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PROCESSING AND PROPERTIES OF MOLYBDENUM SILICIDE INTERMETALLICS CONTAINING BORON

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ABSTRACT

The processing and mechanical properties of Mo-Si-B intermetallic alloys with compositions Mo-26.7Si-7.3B and Mo-12Si-8.5B (at. %) were investigated. The first alloy consisted of the phases Mo_3Si, Mo_5Si_3 (T1) and Mo_5SiB_2 (T2). Attempts to extrude castings of this alloy at 1700 or 1800°C were not successful. Hot isostatic pressing of elemental powders was more promising and room temperature flexure strengths on the order of 200 MPa were reached. The second alloy with the composition Mo-12Si-8.5B could be readily cast and consisted of α-Mo inclusion in a brittle matrix of Mo_3Si and T2. A heat treatment of 1 day at 1600°C in vacuum improved the room temperature strength and fracture toughness. Values on the order of 500 MPa and 10 MPa $m^{1/2}$, respectively, were obtained. Consistent with ductile phase toughening, limited plastic deformation as well as debonding of the α-Mo inclusions were seen on fracture surfaces.

INTRODUCTION

The objective of this task is to develop new-generation corrosion-resistant Mo-Si alloys for use as hot components in advanced fossil energy combustion and conversion systems. The successful development of Mo-Si alloys is expected to improve the thermal efficiency and performance of fossil energy conversion systems through an increased operating temperature, and to increase the service life of hot components exposed to corrosive environments at temperatures as high as 1600°C. While $MoSi_2$ is highly oxidation resistant at elevated temperatures, it is extremely brittle at ambient temperatures and has poor creep resistance at elevated temperatures. Molybdenum compounds with lower Si contents, such as Mo_5Si_3 are potentially less brittle and exhibit higher strengths at elevated temperatures, but do not have the required oxidation resistance. Boron additions appear to resolve the oxidation problem. As early as 1957, Nowotny et al.[1] pointed out that boron-containing silicides possess high oxidation resistance due to the formation of borosilicate glasses. Based on Nowotny et al.'s work, boron-containing molybdenum silicides based on Mo_5Si_3 were recently developed at Ames Laboratory.[2-4] These silicides consist of approximately 25 vol.% of Mo_3Si, 50 vol.% Mo_5Si_3 (T1), and 25 vol.% Mo_5SiB_2 (T2). A typical composition, which is indicated in Fig. 1, is Mo-26.7Si-7.3B, at. % (compositions will always be given in at. %). This alloy has an oxidation resistance comparable to that of $MoSi_2$, and it does not appear to show catastrophic oxidation ("pest reaction") at intermediate temperatures such as 800°C.[4] Also, its creep strength is superior to that of $MoSi_2$. Another class of Mo-Si-B alloys of interest are those developed by Berczik,[5,6] which consist of α-Mo, Mo_3Si, and Mo_5SiB_2 (T2). These types of alloys have also been studied recently by Perepezko and co-workers.[7-9] While their oxidation resistance is inferior to that of the Mo_3Si-T1-T2 alloys, it is likely that it can be improved by minimizing the α-Mo volume fraction, by suitable alloying additions, and/or silicide coatings. The main advantage of the Mo-Mo_3Si-T2 alloys is that they do not consist exclusively of brittle phases. This suggests that fracture toughnesses higher than those of the Mo_3Si-T1-T2 alloys can be achieved.

