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New approach to $MoSi_2$/SiC intermetallic-ceramic composite with B_4C

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The effects of SiC and B_4C additives in the $MoSi_2$ matrix on the microstructures and mechanical properties at room temperature were investigated. Their coefficients of thermal expansion (CTE) were also evaluated up to 1200°C by a thermal mechanical analysis (TMA). The experimental results show that the Mo_2B_5 reinforced phase was formed *in situ* in the hot-pressed $MoSi_2$/SiC/B_4C composites. Both the Mo_2B_5 phase and the SiC phase significantly improved the mechanical behavior of $MoSi_2$. Besides, the SiC with a high content up to 40 vol% could be added into the $MoSi_2$ composite with the B_4C additive. As a result, a dense and homogenous $MoSi_2$/SiC/B_4C composite was obtained, which possessed a relatively high bending strength and fracture toughness. Meanwhile, the CTE of the $MoSi_2$/SiC/B_4C composites linearly decreased with the increasing SiC content, which dropped to 21% at 1200°C in comparison with the pure $MoSi_2$ when adding 40 vol% SiC. This $MoSi_2$/SiC/B_4C composite system is very important for developing new applications at elevated temperature, particularly for high-temperature coating applications.

1. Introduction

$MoSi_2$ has been widely utilized as a high-temperature structural component and the high-temperature protective coatings in the aerospace field, heating elements in thermal treatment technology, and the conductors of integrated circuits in the microelectronic technology due to its high melting point (2030°C), excellent oxidation and corrosion resistance, high electrical conductivity, reasonable density (6.31 g/cm^3), and improvable mechanical properties. $MoSi_2$ has excellent high-temperature properties. It can be used at temperatures up to 1500°C for a long time, and up to 1700°C for a short time due to the formation of a protective silica film on the $MoSi_2$ surface at elevated temperature [1, 2]. $MoSi_2$ is easily shaped at high temperature due to its good ductile property, but it is difficult at room temperature because of its brittle property caused by an insufficient slip system of the polycrystalline $MoSi_2$ similar to most intermetallics [3]. Unfortunately, the mechanical properties of the pure $MoSi_2$ are not sufficient above room temperature. Hence, till now, many elements and compounds have been used to reinforce its mechanical properties and to improve the oxidation-resistance of $MoSi_2$, such as the single elements (Al, Ti, Ta, Ni, B, C), oxides (Sc_2O_3, Y_2O_3, Al_2O_3, ZrO_2, B_2O_3), nitrides (Si_3N_4), carbides (SiC, TiC), and borides (TiB_2) [4–13]. Among them, adding 20 vol% SiC into $MoSi_2$ is considered to be the most effective, which significantly strengthened the mechanical properties and creep resistance of $MoSi_2$ meanwhile, no cracks are observed at the $MoSi_2$/SiC interface [14].

Most studies on $MoSi_2$ are aimed at improving its structures and mechanical properties. In fact, it is very important to eliminate the thermal expansion mismatch between the $MoSi_2$ and the other structural ceramic components at elevated temperature because $MoSi_2$ has a much higher CTE than the general structural ceramics (such as the Si_3N_4). Besides, the $MoSi_2$ composite with a low CTE is very useful for the development of the $MoSi_2$ composite coating on the Mo and Nb alloys, and even on ceramic materials.

Based on above consideration, this research aims to decrease the CTE of the $MoSi_2$ composite by increasing the volume content of SiC as well as to improve the mechanical properties of the $MoSi_2$ composite. Boron and carbon are generally used in reinforcing the mechanical properties of $MoSi_2$ [8, 15], and B_4C is a normal additive in the sintering process of SiC ceramics. From this point of view, B_4C (2.51 g/cm^3) was chosen as another additive to promote the compatibility between the $MoSi_2$ and SiC for the purpose of fabricating the $MoSi_2$/SiC/B_4C composites with an excellent mechanical property and with a low CTE. To the best of our knowledge, this material system, the $MoSi_2$/SiC composite reinforced by B_4C, has not been reported so far.

