



Influence of F⁻ Ions as Flux from Different Resources on Vitrified Bond for Cubic Boron Nitride Grinding Tools

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In this article, the selection of more appropriate flux applied to Na₂O-B₂O₃-Al₂O₃-SiO₂ bonding glass for cubic boron nitride grinding tools was studied. The bending strength of the specimens was tested by three-point bending strength tester and microstructure characteristics of specimens were observed by scanning electron microscopy. Thermal expansion coefficient of bonding glass was tested by high-temperature dilatometer. The results presented that the type of flux had a great effect on the performance of vitrified bond grinding specimens. The refractoriness, fluidity and wettability were improved with the introduction of F⁻ ions no matter in the form of Na₃AlF₆ or CaF₂. Better properties of vitrified bond, such as refractoriness, fluidity and wettability, could be obtained when F⁻ ions was introduced in the form of Na₃AlF₆, however, the mechanical properties of specimens was better when CaF₂ was introduced owing to the feasible expansion value of bonding glass with CaF₂. Therefore, the selection of appropriate resource of F⁻ was determined by various properties of vitrified bond.

Key Words: Cubic boron nitride composites, Bonding glass, Fracture, Mechanical characterization.

INTRODUCTION

Cubic boron nitride (CBN) is a kind of excellent performance and versatile super-hard abrasive materials¹. Due to the eminent performance of cubic boron nitride material, the grinding wheels, made from cubic boron nitride material, are widely applied to grinding for superhard materials, ceramics, glass *etc.*². Compared with tradition grinding wheels, cubic boron nitride grinding wheels are characterized with high speed, high efficiency, high precision, low grinding cost, low environmental pollution³. Therefore, cubic boron nitride grinding tools have a promising demand in the grinding industry.

Cubic boron nitride grinding wheels are composed of cubic boron nitride abrasive grains and bonding matrix. The common bonding materials include metal, resin, vitrified glass and electro-plated⁴. Compared with the other binders, vitrified bond are superior in some aspects, such as lower fracture toughness, higher strength and better self-dressing capability^{5,6}. Owing to the excellent properties above, vitrified bond cubic boron nitride grinding wheels are widely used in modern engineering applications⁷⁻⁹. As to vitrified bond cubic boron nitride grinding tools, it is essential for the cubic boron nitride grains to be embedded in the bonding glass so that they are retained under the forces and temperatures occurring in the grinding zone¹⁰.

Vitrified bond, as a part of cubic boron nitride abrasive wheels, the properties of which determine the performance of cubic boron nitride abrasive wheels. However, there are still challenges to obtain optimal performance, *e.g.* adaptive refractoriness, calculated chemical durability, suited interfacial strength, *etc.* Therefore, in recent years more and more attentions were paid to investigate the properties of vitrified bond, including the study of basic vitrified bond and the effects of additions on the basic vitrified bond. As for the latter, previous studies generally focus on the effects of alkaline or alkaline-earth metal oxides on the properties of vitrified bond¹¹⁻¹². However, only a few studies are reported on the influence of fluoride as flux on the properties of vitrified bond, not to mention the comparison of different F⁻ ions resources on it.

In this work, Na₂O-B₂O₃-Al₂O₃-SiO₂ vitrified bonds with and without F⁻ were prepared. The influences of F⁻ ions in the form of cryolite and fluorite added to Na₂O-B₂O₃-Al₂O₃-SiO₂ vitrified bond system were studied.

EXPERIMENTAL

Vitrified bond of Na₂O-B₂O₃-Al₂O₃-SiO₂ glass system was used for vitrified bond cubic boron nitride grinding wheels. The basic vitrified bond was obtained in the following procedures. Firstly, the raw materials were finely pulverized and

completely blended by means of ball milling for 8 h. Then the mixture were fired at 1300 °C for 4 h and cooled in ice water. Lastly, the glass was dried, crushed and seized. A part of basic vitrified bond introduced F⁻ ions in the form of Na₃AlF₆ and CaF₂ individually, to which was added either 4 wt. % or 8 wt. %. The vitrified bond with and without the above additives were uniaxially pressed into tapered columns and cylinders, which were sintered in an electric furnace used for measuring refractoriness and fluidity. Measurements of the wetting angle were obtained using high-temperature microscope (EM201) by applying the sessile drop method in air. The linear thermal expansion coefficient of the vitrified bond was determined with a high-temperature dilatometer (Netzsch DIL 402C, Germany) at a heating rate of 5 °C/min in air.

