

The effect of $\text{TiO}_2/\text{Al}_2\text{O}_3$ film on the properties of diamond and diamond/glass composites

Weida Hu, Long Wan*, Xiaopan Liu, Junsha Wang and Haochong Zhai

College of Materials Science and Engineering, Hunan University, Changsha, Hunan 410082, People's Republic of China

A titania/alumina ($\text{TiO}_2/\text{Al}_2\text{O}_3$) film was coated on surface of diamond abrasive particles via a sol-gel technique. The effects of $\text{TiO}_2/\text{Al}_2\text{O}_3$ film on the properties of diamonds and diamond/glass composites were investigated. The results showed that the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film could effectively improve the oxidation resistance of diamond, where the initial oxidation temperature of diamond was 600°C in an air environment while oxidation of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond could not be found below 775°C . For a mechanical property investigation, the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond had a better compressive fracture strength (CFS) than that of the uncoated diamond after sintering. When the surface of a diamond was coated with a $\text{TiO}_2/\text{Al}_2\text{O}_3$ film, the contact angle between liquid glass and diamond film decreased from 105° to 60° at 750°C . For the application of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond to diamond/glass composites, it was evident that the performance of the composites was improved.

Key words: Diamond, TiO_2 , Al_2O_3 , Sol-gel, Glass.

Introduction

Owing to high hardness, high strength and good wear resistance, diamond abrasive particles are widely used as cutting, grinding, and polishing tools in modern engineering applications [1-4]. However, there are still challenges to realize the advantages of diamond grinding in industry. Presently, the preparation of a diamond tool and the use of a diamond tool are severely limited above 700°C , where diamond is easily degraded by heat, influencing the performance of diamond tools [5-7]. Furthermore, as the material structure of diamond is different from the matrix such as a metal and vitrified bond (glass), the diamonds are not easy to wet by the matrix, which weakens the retaining force of the diamond particles in the matrix. So, how to improve the performance of diamond to oxidation resistance, graphitization resistance and surface modification are the main factors for improving the lifetime of diamond tools for many researchers [8-9].

Coating the diamond surface with a barrier layer is practical in protecting the diamond from degradation at high temperature and in modifying the surface property of the diamond. The aim of the present study has been coating the diamond with metal, such as Ti, Cu, Cr, etc [10-14]. The active metal coated diamond has the widest range of application for metal bonded diamond tools that are mainly manufactured by hot pressing in a protective atmosphere. However, vitrified bonded diamond tools

are usually prepared by cold pressing and sintering at a high temperature for long periods in an air atmosphere. So then is little effect for the active metal coated diamond by sintering in vitrified bond environment [15].

In other studies, there were novel methods with abrasive grit coatings. Zhang et al. coated diamonds with a Si coating by the method of quasi-atomic layer deposition, which showed that the Si film had a high thermal stability, effectively protecting the diamond from oxidization, and a high bonding strength between the diamond and the vitrified bond system [15]. Zhang et al. coated CBN abrasive particles with a $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ glass via a sol-gel route, which demonstrated the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ glass coating provided a high bonding strength between CBN particles and the vitrified bond system [16].

In our previous study, we obtained TiO_2 film coated diamond particles via a sol-gel route, which showed the TiO_2 film was beneficial to the oxidation resistance of the diamond particles and the grinding performance of the vitrified bond diamond grinding wheel [17]. In this paper, $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond particles were prepared by a sol-gel technique and the effects of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film on the properties of diamond particles and diamond/glass composites were studied.

Experimental

Preparation of $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond particles

The TiO_2 sol was prepared as follows: by stirring, tetrabutylorthotitanate (17.0 ml) and triethanolamine (4.8 ml) were dissolved in ethanol (67.3 ml) at room

*Corresponding author:
Tel : +86-731-88823540
Fax: +86-731-88823540
E-mail: wanlong1799@163.com

temperature then distilled water (0.9 ml) and ethanol (10.0 ml) were mixed together and added, after stirring for 120 minutes, a clear TiO₂ sol was obtained. The Al₂O₃ sol was prepared as follows: by stirring and refluxing at 85 °C, aluminum isopropoxide was mixed with distilled water and nitric acid in the mole ratio of 1 : 90 : 0.2, when the suspension became transparent, the Al₂O₃ sol was obtained.

