B_4C-TiB_2 Composites via Reactive Hot Pressing

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ABSTRACT

B_4C/TiB_2 ceramic composites having 5-10-15 vol % TiB_2 have been prepared via reactive hot pressing of B_4C, TiO_2 and C powder mixture. Reactive hot pressing were carried out at 2273 K and 2373 K applying 50 MPa pressure under argon atmosphere for 1 hour. The effect of TiB_2 amount of composite and sintering temperature on sintering behavior and some mechanical properties of reactive hot pressed composites were investigated. The highest theoretical density that could be achieved, being 99.6 %, was with the composite having 5 % TiB_2 following reactive hot pressing at 2000°C applying 50 MPa pressure under argon atmosphere for 1 hour. The highest strength level achieved with the same composite (B_4C-5 vol.% TiB_2) was 450 MPa. The fracture toughness of the composite was found to be 4.2 MPa. $m^{1/2}$. Increasing TiB_2 content in composites led to increasing porosity in B_4C-TiB_2 samples and decreasing mechanical properties.

Keywords: B_4C-TiB_2, reactive hot pressing.

1. INTRODUCTION

The unique mechanical, physical and thermal properties such as high hardness, high wear resistance, high elastic modulus, high melting point, good chemical stability, low density and high neutron absorption cross-section, make boron carbide (B_4C) ceramics very attractive candidates for many structural applications (cutting tools, wear resistant parts, sand blasting nozzles, armour materials, etc.) /1-4/. However, their widespread use as structural materials has been limited due to their poor sintering behavior, low strength and low fracture toughness. Since covalently bonded boron carbide having very low self diffusivity, it is very difficult to achieve full density with monolithic boron carbide by conventional sintering techniques. To obtain high relative densities in boron carbide ceramics, some sintering additives, extremely high sintering temperatures and in the most case pressure application (uniaxial pressure or isostatic pressure) have been required during the sintering procedure /2, 4/.

Some additives such as C, Al, Fe, Ti, SiC, TiB_2, Al_2O_3, ZrO_2 have been used to improve sintering behavior and mechanical properties /5-12/. Small amount of carbon addition seems to improve sintering behavior of boron carbide /5/. However metallic phase addition reduces the physical and mechanical properties of the ceramic. Addition of small amount of Al_2O_3 increased the sinterability, hardness, elastic modulus, flexural strength and fracture toughness of B_4C /6/. The effects of other additives such as SiC, TiC, WC and BN have also been investigated with limited success in properties /7,8/. Addition of small amount ZrO_2 resulted in excellent mechanical properties of fully dense B_4C /8/.

Two major approaches have been used to develop boron carbide-titanium diboride composites; sintering

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boron carbide and titanium diboride powders /9-12/ and in situ reactive sintering of boron carbide with additions of titanium, titanium oxide or titanium oxide and carbon powders /13-20/. Sintering process have been conducted via pressureless sintering /9, 12-16, 18, 21/, hot pressing /11, 14, 18/ or hot isostatic pressing techniques /22/. Addition of 30 % TiB_2 and pressureless sintering at 2423 K resulted in 99 % of theoretical density and improved mechanical properties in the samples /9/. However, hot pressing of B_4C with 20 % of TiB_2 at 2173 K results in a material of 20 % porosity /11/. Skorokhod et al. /12, 13/ have found that 98.5 % of theoretical density could be reached in the sample containing 15 vol.% TiB_2 by pressureless sintering of B_4C-TiO_2-C starting powders at 2373 K. The bending strength and fracture toughness reached their maximum of 500 MPa and 4.6 $MPa.m^{1/2}$, respectively /13/. By reactive hot pressing of B_4C with the addition of TiO_2 and C at 2273 K applying 20 MPa pressure, 15 vol.% TiB_2 containing B_4C have been produced with flexural strength of 621 MPa and fracture toughness of over 6.1 $MPa.m^{1/2}$ /14/. Goldstein et al. /18/ explained the enhanced sintering of pressureless sintered B_4C/ 28 vol. % TiO_2 powder by the formation of the boron rich solid solution.

