JOURNAL OF MATERIALS SCIENCE 30 (1995) 4027–4031

Effect of B_2O_3 on the microstructure and strength of $SiC/MoSi_2$ composite

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The effect of boron oxide (B_2O_3) on the microstructure and strength of 20% (by volume) silicon carbide (SiC) reinforced molybdenum disilicide ($MoSi_2$) composites was examined. Microstructural analysis using optical and electron microscopes was performed. A standard four-point bending test and Weibull statistics were applied to evaluate the flexural strength of the composites. The addition of boron oxide to composite was found to reduce the processing temperature and the grain sizes, result in formation of glassy boundary phase, and to increase the flexural strength of the composite.

1. Introduction

Although molybdenum disilicide ($MoSi_2$) exhibits excellent high temperature chemical stability and a melting point of near 2030 °C, its poor mechanical performance has severely limited its structural applications. As a result, efforts have been made to strengthen $MoSi_2$ by adding a second phase reinforcing material [1–10]. These $MoSi_2$-based composites were prepared by a hot pressing technique in which high temperature and high pressure are involved. It is therefore desired to decrease processing temperature and/or pressure without reducing the physical and mechanical properties of the resulting composites.

In a previous study, boron oxide (B_2O_3) was found to significantly reduce the sintering temperature of $MoSi_2$ [11]. In this study, we further investigated the use of B_2O_3 additive in SiC reinforced $MoSi_2$ composites. The effect of B_2O_3 on the microstructure and flexural strength of the resulting composites was examined. The benefit of using B_2O_3 was realized in that it resulted in a microstructure which led to a higher flexural strength.

2. Experimental procedure

$MoSi_2$ powders and SiC whiskers were used. As provided by the manufacturers the $MoSi_2$ powders have a purity of 99.9% and an average particle size of 1 μm. The SiC whiskers have an average diameter of 0.4 μm and an average length of 8 μm. The levels of impurities in both materials were not available.

Two $SiC/MoSi_2$ composites, both with 20% (by volume) SiC were prepared by hot pressing. One composite, designated as Composite T, was doped with 500 p.p.m. B_20_3 . The other composite, designated as Composite W, did not have B_2O_3. Desired amounts of $MoSi_2$ powders and SiC whiskers were measured and mixed thoroughly in an aqueous medium. The slurry was then dried overnight to remove all the liquid. After the removal of liquid, the Composite W mixture was hot pressed in 75-cm graphite discs by applying 27.6 MPa of pressure at 1750 °C in an argon atmosphere for 30 min. Composite T was hot pressed by applying 27.6 MPa of pressure at 1600 °C in an argon atmosphere for 45 min. Boron oxide was added to this composite during the mixing stage. As-pressed $SiC/MoSi_2$ specimens were then measured for densities by the Archimedes' method and prepared for microstructural analysis and bending test, at room temperature, for flexural strength. The microstructural analysis was performed using optical microscopy on chlorotrifluoromethane ($CClF_3$) plasma-etched specimens. Specimens were also examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The bending test was carried out using a four point bending technique described in MIL-STD-1942; the preparation of bending bars and the testing procedures can be found in this Standard. In the bending test, the cross-head speed was maintained at $0.51\ \mathrm{mm\,min^{-1}}$ ($0.02\ \mathrm{in\,min^{-1}}$) . For both Composites *W* and *T*, at least 30 bars of each composite type were tested [12]. The load and strain relationship was monitored and recorded by a computer. The maximum load (breaking load) of each bar was used to calculate the flexural strength according to the following equation:

$$S = \frac{3PL}{4bd^2} \tag{1}$$

where *S* is the flexural strength, *P* the breaking load, *L* the outer (support) span, *b* specimen width and *d* specimen thickness. The strength data were then analysed using Weibull statistics [13] as follows

$$\ln\left[\ln\left(\frac{1}{(1-p)}\right)\right] = \ln(S^m) + \text{constrant} \tag{2}$$

where *p* is the probability and *m* the Weibull modulus, which defines the width of data distribution.