2. Experimental

The $MoSi_2$ composites with 0.5, 1.0, 2.0, and 4.6 wt% B_4C and 20, and 40 vol% SiC were fabricated by hot-pressing (30 MPa) in an argon atmosphere (0.1 MPa). Their compositions and preparation conditions are listed in Table I. The raw materials were $MoSi_2$ powders of 2–5 μm (99%, New Metals, Japan), β-SiC powders of 0.29 μm (99%, Ibiden, Japan), and B_4C powders of 10 μm (99%, Kempten Electric Melting Plant, Germany). The powders were milled for 24 hours with SiC balls in methanol. After mixing, drying and sieving, they were hot-pressed into a bulk with a size of 40 × 40 × 5 mm at 1650°C–1750°C. The hot-pressing temperature was measured by monitoring the temperature of the graphite die using a two-color pyrometer. The surface of the graphite die that touched the sample was coated with boron nitride powder to prevent them from sticking together. The compressive stress exerted upon the sample was removed at the beginning of cooling in the hot-pressing in order to decrease the residual stress in the sample.

A phase analysis of the composites was performed by X-ray diffraction (XRD) (Model Dmax 3A, Rigaku, Japan) with a Cu target (40 kV, 20 mA) and graphite monochromator. An optical microscope and scanning electron microscopy (SEM) technique with energy-depressive X-ray analysis (EDAX) were used to observe the microstructures and analyze their chemical compositions. The density measurement was based on Archimedes' principle. The coefficients of thermal expansion were measured up to 1200°C using a thermal mechanical analysis (Model TMA 8140, Rigaku, Japan) with a thermal analysis station (Model TAS100, Rigaku, Japan). Samples for the three-point bending strength measurements were machined to dimension of 36 × 4 × 3 mm. The down span of the measurement was 30 mm and the speed of the crosshead was 0.5 mm/min. Samples for the four-point fracture toughness measurement were machined to 36 mm long, 3 mm wide and 4 mm thick with the notch length of about 1.5 mm and crack tip radii of 0.10 mm. The up span was 10 mm, the down one was 30 mm, and the speed of the crosshead was 0.1 mm/min. The Vickers hardness was measured by a Akashi microhardness tester (Model MVK-E, Akashi, Japan) under the load of 1.96 N. The surface of the samples was ground using an 800-mesh diamond-grinding wheel.

TABLE I Preparation of hot-pressed $MoSi_2$ composites

Sample no.	SiC content (vol%)	B_4C content (wt%)	Hot-pressing temp. (°C)
1	0	0	1650
2	0	4.6	1650
3	20	0	1750
4	20	1.0	1650
5	20	2.0	1650
6	20	4.6	1650
7	40	0.5	1700
8	40	1.0	1700
9	40	2.0	1700
10	40	4.6	1700

3. Results and discussion

Fig. 1 shows the XRD patterns of the pure $MoSi_2$ and $MoSi_2/SiC/B_4C$ composites with various compositions. The pure $MoSi_2$ (sample 1) possessed a single tetragonal phase. Both the $MoSi_2$ and SiC phases were observed in the $MoSi_2$/SiC composite because they are thermodynamically stable at elevated temperature in the phase diagram [16]. The XRD patterns show that the relative intensities of SiC peaks were enhanced by increasing SiC content for the same B_4C content. This was induced by the SiC itself. However, the SiC phase was observed after adding the 4.6 wt% B_4C into the $MoSi_2$ matrix without any addition of SiC (as shown in the curve of sample 2 in Fig. 1). The appearance of the SiC phase in the $MoSi_2/B_4C$ composite was probably caused by the following reaction:

$$8MoSi_2+5B_4C+11SiO_2 \rightarrow 4Mo_2B_5+5SiC+22SiO(g)$$

As already mentioned, the silica always exists in $MoSi_2$ at high temperature. It is very harmful for the creep resistance of the $MoSi_2$ due to its low melting point. This reaction led to a reduction of the silica in the $MoSi_2$. It was of benefit to improve the mechanical properties

