Sintering of Low-Melting Glass Powders and Glass-Abrasive Composites

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Abstract: Sintering of glass powders in Na₂O-B₂O₃-SiO₂ and PbO-ZnO-B₂O₃-SiO₂ systems as well as of their mixtures has been studied. The process of sintering is shown to change because of crystallization of the glass of the PbO-ZnO-B₂O₃-SiO₂ system. Addition of diamond or cubic boron nitride to glass powders affects shrinkage in sintering composites. Sintering of powders of lead-containing glass proceeds by the mechanism of viscous flow.

Keywords: Sintering; Glass powders; Diamond; Cubic boron nitride; Glass-abrasive composites.

1. Introduction

In the production of abrasive tools of superhard materials (diamonds and cubic boron nitride), glasses of various systems are used as binders of ceramic bonds. One of the basic operations in making the working layer of abrasive tools is sintering, in the course of which...
the structure of the abrasive-containing layer is formed. In most cases, sintering in these systems occurs with liquid phase participation. At present it is commonly supposed that the highest degree of densification in liquid-phase sintering with a sufficient wetting of particles with the liquid is caused by capillary contraction and rearrangement of solid particles.

Kuczynski [1] showed that sintering of glass spheres occurs by the viscous flow mechanism. Mackenzie and Shuttleworth [2] as well as Kingeri and Berg [3] found that the initial rate of sintering of glass powders is directly proportional to the surface tension and inversely proportional to the particle size and the viscosity of glass.

When studying the effect of particle shape on shrinkage of densified glass powder, Culter and Henrichsen [4] ascertained that glass powders with a high specific surface densify five times faster than glass powders with perfectly spherical particles.

Czarwinski [5] considered the process of sintering of glass as heat treatment that causes the grains to adhere to one another. He believed that that during the first stage of sintering, glass powder transforms into a low-strength porous material. During the second stage density can become equal to that of monolithic glass.

Various aspects of the kinetics of sintering of glass powders were considered in fundamental studies of Frenkel [6], Geguzin [7] and Scherer [8-10]. It should be, however, noted that the existing theory of sintering is based on idealized models. In practice, the use of this theory involves difficulties. Even with the apparent simplicity, sintering of glass powders and composites has not been adequately studied.

Sintering of glasses that crystallize when heat-treated is more complicated as in this case sintering is accompanied by crystallization. When a powdered crystallizable glass is heat-treated, before crystallization sintering proceeds at the cost of viscous flow of initial glass. At a certain stage the crystallization starts, accompanied by a decrease in the amount of the glass phase and an increase in the materials viscosity. As a result, the rate of sintering that proceeds at the cost of viscous flow decreases. In the course of crystallization sintering is to a great degree affected by the vacancy diffusion mechanism. The contribution of each sintering mechanism to densification of the material depends on the phase and chemical compositions, structure and parameters of the heat treatment of the material [11].

Thus, the complexity of sintering of crystallizable glasses with participation of a liquid phase is in simultaneous proceeding of the processes of sintering, crystallization, redistribution of the amount and composition of phases, the formation of a rigid skeleton and variations in the system viscosity.

2. Experiments and Results

We have studied sintering of glass powders of Na$_2$O-B$_2$O$_3$-SiO$_2$ (silicate glass) and PbO-ZnO-B$_2$O$_3$-SiO$_2$ (lead glass), which can be applied to ceramic bonds of abrasive tools. To get the idea of the kinetics of glass sintering, we have studied sintering of spherical particles of the above glasses. Both glasses were sintered by a classical scheme via the formation of a neck and merging of particles into one sphere. Of interest is co-sintering of particles of the two glasses. In this case, first the spheres intergrow (Fig. 1). Then, low-melting lead glass covers the silicate glass and the system becomes a two-layer sphere. This is possible because of the high wettability of silicate glass with lead glass. At temperatures above 450ºC, the contact angle measured for the lead glass on the silicate glass is below 70º, while at 525ºC it is 20º.
Sintering of glass powders is to a large degree temperature dependent. Thus, an increase in the sintering temperature from 360 to 380°C increases shrinkage of a lead glass by a factor of two and an increase to 400°C by a factor of 3.3. When mixtures of glass powders are sintered under these conditions the difference in shrinkage is lower.