3. Results

The average densities of Composites W and T were determined to be 5.54 g cm^{-3} (97.4% of the theoretical density) and 5.58 g cm^{-3} (98.1% of the theoretical density), respectively. The theoretical density of (20 vol % SiC + 80 vol % $MoSi_2$) composite is taken to be 5.69 g cm^{-3}. Microstructural analysis on both as-processed and etched specimens indicates little porosity. The distribution of SiC in $MoSi_2$ was found to be uniform in both Composites W and T as shown in Fig 1(a) and (b), respectively. The average grain size in Composite W is larger than that of Composite T as shown in Fig. 2. The grain sizes of Composite W range from 2 to 8 μm and the average was estimated to be approximately 5 ± 0.5 μm. The grain sizes of Composite T range from 2 to 7 μm and the average was estimated to be approximately 3 ± 0.4 μm. SEM analysis (Fig. 3) shows that agglomeration of SiC whiskers occurred in both composites, with that in Composite W being more severe.

Fig. 4 is a TEM bright field image of Composite W showing two grains at the grain boundary of $MoSi_2$. Micro-diffraction analysis and energy dispersion X-ray spectroscopy (EDX) indicate that the grain at the left is hexagonal SiC, while the one at right is amorphous SiC. The grain boundary of $MoSi_2$ appears to be very sharp and no other grain boundary phase was found. For Composite T an additional phase located at grain boundaries was found, as shown in Fig. 5. The bright spot in this figure shows no peak during elemental analysis by EDX and is amorphous as indicated by micro-diffraction analysis. It is believed that this amorphous particle contains boron. It also appears that the grain boundary is pinned or dragged by this particle.

To evaluate the mechanical properties of the resulting composites, 45 and 32 flexural specimens of Composites W and T, respectively, were tested. The average flexural strength of Composite W is 456.9 MPa and 689.3 MPa for Composite T. The data were analysed using Equations 1 and 2 and the result is plotted in Fig. 6. In both cases the strength data were widely scattered. It also appears that Composite T has higher strength and a narrower data distribution. Table I lists some statistics for both data groups. For comparison, the average flexural strength, 273.3 MPa, of $MoSi_2$ processed previously by the same fashion is also included [14]. The increase in flexural strength due to the addition of SiC is obvious.

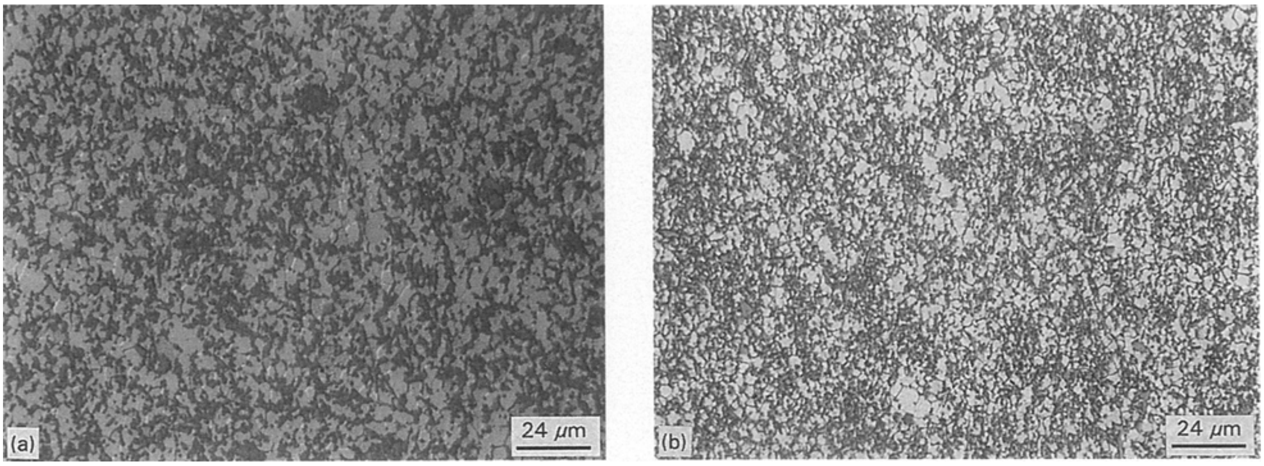

Figure 1 The distribution of SiC in $MoSi_2$ was found to be uniform in (a) Composite W and (b) Composite T.

