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Mechanical performance of foam glass with nanoscale structure elements

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Abstract. The paper presents experimental data on studying the strengthening of glass foam material. Glass foam material is foamed glass of increased strength achieved due to nanoscale structural elements. Glass foam is obtained through thermal treatment of noncrystalline matrix containing crystalline material in the silica state. It is shown that strengthening of glass foam material is achieved by structuring the noncrystalline partition. New technique of strengthening is proposed due to the formation of nanoscale globules of noncrystalline matrix. Self-organization of spherical nanoscale globules. New technique for glass foam strengthening. For the first time the phenomenon of strengthening inter-pore partition of glass foam was established. The principle of the process consists in the formation of noncrystalline matrix with a specific globular structure.

1. Introduction

The phenomenon of materials strengthening has been studied and examined for a long time. Such classical studies are known as those of A.A. Bochvar, M.L. Bernstein, R. Zimmermann [1, 2]. They describe the techniques, schemes and classifications of strengthening for various materials. All strengthening techniques can be divided into two groups. The first group of materials (mostly metal) with a crystalline structure is well described by the classical dislocational model of strengthening. The second group of materials (non-metal) with a noncrystalline structure can be described by the non-dislocational model of strengthening. For example, Ref. [3] proposes the strengthening technique due to the clusters in the noncrystalline structure. Refs. [4, 5, 6] explain strengthening at inelastic deformation particularly by non-dislocational mechanisms. In particular, it is grain boundary sliding and movement of vacancies at boundaries. The work by Kozlov E.V. [7] directly indicates the observed critical grain size after which the amorphized material is strengthened in a dislocation-free mode due to the boundaries of nanostructural formations.

It is believed that the main cause of strengthening at dispersion hardening is elastic stress created by the separation of the second phase [4-6]. In case of noncrystalline bodies (glass) the Griffiths model is more common. It describes strength properties of glass with the use of energy fracture model. According to the model, the glass fracture is caused by the strain concentrators at the glass surface. In glass-ceramic materials where noncrystalline phase may reach up to 90 and 95%, the stress in the interface of crystalline phases and noncrystalline matrix cannot lead to the strengthening of the material as a whole. For the glass foam materials examined in this paper neither the first nor second model is applicable due to the following reasons: no separation of the second crystalline phase in the

first crystalline phase; no continuous surface of the noncrystalline matrix, and presence of multiscale random pores.

The paper examines the process of glassceramic foam material strengthening. This material is manufactured of semiprocessed product – the quenched cullet synthesized at relatively low temperatures ($< 950\text{ }^{\circ}\text{C}$). It is already at this stage when the quenched cullet contains glass phase in a noncrystalline state. It ensures the pyroplastic state of the material at the stage of repeated thermal treatment (sponging) of the quenched cullet. The quenched cullet is a noncrystalline matrix containing residual silica particles with the size up to 200 nm.

2. Results and discussion

The foam materials were produced according to the two-stage technology developed by the authors [8, 9]. Such crystal and noncrystalline silica-containing rocks as silica sand, diatomite, flint, silica clay, and perlite were sampled as a feedstock. The samples of foam material were obtained with the content of residual crystalline material from 5 to 20 % by volume. It was established that the strength of experimental samples increased from 1.8 to 3 MPa as the crystalline phase particle size decreased from 1,000 to 300 nm.

During the formation of submicron crystalline phase in the glass the change in its energy characteristics is observed [10]. The maximum strengthening effect should be expected if the microstructure of crystalline phase is significantly different from the equilibrium for this phase. The paper by academician N.P. Lyakishev shows that material with specific properties should consist of crystallites or mixture of nanoscale crystals and noncrystalline phase [11]. Therefore, the foam material synthesized from the quenched cullet is essentially “simulated” by these principles.

For the samples with fixed amount of residual crystalline material (5 % on average) and different size of particles the experimental dependence was established (Figure 1). Assuming that the minimum critical size of crystalline phase particles is equal to 10 nm [7], the maximum theoretical strength of the foam material was calculated, which amounted to 5 MPa. In case of the glass foam the noncrystalline matrix of which contains no crystalline material, this value does not exceed 1.5 MPa [12].

