ELSEVIER

Ceramics International 28 (2002) 425–430

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Microstructure and mechanical properties of hot-pressed B_4C/(W,Ti)C ceramic composites

Jianxin Deng*, Jun Zhou, Yihua Feng, Zeliang Ding

Department of Mechanical Engineering, Shandong University, Jinan 250061, Shandong Province, PR China

Received 12 July 2001; received in revised form 30 July 2001; accepted 11 October 2001

Abstract

In this paper, B_4C/(W,Ti)C ceramic composites with different content of solid-solution (W,Ti)C were produced by hot pressing. The effect of (W,Ti)C content on the microstructure and mechanical properties of B_4C/(W,Ti)C ceramic composites has been studied. Results showed that a chemical reaction took place for this system during hot pressing, and resulted in a $B_4C/TiB_2/W_2B_5$ composite with high density and improved mechanical properties compared to monolithic B_4C ceramic. Densification rates of the B_4C-based ceramic composites were found to be affected by addition of (W,Ti)C. Increasing (W,Ti)C content led to an increase of the densification rates of the composites. The sintering temperature was lowered from 2150 °C for monolithic B_4C to 1850 °C for the B_4C/(W,Ti)C composites. The fracture toughness and flexural strength continuously increased with increasing (W,Ti)C content up to 50 wt.%, while the hardness decreased with increasing (W,Ti)C content. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: B. Microstructure; C. Mechanical properties; B_4C; (W,Ti)C; Ceramic composites

1. Introduction

Boron carbide (B_4C) is one of the most useful ceramics in modern engineering applications because of its high hardness, high wear resistance, high melting point, good chemical inertness, high Young's modulus and thermal conductivity as well as high cross-section for neutron absorption [1–3], that make it promising candidates for wear resistance components, where metallic components achieve only unsatisfactory service lives, owing to inadequate wear resistance. B_4C is best recognized for its hardness and abrasion resistance. After diamond and cubic boron nitride, B_4C is the third hardest of the technically useful materials. Sandblasting nozzles made of dense sintered B_4C are extremely wear resistance. Under highly abrasive conditions B_4C outperforms other hard materials [3–5]. Moreover the low density of B_4C and its high Young's modulus recommend this material for the construction of light-weight armour, as is need in the military helicopter and similar aero-applications [2,3]. B_4C can also be used advantageously to control the neutron flux of nuclear reactors.

Compared with the ceramics such as Si_3N_4, SiC, ZrO_2, etc., the strength and fracture toughness of monolithic B_4C ceramic material is rather lower (about 200–400 MPa), and its fracture toughness is about 2–3 $MPa.m^{1/2}$ [1–3]. Moreover, the poor sinterability of B_4C limits its application because both high temperature and high pressure are required for a complete densification [6–8]. Unlike alumina, B_4C can not be toughened by the dilational tetragonal–monoclinic transformation of ZrO_2 or HfO_2, simply because these oxides react with the matrix and form compounds such as ZrB_2, B_2O_3, and CO [9]. In earlier studies [9–14], some of the B_4C-based-composites, e.g. B_4C/TiB_2, $B_4C/TiB_2/MB_2$, B_4C/MB_2, B_4C/Al, B_4C/SiC, have been developed and used in various applications, mechanical properties and microstructure studies on them are also extensively carried out. It has been shown that the additions of secondary phases to the B_4C matrix can improve its mechanical properties, i.e. fracture toughness and flexural strength.

In this paper, B_4C-based ceramic composites with different content of solid-solution (W,Ti)C were produced

* Corresponding author. Tel.: +86-531-2940-972; fax: +86-531-2955-999.

E-mail address: dengjx@jn-public.sd.cninfo.net (J. Deng).

0272-8842/02/$22.00 © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.
PII: S0272-8842(01)00113-4

using hot pressing techniques. The mechanical properties and the microstructure of this composite have been studied. Particular attention was paid to the effect of (W,Ti)C additions on the mechanical properties and microstructure.

