Foam-Glass-Crystal Materials

O. V. Kazmina and B. S. Semukhin

Abstract This chapter presents a comprehensive study of the structure, physical and mechanical properties of FGCM obtained from natural siliceous materials. The scientific principles of controlled formation of FGCM macrostructure and technological aspects of its production have been formulated in this chapter. At this, the strength of foamed materials exceeds the strength of the foamglass 3–4 times as much due to the effect of nanoscale crystals in a vitrified matrix. It has been shown that the physical and mechanical properties of foamglassceramic material depend on the number and the size of a crystalline phase. The increase of mechanical strength as compared to the foamglass can be provided by the particle sizes of a crystalline phase of less than 1 μm. Maximum strength depending on the volume rating of the residual crystalline phase accounts for 25 % for less than 1 μm size, and 5–7 % at a size decrease down to 300 nm. With the increase of the crystalline phase size up to 10 μm and higher, the compressive strength of material decreases.

1 Introduction

The problems of energy saving are the foremost in the industrial and construction sectors of economics in all developed countries. The analysis of the experience shows that one of the most effective ways to address the energy saving is the use of high-performance heat-insulating materials. Currently, the promising building materials are materials which combine high heat-proofing and structural

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O. V. Kazmina (✉)
National Research Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk, Russia634028,
e-mail: kazmina@tpu.ru

B. S. Semukhin
Institute of Strength Physics and Materials Science of the Siberian Branch of RAS, 2/4
Akademichesky Avenue, Tomsk, Russia634021,
e-mail: bss@ispms.tsc.ru

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properties, fire safety and durability. The significant scientific and practical experience of their production and use was acquired. At present, there is a vast literature on heat- and sound-insulating construction materials. It covers such aspects as technological, environmental, physical and chemical production of these materials.

One of the high-efficient heat-insulating materials that meet the requirements of environmental safety is foam glass.

Industrial waste utilization and reduction of industrial atmospheric emissions is closely connected with technical and economic problems of resource and energy saving as well as environmental protection aspects. Foam glass production is one of the efficient trends of utilization of both industrial and domestic waste glass. At the same time, the problem of cullet recycling is relevant as before, because it is so far one of the most hardest to utilize hard domestic waste.

The amount of cullet required for foam glass production is obtained by the traditional glass technology including glass manufacturing in industrial furnaces. The glass melting process is connected with generation of a considerable amount of gaseous dust air and chimney gas emissions containing end products of fuel combustion (CO_2, N_xO_y and others), and stack solids (B_2O_3, Fe_2O_3, As_2O_3). Therefore, taking into account the number of production and economic features of glass manufacturing, the foremost task is a pre-synthesis of quenched cullet from natural or industrial raw materials using energy-saving technology in order to escape the glass melting process. Low-temperature synthesis of quenched cullet is, on the one hand, economically feasible due to the absence of such energy-intensive glass manufacturing operations as fining and homogenization of the glass mass. On the other hand, this is the way to lower hazardous emissions in terms of furnace end gases.

Foam glass produced on the basis of glass cullet is composed of 100 % silicate glass which is not, practically, influenced by chemical reagents, is not a nutrient medium for fungus, mold, and is an ideal barrier for insects and rodents. Resistance of foam glass to putrefaction and the absence of a nutrient medium for mold and spread of mold and fungus are especially important when the foam glass is used in closed nonaerated space of roofs, walls, and basements. The absence of organic matter ensures the escaping of situations connected with the destruction of heat-insulating materials under the influence of the bioactive environment. Due to the specific structure of the foam glass with closed impermeable pores, at negative or variable temperatures and actuation of steam migration inside the material, a possibility of accumulation of water particles and steam is excluded as well as their condensation on the surface of interpore partitions which can be destructed in the weaker areas as a result of water and glass interaction. Therefore, one of the most important properties of the base glass is its chemical resistance.

Chemical resistance of glass is its capability to withstand the destructive effect of water, moisture, atmospheric gases, salt solutions, and various chemical reagents. Chemical resistance of glass mainly depends on its chemical composition, particularly, on the content of silicon and alkali metal oxides. Introduction of silicon oxide into glass considerably increases the its resistance while alkali metal oxides decrease it. When changing the glass composition, its chemical properties are also changed. As a rule, potash soda-ash glasses increase chemical resistance of glass.

At this stage, the study of ecotoxicological indicators of FGC (foam-glass-crystal materials), which is produced from natural and industrial raw materials based on low-temperature synthesis of quenched cullet, is conducted in comparison with the commercial types of foam glass synthesized from secondary glass cullet, e.g. FOAMGLAS® (Pittsburgh Corning www.foamglas.com). The eco-toxicological assessment procedure should pay a special attention to the study of toxic substances effect on the environment which can emit from the material while in operation.

FOAMGLAS® emits no harmful substances, such as formaldehydes, styrenes, or fire-proofing compounds, fibres, chlorofluorocarbons (CFC/HCFC) etc. that are detrimental to health. Ecological and biosafety of FOAMGLAS® offers optimum construction solutions not only for rooms where a high degree of air purity is required (hospitals, museums, schools, offices, waiting rooms, high-tech production facilities, etc.) but also in locations where there are special bacteriological and hygienic requirements (slaughterhouses, cheese factories, dairies, industrial kitchens, canteens, restaurants, swimming pools, etc.). All approved accessory products for the systems also aim to satisfy low-emission standards.