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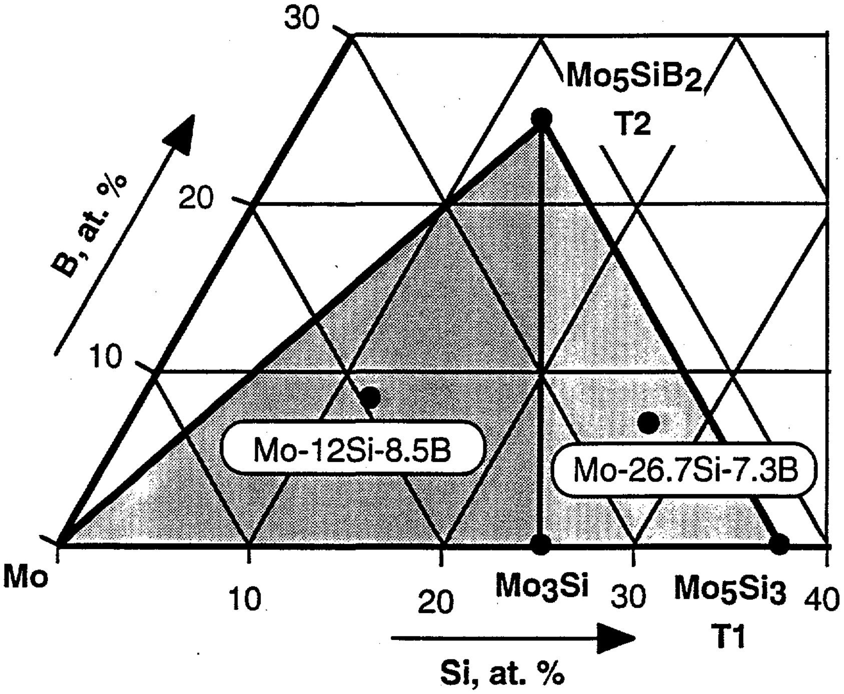

Figure 1: Schematic section of the ternary Mo-Si-B phase diagram showing the phases and alloy compositions of interest.

The present work describes our experience with the processing of these two classes of Mo-Si-B materials. Microstructural information as well as mechanical property measurements will be presented.

RESULTS AND DISCUSSION

PROCESSING AND MECHANICAL PROPERTIES OF Mo-26.7Si-7.3B

A Mo-26.7Si-7.3B extrusion carried out at 1800°C in fiscal year 1997 was unsuccessful, probably due to the formation of liquid phases. Therefore, an extrusion of this composition was repeated at 1700°C. Ingots were arc-melted from commercially pure elements and drop-cast into 25 mm diameter MgO molds. The MgO molds resulted in slow cooling, thus minimizing macrocracking. Several ingots prepared in this manner were put into a Mo-can with an outer diameter of appr. 50 mm, sealed by electron-beam welding, and extruded at 1700°C with an area reduction of 1:4. However, only about 200 mm of rod was extruded before the maximum capacity of the die assembly was reached, at which point the extrusion process had to be discontinued. The extruded material showed profuse cracking. It is concluded that extrusion of cast material with the above composition is very difficult, because extremely high loads and stresses are required at "low" temperatures such as 1700°C, whereas partial liquid phase formation occurs at high temperatures such as 1800°C.

Another processing option is powder metallurgy (PM). Previous work seemed to indicate that hot-pressing of $MoSi_2$, Mo, and B powders resulted in incomplete densification.[10,11] A more detailed analysis showed, however, that the dark spherical features (with typical sizes of 2 μm) seen in scanning electron micrographs were not cavities, but instead glass particles containing primarily Si and O. Since then, additional powder-metallurgical processing has been carried out. In order to reduce surface area and oxygen content, coarse elemental powders (> 100 µm) were blended in an Ar glove box and hot-pressed in graphite dies at temperatures ranging from 1600 to 1700°C and pressures of about 50 MPa. Even after annealing at 1700°C, homogenization was not achieved and microcracks were often observed. SiO_2 inclusions were occasionally seen. In another PM experiment, mixtures of elemental Mo, Si, and B powders with sizes < 45 µm were blended in an Ar glove box, filled into Nb cans, outgassed at 400°C in vacuum, sealed by electron-beam welding, and hot isostatically pressed (HIPed) at 1650°C and 200 MPa. Again, SiO_2 inclusions were seen. Similar to the coarse powders, full equilibration was not achieved, since particles consisting primarily of Mo were seen (Fig. 2). The distribution of the phases was quite inhomogeneous. For example, coarse Mo particles were surrounded by fine T2 particles. However, only occasional microcracking was seen. Improved PM processing is in progress.

Three-point flexure specimens with a cross section of 3x4 mm were tested with a span of 20 mm and a crosshead speed of 10 µm/s. The fracture strengths σ_f were evaluated as $1.5 x P_f/(wt^2)$, where P_f is the load at which fracture occurs, w is the specimen width, and t the specimen thickness. The fracture strengths of the PM materials are listed in Table 1. They are significantly higher than those for the corresponding cast materials, which are only on the order of 100 MPa.[10,11]

Instead of elemental powders, prealloyed powder obtained by breaking up a casting into -325 mesh powder was also HIPed (1600°C/200 MPa). This material was more homogeneous than the material made from elemental powders and had a slightly higher room temperature strength (see Table 1).

