THE INTERACTION OF DIAMOND AND BORON NITRIDE WITH CRYSTALLINE GLASS DURING THE COMPOSITE SYNTHESIS

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Abstract

The interaction process of glass with cubic boron nitride (βBN) and diamond has been studied under dynamic and isothermal conditions. It has been revealed that with the interaction of fluorine-containing glass on the basis of boron alliuminiumsilicate with the abrasives higher than the softening temperature of glass in parallel occurs a stable phase separation. The crystallization process is expressed by the anomalous change of the glass viscosity within the temperature range of 420-440°C. The study of microstructure of the composite has revealed that the formation of the crystalline phase on the interface of "melt – βBN" "melt – diamond" suppresses the abrasive oxidation. The release of stable crystal phases is observed at high-temperature heat treatment of the composite.

Key words: *glass, crystallization, diamond, boron nitride, caking, composite materials*

INTRODUCTION

Manufacture of tools on the basis of superhard materials (SHM) as diamond and cubic boron nitride (βNB), characterized by a wide variety of used binders, which occupy most of the volume of the composite material, and largely determine its performance. Abrasive tool manufacturing processes for ceramic or glass bonded require high temperature firing[1] . Depending on the binder used and the heat treatment history during cooling at the boundary abrasive can be glassy or with crystalline phase. In most cases the compaction and sintering processes of the composite material occurs with the liquid phase. With the emergence of a liquid phase the reactivity of the system components greatly increases. It should be noted that the oxidation process for both diamond and boron nitride is a high temperature process, but the minimum temperature of oxidation is observed at 400^0C [2,3]. Well-known glass-like matrix (ligaments) and the technology of composite materials for the instrumental purposes do not allow to implement adequately high mechanical properties of diamond and boron nitride due to aggressive interactions at the interface between the melt-solid phase (diamond, βNB) and oxidation of abrasives, worsening their adhesion to the matrix along with the mechanical properties. Compositions of glasses that are used to produce an abrasive tool are synthesized on the basis of low-melting alkali borosilicate systems modified ZnO, Al_2O_3, ZrO_2, MoO_3, alkaline earth metal oxides, etc.[4, 5]. The main task for technological processes for the production of composite materials is the protection from oxidation of abrasives and preserve of the mechanical characteristics of cutting element composition.

The main problem in creating a composite of abrasive tools is the ability to control the processes of physical and chemical interaction at the interface "abrasive -glass". Reducing the speed of interaction between the components of the composite at high temperatures is a complex task, since activation barriers easily overcome in the presence of melt. Due to low chemical stability and mechanical strength the use of low-melting glasses with low glass transition temperatures is impractical. Consequently, it seems more promising for the creation of kinetic difficulties of contact interaction between the composite components. Conversion of glass into a thermodynamically more stable state can be achieved by directional crystallization of molten glass to form a coating on the abrasive pyroceramics and reduce the driving force of the interaction between the SHM and oxidation. Numerous studies have revealed that the grains of diamond and boron nitride in the composite are held

[1] Kovalchuk, Yu.M. (1984)
[2] Novikov, N.V, Aleshin V.G., Bogatyrev, G.P, Crook, V.B. (1987)
[3] Kuzey, A. M., Knyazyan, N. B., Frantskevich, A. V. (2015)
[4] RU Patent 2106237(1998)
[5] US Patent 5203886A(1993)

by mechanical fastening with a ligand. The strength in fixing abrasive pyroceramic conjunction ensured by small areas of interaction thickness and a relatively high glass-ceramic wear resistance compared to the original glass. Pyroceramic fiberglass differs considerably higher in thermal conductivity values (5-8 times more than the original borosilicate glass), which is of great importance for the abrasive tool given that in the work area relatively high temperatures are developing.

As a basis for the development of pyroceramics coatings on diamond and boron nitride glasses of fluorine systems such us B_2O_3-SiO_2-AI_2O_3 (AlF_3) -Me_2O (MeF); Me-Li, K, Na) were used. The choice of a system was defined by the wide area of glass, low-melting glass, reduced values of the spreading temperature, lack of propensity to spontaneous crystallization and sufficient chemical resistance. To initiate the crystallization process of the glass batch was administered from 2.0 to 7.5 wt. % sodium fluoride and calcium.