2. Experimental procedure

2.1. Materials and processing

The starting powders used to fabricate the B_4C/(W,Ti)C composites are listed in Table 1 with their particle size, purity and manufacturer. B_4C was used as the baseline material. Additions of solid-solution (W,Ti)C particles were added to the B_4C matrix. The range of (W,Ti)C additions to the B_4C was from 0 to 50 wt.%. The combined powders were prepared by wet ball milling in alcohol for 150 h with cemented carbide balls. The material was fabricated using colloidal and ultrasonic processing techniques. Filter pressing was used to consolidate the multi-component slurries into green bodies approximately 60 mm in diameter and 20 mm thick. Following drying, the final densification of the compacted powder was accomplished by hot pressing with a pressure of 35 MPa in argon atmosphere for 20–70 min to produce a ceramic disk. The maximum temperature employed for hot pressing was less than 2200 °C.

2.2. Material characterization

Densities of the hot-pressed disks were measured by the Archimedes's method. Test pieces of 3×4×36 mm were prepared from the disk by cutting and grinding using a diamond wheel and were offered for measurement of flexural strength, Vickers hardness and fracture toughness. Three-point-bending mode was used to measure the flexural strength over a 30 mm span at a crosshead speed of 0.5 mm/min. The fracture toughness measurement was performed using the indentation method in a hardness tester (ZWICK3212) using the formula proposed by Cook and Lawn [15]. On the same apparatus the Vickers hardness was measured on polished surface with a load of 98 N. Data for hardness, flexural strength, and fracture toughness were gathered on five specimens.

XRD (D/max-2400) analysis was undertaken to identify the crystal phases present after sintering. The microstructures of sintered materials were studied on fracture surfaces and polished section by scanning electron microscopy (Hitachi S-570) and optical microscopy.

Table 1
Particle size, purity and manufacture of starting powders

Starting powder	Average particle size (μm)	Purity (%)	Manufacture
B_4C	3–5	>95	Mudanjiang abrasive works
(W,Ti)C	1–2	>99	Zhuzhou cemented carbide works

3. Results and discussion

3.1. X-ray diffraction phase analysis

Fig. 1 shows the X-ray diffraction analysis of the B_4C/30 wt.% (W,Ti)C ceramic composite before and after sintering at a temperature of 1850 °C for 30 min. It is obvious from Fig. 1 that TiB_2 and W_2B_5 are newly formed phases, and resulted from the reaction of B_4C with TiC and WC. No trace of WC or TiC was found in the sintered materials when these phases had been added in the powder compacts prior to sintering, showing that a complete reaction occurred during sintering. The reaction formulas are as follows [16]:

$$B_4C + TiC \rightarrow TiB_2 + C \quad (1)$$

$$B_4C + WC \rightarrow W_2B_5 + C \quad (2)$$

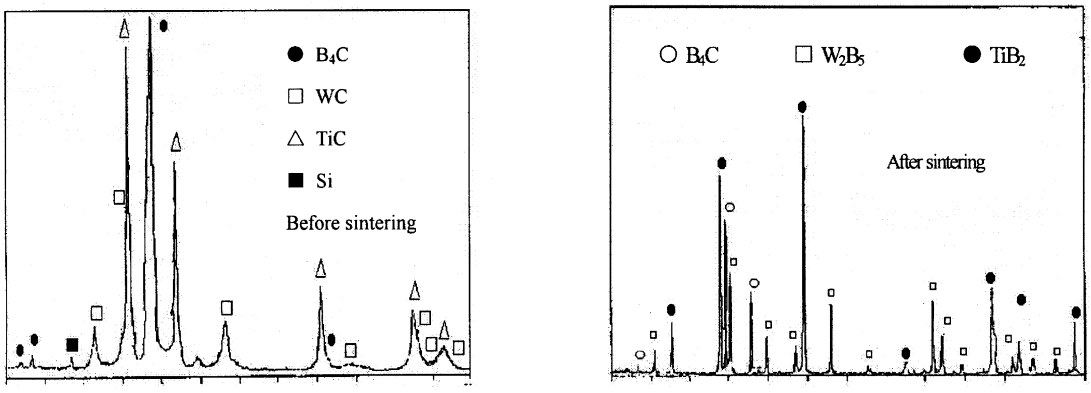

Fig. 1. X-ray diffraction analysis of the B_4C/30 wt.% (W,Ti)C ceramic composite before and after sintering.