Green specimens prepared by mixing with cubic boron nitride grains, vitrified bond and temporary bond, were pre-pressed to shape the rectangle bars with a dimension of 30 mm × 6 mm × 4 mm. The specimens were sintered at the temperature of 760, 780, 800, 820 and 840 °C respectively at a heating rate of 5 °C/min, up to the sintering temperature holding for 2 h and then cooled to the room temperature naturally. Bending strength of the specimens was tested by C158ASTMinMTS machine at a cross-head speed of 0.6 mm/min. The microstructures of the fracture surfaces of specimens were evaluated by scanning electron microscope (Phillips XL30) at an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Refractoriness: Refractoriness is one of the important factors to estimate the sintering temperature of cubic boron nitride abrasive grinding tools, so obtaining the accurate refractoriness data is of great necessary. In this work, the elements fluoride was introduced into the basic vitrified bond system with various resources and different contents. F⁻ ions was imported by Na₃AlF₆ and CaF₂ respectively. Fig. 1 showed the refractoriness of vitrified bond with and without addition of Na₃AlF₆ or CaF₂. It was clear that F⁻ whether in the form of Na₃AlF₆ or CaF₂ had great effect on refractoriness of vitrified bond. The refractoriness of vitrified bond decreased with the introduction of F⁻ ions no matter whether in the form of Na₃AlF₆ or CaF₂. Moreover, the degree of refractoriness reduction was connected with the amount of F⁻ ions, it was visible that the refractoriness decreased gradually with the increasing of F⁻ ions no matter as Na₃AlF₆ or CaF₂. That was because F⁻ ions, in bonding glass, broke down the Si-O tetrahedron by means of making the original bridge oxygen change into non-bridging oxygen. Especially, the saturation price would come into being when F⁻ ions dissolved the network, which caused the network no longer being linked together. And more F⁻ ions could dissolve the liquid-like network more acutely. Therefore, it made the structure of glass network become loose and the melting point reduce.

Meanwhile, resources of F⁻ ions affected the refractoriness of vitrified bond in varying degrees. Fig. 1 also revealed that the vitrified bond containing F⁻ ions in form of Na₃AlF₆, as opposed to intermingling with F⁻ ions in the form of CaF₂, had lower refractoriness when the content of Na₃AlF₆ or CaF₂ was equal. Refractoriness of vitrified bond reduced by 61 °C

when the introduction of Na₃AlF₆ reached 8 wt. % while refractoriness of bonding glass with the same quality of CaF₂ reduced only by 16 °C. That's because Ca²⁺ characterized with higher electric-field intensity played the role of aggregation, which could make the structure of bonding glass compact to a certain extent. Moreover, Na₃AlF₆ would import more F⁻ ions when the mass of the two additions kept equal, which also led to melting point reduce more acutely. Consequently, when F⁻ ions were introduced into the glass network, glass-fused temperature would decrease to some extent, besides, the effect of Na₃AlF₆ on refractoriness was more obvious than that of CaF₂.

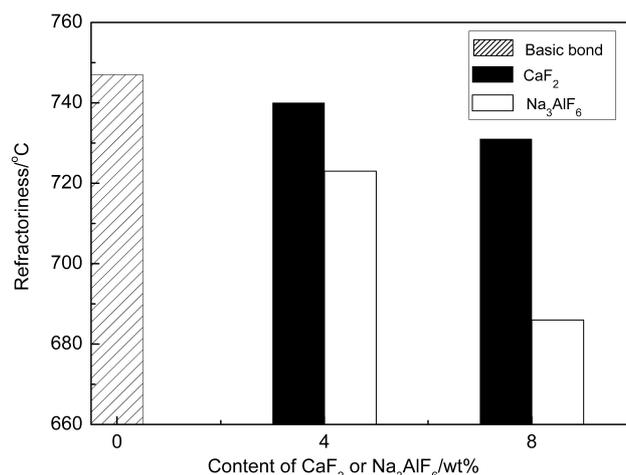


Fig. 1. Refractoriness of vitrified bond with different content of Na₃AlF₆ or CaF₂

