

## Effects of $ZrO_2$ on physical and mechanical properties of vitrified bond CBN composite materials

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The effects of  $ZrO_2$  on the physical and mechanical properties of vitrified bond and vitrified boron nitride (CBN) composites were systematically investigated. The basic vitrified bond ( $B_2O_3-Al_2O_3-SiO_2-Li_2O-Na_2O$ ) and  $ZrO_2$  make up the vitrified bond, and then constitute the vitrified CBN composites consists together with CBN abrasives. The addition of  $ZrO_2$  has a certain influence on refractoriness, liquidity, bending strength of vitrified bond. With the increase of adding amount of  $ZrO_2$  the refractoriness of vitrified bonds gradually rises, and fluidity of vitrified bonds becomes lower. When the  $ZrO_2$  addition amount reaches a certain extent, the crystalline phase- $ZrSiO_4$  will appear during the sintering process. In addition, the  $ZrO_2$  can add to a certain extent, improve the strength of the bond and CBN composites, when  $ZrO_2$  addition amount of 8 wt.%, the performance of the vitrified bond is the most. Its value changes from 69.74 MPa to 87.45 MPa.

**Key words:** Vitrified bond, CBN,  $ZrO_2$ , Refractoriness, Bending strength.

### Introduction

CBN abrasive tools are a group of high performance super hard composite materials with excellent abrasion resistance and good thermal conductivity. Owing to the excellent properties, CBN grinding tools are becoming one of the most potential tools in modern engineering applications [1-3]. Besides the characteristics of abrasive themselves, the mechanical properties of grinding tools mainly depend on the performance of bond systems and combination state between bond systems and abrasives. In comparison with other types of grinding tools, vitrified bond grinding tools show outstanding properties on account of excellent properties of the vitrified bond materials, such as high strength, good wear resistance, thermal stability, fatigue resistance, excellent oxidation resistance and controllable porosity. However, at the same time we must also see that the disadvantage for vitrified bond grinding tools is brittle, and vitrified bond CBN abrasives are easily broken and fractured [4-6]. And with the improvement of requirements on machining precision and machining quality, the development of vitrified bond systems for CBN abrasives cannot meet it. As a consequence, investigations on the improvement of vitrified bond properties should be carried out. The purpose is to pursuit higher performance vitrified bond CBN grinding wheel.

Previous studies have investigated the influences of different additives and their content on the mechanical properties. Yang et al. [7] studied the combination of

Vitrified bonds in an  $Al_2O_3-B_2O_3-Na_2O-CaO$  system in order to obtain CBN grinding wheels of high flexural strength. Li et al. [8] studied the effects of  $Al_2O_3$ ,  $B_2O_3$ ,  $Na_2O$  and  $SiO_2$  on nepheline formation in borosilicate glasses. The results show that the effect of  $B_2O_3$  is somewhat stronger than the effect of  $SiO_2$  and the effect of  $Al_2O_3$  is stronger than the effect of  $Na_2O$ . Demirkesen et al. [9] found that adding  $Al_2O_3$  into the  $Li_2O-ZnO-SiO_2$  glass-vitrified could significantly reduce the thermal expansion of glass-vitrified bond. Hu and Cui et al. [10, 11] found that the  $B_2O_3$  had a significant effect on crystallization temperature. With the increase of  $B_2O_3$  content, the glass transition temperature and the first crystallization peak temperature decreased, while the second crystallization peak temperature increased. Wang and li et al. [12-15] studied the influence of  $CaO$ ,  $ZnO$ , and  $TiO_2$  etc on the vitrified bond, and found that it would improve the performance of the vitrified bond to a certain extent with a small amount of oxide. Hou et al. [16-19] added nano  $AlN$  into vitrified bond, and found that it would improve the performance of vitrified bond such as the refractoriness, the bending strength and the thermal expansion. In addition, when its content is 6 wt.%, the performances of vitrified bond are optimal.

At present, although the low temperature vitrified bond has been solved, but the strength and wear resistance of vitrified bond are still insufficient.  $ZrO_2$  is a kind of high temperature refractory oxide, and the crystal will change under the high temperature [20-23]. It has good toughening effort for vitrified bond. In this paper,  $B_2O_3-Al_2O_3-SiO_2-Li_2O-Na_2O$  vitrified bond with and without addition of  $ZrO_2$  was prepared, and vitrified bonded CBN composite was manufactured.

