Optica Applicata, Vol. XXX, No. 4, 2000

Effect of adding Vycor-type microporous glass to the glass of $PbO–ZnO–B_2O_3$ system

BARBARA STANIEWICZ-BRUDNIK, KAZIMIERA MAJEWSKA-ALBIN

Institute of Metal Cutting, ul. Wrocławska 37A, 30–011 Kraków, Poland.

BERNARDETA PROCYK

University of Mining and Metallurgy, al. Mickiewicza 30, 30–059 Kraków, Poland.

The paper presents the results of investigation on the physicochemical properties of lead -zinc-boron system intended for use as vitrified bonds for cubic boron nitride (cBN) tools in which the glass of sodium-aluminium-borosilicon system is applied as a modified filler. For investigation purposes the following techniques were employed: DTA, XRD, and helium pycnometry, EDAX, scanning microscopy with EDS microanalysis and capillary condensation of nitrogen. The sinters tested have been found useful as vitrified bonds for cubic boron nitride tools. The addition of microporous glass in an amount of 1% by vol. has the most favourable effect on the mechanical parameters of sinters.

1. Introduction

The glasses of the $PbO–ZnO–B_2O_3$ system characterised by specific physicochemical properties (low-melting temperature < 1200 °C, low TLEC coefficient $< 5 \times 10^{-6}$ 1/deg, good wettability of the cBN substrate $\Theta < 30$ °) were applied to the vitrified bonds meant for tools of extra-hard materials (diamond, cubic boron nitride) [1]–[4].

The vitrified bonds include multicomponent glass systems and their devitrificates. The efficiency of their application depends on:

– the chemical constitution determining definite physicochemical properties,

– the way the bond and abrasive grains interact (the possibility of chemical reactions with abrasive grains),

– the type of abrasive grains (mono-, poly- and microcrystalline),

– the method of heat treatment of products.

2. Experimental stage

Two glass sets were selected for investigations:

– the basic set chosen from the $PbO–ZnO–B_2O_3$ glass system used as a bond for cBN tools,

– the modified filler from $Na_2O–Al_2O_3–B_2O_3–SiO_2$ glass system, with variable content of particular oxides and with small additions of manganese oxide, zirconium oxide and vanadium oxide.

The glasses were synthesised from high purity raw materials and were melted in the corundum crucibles at 1250 °C. Eight glasses were obtained and five sets were taken for the research (Tab. 1). The obtained glasses were absolutely transparent and light green coloured.

Table 1. Chemical constitution of oxides of the basic glass system (mol%).

Basic oxides	1	2	3	4	5
ZnO	58	56	55	53	50
PbO	14	12	10	8	6
B_2O_3	25	25	25	25	25
SiO_2	2	6	9	13	18
Li_2O	1	1	1	1	1

The following glass properties were taken into account:
- density (helium pycnometry method),
- microhardness (Vickers method),
- bond strength (Zwick 1435 machine),
- TLEC coefficient during heating and cooling,
- wettability of the cBN and corrundum substrate.

The microporous glass of the Na_2O–Al_2O_3–B_2O_3–SiO_2 system used for modification of the mechanical properties of vitrified bond has the following parameters:
- density 2.2795 g/cm^3,
- TLEC 4.5×10^{-6} 1/deg,
- microhardness HV 4.5 GPa,
- bond strength 70.5 MPa,
- Young's modulus 69.5 GPa,

In order to obtain the microporous glass the initial material was subjected to additional heat treatment at 575 °C for 24 hours. During this process the glass underwent strong turbidity as a result of separating the borate (precipitation of sodium borate). The occurring heterogeneity have a drop character with the tendency for coalescence. The occurrence of simultaneous binodal and spinodal decompositions can be observed in this glass. Next, the glass was crushed and subjected to hot chemical treatment in the 1 mol/l HCl solution for 4 hours to leach the precipitated borate phase. The glass powders obtained in this way add the specific surface area of 105 m^2/g, the average pore diameter of 3.76 nm and micropore volume of 28.7 m^2/g.

3. Results and discussion

The results of the investigation are compared in Table 2 (at the average from 3 to 10 measurements dependent on properties of glass system). The difference between TLEC coefficients did not exceed 10%.

