

THE DEVELOPMENT OF VITREOUS COUPLING AGENTS USED FOR THE PRODUCTION OF ABRASIVE TOOLS

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Abstract

The interaction process of glass with cubic boron nitride has been studied under dynamic and isothermal conditions. It has been revealed that the interaction of molding glass with β BN is accompanied by the glass crystallization. The beginning of the crystallization process is demonstrated by anomalous change of the glass viscosity within the temperature range of 420-440°C. The study of microstructure has discovered that the formation of crystalline phase on the interface of "melt – β BN" suppresses the abrasive oxidation.

Key words: diamond, boron nitride, glass, crystallization, borosilicate

INTRODUCTION

Development of new glassy and glass-ceramic materials used in the preparation of cutting compositions along with ensuring optimal characteristics and a predetermined structure is a very important goal of science of materials. The processes occurring at the interfaces with the interaction of glass and super hard material largely determine not only the mechanical properties, but also the conditions of formation of composite materials.¹

Reducing the speed of interaction between the components of the composite at high temperatures is a difficult task, since the system " β BN - glass" activation barriers are easily overcome due to the softened glass high aggressiveness. Therefore, to reduce the driving force of the interaction between the abrasive and oxidation should simultaneously with the initial softening at the glass coating β BN implement directed parallel to form a glass crystallization pyro-ceramics coating. The main objective in this study is to ensure minimum interaction zone to produce a durable junction devoid of residual stress.²

The proposed project is aimed at the synthesis of glass-like binding materials with low soldering and sintering temperature for making grinding tools. In order to reduce the reaction temperature in powder systems of C(β BN) - glass-like binding materials - inert filler type and to change the mechanism of interaction at the melt - solid interface, it is proposed to use a mixture of low-melting and high-melting sintered glasses with certain physical and mechanical parameters.

To create a solid for β BN glass, and further the layer was pyroceramics glass system used fluorine $B_2O_3-SiO_2-AlF_3-Me_2O$ (MeF); Me-Zn,Ca; Me-Li, K, Na). To initiate the crystallization process of the glass batch was administered from 2.0 to 7.5 % of calcium fluoride wt.

The main issue during composite materials synthesis is the ability to control the processes of physical and chemical interaction at the interface glass - abrasive. Differences in the chemical potentials of the elements that make up the composite, directs the flow of the atoms, causing diffusion phenomenon, diffusion reaction, and a large thickness of interaction zone $\sim 0.5 - 3.0$ microns. Oxidation of the abrasive particles at high temperature heat treatment reduces the strength of particles and reduction of grain strength retention.

¹ Polyanskaya, N. D. (1982), Shilo, A. E. (1988)

² Gordeev, I. S., Ordanyan, S. S. (2012)

Strong adhesion composition components in liquid-phase sintering materials in the presence of glassy phase can only be achieved with good wetting of softened solids or melted glass, which precedes the processes of dissolution and diffusion. Hence the problem of obtaining composites, the structure of which is reduced the transition layer "fiberglass -abrasive" as much as possible, with high mechanical characteristics. To reduce the aggressiveness of the melt glass the parallel ongoing process of sintering and composite components ceramisation had been done.

EXPERIMENTAL PART RESULTS AND DISCUSSION

Glass ceramic materials obtained directionally solidified glasses are microheterogen polycrystalline materials, in which the crystalline phase composition concentration can vary over a wide range (from 30% or more). Metastable glass composition can bring phase separation of the crystalline phase to the glass composition and simultaneously facilitate the formation of a phase boundaries. During the transition of the original microliquid glass to crystalline structure the material properties are being changed, especially the coefficient of linear expansion is changing dramatically. Also changes the softening temperature of the residual glass phase, mechanical properties, etc.

In borosilicate glass-forming systems the availability of metastable phase separation phenomenon determines the formation in the microstructure of the glass phase boundaries. This phenomenon facilitates the occurrence of crystal nuclei and promotes the flow of the process more intensive directional crystallization of glass during its heating.³For the synthesis of glasses with low softening temperature composition was chosen, which lies on the border of fields crystallization metaborate and sodium metasilicate. The total number of input alkali oxides was 28.5%. A clear glass content of up to 2.5% CaF_2 , then turn opalescent, and the introduction of more than 4.5% CaF_2 - intensive jamming glass came out.

