

# Densification and mechanical properties of mullite/TiO<sub>2</sub>-coated B<sub>4</sub>C composites

Hailei Zhao\*, Keisuke Hiragushi, Yasuo Mizota

*Okayama Ceramic Research Foundation, 1406-18 Nishikatakami, Bizen, Okayama 705-0021, Japan*

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## Abstract

Mullite/TiO<sub>2</sub>-coated B<sub>4</sub>C composites with up to 40 wt.% B<sub>4</sub>C were fabricated by coating B<sub>4</sub>C powders with Ti-chelate compounds via a sol-gel method prior to the hot-pressing of mullite/B<sub>4</sub>C mixtures at 1600 °C for 1 h. The effects of TiO<sub>2</sub>-coated B<sub>4</sub>C on the densification and the mechanical properties of mullite/B<sub>4</sub>C composites were investigated. TiO<sub>2</sub> reacts with B<sub>4</sub>C at high temperatures to produce B<sub>2</sub>O<sub>3</sub> and TiB<sub>2</sub>, both seems to be favorable for the densification of mullite/B<sub>4</sub>C composites. The formation of TiB<sub>2</sub>, besides, may lead to the generation of thermal residual stresses, which is deemed to be beneficial to the fracture toughness but detrimental to the flexural strength. The mechanical properties of mullite/B<sub>4</sub>C composites such as hardness, flexural strength and fracture toughness, are enhanced remarkably with the increasing addition of B<sub>4</sub>C. However, with a B<sub>4</sub>C addition more than 20 wt.%, the flexural strength tends to decrease gradually, probably due to the increasing residual stresses originated from the thermal mismatch of TiB<sub>2</sub> with mullite and B<sub>4</sub>C matrix. B<sub>4</sub>C contents above 30 wt.% easily cause the aggregation of B<sub>4</sub>C particles in mullite matrix, which will lower the degree of improvement in fracture toughness.

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## 1. Introduction

Boron carbide (B<sub>4</sub>C) has attracted much attention due to its interesting properties such as high hardness, low density and high melting point. It has been profoundly used in various wearing systems. However, the relatively low sinterability owing to its rigid covalent bonds and associated low ions diffusion mobility has restricted its wide application as structural materials. Many efforts have been made to improve the densification of B<sub>4</sub>C by introducing sintering aids including non-oxides (AlF<sub>3</sub>, TiB<sub>2</sub>, W<sub>2</sub>B<sub>5</sub>, SiC, TiC), oxides (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>), and metals (Al, Mg, Ni, Fe, Cu, Si) as well as B and C.<sup>1–11</sup> On the other hand, B<sub>4</sub>C, as a reinforcement, appears to be a promising candidate in improving the performance of structural materials. Some works have been attempted to incorporate B<sub>4</sub>C into metal materials to enhance its mechanical properties.<sup>12–14</sup> Also, many interesting

results were reported recently to reinforce the non-oxide ceramic by addition of B<sub>4</sub>C particle to its matrix.<sup>15,16</sup> However, there have been a very limited number of studies using B<sub>4</sub>C as a strengthening agent for oxide ceramic material, simply because of its chemical incompatibility with the oxide matrix.<sup>17,18</sup> A potential method to inhibit this reaction between B<sub>4</sub>C and the oxide matrix is to produce a coating layer, serving as a barrier, on the surface of B<sub>4</sub>C particles prior to inserting it into an oxide matrix.

Mullite and mullite-matrix composite are important structural materials because of their excellent high temperature performance.<sup>19</sup> The disadvantages of mullite materials are their relative low toughness and strength at ambient temperature.<sup>20,21</sup> One strategy that has been widely adopted by many investigators to toughen ceramic is the incorporation of rigid particles into ceramic matrix. Thus, the addition of B<sub>4</sub>C to mullite matrix may have the potential to improve its mechanical properties due to the toughening by particle inclusion. In this study, Ti-containing organic compound has been investigated as a coating substance to reduce the reactivity of B<sub>4</sub>C with mullite.

\* Corresponding author at present address: Department of Inorganic Nonmetallic Material, Materials Science and Engineering School, University of Science and Technology Beijing, Beijing 100083, China.

*E-mail address:* zhhailei@yahoo.com (H. Zhao).