Table 2. The sets of selected properties of glass systems.

No. of glass	Density [g/cm^3]	T_{melt} [°C]	TLEC × 10^{-6} [1/deg]	R_{sg} [MPa]	HV [GPa]	Θ cBN substrate [deg]
1	4.462	695	3.8–5.1	40	2.0	22
2	4.542	850	3.5–4.8	48	3.4	30
3	4.361	790	4.6–6.5	46	2.8	25
4	5.350	900	2.0–16	49	3.2	19
5	5.911	900	3.0–19	53	3.6	24

3.1. Structural investigation – DTA

The DTA investigation was carried out on the glass sample, using the derivatograph instrument with heating speed 10 °C/min. from room temperature to melting point.

The course of DTA diagrams give the following information about the thermal effects:

– one endothermic effect caused by the transformation, exhibiting as a beginning of declination from the basic line characterized by the following temperatures: 520, 530, 535, 530, 525 °C,

– the second endothermic effect connected with the dilatometric soft point and characterized by the following temperatures: 560, 565, 590, 600, 590 °C,

– egzothermic effect resulting from the sintering, characterized by the following temperatures: 700 645, 640, 640, 630 °C.

3.2. Investigation on wettability

Good wettability of the grains to the bonds is a factor which determines glass applicability for abrasive tools. It also induces the formation of strong bridges between individual grains. The lower the value of the extreme wetting, the better the wettability. It was assumed that the value of Θ should be lower than 30°. That would provide better adhesion of the bond to the grain surface, enhancing thus the binding power of the bridges. The measurements of the wetting angle were carried out using a high temperature microscope of Leitz-Wentzler type, by means of the drop sessile method, in the air atmosphere [4].

Table 3. Wettability of the basic glass systems of the borazon substrate and with the addition of microporous glasses.

Wettability [°]				
No. of glass	Basic glass	Addition of microporous glasses [% by vol.]		
		1	2	3
1	22	28	34	36
2	30	34	38	40
3	25	29	33	39
4	19	26	31	32
5	24	30	35	42

The electrocorundum and borazon substrates (cleaned earlier in the bath) were used for the investigation. The samples had cubic shape ($a = 3$ mm). The results are shown in Tab. 3. All of the glass systems under investigation had very good wettability of electrocorundum and borazon substrates ($\Theta < 22-30°$) and the addition of microporous glass (1, 2, 3 % by vol.) increased the temperature at which the value of the extreme wetting angle was the lowest (temperature increase of about 15–20 °C) without changing its minimal value ($\Theta < 34$).

3.3. Investigation of the grain boundary phase

The range of chemical reaction of vitrified bond and extrahard grain is the more accurate evaluation criterion for the choice of vitrified bond during heat treatment. The cohesive bond strength of vitrified bond and strength of grain–bond interafce decide about the bond strength of the abrasive sinter.

The interface layers, forming on the boundary phase, determine the degree of interaction between vitrified bond and abrasive grain from extrahard materials. For the investigation of the grain boundary phase phenomena the scanning microscope with EDS microanalysis of the fresh fracture vitrified bond-substrate was applied. The results of the observations are shown in Fig. 1 (**a**–**f**).