The BTU institute (Buro fur technischen Umweltschutz, Reiskirchen, Germany www.btu-umwelt.de) has gathered data on different parameters (e.g. length of service-life, primary energy content, price, thermal conductivity, costs of disposal or recycling and technical or application polyvalence) of the principal industrially-manufactured insulation products in the market. By applying a mathematical formula and with the weighting coefficients (per category from 1 to 5, with 1 being "negative" and 5 "very positive"), an examination of the parameters under consideration leads to different results per group of products and is expressed by the profitability index (R). The higher the R-value, the better the product evaluation.

For FOAMGLAS® the profitability index—a characteristic value for ecological and economic evaluation, involving a number of parameters—leads to the value 45.5. This result positions FOAMGLAS® amongst the leading products in overall economic/ecological assessment.

FGC falls within the scope of the Law of the Russian Federation (the Technical Regulations of the Safety of buildings and facilities), which claims the following: Building materials and products must not extent damage effect on humans and the environment; they must not contain and emit harmful substances in such concentrations or combinations that could influence directly or indirectly humans, or animals, or plants; concentration of harmful substances in the air of working area and habitable rooms must not exceed the normative values stated by the RF legislation in the field of sanitary-epidemiological welfare of population.

Physicotechnical properties of foam glass are specified mainly by its production technique, chemical composition and foaming mixture, the kind and the quantity of gasifier, sponging and fritting modes. Changing these factors one can obtain material of different density, strength, heat conductivity, water absorption [1-3]. Depending

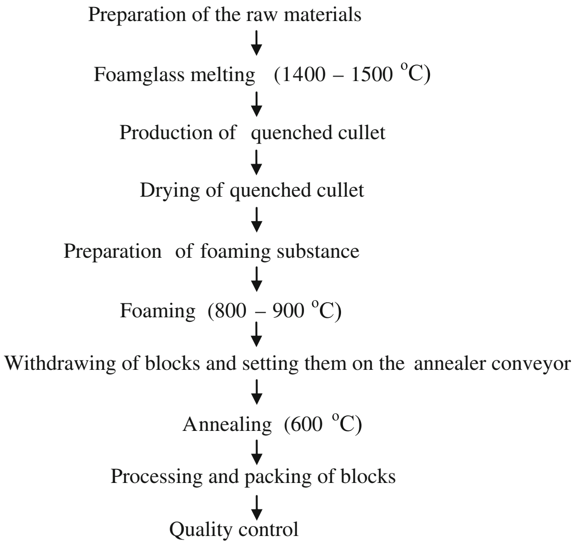


Fig. 1 Flow chart of the powder mode of foam glass production (two-stage process)

on its application, foam glass is classified into heat-insulating, sound-insulating and specific high-temperature. European production widely practises heat-insulating foam glass with density of 200 kg/m^3. Foam glass production technique includes silicate glass grinding, mixing with foaming additive of carbonic or carbonate type and thermal treatment of the mixture at 750–850 °C temperatures.

Foam glass industrial production is mainly based on the powder mode of two-stage process, the flowsheet of which is given in Fig. 1 [4]. The advantages of the two-stage production mode are as follows: minimum sponging time; a complete use of fritting furnace space due to minimum clearance between the glass blocks arranged; the minimum number of forms to be returned to production upon a completion of the sponging process neglecting the long cycle of foam glass fritting. Figure 2 illustrates the plan of the foam glass area designed by the Glamaco Company (Germany).

The global experience shows that it is not always feasible to utilize foam glass in the form of blocks or plates. In a number of cases, the foam glass is used in the form of gravel or crushed stone for building, e.g. as heat-insulating bulk material or concrete filler. A great experience has been accumulated in the field of utilizing foam-glass crushed stone Schaumglas Schotter and gravel Poraver. Production of small granules of heat-insulating material is always more profitable from the viewpoint of heat exchange. In producing block-like foam glass, up to 80 % of the length of the tunnel furnace and, as a consequence, up to 80 % of time is spent on the slow cooling of material. The quenching and productivity improvement result in considerable internal tensions and destruction of blocks. It is the principle of quenching which foam-glass crushed stone Schaumglas Schotter production is being based on: the foam glass is leaves the furnace at a rather high speed, then additionally cooled, and as a result of this crushed stone is obtained.