An alternative pressure assisted sintering technique called spark plasma sintering (SPS) have been also tried to produce B_4C-TiB_2 composites at lower sintering temperatures. Fully densified composites obtained at 1973 K SPS temperature applying 100 MPa pressure /20/.

In the present study, B_4C, TiO_2 and C powder mixture have been subjected to reactive hot pressing technique to fabricate B_4C-TiB_2 composites. The effect of TiB_2 content and hot pressing temperature on sintering behavior and mechanical properties of hot pressed composites were investigated.

2. MATERIALS AND METHODS

Boron carbide (HP grade, H.C.Starck, Germany), TiO_2 (>99 % purity) and carbon black (Elftex 125, Cabot, Spain) were used to prepare ceramics B_4C containing 5-15 vol. % TiB_2 composites.

Sintering procedure was performed in a graphite resistance vacuum hot press HP W 150/200-2200-100 (FCT System GmbH, Germany). Samples having 42 mm in diameter and 5 mm in thickness were prepared by reactive hot pressing at 2273 K and 2373 K applying 50 MPa pressure for 1h under argon. Heating rate was 10 K/min. After sintering, sample densities were determined by Archimed's technique. To identify the crystalline phases, X-ray diffraction of Cu Kα was employed using Panalytical X-Pert Pro equipment. For measuring flexural strength, test pieces were cut from reactive-hot-pressed samples with a diamond wheel, and three point bending test conducted according to ASTM E 399-90. Bending strength levels were measured by using Instron1195 universal test machine with a cross-head speed of 1 mm/s. For all measurements six specimens have been used for each composition. Hardness and fracture toughness measurements were performed on micro Vickers Straus Duramin A-300, by applying 2 kg load. Fracture toughness values were calculated by using Anstis equation /20/.

$$K_{Ic} = 0.016\,(E/H)^{1/2} \times (P/C^{3/2}) \qquad (1)$$

where K_{Ic} is the fracture toughness, E-elastic modulus, H-hardness, P-load, 2C-full crack length produced by Vickers H_v indentation.

Microstructures of the materials were studied using a field emission scanning electron microscope JEOL 7100 FEG-SEM for backscattered electron images.

3. RESULTS AND DISCUSSION

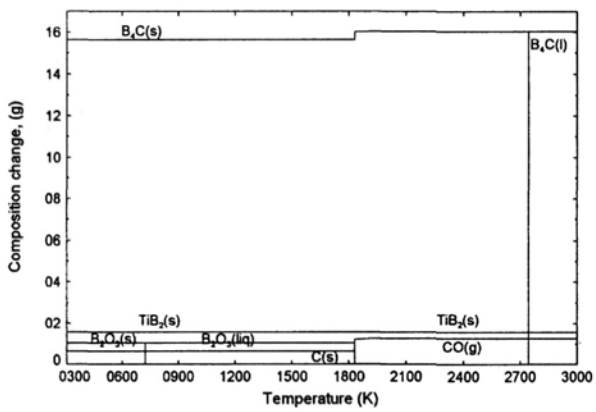
3.1 Thermodynamic Consideration and Phase Formations

$$2B_4C + 2TiO_2 + 3C = B_4C + 2TiB_2 + 4CO \qquad (1)$$
$$5/2B_4C + 3TiO_2 = 3TiB_2 + 2B_2O_3 + 5/2C \qquad (2)$$
$$B_4C + TiB_2 + 2B_2O_3 + 7C = 2B_4C + TiB_2 + 6CO \qquad (3)$$

"Reaction" module of Factsage 6.0 /23/ showed that above reaction (1) was thermodynamically possible even at room temperature. In order to understand the reaction mechanisms, "Equilib" module of the Factsage

was used to simulate the reaction (1) at different temperature considering starting amount of B_4C, TiO_2 and C powders to obtain 5 vol.% TiB_2 containing B_4C-TiB_2 tablet having 42 mm diameter and 5 mm thickness and result was shown in Fig. 1. The reaction (1) consists of two main reactions. The first one is the reaction of TiO_2 with B_4C to form TiB_2, B_2O_3 and C (Reaction 2); the second is the reaction of intermediate products with C to form B_4C, TiB_2 and CO (Reaction 3). The calculation results also indicate that all solid C oxidized to CO above 1831 K. TiC formation is not possible thermodynamically.