**Fig. 1** Kinetics of co-sintering of spheres of lead and silicate glasses.

To assess the kinetics of the sintering process, we have studied the time dependence of densification at various temperatures $\lg \frac{\Delta l}{l_0} = f (\lg \tau)$ (Fig. 2), where $\frac{\Delta l}{l_0}$ is the linear relative shrinkage of the material; $\tau$ is the densification time.
Fig. 2 Densification of glasses depending on time at different temperatures: a) lead glass - 360 (1), 380 (2) and 400°C (3); b) silicate glass - 520 (1), 540 (2) and 560°C (3); c) mixture of glasses in the ratio of 1:1 - 440 (1), 460 (2) and 480°C (3).

Sintering of glasses and their mixtures occurs in three stages and the process of sintering of mixture proceeds less actively than for initial glasses. This fact is supported by the calculated values of the sintering activation energy. For lead glass, the activation energy was found to be 138 kJ/mol, for silicate glass 120 kJ/mol, and for a mixture of these glasses in the ratio of 1:1 it was 177 kJ/mol. The lower activation energy of sintering of the mixture of powders of the above glasses is attributed to the fact that sintering in this case is accompanied by mutual diffusion and crystallization of the glasses. Fig. 3 shows DTA curves obtained for initial glasses and their mixtures. A comparison between the range of crystallization based on the DTA and time and temperature dependences of the shrinkage logarithms shows that in a number of cases the temperatures of the changes in properties coincide. Thus, for the one-to-one ratio mixture of the glasses under study, the range of crystallization is from 420 to 520°C and the change in the mode of shrinkage is observed at 480°C (Fig. 2c).

A material produced by co-sintering of two glasses of different chemical compositions can be considered as a system having an unlimited mutual solubility. Intermediate stages contain phases of initial glasses and a solid solution of a variable concentration. As a result of sintering, one phase is formed.

Sintering of glass-abrasive materials has been studied by adding 25 vol.% AC4125/100 or ACM 10/7 diamond powders or KP 125/100 cubic boron nitride (cBN) powders to the above glasses.

Addition of powders of superhard materials (SHM) to lead glass reduces shrinkage of the material at a sintering temperature of 400°C as compared with initial glass because of the formation of a spatial skeleton from SHM particles that prevent movement of SHM particles (Fig. 4). The presence of diamonds and cBN powders in a composite reduces shrinkage by a factor of 1.85.

Addition of SHM powders to silicate glass has a similar effect, i.e. at a sintering temperature of 600°C shrinkage is reduced by a factor of 1.5 (Fig. 5).

Addition of KP 125/100 powder to the mixture of glasses reduces shrinkage at a sintering temperature of 500°C by a factor of 3.1 and addition of AC4 125/100 diamonds by a factor of 4.1 as compared to shrinkage of a mixture of glasses without SHM powders (Fig. 6).
The SHM effect on sintering of materials that are mixtures of glasses is explained as follows. At a sintering temperature of 500°C lead glass transforms into a plastic state and wets the silicate glass and SHM powders. Calculations of the Gibbs free energy of possible reactions between the glasses and SHM show that under the given conditions, such an interaction is possible [12]. Interacting with diamond and cBN, lead glass impairs the interaction with silicate glass (impairs wetting, hinders diffusion processes, etc.). Therefore, composites containing a mixture of glasses and SHM show much smaller values of shrinkage than a mixture of glasses. This is most clearly seen when diamond micron powders are added. The amount of diamond grains in the composite with ACM 10/7 diamond powder is higher than that in the composite with AC4 125/100 diamonds by three orders of magnitude. Therefore, the shrinkage value of the composite containing the mixture of glasses and ACM 10/7 diamonds is three times less than that of the composite with AC4 125/100 diamonds.

It is of interest to consider the processes proceeding in a microvolume of the material, e.g., between a small number of particles of glass and diamond (cBN). In actual practice, of importance is the relationship between the numbers of particles being sintered and the particle sizes. Our calculations have shown that when large diamonds are used (the diamond content of composites is constant and makes 25 vol.%, which corresponds to the standard for abrasive tools of SHM), for every diamond particle of AC4 125/100 powder there are 30 particles of a glass powder 60 µm or 820 particles of a glass powder 20 µm in grit size. Thus, the relationship between the SHM particle size and glass particle size can essentially affect the shrinkage of the composite.
To define the effect of the SHM substrate surface on sintering of glass powders, we have studied the kinetics of sintering of glass powders on diamond and cBN substrates. Sintering of lead glass on a diamond substrate proceeds more intensively than on a neutral substrate \( \frac{\Delta \ell}{\ell_0} : \frac{\Delta \ell}{\ell_0} \) is the ratio between the linear relative shrinkage during sintering on a diamond or cBN substrate and linear relative shrinkage during sintering on a neutral substrate, which is unwettable with glass, see Tab. I).

