JMEPEG (2008) 17:838–841
DOI: 10.1007/s11665-007-9182-4

1059-9495/$19.00

Pressureless Sintering of TiB_2-B_4C Ceramic Matrix Composite

H.R. Baharvandi and A.M. Hadian

(Submitted February 4, 2007; in revised form November 10, 2007)

The effect of TiB_2 addition on sinterability and mechanical properties of B_4C material was investigated. It was found that addition of TiB_2 aids the sintering process and permits pressureless sintering at temperatures between 2050 and 2150 °C. This also alleviates grain growth during sintering. The relative density reaches 98.5% of the theoretical density by increasing the percentage of TiB_2 in the composition. The mechanical properties such as hardness, fracture toughness, and bending strength were improved remarkably by addition of TiB_2.

Keywords boron carbide, ceramic, composite

1. Introduction

Boron carbide is characterized by a very high hardness (Vickers hardness 40-60 GPa) and a very low density (2.52 g/cm^3), desirable for many industrial applications (Ref 1-22). However, the use of monolitic boron carbide is limited by its low strength, low toughness, poor sinterability and machinability. Since B_4C is very difficult to sinter with higher approximately 80% of the theoretical density, a variety of second phases have been added as sintering aids (Ref 1-20). Nonoxide ceramics such as SiC (Ref 1-3), TiC (Ref 4) and C (Ref 5-7) have also been found to be very affective as sintering additives for B_4C. Metallic sintering aides such as Al (Ref 8), Si (Ref 18), Ti (Ref 19), Mg and Fe are frequently added to provide a medium for liquid phase sintering. Metallic phases at the grain boundaries generally deteriorate the unique properties of hard ceramics. However, in these cases, either a large amount of a second phase or very high sintering temperatures are required for full densifications (Ref 1-18). Oxides are scarcely used as sintering aids for B_4C, mainly because of the chemical instability of B_4C with respect to many oxides (Ref 21, 22). In other words, B_4C reacts with other oxides during sintering to form new compounds that might determine the unique properties of B_4C. However, recently, Kim observed that the addition of small amounts of Al_2O_3 increases the sinterability of B_4C remarkably (Ref 1, 22).

Research has been done to study the effect of additional TiB_2 on the properties of B_4C. Shorokhod studied the formation of TiB_2-B_4C composite via in situ reaction of B_4C-C-TiO_2 (Ref 23). Other researchers have measured mechanical properties of the same composite material prepared by hot-pressing or spark plasma sintering methods (Ref 24-30). All the previous researches emphasize the effectiveness of TiB_2 on mechanical properties of B_4C material.

All these techniques either require expensive processing equipments or as for the in situ method need complicated processing route (Ref 23-30). In the present study, the effect of TiB_2 addition on the pressureless sintering and densification behavior of B_4C has been investigated. Mechanical properties, such as hardness and fracture toughness of B_4C, have been measured and correlated with the variation in density and composition of the body.

2. Experimental Procedure

High-purity B_4C (B:C ratio of 3.8-3.9) and high-purity TiB_2 powders were used as starting materials. The average size and the specific surface area of B_4C powder were measured to be 1.33 μm and 6.64 m^2/g, respectively. Up to 30 wt.% of TiB_2 was added as the sintering aid. The powders were ball-milled in isopropyl alcohol for 8 h using high-purity Al_2O_3 balls. The mixture was then dried in a rotary vacuum evaporator, and passed through a 60-mesh screen. The powder mixtures were cold-pressed under 80 MPa into samples having $30\times3\times60$ mm^3 dimensions. The green samples were then sintered using a microprocessor controlled graphite element vacuum furnace. The heating and cooling rates were 10 °C/min and furnace cooling, respectively.