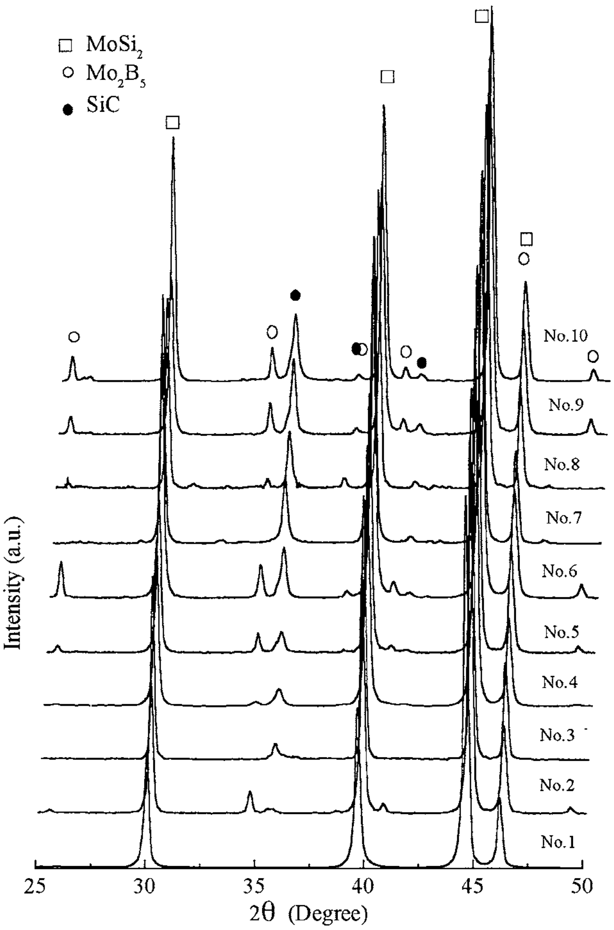

Figure 1 XRD patterns of pure $MoSi_2$ and $MoSi_2/SiC/B_4C$ composites (from sample 1 to 10).

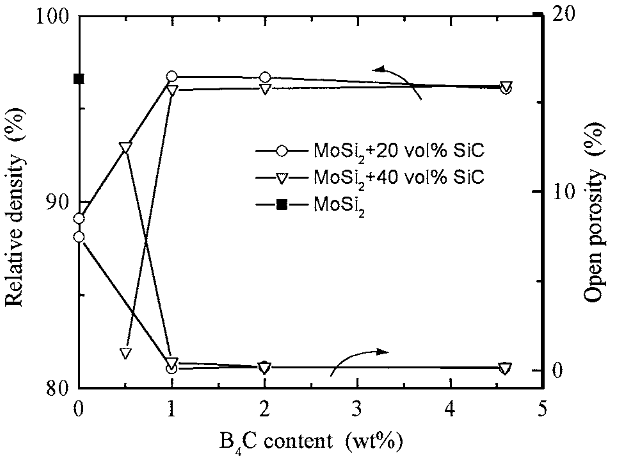

Figure 2 Densities of the $MoSi_2/SiC/B_4C$ composites.

of the $MoSi_2$. Simultaneously, it is worthy noting that the relative intensity of the SiC peaks in XRD patterns was also strengthened with increasing the B_4C content for same SiC content. This result further confirmed the existence of the above solid-state reaction in the $MoSi_2$-B_4C material system. On the other hand, it was of interest that a new Mo_2B_5 phase was found in the $MoSi_2$, $MoSi_2/SiC$ composites with B_4C except for $MoSi_2/SiC$ with 0.5 wt% B_4C (perhaps the amount was not enough to be observed by the XRD). The relative intensity of the Mo_2B_5 peaks increased with the increasing B_4C content. The effect of the Mo_2B_5 phase on the mechanical property and thermal expansion of the $MoSi_2$ composite will be discussed later.