**Tab. I** Effect of the sintering temperature and substrate material on shrinkage of lead glass.

| Temperature (°C) | Diamond | cBN |
|------------------|---------|-----|
| 360              | 3.5     | 3.1 |
| 380              | 2.1     | 2.2 |
| 400              | 2.0     | 1.7 |

An increase in the sintering temperature from 360 to 400°C decreases the ratio from 3.5 to 2.0 for a diamond substrate and from 3.1 to 1.7 for a cBN substrate. The use of diamond and cBN substrates intensifies sintering, but the temperature increase causes the contacting materials to interact, which hinders sintering.

Sintering of silicate glass on diamond and cBN substrates also proceeds more intensively than on a neutral substrate (Tab. II).

**Tab. II** Effect of the sintering temperature and substrate material on shrinkage of silicate glass.

| Temperature (°C) | Diamond | cBN |
|------------------|---------|-----|
| 520              | 1.15    | 1.10|
| 540              | 1.15    | 1.10|
| 560              | 1.50    | 1.65|

An increase in the sintering temperature from 520 to 560°C increases the ratio between the relative shrinkages from 1.15 to 1.5 for a diamond substrate and from 1.1 to 1.65 for a cBN substrate. Unlike lead glass, which is found to interact with substrates, in this temperature range silicate glass interacts neither with diamond nor with cBN. This is the reason why the ratio between the relative shrinkages increases with temperature.

Thus, it may be concluded that during sintering glass-abrasive composites, the process is affected not only by the size of the glass and abrasive particles but also by the chemical compositions of the glass and abrasive.

The processes of sintering of SHM-containing composite materials with the participation of a liquid phase are the key processes in making tools of SHM on vitrified bonds. The regularities of densification are defined by the sintering mechanism that acts in the material during heating.
The authors of [13-14], who have generalized the results of other researchers, divide sintering with a liquid phase into the three following stages: a change in the particle orientation caused by surface tension, dissolution-deposition, recrystallization and growth of grains because of the formation of a rigid skeleton.

In early stages, the sintering kinetics can be expressed as [7]:

\[ \frac{\Delta l}{l_0} = K \cdot \tau^n, \]

where \( \frac{\Delta l}{l_0} \) is the linear relative shrinkage of the material; \( \tau \) is the sintering time; \( K \) is the constant dependent on the material composition and temperature; \( n \) is the exponent dependent on the sintering mechanism.

As a first approximation, the temperature dependence of the constant \( K \) is as follows:

\[ K = K' \cdot e^{\frac{Q}{RT}}, \]

where \( K' \) is a constant; \( Q \) is the apparent activation energy of sintering; \( T \) is the absolute temperature; \( R \) is the gas constant per mol.

We try to ascertain the mechanism of sintering of a lead glass on an example of the PbO-B_2O_3 system, for which the necessary reference data can be found in literature. According to Frenkel and Kingeri [6, 13], sintering of glass powders proceeds by the viscous flow mechanism through a cooperative motion of atoms. To describe the shrinkage that is found from the moving closer of centers of two particles, Kingeri proposed the following equation:

\[ \frac{\Delta \tau}{\tau} = \frac{3\Delta l}{l_0} = \frac{2.9\sigma \cdot r}{4\eta \cdot \tau}, \]

where \( \frac{\Delta \tau}{\tau} \) is the volumetric relative shrinkage of the material; \( \frac{\Delta l}{l_0} \) is the linear relative shrinkage of the material; \( \tau \) is the densification time; \( \sigma \) is the surface tension; \( \eta \) is viscosity of the liquid phase and \( r \) is the particle size.

Judging from the author’s assumptions (without regard for the space of pores), the equation should describe the initial values of shrinkage. In reality, by substituting the known values of surface tension [15], viscosity of the glass melt [16] and particle size, we obtained the calculated values of shrinkage, which differ from the experimental values by 10% at a holding time below 10 min. Based on this, one may conclude that at the initial stage sintering of glass powders follows the viscous flow mechanism.