3.2. Densification and microstructural characterization

Densification rates of the B_4C-based ceramic composites were found to be affected by additions of (W,Ti)C. Increasing content of (W,Ti)C led to increase the densification rates of composites relative to monolithic B_4C as can be seen in Fig. 2 and Table 2. The sintering temperature was lowered from 2150 °C for monolithic B_4C to 1850 °C for B_4C/(W,Ti)C composites.

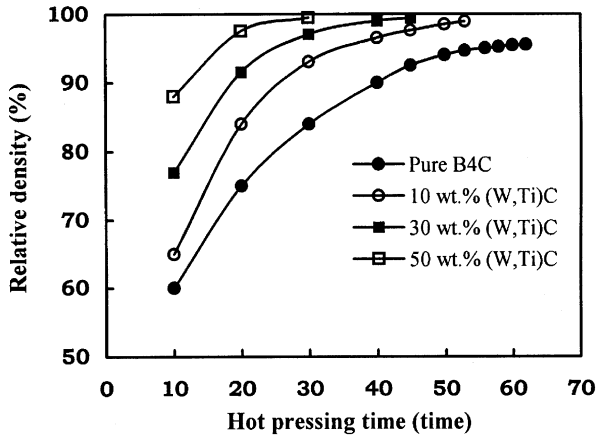

Fig. 2. Densification behavior under hot-pressing conditions of monolithic B_4C and B_4C/(W,Ti)C ceramic composites.

Figs. 3 and 4 show the SEM micrographs of the fracture surfaces of monolithic B_4C and the B_4C/30 wt.% (W,TiC) composite respectively. From these SEM micrographs, different morphologies and grain sizes of the composites and the hot pressed B_4C matrix can be seen clearly. The monolithic B_4C exhibited a flat fracture surface, resulting from the transgraular fracture mode, and there are a lot of obvious pores located at the B_4C grain boundary. A remarkable increase of the grain size (6–10 μm) was also observed. While the composite showed an intergranular fracture mode, and the grain sizes were ranged from 0.5 to 1.5 μm. The second phase seems to have inhibited the grain growth of B_4C by slowing down the grain boundary movement.

Fig. 5 shows typical microstructures from the polished surface of hot-pressed B_4C/30 wt.% (W,Ti)C ceramic composite. The gray areas as identified by EDX analysis are B_4C and the white areas are of TiB_2 (W_2B_5). As can be seen that TiB_2 (W_2B_5 particles are quite uniformly distributed throughout the microstructure. It is apparent from these SEM micrographs that the TiB_2 (W_2B_5) particles were well-distributed in the B_4C matrix. Some of the voids can also be seen in Fig. 5. This is due to the falling off of the B_4C particles during polishing because of weak bonding of the matrix–particle.