Fig. 1: Simulation result of reaction of $2B_4C_{(s)}$ +



$2TiO_{2(s)} + 3C_{(s)} = B_4C_{(s)} + 2TiB_{2(s)} + 4CO_{(g)}$ at different temperatures under 1 atm.

Powder mixtures containing proper amount of B_4C, TiO_2 and C to obtain B_4C-TiB_2 composites having 5, 10 and 15 vol.% TiB_2 were reactive-hot- pressed at 2273 K and 2373 K under 50 MPa pressure for 1 hour in an argon atmosphere, and the XRD patterns of samples are given in Fig. 2 and Fig. 3, respectively. Phases observed in these products are only B_4C, TiB_2 and C. Unreacted TiO_2 was not observed in XDR patterns of hot pressed samples. Increasing amount of TiO_2-C content in starting powders led to an increase in the peak intensities of TiB_2 of the samples. However, a significant peak of unreacted C was observed in the composites in which 15 vol.% TiB_2 was expected to form.

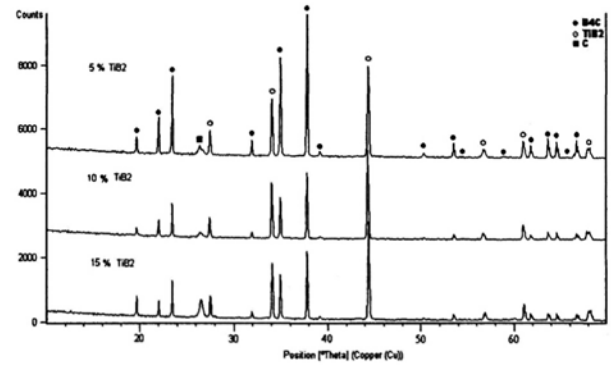


Fig. 2: X-ray diffractograms of specimens applied reactive-hot-pressing at 2273 K 50 MPa for 1 hour under argon gas.

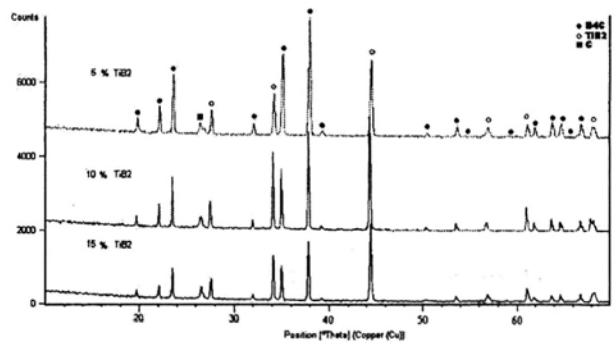


Fig. 3: X-ray diffractograms of specimens applied reactive-hot-pressing at 2373 K, 50 MPa for 1 hour under argon gas.

3.2 Relative Density of Reactive Hot Pressed Samples

Density values of composites reactive-hot-pressed at 2273 K and 2373 K applying 50 MPa pressure for 1 hour under argon are given in Table 1. Increased TiB_2 content in composites led to a decrease in the relative densities due to unreacted C at both temperatures. However the densities of reaction-hot-pressed composites containing 5 and 10 vol. % TiB_2 at 2373 K showed a small decrease as compared to the composites obtained at 2273 K.

Table 1
Relative densities of samples reactive-hot-pressed at 2273 K and 2373 K applying 50MPa pressure under argon for 1 hour.

	Relative Density (%) at 2273 K	Relative Density (%) at 2373 K
B_4C-5% vol. TiB_2	99.6	99.3
B_4C-10% vol. TiB_2	99.6	99.0
B_4C-15% vol. TiB_2	97.2	97.2

3.3 Mechanical Characterization Results

Figure 4 illustrates the variation of hardness versus the amount of TiB_2 in the composites for both reactive hot pressing temperatures. For both temperatures, by increasing TiB_2 content from 5 vol. % to 15 vol. % the hardness decreased. This is due to the fact that the structures of composites containing high amount of TiB_2 are porous, and that the hardness of TiB_2 compared to matrix phase (B_4C) is lower. As can be seen, the highest hardness value obtained was about 34 GPa for the samples having 5 and 10 vol. % TiB_2 reactive-hot-pressed at 2273 K.

