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A Mo–Si–B intermetallic alloy with a continuous α-Mo matrix

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Abstract

A novel technique for fabricating high-temperature molybdenum–silicon–boron intermetallic composites is described. Vacuum annealing of silicide particles resulted in a loss of Si, and consequently a Mo solid solution layer, at the surfaces. Subsequent consolidation produced a microstructure of silicide particles bonded by a continuous Mo matrix. The α-Mo imparted significant room temperature fracture toughness. © 2002 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Mo–Si–B alloys consisting of the intermetallic phases Mo_3Si and Mo_5SiB_2 (T2) as well as a Mo solid solution phase (α-Mo) are of interest as oxidation-resistant high-temperature structural materials. These types of alloys have been described in two patents by Berczik [1,2] and their phase relations have been examined by Perepezko and co-workers [3,4]. Their oxidation resistance was screened by Schneibel et al. [5]. Typically, it increases with increasing Si and B concentrations. The mechanical properties of this class of alloys have been studied by Liu et al. [6], Nieh et al. [7], Schneibel et al. [5,8], and Choe et al. [9]. The intermetallic phases Mo_3Si and T2 retain high strengths up to 1400 °C [10–13]. However, they tend to be brittle with room temperature fracture toughness values on the order of 3 MPa $m^{1/2}$ [10,14]. Using controlled crack propagation in chevron-notched flexure bars, Schneibel et al. [8] showed that alloys with the composition Mo–12Si–8.5B (at.%) [1] exhibit significantly higher fracture toughness values than Mo_3Si or T2. More rigorous fracture toughness measurements carried out by Choe et al. [9] showed values on the order of 7–8 MPa $m^{1/2}$. The volume fraction of the α-Mo phase in these alloys was approximately 38% and in 2-D cross-sections the α-Mo phase appeared to consist of individual particles. Choe et al.'s results suggested that crack trapping by the α-Mo phase was an important factor contributing to the improvement of the fracture toughness values.

In order to maximize the contribution of the α-Mo phase to the fracture toughness it is desirable

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for the α-Mo phase to be continuously distributed. The advantage of such a microstructure (which is similar to that of Co-bonded WC composites [15]) is that propagating cracks cannot avoid the α-Mo phase. Nieh et al. [7] believe that their powder-metallurgically prepared material with the nominal composition Mo–9.4Si–13.8B had a continuous α-Mo network. Flexure tests with chevron-notched specimens indicated room temperature fracture toughness values on the order of 10 MPa $m^{1/2}$ [6]. However, in order to achieve satisfactory oxidation resistance the α-Mo volume fraction needs to be considerably smaller than the 50 vol% present in that alloy [7]. The goal of the present work is to describe a process capable of producing Mo–Si–B alloys with a continuous α-Mo matrix while at the same time keeping the volume fraction of the α-Mo matrix low (e.g., 20%).

2. Experimental details

Several buttons with the nominal composition Mo–20Si–10B were prepared from elemental materials by arc-melting in a partial pressure of argon. The purities of the Mo, Si, and B starting materials were 99.95, 99.99, and 99.5 wt.%, respectively. The buttons were crushed to $-100/+270$ mesh ($53 \leqslant$ diameter $\leqslant 150$ μm) powder. Steel debris resulting from the crushing process was removed magnetically. As will be described later, the powder surfaces were depleted of Si by annealing in a Mo-mesh vacuum furnace at a pressure of 10^{-3} Pa and a temperature of 1600 °C. Small portions of the annealed powders were ground to a size of -635 mesh ($\leqslant 20$ μm) and examined by powder X-ray diffraction. Some of the powder was sealed in a 10 mm diameter Nb tube which was closed in vacuum by electron-beam welding and consolidated by hot isostatic pressing (HIP) at 1600 °C and 210 MPa for 2 h. Flexure bars were chevron notched with a 0.3 mm thick diamond blade and tested in three-point bending at room temperature. The fracture toughness was evaluated as $K_q = (GE')^{1/2}$, where $E' = E/(1 - \nu^2)$ is the plane strain Young's modulus and $G = W/A$ is calculated from the energy (W) absorbed during the fracture of an area (A) swept out by the propagating crack. The oxygen content of the consolidated material was determined by LECO inert gas fusion. The microstructures of the powder particles and the consolidated material were examined by optical microscopy as well as scanning electron microscopy (SEM) in the back-scattered electron (BSE) image mode. Qualitative chemical analysis was performed by energy dispersive spectroscopy (EDS) in an SEM.