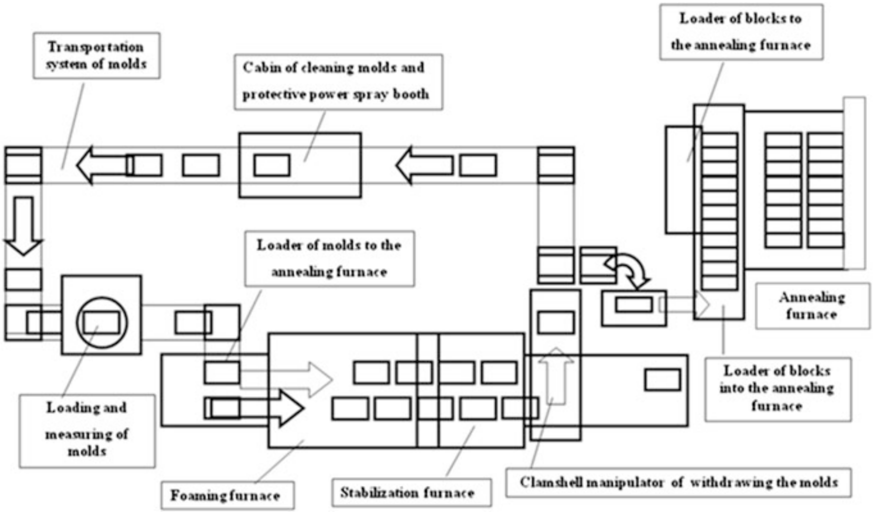


Fig. 2 Plan of the foam glass area in the two-stage mode of production designed by the Glamaco company (Germany)

Raw material used to obtain foam glass according to the classic scheme is broken glass, the composition of which meets the specific requirements. Firstly, they use glasses of a wide melting range, the so-called ‘long’ glasses. Secondly, the glass must contain a component which at the process temperatures would interact with carbon so as to provide gasification. At the same time, broken glass still remains one of the most difficultly utilized components of hard domestic waste. For example, in 2001 the percentage of its recycling in the developed West European countries ranged from 24 to 92 %. Only profiled broken glass undergoes the effective recycling while the low-grade one is stored at hard domestic waste grounds. It leads to the inevitable interaction between the glass and precipitation which results in scavenging of Na^+ ions from the glass surface and formation of alkaline solutions. Especially, it concerns small fractions which possess the largest specific surface and, therefore, define scavenging of the alkaline component to a great extent that negatively influences the environment.

Thus, profiled broken glass of the certain composition is employed to manufacture the qualitative foam glass; its lack is made up by the traditional glass technology. The glass production requires substantial material and energy expenditures. Therefore, taking into account a number of technological and economic glass manufacturing features, the foremost task is to provide the preliminary synthesis of the quenched cullet from the natural or anthropogenic raw materials using the energy saving technology at temperatures not above 950 °C escaping the power-intensive process of glass melting.

This chapter presents a comprehensive study of the structure, physical and mechanical properties of FGCM obtained from natural siliceous materials.

2 Physical and Chemical Principles of the Production of FGC

A foam-glass-crystalline material is an amorphous porous material that contains nanostructural units and exhibits increased strength characteristics as compared to the conventional foam glass manufactured from a glass cullet. The possibility of controlling the structure of foam-glass-crystalline materials is determined by the chemical and granulometric compositions of the initial batch; the nature of the basic glass forming component of the batch, the technology used for preparation of the batch, which brings into operation of the mechanisms and effects of mechanical activation of the mixture; and the regime of heat treatment of the batch under the conditions providing the low-temperature synthesis of the glass granulate.

The glass granulate is the initial raw material for the subsequent foaming and manufacturing of foam-glass articles with specified characteristics. According to the phase composition, this intermediate product is a glassy material containing the residual quartz crystals. The properties of foam-glass-crystalline materials depend not only on the composition and structure of the phases of the glass granulate, which are formed in this material, but also on the size and mutual arrangement of the structural units at the microscale level.

A two-stage method for producing foam glass via the intermediate product (quenched cullet) synthesized by thermal treatment of the mixture of the certain composition was developed at Tomsk Polytechnic University [5]. This product acts as the raw material for the following sponging and obtaining foam-glass-crystal products with the pre-set characteristics. According to the phase composition the quenched cullet represents a vitrified product with residual crystal inclusions which define the density and strength of the end items. The principal procedure for obtaining foam-glass-crystal materials is given in Fig. 3, which outlines three main technological stages, two of which relate to the quenched cullet. The idea of the technology developed lies in the following principles:

- Special preparation of raw materials allows synthesizing a glass ceramic at temperatures not over 950 °C which is the raw material for the foam glass;

Controlling the formation of nano and microstructure of the interpore partition allows regulating the strength and density of the end item. Relatively low temperatures of the glass phase synthesis carried out according to the designed mode, promotes not only energy consumption decrease, but also that of the carbonic acid release. The working operation of the mixture compaction makes possible to lower the air pollution of the working area as well as the general dust emission to the atmosphere.