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The surface morphology of the vitrified bonds has been investigated by using scanning electron microscope (SEM) and the change in composition of the vitrified bonds with X-Ray Diffraction (XRD), and the bending strength of grinding tool samples as well.

## Experimental Procedure

### Sample preparation

The basic vitrified bond was based on a  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Li}_2\text{O-Na}_2\text{O}$  glass system, and the components were introduced in the form of silica, boron trioxide, alumina, lithium carbonate, and sodium carbonate respectively. The raw materials were weighed accurately, milled together for 6 h in a ball mill (ball: powder = 2 : 1), and sieved with a 200# mesh. Table 1 shows the composition of the glass powder used in this study. Then the mixture was melted at 1200 °C for 2 hrs in an electric furnace and then quenched in deionized water. Then to dry and crush the vitrified bond, and to grind it for 24 hours on the ball grinder, through this the vitrified bond was obtained. At last the powder of vitrified bond was obtained by using the standard screen of 200# mesh. The CBN grains (average grain size 120/140#, Henan Funaike Ultra hard Material Co. Ltd., China NO.880) used in this study were shown in Fig. 1. After screened and molded into rectangular bars (37 mm × 6 mm × 6 mm) under 200MPa of pressure. Then the samples were sintered in an electric furnace in air with 2 hrs holding at their respective refractoriness. After sintering, the samples were cooled to room temperature in the furnace.

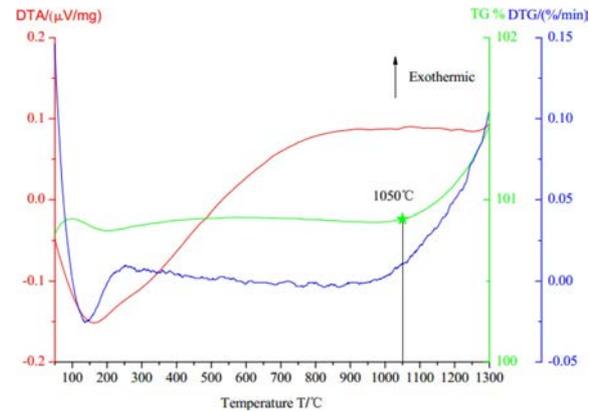
The thermal stability of CBN abrasives has a certain effect on the sintering temperature of vitrified bond

**Table 1.** Compositions of vitrified bonds (wt.%).

Sample	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> O	Na <sub>2</sub> O	ZrO <sub>2</sub>
Zr0	58.7	15.2	11.1	4.9	10.1	0
Zr4	56.4	14.6	10.6	4.7	9.7	4.0
Zr8	54.1	14.0	10.1	4.5	9.3	8.0
Zr12	51.8	13.4	9.6	4.3	8.9	12.0



**Fig. 1.** Morphology of the CBN grains (NO.880).



**Fig. 2.** DTA curve of CBN abrasives.

composite materials, thus it is necessary to determine the oxidation properties of CBN abrasives before sintering test. So, the DTA test was carried out on CBN abrasives. And the heating rate was set to 20 °C/min. The analysis results were shown as Fig. 2. The TG Curve showed that when the temperature reached to 1050 °C, the weight of CBN abrasives began to increase. And it indicates that the oxidation temperature of CBN abrasives is about 1050 °C. In addition, with the increase of temperature, oxidation degree deepened, and the weight of CBN abrasives also corresponding increase. It provides a certain reference for the preparation of vitrified bond CBN composite materials.

### Sample characterization

Refractoriness and fluidity of vitrified bond were measured by Seger-cone and plane flowing method, respectively. The thermal profile of the thermal mechanical analysis was the same as the sintering process shown previously. In order to find out its glass transition temperature, differential thermal analysis test (Netzsch, DSA/DTA TG- STA 449 F3) was carried out for the glass powder. The mechanical properties of samples were characterized by bending strength, and the three-point bending test was performed by a universal testing machine (DYE-300B) universal testing machine at a cross-head speed of 0.5 mm/min. Furthermore, the microstructure of the fracture surfaces of sintered composites was evaluated by scanning electron microscopy (Zeiss Ultra Plus).