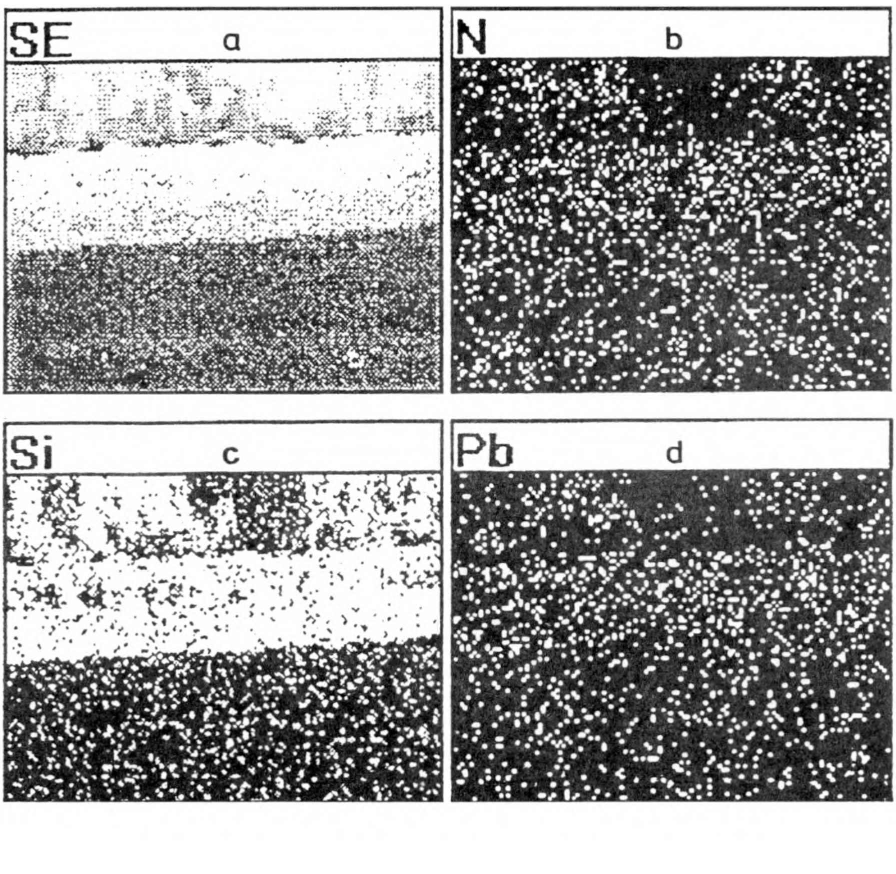

Fig. 1**a**–**d**

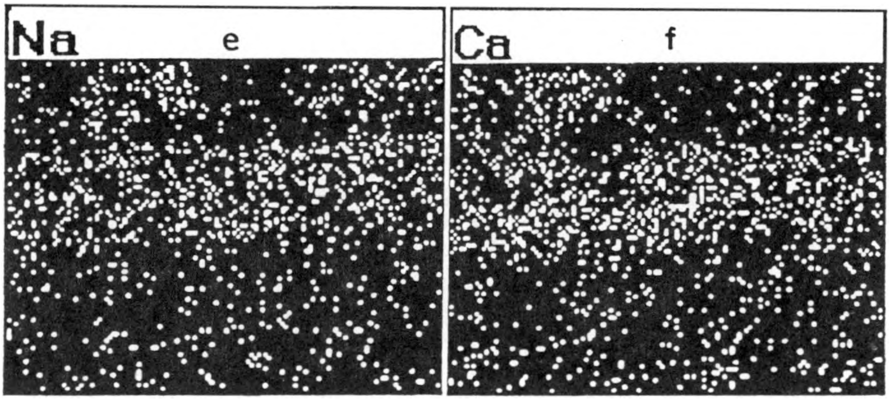

Fig. 1. Scanning electron image of the fresh fracture of the glass No. 2 — borazon substrate (a), and microanalysis of N (b), Si (c), Pb (d), Na (e), and Ca (f).

The observations show that either in the case of electrocorundum substrate, both the clear intermediate zones and consolidation of the substrate structure with strongly marked pores presence can be seen. The results obtained testify to the occurrence of strong reaction between vitrified bond and substrate. A detailed analysis confirms these observations.

3.4. Mechnical properties of glass system

Small amounts (1, 2, 3 % by vol.) of the microporous glass were added in order to enhance the general strength of the sintered samples. The microhardness and bond strength of glass were investigated (Figs. 2, 3). The measurements were carried out on the samples of 10×8 mm and sticks ($50 \times 4 \times 4$ mm) cleaned earlier with the use of cerium oxide. All the results are compared in Tab. 2. The evident influence of the addition of microporous glass on the vitrified bond strength was observed. Its amount of about 1% by vol. enhanced the sinter strength from 46 to 68 MPa. Further increase of microporous glass content did not change the strength value of the sinter.