Compositions of container glasses or the like are considered to be the optimal for foam glass manufacture. The content of oxides required for these glasses consists of the following elements (mas. %): SiO_2 67–72; Al_2O_3 1–6; CaO 7–11; MgO 1–4; Na_2O 14–15. It has been experimentally stated that the most perspective

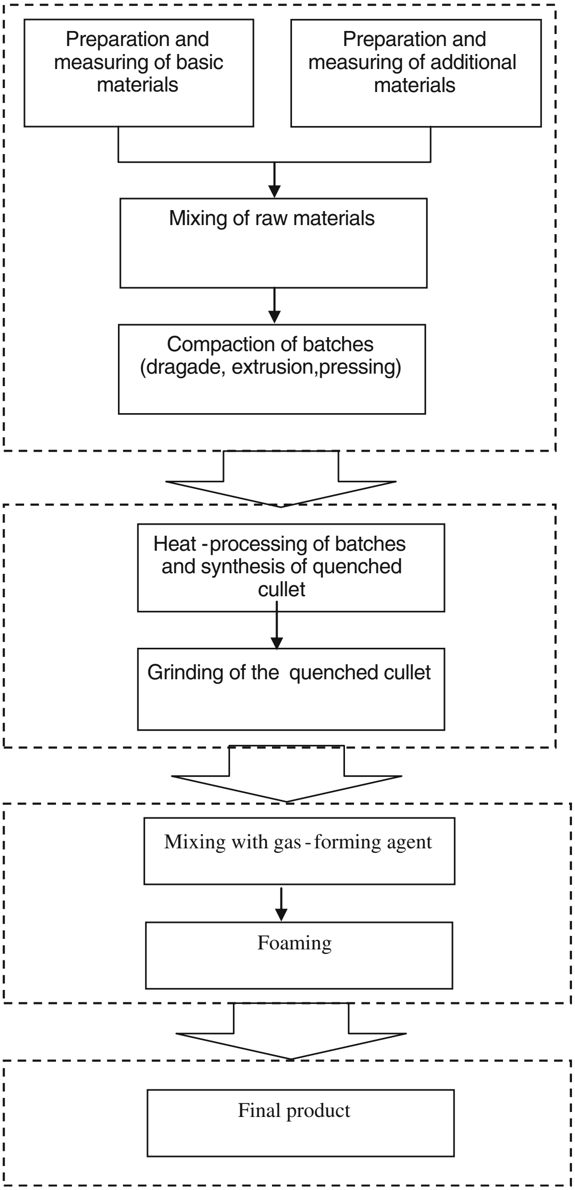


Fig. 3 The principal procedure for obtaining foam-glass-crystal materials

raw material is the breakage of a dark green bottle while less manufacturable is the breakage of float-glass. Table 1 gives typical compositions of silicate glasses used to manufacture foam glass in different countries. Oxides included in the glass composition influence the sponging mode, namely: the temperature, the process duration and also such properties as crystallization, viscosity and surface tension [6].

Table 1 Chemical composition of glasses used for foam glass production

Composition	Content, mass. %						Country
	SiO_2	Na_2O	Al_2O_3	CaO	MgO	B_2O_3	
1	72–73	15.5–16.5	0.5–1	6–6.5	3.5–4	–	Russia
	(73)	(16.1)	(0.8)	(6.3)	(3.8)		
2	55–72	11–18	3–16	9–12		–	Czech
	(64.8)	(14.8)	(9.7)	(10.7)			
3	72–74	13–17	0–2	8–12	–	–	Great Britain
	(73.7)	(15.2)	(1)	(10.1)			
4	70–72.7	14	2–7	4.9–7.6	3	0–3.6	France
	(70.5)	(14)	(4.5)	(6.3)	(2.9)	(1.8)	

In brackets given are average values translated into 100 % glass composition

The use of the raw materials alternative to the broken glass significantly expands the technological possibilities of the foam glass production. The diverse natural and/or anthropogenic feed stock can be utilized as raw materials. The composition and properties of siliceous and silica-alumina raw materials allow synthesizing the quenched cullet on their basis with the following processing until the porous material will be obtained. Controlling the component composition of the mixture and the temperature conditions for thermal treatment, heat-insulating materials can be obtained being rather various in their properties.

The analysis of scientific publications and research findings provided have shown that in order to obtain a low-temperature quenched cullet, the choice of the mixture composition should be carried out in relation to the following conditions:

- The amount of glass formers' oxides and alkali metal oxides in the quenched cullet must be sufficient for a sustainable glass formation, i.e. the content of SiO_2 is in the range of 60–75, and the content of alkali metal oxides is in 13–22 mass % range;
- The number of the glass bath must not be less that 70 % that is necessary to provide plastic state of the mass at the sponging stage;
- The liquid phase must be of the optimal viscosity (103–106 Pa•s) within the sponging range;
- The temperature for the liquid phase formation (glass bath) must not exceed 950 °C.

With a purpose to select the basic glass composition and diminish the amount of preliminarily experiments so as to obtain the quenched cullet, carried out was the analysis of state diagrams of the ternary system Na_2O–CaO–SiO_2 which is the basis for a production of the industrial glasses of more oft-used compositions, namely: container glass, sheet glass, etc. In accordance with the state diagram the industrial silicate glass area is close to the equilibrium field of crystals of wollastonite, devitrite, tridymite. It is these phases which are often demonstrated in glass crystallization. Almost all industrial compositions get one elementary phase triangle $Na_2O \times 2SiO_2$–Na2O × 3CaO × $6SiO_2$–SiO_2 and begin to melt at 725 °C that corresponds to the low-temperature system eutectic.

The analysis of the diagram has shown that the following three groups of compositions correspond to the above stated conditions: (1) compositions with the varying ratio of the basic oxides and the fixed amount of SiO_2 (73 %); (2) compositions with the varying content of CaO and SiO_2 at the fixed amount of the alkaline component (21 %); (3) compositions with the varying content of Na2O and SiO_2 at the fixed amount of alkali-earth metal (5 %) [7].