This paragraph describes the coating process. The artificial diamond particles (mean particle size 300 μm) were put into a copper net and immersed into the above prepared TiO₂ sol for about 1 minute, then with a pull-out speed of the copper net between 1 and 2 cm/minute, dried at 80 °C for about 5 minutes, and this process was repeated 2 times. Then the TiO₂ film coated diamonds were dipped into the Al₂O₃ sol with the same process. After that, the TiO₂/Al₂O₃ film coated diamond particles were put into a ceramic crucible and heated at 100 °C for 30 minutes, then heated at 5 K · minute⁻¹ to 650 °C for 60 minutes in a furnace. When the diamond particles cooled off, the TiO₂/Al₂O₃ film coated diamond particles had been prepared.

Characterization of TiO₂/Al₂O₃ film coated diamond particles

The microstructures and the elemental analysis of the TiO₂/Al₂O₃ film coated diamonds were examined by an environmental scanning electron microscope (FEI QUANTA-200) and energy dispersive X-ray spectroscopy (EDS, EDAX/TSL). The phase structure of TiO₂/Al₂O₃ film coated diamonds were identified by means of X-ray diffraction (XRD, SIEMENS D-5000) with a standard CuKα radiation source and 2θ angle from 20 ° to 80 °. Differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements of the uncoated and the TiO₂/Al₂O₃ film coated diamond particles were performed by a NETZSCH calorimeter (STA-449C) in flowing air, at a heating rate of 10 K · minute⁻¹ from room temperature to 1100 °C. The compressive fracture strength (CFS) of the diamond particles was tested using the single grit method.

Preparation of diamond/glass composites

The diamond/glass composites were prepared by using uncoated and TiO₂/Al₂O₃ film coated diamond particles with powdered glass (Table 1) on a mass ratio of 4 : 6. Mixtures of diamond particles, the glass and a temporary binder were put in a the cold press of 60 MPa for 5 minutes in a 4×5×40 mm mold. The molded composites were sintered in a furnace with an air atmosphere at 10 K · minute⁻¹ to 500 °C for 30 minutes

Table 1. Composition of glass used in this study (sintering temperature: 750 °C).

Glass component	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Li ₂ O	Na ₂ O	K ₂ O
(wt.%)	50.0	20.0	8.0	10.0	9.0	3.0

and 10 K · minute⁻¹ to 750 °C, holding for 60 minutes, 90 minutes and 120 minutes, respectively, then cooled off in the furnace.

Characterization of diamond/glass composites

The wettability of the diamond particles by the glass liquid was studied using the sessile drop method in a nitrogen atmosphere. Considering the small grit size of the diamond particles, a substrate with a CVD diamond film was used in this investigation. The glass powder was pressed into a cylinder (Φ8 mm×6 mm) and the substrate with the cylinder on it was placed into the furnace chamber, followed by heating it to the sintering temperature at a heating rate of 5 K · minute⁻¹. At the sintering temperature, the images of glass droplets on the substrate were taken with a digital camera. The contact angle was defined by the angle that a line tangent to the droplet forms with the horizontal surface. The smaller the contact angle was, the better the wettability was.

The volumes of the diamond/glass composites were measured by Archimedes law and the volume shrinkage/expansion was calculated by Eq. (1): where V_i was the initial volume of the composite before sintering and V_f was the final volume after sintering.

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

The bending strength for each composite was tested using a three-point bending test conducted on a testing machine (DKZ-5000, China). Each sample was tested five times and the average was the result. The hardness of diamond/glass composites was measured by a Rockwell's hardness tester (HR-150DT, Shanghai China) under a load of 30 kgf. The average of ten tests