## Results and Discussions

### Thermal mechanical analysis of vitrified bond and CBN grains

In the DTA analysis on ceramic bond, the heating rate was set to 10 °C/min. Fig. 3 is the DTA curve of ceramic bond. It could be observed that there have obvious endothermic peaks on the DTA curve from 500 to 700 °C, and there is an obvious the endothermic peak at 573 °C on the four kinds of vitrified bond. It could be well explained by phase transformation. At

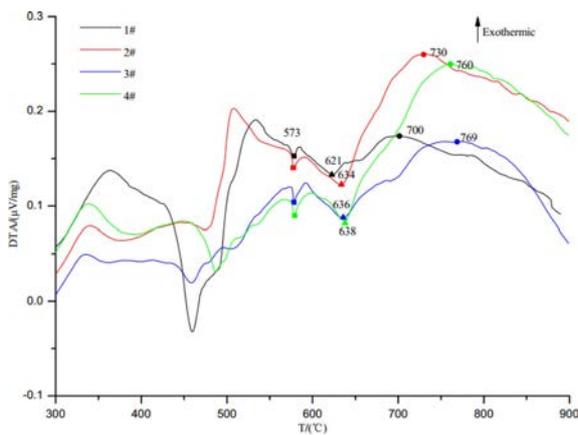


Fig. 3. DTA curve of vitrified bond.

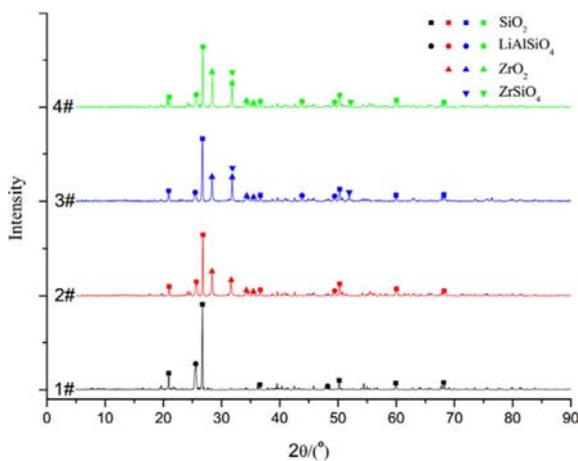


Fig. 4. XRD patterns of the vitrified bonds.

573 °C  $SiO_2$  from alpha phase changed into beta phase. And there was an obvious endothermic peak on 1#, 2#, 3# or 4# vitrified bond respectively at 621 °C, 634 °C, 636 °C, or 638 °C. It indicated that the liquid phase respectively appeared at those temperature points. Additional different degree of exothermic peaks of 1#, 2#, 3# and 4# vitrified bond respectively appeared in 700 °C, 730 °C, 760 °C and 769 °C. Vitrified bond belongs to glass phase materials, and it is a kind of metastable substances in a state of thermodynamic instability. It will have excess energy release, when the vitrified bond from glassy state into crystalline state. So the upward exothermic peak appeared on the DTA curve. And the exothermic peaks are considered as the crystallization exothermic peak. With the increase of the relative contents of  $ZrO_2$ , the position of crystallization exothermic peak shift in the direction of high temperature. After over the peak, as temperatures continue to rise, it began to decline in the DTA curve. And it could be interpreted as liquid phase has appeared in vitrified bond, and it consistent with the results of refractoriness test.

#### Phase composition of the vitrified bond

Fig. 4 shows the XRD patterns of the vitrified bonds

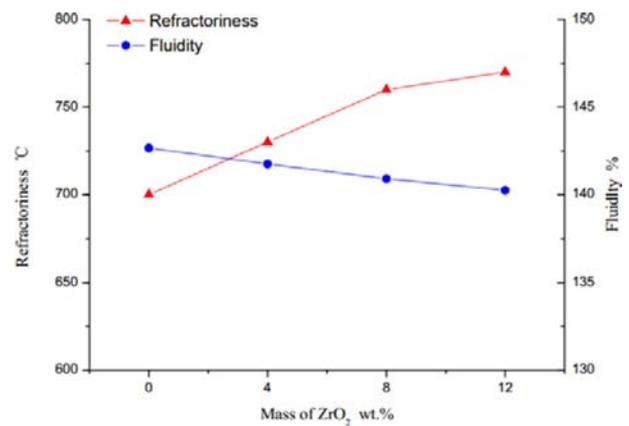


Fig. 4. Refractoriness and high-temperature fluidity of the vitrified bonds.