The research findings have shown that the optimal glass content appropriate to obtain the foam glass under the low-temperature technology, is the composition with rather high content of SiO_2 (72–74 mass %) and the ratio of basic oxides CaO/Na_2O within the range of 0.2 ÷ 0.9 that corresponds to the sufficient viscosity of the glass bath and stable glass formation.

For test experiments the compositions characterized by the ratio of the basic oxides were selected within the following limits: the amount of Na_2O ranges from 14.5 to 21 %; the amount of CaO ranges from 5 to 13 %. The state diagram of Na_2O–CaO–SiO_2 system illustrates that the given compositions limit the area of glass formation with the various component ratio.

The change of the composition along the line connecting points 1 and 2 is accompanied by the decrease of Na_2O and the increase of the melting temperature which does not exceed 950 °C.

The first composition is eutectic with melting temperature of 725 °C; in the second composition the share of the liquid phase forming in the temperature range of 800–950 °C changes from 45 to 80 %. For all that, one can expect that real temperatures of mixture treatment will be lower due to the impurity substances presented in raw materials. To obtain the quenched cullet based on siliceous raw materials the following two boundary compositions were chosen (mass %): SiO_2—74; CaO—5; Na_2O—21 and SiO_2—73; CaO—11; Na_2O—16.

To synthesize the glass phase of the chosen compositions the two-component mixture is required which includes the siliceous and alkaline material in the form of soda ash. In the lack of alkali-earth oxides in raw materials, the mixture is corrected by the additional introducing of chalk or dolomite.

The adequacy of siliceous raw material for quenched cullet production is defined by three main indicators: chemical, phase and granulometric compositions. In this case, siliceous materials with the following oxide content (mass %) are the most adequate for quenched cullet production: silicon not less than 83; aluminum up to 7; the total amount of alkali-earth oxides up to 13; ferrum not over 10.

The phase content of siliceous materials is of significant meaning for low-temperature synthesis of the glass phase. The presence of amorphous component SiO_2 creates favorable background for solid-phase reactions and allows lowering temperature of glass synthesis in comparison with crystalline silica. In this case, the most optimal are high-silica amorphous rocks because the silicate glass is an amorphous material which contains over 70 % of SiO_2. However, it should be taken into consideration that silicate glasses which contain coloring oxides tend to be crystallized, for example, ferric oxide at the repeated thermal treatment. The presence of the residual crystal phase in the quenched cullet may promote crystallization which is promoted as well by the high specific surface of initial mixtures. Therefore, it is important to take into account the qualitative ratio between the crystal and amorphous phase components in the siliceous mixture component.

Below given are the experimental findings for siliceous raw materials which meet the stated requirements in terms of such materials as sand, marshallite, diatomite and flask (Table 2). The chemical composition of these materials is represented by rather a high content of SiO_2 and the presence of impurities which are not harmful because of their inclusion in the glass composition and taking into account in the mixture calculating.

The experiment data showed that the residual content of crystals remains at the level of 10–23 %; the largest amount of the glass phase has the quenched cullet based on marshallite and flask. The mixture based on the material with amorphous SiO_2 shows more higher chemical activity at the stage of silicate and glass formation.

It has been stated that with the increase of the mixture treatment temperature the content of the crystal phase decreases for all compositions. In case of using diatomite and flask, the temperature decreases down to 850 °C with the further stabilization of the residual silica amount. Obviously, it is connected with relatively low temperature of the mixture melting and the early approach of high-

Table 2 Properties of siliceous raw materials and quenched cullet produced on their basis

Indicators	Siliceous raw materials			
	Silica sand	Marshallite	Diatomite	Flask
Chemical composition, mass %:				
SiO_2	98.15	95.7	86.44	83.00
$Al_2O_3 + TiO_2$	0.73	2.10	5.30	5.25
$CaO + MgO$	0.09	1.4	1.27	3.52
Fe_xO_y	0.05	0.27	1.60	2.72
Phase composition, volume, %:				
Crystal forms SiO_2	98	95	14	13
Amorphous opal	–	–	70	57
Silica-alumina crystal phases	2	5	16	30
Specific surface of prepared rock, cm^2/g	3,484	5,500	14,510	16,150
Maximum temperature of mixture treatment, °C:	Thermal treatment of mixture			
Composition (I)	930	875	830	810
Composition (II)	880	840	850	825
Crystal phase amount for quenched cullet, mass %:	Quenched cullet properties			
Composition (I)	16	1	13.7	2.65
Composition (II)	23	10.38	14.92	6.14
Plastic state temperature of quenched cullet, °C:				
Composition (I)	800	748	777	740
Composition (II)	850	823	845	841

viscosity liquid phase which takes disjoining effect and lowers the dissolution of crystal SiO_2. The glass formation process for sand mixtures is not complete (the amount of crystal phase is 23 %). Thus, it is advised to treat the mixture at higher temperatures or provide the additional preparation of the mixture using mechanical activation.