Fluidity and wettability: It had been proved that vitrified bond with satisfying fluidity and wettability were beneficial to obtain excellent performance abrasive tools owing to the formation of strong bond bridges between abrasive grains¹³. Optimal high temperature fluidity and wetting behaviour in liquid glass and solid cubic boron nitride systems was critical for improving the interface performance. In this study, higher fluidity and perfect wettability were obtained by introducing F⁻ ions no matter in the form of Na₃AlF₆ or CaF₂. Fig. 2, showed the fluidity and wettability of the vitrified bond with addition of Na₃AlF₆ or CaF₂ at the same temperature respectively. From Fig. 2a, it was obvious that Na₃AlF₆ and CaF₂ could improve the fluidity of vitrified bond, the fluidity increased from 118.04 to 131.75 % when CaF₂ was introduced, while the fluidity increased to 183.75 % when Na₃AlF₆ was imported. As to wettability, the wetting angle, a common characteristic of solid-liquid-vapour system, was widely used for measuring the degree of wetting properties^{14,15}. The glass with a lower wetting angle presented better wetting ability. It could be seen (Fig. 2b) that there was a good surface wettability of the glass on the cubic boron nitride substrate. From Fig. 2, we could draw a conclusion that fluidity and wettability were related with the content of F⁻ ions and the resources of F⁻ ions. With the increasing of the content of F⁻ ions, the fluidity increased while the wetting angle decreased, in other words, the fluidity and wettability of vitrified bond were improved. Besides, the vitrified bond added Na₃AlF₆ processed better fluidity and wettability than that of CaF₂ when the mass of additives was equal.

On comparing the Fig. 1 with Fig. 2, it was clear that the fluidity and wettability were correlative with refractoriness, the vitrified bond with lower refractoriness had higher fluidity and wettability. Just like the effect on refractoriness, Na_3AlF_6 had greater influence on fluidity over CaF_2 . The reason was similar to that of the refractoriness. According to the analysis of refractoriness, the vitrified bond with addition of CaF_2 had denser structure compared to that of Na_3AlF_6 owing to the aggregation of Ca^{2+} in the bonding glass network.

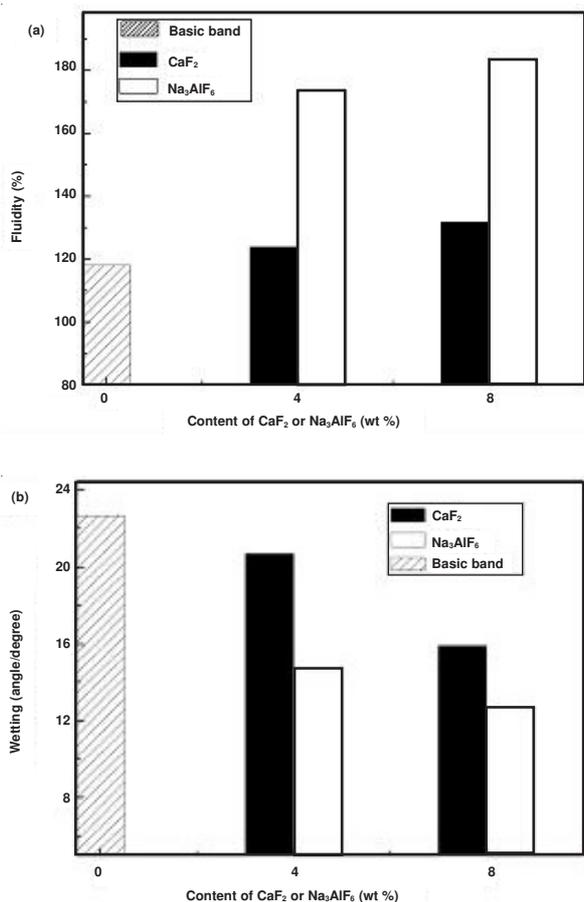


Fig. 2. Fluidity and wettability of vitrified bond with different contents of Na_3AlF_6 or CaF_2 : (a) fluidity; (b) wettability