The time dependence of shrinkage plotted in logarithmic coordinates shows that sintering of a glass powder occurs in three stages. It follows from [13] that densification of highly viscous materials, to which glass belongs, as a rule, should proceed in one stage and the time of total densification of such materials is defined by the formula: \( \tau = \frac{1.5}{\sigma} \cdot \frac{r \cdot \eta}{\sigma} \). For lead glass in the PbO-B_2O_3 system, this time is 150 min.
3. Conclusions

We have ascertained that sintering of glass powders of Na$_2$O-B$_2$O$_3$-SiO$_2$ and PbO-ZnO-B$_2$O$_3$-SiO$_2$ systems as well as mixtures thereof proceeds in three stages and shrinkage increases with increasing temperature. For crystallizable glasses, when the temperature range of crystallization coincides with the temperature range of sintering, shrinkage decreases. For these glasses, during the first stage of sintering, a liquid phase appears and reorientation of particles occurs, which causes densification of the material. In the second stage, liquation, nucleation and growth of crystalline phases proceed in the softened glass and the last third stage consists of densification of the material because of the growth of crystalline phases.

Addition of diamonds or cBN to glasses or their mixtures results in a decrease of shrinkage of a glass-abrasive composite as compared to that of glasses by a factor of 1.5–4.1 depending on the composite composition. Sintering of glass powders of Na$_2$O-B$_2$O$_3$-SiO$_2$ and PbO-ZnO-B$_2$O$_3$-SiO$_2$ systems is more intensive on diamond and cBN substrates. Shrinkage of silicate glass increases with temperature. Shrinkage of lead glass decreases with an increase in temperature since the beginning of the interaction at the glass-SHM interface.

References

1. G. Kuczynski, Study of sintering of glass, J. Appl. Phys., 20 (12) (1949) 1160–1163.
2. J. Mackenzie and R. Shuttleworth, Proc. Phys. Soc., 62 (12) (1949) 833–852.
3. W. D. Kingery and M. Berg, Studies of initial stages of sintering solid by viscous flow, evaporation – condensation and sell-diffusion, J. Appl. Phys., 26 (10) (1955) 1205–1206.
4. J. Culter and R. Henrichsen, Effect of particle shape on the kinetics of sintering of glass, J. Amer. Ceram. Soc., 51 (10) (1968) 604–605.
5. C. Czarwinski, Szklo i Ceram, 19 (1968) 72–75.
6. Ye. I. Frenkel, Viscous flow in crystalline bodies, Zhurnal Eksperimentalnoi i Teoreticheskoi Fiziki, 16 (1) (1946) 29-38. (in Russian)
7. Ye. E. Geguzin, Physics of sintering, Nauka, Moscow, 1984. (in Russian)
8. G. W. Scherer, Sintering of low-density glasses: I. Theory, J. Amer. Ceram. Soc., 60 (5–6) (1977) 236–239.
9. G. W. Scherer and D. J. Bachman, Sintering of low-density glasses: II. Experimental study, J. Amer. Ceram. Soc., 60 (5–6) (1977) 239–243.
10. G. W. Scherer, Sintering of low-density glasses: III. Effect of a distribution of pore sizes, J. Amer. Ceram. Soc., 60 (5–6) (1977) 243–247.
11. T. I. Fedoseeva, Studies of the synthesis conditions and the development of acid-proof glass-ceramic materials on the basis of fused basalts using the thermoplastic method of the ceramic technology, Author’s Abstract of the Cand. Sci. (Eng.) Dissertation, Moscow, 1970. (in Russian)
12. A. E. Shilo, Glass Coatings for Powders of Superhard Materials, Naukova Dumka, Kiev, 1988. (in Russian)
13. W. D. Kingeri, Introduction to Ceramics, Stroyizdat, Moscow, 1967. (Russian translation)
14. V. N. Eremenko, Yu. V. Naich and I. A. Lavrinenko, Sintering with the Liquid Metal Phase Present, Naukova Dumka, Kiev, 1968. (in Russian)
15. W. Eitel, The Physical Chemistry of the Silicates, University of Chicago, Chicago, 1954.
16. O. V. Mazurin, M. V. Streletsina and T. P. Shvaiko-Shvaikovskaya, Properties of Glasses and Glass-Forming Melts, Handbook, Vol. 2, Nauka, Leningrad, 1975. (in Russian)