Thus, in order to obtain the quenched cullet at relatively low temperatures one can utilize fine-dispersed siliceous materials in the capacity of the mixture component taking into account the following factors:

- The use of quenched cullet with the glass phase amount of over 80 % allows obtaining foam-glass-crystal material of up to 250 g/cm^3 density; 3 MPa strength and 6 % water absorption;
- The amount of the glass phase of the quenched cullet increases along with the increase of amorphous component in the siliceous mixture component.

3 Foam-Glass-Crystal Materials Structure

In this section, the experimental results of the analysis of FGC structure on different structural levels are presented. To determine the structure of the samples obtained, the optical and electron microscopy was used. The elemental composition of interpore partitions was detected with of high resolution scanning electron microscope JSM-7500FA and equipped with X-ray microanalyzer. Before recording, the samples were covered with a thin platinum layer. Recording was carried out at the following modes: accelerating voltage of the electron beam of 10–15 kV; working distance of 20–50 mm; and magnification up to 100,000 times.

The X-ray structural analysis of the phase composition of quenched cullet and foamed material was carried out using DRON-3 M diffractometer with Cu Kα radiation with monochromatization of a diffracted beam by a pyrolitic graphite crystal.

The energy characteristics of a submicron crystalline phase differ from those of the starting material [8]. A maximal enhancement in the strengthening of material might be expected if the crystalline phase microstructure is far from equilibrium. According to Academician N. P. Lyapishev, a material having specific properties would be composed of crystallites or of a mixture of nanometer-sized crystals and amorphous phase. Indeed, the foam glass material manufactured from glass granulate is in conformity with the latter principles [9].

The experimental dependence illustrated in Fig. 4 was obtained for the test samples, which had a predetermined content of residual crystalline phase (5 % on the average) and differed in the size of crystalline phase particles. By assuming that the minimal critical size of crystalline phase particles is 10 nm, the maximal theoretical strength was calculated for foam glass material; the value obtained is 5.0 MPa. In the case of foam glass whose amorphous matrix contains no crystalline phase this value is not greater than 1.5 MPa [10].

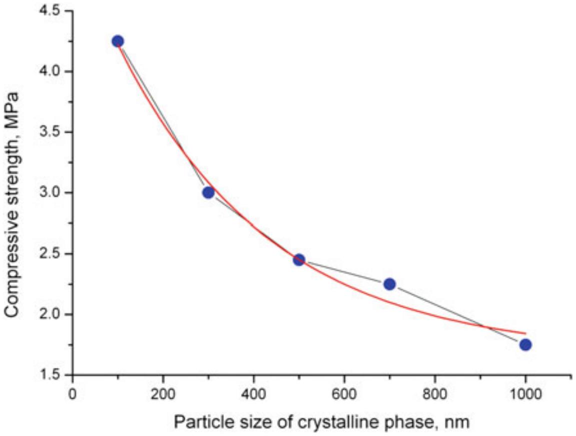


Fig. 4 The strength of foam glass material versus particle size of crystalline phase

The particle size of residual crystalline phase can be no further reduced; therefore, one can employ an alternative method for strengthening of amorphous matrix by changing its internal structure. Compressive strength values were obtained experimentally for all the test samples of foam glass material. This data suggests that an enhancement in the strength of materials (up to 4.3 MPa) was achieved due to the occurrence in their interpore partitions of spherical formations (spheroids).

High resolution electron microscope images show spheroids having sizes of 60–160 nm, which occur in the amorphous matrix of these materials. No formations of this kind were found to occur in the interpore partitions of common foam glass and glass ceramics whose matrix contains residual quartz particles having size >200 nm (Fig. 5). Figure 5 clearly illustrates a complex hierarchy of single spheroids and groups of spheroids. An X-ray dispersion analysis suggests the occurrence of nonuniformly distributed silicon in the amorphous matrix of the interpore partition: the maximal silicon concentration is observed in the vicinity of interpore partition and the minimal, within the interpore partition (Fig. 6). The formation of spheroids would evidently cause redistribution of silicon in the interpore partition. It is thus concluded that the main silicon-containing structural elements are nanospheroids which gather mostly in the vicinity of interpore partition.

It is thus found that the structural changes of a strengthened foam glass material are due to a change in the structure of its amorphous matrix rather than to the occurrence and structure of residual crystalline phase. This conclusion seems inconsistent with the conventional scheme discussed in the literature [11-13]. However, the experimentally observed behavior of the glass ceramic is in accord with a structure, which enables minimization of the energy of the entire material volume at the expense of the main (amorphous) component.