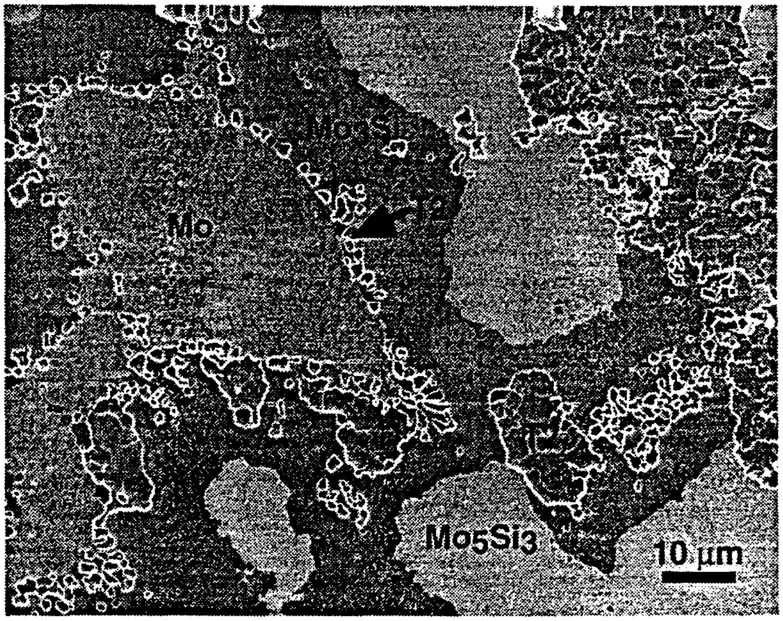

Figure 2: SEM micrograph of polished and etched (Murakami's etch) Mo-26.7Si-7.3B HIPed from elemental powders.

Table 1. Room temperature flexure strengths of PM Mo-26.7Si-7.3B

Processing	Flexure Strengths, MPa
HIPing from elemental powders (476-2HI)	199, 194
HIPing from prealloyed powder (459F)	220, 211, 235

CAST Mo-12Si-8.5B (at. %)

Figure 3 is an SEM micrograph of cast and annealed (1 day/1600°C/vacuum) Mo-12Si-8.5B. The different phases were identified by energy dispersive spectroscopy and several phase particles are annotated. The T2 phase appears etched, the α-Mo phase is the brightest phase, and the third phase is Mo_3Si. The α-Mo occurs discontinuously in a brittle matrix of Mo_3Si and T2.

The strength of Mo-12Si-8.5B was examined by 3-point flexure tests. As would be expected from the microstructure in Fig. 3, no plastic deformation was noted prior to fracture. The measured flexure strengths are summarized in Table 2. The strength is lowest for the as-cast condition. An anneal for 1 day at 1600°C in vacuum appears to increase the strength slightly. One possible reason for this might be a reduction of the concentration of Si and B in the α-Mo phase. This reduction might increase the ductility of the Mo and reduce the flaw sensitivity of the material. Since the ductile-to-brittle transition temperature of Mo and its alloys is usually above room temperature,[12] two tests were carried out at 500°C in air. The significantly higher strength at 500°C is consistent with improved mechanical properties of the α–Mo phase at 500°C, as compared to room temperature. The specimens darkened during the testing, which lasted approximately 1 h at 500°C. However, they showed no evidence for a pest reaction.