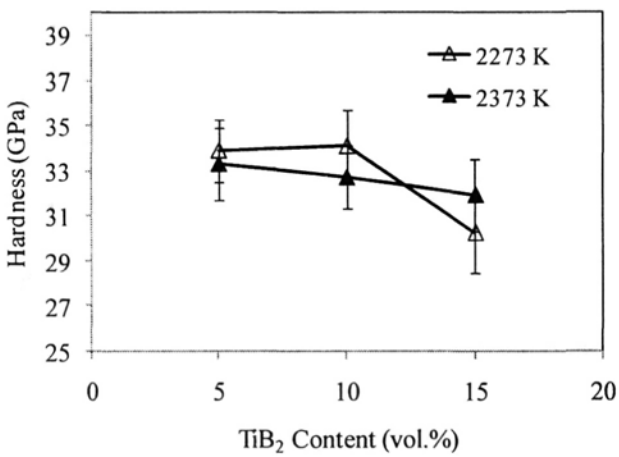


Fig. 4: Effect of TiB_2 content on hardness of the composites reactive-hot-pressed at 2273 K and 2373 K applying 50MPa pressure under argon for 1 hour

The variation of bending strength as a function of TiB_2 percent is given in Figure 5. The bending strength decreases from 450 MPa to 330 MPa for samples with 5 vol.% TiB_2 to 15 vol. % TiB_2 reactive-hot-pressed at 2273 K. For samples reactive-hot-pressed at 2373 K, the bending strength values varied between 415 MPa and 370 MPa with the increasing TiB_2 content. The decrease in flexural strength values are caused by the decreasing relative density as the TiB_2 content in composites were increased.

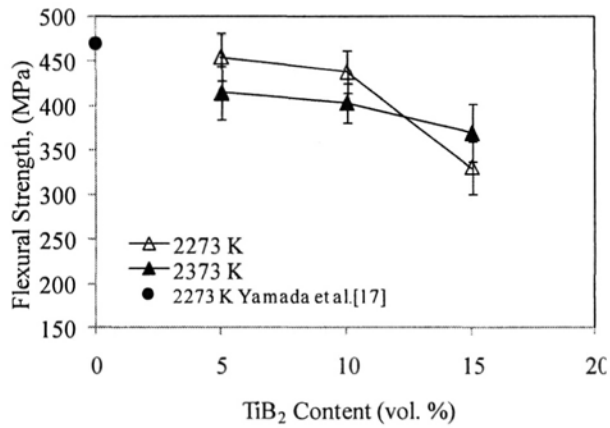


Fig. 5: The variation of flexural strength as a function of TiB_2 content in composites reactive-hot-pressed at 2273 K and 2373 K applying 50 MPa pressure under argon for 1 hour

Fracture toughness values of composites are given in Table 2. These values changed between 4.3 and 3.9 $MPa.m^{1/2}$ for composites containing 5 and 10 vol. % TiB_2 reactive-hot-pressed at 2273 K and 2373 K. The fracture toughness of the composites containing 15 vol. % TiB_2 could not be determined due to their high porosity. The fracture toughness of monolithic B_4C ceramics fabricated by hot pressing at 2273 K applying 50 MPa pressure was measured as 2.6 $MPa.m^{1/2}$ by Yamada et al./17/. As compared to the monolithic B_4C, highly densified composites having 5 and 10 vol. % TiB_2 showed improvement in fracture toughness. Many researchers explained this improvement by the difference in thermal expansion coefficients of B_4C and TiB_2. Due to the thermal expansion mismatch between B_4C and TiB_2, residual stress is generated around the TiB_2 particles during cooling, which results in the

formation of microcracks and deflection of propagating cracks /9, 17, 21/. Figure 6 shows crack deflection observed around the TiB_2 particles in polished B_4C-5 vol. % TiB_2 composites by using Vickers diamond indenter.

Table 2

Fracture toughness values of composites reactive-hot-pressed at 2273 K and 2373 K applying 50MPa pressure under argon for 1 hour.

