



ASSESSMENT OF PROCESSING ROUTES AND STRENGTH OF A 3-PHASE MOLYBDENUM BORON SILICIDE (Mo_5Si_3 - Mo_5SiB_2 - Mo_3Si)

J.H. Schneibel, C.T. Liu, L. Heatherly, and M.J. Kramer[†]
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6115, U.S.A.
[†]Iowa State University, Ames Laboratory, Ames, IA 50011-3020, U.S.A.

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1. Introduction

High temperature components such as furnace elements are often fabricated from MoSi_2 . An interesting alternative to MoSi_2 are molybdenum boron silicides consisting of Mo_5Si_3 , Mo_3Si , and Mo_5SiB_2 (1–4). First, these Mo-Si-B intermetallics possess a high temperature oxidation resistance comparable to that of MoSi_2 (1,3). Second, they do not show catastrophic oxidation (“pest reaction”) at intermediate temperatures such as 1100 K (3). Third, these three-phase materials may possess a higher fracture resistance than MoSi_2 . Fourth, their creep strength is vastly superior to that of MoSi_2 and most composites based on MoSi_2 (2).

In 1957, Nowotny et al. (4) investigated the Mo-Si-B phase diagram at 1873 K. The section of this phase diagram relevant to the present work is shown in Fig. 1. The phases of interest are Mo_3Si with the cubic A15 structure (cP8) containing 8 atoms per unit cell, Mo_5Si_3 with the tetragonal D8_m structure (tI32) with 32 atoms per unit cell, and Mo_5SiB_2 with the tetragonal D8_1 structure (tI32). Nowotny et al. referred also to two articles published in 1954 which suggest 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 studied at Ames Laboratory (1–3). A typical composition is Mo-31.4 Si-8.1 B, at.% (Mo-13 Si-1.3 B, wt%) and consists of approximately 50 vol.% Mo_5Si_3 (T1), 25 vol.% Mo_3Si , and 25 vol.% Mo_5SiB_2 (T2).

At present, the mechanical properties of these new Mo-Si-B intermetallics have not been fully explored. One reason for this is simply the unavailability of sufficiently large parts with a sound microstructure. The goal of this work was therefore to explore the processing of these materials by several different routes such as powder and ingot metallurgy, and examine the resulting microstructures. In addition, some post-processing (hot isostatic forging, extrusion) was carried out. The flexure strength of the differently processed materials was characterized and interpreted in terms of their microstructures. Some additional work not described in this article may be found elsewhere (5).

2. Experimental Details

Powder metallurgical processing was carried out by mixing MoSi_2 (10 μm), Mo (2–8 μm), B (<45 μm), and graphite powders in argon and hot-pressing them in vacuum in a 60 mm diameter graphite

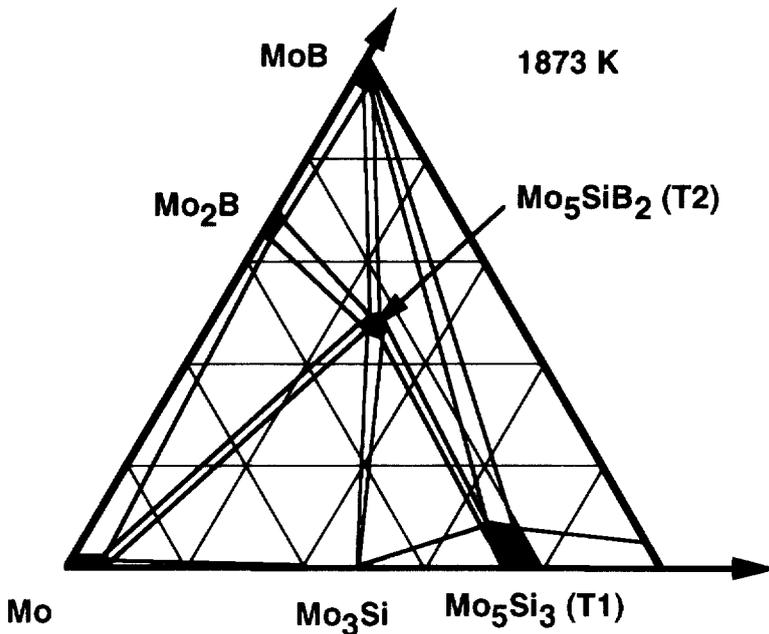


Figure 1. Section of the Mo-Si-B phase diagram at 1873 K [after Nowotny et al. (4)]