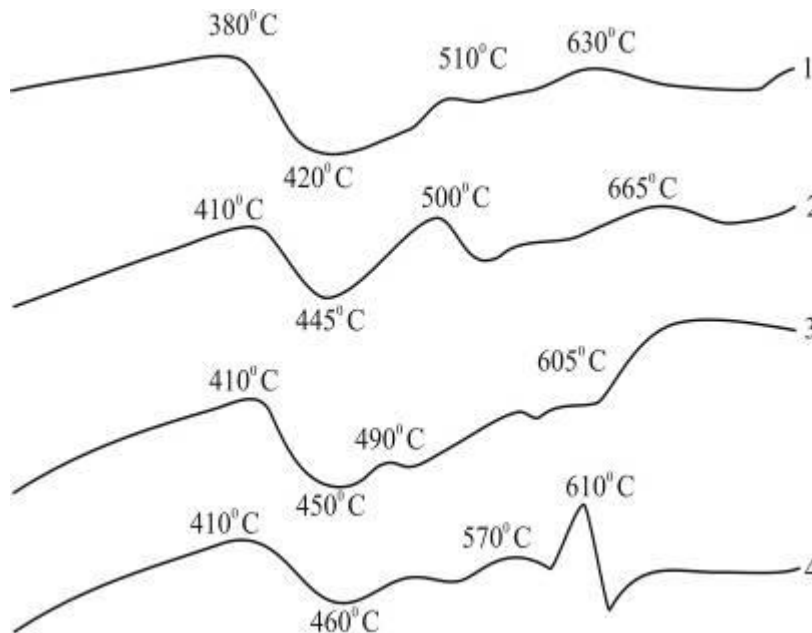


Fig. 1. Thermograms of glasses and compositions:

1. glass BA-3(2,5 % CaF_2), 2. glass BA-3 (5.0 % CaF_2), 3. glass BA-3 (50 %), βBN -(50 %), 4. glass BA-3(49.5 %), βBN -(49.5 %) Al-1.0% .

³ Sarkisov, P. J. (2003)

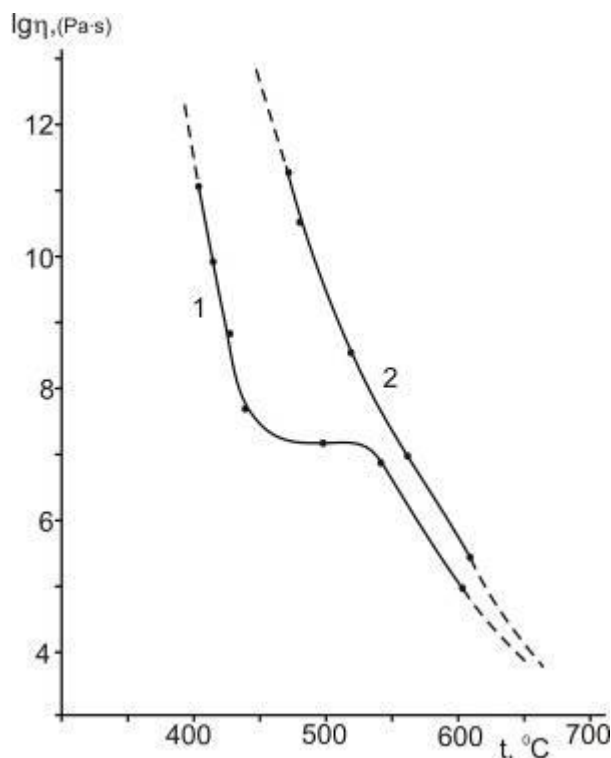


Fig. 2. Temperature dependence of the composition № 3 during heating (1) and cooling (2).

To the study the interaction of borosilicate glass with β NB during heat treatment method of DTA has been applied. As a result of the DTA studied composition can be divided into two groups. In the first group compositions do not appear exoeffect glass crystallization (the content of $B_2O_3 > 35\%$ $CaF_2 \leq 2,0\%$) on the DTA curves. These compositions are characterized by high content of B_2O_3 . The absence of crystal formation in these new formulations during heat treatment confirmed by XRD of the samples treated by the method of mass crystallization. A characteristic feature of the rest of the composition is the presence of exothermic peak of crystallization, following the thermal effect, manifested as a result of the glass matrix composition softening (Fig.1. 1.cr.3 and 4). In the DTA curves of glasses containing 2.5 and 5.0% CaF_2 (Fig.1 cr.1i 2), the formation of the exothermic effect in the region 500-510 °C, testifying to the crystallization of one phase.