## 2. Experimental procedure

Boron carbide (Wako Pure Chemical Industries, LTD, Japan) and di-*i*-propoxy bis acetylacetonato titanium (T-50, Nisso Chemical Industries, Ltd., Japan) were used as a starting material and a coating substance, respectively. Mullite powders were synthesized by gelling a mixture of silica and alumina sols (all from Nissan Chemical Industries, LTD, Japan) via sol-gel method prior to calcining at 1300 °C for 2 h. The synthesized mullite powder and commercial boron carbide powder were ball-milled respectively in ethanol for 48 h with high-purity Al<sub>2</sub>O<sub>3</sub> balls. Powder characterization was conducted after a 30-min ultra-sound deagglomeration by the BET method. The specific surface area of mullite and B<sub>4</sub>C powders is 8.2 and 6.1 m<sup>2</sup>/g, respectively.

The obtained B<sub>4</sub>C powder was firstly dispersed into ethanol containing the desired amount of T-50 by using a homogenizer for 30 min and followed by an ultrasonic stirring for 10 min, then dried with a rotary evaporator under reflux condition. The B<sub>4</sub>C powders coated by titanium chelate compound were heat-treated at 300 °C in air for 2 h to decompose the organic radical and thus create a TiO<sub>2</sub> coating layer on the particle surface of B<sub>4</sub>C. Carbon analysis at 500 °C indicated that almost no carbon element was remained in the coating layer after 300 °C-heat treatment. The coating amount of TiO<sub>2</sub> on B<sub>4</sub>C powders was 2, 4 and 6 wt.%, respectively. The TiO<sub>2</sub>-coated B<sub>4</sub>C powders were blended with mullite powders in ethanol at a ratio of 10–40 wt.% B<sub>4</sub>C in mullite powder in a homogenizer, and then dried in a rotary vacuum evaporator. They were hot-pressed in a boron nitride lined graphite die (φ50 mm) at 1500 and 1600 °C, respectively, with an applied load of 30 MPa in a flowing Ar atmosphere for 1 h.

Phase identification was conducted by X-ray diffraction (XRD) analysis. The bulk density was measured by the Archimedes method. Theoretical densities were calculated using the rule of mixtures on the basis of starting blends. The samples for mechanical testing were cut and ground with a diamond wheel, then the tensile surface of the specimens was polished with diamond slurries down to 1 μm and the edges were beveled. The dimensions of all specimens tested in this investigation were 3×4×36 mm. The flexural strength was measured by a three-point flexural test and the bending load was applied parallel to the hot-pressing axis with span 30 mm and crosshead speed of 0.5 mm/min. Hardness ( $H_V$ ) was evaluated by Vicker's indentation under 98 N load with a loading duration of 10 s in air. Fracture toughness ( $K_{IC}$ ) at room temperature was determined simultaneously by the indentation fracture (IF) method.  $K_{IC}$  values were calculated using the following empirical equation for a median crack:

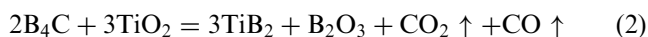
$$K_{IC} = 0.203(c/a)^{-3/2} H_V a^{1/2} \quad (1)$$

where  $c$  and  $a$  are the lengths of a median crack and half of a diagonal of an indentation, respectively. The microstructure of samples was characterized by scanning electron microscopy (SEM, JSM-6400, Jeol Ltd., Japan). The SEM specimens were precoated with carbon to eliminate charging.