	Fracture Toughness, ($MPa.m^{1/2}$)	
	2273 K	2373 K
B_4C-5% vol. TiB_2	4.2 ± 0.4	4.1 ± 0.6
B_4C-10% vol. TiB_2	4.3 ± 0.4	3.9 ± 0.3
B_4C-15% vol. TiB_2	n.d.	n.d.

n.d.: not determined

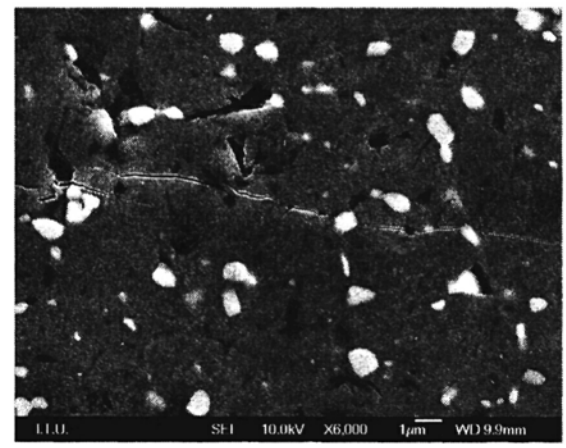


Fig. 6: Crack deflection on B_4C- 5 vol.% TiB_2 composite.

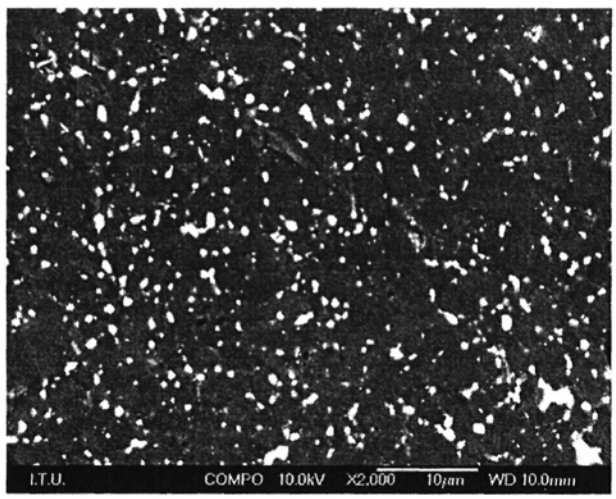


Figure 7 (a)

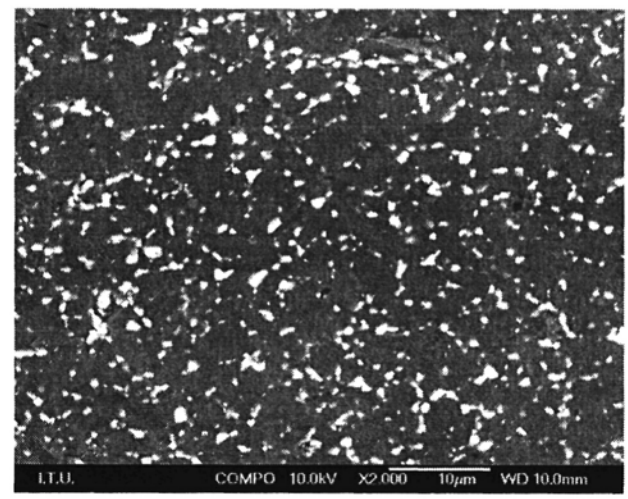


Figure 7 (b)

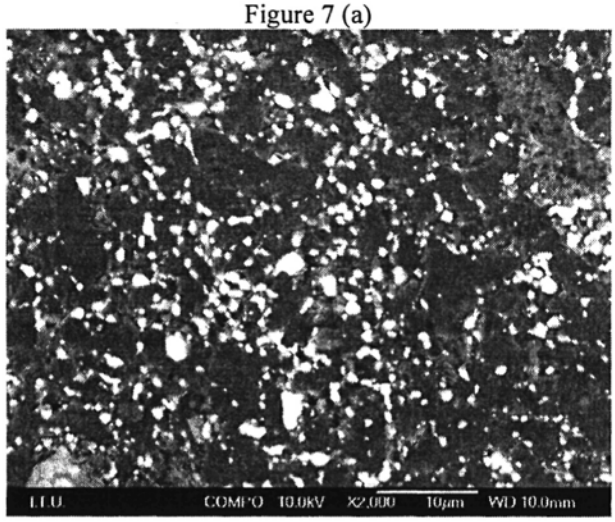


Figure 7 (c)