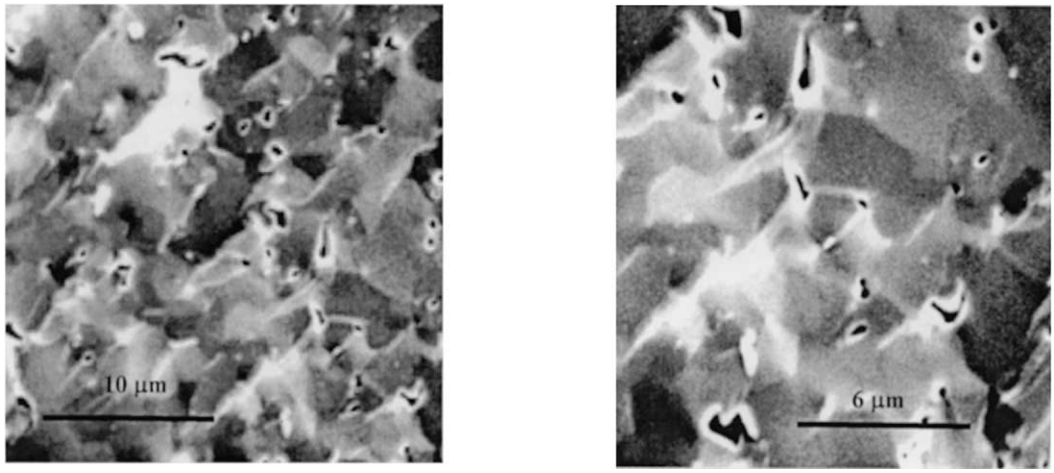

Fig. 3. SEM micrographs of the fracture surfaces of pure B_4C.

Table 2
Sintering parameters, densities and microstructures of the hot-pressed B_4C-based ceramic composites

Sample	Sintering parameter (35 MPa)		Relative density (%)	Grain size (μm)	Crystalline phases
	Temperature (°C)	Time (min)			
B_4C	2150	65	95.0	6–10	B_4C
B_4C/10 wt.% (W,Ti)C	1850	50	98.5	1–2	B_4C, TiB_2, W_2B_5
B_4C/30 wt.% (W,Ti)C	1850	40	99.2	0.5–1.5	B_4C, TiB_2, W_2B_5
B_4C/50 wt.% (W,Ti)C	1850	30	99.5	<1	B_4C, TiB_2, W_2B_5

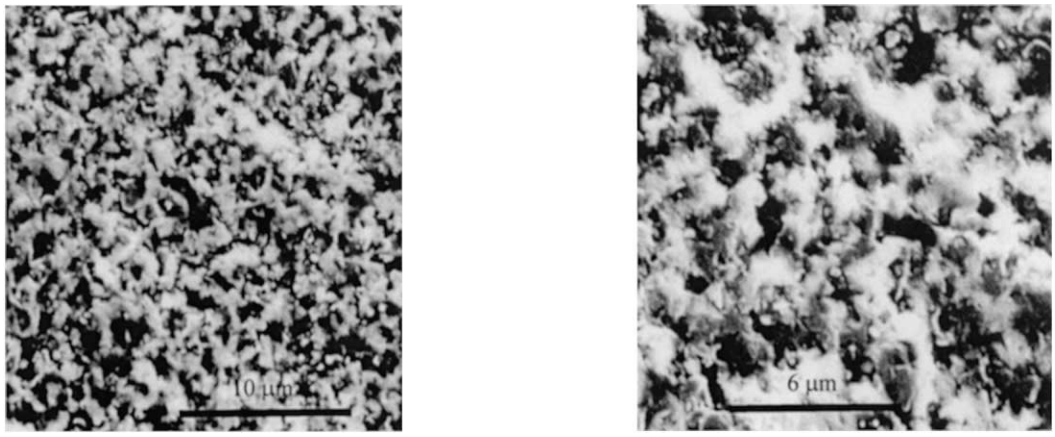

Fig. 4. SEM micrographs of the fracture surfaces of B_4C/30 wt.% (W,Ti)C composite.

Fig. 5. Typical microstructures of the polished surface of B_4C/40 wt.% (W,Ti)C composite.

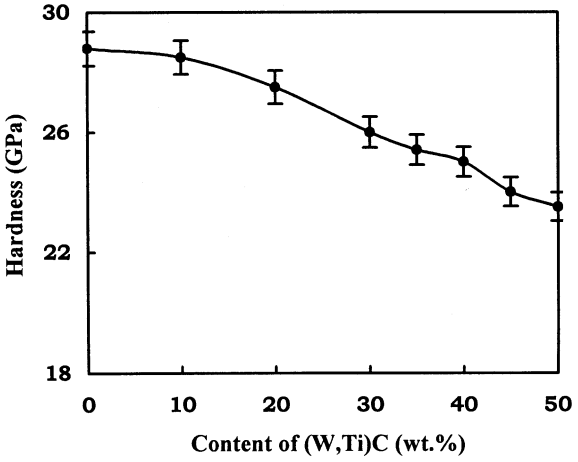

Fig. 7. Variation of composite hardness with (W,Ti)C additions.