3. Experimental results and discussion

The goal of this research is to fabricate Mo–Si–B intermetallic particles with α-Mo surface layers, and consolidate them in order to create a microstructure consisting of intermetallic particles bonded by a continuous matrix of α-Mo. According to the Mo–Si–B ternary phase diagram [3] Mo–20Si–10B in thermodynamic equilibrium at 1600 °C consists exclusively of Mo_3Si and T2, without any α-Mo. Powder particles of Mo–20Si–10B were annealed for 16 h at 1600 °C in vacuum. A cross-section of a particle (Fig. 1) shows a surface layer of α-Mo. The formation of the α-Mo surface layer is attributed to the loss of silicon by evaporation of SiO as described by Kofstad [16]. According to Kofstad evaporation of SiO at 1600 °C will occur

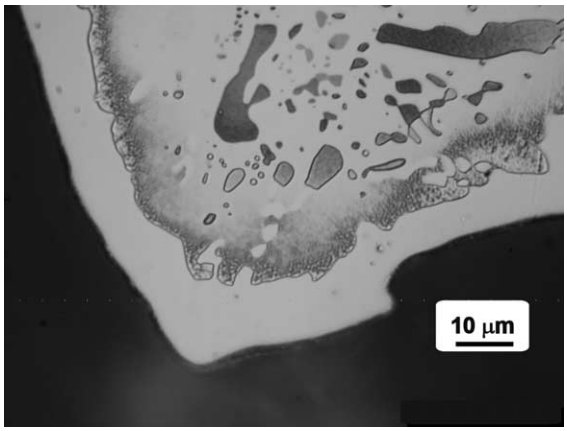

Fig. 1. Optical micrograph of polished and carbon-coated section of Mo–20Si–10B powder particle after 16 h at 1600 °C in vacuum. The approximately 10 μm thick α-Mo layer around the particle is clearly visible.

at oxygen partial pressures as high as 1000 Pa, while the pressure during our anneals was only 10^{-3} Pa.

Using a mixture of known amounts of Mo_3Si and Mo powders and the ratio of the intensities of the Mo(2 0 0) and Mo_3Si(2 1 1) X-ray diffraction peaks (evaluated from the peak areas), the Mo/Mo_3Si ratio of the annealed Mo–20Si–10B powders was determined. The T2/Mo_3Si ratio was calibrated by X-ray diffraction of the as-cast powders (which consisted almost exclusively of Mo_3Si and T2) using the T2(3 1 0) and Mo_3Si-(2 1 1) peak intensities and the T2/Mo_3Si phase ratio taken from the phase diagram. Using these calibrations, the evolution of the phase volume fractions with annealing time was calculated and is shown in Table 1. The increase in the α-Mo volume fraction is approximately proportional to the square root of the time (Fig. 2) suggesting diffusion controlled kinetics of the SiO evaporation, i.e., the rate of the process is controlled by diffusion of Si through the α-Mo layer surrounding the particles. A precise $t^{1/2}$ law is not expected for several reasons. During annealing the width of the diffusion layer around the smaller particles may become as large as the particle radius. The sintering taking place during annealing will remove surface area due to neck formation between adjacent sintering particles. It should also be pointed out that the volume fraction analysis is only approximate since a fourth phase, Mo_2B, was found in the powder diffraction pattern corresponding to an annealing of 64 h. The Mo_2B formed presumably by the reaction:

$$Mo_5SiB_2 + 1/2O_2 \rightarrow 2Mo_2B + SiO + Mo \qquad (1)$$

Table 1
Evolution of the volume fractions (in %) of the α-Mo, Mo_3Si and T2 phases of Mo–20Si–10B powders during annealing at 1600 °C in vacuum

Annealing time (h)	α-Mo	Mo_3Si	T2
0	0.4	59.8	39.8
1	2.1	57.3	40.6
4	10.2	45.8	44.0
16	13.3	40.7	46.0
64	19.1	36.4	44.5

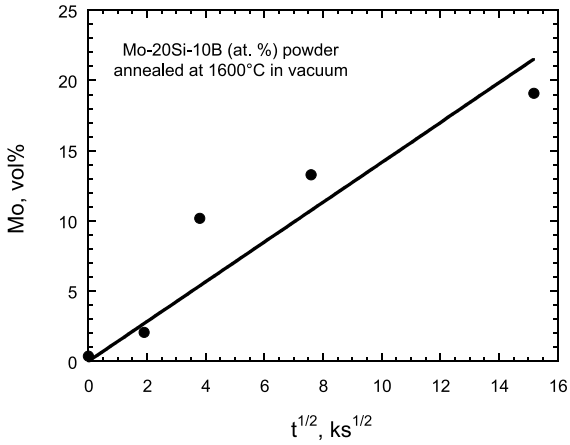

Fig. 2. Increase of the α-Mo volume fraction of Mo–20Si–10B (at.%) powder during annealing in vacuum at 1600 °C.