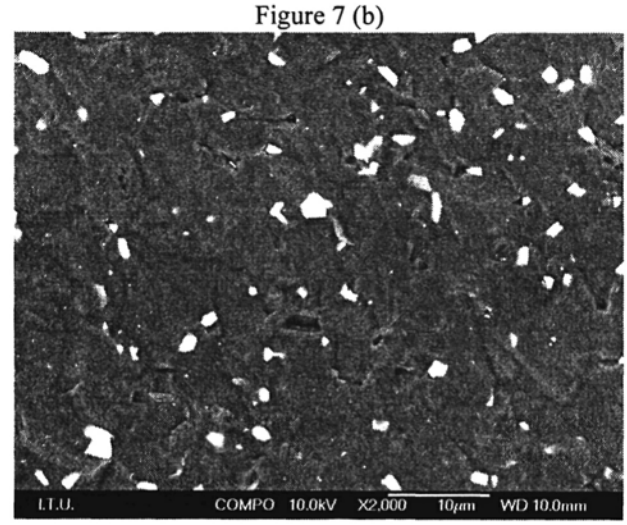


Figure 7(d)

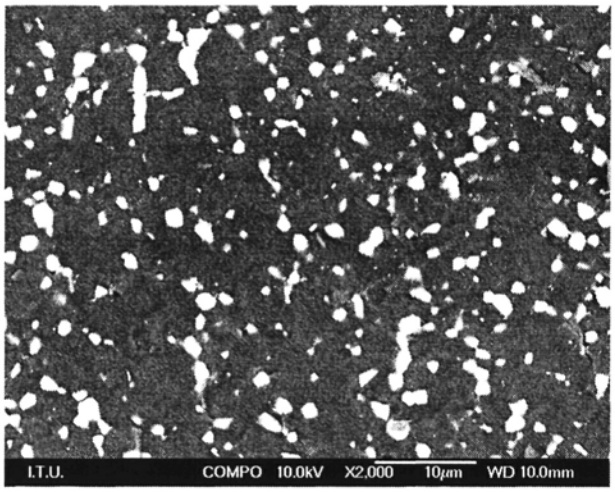


Figure 7(e)

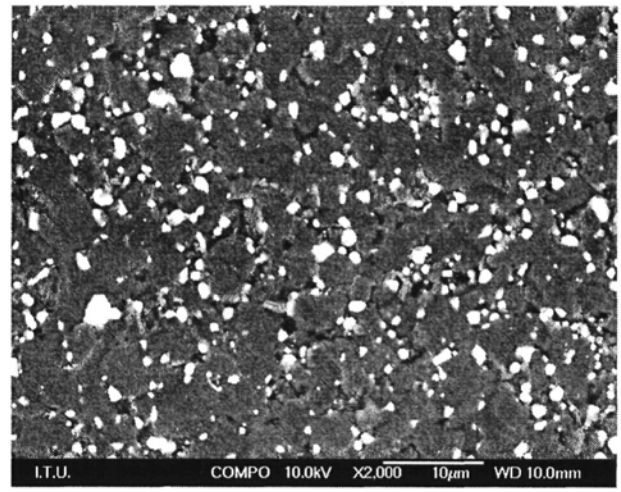


Figure (f)

Fig. 7: Microstructures of B_4C-TiB_2 composites reactive-hot-pressed at two different temperatures: (a) 5 vol. % TiB_2 (b) 10 vol. % TiB_2 (c) 15 vol. % TiB_2 at 2273 K (d) 5 vol. % TiB_2 (e) 10 vol. % TiB_2 (f) 15 vol. % TiB_2 at 2373 K

3.4 Microstructural Observation

Figure 7 shows microstructures observed in the fractured surface of the B_4C-TiB_2 composites. In these micrographs,TiB_2 particles appear as white areas due to high atomic number of Ti. In the composites reactive-hot-pressed at 2273 K, TiB_2 particles were highly dispersed whereas a large number of aggregated TiB_2 particles existed in the composites reactive-hot-pressed at 2373 K. For both reactive hot pressing temperatures the microstructures of composites prepared to form 15 vol. % TiB_2 (Figures 7c and 7f) showed high porosity and less homogeneity.