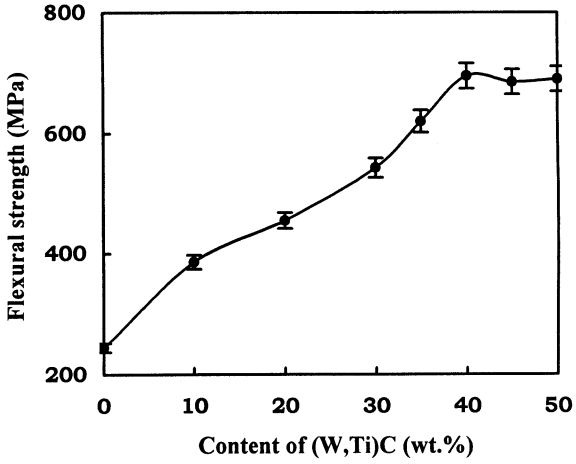

Fig. 6. Variation of composite flexural strength with (W,Ti)C additions.

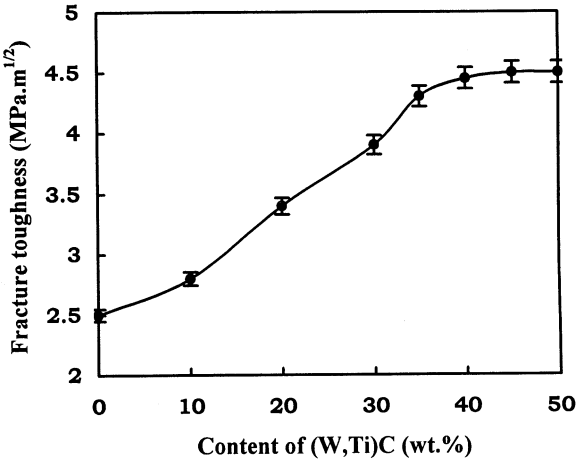

Fig. 8. Variation of composite fracture toughness with (W,Ti)C additions.

3.3. Mechanical properties

Fig. 6 shows the effect of (W,Ti)C addition on the flexural strength of B_4C. It was found that the flexural strength continuously increased with increasing (W,Ti)C content up to 50 wt.%, and rose from 245 MPa for hot-pressed monolithic B_4C to 690 MPa for B_4C/50 wt.% (W,Ti)C composite, representing a maximum

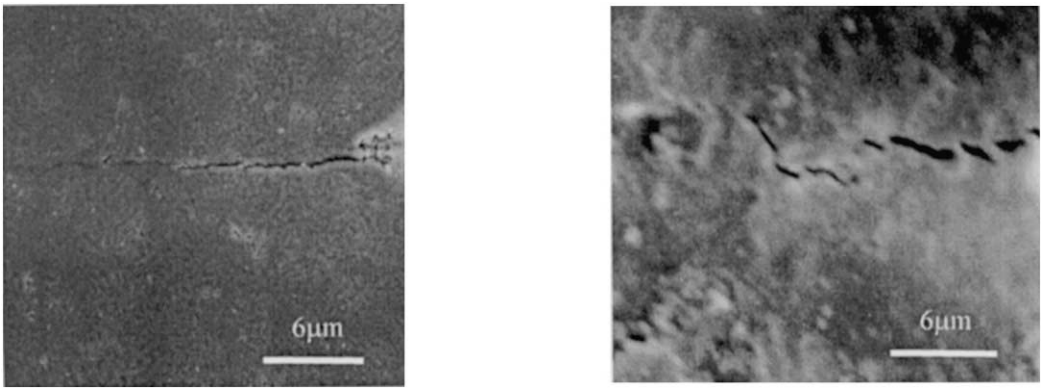

Fig. 9. Crack path produced by Vickers indentation on the polished surface of hot-pressed (a) monolithic B_4C, (b) B_4C/30 wt.% (W,Ti)C composite.

strengthening increase of 445 MPa. The flexural strength of the composite is greatly improved with respect to the matrix when the composite are nearly fully dense (Table 2) and with finer microstructure. So strong grain refinement, higher density, more uniform microstructure associated with the reduction of porosity may be the direct consequence of the higher strength of the composites.