die at 1873 K and 48 MPa. The carbon was added to reduce the oxygen content. For processing by ingot metallurgy, pure elemental materials were repeatedly arc-cast in argon, followed by drop-casting in argon into copper or sand molds with a diameter of 25 mm and a length on the order of 80 mm. Unless otherwise stated, compositions will be given in at.%. Isothermal forging was carried out in a graphite hot press. A cylindrical ingot prepared by drop casting into a Cu mold was placed in a Mo can with an outer diameter of 50 mm. The can was evacuated, sealed, and extruded at 2073 K with an area reduction of 1:4. Metallographic specimens were etched with Murakami's etch and examined by optical and scanning electron microscopy (SEM) as well as energy-dispersive and wave-length dispersive spectroscopy (EDS and WDS). Powder x-ray diffraction patterns were also obtained. The oxygen and carbon contents were determined by inert gas-fusion analysis of pieces with a mass of ~ 100 mg. Flexure bars with cross sections of 3×4 mm were electrodischarge machined, ground, and tested in air by 3 point bending with a span of 20 mm and a cross-head speed of $10 \mu\text{m/s}$. Also, several flexure tests were performed in a 3-point SiC bend test fixture (15 mm span) at 1473 K in air. A tensile test with a ground buttonhead specimen with a gage length of 20 mm and a diameter of 3.2 mm was also performed.

3. Results and Discussion

Powder metallurgical processing

Specimen MSB1 was hot-pressed from MoSi_2 , Mo, B, and graphite powders at 1873 K and 48 MPa. Table I shows its oxygen and carbon content. As would be expected from the powder processing route, the oxygen content was very high.

Figure 2 illustrates the microstructure of a polished and etched specimen of alloy MSB1. Although Fig. 2 shows no microcracks, a more detailed examination of the metallographic specimen revealed

TABLE I
Processing and Compositions of Mo-Si-B Alloys

Sample ID	Processing*	Nominal Composition, at.%	Oxygen, wppm	Carbon, wppm
MSB1	PM/HP	Mo-26.6 Si-7.2 B-0.8 C	7482	1729
MSB418 (center)	IM (Cu mold)	Mo-26.7 Si-7.3 B	486	206
MSB418 (surface)	IM (Cu mold)	"	222	1400
MSB425	IM (sand mold)	"	280	170

*PM = powder metallurgy; HP = hot pressing; IM = ingot metallurgy.

occasional microcracks. Numerous quasi-equilibrium pores are seen. These pores have either not been fully removed by the hot-pressing, or they have been stabilized by trapped CO/CO₂. Also, some grains may have fallen out during polishing. Analysis of the different phases was carried out following the procedure developed by Meyer et al. (2): the T2 phase (Mo₅SiB₂) was readily etched by Murakami's etch, and the three major phases, Mo₃Si, T1, and T2 were identified by their Mo:Si ratios. Powder x-ray diffraction showed almost exclusively these three phases. Occasionally Mo-rich particles containing no or only little Si were found by EDS (which did not detect B reliably). Since a small extra peak in the powder x-ray diffraction pattern was consistent with MoB₂, these particles may have been MoB₂. The fact that the three-phase Mo₃Si-T1-T2 equilibrium corresponding to the nominal composition has not been reached is consistent with recent results by Perepezko et al. (6). These authors found that annealing of Mo-7 Si-14 B (which is in the Mo-T2 two-phase field) for 150 h at 1873 K did not establish complete phase equilibrium. In particular, some Mo₃Si was still found. Since the hot-pressing in this work was carried out at 1873 K, it is not surprising that full equilibrium was not reached.