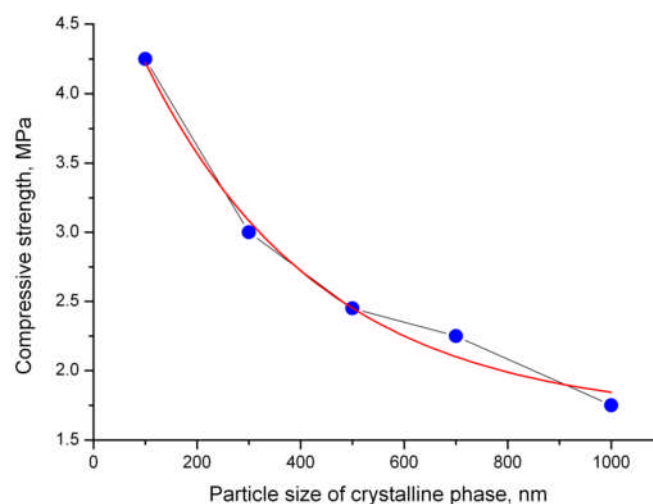


Figure 1. The strength of the foam material as a function of the crystalline phase particle size.

Since it proves to be impossible to strengthen the noncrystalline matrix due to the subsequent reduction of the particle size in the residual crystalline material, there is another option to alter the material strength. The strength of the partition can be changed due to the modification in the matrix internal structure. The strength values at compression determined for all experimentally obtained samples of foam material showed that the increased strength (4.3 MPa) is typical for those ones having

the noncrystalline matrix of the interpore partition with the observed nanoscale spherical elements (spheroids). In electron micrographs of high resolution there are spheroids observed in the noncrystalline phase with the size of 60 to 160 nm. Such spheroids are not found in the interpore partitions of conventional glass foam and glassceramic foam material samples with the size of residual silica particles over 200 nm (Figure2). Figure2 distinctively shows a complex hierarchical arrangement consisting of both separate spheroids and their groups. X-ray dispersion analysis of the silicon content in the partition noncrystalline matrix shows its non-uniform distribution. The maximum concentration is observed at the partition boundary, whereas the minimum one – in the middle (Figure 3). The formation of spheroids leads to the redistribution of silicon in the partition. It implies that nanospheroids are main silicon-containing structural elements that are accumulated mostly by the partition boundaries.

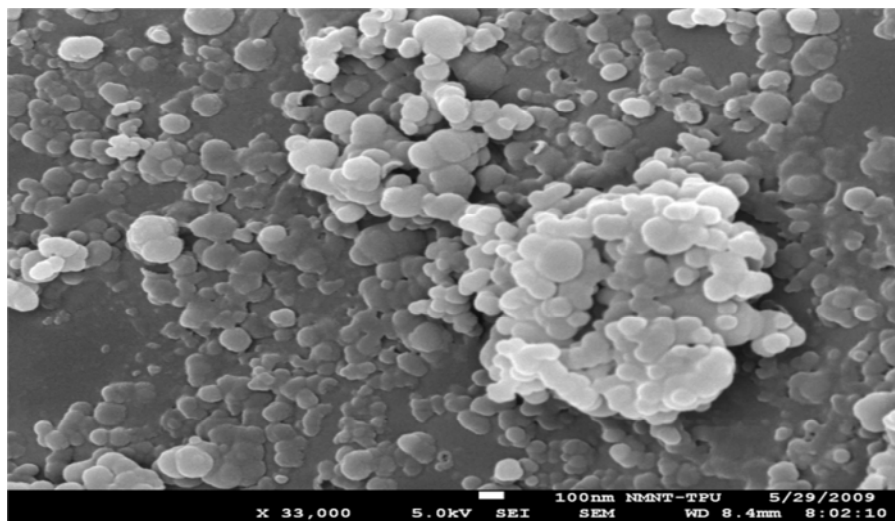


Figure 2. Electron micrograph of the spheroids in the foam material interpore partition.

Thus, the modification of the strengthened glass foam structure is determined not by the structure and presence of residual crystalline material, as it was expected, but by the change in the noncrystalline matrix structure. On the one hand, it is inconsistent with the scheme described in the scientific literature, and on the other hand, such behavior of glass-ceramic material agrees with the structure where the minimization of energy of the whole material is performed due to the energy minimization of basic (noncrystalline) component only. In the course of sponging the material by itself modifies the structure of the noncrystalline matrix. Spheroids are formed, which are referred to as “globules” in minerals-related literature. For example, Ref. [13] gives experimental evidence on the existence of globules in silicon oxide and proposes the mechanisms of their formation. The author believes that the spherical globule has different packing density of SiO_4 tetrahedrons in the centre and on the surface. The globule internal area has more incoherent packing of SiO_4 tetrahedrons, as compared to the nucleus. The general view of a globule is a three-dimensional particle with the structure similar to that of silica or cristobalite, on the surface of which there are one-dimensional Si_2O_5 chains – dimers, trimers, and monomers of silicic acid or sodium silicate. This paper assumes that globules have an intermediate position between crystalline and noncrystalline state. Other studies [14, 15] also give numerous experimental evidences on the formation of silicon oxide globules. According to the data of X-ray diffraction and thermography, the globules internal composition can be presented as a disordered set of nanocrystals and noncrystalline areas.

