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Improvement of thermal stability of diamond by adding Ti powder during sintering of diamond/borosilicate glass composites

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Abstract

Oxidization of diamond in the sintering process of diamond/glass composites results in thermal degradation of diamond and uncontrolled expansion of the bulk composites with many irregular pores, causing low bending strength of the composites. In this paper, Ti powder was used as oxygen getter due to its excellent affinity with oxygen. The results showed the diamond grits got good protection from oxidation during sintering due to the prior reaction of Ti powder with oxygen. As a result, expansion phenomenon was inhibited and bending strength was improved for the composites due to the Ti additives. TiO_2, as oxidization product of Ti, could enter into the glass network. The maximum bending strength and minimum volume expansion values were obtained for the composites with 6 wt.% Ti powder. This content resulted in a decrease of volume expansion from 22.78% to −25.0%, and an increase in bending strength from 28.49 MPa to 100.54 MPa.

Keywords: TiO_2; Cutting tool; Glass; Composites; Oxidization resistance

1. Introduction

Due to diamond's superior hardness and high wear resistance, diamond tools are used widely for grinding, cutting, drilling, and polishing strong materials, such as concrete, advanced ceramics, cemented carbides, and other hard materials.[1–3] These diamond tools are normally made of a composite material in which diamond particles are mixed together with a powder binding matrix and sintered. Three different bond systems, including resin, metal, and vitrified, are currently employed for the bonding of diamond grits into composite blocks.[4–6] Among these three categories of bonding agents, the vitrified bond has a relatively higher strength to hold the abrasive grains together, and a relatively easier dressing operation.[7,8] In vitrified wheels wear can occur through brittle fracture of the bond materials, allowing rapid emergence of new abrasives for continued grinding. Vitrified bonds are also of interest because the porosity level of the bond can be tailored to control bond facture, so that self-sharpening is facilitated and continuous grinding is established.[9–11]

Vitrified diamond tools are often fabricated using cold pressing at the sintering temperature of 700–900 °C and the bending strength are usually tens of MPa.[5,12–14] The highest strength reported is 37.1 MPa, which was the borosilicate glass composites with 90–106 μm diamonds prepared at 780 °C.[14] One major issue is oxidation and graphitization for diamond grains.[14–16] This would degrade the diamond grains and produce numerous pores in the matrix which weaken the retaining force of the grits and the bending strength of the composites.[14,17] In order to prevent thermal degradation of diamond grains, most bonding processes must be restricted to a certain temperature, resulting in a weak adhesion between diamond grains and bonds. A typical result of this insufficient adhesion is the significant pull-out of the diamond grains. A high sintering temperature is benefit to decrease the viscosity of the bonds melt, improve the wettability of diamonds by the melt,[17,18] and consequently obtain a full densification of the bonds and an excellent bonding strength between diamond grains and the bonds. Consequently, it is necessary to be sintering at high temperatures for a long time to achieve a high strength for the composites and a strong adhesion between

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diamond grains and bonds. In addition, an air atmosphere is also essential to remove organic impurities in the raw materials and organic binders introduced during cold pressing. So it is worth studying how to improve oxidization resistance of diamonds at high temperatures in air atmosphere.

The main focus in this paper is on realization of diamond/borosilicate glass composites prepared at a high temperature to assure a strong adhesion between the grains and the matrix but without thermal degradation of the grains. Active elements, which have an efficient getter for oxygen, are expected to provide sufficient oxidation resistance to the grains.

2. Experimental

Commercial grade borosilicate glass powder was used, and its composition is shown in Table 1. Synthetic diamond powder of crystal size 75–90 μm from Element Six Ltd., and Ti powder of particle size less than 5 μm were used. The matrixes used for those diamond/borosilicate glass composites were the borosilicate glass and Ti powder, and the respective batches prepared in the required composition were placed with ethanol and well mixed for 24 h in a ball mill. In order to investigate the effects of Ti contents on the properties of the diamond/borosilicate glass system, 0–10 wt.% Ti contents were selected. The batches were then fired at 80 °C for 48 h in an electric furnace. The Ti/glass matrix batches were cold pressed and then examined using

Table 1
Chemical composition of the borosilicate glass (wt.%).