Ingot metallurgical processing

Alloys with the composition Mo-26.7 Si-7.3 B were drop-cast into molds made from materials with different thermal conductivities in order to examine the effect of the cooling rate on the microstructures that developed during solidification and cool-down. Casting into a 25 mm diam. Cu mold produced ingots which appeared to be uncracked as judged by visual examination of the outside. However, sectioning and polishing of these ingots always revealed macroscopic cracking. The microstructure of

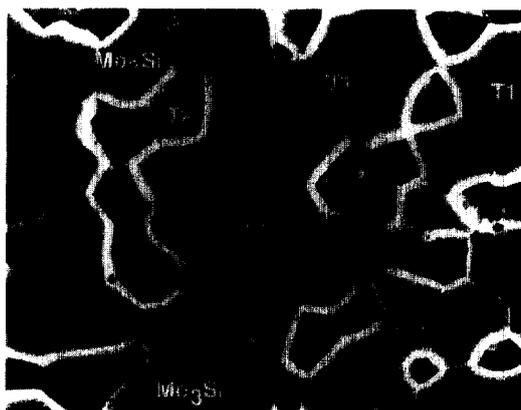


Figure 2. SEM micrograph of polished and etched alloy MSB1 (Mo-26.6 Si-7.2 B-0.8 C).

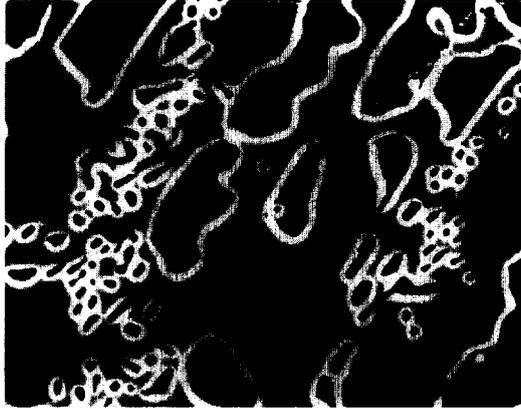


Figure 3. SEM micrograph of polished and etched section of Mo-26.7 Si-7.3 B cast into a 25 mm diam. Cu mold (MSB418) and annealed for 24 h at 1673 K in vacuum. A microcrack is indicated by an arrow.

a cast and annealed specimen is shown in Fig. 3. Voids such as those in the powder metallurgical material were not detected, but microcracks were occasionally observed (see arrow). As expected, the ingot metallurgical alloys contained much less oxygen than the powder metallurgical ones (see Table I). Since no carbon was intentionally added, the carbon contents were generally low (with the exception of one measurement near the surface of specimen MSB418).

Casting Mo-26.7 Si-7.3 B into a 25 mm diam. SiO₂ (sand) mold resulted in much lower cooling rates and reduced macroscopic cracking. An approximately 1 mm thick reaction zone was observed on the outside of the ingot. A typical microstructure of the interior of this ingot is illustrated in Fig. 4. As compared to Fig. 3, more microcracking is seen. Although a quantitative analysis has not been carried out, it appears that the lower cooling rate enhanced microcracking. Slow cooling results in larger grain/phase sizes than fast cooling. Since Mo₅Si₃ is likely to exhibit anisotropic thermal expansion (1), the large grain/phase size encountered during slow cooling is consistent with enhanced microcracking.



Figure 4. SEM micrograph of polished and etched section of Mo-26.7 Si-7.3 B cast into a 25 mm diam. sand mold (MSB425). Several microcracks are indicated by arrows.

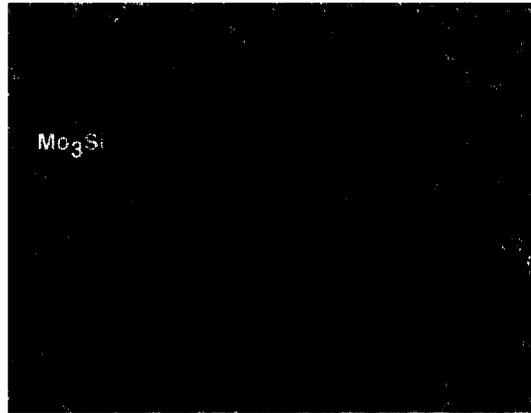


Figure 5. SEM micrograph of a polished and etched section of extruded Mo-Si-B (MSB418-E).