The hardness of B_4C/(W,Ti)C composite was found to decrease with increasing (W,Ti)C content as it can be seen in Fig. 7. As the TiB_2 (W_2B_5) is less hard than B_4C, the hardness of the composite decreased with increasing (W,Ti)C content. In addition, the reason for the lower hardness exhibited by the composites compared to the monolithic B_4C may be caused by the residual stress field generated in the sintered composite material due to the thermal expansion coefficient mismatch (see Table 3).

Fig. 8 shows the variation of fracture toughness with (W,Ti)C content, exhibiting a maximum value of 4.5 $MPa.m^{1/2}$ for 50 wt.% (W,Ti)C composite. The trend of the fracture toughness is the same as that of the flexural strength. The fracture toughness continuously increased with increasing of (W,Ti)C content up to 50 wt.%, and rose from 2.5 $MPa.m^{1/2}$ for hot-pressed monolithic B_4C to 4.5 $MPa.m^{1/2}$ for 50 wt.% (W,Ti)C/B_4C composite, representing a maximum toughening increase of 2.0 $MPa.m^{1/2}$.

For particle composites, several toughening mechanisms have been proposed [17–20], crack pinning, crack deflections, microcracking, crack bridging, and residual stresses. A number of these mechanisms can be active at the same time, making it difficult to indicate a prevailing phenomenon. In the present case, since the thermal expansion coefficients of the constituent phases are quite difference (see Table 3), the fracture toughness increase can be attributed more probably to the mechanisms such as residual stresses and microcracking.

Table 3
Properties of B_4C, TiB_2 and W_2B_5 [1–3]

	Density (g/cm^3)	Melting point (°C)	Hardness (GPa)	Elastic modulus (GPa)	Thermal expansion coefficient (10^{-6}/K)
B_4C	2.52	2450	29–46	445	4.5–5.5
TiB_2	4.52	2790	25–33	529	8.1
W_2B_5	13.03	2365	27		7.8

Fig. 9 shows the path of a crack produced by Vickers indentation on the polished surface of hot-pressed monolithic B_4C and B_4C/30 wt.% (W,Ti)C composite respectively. Fig. 10 is a portion of Fig. 9(b) at higher magnification. It is noted that by incorporating (W,Ti)C into B_4C, the cracks were deflected considerably and consequently their propagation was inhibited in the case of the composite, while crack deflection rarely occurred in the monolithic B_4C. The crack deflection was thought to be caused by the residual stress generated by the difference in the thermal expansion coefficient between B_4C and TiB_2 (W_2B_5) in the composites. Thus, the improvement of fracture toughness is attributed to the crack deflection mechanism triggered by internal stresses due to the thermal expansion coefficient mismatch of B_4C matrix and TiB_2 (W_2B_5) dispersed phases.

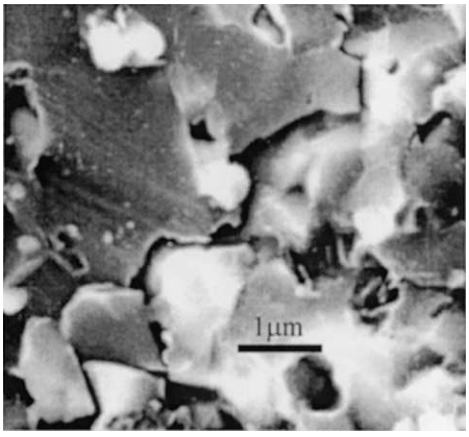

Fig. 10. Crack path produced by Vickers indentation on the polished surface of hot-pressed B_4C/30 wt.% (W,Ti)C composite at higher magnification.

