JOURNAL OF MATERIALS SCIENCE 25 (1990) 580–584

Improvements in mechanical properties of TiB_2 by the dispersion of B_4C particles

EUL SSON KANG, CHONG HEE KIM
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, PO Box 131, Cheongryang, Seoul, Korea

Densities up to 99% of the theoretical value were achieved by hot-pressing of TiB_2–B_4C composites at 1700° C for 1 h using 1 vol% Fe as a sintering aid. The microstructure consists of dispersed B_4C particles in a fine-grained TiB_2 matrix. Addition of B_4C particles increases the fracture toughness of TiB_2 (to 7.6 MPa m$^{1/2}$ at 20 vol% B_4C) and yields high fracture strength (to 700 MPa at 10 vol% B_4C). Microstructural observations indicate that the improved strength is a result of a higher density, smaller grain size and intergranular fracture, and the toughness increase is a result of crack deflection around the B_4C particles.

1. Introduction

Titanium diboride which is mainly covalently bonded, has a high melting point (2980° C) and high hardness (2300–2800 kg mm^{-2}) [1, 2]. Also it has a good thermal and electrical conductivity. It is wet by molten metals, resists molten metals and molten halides [3]. Sintered TiB_2 components have been used as cathodes for Hall Heroult cell [4]. Moreover TiB_2 ceramics can be used as light weight armour materials and cutting tools [2, 5]. These superior properties of TiB_2 make it possible that TiB_2 based ceramics could be used as structural materials. But it's use is restricted because of an intrinsic brittle character of TiB_2 like other ceramics. Therefore the improvement of fracture toughness of TiB_2 ceramics is required for the application of structural materials.

Fracture toughness can be increased by several mechanisms, such as phase transformation, microcracking, crack deflection toughening, etc. [6–8]. All of these mechanisms are available in some ceramics, however crack deflection toughening is used to optimize high temperature toughness due to its independence on temperature [9].

Crack deflection can occur when a propagating crack tip meets a residual strain field or a reduced grain boundary. This deflection improves the fracture toughness, because the crack driving force at the crack tip is reduced [10, 11]. Some investigations have demonstrated strength and toughness increase in a ceramic matrix by the dispersion of a second phase which has a slightly different thermal expansion coefficient and elastic modulus from those of the matrix [8, 12, 13]. In these cases, toughening and strengthening were attributed to crack deflection caused by the interaction of the crack tip with a residual strain field that surrounded the second phase inclusions [8, 12, 13].

In the present work, the improvements in mechanical properties of TiB_2 by B_4C dispersions were studied using iron as a sintering aid. It was revealed that iron and B_4C were appropriate additives for the sintering of TiB_2 in our previous work [14]. The sintering was conducted via hot-pressing at the condition of 1700° C and 35 MPa. Microstructures of TiB_2 based ceramics correlated with B_4C addition are presented, and the role of B_4C addition on the fracture strength and fracture toughness are discussed.

2. Experimental procedure

Titanium diboride (Japan New Metal Co. Ltd., Tokyo, Japan) and boron carbide (Tetrabor, Electroschmelzwerk Kempten GmbH, Munchen, FRG) powders were used as-received. The major impurities in TiB_2 were oxygen (0.46 wt %), carbon (0.43 wt %) and nitrogen (0.38 wt %). The average particle size of TiB_2 and B_4C was about 2.4 and 2.5 μm, respectively.

The titanium diboride powders together with boron carbide and 1 vol % iron (Teledyne Wah Chang, Albany, OR) were mixed in a polypropylene bottle with TiB_2 balls in acetone and then dried at room temperature. The composition of powder mixtures were selected so that the contents of B_4C in the final sintered body were 0, 10, 20 and 30 vol %, respectively. The dried powders after being screened to -60 mesh were used for hot-pressing.