In the course of foaming process, the structure of amorphous matrix would change spontaneously; in so doing, spheroids are formed. Here a remark is in

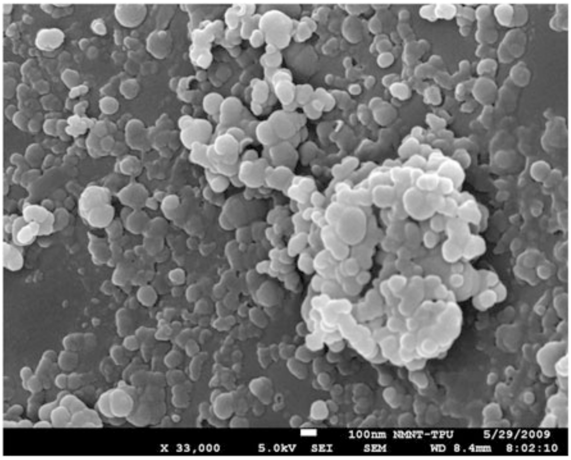


Fig. 5 The electron microscope image of spheroids in the interpore partition of foam glass material

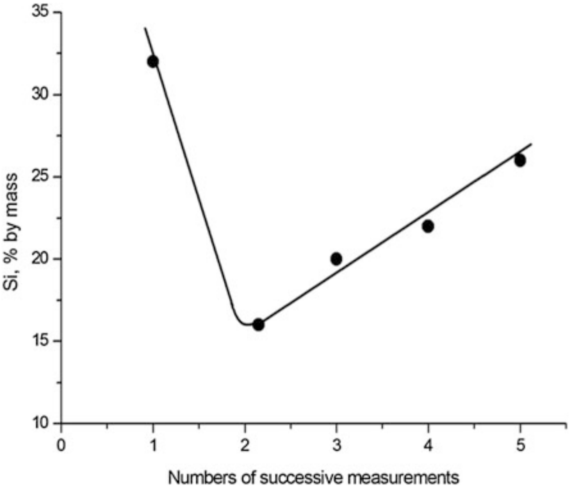


Fig. 6 Silicon content distribution in the interpore partition

order: when dealing with minerals, spheroids are called ‘globules’. The experimental evidence for the occurrence of globules in silica and the mechanisms involved in their formation are discussed elsewhere [14]. It is assumed that a spherical globule has a loosely packed body, while its core has a close-packed arrangement of SiO_4 tetrahedrons. The general aspect of a globule is that of a 3D particle having a quartz- or crystobalite- type structure; on its surface are arranged unidimensional SiO chains, i.e. mono-, di- and trimers of silicic acid or sodium silicate. Such a globule is taken to be an intermediate state between crystalline and amorphous matter. Abundant experimental evidence for silica globule formation is available [15, 16]. X-ray diffraction analysis and thermography data suggests that the globule structure is a set of randomly distributed nanocrystallites and amorphous areas.

Using IR spectroscopy technique, investigations were carried on for the test samples of silica gel and synthetic amorphous aluminosilicate. The spectra obtained show a band 1,200 cm^{-1}, which corresponds to globule formation [14]. This suggests that on the crystal surface have appeared fragments of SiO_4 tetrahedrons, which make an angle of 180^o with one another; some of these fragments are composed of two or three tetrahedrons joined together to make a kind of chain.

The IR spectra obtained for glass ceramic samples are found to show a new line 1,249.6 cm^{-1}, which is absent from the IR spectra of foam glass. On the base of IR spectra and micrographs obtained one can evidently assume that the amorphous component of the interpore partition has a globular structure. It is for the first time that globules are discovered in the amorphous matrix of foam glass material. It is these globules that are responsible for a sudden enhancement in the strength of foam glass material. It is emphasized that the microstructure of interpore partition is composed of amorphous matrix, which contains residual quartz particles (≤ 5 %) having size ~ 200 nm and globules having size ≤ 100 nm.

The strength of amorphous materials is generally attributed to the action of several mechanisms, with the main mechanisms being shearing and local jumps. In the former case, the deformation is assumed to involve shearing of one amorphous cluster (globule) against another to cause dissipation of energy [17]. In the latter case, it is assumed that a jump-wise change of atoms positions would occur within a cluster (globule). It was proposed recently that, in addition to the above mechanisms, one should taken into account another factor, which might also be responsible for material strengthening, i.e. nanostructure formation within the deformation bands [18-22]. In our experiments the strengthening of foam glass materials is largely due to two processes: (1) a decrease in the particle size of residual crystalline phase and (2) formation of nanospheroids (globules) in the amorphous matrix. In the former case, an enhancement in the strength of material is ≤ 3 MPa and in the latter case, one can achieve theoretical strength ≤ 5 MPa. In the course of deformation, the dissipation of energy would mainly occur in material areas containing close-packed globules, with the volume fraction of globules being ≤ 95 %.

A new type of deformation strengthening has been observed for the first time. This involves spontaneous formation of nanometer-sized spherical globules within the amorphous matrix of the deforming material. The model of strengthening proposed for amorphous materials in is validated by the experimental results discussed herein.

4 Mechanical Properties

Foamglass is one of the universal high-performance heat and sound-insulating materials whose scope of use as a structural material is impartially limited by the compressive strength indicator (not over 1.5 MPa) that depends on the nature and structure of material, i.e. ‘glass foam’ with the pore partition thickness up to 50 mkm.

The foam glass-crystal material high-strength characteristics as compared to the traditional foam glass technology based on the use of cullet. The increase of mechanical strength of foam glass allows widening its scope of use as a structural material.

The research findings of the fracture process of foam glass-crystal samples obtained *in vitro* as well as the relation between the structure and mechanical strength are discussed in this Report.