SiO_2	Al_2O_3	B_2O_3	Na_2O	Fe_2O_3	K_2O
43.8	14.6	24.2	10	0.8	6.7

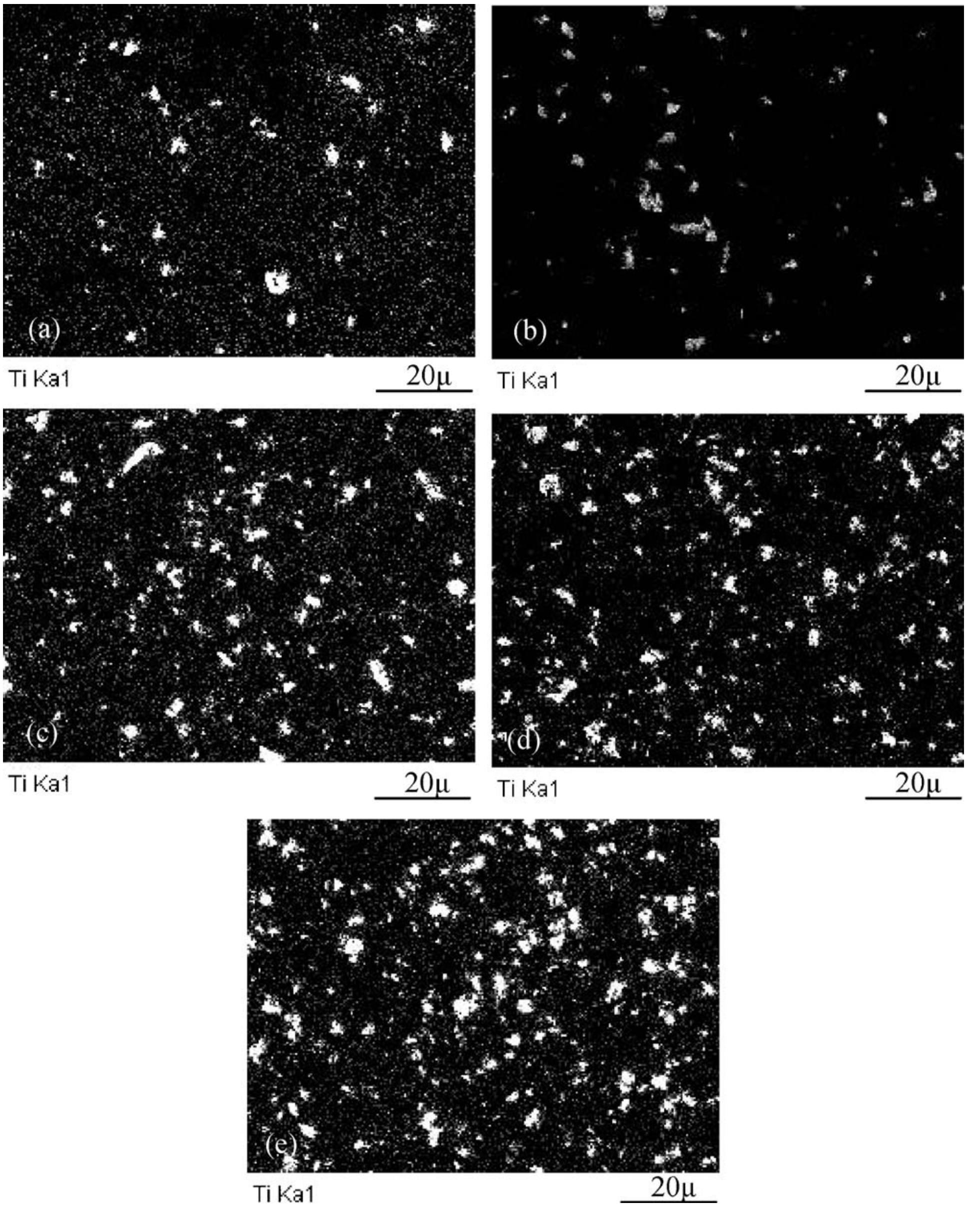

Fig. 1. EDS analysis of the composite matrices with: (a) 2 wt.% Ti; (b) 4 wt.% Ti; (c) 6 wt.% Ti; (d) 8 wt.% Ti; (e) 10 wt.% Ti.