The hot-pressing was accomplished as follows. The granulated powder mixtures were loaded into a graphite die with inner diameter of 20 mm. The cylindrical surfaces and punch faces of the dies were lined with a BN coating. The amounts of powder were selected so that the thickness of the resulting ceramic discs was 4 mm thick. The powder charged die was fired in a furnace (Centorr Associates, Inc., Suncook, New Hampshire, USA) with a tungsten-mesh heating element to 1700° C in argon atmosphere. Heating rate was 20° C min^{-1}. Uniaxial pressure was applied to the die punches via the pressure rams to the total pressure of 35 MPa. The shrinkage during soaking time mostly occurred in 30 min. So 60 min was enough time for obtaining fully dense TiB_2 ceramics at that condition.

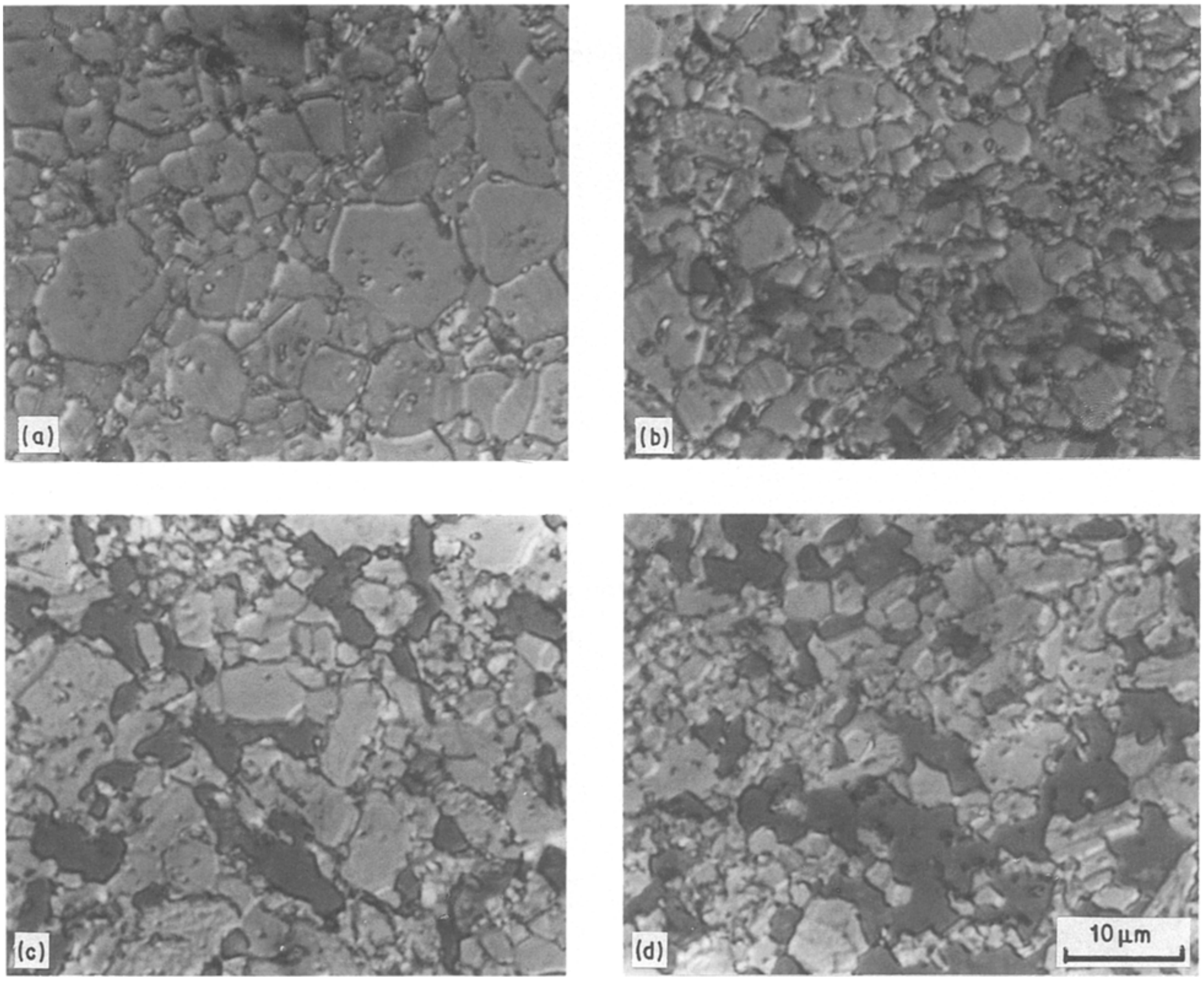

Figure 1 Optical micrographs of TiB_2-based ceramics with various compositions of B_4C. Bright phases are TiB_2 grains and gray phases are B_4C grains. Specimens with the compositions of (a) TiB_2–1 Fe, (b) TiB_2–10 B_4C–1 Fe, (c) TiB_2–20 B_4C–1 Fe and (d) TiB_2–30 B_4C–1 Fe were hot-pressed at 1700° C, 35 MPa for 1 h.

The surfaces of hot-pressed discs were removed, and then the sintered density of the specimen was determined by the Archimedes method. The theoretical densities were calculated by using a rule of mixture, assuming that only TiB_2, B_4C and Fe were present because other phases were not detected by XRD.

The grain structure was revealed by chemical etching of polished specimens in 10 HCl–1 HNO_3 solution at room temperature for 30 sec. The microstructure was observed using an optical microscope in an interference contrast mode, and fracture surface was observed using scanning electron microscope (SEM, Model 200 CX, JEOL, Tokyo, Japan).

