Microstructures and mechanical properties of TiN–TiB₂–Ti₅Si₃ composites in-situ fabricated by spark plasma sintering

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Various TiN–TiB₂–Ti₅Si₃ composites have been synthesized via spark plasma sintering of Ti, BN and Si₃N₄. The reaction process analysis indicates that Ti₅Si₃ forms earlier than TiB₂. The reaction heat as well as the Joule heat may prompt the melting of Ti₅Si₃, making it infiltrate into TiN and TiB₂. Thus, the composites can be further densified with the in-situ addition of Ti₅Si₃. For TiN–TiB₂–Ti₅Si₃ composites, the maximum fracture toughness was $4.5 \pm 0.3 \text{ MPa}\cdot\text{m}^{1/2}$, and maximum flexural strength was $601.1 \pm 28.5 \text{ MPa}$, which were both quite higher than those of TiN–TiB₂ composites. The related toughening and strengthening mechanisms were proposed from microstructural analysis.

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Key-words : TiN–TiB₂–Ti₅Si₃, Ceramic-matrix composites (CMCs), Intermetallics, Mechanical properties, Spark plasma sintering

[Received January 19, 2009; Accepted August 20, 2009]

1. Introduction

High-temperature structural ceramics such as TiN, TiC and TiB₂ have high melting points, high Vickers hardness, and good electrical conductivity.^(1–5) Their monolithic materials as well as composites such as TiN–TiB₂ and Ti(C,N)–TiB₂ can be widely used as crucibles, wear resistant parts, cutting tools, or electrodes.^(4–6) However, the strong covalent nature in these ceramics made the consolidation difficult and fracture toughness too low to be suitable for industrial application. In order to solve the puzzle, metallic additives were incorporated into the ceramic matrix because metallic additives allow the liquid-phase sintering of ceramic materials (avoiding the expensive high-pressure and temperature sintering techniques).^(7–10) But as binders for consolidating ceramics, metallic additives such as iron, aluminum, cobalt and nickel have fundamental shortcomings of poor corrosion resistance, high cost, environmental toxicity, etc.

Recently, intermetallics such as NbAl₃, TiAl₃, Fe₄₀Al, and so on have been proposed as alternative binders.^(11–15) As a potential high temperature intermetallic structural material, Ti₅Si₃ possesses the advantages of high melting point (2130°C), low density (4.32 g/cm³) and excellent oxidation resistance at high temperature.^(16–19) It has been proved that the addition of Ti₅Si₃ can greatly improve the oxidation resistance of TiN-based composite coatings.⁽¹⁷⁾ However, fabrication and characterization of bulk ceramic-based composites containing Ti₅Si₃ as a sintering binder can hardly be reviewed yet.

In this paper, novel bulk dense TiN–TiB₂–Ti₅Si₃ composites were reaction synthesized from commercially available Ti, BN and Si₃N₄ by spark plasma sintering. Microstructural tailoring by changing phase compositions of the composites was attempted to get better mechanical properties. Reaction process and microstructural analysis were explored to declare related densification, toughening, and strengthening mechanisms.

2. Experimental procedure

Bulk TiN–TiB₂–Ti₅Si₃ composites were fabricated from the raw powder mixtures of Ti, BN and Si₃N₄, the characteristics of which are shown in **Table 1**. Six groups of powder mixtures were prepared according to formula (1) ($x = 0, \frac{1}{30}, \frac{1}{15}, \frac{1}{10}, \frac{1}{5}, \frac{1}{2}$), which are labeled as No.1, 2, 3, 4, 5 and 6, respectively. After being mixed and dried, the mixtures were sintered by a SPS apparatus (SPS-2040, Sumitomo Coal Mining Co.) in vacuum (less than 6 Pa). The employed heating rate was 100–200°C/min, the applied pressure was 60 MPa, and the holding time was about 5 min at the sintering temperature of 1400°C before turning off the power. A typical densification behavior of the sintered composites is shown in **Fig. 1**.