sintered at their respective refractoriness in argon atmosphere. From the analyzing results of 1# vitrified bond it can be seen that the basic vitrified bond mainly consists of crystalline phase  $SiO_2$  and residual glass phase such as  $LiAlSiO_4$ . Compared with the basic vitrified bond, there appear the diffraction peaks of  $ZrO_2$  in 2# vitrified bond. And with the increasing of  $ZrO_2$ , the crystalline phase- $ZrSiO_4$  appeared in 3# and 4# vitrified bond. It indicates that only when the  $ZrO_2$  addition amount reaches a certain extent, the crystalline phase- $ZrSiO_4$  will appear during the sintering process. It is deduced that due to its low thermal expansion, high thermal conductivity, and strong chemical stability toughness, the presence of  $ZrSiO_4$  will play a positive role on the thermal and mechanical properties.

#### Refractoriness and high-temperature fluidity of the vitrified bonds

Refractoriness and high-temperature fluidity are the most widely used parameters for estimating the Sintering temperature and the flowing ability of vitrified bond. Sintering temperature determines the stability of vitrified bond CBN composite materials to a certain extent. And outstanding flowing ability of vitrified bond to abrasives has great influence on the interface status between the bonds and the abrasive grains. After joining the  $ZrO_2$ , the refractoriness of vitrified bonds has been improved. The Fig. 3 shows that the addition of  $ZrO_2$  can improve the melting temperature of vitrified bonds to some extent. And it can be seen that the addition of  $ZrO_2$  has large effect on the fluidity of vitrified bond. As shown in Fig. 4, the fluidity of vitrified bonds with  $ZrO_2$  is lower than that without  $ZrO_2$  at the optimal sintering temperature. Moreover, it is clear that higher amount of  $ZrO_2$  results in lower fluidity of vitrified bonds.

#### Microstructures of vitrified bond CBN composites

Fig. 5 shows the SEM impact fracture morphologies of vitrified bond with different amount of  $ZrO_2$  (0 wt.%,

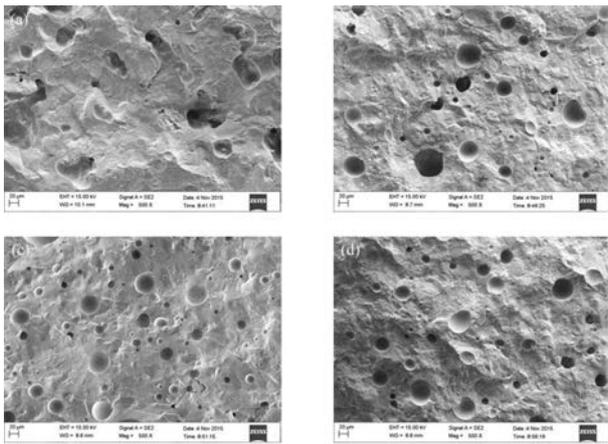


Fig. 5. Fracture morphologies of vitrified bond with different amount of  $ZrO_2$ .

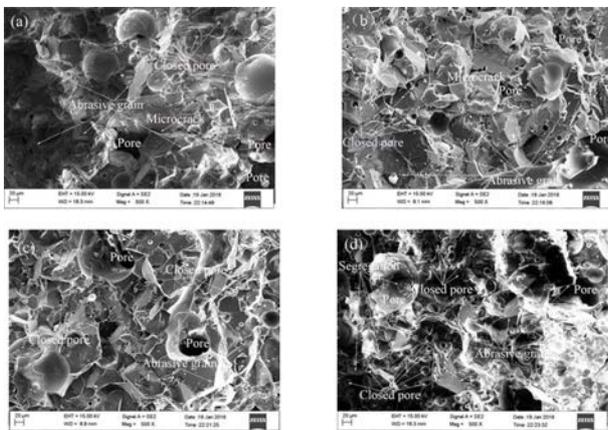


Fig. 6. Fracture morphologies of CBN composites with different amount of  $ZrO_2$ .

4 wt.%, 8 wt.%, 12 wt.%). They were significantly different. From Figs. 5(a-d), it could be observed that a certain number of closed porosity of the specimens formed, and the addition of  $ZrO_2$  does not affect the formation of porosity. Compared with the specimens with vitrified bond 1#, 2#, and 4# in Figs. 5(a, b and d), the specimens with vitrified bond 3# (Fig. 5(c)) had relatively uniform pore structure. It (3#  $ZrO_2$  8wt.%) shows that the size and the distribution of the pores are uniform, and most of the porosities are spherical. So the stress concentration will not be formed, and it also enhances the mechanical properties of the vitrified bond to some extent. In addition, when the content of  $ZrO_2$  reached 12 wt.%, the segregation of  $ZrO_2$  appeared, and the sample fracture is not smooth.