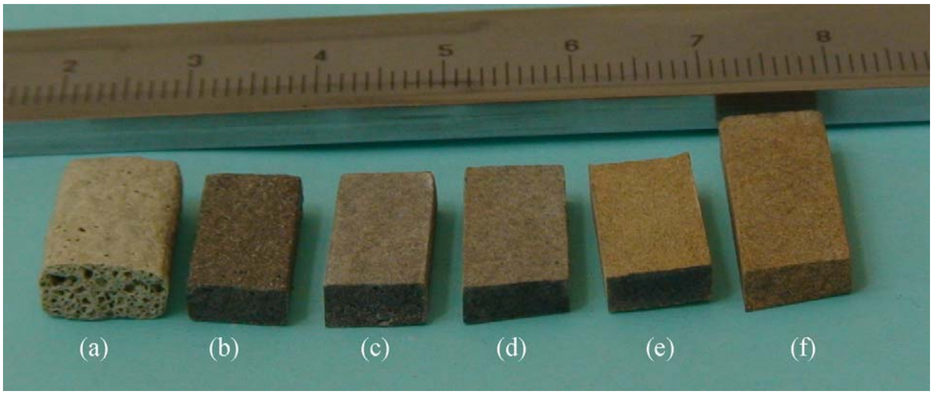

Fig. 2. Pictures for the sintered composites sintered at 850 °C with different Ti contents: (a) 0 wt.%; (b) 2 wt.%; (c) 4 wt.%; (d) 6 wt.%; (e) 8 wt.%; (f) 10 wt.%.

a S4800 field emission scanning electron microscope (SEM) attached to an energy-dispersive spectroscope (EDS) to observe the Ti distributions in the matrices.

All composite specimens were made by cold pressing and sintering. According to our previous studies, diamonds (65–85 μm) in the borosilicate glass melt at air atmosphere began to be oxidized at 817.7 °C.[17] So, the sintering temperature selected in this study was 750 and 850 °C, respectively. The weight percent of the diamonds were approximately 35% for all composites. The well-mixed powders of the diamond grits, the Ti/glass binding powders, and a temporary binder were pressed at 120 MPa for 3 min in a 40 mm × 8 mm × 2 mm mold. The composites were sintered under air atmosphere at 10 °C/min to 400 °C, holding for 30 min, and 10 °C/min to 750 or 850 °C, holding for 120 min. They were then cooled in the furnace.

The volumes of the bulk composites were measured by Archimedes law, and the volume expansion was calculated according to Eq. (1):

$$\Delta V = \frac{V_f - V_i}{V_i} \times 100 \qquad (1)$$

where V_i is the initial volume of the samples before sintering and V_f is the final volume after sintering.

The bending strength for each bulk composite was tested by using a three-point bending test conducted on a DKZ-5000 testing machine. Five tests were repeated for each sample, and the results were averaged. The resulting fracture surfaces from the bending tests were examined by SEM.

The diamond grits in the bulk composites were separated by mixture of hydrofluoric acid and sulfuric acid. The surface images and the compressive fracture strengths (CFS) of the grits before and after sintering were measured using SEM and the single grit method, respectively.

The thermal behavior of the powdered diamond/glass composites with various Ti contents was investigated by differential scanning calorimeter and thermogravimetry (DSC-TG) were conducted with a NETZSCH differential scanning calorimeter (Model STA449C, Germany). The samples were heated at 20 °C/min up to 1000 °C in flowing air.

The phase determination for all composites sintered at 850 °C was measured by means of X-ray diffraction (XRD). The measurements were carried out using a D/Max-2500pc diffractometer equipped with a standard Cu Kα radiation source employing a step size of 0.02° in 2θ. The range of 2θ angles is from 20° to 100°.