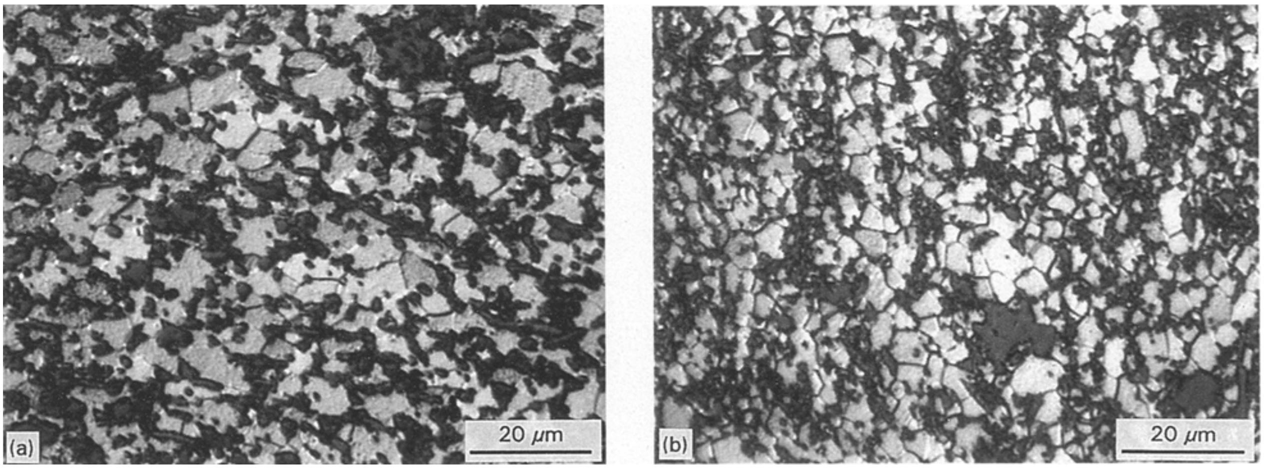

Figure 2 The average grain size in (a) Composite W (5 μm) is larger than that of (b) Composite T (3 μm).

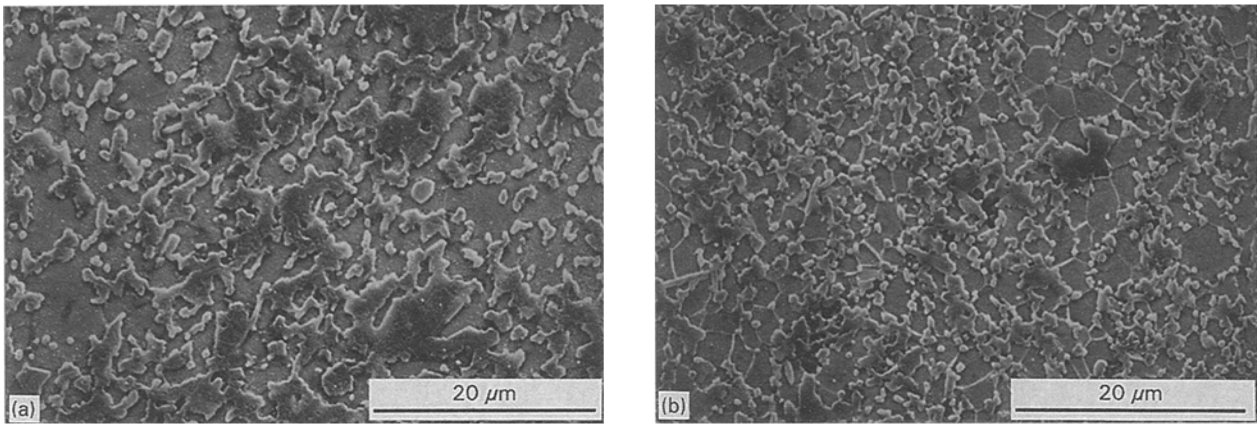

Figure 3 SEM analysis shows that more severe agglomeration of SiC whiskers occurred in (a) Composite W than in (b) Composite T.

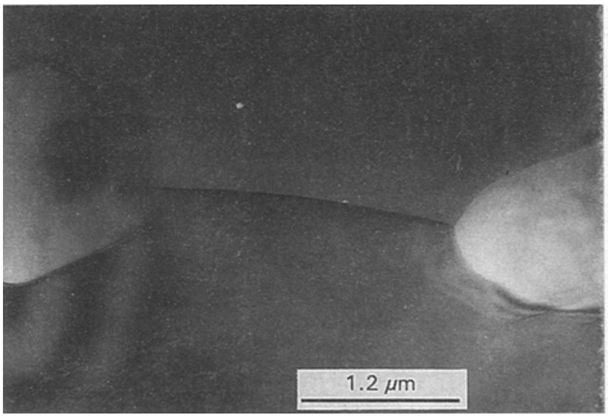

Figure 4 TEM bright field image showing two SiC grains located at a sharp grain boundary.