The bar specimens of the required dimensions (1.2 mm thick and 1.5 mm width) were cut from the discs by an oil-lubricated diamond saw and then the surfaces were ground in the direction parallel to the bar length with 6 μm diamond grinding wheel, and edges were similarly bevelled. Flexural strength was measured by three-point bending with a 12 mm span at a loading rate of 0.5 mm min^{-1}. Fracture toughness was measured by indentation method using a Vickers indenter [15] with an applied load of 98 N.

3. Results and discussion

3.1. Microstructure

It is well known that densification of pure TiB_2 ceramics to a reasonably high sintered density is difficult because of its high melting point (2980° C) and low bulk diffusivity [16]. Densification has been enhanced with a small addition of iron or nickel to TiB_2 using either pressureless sintering or hot-pressing [2, 14]. In the present work, iron was used as a sintering aid for obtaining a fully dense TiB_2 ceramics (up to 99% of theoretical density), so that the effect of porosity on the fracture toughness might be minimized.

The microstructures of TiB_2 ceramics with 1 vol % Fe containing from 0 to 30 vol % B_4C are shown in Fig. 1, and their densities and average grain sizes are given in Table I. The microstructures show that the specimens contain equiaxed TiB_2 grains (4–7 μm in size) and 3–5 μm B_4C grains dispersed in the matrix. The addition of B_4C slightly increased the density of sintered body, and reduced the average grain size of TiB_2 because B_4C acted as a grain growth inhibitor [14]. These results suggest that the addition of B_4C may improve mechanical properties of TiB_2 ceramics because of its higher density and smaller grain size.

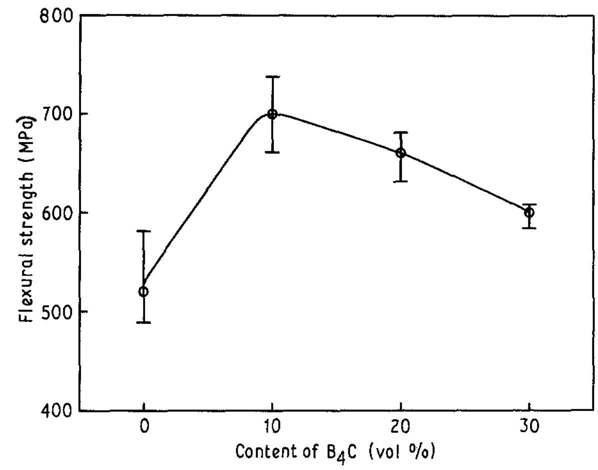

Figure 2 Room temperature flexural strength of TiB_2 with 1 vol % Fe as a function of B_4C content. Error bars represent minimum and maximum value of five test specimens.