For microstructural examinations, dense sintered bodies were surface ground and polished with diamond paste down to 1 μm surface finish. The polished surfaces were then electrically etched in a 0.1% KOH solution with a current density of 0.1 A/cm^2 for 10-20 s. Microstructures of the specimens were observed using a scanning electron microscope and the phases were characterized by X-ray diffraction (XRD) method. The density was measured by Archimedes method. An approximate theoretical density was calculated for the various compositions of B_4C-TiB_2 system (Ref 12).

For mechanical testing, samples were cut to dimensions of $3\times4\times45$ mm^3 and ground with an 800-grit diamond-grinding wheel. The tensile side of the specimens was polished with

H.R. Baharvandi, Department of Metallurgy and Materials, Faculty of Engineering, University of Tehran, Tehran, Iran; and **A.M. Hadian**, University of Malek Ashtar, Tehran, Iran. Contact e-mail: baharvandee@yahoo.com.

diamond paste down to 1 μm finish. The edges of the tensile side of the specimens were rounded with a radius of 0.15 ± 0.05 mm. To measure the hardness, a Vickers indenter was used with a load of 1.96 N. The flexural strength was measured by four-point flexural test method using a universal testing machine with a crosshead speed of 0.5 mm/min. The inner and outer spans of the jig were 20 and 40 mm, respectively. The fracture toughness of the specimens was determined by the indentation strength method. After indenting the polished surface at 98 N with a Vickers indenter for 15 s, the fracture strength was measured with the four-point flexural configuration (Ref 13). For each set of mechanical tests at least five samples were tested.

3. Results and Discussion

Figures 1 and 2 show SEM images indicating the influence of TiB_2 on densification of boron carbide. From the figures, it can be seen that by increasing the sintering temperature from 2050 to 2150 °C, the amount of porosity has decreased remarkably with an increase in grain size. The white phase is TiB_2 and the dark phase is B_4C. The figures also indicate that addition of TiB_2 has resulted in reduction of porosity in both samples. Compared to Fig. 2(a), less porosity is observed in the samples sintered at 2150 °C [Fig. 2(b)]. It is also apparent that the grain size in these samples is smaller than that of the additive-free samples. In order to quantify the size of the grains, the polished surfaces of some B_4C and B_4C-TiB_2 samples were thermally etched and the grain sizes were measured (Table 1).

This indicates that TiB_2 has acted as a grain growth inhibitor in this case. The same effect has been reported for graphite and carbon black by other researchers (Ref 5-7). The better sinterability will result in increasing density. Figure 3 shows the variation of relative density as a function of TiB_2 addition. The figure indicates that by increasing the amount of TiB_2 the relative density increases. It is also apparent that this value is higher for the samples sintered at 2150 °C. A density value of 98.5% of the theoretical density was obtained for the samples having 30% TiB_2 and sintered at 2150 °C, whereas the density of the samples sintered at 2050 °C was about 96.5 of TD.

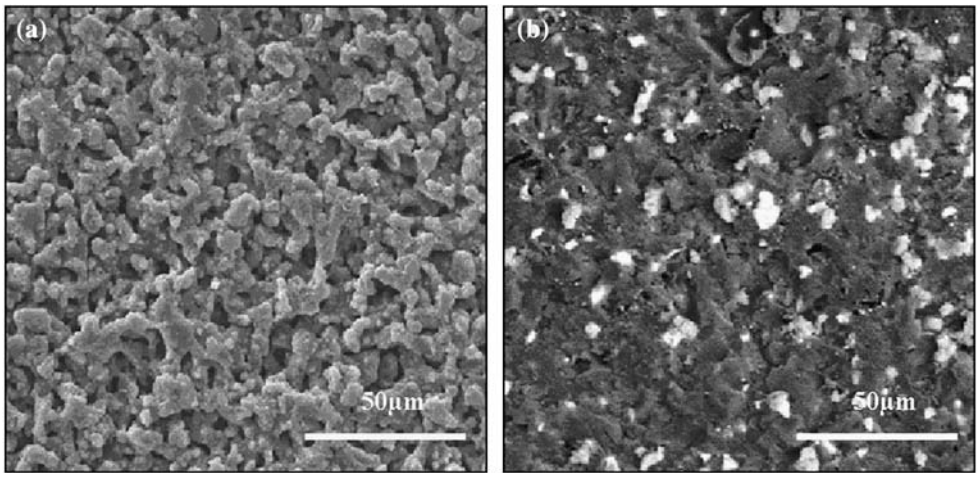

Fig. 1 SEM micrographs of samples sintered at 2050 °C for 1 h. (a) B_4C-free TiB_2 and (b) B_4C-30% TiB_2