Isothermal forging

An attempt was made to isothermally forge a cylindrical section (25 mm in diameter, 20 mm high) of an alloy cast into a sand mold (MSB425). This experiment was carried out in a hot-pressing unit. An initial pressure of 35 MPa was applied. Consistent with the excellent high temperature strength of this material, no deformation occurred at temperatures up to 2073 K. At 2123 K, the specimen deformed to half its initial height in approximately 1 ks. Its external appearance after the forging suggested that the material was partially liquid during deformation. Microstructural analysis showed that additional voids and cracks had formed during the processing, probably as a result of the partial liquid formation.

Extrusion

A casting with the nominal composition Mo-26.7 Si-7.3 B (MSB418) was extruded in a Mo can at 2073 K. The area reduction was 4:1. The extruded material exhibited severe cracking and porosity and only small pieces were available for metallographic examination. Figure 5 shows an SEM micrograph of the extruded material. The microstructure consisted of large particles of Mo_3Si (dark phase) in a fine-scale multi-phase matrix. X-ray analysis revealed Mo and T2, in addition to Mo_3Si . The multiphase matrix found in-between the Mo_3Si particles is depicted at a higher magnification in Fig. 6. WDS showed its average matrix composition to be Mo-16 Si-4 B. According to the phase diagram, the fine-grained matrix consists therefore of Mo, Mo_3Si , and T2. Since the nominal composition of the extruded material corresponded to a 3-phase mixture of Mo_3Si , T1, and T2, it appears that the Mo content of the extruded material increased by a reaction with the Mo can. Since liquid phase formation was observed during isothermal forging of Mo-26.7 Si-7.3 B at 2123 K, and since the presence of the Mo extrusion can may have reduced the solidus temperature even further, liquid phase formation must have been a factor in the extrusion experiment. Nonetheless, the extremely fine-grained Mo- Mo_3Si -T2 microstructure is worth noting.

Mechanical properties

The room temperature tensile strength of the powder metallurgical alloy MSB1 was determined to be 186 MPa. Fracture occurred in a brittle manner without prior yielding. It was therefore decided to carry out several flexure tests in order to obtain statistical information. The results are represented in the

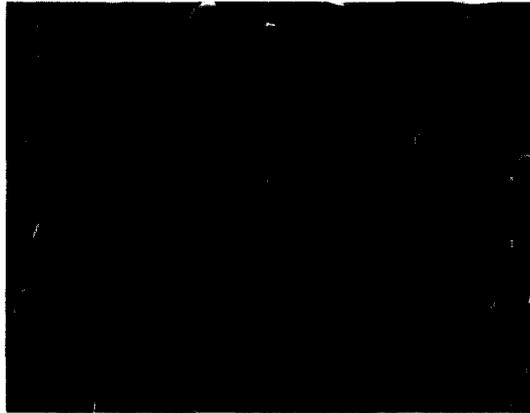


Figure 6. High magnification SEM micrograph of matrix region of polished and etched section of extruded Mo-Si-B (MSB418-E).

Weibull plot in Fig. 7. They indicate that flexure strengths of up to 300 MPa may be obtained. The value of the Weibull modulus (namely, 12) was relatively low and is consistent with the presence of numerous flaws in this material. Significantly better properties would be expected for optimized processing. Table II shows that the flexure strength at 1473 K was substantially higher than that at room temperature. The two specimens tested at 1473 K showed quite different strengths indicating again the flaw sensitivity of this material. Possible reasons for the high observed strengths (up to 604 MPa) may involve crack healing, borosilicate glass formation at crack tips, or incipient plasticity. The strengths of the powder metallurgical Mo-Si-B materials compare favorably to those published for MoSi_2 and $\text{MoSi}_2/\text{SiC}_w$ composites (see Table II).