From the experimental results, the relative density of the $MoSi_2/B_4C$ composite (4.6 wt% B_4C) increased up to 97.76% from the pure $MoSi_2$ of 96.60% after hot-pressed at 1650°C. The pure $MoSi_2/SiC$ composites (20 vol% SiC) exhibited a poor density of 89.12% even if the sintering temperature was raised up to 1750°C. By adding the proper B_4C content, the relative densities of the $MoSi_2/SiC$ composites were greatly increased as shown in Fig. 2. As a consequence, most $MoSi_2/SiC$ composites with B_4C additive were basically the same as the pure $MoSi_2$ in relative density. This indicates that the proper amount of B_4C could effectively improve the density of the $MoSi_2$ composites. Besides, for the $MoSi_2$ composites with the 20 vol% SiC additive, the relative density increased with the increasing B_4C content at the beginning, and then reached a maximum value, followed by a slow decrease. The relative density of the $MoSi_2$ composites with 40 vol% SiC remained unchanged with the increasing B_4C content after attaining the maximum value. The open porosity of the composites was contrary to the corresponding density as shown in Fig. 2. According to the above discussion, the perfect relative density could be obtained by adding above 1.0 wt% B_4C into the $MoSi_2$ composites along with SiC of 20 vol% and 40 vol%.

Fig. 3 shows the optical microscope photographs of the pure $MoSi_2$ and $MoSi_2/SiC/B_4C$ composites. They were observed after etching in the solution with a volume ratio of $HNO_3 : HF : H_2O = 2 : 1 : 5$ at room temperature. The pure $MoSi_2$ had a single phase with a small silica phase that appeared in the photograph in the form of small black dots as shown in Fig. 3a. The other samples consisted of several phases that were uniformly distributed in the composites. The existence of the second-enforcement phase, Mo_2B_5, was confirmed by the EDAX analysis. This Mo_2B_5 phase was formed *in situ* during the hot-pressing of the $MoSi_2$-B_4C composites at 1650–1700°C. It obviously blocked the growth of the $MoSi_2$ grains, so that the grain size of the $MoSi_2$ decreased with the increasing SiC and B_4C contents. The ultrafine microstructure was also found in the $MoSi_2$ composite with 40 vol% SiC and 4.6 wt% B_4C (Fig. 3h). Generally, the formation of silica will weaken the mechanical properties of the $MoSi_2$. However, the silica phase was not found in the $MoSi_2/SiC/B_4C$ composites based on the EDAX analysis. This indicates that the existence of the Mo_2B_5 phase hindered the formation of silica from the $MoSi_2$ matrix. Moreover, the appearance of the Mo_2B_5 phase would promote improvement of the mechanical properties of the $MoSi_2$ composites as reported by Watanabe and coworkers [17], who chose Mo_2B_5 as the reinforcement phase to improve the mechanical properties and oxidation-resistance of $MoSi_2$. The *in situ* formation of this reinforced phase also avoided the mismatch between the matrix and the additive phase, thus leading to improvement of the mechanical properties [7, 16, 18]. Therefore, the Mo_2B_5 reinforced phase played an important role in adjusting the properties of $MoSi_2$. Besides, a small SiC phase was observed by EDAX in the $MoSi_2/B_4C$ composite without the SiC additive, which was consistent with the XRD analysis detailed above. A little Si-B phase was also found in the composites. The formation of this glass-like phase favored to raise the creep ratio at elevated temperature.

The CTE curves of the various $MoSi_2$ composites are presented in Fig. 4. The CTE increased with the increasing temperature and the addition of SiC could effectively decrease the CTE. In comparison with the pure $MoSi_2$, the CTE of the composites dropped 21% at 1200°C. The lowest CTE could be achieved in the $MoSi_2$ composite with the co-addition of 40 vol% SiC and 4.6 wt% B_4C. Fig. 5 shows the CTE change of the $MoSi_2/SiC$ composites with 1.0 wt% B_4C at 1200°C, which was situated between the pure $MoSi_2$ and SiC, and linearly reduced with the increasing SiC content. However, the B_4C additive had only a slight influence on the CTE in these composites by comparison with the SiC additive. This implied that the change in the CTE mainly depended on the change in the SiC content.

Fig. 6 shows the mechanical properties of the $MoSi_2$ composites at room temperature. Obviously, the microhardness of the $MoSi_2$ composites was much higher than that of the pure $MoSi_2$ and in proportion to the contents of SiC and B_4C. As stated in the above discussion of the XRD analysis, the SiC and B_4C additives induced the SiC and Mo_2B_5 phases in the $MoSi_2$ matrix. The hardness of both SiC and Mo_2B_5 is much higher than $MoSi_2$. They are 19 GPa, 23 GPa and 9 GPa, respectively [7]. Accordingly, a high hardness can be achieved in the $MoSi_2$ composites with SiC and B_4C additives.