4. CONCLUSION

B_4C-TiB_2 composites having 5, 10 and 15 vol. % TiB_2 were fabricated by reactive hot pressing of B_4C-TiO_2-C mixtures applying 50 MPa pressure under argon for 1 hour at 2273 K and 2373 K. The composites containing 15 vol. % TiB_2 resulted in lower density and degraded mechanical properties for both temperatures.

Nearly fully dense composites containing 5 and 10 vol.% TiB_2 obtained by reactive hot pressing at 2273 K applying 50 MPa pressure under argon for 1 hour. These dense composites showed an increase in fracture toughness compared to monolithic boron carbide.

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REFERENCES

1. F. Thevenot, *J. Eur. Ceram. Soc.*, **6**, 205-225 (1990).
2. A.W. Weimer, *Carbide, Nitride and Boride Materials Synthesis and Processing*, Chapman&Hall, London, (1997).
3. W.C. Johnson, *Am.Ceram.Soc. Bull.*, **80**, 64-66 (2001).
4. A.G. Evans, *J. Am. Ceram. Soc.*, **73-2**, 187-206(1990).
5. K.H. Schwetz and W. Grellner, *J. Less-Common Met.*, **82**, 37-47 (1981).
6. H-W. Kim, Y.-H. Koh and H-E. Kim, *J.Am.Ceram Soc.*, **83-11**, 2863-2865(2000).
7. L.S. Sigl, *J. Eur. Ceram. Soc.* , **18**, 1521-1529 (1998).
8. H-W. Kim, Y.-H. Koh and H-E. Kim, *J. Mater. Res.*, **15**, 2431-2436(2000).

9. H.R. Baharvandi, A.M. Hadian and A. Alizahed, *Appl. Compos Mater.*, **13**, 191-198 (2006).
10. T.K. Roy, C. Subramanian and A,K. Suri, *Ceramics International*, **32** ,227-233 (2006).
11. K.F. Cai, C.W. Nan, M. Schuecker, E. Mueller, *J. Alloys and Compounds*, **350**, 313-318 (2003).
12. T.S. Srivatsan, G.Guruprasad, D. Black, R.Radhakrishnan and T.S.Sudarshan, *Powder Technology*, **159**, 161-167 (2005).
13. VI. V. Skorokhod and V.D.Kristic, *Pow. Metall. and Met. Ceram.*, , Vol **39**, Nos.7-8, 414-423 (2000).
14. VI. V. Skorokhod and V.D.Kristic, *Pow. Metall. and Met. Ceram.*, Vol **39**, Nos.9-10, 504-513 (2000).
15. VI. V. Skorokhod and V.D.Kristic,, *J. Mater. Sci. Letters*, **19**, 237-239 (2000).
16. L. Levin, N. Frage and M.P. Dariel, *Int. J. Ref. Met. & H. Mat.*, **18**,1231-135 (2000).
17. S. Yamada, K. Hirao, Y. Yamauchi and S. Kanzaki, *J.Eur. Cer. Soc.*, **23**, 1123-1130 (2003).
18. A. Goldstein, Y. Yeshurun and A. Goldenberg, *J.Eur.Cer.Soc.*, **27**, 695-700 (2007).
19. J. Sun , C. Liu, and C. Duan, *Mat.Sci.and Eng. A* , **509**,89-93 (2009).
20. D.V. Dudina, D.M.Hulbert, D. Jiang, C. Unuvar, S.J. Cytron and A.K. Mukherjee, *J.Mat. Sci.*, **43**, 3569-3576(2008).
21. V. Skorokhod, M.D. Vlajic and V.D. Krstic, *J. Mater. Sci. Letters*, **15**,1337-1339(1996).
22. L.S. Sigl, *J.Eur.Cer.Soc.*, **18** , 1521-1529 (1998).
23. FactSage 6.0 Thermochemical Software for WindowsTM. *Thermfact and GTT-Technologies*, (2009).