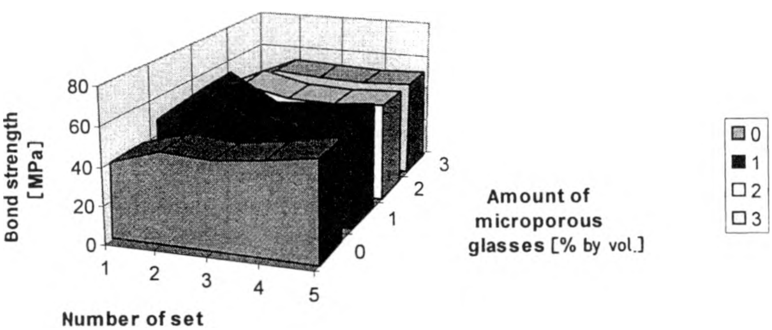

Fig. 2. Bond strength of glass versus the amount of microporous glasses.

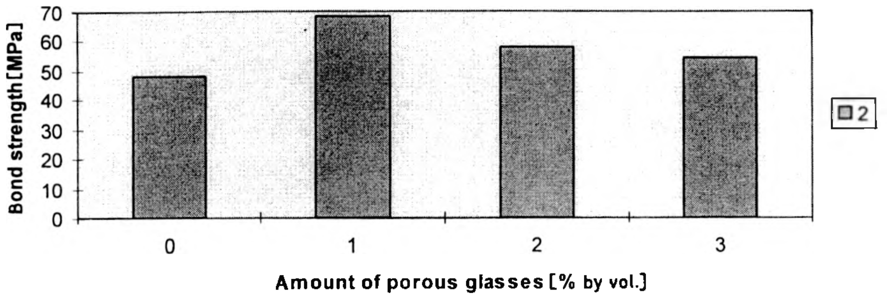

Fig. 3. Bond strength of glass versus the amount of porous glasses for set 2

4. Conclusions

Based on resuts of investigations the follwing conclusions can be drawn:

1. The sinters we have tested can find application as vitrified binders for cubic boron nitride tools.

2. Sinters of the basic glass system and sinters with the addition of a microporous glass, used as a as modified filler have good wettability of borazon and electrocorundum substrates. In all the cases the wetting angle was smaller than 30°.

3. The addition of microporous glass in an amount 1% by vol. has the most favourable effect on the mechanical parameters of the sinters.

4. Sinters of both the basic glass and those containing the microporous glass fulfil the usability criterion as a binding material for cBN tools since their properties such as:

– basic glass microhardness is 3.6 GPa, while the microhardness of sinter containing microporous glass is 5.5 – 6.0 GPa,

– bond strength of basic glass is 48 MPa, while the bond strength containing microporous glass is 68 MPa,

– TLEC coefficient $(3.8-5.1)\times 10^{-6}$ 1/deg (set 2),

– wettability (borazon substrate) 22°,

are better than assumed.

Acknowledgments – The work was partly supported by the State Committe for Scientific Research (KBN), Poland, under projects: 7 S 201, 005 007 and 7 T08D 034 13.

References

[1] STANIEWICZ-BRUDNIK B., MAJEWSKA-ALBIN K., KŁAPUT E., *et al.*, Szkło i Ceramika, No. 1 (2000), 4 (in Polish).

[2] STANIEWICZ-BRUDNIK B., MAJEWSKA-ALBIN K., PROCYK B., *Some aspects of crystallizations in the glasses of the* $ZnO–B_2O_3–SiO_2–PbO–Li_2O$ *system assigned as vitrified bonds for tools of superhard materials*, [In] Intern. Symp. on Glass Problems, Istanbul (Turkey, September 4–6, 1996, Vol. 2, p. 192.

[3] STANIEWICZ-BRUDNIK B., MAJEWSKA-ALBIN K., PROCYK B., STOCH. L., *The glasses of PbO–ZnO–B_2O_3–SiO_2 system with addition of microporous glasses as the components of binders for cBN tools*, [In] Proc. 17th Intern. Congress on Glass, Beijing (China), 1995, Vol. 5. p. 441.
[4] NOVOSELOVA I.A., Sverhtverdye Materialy, No. 6 (1996), 43 (in Russian).
[5] PROCYK B., STOCH L., KIELSKI A., WODNICKA K., *Microporous glasses for proecological applications*, [In] Proc. Intern. Conf. Exhib. Kraków 2000, p. 165.

Received September 18, 2000