Bending strength: The main factor affecting bending strength of cubic boron nitride grinding wheels was the properties of bonding glass. The bending strength of samples with different vitrified bond at various temperatures were shown in Figs. 3a and 3b. It was obvious that F^- ions had great influence on the bending strength of samples, with the increasing of F^- ions no matter in the form of Na_3AlF_6 or CaF_2 , the mechanical properties of cubic boron nitride grinding samples increased. From Fig. 3a, it is clear that Na_3AlF_6 could enhance the bending strength of the samples. The maximum value of bending strength increased from 50.8 to 56.8 MPa with the addition of Na_3AlF_6 . Fig. 3b showed the influence of CaF_2 on the strength of the samples, the maximum value increased by 15 MPa. Compared Fig. 3a with Fig. 3b, the different resources of F^- influenced the bending strength in different degree, the maximum value of samples with CaF_2 was higher than the samples with Na_3AlF_6 .

From all the above studies, the samples with addition of CaF_2 showed the more satisfying bending strength although bonding glass with Na_3AlF_6 showed better fluidity and wettability. This might attribute to bonding glass with CaF_2 exhibited relatively feasible expansion value. Consequently, in order to obtain excellent performance cubic boron nitride grinding wheel, all related properties of bonding glass should be considered.

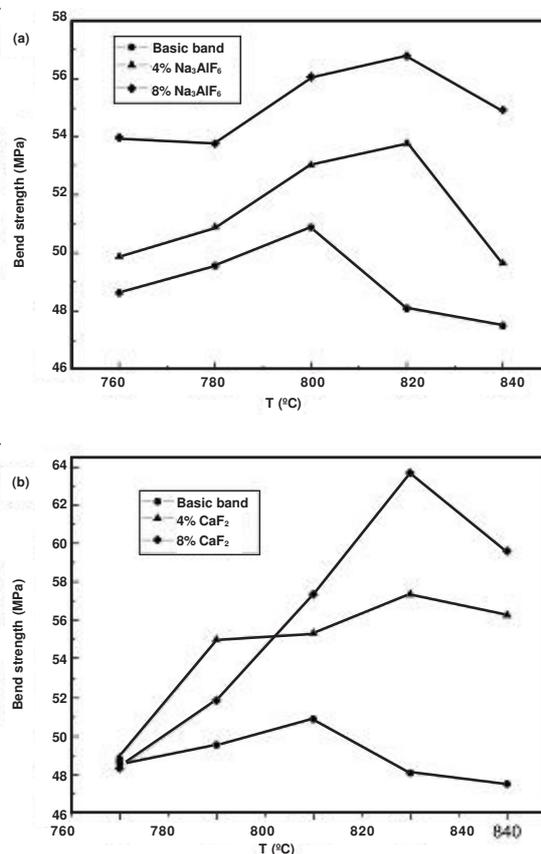


Fig. 3. Bending strength of samples with different contents of Na_3AlF_6 or CaF_2 at various temperatures: (a) with Na_3AlF_6 ; (b) with CaF_2

Thermal expansion coefficient: Thermal expansion coefficient is an important parameter for vitrified bond grinding tools. The performances of cubic boron nitride grinding tools could be improved if the thermal expansion coefficient of bonding glass was approximate with that of cubic boron nitride abrasive grains. In order to obtain good adhesion between the vitrified bond and the abrasive grain, ideally, the thermal expansion coefficient should keep the same, because thermal matching avoids stresses forming at interfaces when the grinding wheel cools after firing. In order to figure out the reason why samples with CaF_2 possessed more excellent mechanical properties, the thermal expansion coefficient of bonding glass with 8 wt % CaF_2 was tested. The average coefficient of thermal expansion coefficient in the range of temperatures from 50 to 650 °C was $5.56 \times 10^{-6}/^\circ\text{C}$, which matched with the thermal expansion value of cubic boron nitride abrasives ($3.5 \times 10^{-6}/^\circ\text{C}$) well (Fig. 4). As a result, owing to bonding glass with 8 wt % CaF_2 exhibited relatively feasible expansion value, the mechanical properties of the vitrified bond grinding samples was strengthened.