4. Conclusions

B_4C/(W,Ti)C ceramic composites with different content of solid-solution (W,Ti)C were produced using hot pressing techniques. Particular attention was paid to the effect of (W,Ti)C additions on the mechanical properties and microstructure. Results showed that:

1. Chemical reaction took place for this ceramic system during hot pressing sintering, and resulted in a $B_4C/TiB_2/W_2B_5$ composite with high density and improved mechanical properties compared to pure B_4C ceramic.
2. Densification rates of the B_4C-based ceramic composites were found to be affected by additions of (W,Ti)C. Increasing content of (W,Ti)C led to increase the densification rates of the composites. The sintering temperature was lowered from 2150 °C for monolithic B_4C to 1850 °C for B_4C/(W,Ti)C composites.
3. The fracture toughness and flexural strength continuously increased with increasing (W,Ti)C content up to 50 wt.%, while the hardness decreased with increasing (W,Ti)C content.

Acknowledgements

This work was supported by the National Science Foundation of China (Grant No. 59805012).

References

[1] F. Thevenot, Boron carbide—a comprehensive review, Journal of the European Ceramic Society 6 (1990) 205–225.
[2] M.V. Swain, Structure and properties of ceramics, in: Material Science and Technology, Vol. 11, VCH Verlagsgesellschaft mbH, Weinheim, 1994, pp. 153–232.
[3] H. Knoch, Non-oxide technical ceramics, in: 2nd European Symposium on Engineering Ceramics, Elsevier Applied Science, Amsterdam, 1987, pp. 151–169.
[4] K.A. Schwetz, L.S. Sigl, J. Greim, Wear of boron carbide ceramics by abrasive waterjets, Wear 181–183 (1995) 348–355.
[5] R.J.K. Wood, D.W. Wheeler, D.C. Lejeau, Sand erosion performance of CVD boron carbide coated tungsten carbide, Wear 233–235 (1999) 134–150.
[6] S.L. Dole, S. Prochazka, R.H. Doremus, Microstructural coarsening during sintering of boron carbide, Journal of the American Ceramic Society 72 (6) (1989) 958–966.
[7] S.L. Dole, S. Prochazka, Densification and microstructure in boron carbide, Ceramic Engineering Science Proceedings 16 (1985) 1151–1160.
[8] Z. Panek, The synthesis of SiC/B_4C ceramics by combustion during hot pressing, Journal of the European Ceramic Society 11 (1993) 231–236.
[9] L.S. Sigl, Microcracking in B_4C/TiB_2 composites, Journal of the American Ceramic Society 78 (9) (1995) 2374–2380.
[10] R. Telle, G. Petzow, Strengthening and toughening of boride and carbide hard material composites, Material Science and Engineering A105/106 (1988) 97–104.
[11] T. Grazian, A. Bellosi, Production and characteristics of B_4C/TiB_2 composites, Key Engineering Materials 104–107 (1995) 125–132.
[12] M. Ingaki, Research and development on carbon/ceramic composite in Japan, Carbon 29 (3) (1991) 287–293.
[13] A.K. Bhattacharya, J.J. Petrovic, Ductile phase toughening and R-curve behavior in a B_4C–Al cermets, Journal of Material Science 27 (1992) 2205–2210.
[14] T. Jun, T. Shouhong, C. Zhongming, Strengthening and toughening of B_4C/TiB_2 multiphase ceramics, Journal of Inorganic Materials 12 (2) (1997) 169–174.
[15] R.F. Cook, B.R. Lawn, A modified indentation toughness technique, Journal of the American Ceramic Society 66 (11) (1983) C200–C201.
[16] T. Guohong, Hot press reaction sintering and mechanical properties of boron carbide, Materials Science Progress 7 (6) (1993) 517–520.
[17] A.G. Evans, Perspective on the development of high toughness ceramics, Journal of the American Ceramic Society 73 (2) (1990) 187–195.
[18] R.W. Steinbrech, Toughening mechanisms for ceramic materials, Journal of the European Ceramic Society 10 (1992) 131–142.
[19] M. Taya, S. Hayashi, A.S. Kobayashi, Toughening of a particulate-reinforced ceramic matrix composite by thermal residual stress, Journal of the American Ceramic Society 75 (5) (1990) 1382–1391.
[20] B. Lin, T. Iseki, Effect of thermal residual stress on mechanical properties of SiC/TiC composites, British Ceramic Transactions 91 (1992) 1–5.