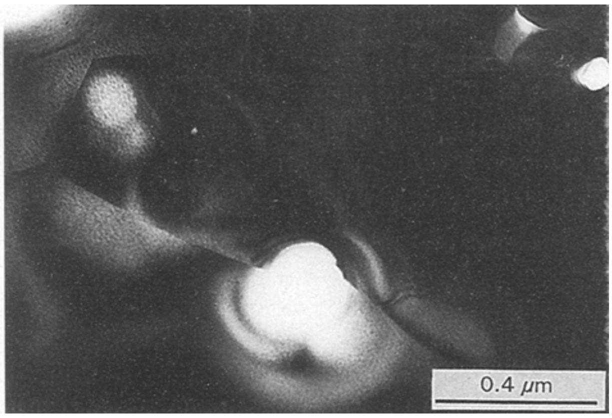

Figure 5 TEM bright field image showing an amorphous particle (the bright spot) located at the grain boundary of $MoSi_2$. It also appears that the grain boundary is pinned or dragged by this particle.

4. Discussion

The advantages of using an additive during a sintering process have been realized for decades. It is well known that by adding only 250 p.p.m. of MgO to Al_2O_3, not only the densification temperature is lowered but also a near theoretical density can be obtained [15]. Although the mechanism by which an additive influences sintering is still debatable, the fact is that it results in smaller grain sizes and uniform microstructure, and reduces sintering temperatures accordingly. For pressurized sintering, densification can occur by the mechanisms that take place during pressureless sintering [16]. In addition, it is noted that grain growth is insensitive to pressure. In the current study, pressurized sintering was used to prepare 20% SiC/$MoSi_2$ composites. In one process, no additive was added and the processing temperature was 1750 °C. In the other process, B_2O_3 was used as an additive and similar final density (5.58 $g\,cm^{-3}$ versus 5.54 $g\,cm^{-3}$) was achieved at 1600 °C, which is 150 °C lower. The composite with B_2O_3 additive also has a smaller average grain size (3 μm versus 5 μm). This may be due to either the use of B_2O_3 as an additive [15,17–22] or the lower processing temperature. However, the average grain sizes of $MoSi_2$ processed at 1600 °C and 1800 °C are 15.3 μm and 20.5 μm, respectively [23]. A decrease in the average grain size of 25% was observed when the temperature was reduced by 200 °C. In the current study, a decrease in the average grain size of 40% was observed as the temperature was reduced by 150 °C. It is therefore believed that in the current case, the temperature contribution on reducing the average grain size is minor. The average grain size was reduced primarily due to the use of B_2O_3. The mechanism of microstructural control due to the use of B_2O_3 is explained by the so-called second phase model [14, 15]. As seen from TEM analysis, second phase formation occurred at grain boundaries in Composite T. The exact composition of the second phase found is not known, but it is thought to be a form of borate glass [24]. The second phase model states that the formation of a second phase at the grain boundary occurs, due to the addition of additive, to pin the grain boundary and result in a smaller grain. The effect due to pinning mechanism on the sintering kinetics has been explained in terms of impurity-drag effect [25]. Due to the presence of a second phase, the grain boundary velocity, V_b is reduced to

$$V_b = \frac{FM_b}{(1 + K_1QC_0)} \tag{3}$$

where F is driving force, M_b the grain boundary mobility, K_1 a constant, Q the partition coefficient and

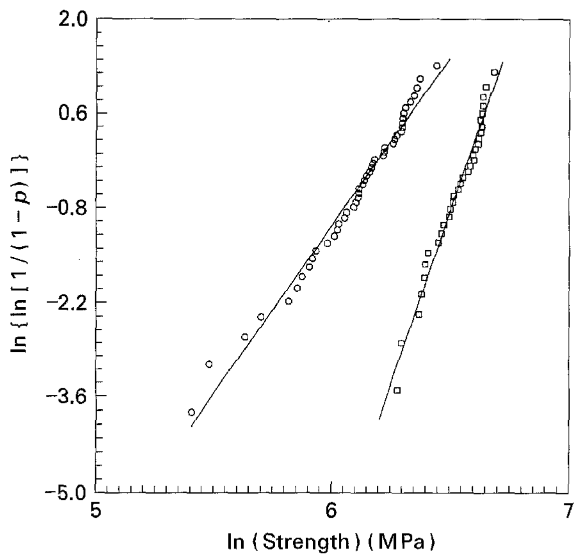

Figure 6 Weibull plots of flexural strength data of Composites W and T. ○ Composite W, Weibull modulus = 4.99; □ Composite T, Weibull modulus = 10.23.