The as-sintered samples were ground and polished. Archimedes' method was adopted to identify the degree of densification. After being polished, the microstructure analyses of the samples were conducted by X-ray diffraction (XRD, D/MAX-2550V, Rigaku Co.), field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL Ltd.), and Transmission electron microscopy (TEM, JEM2010). Some samples were machined and polished to 2 mm × 3 mm × 18 mm bars for mea-

Table 1. Characteristics of Raw Powders Used in this Paper

Raw materials	Purity (%)	Grain size of the powders by (μm)				
		10%	50%	90%	97%	D ₅₀
Ti	99.4	3.34	9.75	18.74	26.7	12.49
BN	99	0.30	1.28	6.41	8.98	2.57
Si ₃ N ₄	99	0.29	1.23	4.17	6.08	1.95

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suring the three-point bending strength with a span of 12 mm. Vickers hardness (H_v) of the polished samples were measured by indentation technique (Wilson-wolpert Tukon[®] 2100B). The fracture toughness K_{IC} of composites was calculated using the following formula:

$$K_{IC} = P(\pi C)^{-3/2} \cot \beta \quad (2)$$

Where $2c$ was the length of crack, Load $P = 98\text{N}$ and $\beta = 68^\circ$.

Six measurement runs were carried out to determine the average value of flexural strength, Vickers hardness and fracture toughness.

3. Results and discussion

Figure 2 shows the XRD patterns of the as-sintered composites by spark plasma sintering at 1400°C for a holding time of 5 min. It is found that the composites are composed of TiN, TiB₂, and Ti₅Si₃ phases. No other phases can be detected. Therefore, it is believed that reaction (1) was accomplished in the spark plasma sintering process, that is to say, Ti, BN and Si₃N₄ were fully reacted to the target composites. Hence, the theoretical densities of the composites were calculated following a rule of mixture from the theoretical ones of TiN, TiB₂, and Ti₅Si₃. Finally, the relative densities of the composites were obtained by division of measured densities to the theoretical ones.

In **Table 2**, the relative densities and mechanical properties of the composites vs theoretical volume contents are presented. It is clear that with the increase of Ti₅Si₃ contents, relative densities of the TiN–TiB₂–Ti₅Si₃ composites increase accordingly. For the No.1 sample without Ti₅Si₃ phases, the relative density is only 96.1%, but that of No.6 sample reaches nearly fully dense of

99.2% with a Ti₅Si₃ content of 37.8%. In order to explain why the addition of Ti₅Si₃ can increase the relative densities of the TiN–TiB₂–Ti₅Si₃ composites, the reaction process as well as the microstructure of the No.5 sample is studied in detail as follows.

The XRD patterns of the No.5 sample sintered at different temperatures are shown in **Fig. 3**. From this figure, it can be found that the peaks of Ti₅Si₃ appear at 1000°C , but the peaks of TiB₂ appear later at 1200°C . This indicates that Ti₅Si₃ forms earlier than TiB₂ in fabrication process. It is because that formula (1) can be divided into formula (3) and formula (4), and the formation Gibbs energy of formula (3) is more negative than that of formula (4).^{20,21)}

As Ti₅Si₃ has a lower melting point than that of TiN and TiB₂, it could melt locally by the heat from the strong exothermic reaction and the Joule heat generated from the current passing through the sample (because TiN, TiB₂ and Ti₅Si₃ are all electrically conductive) as well as the graphite die.^{22,23)} Then, it would infiltrate rather well between the TiN and TiB₂ crystallites, as claimed in literature.²²⁾ The TEM images of the No.5 samples in **Fig. 4** further confirm our conjecture. Figure 4 shows the distribution of TiN, TiB₂, and Ti₅Si₃ phases, and the corresponding electron diffraction patterns. It is clear that TiN(1) and TiB₂(1) grains are separated by Ti₅Si₃(1), Ti₅Si₃(2), and Ti₅Si₃(3). At the same time, TiN(1) was also surrounded by Ti₅Si₃ grains. Thus Ti₅Si₃ can act as a binding phase for the densification of TiN–TiB₂.

Fig. 1. Typical densification behavior in the spark plasma sintering process.

Fig. 2. X-ray diffraction patterns of the as-sintered TiN–TiB₂–Ti₅Si₃ composites at 1400°C for a holding time of 5 min.