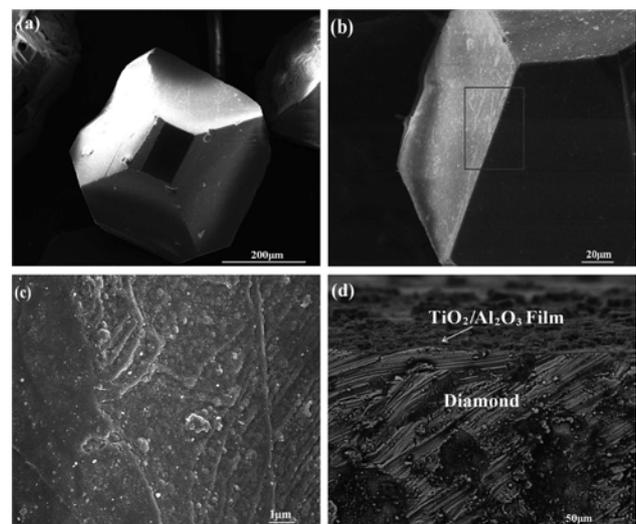


Fig. 1. Scanning electron microscope (SEM) image of (a) uncoated diamond, (b) TiO₂/Al₂O₃ film coated diamond, (c) TiO₂/Al₂O₃ film on diamond surface, (d) cross-section of TiO₂/Al₂O₃ film coated diamond.

was the hardness value. The fracture surfaces of the diamond/glass composites were examined by an environmental scanning electron microscope (FEI QUANTA-200).

Results and discussion

Characterization of TiO₂/Al₂O₃ film coated diamond particles

Fig. 1 shows the SEM image of the uncoated and TiO₂/Al₂O₃ film coated diamond particles. Fig. 1(a) shows that the uncoated diamond surface was smooth. The coated diamond is shown in Fig. 1(b). The EDS (Table 2) analysis of the rectangular area in Fig. 1(b) indicates that the film coating on the surface of diamond was composed of the elements O, Ti, Al, and the C element was derived from the diamond particles. In Fig. 1(c), the surface topography of the TiO₂/Al₂O₃ film on the diamond surface is a stratiform construction, which is related to the step repeat of the coating process. Fig. 1(d) represents a cross-sectional view of a TiO₂/Al₂O₃ film coated diamond particles, which demonstrates the film coating on the surface of a diamond particles has a thickness of about 5 μm.

Fig. 2 shows the XRD spectra of the TiO₂/Al₂O₃ film coated diamond particles sintered at 650 °C and 750 °C. The diffraction peaks at 2θ = 43.9 ° and 75.5 ° are associated with the (111) and (220) planes of cubic diamond. It may be clearly seen in the XRD spectra that the crystal structures of the TiO₂/Al₂O₃

film were comprised of anatase, rutile and γ-Al₂O₃. As the temperature rose from 650 °C to 750 °C, the crystalline nature of γ-Al₂O₃ became more obvious.

Performance of the TiO₂/Al₂O₃ film coated diamond particles

Fig. 3 shows the DSC-TG curves of the uncoated and TiO₂/Al₂O₃ film coated diamond particles. What may be noted from Fig. 3(a), there is a big exothermic peak from 600 °C to 1000 °C in the DSC curve. The initial oxidation temperature for the uncoated diamond particles was 600 °C in flowing air, which was possibly oxidized by oxygen from the air atmosphere above 600 °C as Eqs. (2) and (3).



However, in Fig. 3(b), the coating of TiO₂/Al₂O₃ film was able to provide an effective thermal protection for the diamond particles at a high temperature and prevented the diamond particles directly contacting the oxygen in the air atmosphere, so the initial oxidation temperature of the TiO₂/Al₂O₃ film coated diamonds was 775 °C in flowing air, which was elevated by more 175 °C than that of the uncoated diamond particles. In

Table 2. Energy dispersive X-ray spectrometer (EDS) analysis of the TiO₂/Al₂O₃ film coated diamond in the rectangular area of Fig. 1(b).

Element	Mass fraction/%	Mole fraction/%
C	83.40	89.35
O	09.44	07.59
Al	05.42	02.59
Ti	01.74	00.47

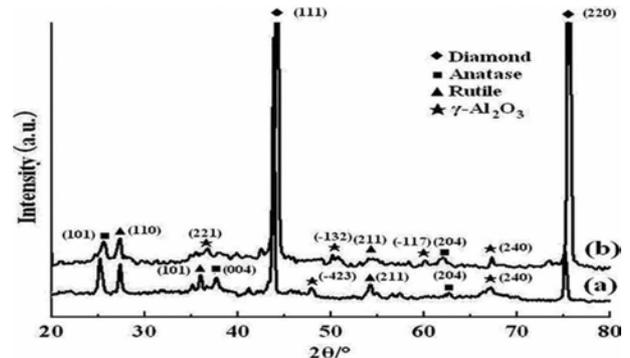


Fig. 2. X-ray diffraction (XRD) patterns of TiO₂/Al₂O₃ film coated diamond particles: (a) 650 °C and (b) 750 °C.

