a continuous submicro- and micro-scale α-Mo matrix in which the sub-micron Mo_3Si/Mo_5SiB_2 particles were distributed. Addition of Zr to Mo-12Si-8.5B alloy promoted to form spherical nano-scale intermetallic Mo_2Zr and ZrO_2 particles, which were mainly located at the grain boundaries (GBs) as well as partially within the grains. The microstructure of Mo-12Si-8.5B-xZr alloys was remarkably refined by these Mo_2Zr/ZrO_2 nanoparticles. Additionally, results of mechanical properties indicated that the Zr addition improved the hardness, compression strength, yield strength and flexure strength of alloys. In particular, the Mo-12Si-8.5B-2Zr alloy exhibited extremely high compression strength (3.38 GPa), yield strength (3.17 GPa) and flexure strength (1.15 GPa). Quantitative analyses indicate that both fine-grained strengthening and Zr-rich particle strengthening mechanisms play a significant role in strengthening the Mo-Si-B-Zr alloys, the strengthening is dominantly governed by grain size reduction. Furthermore, Zr getters detrimental oxygen by synthesizing ZrO_2 distributed at grain/phase boundaries, which contributes to increasing the GBs cohesion. Fracture surfaces revealed that the fracture mode transformed from intergranular to transgranular fracture owing to Zr addition.

1. Introduction

Three-phase Mo-Si-B alloys with excellent high-temperature capabilities are potential candidates for high temperature (> 1100 °C) structural applications in the aerospace and power generation industry [1–4]. Mo-Si-B alloys usually consist of a molybdenum solid solution (α-Mo) providing adequate toughness and the two intermetallic compounds Mo_3Si and Mo_5SiB_2 (T2) forming a protective boro-silicate glass layer for oxidation resistance [5]. Therefore, the present research focuses on the Mo-Si-B alloys with nominal composition of Mo-12Si-8.5B (at.%) which possesses adequate Si and B contents, and the Mo-12Si-8.5B alloy has potential to present good oxidation resistance [6]. However, this alloy exhibits minimum brittle-to-ductile transition temperatures (BDTT) of around 1100 °C, which does not satisfy the requirements of structural material.

It is well known that the concentration of detrimental interstitials (particularly oxygen [7]) at GBs results in the GBs embrittlement which influences the BDTT of Mo-based alloys significantly, reducing the strength and ductility of alloys. The reduction in grain size of Mo-based alloys is a common approach to overcome this issue, because it can reduce the concentration of these interstitials on the GBs below a critical level [8]. Only refining the grain size of material may have a negative impact on the creep performance at high temperatures and be difficult to obtain the comprehensive performance [9]. Another approach which is widely accepted is microalloying with suitable elements that not only refine the grain size of material but also suppress oxygen and nitrogen segregation at the GBs, in order to enhance the cohesive strength of GBs and compensate for the lack of high-temperature properties [10]. Numerous studies reported that microalloying with appropriate elements in Mo and Mo-Si alloys could achieve the desired effects. Miller and Bryhan [11] found that by adding Zr, Al, C and B into the 6.35-mm-thick Mo weldments, a momentous improvement in the tensile ductility from the traditional 3–20% had been achieved. The segregation of Zr, B and C to GBs can inhibit O segregation. Recently, H. Saage et al. [9] revealed that the role of Zr addition was to reduce segregation of Si and O at the GBs of Mo-1.5 at.% Si-based alloys and simultaneously enhance the cohesive strength of the GBs. Thus, the ductility of the material was improved significantly.

In the multiphase Mo-Si-B alloys, J.H. Schneibel et al. demonstrated that Zr addition was benefit for improving the fracture toughness of Mo-

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12Si-8.5B alloy [12]. Additionally, K. Morita et al. [13] pointed that bend strength of Mo-Si-B alloys was improved with addition of Zr, which resulted from the fine-grained microstructure. The ZrO_2 particles which were located at GBs impeded GBs movement and stabilized a small grain size of alloys. Besides, C. Hochmuth et al. reported that Mo-Zr precipitates and ZrO_2 phases were distributed at GBs and within the grains, which improved the creep properties of Mo-Si-B-Zr alloy [10].