Endoeffect at 600-610 °C associated with a liquidus temperature of the system. In the DTA curve of the composite containing 50% glass BA-3 and 50% β BN (Fig.1cr.3) glass crystallization thermoeffect is shifted to the low-temperature region by 10 °C, which appears to be associated with the formation of phase boundaries at stirring the starting composition components. To reduce oxidation effects of atmospheric oxygen on β NB the 1.0% aluminum was introduced in one of the compositions. DTA of the mixture (Fig.1.kr.4) has a broad area of the glass transformation temperature and a pronounced exothermal with a maximum at 610 °C. The positive effect of the metal introduced in the process of sintering and an abrasive protection from oxidation confirms the absence of weight loss the initial mixture during its high-temperature heating. However, a composite material characterized by a high porosity and uneven distribution around the abrasive composite volume.

Structural transformations occurring in the softened glass when the temperature increases, clearly represented in the viscosity change. The crystallization process at continuous heating with thermostatic glass or composite by viscosity measured may have an almost complete character, which makes it possible to determine the process of spreading and glass crystallization viscosity

characteristics⁴. Figure 2 shows the curve of the temperature dependence of the viscosity of the composition based on the jamming glass BA-3, based on the results of measurements of the viscosity by indentation. The analysis of the temperature dependence of the viscosity curve shows that the progress on the part of the curve corresponds to the high-field 400-450°C, viscous flow characteristic of normal fluids. Composite viscosity with increasing temperature is gradually reduced to $\sim 10^7 \cdot 8 \text{ Pa}\cdot\text{s}$. Crystallization expressed extreme change in viscosity at 450-550°C temperatures, causing a break in the viscous flow curve. With further increase of temperature, the crystalline phase melts and viscosity of the composition decreases.

The curve of the temperature dependence of the viscosity is similar to the flow of low viscosity glassy systems. The composition viscosity curve during cooling shows that the increase in viscosity occurs while structuring at $\sim 10^5 \text{ Pa}\cdot\text{s}$, after spreading and coating the particles of βNB with softened glass.

A clearer picture of the nature of phase separation in the glass and morphological characteristics of the composite material depending on the composition and heat treatment temperature was obtained by electron microscope. Figure 3 shows electron microscope images of glass, heat-treated glass and composite materials.