TABLE I Statistics of strength data for SiC/$MoSi_2$ composites

Material	Flexural Strength (MPa)			Weibull modulus
	Minimum	Average	Maximum	
$MoSi_2$		273.7		
Composite W	222.3	456.9	629.7	5.0
% increased over $MoSi_2$		66.9		
Composite T	533.9	689.3	799.9	10.2
% iincreased over $MoSi_2$		151.8		
% increased over Composite W		50.9		

C_0 the bulk concentration of the second phase. When there is no second phase, C_0 is zero. In addition, the presence of SiC at grain boundaries is believed to have a similar effect on grain growth. When the average grain size of monolithic $MoSi_2$ is compared to that of composite, the former appears to have much larger average grain sizes, indicating grain growth is prohibited due to the addition of SiC.

The use of B_2O_3 also greatly increased the flexural strength of resulting composite. As shown in Table I, the average flexural strength of Composite T (689.3 MPa) is 50% higher than that of Composite W (456.9 MPa). The use of whiskers to reinforce a material is also realized. Several microstructural differences between Composites W and T were observed. The first one is the degree of agglomeration of SiC whiskers. The agglomeration of SiC in Composite W is more severe than that in Composite T. This is perhaps due to the fact that the boron oxide might reduce the attraction among SiC whiskers although there was only 500 p.p.m. of boron oxide added. This results in different shapes of the reinforcing SiC phase. As shown in Fig. 3, the SiC phase in Composite W has a lower aspect ratio than that in Composite T. Theoretical analysis has shown that the higher the aspect ratio of a reinforcing phase, the better is the strength of resulting composite [26]. The agglomeration also resulted in different sizes of SiC phase. It has been reported that compressive strength of SiC whiskers-reinforced ceramics was inversely related to whisker size [27]. The effect was due to whisker-crack interaction and whisker pull-out. Since both mechanisms are likely to occur in flexural tests [14], it is believed that smaller whisker sizes in Composite T led to the higher strength. The third microstructural difference is the spacing between the reinforcing phase. Due to the agglomeration, the spacing is smaller in Composite T. Similarly to the dislocation movement, this might result in a higher barrier to crack propagation and therefore result in higher strength. The fourth microstructural difference is the average grain size. The average grain sizes were estimated to be 5 ± 0.5 μm and 3 ± 0.4 μm for Composites W and T, respectively. In addition, the interaction of cracks and the glassy phase at grain boundaries can also contribute to the higher strength through crack deflection, crack bowing, or ductile phase toughening [26, 28–30]. As the strength test was conducted at room temperature, the glassy phase may not undergo yielding. Therefore, it is likely that either crack deflection or crack bowing mechanism was governed so that the stress intensity was reduced and therefore higher room temperature strength was observed. However, it is noted that the glassy phase may actually decrease the composite strength at elevated temperatures [31].

It was also found in this study that the flexural strength of both composites was scattered widely. The Weibull moduli of Composites W and T were 5.0 and 10.2, respectively. Both values indicate the brittle nature of SiC/$MoSi_2$ and suggest a need for a statistical approach to evaluate the strength data of the composite system. The change of Weibull modulus from 5.0 to 10.2 is not considered to be significant. For comparison, brittle alumina ceramic has a Weibull modulus of about 7 to 12 [32] and for steel it is 58 at room temperature [33].

5. Conclusions

1. B_2O_3 was found to be beneficial for the processing of SiC/$MoSi_2$ composite. It reduced the processing temperature and resulted in higher flexural strength.
2. Severe SiC agglomeration was found in Composite T which did not have added B_2O_3. This altered the morphology of SiC phase and the spacing between SiC phase such that the flexural strength of the resulting composite was degraded.
3. Composite doped with B_2O_3 exhibits smaller grain sizes and a glassy boundary phase. As compared to the composite without B_2O_3 doping, a higher flexural strength was obtained for this composite.
4. Both SiC/$MoSi_2$ composites studied were found to be brittle, which would require statistical analysis on the strength data. Weibull statistics were applied and the Weibull moduli of two data groups were determined to be 5.0 and 10.2.

Acknowledgements

The author would like to acknowledge the support for the study from Defense Advanced Research Projects Agency under Contract No. DAAH01-91-C-R156.

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Received 8 September 1994
and accepted 21 February 1995