The bending strength and fracture toughness of the $MoSi_2$ composites were also investigated at room

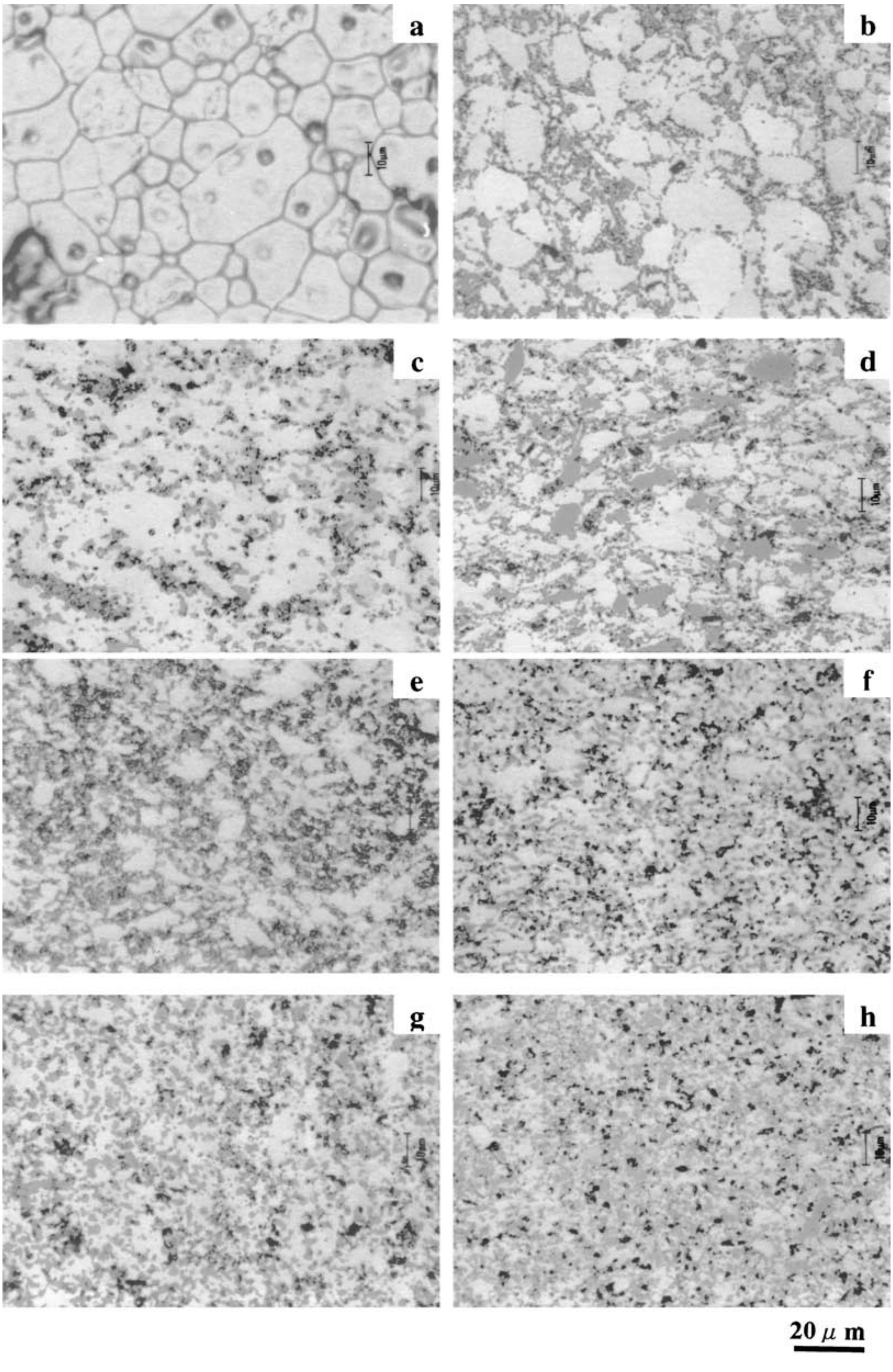

Figure 3 Optical microscope photos of pure $MoSi_2$ and $MoSi_2/SiC/B_4C$ composites: a(sample 1); b–d(sample4–6); and e–h(sample 7–10).