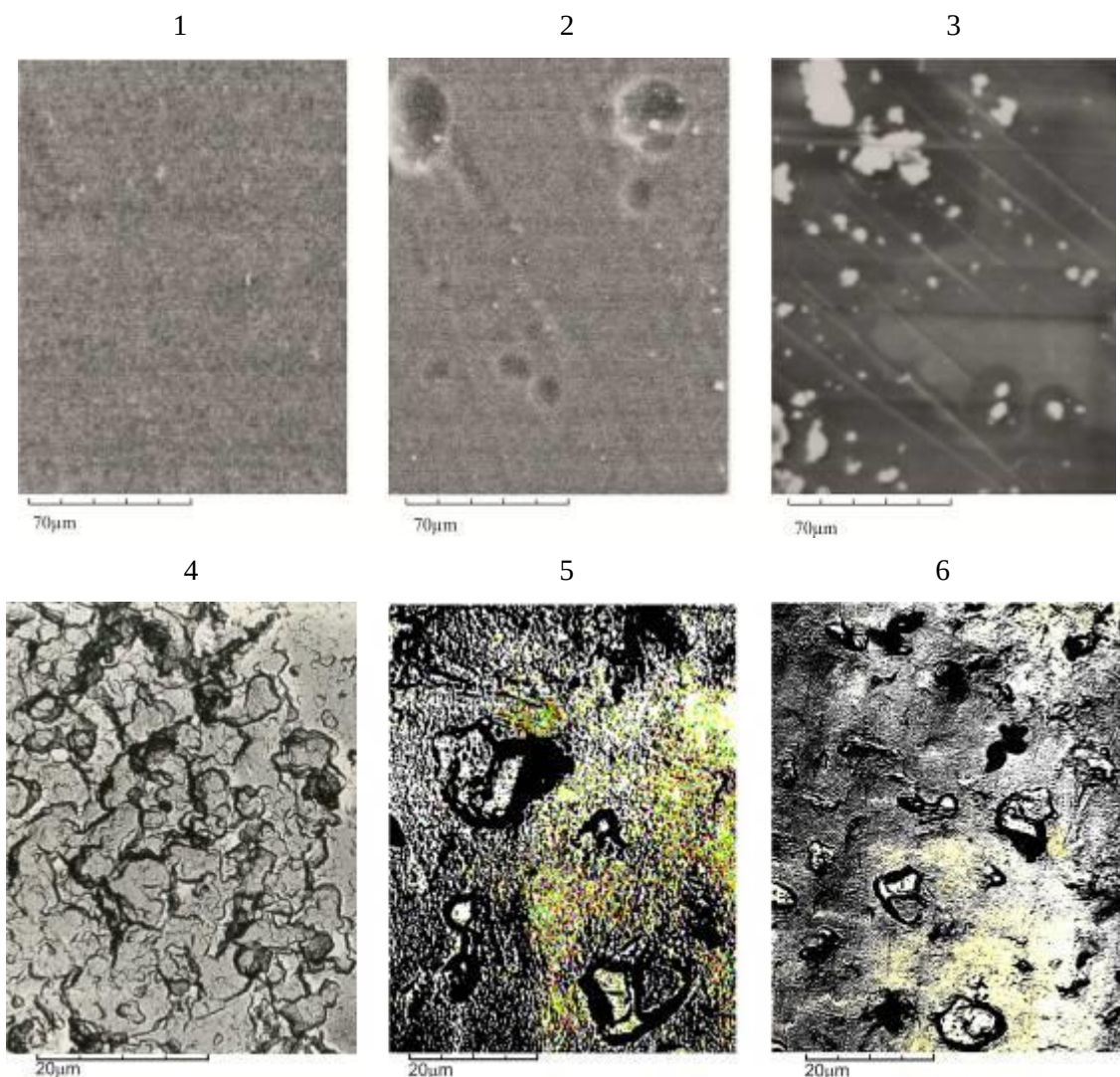


Fig. 3. Microstructure of glasses and composite material “glass- βBN ”.

⁴ Nemilov, S. V. (1992)

1. Initial glass BA-3 without NaF and CaF₂; 2. Glass BA-3 with 3.0 % NaF and 5.0 % CaF₂; 3. Glass BA-3 (3.0 % NaF, 5.0 % CaF₂) – 15 minutes of thermal treatment at 500°C; 4. Glass BA-3 (NaFCaF₂) – 120 minutes of thermal treatment at 500°C; 5. Composition of 50% BA-3, 50% βBN glasses, 60 minutes of sintering at 600°C; 6. Composition of 49.5 % BA-3, 49.5 % βBN, 1%Al glasses, 60 minutes of sintering at 600°C.

Images show that the initial glass (Figure 3.1) of borosilicate composition that does not contain fluoride and NaF of CaF₂, has microinhomogeneous structure and spherical heterogeneities are arranged along straight lines. The microstructure of the glass-containing fluoride represents a two-phase system liquation type. In the picture (Figure 3.2) can be seen portions of phase separation in the form of a droplet phase. This gives us reason to believe that there is not a stable phase separation to form a common interface, but two-phase system without a common border is formed in the form of a droplet phase in the overall matrix. Additional thermal treatment of the glass at a temperature at exothermic peak of DTA curve leads to the formation of partially crystallized glass. Based on a picture (Fig.3.3) crystals distributed throughout the material and separated by a glassy phase. The phase separation is observed with droplet phase of 10 to 40 microns. During prolonged heat treatment at the same temperature (Fig.3.4) sodium metasilicate crystallization enhanced and allocated together with the silicate crystals in a small amount of sodium and potassium metaborate. The crystalline phases, along with a vitreous layer comprise twisted continuous structure of glass-ceramic material. The structures of composites are presented in Figure 3.5 and 3.6. Comparing the microstructure of the glass, the heat-treated, with the structure of composite material (Fig 3.5), a fine structure can be noted in the composite crystallized glass in a two-stage heat treatment. In the picture the formation of pores is not observed, associated with the interaction of the glass. With the boron nitride during prolonged heat treatment. Crystals βBN distributed by glass-ceramic material and practically without of glassy phase.