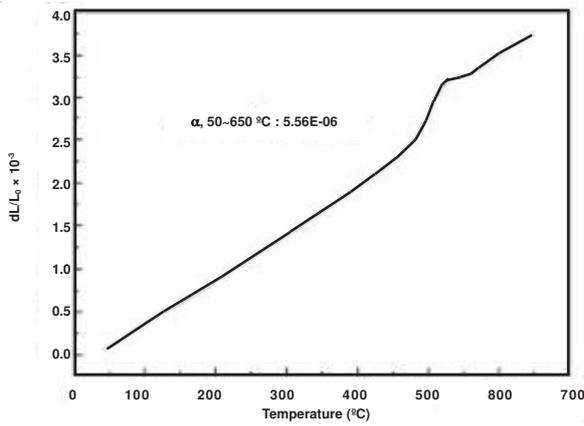


Fig. 4. Thermal expansion coefficient of bonding glass with 8 wt % CaF₂

Microstructure: In order to study the bonding state between the vitrified bond and cubic boron nitride abrasive grains, fracture surfaces of samples were observed by using scanning electron microscopy (SEM). Fig. 5(a-f) showed the fracture surfaces micrograph of samples with various bonding glasses. The state of the connection between abrasive grains and bonding glass could be seen from Fig. 5a. In order to obtain the outstanding properties of samples, abrasive grains should be fully coated by bonding glass. Meanwhile, the denser the bond bridge was, the more excellent the performance of vitrified bond cubic boron nitride grinding wheels would be. Compared with samples with basic bonding glass (Fig. 5b), the fracture surface of samples with the addition of F⁻ ions (Fig. 5c-f) exhibited smaller pores and more denser structure. The effect was much more obvious with the increasing of the addition of F⁻ ions no matter whether in the form of Na₃AlF₆ or