In the Mo-La_2O_3-ZrB_2 alloys, Cheng et al. [14] confirmed that the ductilizing effects of alloys were related to not only volume fractions of ZrB_2 additions but also the sizes, distribution and volume fractions of the second phase particles (La_2O_3 and ZrO_2). However, previous studies based on the detail analysis of the second phase (Mo-Zr precipitates and ZrO_2 phases) are insufficient for Mo-Si-B-Zr alloys.

In this work, mechanical alloying and hot pressing sintering technology were used to prepare Mo-12Si-8.5B-xZr (x = 0, 1, 2, 3, 4) (at.%) alloys. The present work is aimed at investigating the microstructure characteristic, especially, the size, distribution and volume fractions of the second phase particles by reactive synthesis in the Mo-Si-B-Zr alloys. Another objective of this work is to analyze the influence of Zr addition on the mechanical properties of alloys. Also, we try to establish a quantitative relationship between microstructure parameters and mechanical properties.

2. Experimental procedures

Alloys with the nominal composition of Mo-12Si-8.5B-xZr (in at.%, x = 0, 1, 2, 3, 4) were prepared by mechanical alloying and hot pressing sintering, as listed in Table 1. The selected alloys were prepared from high purity powders Mo (99.9 wt%), Si (99.99 wt%), B (99.95 wt%) and ZrH_2 (99.5 wt%), respectively. ZrH_2 with amounts of 1, 2, 3 and 4 wt%, which is reduced to the appropriate zirconium contents of 1, 2, 3 and 4 at.% upon sintering, were added. The entire details of preparation process for Mo-12Si-8.5B-xZr alloys are described as following:

The loading/unloading of powders to/from vials were performed inside a dry Ar-filled glove box. Firstly, the Mo, Si and B powders were measured and mixed according to the target composition. Secondly, the Mo, Si and B powders were placed into a planetary ball mill (Retch PM 400, WC balls and WC vial) with a speed of 150 rpm and a powder-to-ball weight ratio of 1:1 under protective atmosphere (Ar) for 5 h to obtain a homogenous and dispersive powder mixture. Then, the mixed powders were further processed by mechanical alloying (MA) at a high energy state with a rotational speed of 250 rpm and a powder-to-ball weight ratio of 1:10 for 15 h under a protective atmosphere (Ar). Thirdly, the mechanically alloyed powders were added certain composition of ZrH_2 powders. These remixed powders were used to conduct MA in high energy state with a speed of 250 rpm and a powder-to-ball weight ratio of 1:10 under protective atmosphere (Ar) for 5 h. Finally, the ultimate mechanically alloyed powders were wrapped in a graphite ferrule, and compacted in a vacuum environment ($< 10^{-3}$ Pa) inside the graphite dies. Prior to hot pressing, the Mo-Si-B-Zr powder mixtures were annealed at 1200 °C for 1 h to eliminate the internal stress and promote phase precipitation. Hot pressing process was completed under a pressure of 49 MPa at 1600 °C for 2 h to consolidate and densify the alloy.

Density of the Mo-Si-B-Zr alloys was measured by using Archimedes' principle [15]. The crystalline phases of the alloys were characterized by X-ray diffraction (XRD) using a XRD-7000S Diffractometer.

Table 1
Investigated alloys with different Zr contents.