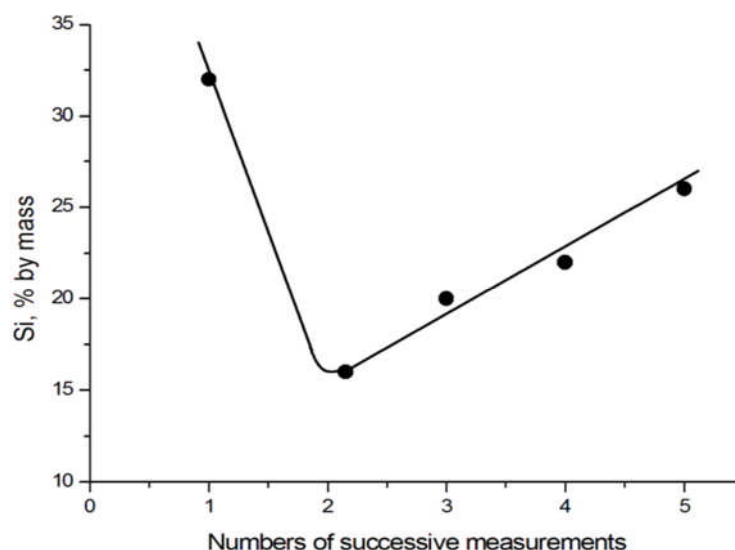


Figure 3. Distribution of silicon content in the interpore partition.

Based upon the IR spectroscopy data presented in Ref. [13] by the example of silica gels and noncrystalline synthetic aluminosilicate, it was shown that the formation of globules in the materials spectra is accompanied by the appearance of the band 1200 cm^{-1} . This is indicative of the fact that fragments of SiO_4 tetrahedrons appeared on the surface of crystals with the angles between them being equal 180° . These fragments can consist of two or three linked tetrahedrons that can be referred to as chains.

In our case, based upon the IR spectroscopy data of the glassceramic foam materials samples the appearance of a new band $1,249.6\text{ cm}^{-1}$ was established, which was not present in the IR spectra of glass foam. It is evident that these data with regard to micrographs can be indicative of the globular structure of the interpore partition noncrystalline component. Thus, we were first to discover the globules of noncrystalline matrix in the glass foam material. We consider that the sharp (abrupt) increase in the glass foam material strength is assigned specifically to them. Upon that, the microstructure of the high-strength foam material partition consists of the noncrystalline matrix with the present particles of residual silica (not more than 5% with the size of about 200 nm) and globules (100 nm and less in size).

The strength of nanoncrystalline materials is generally assigned to several mechanisms. The mechanisms of shift and local jumps are presented as basic ones. In the first case part of noncrystalline cluster (globule) is displaced at the deformation along the other one and dissipates the energy [16]. In terms of the second mechanism it is proposed to consider possible the abrupt displacement of individual atoms within a cluster (globule). More recent studies, in addition to these mechanisms, propose considering the formation of nanostructures in the deformation bands as a strengthening factor [17-21]. In our experiments the strengthening of foam material is related to two processes: 1) decreasing of the particle size in residual crystalline material; 2) formation of nanoscale spheroids – globules in the noncrystalline matrix of glass foam material. In the course of the first process – the change of the crystal size (Figure1) the strength of 3 MPa is reached, and at the introduction of the second process a theoretical strength of 5 MPa can be attained. The major energy dissipation at the deformation is performed by the areas with densely packed globules, with the volume content of which can amount to 95% in the material.

For the first time a new type of strengthening is observed in the noncrystalline material, that is the self-organization of nanospherical globules in the body of noncrystalline matrix. The strengthening model of noncrystalline materials with nanocrystal components proposed in Ref. [11] has been proved by the research conducted in our paper.

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