As a result of X-ray diffraction by thermal treatment glassy bond stands sodium fluoroborosilicate Na₂B [SiO₄] F, and in the long-term heat treatment of the composite along with borosilicate also stands triple fluoroborate of Li₂NaZn(B₃O₆F₂) composition. Thermogravimetric studies of composite showed that during the glass sintering sharply decreases βBN oxidation and weight loss during the heat treatment are reduced almost an magnitude of order. Phase changes, occurring in the process of crystallization of glass, not only determine the change in the morphology of the composite but also its properties change. As seen from the composite microstructure pictures almost no pores formed by reacting as from softened glass with an abrasive as well as a consequence of melting of crushed glass, preventing the exit of air due to the high surface tension of the glass.

Between the glass and the abrasive in the synthesis of composite materials, in view of lack of wetting with the molten glass of surface of boron nitride, may occur only mechanical connection, which is not strong enough, because it is formed only by the roughness of the abrasive surface. Favorable influence of an increase of the surface area of section on the glass adhesion with nitrides, carbides, metals and others and in those cases when on the process conditions (spraying, and quenching the melt and others) contact dissolution of the contiguous phases of system does not occur.⁵ It is generally known that the properties of the composite materials obtained by sintering powders on the basis of glassy binder dispersion depend on the initial materials, the particle distribution according to sizes and regime of heat treatment. On fig. 4 shows the dependence of the change in density, shrinkage and temperature coefficient of linear expansion (TCLE) of the cakes of mixtures of glass powders and βBN (BA-3/BN=1) in the process of sintering. As it can be seen from the given curves in the initial stage of sintering, certain expansion of a model is observed, which is further changed by shrinkage. Apparently, during the heating to the isothermal hold temperature, i.e., at the transition of glass into viscous- fluid condition, the bubbles generated due to the high viscosity and surface tension of the melt have low removal rate.

⁵ Ivensen, V A. (1985)

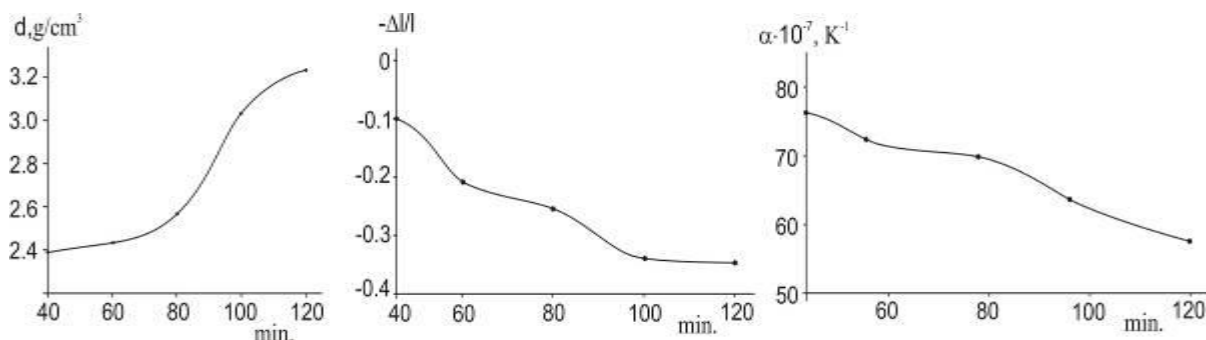


Fig. 4. Dependence of density (a), the shrinkage (b) and temperature coefficient of linear expansion (c) of composites from different duration of the isothermal holding at 600° C