Technological specificity of the compound glass with abrasives characterised with the grip achieved by wetting and simultaneous interaction of a solid body of molten glass, which greatly impairs the characteristics of the instrument. Consequently, an urgent problem is to reduce interaction of glass with abrasives during the heat-treatment and obtaining the composite with high wear resistance and hardness. To reduce the aggressiveness of the glass melt processes of sintering of composite components and glass ceramization were parallelly ongoing.

EXPERIMENTAL PART AND DISCUSSION OF THE RESULTS

In systems of complex chemical composition containing two or more basic glass-forming oxides (SiO_2, B_2O_3, AI_2O_3, etc.), there is a phenomenon of immiscible phases, which largely restricts the field of creation of homogeneous glass. Creating glass ceramic materials was made possible by the discovery of ways to regulate the phase transformations in the glasses and resulting in a uniform bulk crystallization to form glass-ceramics with fine-grained structure in the presence of 10 to 70% glassy. One of the important issues that are of great practical importance in the phase separation of glass, is the mutual distribution of the resulting phases. For glasses metastable separation process is characterized by all of the phase separation patterns, the inherent immiscibility stable melts, with the only difference that the phase separation in this case occurs at higher viscosities. Low diffusion rates at high values of the melt viscosity of the raw glass formation cause fine structure in which one phase is uniformly distributed in the other[6] .

Melting of glass held in electric furnace heaters with carborundum corundum crucible in an oxygen atmosphere at temperatures above ~ 250 300^0 liquidus temperature of the system. The crystallization ability of the glass crystallization temperature interval was evaluated by the DTA curves of glass powders. It was revealed that glasses may be perspective with a softening temperature 440-480^{O}C having composed 24-30% of alkali metal oxides and fluorides, at a content of 12% (ZnO + ZnF_2).

For the synthesis of glasses with low temperature of softening composition was chosen, which lies on the border of fields crystallization of metaborate and sodium metasilicate of the studied systems. 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. With a controlled temperature range of crystallization in the initial glass containing 3,0% NaF and 5.0% CaF_2 ceramic glass has been developed.

For the study of the interaction of borosilicate glass with a diamond and βNB during the heat treatment methods of differential thermal (DTA) and thermo-gravimetric (TG) analysis were applied. Study of the characteristic glass temperature, phase transition temperature effects, processes of interaction with the glass melt abrasives and oxidation were performed on Q-1500 derivatograph in air at a temperature rise of 10 C^O / min. The content of abrasives in composite mixtures investigated was ~ 50.0 masc. %.

[6] Varshal, B.G, Mazurin, O.V.(1991)

The viscosity of the glass at a rate has been determined during ceramization indentation of cylindrical interference indentra in the glass plate.

Fig. 1 and 2 show the thermal image and weight loss of abrasives and fiberglass under dynamic and isothermal heat treatment conditions. When considering the DTA abrasive powders, it is clear that intensive oxidation of diamond in air is observed in 630° C, but the beginning of the oxidation process is fixed with 440° C. With increasing temperature, the diamond is oxidized more, and the total losses of up to 850°C are 3.4%. Intensive diamond oxidation above 700 ° C in the DTA curve recorded exothermic effect with a maximum at 805°C. At TG curve in the temperature range there is a significant mass loss. βNB interaction with air in the same conditions, is much lower, minimum temperature oxidation process start recorded at 600°C. Less oxidation of boron nitride predetermines their low loss and high temperature treatment at a temperature of 900°C due to oxidation losses are 0.4%.