3. Results and discussions

The EDS results of the composite matrices with various Ti contents are shown in Fig. 1. The dark background and the bright islands represent the borosilicate glass and the Ti particles, respectively. The Ti particles are distributed throughout the entire bulk and have generally a regular rounded shape. The sizes of the particles are in the range of 3–7 μm. These mean that Ti powders did not agglomerate and had a good distribution in the glass matrix.

Fig. 2 shows pictures of diamond/borosilicate glass composites with different Ti contents sintered at 850 °C for 120 min. The composite without Ti additive showed an obvious expansion. The composites with various Ti contents were compacter than those without Ti additive.

The effect of Ti contents on the bending strength and volume expansion rate of the diamond/borosilicate glass composites sintered at 850 °C for 120 min is illustrated in Fig. 3. The composite without Ti additive showed a high expansion ratio (22.78%) and a low bending strength (28.49 MPa). Ti additive did improve the bending strength of the composites and decrease their volume

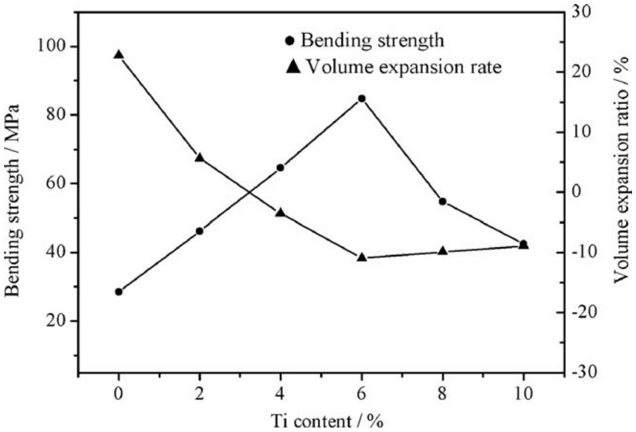

Fig. 3. Bending strength and shrinkage/swelling of the composites with different Ti contents, sintered at 850 °C for 120 min.

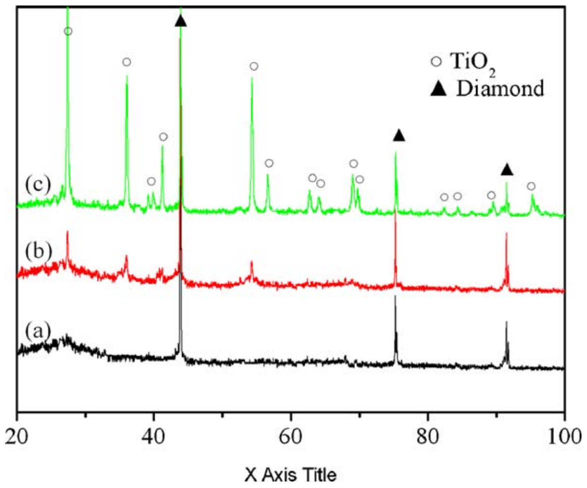

Fig. 4. XRD spectra of the composites sintered at 850 °C with (a) 4 wt.%; (b) 6 wt.%; (c) 8 wt.% Ti.

expansion rates. These results are in good agreement with those of Fig. 2. The composite gained extreme values of the bending strength and the volume expansion rate when Ti content was 6 wt.%. This content resulted in a volume expansion rate of −25.0%, and a bending strength of 84.94 MPa.

X-ray diffraction patterns were obtained for all specimens; examples for the samples with 4 wt.%, 6 wt.% and 8 wt.% Ti are shown in Fig. 4(a)–(c), respectively. Characteristic peaks of cubic diamond and vitreous phase can be clearly observed for all patterns. When Ti content was lower than 6 wt.%, except for cubic diamond and vitreous phase, no peak was found. This result implied that Ti had been oxidized into TiO_2 and resolved into the glass structure. So the bending strength of the composite improved with increasing Ti contents when Ti content was lower than 6 wt.%. Rutile TiO_2 peak could be confirmed for the composites in which Ti content was higher than 6 wt.%, and rutile TiO_2 increased with further increasing Ti contents. Because rutile TiO_2 could not enter into the glass structure, the bending strength of the composites decreased with increasing Ti contents when Ti content was higher than 6 wt.%. In all cases, diamond was protected from being oxidized due to oxygen was consumed by Ti, and the expansion of the composites resulted from oxidization of diamond was inhibited.