The cast silicides contained many more microcracks than the powder metallurgical ones. They are thus expected to have lower room temperature strengths than the powder metallurgical ones. Table II shows this to be the case. Consistent with the formation of additional flaws, isothermal forging at 2123 K did not improve the room temperature strength. Analogous to the powder metallurgical material, the 1473 K flexure strength of the cast material is 2 to 3 times higher than that at room temperature (see Table II). Again, this points out the importance of optimizing the processing of these materials in order to achieve satisfactory room temperature mechanical properties. In the case of the ingot metallurgy

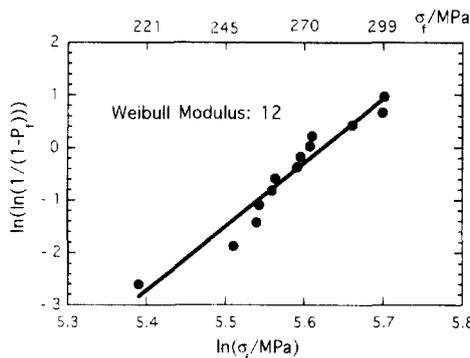


Figure 7. Weibull Plot of the 3-point flexure strength of MBS1 (Mo-26.6 Si-7.2 B-0.8 C). P_i is the fracture probability of σ_i , the maximum outer fiber stress.

TABLE II
Three-Point Flexure Strengths of Mo-Si-B Silicides, and Four-Point Flexure Strengths for Monolithic MoSi₂
and MoSi₂-SiC Composites

Specimen Number	Processing*	Specimen Condition	Test Temperature, K	Fracture Strength, MPa
MSB1	PM	as-pressed (13-specimens)	293	270(average)
"	PM	as-pressed	1473	460
"	PM	as-pressed	1473	604
MSB425	IM	as-cast	293	119
"	IM	as-cast	293	105
"	IM	as-cast	293	114
"	IM	isothermal forging at 2123 K	293	95
"	IM	isothermal forging at 2123 K	293	110
"	IM	as-cast	1473	221
"	IM	as-cast	1473	283
MoSi ₂ (Ref. 7)	PM	hot-pressed at ≈1900 K	293	150
MoSi ₂ (Ref. 8)	PM	hot-pressed	293	242
MoSi ₂ (Ref. 8)	PM	hot-pressed	1473	326
MoSi ₂ -20 vol% SiC _w (Ref. 7)	PM	hot-pressed at ≈1900 K	293	310

*PM: powder metallurgy; IM: ingot metallurgy.

materials, improved secondary processing will be required in order to minimize the size and number density of microcracks. Since partial liquid formation has been found at temperatures near 2073 to 2123 K, processing temperatures lower than those values will be required.

4. Conclusions

Molybdenum-silicon-boron intermetallics with compositions near Mo-26.7 Si-7.3 B were fabricated by several processing techniques. Each technique has its own advantages and limitations. The main conclusions for the different techniques are as follows:

1. Powder processing resulted in macrocrack-free material containing only occasional microcracks. Powder processed material exhibited a reasonably high strength at room temperature and excellent strength at 1473 K (up to ~600 MPa). However, significant porosity and high concentrations of oxygen were found. Improvements in powder handling and higher processing temperatures and/or pressures would be required to optimize the powder metallurgical fabrication.
2. Ingot metallurgy resulted in much lower oxygen concentrations than powder metallurgical processing. Depending on the cooling rate during solidification, either macrocracks or microcracks were prevalent. It may therefore be difficult, or even impossible, to produce sound as-cast material with this particular composition.
3. Isothermal forging needs to be carried out at temperatures below 2123 K in order to avoid liquid phase formation. However, very high stresses would be required to deform the material at these lower temperatures.
4. Extrusion in Mo cans needs to be carried out at room temperatures below 2073 K, since our results indicate liquid phase formation at 2073 K. An extremely fine microstructure has been found in the extruded material.

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