In addition to examine the holding effect of vitrified bond on CBN abrasives, the concentration of 100% CBN composite material was made, and the section morphology of CBN composites were analyzed. The results were shown in Fig. 6. The differences of fracture morphologies of CBN composites are not very obvious. The size and distribution of the pores are non-uniform, and some small, close pores can be observed.

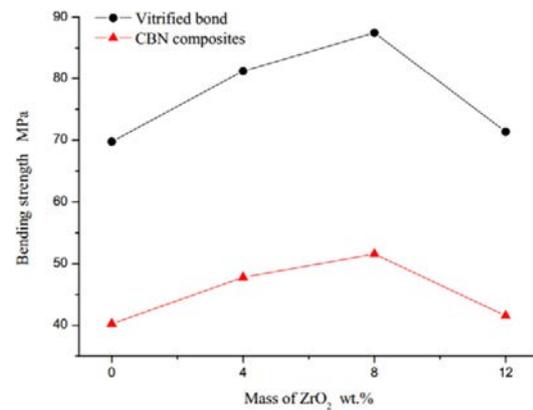


Fig. 7. Bending strength of vitrified bond samples and CBN composites.

From Fig. 6(a), it can be observed that the crack propagates primarily along the vitrified bond bridge. With the addition of  $ZrO_2$  the micro cracks gradually disappeared, and Fig. 6(c) was better than Fig. 6(b) in inhibiting the microcrack. When the content of  $ZrO_2$  reached 12 wt.%, the segregation of  $ZrO_2$  began to appear, and the details were shown in Fig. 6(d). This result indicates that the  $ZrO_2$  modified  $Na_2O-Li_2O-B_2O_3-Al_2O_3-SiO_2$  vitrified bond in this work results in inhibiting the microcrack, and the content of  $ZrO_2$  is not the more the better.

### Effect of $ZrO_2$ on the bending strength of vitrified bond CBN composites

Bending strength is the important parameter used to characterize the mechanical properties of the grinding tools. The values are closely related to the strength of vitrified bond and the combination state between vitrified bond and abrasive grains. The samples with higher bending strength always own higher Micro hardness. Bending strength (Five values take average) of vitrified bond samples and CBN composites with different vitrified bond sintering could be seen in Fig. 7.

Under the same soaking instance, after the introduction of  $ZrO_2$ , the  $Na_2O-Li_2O-B_2O_3-Al_2O_3-SiO_2$  vitrified bond is dense, and the bending strength of vitrified bond samples and CBN composites exhibits an earlier increase and later gradual decrease with the increasing of  $ZrO_2$ . When the content of  $ZrO_2$  reached 8 wt.%, the relatively high value of vitrified bond samples and CBN composites respectively reached 87.45MPa and 51.58 MPa. However, with the content of  $ZrO_2$  further increasing, the bending strength of vitrified bond samples and CBN composites respectively reduced to 71.35 MPa and 41.43 MPa. It indicates that the content of  $ZrO_2$  is not the more the better and it is better not exceed 8 wt.%.

### Conclusions

The effect of  $ZrO_2$  on the microstructures and

mechanical properties of SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Li<sub>2</sub>O-Na<sub>2</sub>O vitrified bond CBN composites were investigated in this work. The addition of ZrO<sub>2</sub> could enhance the refractoriness, reduce liquidity, and improve the strength of the vitrified bond, and it is beneficial to improve CBN composite material properties. After joining the ZrO<sub>2</sub>, the refractoriness of vitrified bonds has been improved. And the fluidity of vitrified bonds with ZrO<sub>2</sub> is lower than that without ZrO<sub>2</sub> at the optimal sintering temperature. It had demonstrated that appropriate amount (8 wt.%) of ZrO<sub>2</sub> introduced into the SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Li<sub>2</sub>O-Na<sub>2</sub>O vitrified bond could enhance the bending strength of the specimens from 69.74 MPa to 87.45 MPa. The interfacial combination state of the specimens with the vitrified bond containing 8 wt.% ZrO<sub>2</sub> was more excellent comparing with other compositions (0 wt.%, 4 wt.% and 12 wt.%).

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