TABLE I Relative densities and grain sizes of TiB_2 and B_4C of TiB_2-based ceramics as a function of B_4C content

		B_4C content (vol %)			
		0	10	20	30
Relative density (%)		99.0	99.5	99.5	97.5
Grain size*	TiB_2	6.38	4.88	4.42	4.28
(μm)	B_4C	–	2.97	4.12	4.54

*Measured by line intercept method.

3.2. Fracture strength

Figure 2 shows the room temperature flexural strength of TiB_2 ceramics with 1 vol % Fe as a function of B_4C content. The flexural strength has a maximum value of 700 MPa at the composition of TiB_2–10 vol % B_4C–1 vol % Fe, and it decreased slowly with further increase of B_4C content. The strength of a polycrystalline ceramic is influenced by many factors, such as grain size, porosity (or density), fracture mode, etc. Low porosity (or high density), small grain size and intergranular fracture are necessary conditions which can show high strength.

As B_4C was added to TiB_2 ceramics, the grain size of TiB_2 was reduced and density was slightly increased as mentioned in the previous section. Furthermore, intergranular fracture occurred when B_4C was added to TiB_2 ceramics, whereas the fracture mode of the specimen without added B_4C was mainly transgranular, as shown in Fig. 3. These may be the reasons why the strength is increased as B_4C is added to TiB_2 ceramics. As B_4C content exceeds 20 vol %, the strength is slightly decreased. These results can be explained by microstructural changes. As shown in Fig. 4, abnormally grown B_4C grains (about 40 μm) are observed in specimens with both 20 and 30 vol %