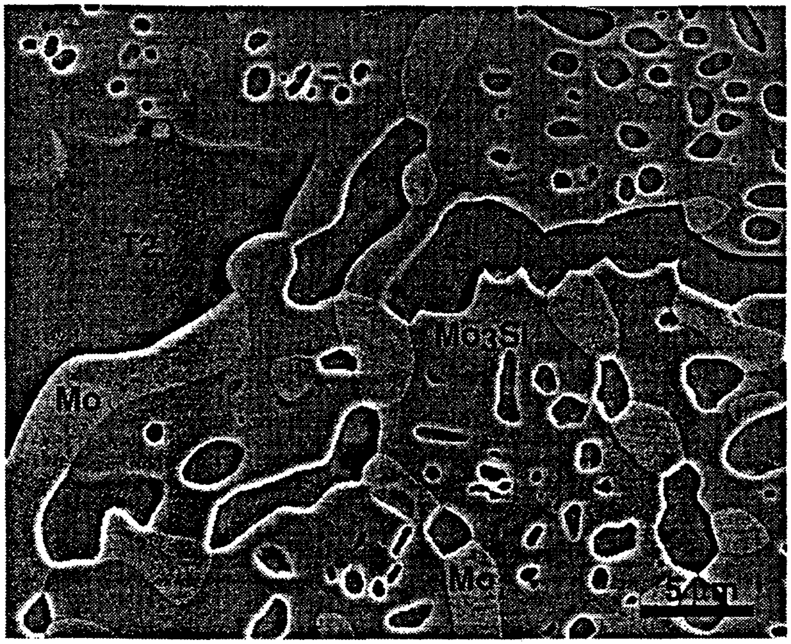

Figure 3: SEM micrograph of cast and annealed (1 day/1600°C/vacuum) Mo-12Si-8.5B, after polishing followed by etching with Murakami's etch.

Room temperature fracture toughnesses were measured by determining the energy dissipated during the controlled 3-point fracture of chevron-notched specimens. Similar to the flexure specimens, a cross section of 3x4 mm, a span of 20 mm, and a crosshead speed of 10 μm/s were employed. During the testing, crack nucleation started at the apex of a triangle with a height of about 2 mm and a base of about 3 mm (see schematic of cross section in Fig. 4).

Table 2. Three-point flexure strengths of cast Mo-12Si-8.5B (at. %)

Specimen Number	Condition	Temp, C	Flexure Strength, MPa
531#1	as-cast	20	457
531#2	as-cast	20	455
531-A1#1	1d/1600C/Vac	20	484
531-A1#2	1d/1600C/Vac	20	539
531-A2#1	1d/1600C/Vac	500	722
531-A2#2	1d/1600C/Vac	500	697

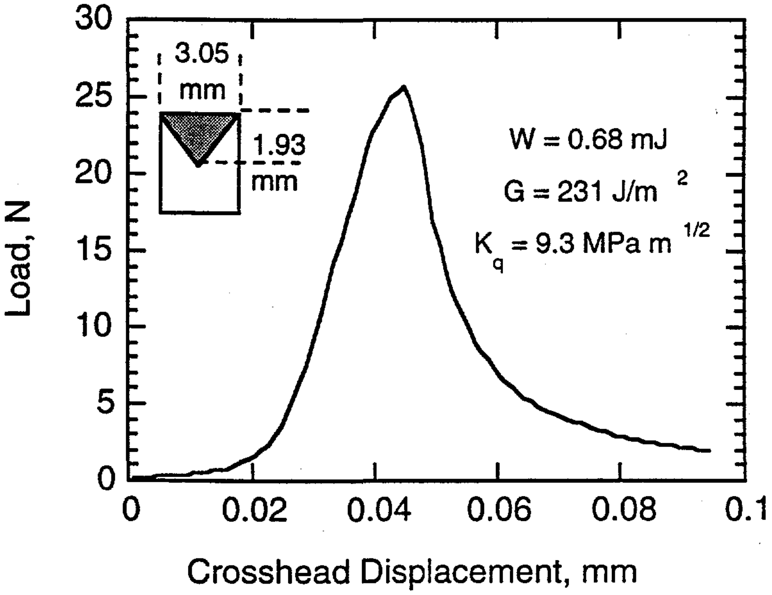

Figure 4: Load-displacement curve obtained during the controlled fracture of a chevron-notched specimen of Mo-12Si-8.5B annealed for 1 day at 1600°C in vacuum.