## 3. Results and discussion

In order to suppress the reaction between mullite and B<sub>4</sub>C, di-*i*-propoxy bis acetylacetonato titanium was used as a coating substance in the present research. Various amounts of it were coated on B<sub>4</sub>C powders by a sol-gel method to produce 0.5, 1, 2, 4 and 6 wt.% TiO<sub>2</sub> coating layer on B<sub>4</sub>C particle surface, respectively, by a heat-treatment at 300 °C in air for 1 h. The XRD patterns of samples composed of 80 wt.% mullite and 20 wt.% B<sub>4</sub>C uncoated or coated by different amounts of TiO<sub>2</sub>, and sintered at 1600 °C in Ar atmosphere are shown in Fig. 1. It should be noted that B<sub>4</sub>C was difficult to be detected by XRD in this experiments for all of the investigated samples of mullite/B<sub>4</sub>C composite, probably due to the intrinsic nature of lower X-ray scattering in B and C. From Fig. 1 we can see that B<sub>4</sub>C reacts with mullite to form α-Al<sub>2</sub>O<sub>3</sub> and Al<sub>3</sub>SiB<sub>48</sub> such that no mullite remains when uncoated B<sub>4</sub>C is used, showing a high reactivity of B<sub>4</sub>C with mullite. After coating with Ti-chelate compound, this reaction can be suppressed to some extent. The peak intensities of α-Al<sub>2</sub>O<sub>3</sub> and Al<sub>3</sub>SiB<sub>48</sub> phases decrease with increasing amount of TiO<sub>2</sub> and eventually disappear above 2 wt.% TiO<sub>2</sub>, indicating that 2 wt.% TiO<sub>2</sub> is enough to inhibit the reaction between mullite and B<sub>4</sub>C.

In order to investigate the effect of TiO<sub>2</sub> on the densification and mechanical properties of mullite/B<sub>4</sub>C composites, samples composed of 90 wt.% mullite and 10 wt.% B<sub>4</sub>C coated by different amounts of TiO<sub>2</sub> were hot-pressed at 1600 °C in Ar for 1 h. Fig. 2 shows the changes of flexural strength and fracture toughness as a function of the amount of TiO<sub>2</sub>. The relative density of each sample is also indicated in the dash frame. As can be seen from Fig. 2, the fracture toughness exhibits an approximately linear increase with the addition of TiO<sub>2</sub>. The flexural strength increases with an increasing amount of TiO<sub>2</sub> up to 4 wt.% but then tends to become constant upon further additions of TiO<sub>2</sub>. This is considered to be related with the following reaction:



that occurs on the surface of B<sub>4</sub>C particles at high temperatures, as evidenced by the XRD pattern of TiO<sub>2</sub>-coated B<sub>4</sub>C powder heat-treated at 1350 °C in Ar atmosphere (shown in Fig. 3).

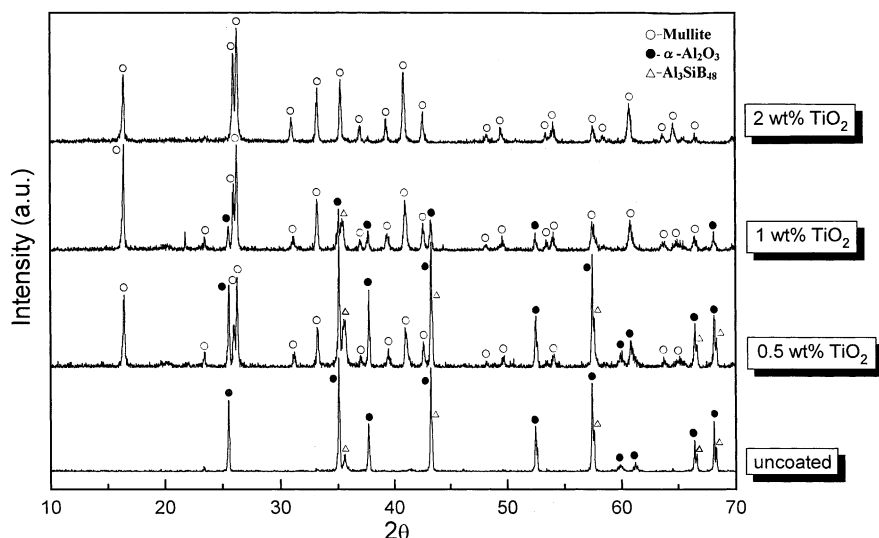


Fig. 1. XRD patterns of samples composed of 80 wt.% mullite and 20 wt.%  $B_4C$  uncoated or coated by different amounts of  $TiO_2$ , sintered at  $1600\text{ }^\circ\text{C}$  in Ar.