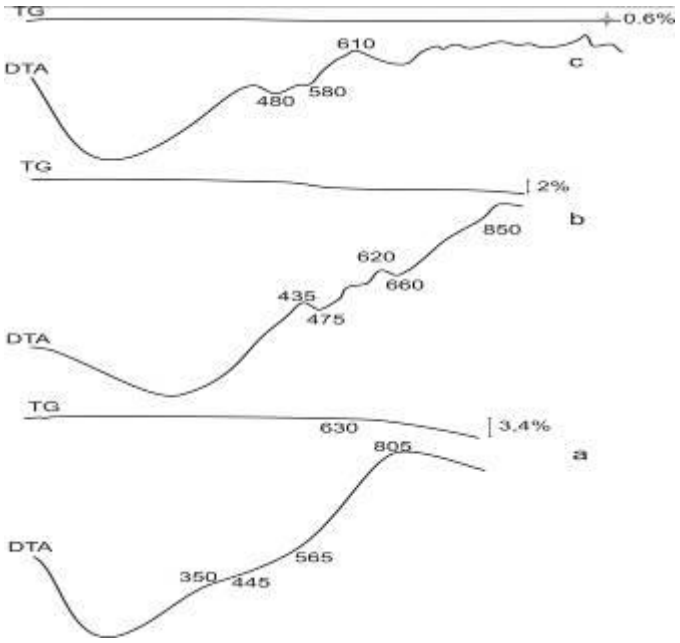


Fig. 1. Thermograms and weight loss of the diamond (a) and glass composition under dynamic (b) and isothermal conditions (c) of thermal treatment

The thermogram of the original glass is characterized by endothermic peak at 445 ° C, glass softening associated with BA-3, two exothermic effects of crystallization at 500 ° C and 630 ° C, and the melting phase endoeffect of crystallizing at 760 ° C (liquidus temperature)[7]. DTA curve of a composite containing 50% glass BA-3 and 50% of diamond and the heat-treated in a dynamic mode (Fig.1.b) effect due to softening of glass (transformation interval) at 30°C is shifted to the high temperature region, which, apparantely can be explained by the interaction of the softened glass with the abrasive. Board formation in 500-550°C is due to diamond simultaneous processes of interaction with the melt and crystallization of the latter. The demonstration of bias and lack of a second exothermic peak temperature of crystallization effect indicates the allocation of high-crystalline phase. Weight loss during the heat treatment of the composite up to 850 ° C is much lower loss of diamond and does not exceed 2%. At an isothermal heat treatment of the composite at 600 ° C is a characteristic feature of the undulating form of the DTA curve, indicating an increase in the crystallinity of the

[7] Grigoryan, T.V., Manukyan, G.G.,Toroyan, V.P., Avetyan, R.A., Petrosyan, M.Z., Franckevich, A.V., Kuzey, A.M., Knyazyan, N.B.(2015)

glass-ceramic in long-term treatment. By ceramization and formation on the surface of the diamond coating sustained weight loss of the composite are reduced to 0.6%.

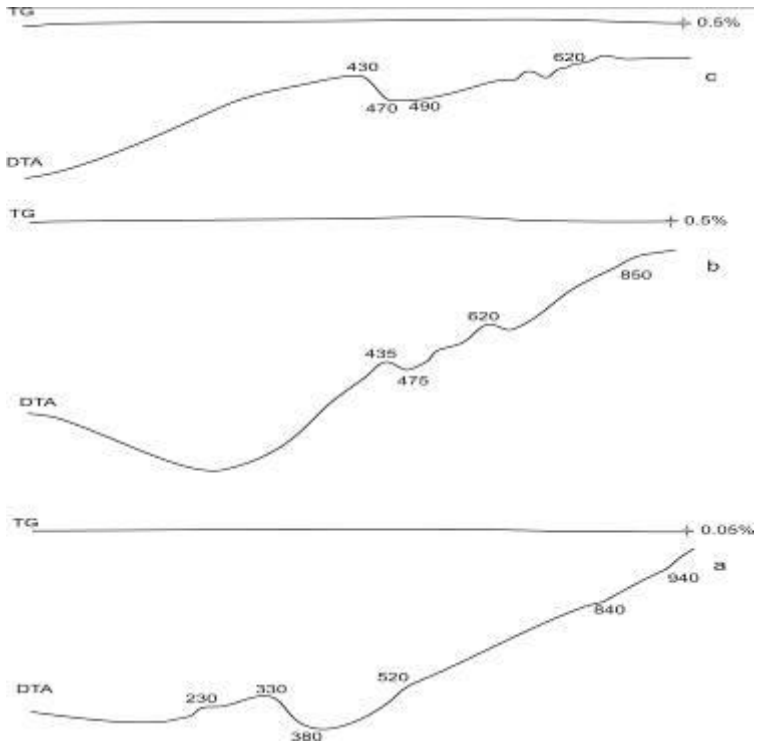


Fig. 2. Thermograms and weight loss of cubic boron nitride (a) and glass composition under dynamic (b) and isothermal conditions (c) of heat treatment