The isothermal holding of models with different time of sintering accelerates the shrinkage, which is significant with the duration of sintering of more than 80min. A certain braking of shrinkage process of models in the interval of endurance 60-80min. is connected with the phase transitions in the glass and isolation of crystalline phases. As a result, the glass crystallization with separation of borosilicate and borate the motion of changes in the values of density and temperature coefficient of linear expansion of samples slows down. With the duration of heat treatment of models -120min selection of stable fluorine-containing crystalline phases practically completes with the formation of glass-ceramic material with a density of about 3.14 g /sm3 (fig. 4. a.). Increasing the time of sintering leads to an increase in the strength of coupling components of the composite material, as it increases the degree of interaction at the interface "glass- β BN melt" ⁶. It should be noted that due to the practical absence of surface wettability abrasive glass melt sharply decreases the diffusion rate, and the allocation of gas through the melt. Consequently, a bubble in the intermediate layer of glass and the abrasive can be maintained and during cooling of the composite and reduce the mechanical characteristics of the tool. From the given dependences it can also be seen that the acceleration of the densification process is observed in a significant reduction of temperature coefficient of linear expansion of the composite. Boron nitride has a low value of temperature coefficient of linear expansion (according to various data varies from 25 to 47 · 10-7K-1) and practically remains constant in the investigated temperature range. Consequently, the devitrication of glass not only increases the density of composite, but also increases the hydrostatic compression of gas in the interphase boundary abrasive– devitrified glass contributing to the release of gas due to the formation of glass-ceramic material with a low coefficient of linear expansion.

Due to the above stated glass devitrication by heat treatment, is conducive to a material with a low coefficient of thermal expansion can not only reduce the aggressive influence on the molten glass abrasive, but also increase the rate of release of bubbles and a more dense, mechanically strong material.

During sintering of the composite mixtures containing the metal aluminum, there is excessive foaming and non-uniform distribution of the abrasive material obtained by volume (Figure 3.5). The picture shows nonuniform portions related, it seems to form pores during the oxidation of aluminum.

⁶ Kuzey, A. M., Knyazyan, N. B., Frantskevich, A. V. (2015)

CONCLUSION

Thus, the heat treatment of the low-melting heterogeneous glass simultaneously causes glass spreading and abrasive crystallization. The process of crystallization is expressed in abnormal changes in viscosity of the glass in the area of 420-440°C temperatures. The study of the microstructure of specs found that the formation of glass-crystalline phase at the interface "melt - β BN" suppresses the oxidation of the abrasive.

Glass formation and melting diagrams have been studied for boronalumina and borosilicate systems containing alkali metal fluorides, the conditions of formation of a compact glassceramic structure have been investigated.

REFERENCES

- Gordeev, I. S., Ordanyan, S. S. (2012), "Composite materials cubic boron nitride-silicon carbide-silicon" [Kompozitsionnyye materialy kubicheskoy nitrid bora- karbid kremniya- kremniy], Materials Issues, No 3, pp. 29-37.
- Ivensen, V. A. (1985) "Phenomenology of sintering and some questions of the theory" [Fenomenologiya spekaniya i nekotoryye voprosy teorii] M.: Metallurgy, 247p.
- Kuzey, A. M., Knyazyan, N. B., Frantskevich, A. V. (2015), "Diamond abrasive composites materials on the basis of highly porous glass-ceramic ligaments". [Almaznoabrazivnyye kompozitsionnyye materialy na osnove vysokoporistykh steklokeramicheskikh svyazok] X Int. Conf. "Modern methods and technologies of creation and processing of materials", Minsk, pp. 140-144
- Nemilov, S. V. (1992), Viscous flow of glasses due to their structure. Application of the theory of speeds processes. [Vyazkoye techeniye stekol v svyazi s ikh strukturoy. Primeneniye teorii skorostey protsessov] Phys. and Chem. of Glass, Vol.18, No1, pp.3-44.
- Polyanskaya, N. D. (1982) Interaction of diamond with oxidizing environments. Adhesion of melts and soldering of materials [Vzaimodeystviye almaza s okislyayushchimi sredami. Adgeziya rasplavov i payka materialov.] Kiev, Vol. 9, pp. 55-62.
- Sarkisov, P. J. (2003), "Recent achievements in the field of glass-ceramic materials" [Posledniye dostizheniya v oblasti steklokristallicheskikh materialov] Proceedings of Int. Conf. "Science and technology of silicate materials", Ed. ATEC, Moscow, pp. 54-61.
- Shilo, A. E. (1988), Glass coatings for powders of superhard materials [Steklopokrytiya dlya poroshkov sverkhтвердых materialov], Nauk. Dumka, Kiev, 208p.