temperature. As a result, the bending strength and fracture toughness of the composites were significantly higher than the pure $MoSi_2$ (345.9 MPa, 4.27 $MPa \cdot m^{-1/2}$, respectively). Among them, the effect of the SiC additive on the mechanical properties was more significant than the B_4C additive. This is in agreement with the effect of the additive on the CTE discussed above. The maximum bending strength reached 710 Mpa for the $MoSi_2$ composite with 40 vol% SiC and 1.0 wt% B_4C. Correspondingly, the maximum fracture toughness appeared in the $MoSi_2$ composite with 40 vol% SiC and 4.6 wt% B_4C, which is about 7 $MPam^{1/2}$. This suggests that the SiC plays an important role in the improvement of the bending strength and the fracture toughness. It is also noted that the B_4C content should be carefully controlled since the *in situ*

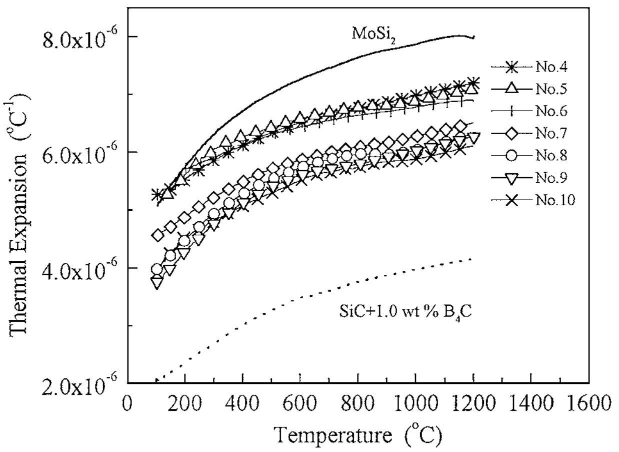

Figure 4 The CTE curves of various $MoSi_2$ composites.

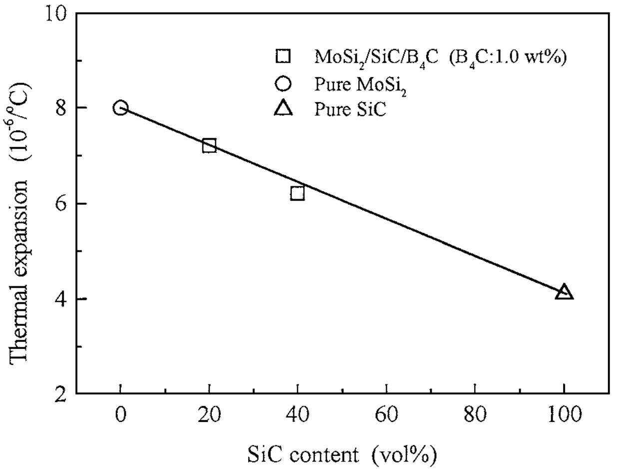

Figure 5 The CTE as a function of the SiC content at 1200°C.

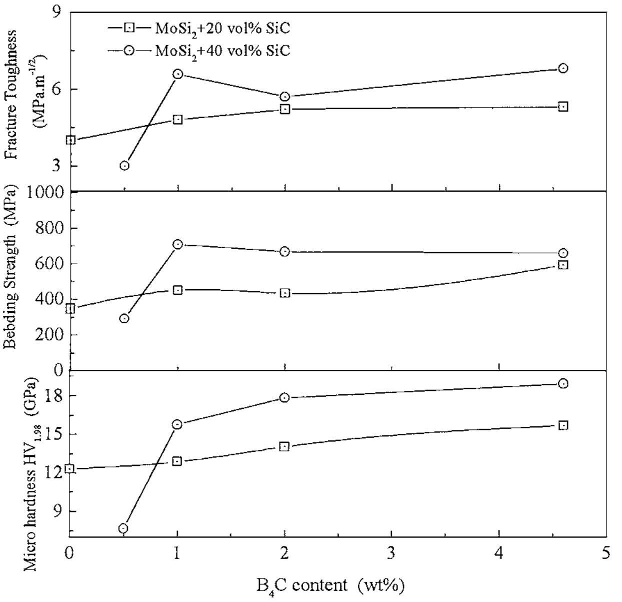

Figure 6 The mechanical properties of various $MoSi_2$ composites.