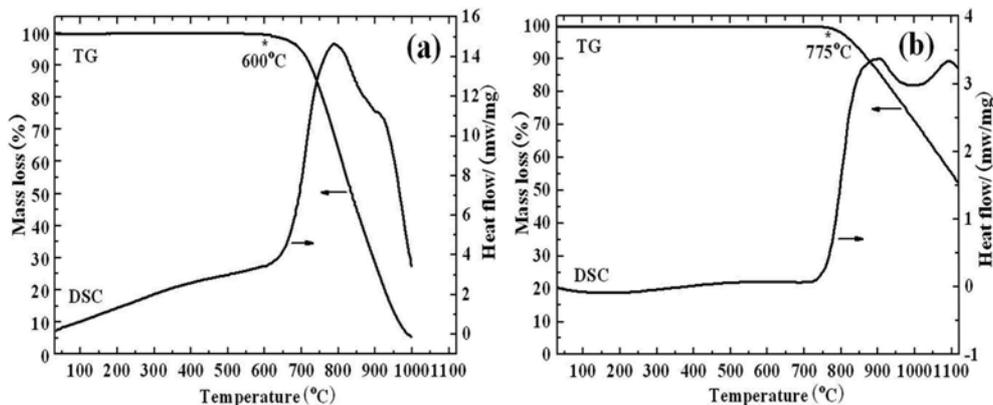


Fig. 3. DSC-TG curves of the two different types of diamond particles in an air environment (a) uncoated diamond particles, (b) TiO₂/Al₂O₃ film coated diamond particles.

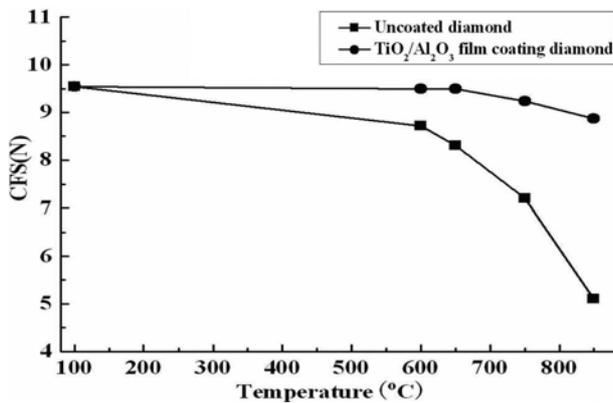


Fig. 4. Compressive fracture strength (CFS) results of the uncoated and TiO₂/Al₂O₃ film coated diamond particles sintered at different temperatures for 60 minutes.

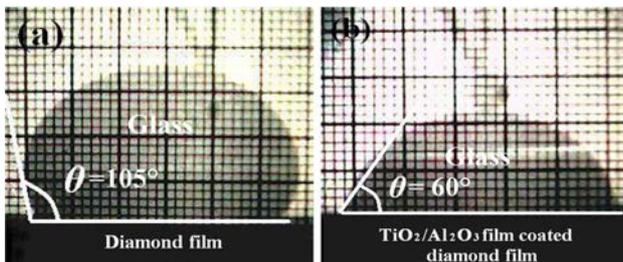


Fig. 5. Contact angle of liquid glass on (a) diamond film, (b) TiO₂/Al₂O₃ film coated diamond film.

our previous study [17], for the TiO₂ film coated diamond particles, the initial oxidation temperature was 650 °C, which was also lower than the TiO₂/Al₂O₃ film coated diamond particles. From the analysis of the DSC curves, the value of the heat flow was smaller than that of the uncoated diamond particles, which indicated that the rate of oxidation for TiO₂/Al₂O₃ film coated diamond particles was also smaller than that of the uncoated diamond particles. For example, at 850 °C, the mass loss of the uncoated diamond particles sharply decreased 55% whereas the mass loss of the TiO₂/Al₂O₃ film coated diamond particles was just 10%. The special exothermic peak at 1100 °C is related to the change of crystal structure from γ -Al₂O₃ to α -Al₂O₃.