As compared to Mo_3Si, which is expected to yield three Mo atoms for each Si atom removed, the Mo-yield of T2 is comparatively small. Nevertheless, with increasing annealing time the amount of T2 is expected to decrease. Table 1, on the other hand, shows a tendency for the T2 volume fraction to increase. Reasons for this are the changes in the volume fractions of the other phases and the fact that the formation of the Mo_2B phase was ignored. The crucial point, namely, the formation of substantial amounts of α-Mo, has however been clearly demonstrated.

The processing of Mo–Si–B with the desired microstructure was carried out in the following way: Mo–20Si–10B powder was annealed at 1600 °C in vacuum for 24 h resulting in slight sintering of the powder. The powder was carefully broken up in order to separate the particles while not breaking them, and in order to expose those areas on the powder particles that might not have lost silicon during the first anneal. After a second anneal for 24 h at 1600 °C, the powder was broken up again and HIPed in an evacuated and sealed Nb tube. The oxygen content after HIPing was determined to be 338 wppm. The BSE–SEM in Fig. 3 shows that the intended microstructure has indeed been obtained—it is a composite of intermetallic particles (dark) bonded by a continuous matrix of α-Mo (bright). Point counting indicated a α-Mo volume fraction on the order of 30%. The

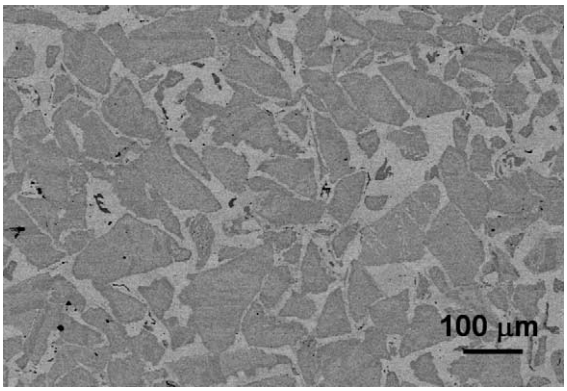

Fig. 3. SEM–BSE micrograph of a Mo–Si–B alloy fabricated from Mo–20Si–10B powder that was annealed for 2 days in vacuum at 1600 °C prior to consolidation by HIPing: intermetallic particles (dark); α-Mo (bright).

room temperature fracture toughness was determined from the controlled fracture of two chevron-notched specimens and found to be on the order of 14 MPa $m^{1/2}$ (see Table 2). This value is considerably higher than the value of 10 MPa $m^{1/2}$ obtained by Liu et al. [6] for a Mo–Si–B alloy with a higher α-Mo volume fraction (≈50%) [7]. The reason for the difference is that the fracture toughness is not only determined by the volume fraction of the toughening α-Mo, but also by its scale. Typically, the fracture toughness values increase with increasing volume fraction of the toughening phase and decrease when its scale decreases [17]. Since Liu et al.'s alloy had a fine particle size on the order of 3 μm (i.e., a much finer microstructural size than our alloy) it is not surprising that its fracture toughness is relatively low.

In previous work, we fabricated a Mo–Si–B specimen by HIPing of a mixture of Mo_3Si, T2, and Mo powders [8]. This specimen consisted of coarse (<150 μm) intermetallic particles in a nearly continuous α-Mo matrix with a volume fraction on the order of 38%. Its room temperature fracture toughness was on the order of 15 MPa $m^{1/2}$. However, the processing technique based on mixing Mo_3Si, T2, and Mo powders is not likely to produce a continuous α-Mo matrix when the α-Mo volume fractions are small, e.g., 20% or 30%. This is where the technique presented in this paper has a definitive advantage. In order to achieve thin continuous Mo-layers during annealing of the powders, it will however be necessary to carry out more frequent, or continuous, mixing of the powders. By varying the size of the intermetallic powder particles and the volume fraction of the α-Mo layer on their surfaces it is anticipated that a wide range of microstructures and properties can be achieved.

Table 2
Fracture toughness K_q determined from the absorbed energies W and the areas A swept out by cracks propagating during the fracture of chevron-notched specimens[a]

A, mm^2	W, mJ	G, J/m^2	K_q, MPa $m^{1/2}$
2.60	1.32	507.8	13.5
3.08	1.98	642.9	15.1

[a] The elastic modulus and Poisson's ratio were taken to be 327 GPa and 0.29 [8].

4. Conclusions

A fabrication technique capable of producing Mo–Si–B alloys with a microstructure consisting of Mo_3Si and T2 particles bonded by a continuous α-Mo matrix has been developed. By varying the size of the intermetallic particles and the α-Mo volume fraction it is anticipated that alloys with a wide combination of properties can be fabricated. In this way, it will be possible to engineer Mo–Si–B alloys with the desired combinations of oxidation resistance, creep strength, and fracture toughness.

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