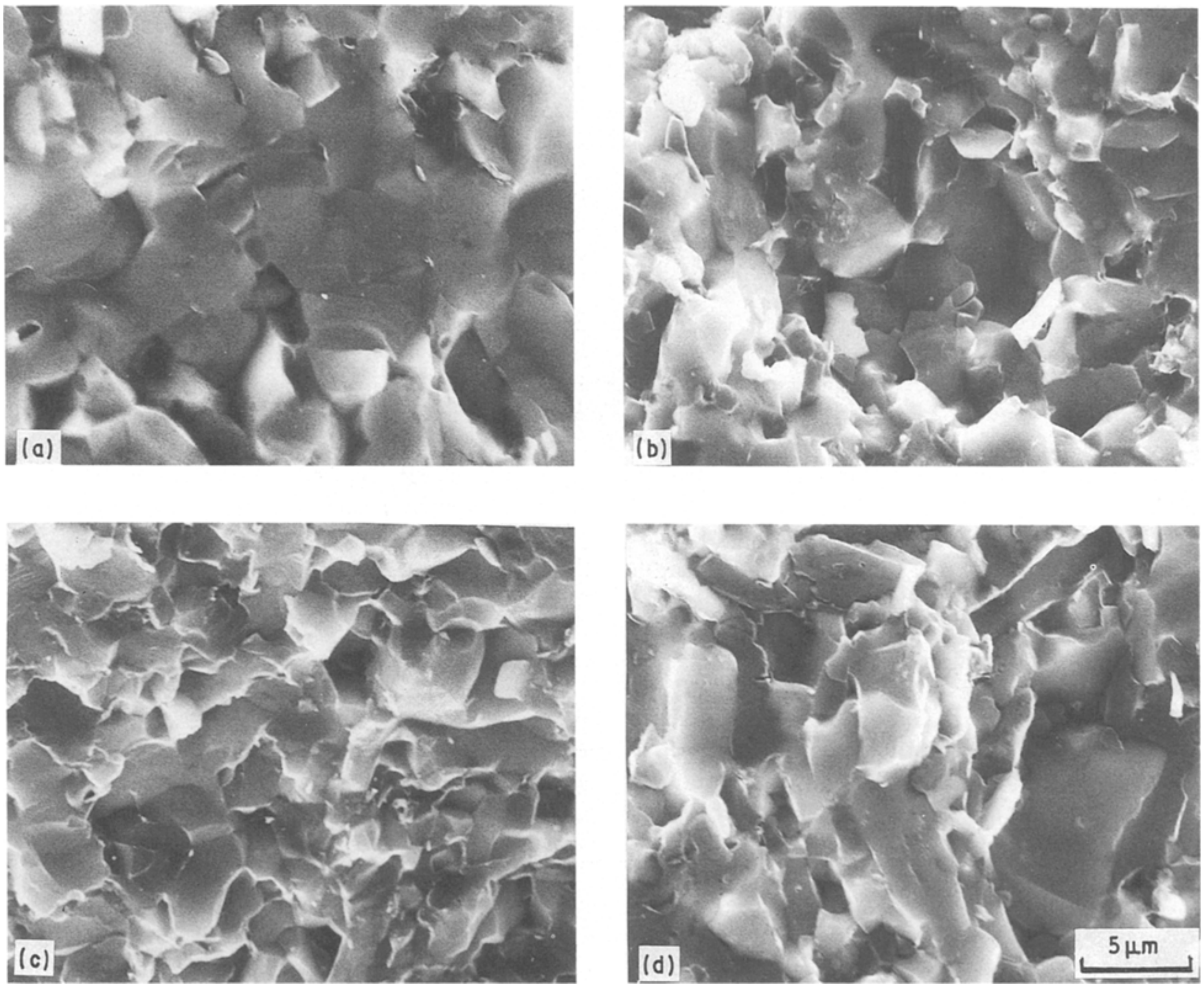

Figure 3 Scanning electron micrographs of TiB_2-based ceramics with various compositions of B_4C. Specimens with the compositions of (a) TiB_2–1 Fe, (b) TiB_2–10 B_4C–1 Fe, (c) TiB_2–20 B_4C–1 Fe and (d) TiB_2–30 B_4C–1 Fe were hot-pressed at 1700° C, 35 MPa for 1 h.

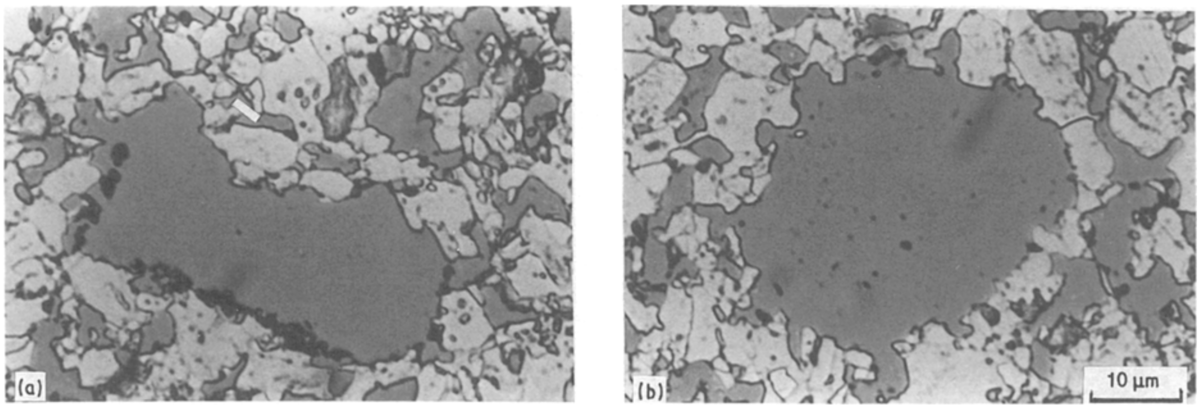

Figure 4 Optical micrographs showing the abnormally grown B_4C grain in the specimens with the compositions of (a) TiB_2–20 B_4C–1 Fe and (b) TiB_2–30 B_4C–1 Fe.