Fig. 4 gives the CFS results of the two different diamond particle types sintered at different temperatures for 60 minutes. At 100 °C, there was no any significant difference in the values of CFS for the two different diamond particle types. But when the temperature was increased from 600 °C to 850 °C, it may be clearly seen that the decreasing degree of the CFS of the uncoated diamond particles was faster than that of the TiO₂/Al₂O₃ film coated diamond particles. This could be confirmed by the DSC-TG data, as the uncoated diamond particles were oxidized from 600 °C, so the CFS of the uncoated diamond particles was remarkably decreased due to thermal damage. However, for the TiO₂/Al₂O₃ film coated diamond particles, possibly due to the elimination of the surface defects on the

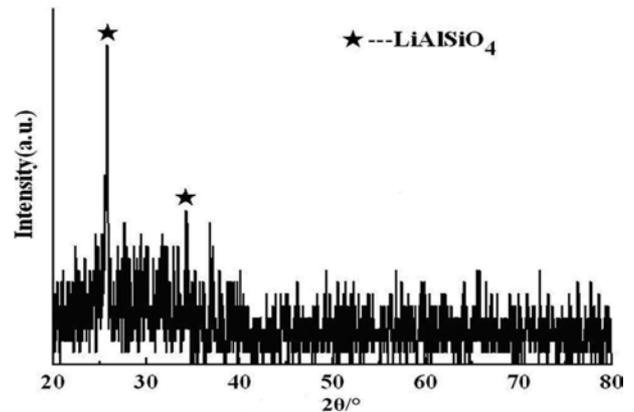


Fig. 6. XRD pattern of the glass sintered at 750 °C.

Table 3. The performance of the different diamond/glass composites sintered at 750 °C (A, the sintered composites prepared by the uncoated diamond particles and B, the sintered composites prepared by the TiO₂/Al₂O₃ film coated diamond particles).

Composites	holding time (minutes)	Volume expansion (%)	Hardness (H _{RC})	Bending Strength (MPa)
A-1	60	28.2	46.5	30.1
A-2	90	40.6	37.8	26.3
A-3	120	60.4	30.2	18.7
B-1	60	12.1	48.1	38.4
B-2	90	11.8	50.7	40.7
B-3	120	9.5	53.9	42.1

diamond particles by the TiO₂/Al₂O₃ film and resistance to heat-oxidation, the coated diamond particles were able to possess higher CFS values than the uncoated diamond particles above 600 °C.

Performance of the diamond/glass composites

Outstanding high temperature wettability behavior in a liquid glass and solid diamond film system is critical for improving the interfacial performance. The effect of liquid glass on the wettability of the uncoated diamond film and the TiO₂/Al₂O₃ film coated diamond film at 750 °C in a nitrogen atmosphere may be seen from the changes of the contact angle θ in Fig. 5. The lower the value of the contact angle is, the better the wettability of the liquid glass is. In Fig. 5(a), the contact angle between the liquid glass and the uncoated diamond film was about 105 °, while the contact angle between the liquid glass and the TiO₂/Al₂O₃ film coated diamond film was about 60 ° in Fig. 5(b). The XRD pattern of the liquid glass sintered at the same temperature is shown in Fig. 6, where the diffraction peaks at $2\theta = 25.2^\circ$ and 34.1° are associated with the $(-1\ 1\ 2)$ and $(-2\ 1\ 0)$ planes of monoclinic LiAlSiO₄. From the present investigation, as the crystal structure of diamond was cubic and the chemical bond was hybrid orbital sp³, so the diamond film was not

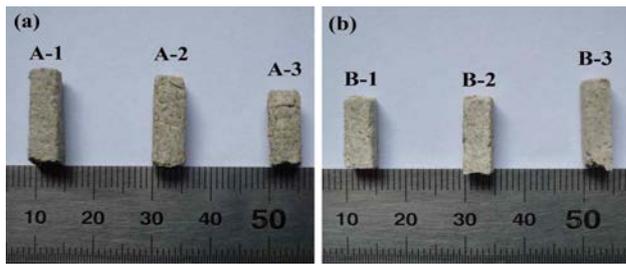


Fig. 7. (a) the diamond/glass composites prepared by the uncoated diamond particles, (b) the diamond/glass composites prepared by the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond particles, sintered at 750 °C.