Table 2. Theoretical Volume Contents vs Relative Densities and Mechanical Properties of the TiN–TiB₂–Ti₅Si₃ Composites by Spark Plasma Sintering

No.	x	Calculated contents (vol%)			Relative density (%)	Hardness (GPa)	Fracture toughness (MPa·m ^{1/2})	Flexural strength (MPa)
		TiN	TiB ₂	Ti ₅ Si ₃				
1	0	59.7	40.3	0.0	96.1	16.8 ± 0.8	3.0 ± 0.2	488.7 ± 41.9
2	1/30	57.7	36.5	5.9	96.6	16.5 ± 0.3	3.1 ± 0.2	601.1 ± 28.5
3	1/15	56.0	33.3	10.7	97.1	16.0 ± 0.4	3.5 ± 0.3	531.8 ± 53.8
4	1/10	54.5	30.7	14.8	97.9	14.3 ± 0.7	3.5 ± 0.2	522.6 ± 38.9
5	1/5	51.4	24.8	23.9	98.9	14.3 ± 0.4	4.5 ± 0.3	451.2 ± 46.7
6	1/2	46.5	15.7	37.8	99.2	14.2 ± 0.6	3.3 ± 0.2	387.2 ± 44.1

Fig. 3. X-ray diffraction patterns of the as-sintered No.5 sample at different temperatures for a holding time of 5 min.

Fig. 5. SEM image of crack propagation in the No.5 sample sintered at 1400°C for a holding time of 5 min.

Fig. 4. (a) TEM image of the as-sintered No.5 sample at 1400°C for a holding time of 5 min and the corresponding electron diffraction patterns of (b) TiN, (c) TiB₂, (d) Ti₅Si₃.

It is known that the Vickers hardness of TiN and TiB₂ is 20 and 33 GPa, but the Vickers hardness of Ti₅Si₃ is only about 9.5 GPa.^{2),3),24)} Therefore, it is obvious that addition of Ti₅Si₃ would decrease the hardness of the composites, as is shown in Table 2. But the fracture toughness does not follow the same trend, although the fracture toughness of Ti₅Si₃ is just as low as 2.5 MPa·m^{1/2}.^{18),19)} It is known that the toughness of a material is determined by not only its composition, but also the ability of its microstructure to dissipate deformation energy without propagation of the cracks.²⁵⁾ In ceramics, well-known toughening mechanisms are based on crack ligament bridging and crack deflection. Interestingly, crack deflection and crack bridging are identified in Fig. 5, which can explain the highest fracture toughness value of sample 5 among the No.1–6 samples.

Similarly, the flexural strength of the composites does not simply decrease or increase with the change of Ti₅Si₃ contents. The No.2 sample has the highest flexural strength of 601 MPa among the No.1–6 samples. This can also be explained from the microstructural analysis. Figure 6 shows the SEM images of the fracture surfaces of the No.1–6 samples. It is clear that samples of

Fig. 6. SEM images of fracture surfaces of the No.1–6 samples.

No.2 and 3 have the finer microstructures among all 6 samples. According to the hall-patch formula, this kind of fine microstructure would be much helpful for the improvement of the strength of the solid composites.²⁶⁾ The thermal expansion mismatch may also be one reason for the highest strength of the No.2 sample.^{16),26),27)} Therefore, in order to obtain better mechanical properties, further microstructural tailoring is necessary and is underway through careful controlling of the different processing parameters (e.g. phase compositions, sintering temperature and holding time).^{1),11),26)}

4. Conclusions

TiN–TiB₂–Ti₅Si₃ composites were in-situ fabricated by spark plasma sintering of Ti, BN and Si₃N₄ mixtures. It was found that with increasing Ti₅Si₃ contents, the relative densities of the TiN–TiB₂–Ti₅Si₃ composites increased correspondingly. The contents of Ti₅Si₃ had also important effects on the mechanical properties

of the composites. The fracture toughness and flexural strength increased with increasing Ti₅Si₃ content up to 23.9 and 5.9 vol%, respectively, and then decreased. For TiN–TiB₂–Ti₅Si₃ composites, the maximum fracture toughness was $4.5 \pm 0.3 \text{ MPa}\cdot\text{m}^{1/2}$, and maximum flexural strength was $601.1 \pm 28.5 \text{ MPa}$, which were both quite higher than those of TiN–TiB₂ composites.

Acknowledgements This work was supported by Natural Sciences Foundation of China (No. 50625414, 50821004), Program of Shanghai Subject Chief Scientist (No. 08XD14046), and Shanghai Nano Science and Technology Special Project (0852nm03300).