The thermal behavior of the composite with 6 wt.% Ti under air has been measured by TG–DSC in order to confirm the protective effect of Ti powder on diamonds. The corresponding TG–DSC curves are shown in Fig. 5(a) and (b), respectively. As shown in Fig. 5 there was an exothermic reaction occurring at 634 °C in DSC curve which related remarkable weight gain in TG pattern and confirmed the oxidation reactions of Ti powder. Around 1000 °C, the composite had a residual mass of 106 wt.%.

According to the results of Figs. 4 and 5, possible reactions can be written as shown below when Ti was added into the diamond/borosilicate glass system:

$$Ti + O_2 \rightarrow TiO_2 \qquad (2)$$

$$C(\text{diamond}) + O_2 \rightarrow CO_2 \uparrow /CO \uparrow \qquad (3)$$

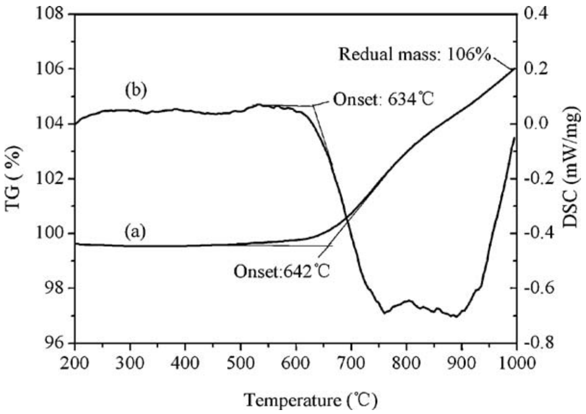

Fig. 5. TG–DSC curves of the composites sintered at 850 °C with 6 wt.% Ti: (a) TG; (b) DSC.

Fig. 6 shows SEM micrographs of the composites without and with 6 wt.% and 8 wt.% Ti content. There were many big pores in the matrix of composites without Ti additives, which resulted in a high expansion ratio and a low bending strength of the composite. These big pores came from oxidation of diamond grits, so the diamond grits was degraded and exposed as shown in Fig. 6(a) and (b). Composites with 6 wt.% Ti additives showed fewer pores and denser structures because oxygen was absorbed by Ti and diamond grits were protected from oxidization, which resulted in a low expansion rate and a high bending strength. Due to oxidization of diamond grits, the composites expanded and the density of the grits became smaller. In addition, the oxidation of the grits means that there is less diamond in the Ti-free specimen. Consequently, the fracture surface of the composites without Ti additives is smoother. It should be noted that there were many particles of 10–25 μm in the composite with 8 wt.% Ti content. These particles were identified as TiO_2 particles by EDS, which were noted in Figs. 4 and 5. The morphologies of TiO_2 particles were shown in Fig. 7(a) and (b). The Ti distribution in the composites with 6 and 8 wt.% Ti content is shown Fig. 8(a) and (b), respectively. Ti distributed well in the composites and the sizes of Ti were far smaller than those before sintering (Fig. 1). This was not only a consequence of the high rate of melting the glass matrix, but also of the large volume fraction of the liquid phase at 850 °C. Additionally, the solubility of Ti in the glass liquid phase was ensured due to a long sintering time.

The morphologies and CFS of the grits separated from these composites by mixture of hydrofluoric acid and sulfuric acid are shown in Fig. 9 and Table 2, respectively. The particles separated from the composite without Ti had many pits on the surface and

Table 2
CFS of the diamond grits used for the sintered composites sintered at 850 °C without Ti and with 6 wt.% Ti.