preferable to be wetted by the liquid glass. When the diamond film was coated with the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coating, the monoclinic $\gamma\text{-Al}_2\text{O}_3$ of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coating was with a similar structure to the monoclinic LiAlSiO_4 , which produced a chemical combination between the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coating and liquid glass in the sintering process [11]. Therefore the contact angle of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond film became smaller than that of the uncoated diamond film.

Table 3 lists the performance of the two different diamond/glass composites sintered at 750 °C for 60 minutes, 90 minutes and 120 minutes. The digital pictures of the two different diamond/glass composites are shown in Fig. 7. The results showed that, for the diamond/glass composite prepared by the uncoated diamond particles, sintered at the 750 °C, based on the analysis of the DSC-TG, the diamond particles were thermally oxidized and the resultant gas remaining in the composites produced the pores. With an extension of the isothermal holding time, the uncoated diamond particles were further oxidized and the pores in the composites increased and became bigger, which expanded the volume of the composites and resulted in inadequate bonding between the diamond particles and the glass matrix. So there was an obvious decrease in both the hardness and the bending strength.

But due to the barrier effect of $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coating, the oxidation and thermal attack of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond particles in the composites was prevented during sintering at 750 °C. In addition, with an increase in the time of isothermal holding, the viscosity of the liquid glass matrix became very low so that the liquid glass could perfectly wet on the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond particles, thus contributing to the densification of the diamond/glass composites. So for the diamond/glass composite prepared with the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond particles, especially at an isothermal holding time of 120 minutes, a close to fully densified structure had been achieved and the volume expansion was the minimum 9.5%. It was also noted that only with an isothermal holding time of 120 minutes could the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond/glass composite be sintered to a maximum hardness value (53.9 H_{RC}) and a maximum bending strength

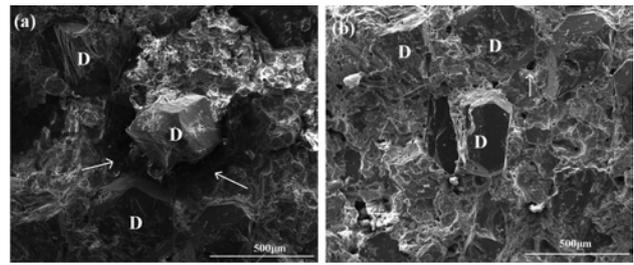


Fig. 8. Scanning electron microscope (SEM) image of (a) the diamond/glass composite prepared with the uncoated diamond particles sintered at 750 °C for 120 minutes, (b) the diamond/glass composite prepared with the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond particles sintered at 750 °C for 120 minutes, D: diamond particles, arrow: pores.

(42.1 MPa). Fig. 8 shows the SEM image of the fracture surfaces for the two different composites sintered at 750 °C for 120 minutes. Clearly, many big pores are visible in the diamond/glass composite prepared with the uncoated diamond particles in fig. 8(a), therefore, the performance was very weak. By contrast, for the diamond/glass composite prepared with the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond particles in fig. 8(b), the glass had a large area of intimate coverage on the diamond particles and there were few small pores, revealing that there should be a high bonding strength between the diamond particles and the glass matrix, so the performance of this composite (B-3) was the best.

Conclusions

- 1) A $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coating on diamond abrasive particles was prepared by a sol-gel process.
- 2) The $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coating could increase the initial oxidation temperature of the diamond particles by 175 °C in an air atmosphere and improve the CFS of the diamond particles in high temperature conditions.
- 3) Compared with the uncoated diamond film, the wettability of a liquid glass coating with the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coated diamond film was decreased from 105 ° to 60 ° at 750 °C.
- 4) For the diamond/glass composites investigation, as the protective effect and surface modification of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ film coating on diamond particles, it consequently decreased the volume expansion of the composites and increased the hardness and the bending strength of the composites.

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