References

- 1) D. L. Jiang, "Fine Ceramic Materials," 1st ed., China Logistics Publishing House, Beijing (2000).
- 2) H. R. Baumgartner and R. A. Steiger, *J. Am. Ceram. Soc.*, 67[3], 207–212 (1984).
- 3) T. Yamada, M. Shimada and M. Koizumi, *J. Am. Ceram. Soc. Bull.*, 59[6], 611–616 (1980).
- 4) K. Shobu and T. Watanabe, *J. Powder. Metall. Soc. Jpn.*, 32[6], 215–218 (1985).
- 5) K. Shobu, T. Watanabe, Y. Enomoto, K. Umeda and K. Tsuya, *J. Am. Ceram. Soc.*, 70[5], C-103–C-104 (1987).
- 6) G. J. Zhang, *Ceram. Int.*, 21[1], 29–31 (1995).
- 7) G. J. Zhang, Z. Z. Jin and X. M. Yue, *J. Am. Ceram. Soc.*, 78[1], 2831–2833 (1995).
- 8) Z. H. Zhang, X. D. He, J. C. Han, W. Qu and V. L. Kvalin, *Mater. Lett.*, 56[3], 183–187 (2002).
- 9) W. F. Zhang, X. H. Zhang, J. L. Wang and C. Q. Hong, *Mater. Sci. Eng.*, A381[1–2], 92–97 (2004).
- 10) Y. Li, N. Liu, X. B. Zhang and C. L. Rong, *Int. J. Refract. Met. H.*, 26[3], 190–196 (2008).
- 11) S. Schiker, D. E. Garcia, J. Bruhn, R. Janssen and N. Claussen, *Acta. Mater.*, 46[7], 2485–2492 (1998).
- 12) S. K. Bhaumik, C. Divakar, L. Rangaraj and A. K. Singh, *Mater. Sci. Eng.*, A257[2], 341–348 (1998).
- 13) R. Subramanian, J. H. Schneibel, K. B. Alexander and K. P. Plucknett, *Scripta. Mater.*, 35[5], 583–588 (1996).
- 14) M. X. Gao, Y. Pan, F. J. Oliveira, L. Yang, J. L. Baptista and J. M. Vieira, *Mater. Sci. Eng.*, A371[1–2], 277–282 (2004).
- 15) M. Alvarez and J. M. Sánchez, *Int. J. Refract. Met. H.*, 25[1], 107–118 (2007).
- 16) R. Rosenkranz, G. Frommeyer and W. Smarsly, *Mater. Sci. Eng.*, A152[1–2], 288–294 (1992).
- 17) G. Llauro, F. Gourbilleau, F. Sibieude and R. Hillel, *Thin. Solid. Film.*, 315[1–2], 336–344 (1998).
- 18) K. S. Min, A. J. Aredell, S. J. Eck and F. C. Chen, *J. Mater. Sci.*, 30[21], 5479–5483 (1995).
- 19) L. J. Wang, W. Jiang, C. Qin and L. D. Chen, *Mater. Sci. Eng.*, A425[1–2], 219–224 (2006).
- 20) J. S. Byun, J. H. Shim and Y. W. Cho, *Scripta. Mater.*, 50[2], 279–283 (2004).
- 21) J. H. Shim, J. S. Byun and Y. W. Cho, *Scripta. Mater.*, 47[7], 493–497 (2002).
- 22) J. W. Kim, H. S. Chung, S. H. Lee, K. H. Oh, J. H. Shim and Y. W. Cho, *Intermetallics.*, 15[2], 206–210 (2007).
- 23) M. Omori, *Mater. Sci. Eng.*, A287[2], 183–188 (2000).
- 24) D. M. Shah and D. Berczik, *Mater. Sci. Eng.*, A155[1–2], 45–47 (1992).
- 25) J. H. Gong, "Fracture Mechanics of Ceramics," 1st ed., Tsinghua University Press, Beijing (2001).
- 26) Z. H. Jin, J. Q. Gao, G. J. Qiao, "Engineering Ceramic materials," 1st ed., Xi'an Jiaotong University Publishing House, Xi'an (2000).
- 27) M. L. Gu, C. Z. Huang, S. R. Xiao and H. L. Liu, *Mater. Sci. Eng.*, A486[1–2], 167–170 (2008).