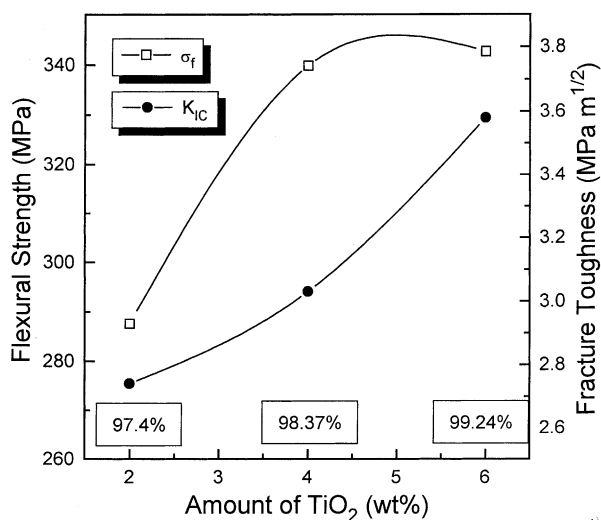


Fig. 2. Flexural strength and fracture toughness of mullite/10 wt.%  $B_4C$  composite hot-pressed at  $1600\text{ }^\circ\text{C}$  as a function of coating amount of  $TiO_2$ , with the indicated relative density.

As shown in Fig. 3,  $TiB_2$  and a little amount of  $Ti_3B_4$  are produced on the surface of  $B_4C$  grains at elevated temperatures. However,  $B_2O_3$  could not be detected by XRD, presumably due to either its low concentration in heat-treated sample or the amorphous state it taking. The formation of  $B_2O_3$  and  $TiB_2$  seems to be favorable to the densification of composite, and besides,  $TiB_2$  may result in the generation of thermal residual stress due to the thermal mismatch of  $TiB_2$  with matrix.  $B_4C$  and mullite have almost the same thermal expansion coefficient ( $4.5 \times 10^{-6}/^\circ\text{C}$  for  $B_4C$  and  $4.0 \times 10^{-6}/^\circ\text{C}$  for mullite),<sup>10,19</sup> whereas that for  $TiB_2$  is some higher ( $7.8 \times 10^{-6}/^\circ\text{C}$ ).<sup>15</sup> Thus, tensile stresses must exist inside the  $TiB_2$  grain but tangential compressive stresses and radial tensile stresses in the surrounding of mullite and  $B_4C$  grains. With the amount of  $TiO_2$  added more  $TiB_2$

formed, causing more residual stresses, which should be responsible for the steady increase in fracture toughness. Based on the above results, 4 wt.%  $TiO_2$  were decided to be used in the following investigation as the coating substance for  $B_4C$  powders.

It should be noted here that  $TiB_2$  was not distinguished in  $1600\text{ }^\circ\text{C}$ -sintered sample composed of 80 wt.% mullite and 20 wt.%  $B_4C$ . This can be ascribed to its lower content in the composite, about 0.4 wt.% to the base of mullite/ $B_4C$  composite, which is too little to be detected by XRD.

Fig. 4 shows the bulk density and relative density of mullite/ $TiO_2$ -coated  $B_4C$  composites hot-pressed at  $1600\text{ }^\circ\text{C}$  for 1 h as a function of  $B_4C$  content. Good densification has been achieved for all samples investigated. The relative density for samples with 10–30 wt.%  $B_4C$  is virtually constant, however, a slight decrease is exhibited by the sample with 40 wt.%  $B_4C$ . On the other hand, the bulk density shows a nearly linear decrease with the addition of  $B_4C$ , which is deemed to be related to the rule of mixtures. The density of  $B_4C$  ( $2.52\text{ g/cm}^3$ ) is lower than that of mullite ( $3.16\text{ g/cm}^3$ ).

The variations of Vicker's hardness, flexural strength and fracture toughness of  $1600\text{ }^\circ\text{C}$ -hot-pressed samples are illustrated in Figs. 5 and 6. Vicker's hardness is obviously enhanced by the addition of  $B_4C$ , which is attributable to the high hardness of  $B_4C$  and the rule of mixtures. With 40 wt.%  $B_4C$  added, a hardness of 18 GPa is obtained, which is 45% higher than that of pure mullite. The increase of hardness is not so obvious in the range of 0–20 wt.%  $B_4C$ , but becomes more significant upon further addition up to 40 wt.%  $B_4C$ . This shows that the slight decrease in relative density with the addition of  $B_4C$  has almost no impact on the hardness increase of mullite/ $B_4C$  matrix.