Conditions	CFS of grits for the composite without Ti (N)	CFS of grits for the composite with 6 wt.% Ti (N)
Before sintering	28	28
After sintering	21	25

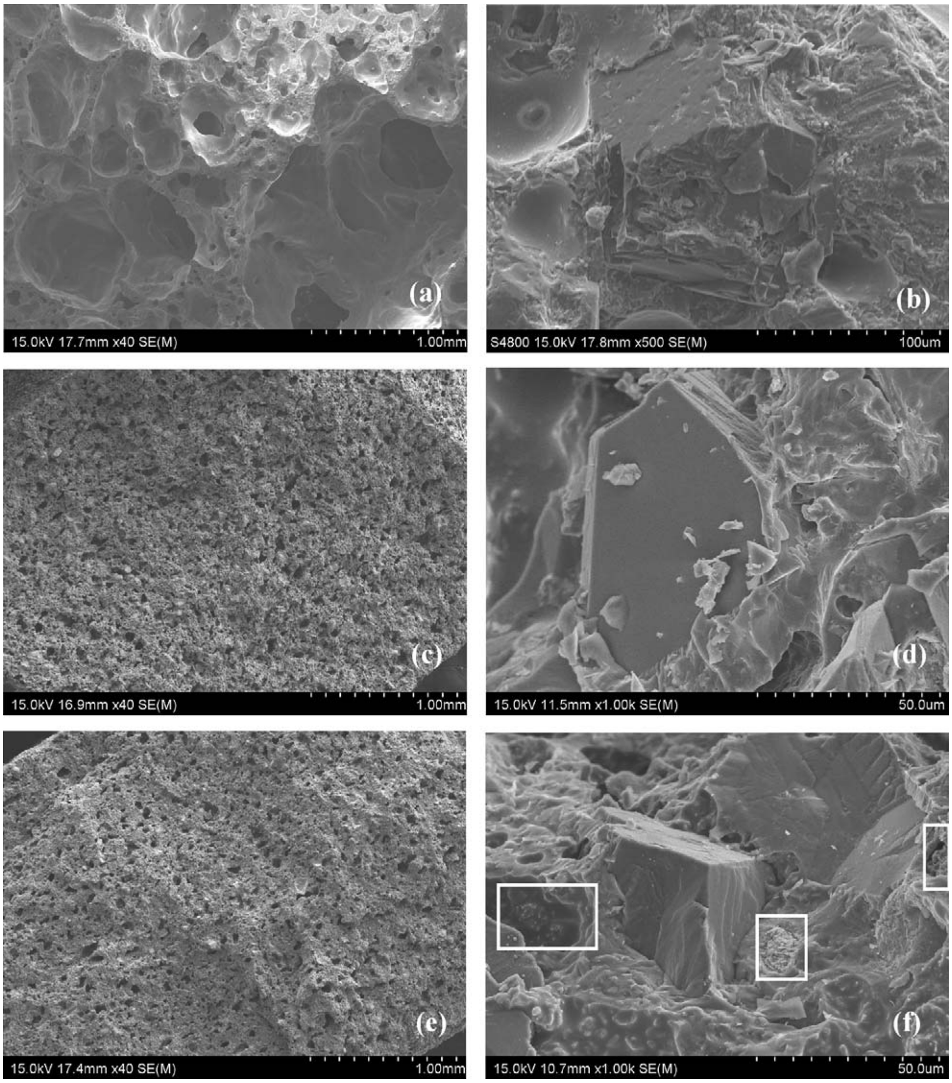

Fig. 6. SEM images of fracture surface of bending test composites sintered at 850 °C: (a) and (b) for the composite without Ti; (c) and (d) for the composite with 6 wt.% Ti content; (e) and (f) for the composite with 8 wt.% Ti content.

possessed a decreased CFS value. While those separated from the composite with 6 wt.% Ti had smooth surface and a higher CFS value. These results further confirm the protective effect of Ti on the grits.