B_4C. Although it is not known why the abnormal grain growth of B_4C occurred, the large B_4C grains may reduce the strength of these composites. In various ceramics, particularly noncubic ceramics, the grain size dependence of fracture strength is related to the residual stress introduced by the anisotropy of thermal expansion coefficient [17–19]. B_4C and TiB_2 are anisotropic. The large B_4C grains diminished strength, as expected.

So it was concluded that the TiB_2 ceramics were strengthened by the dispersions of B_4C particles which reduced the average grain size of the TiB_2 matrix, slightly increased the sintered density, and induced intergranular fracture. As the B_4C content exceeded 20 vol %, the strength slightly diminished, but it was still higher than that of the specimens without B_4C addition.

3.3. Fracture toughness

Figure 5 shows the room temperature fracture toughness of TiB_2 based composites with 1 vol % Fe addition as a function of B_4C content. The fracture toughness of TiB_2 ceramics increased as B_4C content was increased, and reached maximum value at the composition of TiB_2–20 vol % B_4C–1 vol % Fe, and then decreased with further increase of B_4C content. But all of the TiB_2–B_4C composites show a higher toughness than TiB_2 ceramics without B_4C.

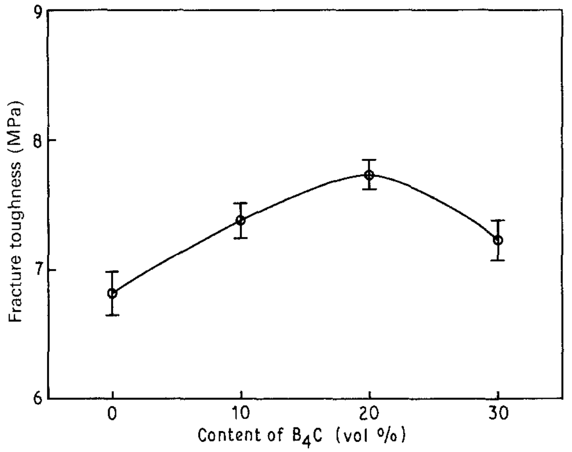

Figure 5 Room temperature fracture toughness of TiB_2 with 1 vol % Fe as a function of B_4C content. Error bars represent standard deviation.

Figure 6 shows crack deflection profiles from Vickers indentation cracks. The crack profile is nearly flat in TiB_2 ceramics with only iron addition, but large amounts of crack deflection occurred in all specimens with added B_4C. These results confirm that the added B_4C has induced crack deflection, which results in the increase of the toughness in TiB_2–B_4C particulate composites. Crack deflection processes can operate when a propagating crack tip interacts with a residual strain field or a weak interface. The crack deflection increases the fracture toughness, because the stress intensity at the propagating crack tip is decreased hence the crack driving force is reduced [10, 11]. The reduced grain-boundary fracture resistance that establishes a basis for crack deflection may be attributed to several interrelated effects. Improper processing can result in residual grain-boundary porosity, or impurities may segregate along a grain boundary [11]. In the present work, the grain-boundary phases in all compositions used here are similar to the Fe–Ti–B compound [14, 20]. Furthermore, the porosity difference in specimens with different composition may be negligible as shown in the microstructure section. So the possibility of crack deflection due to a weak grain boundary can be excluded.

Therefore, it is considered that the crack deflection occurred due to a residual strain field which is introduced during a cooling process because of some differences in modulus and/or thermal expansion coefficient between TiB_2 and B_4C. According to the method of Evans and Langdon [21], the stress at the interface between the B_4C particles and TiB_2 matrix, σ_{mr}, can be calculated to be $\sigma_{mr} = -260$ MPa. This stress resulted in a deflection of a propagating crack, as a result the toughness of these composites was increased.