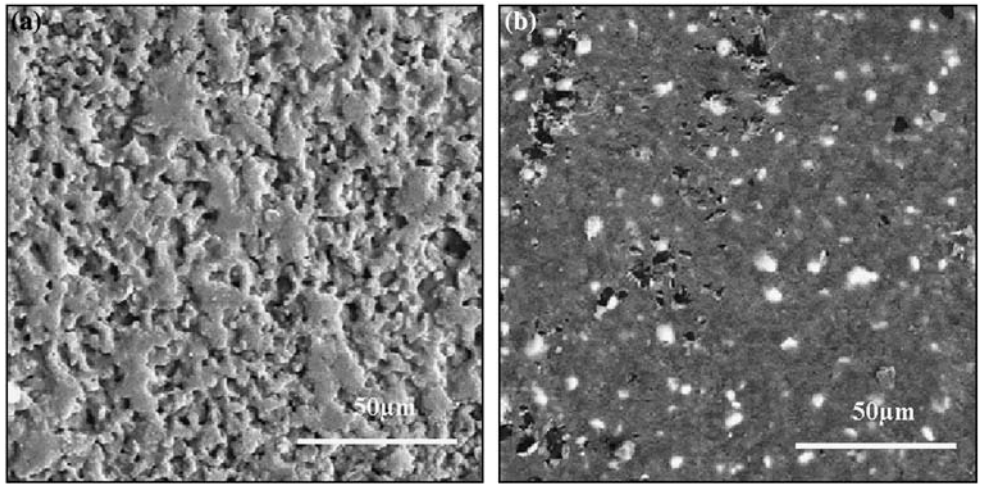

Fig. 2 SEM micrographs of samples sintered at 2150 °C for 1 h. (a) B_4C-free TiB_2 and (b) B_4C-30% TiB_2

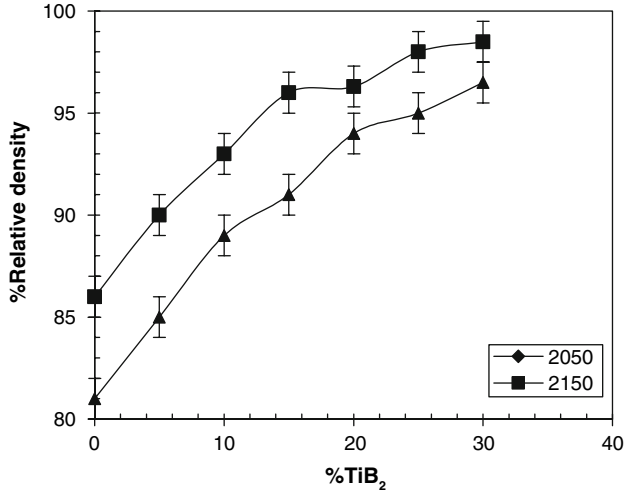

Fig. 3 Effect of TiB_2 addition on relative density of the samples sintered at 2150 °C (■) and 2050 °C (▲)