Due to protection of Ti additives oxidization of diamond grits was inhibited, the CFS of the diamond grits and the density of the composites increased, and boundary condition between the diamond and the matrix would improve. In order to study the main factor in the improvement of the mechanical properties, the composites with 6 wt.% Ti and without Ti were sintered at 750 °C, at which the oxidization of diamonds in the matrix would not occur.[14] The bending strength and volume expansion rate of

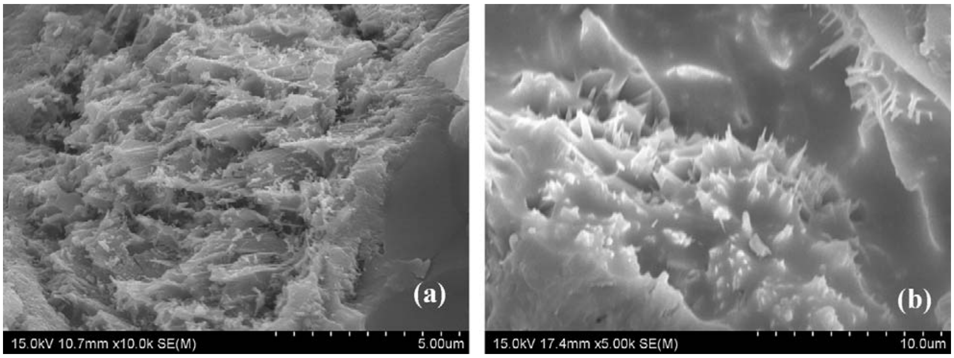

Fig. 7. SEM images of TiO_2 in the bond sintered at 850 °C with different morphologies.

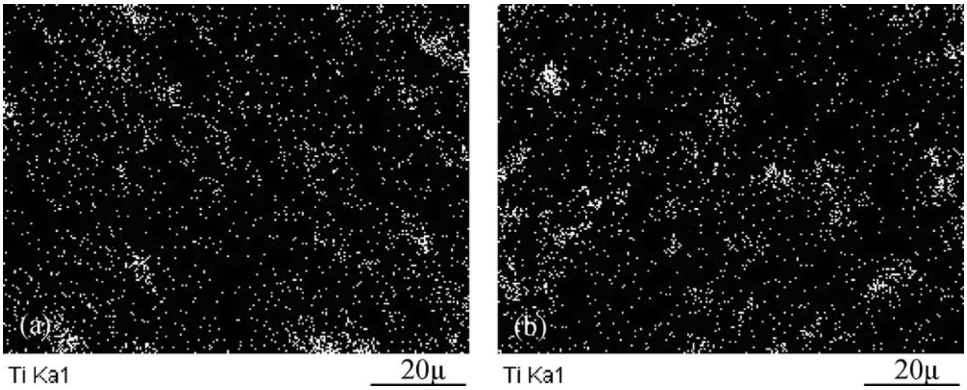

Fig. 8. Distribution of Ti in the sintered composites sintered at 850 °C: (a) 6 wt.% Ti; (b) 8 wt.% Ti.

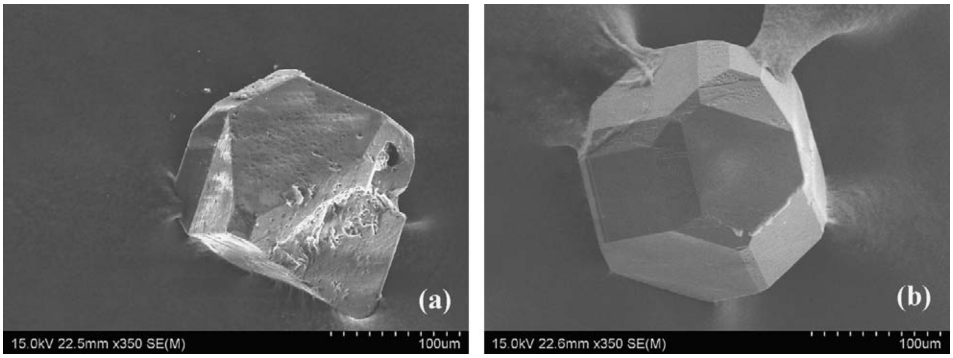

Fig. 9. SEM images of diamond grits separated from composites sintered at 850 °C: (a) without Ti; (b) with 6 wt.% Ti.

the composites and the CFS of the diamond grits are shown in Table 3. SEM photographs of the fractured surfaces of the composites are given in Fig. 10. At this temperature, oxidization of diamond grits were avoided and the mechanical properties of the composites without Ti powders were very near to those with 6 wt.% Ti addition. This implied that effects of Ti addition on boundary condition between diamond grits and the matrix were minimal. As shown in Figs. 6 and 10, it was intergranular