4. Conclusions

TiB_2–B_4C polycrystalline composites with added iron as a sintering aid were hot-pressed up to 99% of theoretical density. Addition of B_4C resulted in a small increase in the sintered density and a decrease in the average grain size of TiB_2. Also the addition of B_4C induced intergranular fracture, whereas the fracture was mainly transgranular in the specimen without added B_4C. As a result, the fracture strength was increased by the addition of B_4C. The addition of B_4C

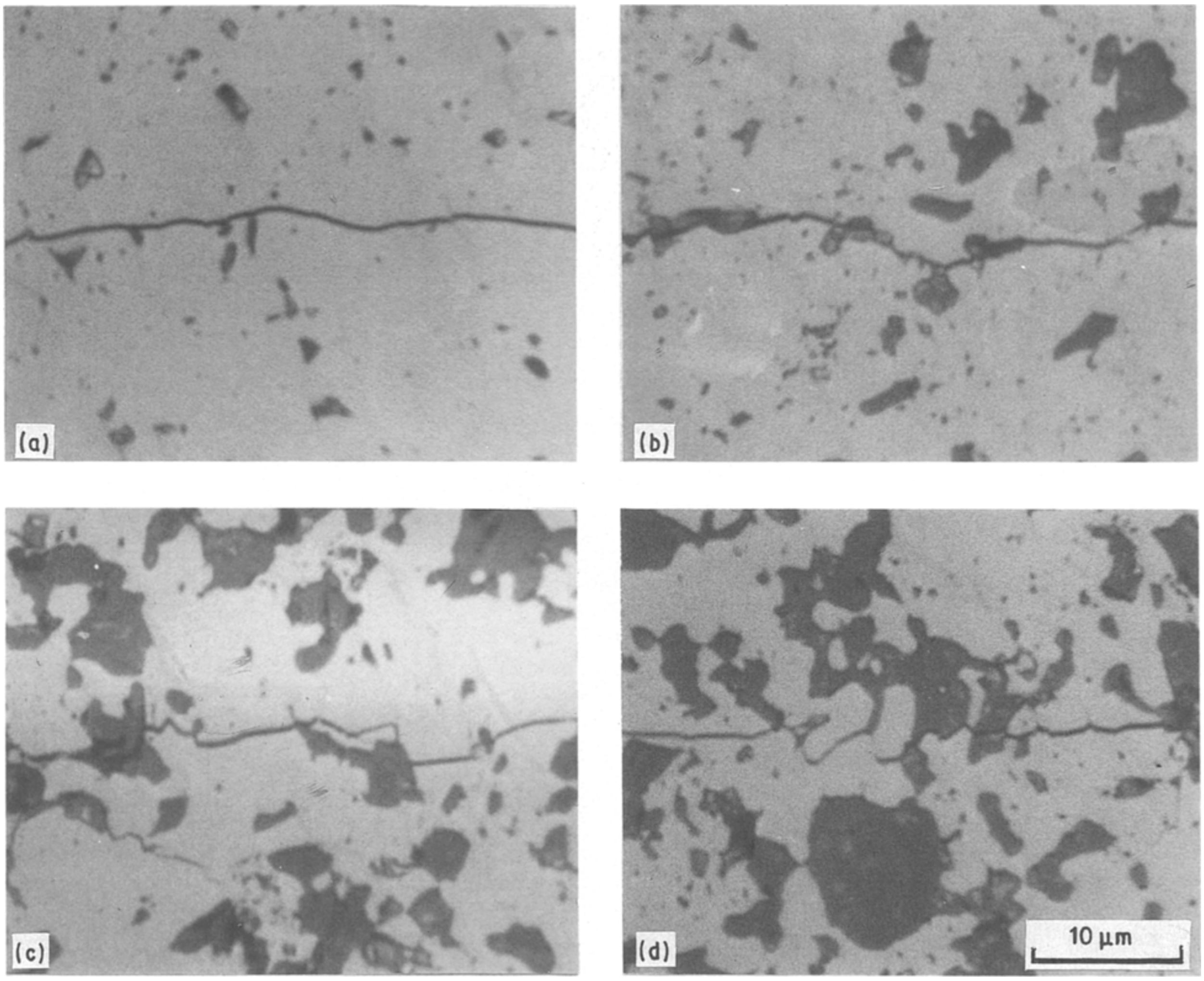

Figure 6 Crack deflection profiles from Vickers indentation cracks in the specimens with the compositions of (a) TiB_2–1 Fe, (b) TiB_2–10 B_4C–1 Fe, (c) TiB_2–20 B_4C–1 Fe and (d) TiB_2–30 B_4C–1 Fe.

also resulted in a considerable increase in the fracture toughness. It was considered that the toughening was ascribed to crack deflection caused by residual strain field which was generated during the cooling process because of differences in the thermal expansion coefficient and/or elastic modulus between TiB_2 and B_4C.

References

1. G. V. SAMSONOV and B. A. KOVENSKAYA, "Boron and Refractory Borides", edited by V. I. Matkovich (Springer-Verlag, New York, 1977) p. 19.
2. V. J. TENNERY, C. B. FINCH, C. S. YUST and G. W. CLARK, "Science of Hard Materials", edited by R. K. Viswanadham (Plenum, New York, 1983) p. 891.
3. T. LUNDSTROM, "Boron and Refractory Borides", edited by V. I. Matkovich (Springer-Verlag, New York, 1977) p. 351.