From the DTA curve of the composite containing 50% glass and 50% BA-3 βBN (Fig. 2 cr.b), it is clear that by heating the composite to a temperature of maximum crystallization of the first characteristic glass temperature (t_g and of t_f) increases about 25-30°C. First thermoeffect of glass crystallization at 20°C is shifted to the low temperature region, as a system for the diamond, due to the formation of phase boundaries at heat treatment of the composition of the initial components. Reducing the maximum tempetarure of second crystallization is 10°C, which can be explained by a decrease of the interface between the abrasive and the softened glass.

Very low weight loss of the composite can be monitored during dynamic heating to form a surface coating βNB pyroceramics and low loss of abrasive.

To reduce the influence of atmospheric oxygen on the oxidation of βNB one of the compositions aluminum metal was introduced in an amount of 1.0%. DTA of the mixture has a wide temperature range of glass transformation and pronounced exothermic effect with a maximum at 610° C. The positive impact of introduced metal and glass ceramisation the process of sintering and an abrasive protection from oxidation confirms the absence of weight loss of the starting mixture in its high-temperature heat treatment. Thus the composite material differed in high porosity and irregular distribution of the abrasive throughout the entire volume of the composite.

The process of sintering and formation of the composite in the presence of the softened glass is due to viscous flow under pressure the small pores are formed. To increase the sealing speed is of great importance not only to the wetting, but also the amount of molten glass[8]. It is known that if the amount of the melt at the sintering temperature is sufficient to fill the void volume between the particles can be

[8] Shilo, A.E., Kharchenko, S.A, Klimenko, N.G.(2008)

expected to complete the seal of the composite. However, excessive increase in the temperature and decrease of the viscosity of the glass can lead to an increase aggressiveness of the melt and reduce adhesion of abrasives with grain binder. Structural transformations taking place in the crystallized glass, above the softening temperature appears to change the viscosity of the medium.

The process of crystallization of the glass in the heating mode without exposure to certain temperatures often remain unfinished, although in the glass crystallization temperature region there is an abnormal variation of viscosity. When heated, the developed glass BA-3, serving in the preparation of binder composites and decreases its viscosity begins to crystallize within the temperature range 520-610 ° C. Depending on the time delay increasing crystallization may limit the spreading of the glass. Analysis of the dependence of the viscosity curve of the glass temperature shows that the course of the curve on a plot of 400 - 450° C corresponds to the area of high-viscosity, viscous flow characteristic of normal fluids. Crystallization began to express a kink in the curve of viscosity in the 450-550° C temperatures and, therefore, it can be assumed that the process of spreading the glass becomes more difficult.

Figure 3 shows the viscosity curves of glass-ceramic material by the time of heat treatment at different temperatures.

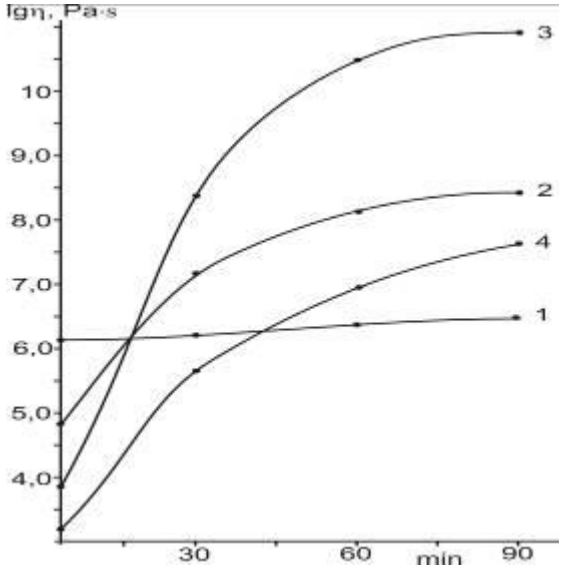


Fig. 3. The dependence of the viscosity - time of heat treatment at temperatures:
1. 450° C; 2. 500° C; 3. 550° C; 4. 600° C

Curves of the crystallized glass viscosity at different temperature and residence time demonstrate the increase in viscosity occurs while structuring in $10^{3,5}$ - 10^5 Pa·s i.e. after spreading and wetting of the diamond and glass βNB. Almost horizontal variation of the viscosity of the heat treatment time at 450° C indicates the primary processes of the initial structuring of glass, which produce crystallization centers[9]. Identification of this temperature allowed to regulate the spreading of abrasives on the glass process and set the duration of the exposure of the first heat treatment step. Depending on the characteristics of crystallization of glasses shutter speed ranged from 40 to 60 minutes. The most significant increase in the volumetric rate of crystallization occurs at a temperature of 550 ° C, as evidenced by high viscosity value glasscrystalline material reaching up to ~ 10^{11}Pa·s.