As shown in Fig. 6, the addition of  $B_4C$  also has significant effects on the flexural strength and the fracture

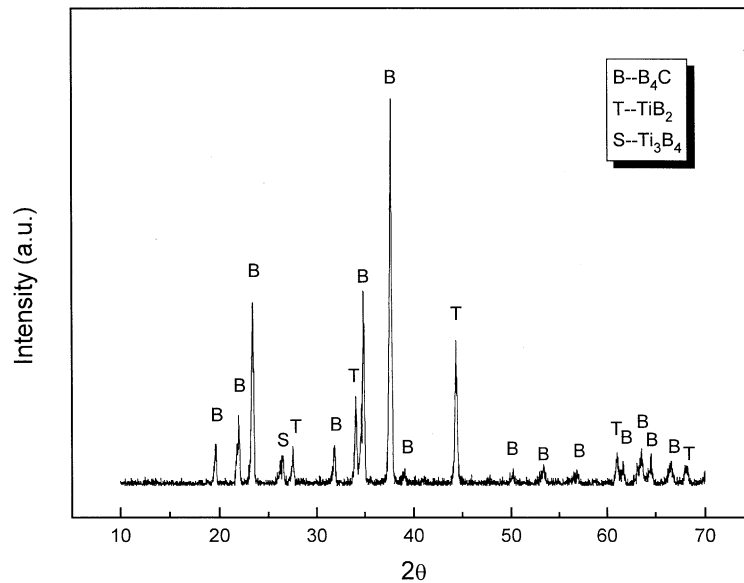


Fig. 3. XRD pattern of 4 wt.%  $\text{TiO}_2$ -coated  $\text{B}_4\text{C}$  powder heat-treated at  $1350^\circ\text{C}$  in Ar atmosphere.

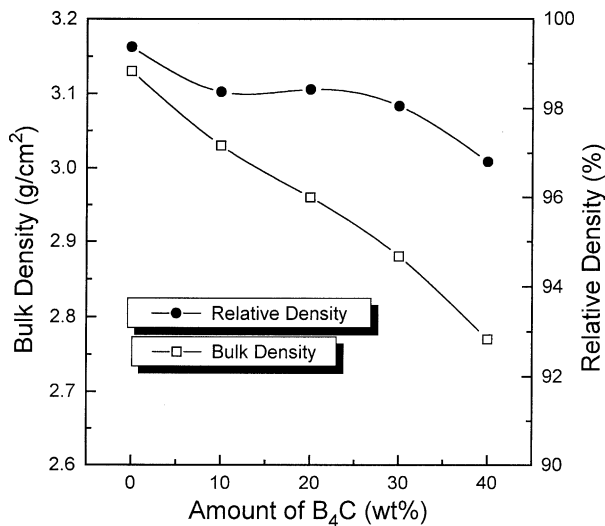


Fig. 4. Bulk density and relative density of mullite/ $\text{TiO}_2$ -coated  $\text{B}_4\text{C}$  composites hot-pressed at  $1600^\circ\text{C}$ .

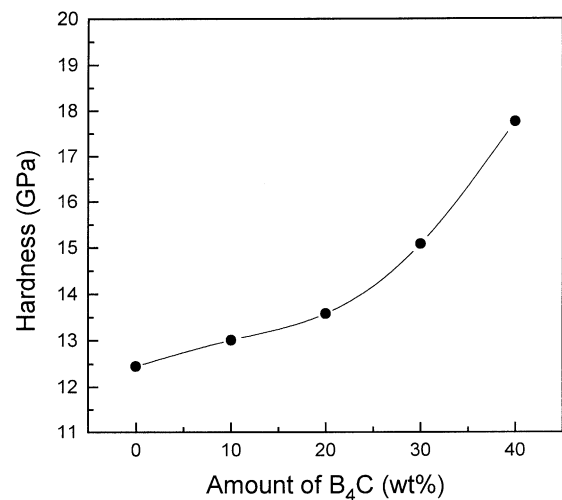


Fig. 5. Vicker's hardness versus the amount of  $\text{B}_4\text{C}$  coated by 4 wt.%  $\text{TiO}_2$ .