Label	MSB	MSB-1Zr	MSB-2Zr	MSB-3Zr	MSB-4Zr
Alloy (at. %)	Mo-12Si-8.5B	Mo-12Si-8.5B-1Zr	Mo-12Si-8.5B-2Zr	Mo-12Si-8.5B-3Zr	Mo-12Si-8.5B-4Zr

Microstructure analyses of the alloys were performed via optical metallography (OM) (GX71 of OLYMPUS) and scanning electron microscopy (SEM) (JEM-6700F). The specimens were polished and etched with Murakami's etch (an aqueous solution of 10 vol% potassium ferricyanide and 5 vol% sodium hydroxide). The detailed microstructure including second phase particles was examined by transmission electron microscopy (TEM) (JEM-200CX). The TEM specimens were mechanically ground to a thickness of 50 μm and then twin jet polished to perforation using a 10 vol% sulphuric acid/alcohol solution at − 25 °C and a 30 V voltage. Energy dispersive spectrometry (EDS) and selected area electron diffraction (SAED) in TEM were employed to characterize the composition and structure of different grains/particles, respectively. The size and volume fraction of grains/particles were statistically evaluated with the help of image process software Image J. In order to obtain the accurate size of the grains/particles, at least 200 random grains/particles were measured. Details about the parameter (size and volume fraction) measurements of grains/particles can be referred to Ref. [16].

Vickers hardness (HV) was measured with a 0.3 kgf and 10 s full-loading time on a TUKON 2100 micro-Vickers's hardness tester and five measurements were conducted on each grip section. The uniaxial compression tests were performed using a computer-controlled machine (HT-2402) at a nominal strain rate of $5 \times 10^{-3}\ s^{-1}$ on samples of dimension of 5 mm × 5 mm × 10 mm (L × W × H) in air at room temperature. The yield strength (values of flow stress at 0.2% plastic strain) was measured by back-extrapolation of the stress/strain curve after yielding in compression tests. The flexure strength values were determined by the three-point bending tests. Flexure specimens with a cross section of 3 mm × 4 mm and a length of 26 mm were electro-discharge machined and ground, and subsequently tested in a universal testing machine (Instron 1185) in a three-point bend fixture with a 20 mm span at room temperature in air. The cross-head speed in flexure strength tests was 0.5 mm/min. In this paper, all the samples were electro-discharge machined, ground, and then polished before testing. All the experiment results are average values of at least five samples.

3. Results and discussion

3.1. XRD analysis and microstructure characterization

Measurement results on the density determined by the Archimedes principle exhibit that all the alloys with different Zr additions have a relative density of above 94%. Fig. 1 shows X-ray diffraction pattern of the MSB-xZr alloys. It presents that all the alloys exhibit α-Mo and two intermetallic phases (Mo_3Si and T2), which are in keeping with the isothermal three-phase section of the Mo-rich portion of the Mo-Si-B phase diagram [17]. Additionally, ZrO_2 phase is observed in MSB-3Zr alloy and MSB-4Zr alloy. It indicates that the ZrH_2 was decomposed to form Zr during sintering, and then ZrO_2 phase was produced through the reaction between Zr and oxygen impurities.

The microstructure of the MSB alloy is depicted in Fig. 2(a). It can be seen that the powder metallurgy method creates fine and homogeneous microstructure. The α-Mo, Mo_3Si and T2 which are all denoted by black arrows are the brightest appearing phase, the slightly darker gray phase and the dark gray appearing phase, respectively. Furthermore, the MSB alloy possesses a continuous α-Mo matrix with homogeneously distributed Mo_3Si and T2 particles, which is similar to Schneibel et al.'s study [18]. In fact, the microstructures of the Zr-containing alloys have characteristic similar to MSB. In addition, the volume fractions of α-Mo phase and intermetallic (Mo_3Si + T2) phase have an average value of about 44% and 56%, respectively, irrespective of the amount of Zr addition (Fig. 2(b)).

The microstructure of the MSB-xZr alloys was further investigated by TEM, as shown in Fig. 3 and Fig. 4. As seen from Fig. 3(a) and 3(b), the α-Mo, Mo_3Si and T2 phases were determined by analyses of the corresponding SAED. In addition, the finely distributed nano-size