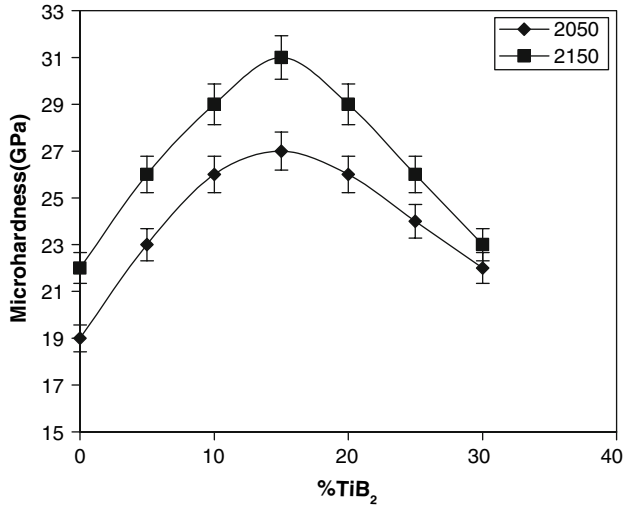

Fig. 4 Effect of TiB_2 addition on Vickers Microhardness of the samples sintered at 2150 °C (■) and 2050 °C (▲)

Table 1 The grain size of samples

Materials composition, wt.%TiB_2	Grain size, μm
2050 (°C)	
0	20
10	15
20	12
30	9
2150 (°C)	
0	30
10	17
20	14
30	10

The higher density has a remarkable effect on mechanical properties of sintered samples. Figure 4 illustrates the variation of hardness vs. the amount of TiB_2 in the compositions. As can be seen, the highest hardness value obtained was about 31 GPa

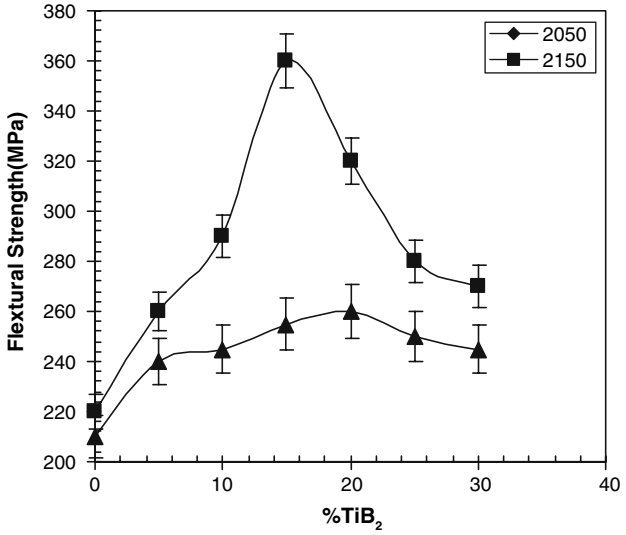

Fig. 5 Effect of TiB_2 addition on fracture toughness of the samples sintered at 2150 °C (■) and 2050 °C (▲)

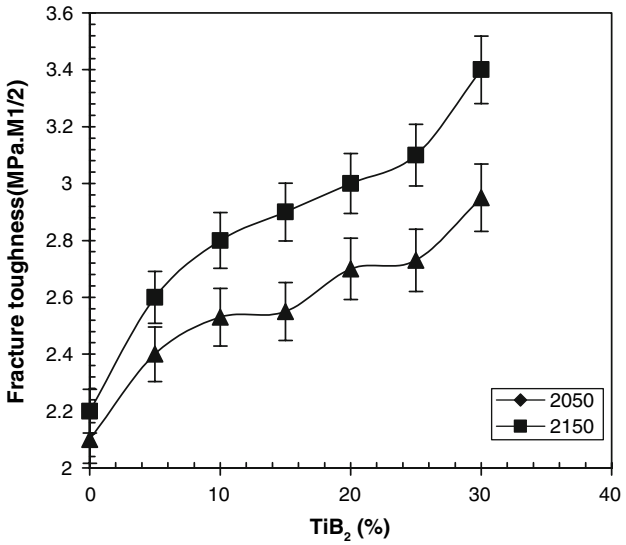

Fig. 6 Effect of TiB_2 addition on fracture toughness of the samples sintered at 2150 °C (■) and 2050 °C (▲)

for the samples having 15% TiB_2 in their composition. This value is very close to the hardness of fully densified pure B_4C materials. By increasing TiB_2 from 15% to 30%, the hardness decreases. This is due to the fact that TiB_2 is a less hard phase compared to B_4C.