4. J. B. TODD, *J. Metals* **33**(9) (1981) 42.
5. M. L. WILKINS, "Boron and Refractory Borides", edited by V. I. Matkovich (Springer-Verlag, New York, 1977) p. 633.
6. R. M. McMEEKING and A. G. EVANS, *J. Amer. Ceram. Soc.* **65** (1982) 242.
7. A. G. EVANS and K. T. FABER, *ibid.* **67** (1984) 255.
8. G. C. WEI and P. F. BECHER, *ibid.* **67** (1984) 571.
9. A. G. EVANS, "Fracture in Ceramic Materials", edited by A. G. Evans (Noyes, New Jersey, 1984) p 1.
10. K. T. FABER and A. G. EVANS, *Acta Metall.* **31** (1983) 565.
11. *Idem, J. Amer. Ceram. Soc.* **66** (1983) c-94.
12. M. K. JANNEY, *Amer. Ceram. Soc. Bull.* **66** (1987) 322.
13. C. H. McMURTRY, W. D. G. BOECKER, S. G. SESHDRI, J. S. ZANGHI and J. E. GARNIER, *ibid.* **66** (1987) 325.
14. E. S. KANG, C. W. JANG, C. H. LEE, C. H. KIM and D. H. KIM, *J. Amer. Ceram. Soc.* to be published.
15. R. H. MARION, "Fracture Mechanics Applied to Brittle Materials," edited by S. W. Freiman (ASTM STP 678, Pennsylvania, 1979) p. 103.
16. H. PASTOR, "Boron and Refractory Borides," edited by V. I. Matkovich (Springer-Verlag, New York, 1977) p. 457.
17. R. W. RICE, S. W. FREIMAN and P. F. BECHER, *J. Amer. Ceram. Soc.* **64** (1981) 345.
18. R. W. RICE and S. W. FREIMAN, *ibid* **64** (1981) 350.
19. P. F. BECHER and M. K. FERBER, *Acta Metall.* **33** (1985) 1217.
20. D. K. KIM and C. H. KIM, *Adv. Ceram. Mater.* **3** (1988) 52.
21. A. G. EVANS and T. G. LANGDON, *Prog. Mater. Sci.* **21** (1976) 171.

*Received 3 January
and accepted 14 April 1989*