Electron microscopic examination revealed glass change features of the glass microstructures at phase transitions and at formation of glass-ceramics and composite materials, depending on the composition of the starting mixtures, the temperature and time of heat treatment.

[9] Smirnov, V.G, Semin(1987)

To detect the activity of fluorides during composites synthesis and oxidation of diamond βNB microstructure of glass composition containing fluoride BA-1, BA-glass 3 - containing 3,0% NaF and 5.0% CaF_2 were studied.

Figure 4 shows electron microscope pictures of composite materials at different temperatures and durations of sintering. Review of images shows that the initial borosilicate glass composition that does not contain fluorides NaF of CaF_2, has microinhomogeneous structure (Fig. 4, a.1), and wetting with βNB occurs at a temperature of 600^0C to form a film.

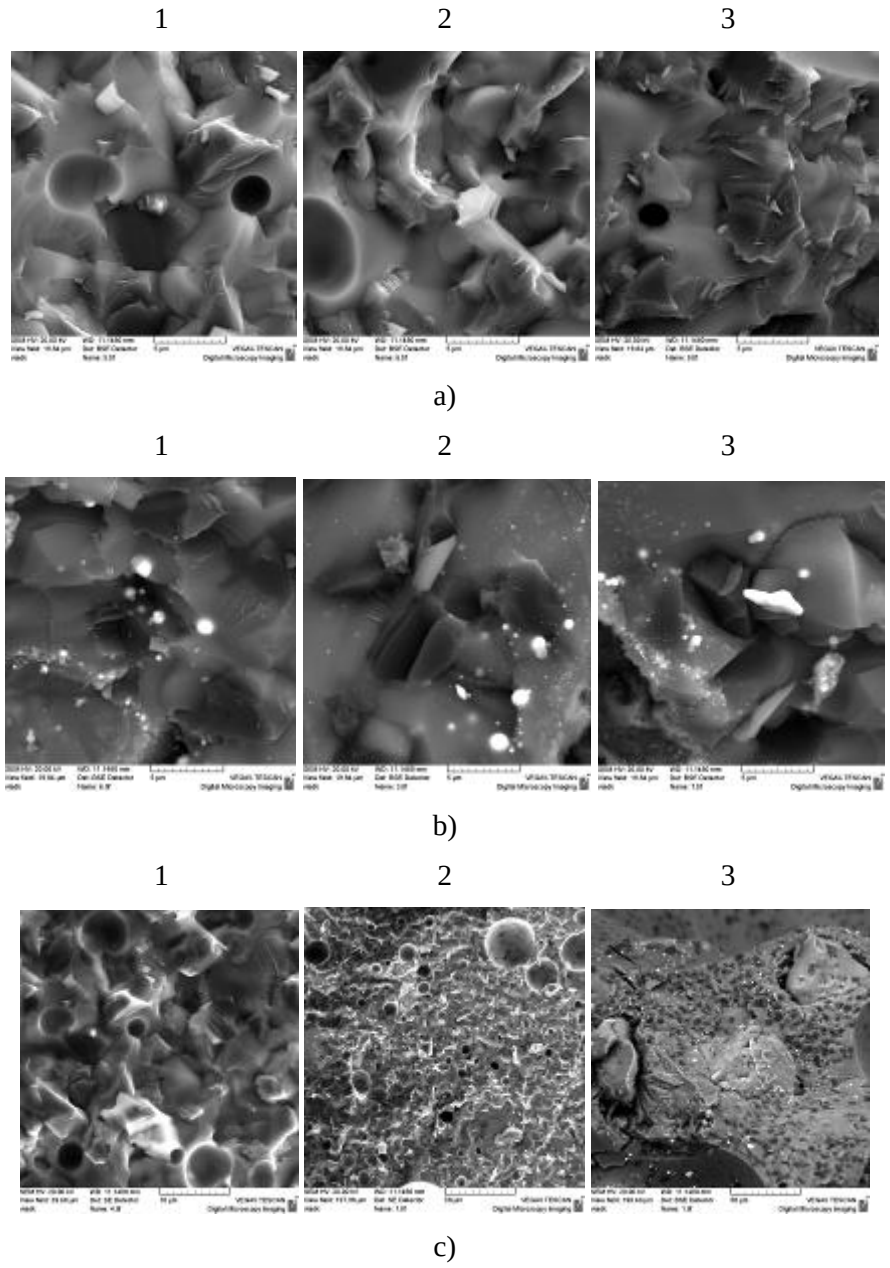


Fig. 4. The microstructure of the glass composite materials "glass- βNB"(a), "glass- diamond"(b), "glass-βNB(diamond)- Al"(c): a) 1- glass BA-1-βNB (600 °C, 15 minutes), 2- glass BA-3 - βNB (650 °C, 0,5 hour), 3- glass BA-3- βNB (650 °C, 1 hour); b) 1- glass BA-1 - diamond (600 °C, 15 minutes), 2- glass BA-3 -diamond (650 °C, 0,5 hour), 3- glass BA-3-diamond (650 °C, 1 hour); c)1- glass BA-3 -βNB+Al (600 °C, 0.5 hour), 2- glass BA-3- diamond + Al (650 °C, 0,5 hour) 3- glass BA-3 - diamond + Al (650 °C, 1 hour)

The presence of pores in glass-matrix is due to the high viscosity glass, retarding the process of separation of gas from the glass. Characteristically, at the interface "glass – grit (abrasive)" there are no pores, due to the low rate of βNB oxidation. When using the fluorine-containing glass and raising the temperature and duration of heat treatment number of pores in the composite is dramatically reduced and the duration of the sintering promotes the release of the primary crystals around the glass-ceramic abrasive (Fig. 4, a.2). Judging from the snapshot, the crystals dispersed throughout the material and separated by a glassy phase. In general, morphology of the transition layer, formed on the surface of βNB grains at higher temperatures (650 ^{0}C), identical to glass film-forming surface morphology without fluorine at 600^{0}C. By increasing