In Fig. 5, the variation of bending strength as a function of TiB_2 percentage has been drawn. From the figure, the bending strength has improved remarkably as a result of TiB_2 addition. With respect to this figure, the bending strength increases from 220 MPa to a value of 345 MPa for samples with 15% TiB_2 and then decreases for samples having higher amount of TiB_2 in their composition. Contrary to the other mechanical properties, the fracture toughness increases for all the samples having up to 30% TiB_2 (Fig. 6). The reason for this behavior seems to be the crack interaction with tougher TiB_2 phase or crack deflection by microcracks around TiB_2

phase. Due to thermal expansion mismatch between TiB_2 and B_4C, microcracking or compression residual stress field exists around TiB_2 phase.

4. Conclusion

1. Addition of TiB_2 has a remarkable effect on grain growth, sinterability, and density improvement of B_4C material.
2. Bending strength and hardness follow the same behavior. These properties improve by addition of TiB_2 to certain amounts and then start to decrease.
3. The fracture toughness increases for all the B_4C-TiB_2 samples, having up to 30% TiB_2.
4. Addition of TiB_2 alleviates B_4C grain growth during sintering process.

Acknowledgment

The authors would like to thank University of Malek Ashtar and University of Tehran for supporting the present project.

References

1. C.C. Philip, Ceramic Composites Containing Spinel Silicon carbide, and Boron Carbide, European Patent No. 921085924, 1999
2. G. Magnani, G. Beltrani, and G. Loris, Pressureless Sintering and Properties of α SiC–B_4C Composites, *J. Eur. Ceram. Soc.*, 2001, **21**, p 633–638
3. G.Q. Weaver, Sintered High Density Boron Carbide, US Patent No. 4320204, 1982
4. L.S. Sigl, Processing and Mechanical Properties of Boron Carbide Sintered with TiC, *J. Eur. Ceram. Soc.*, 1998, **18**, p 1521–1529
5. J.W. Henney and J.W.S. Jones, Novel Powder Processing of Sintered Boron Carbide, British Patent No. 2014193, 1979
6. T. Vasilos and S.K. Dutta, Low Temperature Hot Pressing of Boron Carbide and its Properties, *Am. Ceram. Soc. Bull.*, 1974, **53**, p 435–438
7. S. Dole and S. Prochazka, Densification and Microstructure Development in Boron Carbide, *Ceram. Eng. Sci. Proc.*, 1985, **6**, p 1151
8. H. Lee and R.F. Speyer, Pressureless Sintering of Boron Carbide, *J. Am. Ceram. Soc.*, 2003, **86**(9), p 1468–1473
9. R.F. Speyer and H. Lee, Advances in Pressureless Densification of Boron Carbide, *J. Mater. Sci.*, 2004, **39**(19), p 6017–6021
10. M. Bougoin and F. Thevenot, Pressureless Sintering of Boron-Carbide with an Addition of Polycarbosilane, *J. Mater. Sci.*, 1987, **22**(1), p 109–114
11. S.L. Dole, S. Prochazka, and R.H. Doremus, Microstructural Coarsening During Sintering of Boron-Carbide, *J. Am. Ceram. Soc.*, 1989, **72**(6), p 958–966
12. A. Goldstein, Y. Geffen, and A. Goldenberg, Boron Carbide-Zirconium Boride in situ Composites by the Reactive Pressureless Sintering of Boron Carbide-Zirconia Mixtures, *J. Am. Ceram. Soc.*, 2001, **84**(3), p 642–644