Figure 4 shows a typical load-displacement plot. Integration of this curve provided the absorbed energy W. The fracture toughness was determined either as G=W/(2A), where A is the area of the triangle through which the crack propagated, or as $K_q=(G\times E')^{1/2}$, where $E'=E/(1-\nu^2)$ is the plane strain Young's modulus and ν is Poisson's ratio. By ultrasonic techniques, the room temperature elastic constants were found to be E=327 GPa and $\nu=0.29$. The density was found to be 9.32 Mg/m^3 by He pycnometry. The fracture toughnesses evaluated in this manner are shown in Table 3. The as-cast Mo-12Si-8.5B had a value on the order of 7 MPa $m^{1/2}$. Annealing for 1 day at 1600°C in vacuum improved the fracture toughness to values of 9 to 10 MPa $m^{1/2}$. This suggests that the 1600°C anneal increased the toughening contribution of the α-Mo phase. This finding is in agreement with the increased flexure strength after a 1600°C anneal, since a higher toughness of the α-Mo phase is likely to reduce the flaw sensitivity of the flexure specimens and will thus increase the flexure strength. There is also some indication that the fracture toughness at 500°C may be higher than that at room temperature. However, the increase may be within the error of the testing technique and further verification is needed.

Table 3. Fracture toughness of Mo-12Si-8.5B (at. %)

Specimen Number	Processing	Temp., °C	A, mm^2	W, mJ	G, J/m^2	K_q, MPa m$^{1/2}$
531#3	as-cast	20	3.02	0.4179	138.4	7.2
531#4	as-cast	20	2.75	0.3927	142.8	7.3
531-A1#3	1d/1600°C/Vac	20	2.94	0.6800	231.0	9.3
531-A1#4	1d/1600°C/Vac	20	2.88	0.7750	269.5	10.0
531-A2#3	1d/1600°C/Vac	500	2.62	0.7087	271.0	10.0
531-A2#4	1d/1600°C/Vac	500	2.93	1.0599	361.7	11.6

Figure 5 shows a fracture surface of annealed Mo-12Si-8.5B. This particular image shows α-Mo particles in a matrix of T2. In other micrographs, Mo_3Si was found as well. Similar to the cross section in Fig. 3, the α-Mo forms inclusions in a brittle matrix. Figure 5 shows some evidence for debonding at the Mo-T2 interfaces. Limited ductility of the α-Mo particles is also seen.

The fracture toughnesses of Mo-12Si-8.5B alloys exceeds those of most engineering ceramics. However, in view of the high volume fraction of the α-Mo phase (approximately 40%), higher fracture toughnesses might be expected. It is hoped that further improvements may be achieved by lowering the ductile-to-brittle transition temperature of the α-Mo by suitable alloying additions. Also, processing resulting in a microstructure consisting of T2 and Mo_3Si particles in a matrix (or "binder") of Mo is likely to be more effective with regard to the mechanical properties. The oxidation behavior of these alloys will be examined as well.

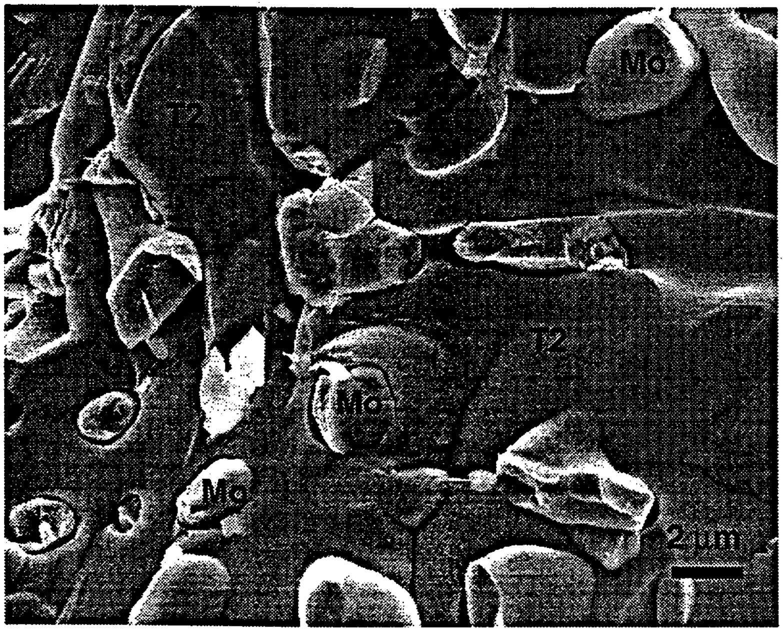

Figure 5: Fracture surface of Mo-12Si-8.5B. Prior to fracture, the material was annealed for 1 day at 1600°C in vacuum.

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