toughness of mullite. The flexural strength increases significantly from 250 to 500 MPa with the addition of 20 wt.%  $\text{B}_4\text{C}$ , followed by a decrease on further addition of  $\text{B}_4\text{C}$ . Two factors are considered to be most likely responsible for the variation of flexural strength. One is the strengthening effect of  $\text{B}_4\text{C}$  and another is the weakening effect of residual stresses and microcracks. It is expectable that the flexural strength of mullite increases with the addition of  $\text{B}_4\text{C}$ . However, residual stress caused by  $\text{TiB}_2$  in situ formed in composite according to Eq. (2) also increases with the increasing amount of  $\text{B}_4\text{C}$ , which is regarded to be detrimental to the flexural strength. The effect of residual stress and microcracks on flexural strength may not be obvious at a lower addition of  $\text{B}_4\text{C}$ , especially the sintered body

being in a high-dense status, whereas it may tend to be prominent when further  $\text{B}_4\text{C}$  added and so more  $\text{TiB}_2$  being formed. As a result, the flexural strength decreases with the addition of  $\text{B}_4\text{C}$  more than 20 wt.%. In addition, the big decrease in flexural strength for sample with 40 wt.%  $\text{B}_4\text{C}$  can be ascribed also, besides the residual stress, to its comparatively lower relative density.

Different from flexural strength, the fracture toughness increases steadily with the addition of  $\text{B}_4\text{C}$ , as shown in Fig. 6. Dispersion toughening is considered to be the main mechanism for the present mullite/ $\text{B}_4\text{C}$  composites in the improvement of fracture toughness. With the increasing addition of  $\text{B}_4\text{C}$ , the effect of crack deflection due to the hard particles of  $\text{B}_4\text{C}$  will be enhanced and thus resulting in the gradual increase in

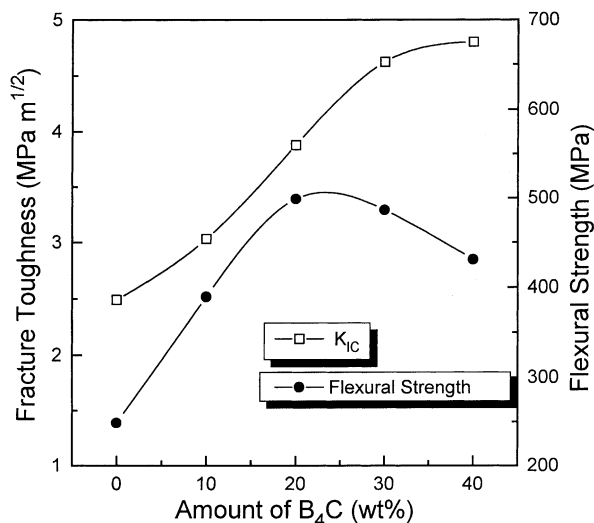


Fig. 6. Effect of B<sub>4</sub>C addition on flexural strength and fracture toughness of mullite/TiO<sub>2</sub>-coated B<sub>4</sub>C composites hot-pressed at 1600 °C.

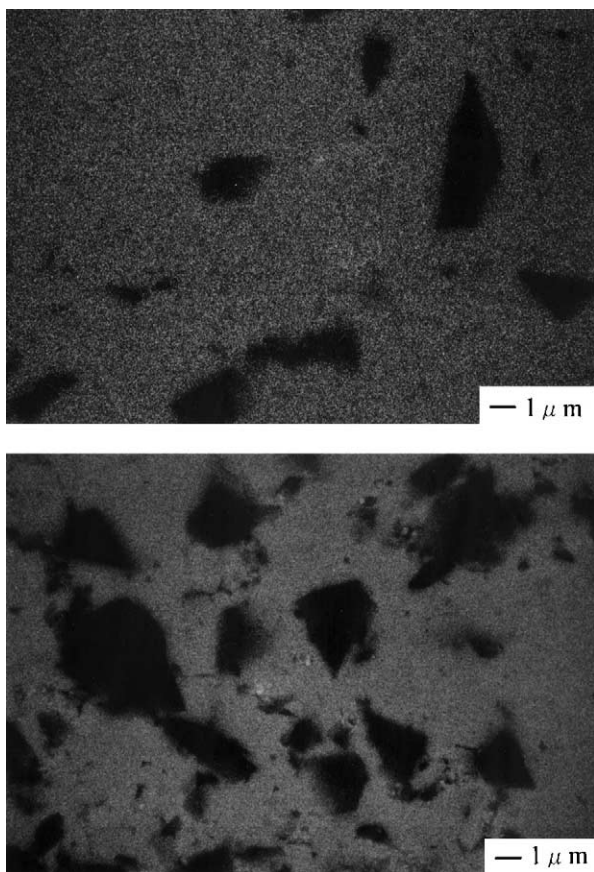


Fig. 7. Backscattered electron image of mullite/B<sub>4</sub>C composites, (a) 10 wt.% B<sub>4</sub>C and (b) 40 wt.% B<sub>4</sub>C.