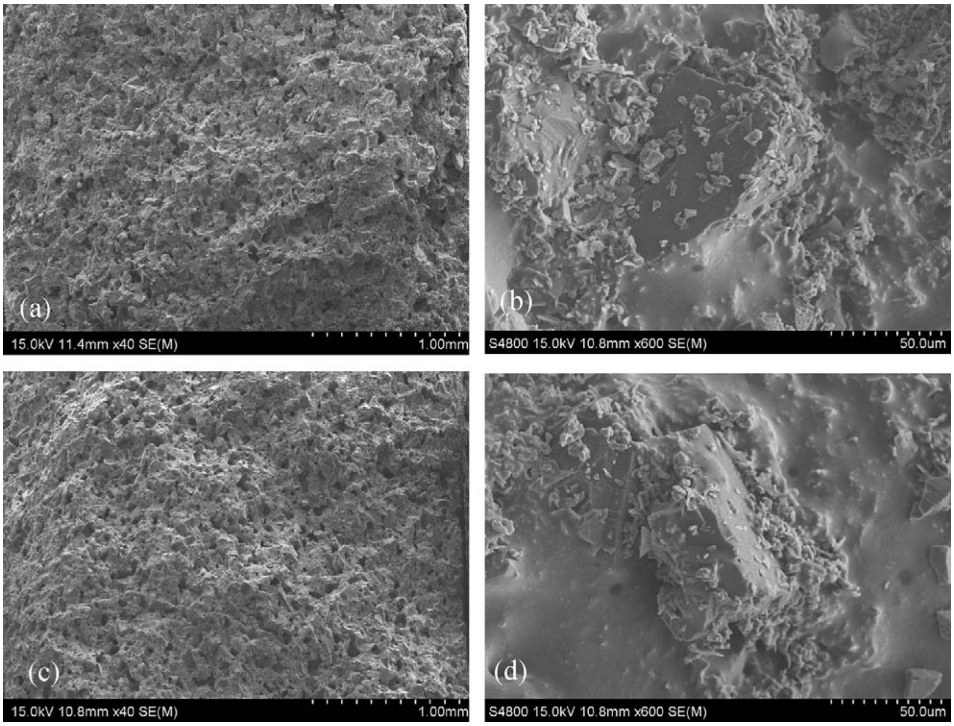

Fig. 10. SEM photographs of the fractured surfaces of the composites sintered at 750 °C: (a) and (b) without; (c) and (d) 6 wt.% Ti.

Table 3
Mechanical properties of the composites sintered at 750 °C for 120 min.

Ti contents (%)	Bending strength (MPa)	Shrinkage/ swelling (%)	CFS of diamonds (N)
0	39.73	−4.97	30
6	40.25	−5.46	32

fracture mode but not transgranular fracture mode observed on the fracture surface of the composites. Consequently, effects of the CFS of grits on the mechanical properties were minimal. The main factor in the improvement of the mechanical properties was the density of the composites.

4. Conclusions

In order to avoid thermal degradation of diamond particles in diamond/borosilicate glass composites, 0–10 wt.% Ti powders were added into the composites. The results showed that Ti could protect diamond grits from oxidation due to its prior reaction with oxygen. So incorporation of Ti powder into diamond/borosilicate glass composites could improve the bending strength and decrease the expansion ratio of the composites. The composites containing 6 wt.% Ti particles obtained the maximum bending strength and the minimum volume expansion rate, which was 74.02 MPa and −20.53%, respectively. The CFS results of the diamond grits separated from the composite without Ti and with 6 wt.% Ti were 21 N and 25 N, respectively. XRD results indicated that during sintering Ti was oxidized and then dissolved into the glass phase when Ti content was lower than 6 wt.%. Rutile TiO_2 peak could be confirmed for the composites in which Ti content was higher than 6 wt.%, and rutile TiO_2 increased with increasing Ti contents. So the amount of 6 wt.% was sufficient for Ti to react with oxygen and could result in a highest bending strength and a lowest expansion rate for the diamond/borosilicate glass.

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