formation of Mo_2B_5 during the hot-pressing process of $MoSi_2$/SiC/B_4C favored the improvement in the mechanical properties of the composites at room temperature, but too much Mo_2B_5 would result in the poor oxidation-resistance at elevated temperature in an oxygen atmosphere [17]. In conclusion, the additive content in the range of 40 vol% SiC and about 1.0 wt% B_4C should be a promising composition for this material system.

4. Conclusions

The second-reinforcement Mo_2B_5 phase was successfully formed *in situ* during the hot-pressing process in the $MoSi_2$ composites with SiC and B_4C. As a result, a dense and homogenous $MoSi_2$ composite with 40 vol% SiC was obtained by adding about 1.0 wt% B_4C. The SiC additive significantly increased the mechanical properties and decreased the CTE of the $MoSi_2$ composite. The B_4C additive promoted the formation of the second-reinforcement Mo_2B_5 in the $MoSi_2$ composites, thus leading to an increase in the microhardness and reduction in the CTE. Typically, the microhardness, the bending strength and fracture toughness of the $MoSi_2$ composite with 40 vol% SiC and 1.0 wt% B_4C reached 16.5 Gpa, 710 Mpa and 6.3 MPam$^{1/2}$, respectively. The CTE of this composite dropped 21% in comparison with the pure $MoSi_2$ at 1200°C. This illustrates that this $MoSi_2$/SiC/B_4C system possesses excellent mechanical properties and a low CTE, and can be used as high temperature elements as well as high-temperature coating materials.

Acknowledgments

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References

1. A. K. VASUDEVAN and J. J. PETROVIC, *Mater. Sci. Eng. A* **155** (1992) 1.
2. X. FAN, T. ISHIGAKI, Y. SUETSUGU, J. TANATA and Y. SATO, *J. Amer. Ceram. Soc.* **81** (1998) 2517.
3. D. J. EVANS, *Phil. Mag.* **75** (1997) 1.
4. M. K. MEYER, A. J. THOM and M. AKINC, *Intermetallics* **7** (1999) 153.
5. K. YANAGIHARA, T. MARUYAMA and K. NAGATA, *ibid.* **3** (1995) 243.
6. J. J. PETROVIC, *Mater. Sci. Eng. A* **192/193** (1995) 31.
7. A. COSTA E SILVA and M. J. KAUFMAN, *Mater. Sci. Eng. A* **195** (1995) 75.
8. *Idem., Intermetallics* **5** (1997) 1.
9. J.-M. TING, *J. Amer. Ceram. Soc.* **77** (1994) 2751.
10. Y. SUZUKI, P. E. D. MORGAN and K. NIIHARA, *ibid.* **81** (1998) 3141.
11. J. SUBRAHMANYAM and R. MOHAN RAO, *J. Mater. Res.* **10** (1995) 1226.
12. H. KUNG, Y. C. LU, A. H. BARTLETT, R. G. CASTRO and J. J. PETROVIC, *ibid.* **13** (1998) 1522.
13. K. TANAKA, K. NAWATA, H. INUI, M. YAMAGUCHI and M. KOIWA, *Intermetallics* **6** (1998) 607.
14. Y. SUZUKI and K. NIIHARA, *ibid.* **6** (1998) 7.
15. K. NIIHARA and Y. SUZUKI, *Mater. Sci. Eng. A* **261** (1999) 6.
16. C. M. WARD-CLOSE, R. MINOR and P. J. DOORBAR, *Intermetallics* **4** (1996) 217.
17. T. WATANABE and K. SHOBU, *MRS Int. Mtg. On Adv. Mats.* **7** (1989) 303.
18. X. FAN, T. ISHIGAKI and Y. SATO, *J. Amer. Ceram. Soc.* **82** (1999) 281.

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