fracture toughness of composites. On the other hand, the microcracks or thermal residual stress originated from the thermal mismatch of TiB<sub>2</sub> with mullite/B<sub>4</sub>C matrix is believed also to contribute to the enhancement of fracture toughness. The residual tensile stresses in the

radial direction of TiB<sub>2</sub> may easily allow the realization of crack bending or even crack microcracking during crack propagation.<sup>10,17</sup> Both the dispersion of B<sub>4</sub>C and the residual stress can increase the energy consumption during fracture process in the mullite/B<sub>4</sub>C composite via deflecting and bending the traveling cracks, and eventually changing the path of crack propagation, which is frequently observed in other systems.<sup>22,23</sup>

However, more addition of B<sub>4</sub>C particle readily cause the aggregation of B<sub>4</sub>C particles towards a relatively larger unit composed of several original B<sub>4</sub>C particles, as revealed by the SEM micrographs in Fig. 7. Only one times of deflection against the traveling crack can be implemented by this aggregated unit during crack propagation. In other words, the aggregated unit just acts as one particle of B<sub>4</sub>C in crack deflection process. This may weaken the effect of dispersion toughening, thus resulting in the slow increase in fracture toughness, as exhibited by sample with 40 wt.% B<sub>4</sub>C. Taking into account of the overall properties, 30 wt.% B<sub>4</sub>C/mullite composite, having a low density (2.89 g/cm<sup>3</sup>), a relatively high flexural strength (475 MPa) compared to the pure mullite, as well as an excellent fracture toughness (4.6 MPa·m<sup>1/2</sup>), is probably a good candidate as light-type structural materials for high-temperature applications.

#### 4. Conclusion

The reaction between mullite and B<sub>4</sub>C are suppressed by coating the B<sub>4</sub>C powders using Ti-chelate compound to form a TiO<sub>2</sub> layer on the surface of B<sub>4</sub>C particle. The effects of the amount of TiO<sub>2</sub> coating on B<sub>4</sub>C particles on the densification and the mechanical properties of mullite/B<sub>4</sub>C composite were investigated. TiO<sub>2</sub> will react with B<sub>4</sub>C at high temperatures to produce B<sub>2</sub>O<sub>3</sub> and TiB<sub>2</sub>. The former seems to be beneficial to the densification of mullite/B<sub>4</sub>C composite, while the latter will lead to the thermal residual stresses or microcracks at the grain boundary, which is favorable to the improvement of fracture toughness but detrimental to the flexural strength at a relatively high TiO<sub>2</sub> content. Considering the overall properties, 4 wt.% TiO<sub>2</sub> is selected as an optimum amount of coating substance for B<sub>4</sub>C powders.

Fully condensed mullite/TiO<sub>2</sub>-coated B<sub>4</sub>C composites are obtained by hot-pressing at 1600 °C for 1 h under 30 MPa. The mechanical properties of mullite/B<sub>4</sub>C composites, such as hardness, flexural strength and fracture toughness, are enhanced remarkably with the increasing addition of B<sub>4</sub>C. However, when the addition of B<sub>4</sub>C exceeds 20 wt.%, the flexural strength decreases. This can be ascribed to the thermal residual stress around the B<sub>4</sub>C particles originated from the thermal mismatch of TiB<sub>2</sub> with mullite/B<sub>4</sub>C matrix. From the view point of practical application, the composite of mullite/30 wt.%

B<sub>4</sub>C coated by 4 wt.% TiO<sub>2</sub> with a low density (2.89 g/cm<sup>3</sup>) and a high flexural strength (475 MPa) as well as an excellent fracture toughness (4.6 MPa.m<sup>1/2</sup>) is probably a good candidate for light-type structural materials at high-temperature.

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