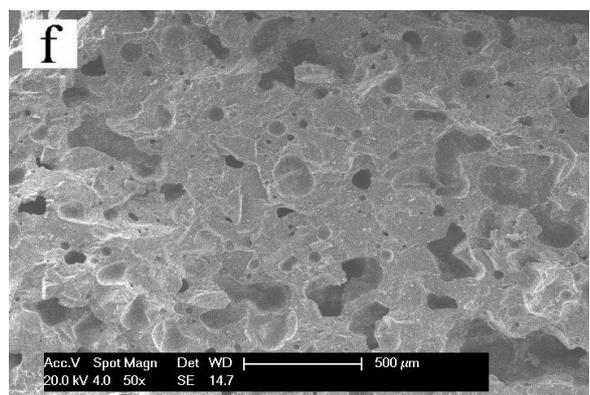
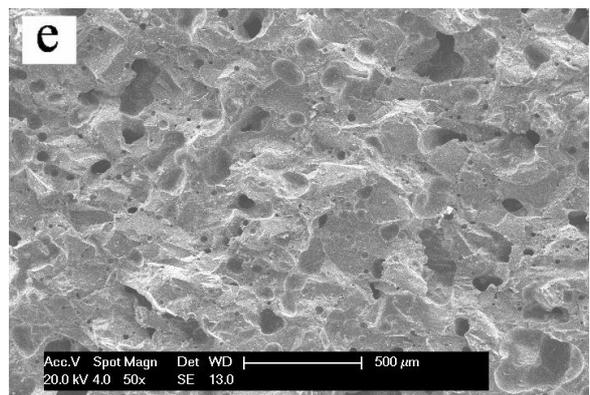
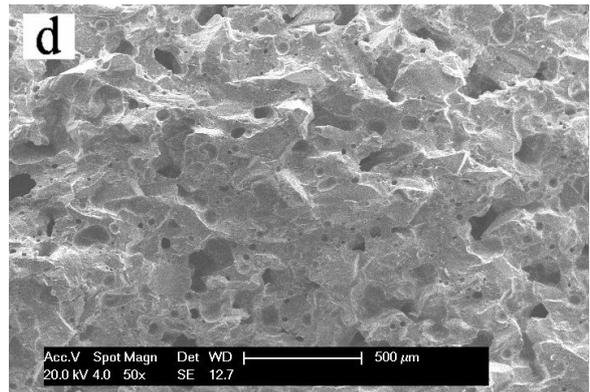
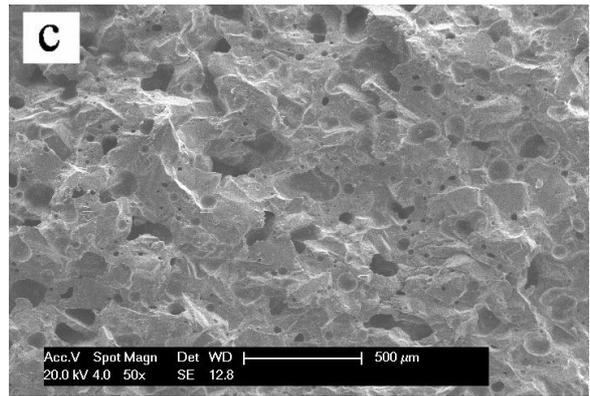
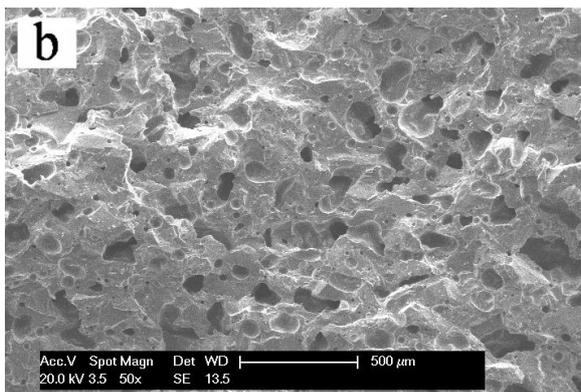
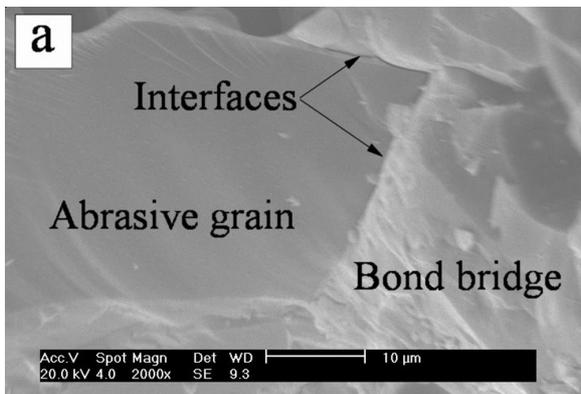


Fig. 5. Microstructure of samples with different contents of Na₃AlF₆ or CaF₂ sintered at optimal temperature; (a) 0 % F⁻; (b) 0 % F⁻; (c) 4 % Na₃AlF₆; (d) 8 % Na₃AlF₆; (e) 4 % CaF₂; (f) 8 % CaF₂

CaF₂. Besides, the structure of the samples with CaF₂ (Fig. 5e,f) was more compact than the samples with Na₃AlF₆ (Fig. 5c,d), evenly, cubic boron nitride abrasive grains was covered

fully. That, on the other way, explained why the samples with CaF_2 had better mechanical properties over the samples with Na_3AlF_6 .

Conclusion

In order to obtain appropriate bonding glass, the effect of F^- ions as flux applied to glass bonding system in the form of Na_3AlF_6 and CaF_2 was investigated. In this study, glass binder with different form of F^- ions in various contents were chosen to make a series of experiments. According to the analysis, the introduction of F^- ions was beneficial to the performances of the glass binder for the cubic boron nitride grinding wheels, such as reducing refractoriness, boosting fluidity and wettability. Moreover, the influence of Na_3AlF_6 on the vitrified bond in above aspects was more obvious than CaF_2 .

Although the glass bonding with the introduction of CaF_2 characterized with a little higher refractoriness and lower fluidity, presented proper thermal expansion coefficient, which was benefited for the performance improvement of the vitrified bond cubic boron nitride grinding tools. As a result, the function of CaF_2 as flux in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ system vitrified bond for cubic boron nitride grinding wheels was more remarkable than that of Na_3AlF_6 . Besides, in order to obtain excellent performance cubic boron nitride grinding wheel, all related properties of bonding glass should be considered.

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