13. K.A. Schwetz, Mechanical Properties of Injection Moldod B_4C-C Ceramics, *J. Solid State Chem.*, 1997, **133**, p 66–76
14. D. Stibbs, C.G. Brown, and R. Thompson, Dense Sintered Boron Carbide Containing Beryllium Carbide, US Patent No. 3146571, 1973
15. S. Prochazka, Sintering Boron Carbide Containing Beryllium Carbide, US Patent No. 4005235, 1997
16. A.K. Kundsen and W. Rafaniello, Titanium Diboride/Boron Carbide Composites with High Hardness and Toughness, US Patent No. 4957884, 1990
17. T. Graziani and A. Bellosi, Production and Characteristics of B_4C/TiB_2 Composites, *Key Eng. Mater.*, 1995, **104–107**, p 125–132
18. K.-F. Cai and C.-W. Nan, The Effect of Silicon Addition on Thermoelectric Properties of a B_4C Ceramic, *Mater. Sci. Eng. B*, 1999, **67**, p 102–107
19. L. Levin, N. Frage, and M.P. Darriel, The Effect of Ti and TiO_2 Addition on the Pressureless Sintering of B_4C, *Metall. Mater. Trans. A*, 1999, **30**(12), p 3201–3210
20. C.C. Wu and R.W. Rice, Porosity Dependence of Wear and Other Mechanical Properties on Fine-grain Alumina and Boron Carbide (B_4C), *Ceram. Eng. Sci. Proc.*, 1985, **6**, p 977–994
21. H.-W. Kim, Y.-H. Koh, and H.-E. Kim, Densification and Mechanical Properties of B_4C with Al_2O_3 as a Sintering Aids,, *J. Am. Ceram. Soc.*, 2000, **83**(11), p 2863–2865
22. V.V. Shorokhod, M.D. Vlajic, and V.D. Kristic, Pressureless Sintering of B_4C–TiB_2 Ceramic Composites, *Mater. Sci. Forum*, 1998, **282–283**, p 219–224
23. V.V. Skorokhod, Processing, Microstructure, and Mechanical Properties of B_4C-TiB_2 Particulate Sintered Composites I: Pressureless Sintering and Microstructure Evolution, *Powder Metall. Metal Ceram.*, 2000, **39**(9–10), p 504–513
24. S. Yamada, K. Hirao, and S. Sakaguehi, Microstructure and Mechanical Properties of B_4C-CrB_2 Ceramics, *Key Eng. Mater.*, 2002, **206–213**, p 811–814
25. K.F. Cai, C.W. Nan, M. Schmuecker, and E. Mueller, Microstructure of Hot-pressed B_4C–TiB_2 Thermoelectric Composites, *J. Alloys. Compd.*, 2003, **350**(1–2), p 313–318
26. A. Li, Y. Zhen, Q. Yin, M. Laipeng, and Y. Yansheng, Microstructure and Properties of (SiC, TiB_2)/B_4C Composites by Reaction Hot Pressing, *Ceram. Int.*, 2006, **32**(8), p 849–856
27. T.S. Srivatsan, G. Guruprasad, D. Black, M. Petraroli, R. Adhakrishnan, and T.S. Sudarshan, Microstructural Development and Hardness of TiB_2–B_4C Composite Samples: Influence of Consolidation Temperature, *J. Alloys Compd.*, 2006, **413**(1–2), p 63–72
28. M. Kakazey, M. Vlasova, J.G. Gonzalez-Rodriguez, M. Dominguez-Patino, and R. Leder, X-ray and EPR Study of Reactions between B_4C and TiO_2, *Mater. Sci. Eng. A*, 2006, **418**, p 111–114
29. T.S. Srivatsan, G. Guruprasad, D. Black, R. Radhakrishnan, and T.S. Sudarshan, Influence of TiB_2 Content on Microstructure and Hardness of TiB_2–B_4C Composite, *Powder Technol.*, 2005, **159**(3), p 161–167
30. Z. Yuhu, L. Aijua, Y. Yansheng, S. Ruixi, and L. Yingcai, Reactive and Dense Sintering of Reinforced-toughened B_4C Matrix Composites, *Mater. Res. Bull.*, 2004, **39**(11), p 1615–1625