the duration of heat treatment composition is formed with a decrease of the interaction of the residual glass phase in glass-ceramic structure with boron nitride. According to the RFA results in the first heat treatment step sodium flourine borosilicate is released during crystallization Na_2B [SiO_4] F, further heating leads to formation of sodium fluoroborate $Li_2NaZn(B_3O_6F_2)$ along with flourine borosilicate. TG study showed that glass-ceramic formation on the surface of the abrasive dramatically reduces with βNB the oxidation process. The weight loss during heat treatment of the composite is reduced almost by an order. Comparison of the microstructure of composites based on the structure of the diamond composite material (Fig. 4 b), shows that fine structure can be noted in the composite crystallized glass by heat treatment and the absence of a pore in the glass in the transition layer. This indicates diamond less intensive interaction with the softened glass even after prolonged sintering a composite material. Also, this is evidenced by very low loss and weight of samples isothermally at one hour (Fig.1c ,Fig.2c). Additional introduction of aluminum metal in outgassing leads to a strong decrease during sintering and adhesion of the abrasive grains on the surface of the glass (Fig. 4 c). At 600^{0}C oxidation processes are slowed because of the interaction of the high viscosity of the molten glass, contributing to the formation of large pores in the composite. Intensive oxidation and interaction of composite components at high temperature (650 ^{0}C) causes the formation of a large number of minure pores (Figure 4 in c. 2, 3) and reducing the mechanical characteristics of the composites.

CONCLUSION

During the heat treatment of the low-melting glass of liquidous structure processes of glass spreading on abrasive and its crystallization simultaneously occur. The process of crystallization is expressed in abnormal changes in viscosity of the glass in the temperature range 420 - 440^{0}C. As a result of studying the microstructures of caking it has been found that the formation of glass-crystalline phase at the interfaces "melt - diamond" and "melt - βBN" suppresses the oxidation of the abrasive.

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