There are two extreme cases of a body behavior at the external load application. In the first case, which corresponds to an ideal solid, deformation is proportional to the stress imposed. The second extreme case is viscous fluid for which the deformation rate equals to the applied load divided by the coefficient of viscosity. Amorphous solids are neither perfectly elastic nor perfectly viscous ones and combine both elasticity and viscosity properties. It means that complete deformation of the amorphous solid is likely to consist of two parts—elastic and viscous. In case of foam glass, this phenomenon appears to the specific degree because the 'classical' glass is fractured in perfectly brittle way according to the Griffiths' model, while the foam glass and the foam glass-crystal material display both elastic and viscous components.

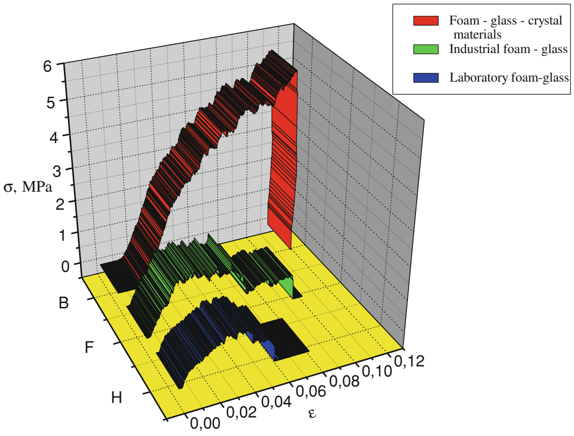
To analyze the mechanical properties, and specifically to define the tensile ultimate strength of foam glass, some tests were conducted by means of the universal machine 'Instron 1185' with the load range between 0–100 N and 0–100 kN. The measurement accuracy was ±0.5 % of the display value, or ±0.25 % of the load scale used. In compliance with the recommendations given by the Russian State Standards (ГОСТs), Р ЕН 826–200 "Heat-insulating products used in construction. Method of compression characteristics' detection", tests were carried out at rate of 2 mm/min. Foam glass samples in the form of rectangles or cubes underwent the test for compression down to their complete fracture with registering strain diagram in the automatic mode. For the comparative analysis three kinds of samples were chosen, namely: foam glass-crystal materials, industrial foam glass and laboratory foam glass obtained from cullet.

Figure 7 presents the generalized view of dependencies σ–f(ε) which shows that the dependence characters for foam glass samples obtained from cullet are similar, while those ones of the foam glass-crystal material are different. The value of the tensile ultimate strength of the foam glass-crystal samples is considerably higher (2–3 times) as compared to the foam glass. This significant difference can be explained by the material structure including the size of pores and interpore partitions, the composition and structure of the amorphous component.

To describe the deformation curve of the foam glass-crystal material the synergetic approach was applied, which was described by Prof. Olemsky in his work on fluid vitrification [23]. It was shown in this work that within the synergetic equations the modified Maxwell equation is in compliance with the experiment for the viscoelastic medium:

$$\sigma = -\sigma/\tau_{\sigma} + g\,\sigma\,\varepsilon\,T \qquad (1)$$

Fig. 7 Compression test curves of foam glass materials



The first summand is responsible for the dissipative process of stress relaxation to the equilibrium value, and for the microscopic Debye time of 10^{-12} s at that. This time appears in the well-known Zhurkov formula which describes the interrupting time and rupture stress σ_p relation [24]:

$$\tau = \tau_0 \exp[(U_0 - \gamma\, \sigma_p) = kT \tag{2}$$

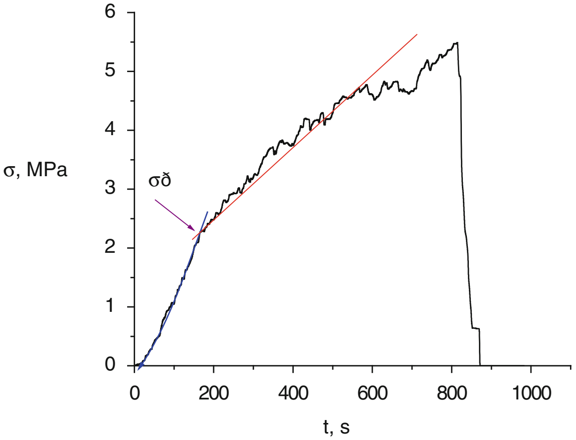
The second summand of Eq. (1) defines the self-organization process.

Thus, the elementary deformation curve σ (ε) includes not one but two sections. The first section is elastic, Hookian, and has a wider slope angle; the second section is more gradient and responsible for plastic deformation processes. Taking into account the deformation module defect at transition from Hookian stage to the plateau of the plastic flow adequately reflects the vitrification process in terms of synergistic concepts. In the case described, the deformation curve of the foam glass-crystal material actually consists of two segments specified by the suggested synergetic model and Zhurkov's model (Fig. 8).

It should be noted that in compression testing of foam glass, the abrupt fraction of samples typical for brittle materials has almost never been observed. With the increase of the load the sample becomes deformed, and at the same time, thin partitions of cells are sequentially fractured on the fixed thrust face. The received glass powder is pressed into the anew fractured cells.

The elemental composition of interpore partitions was detected by the electronic microscope JSM-7500FA equipped with the power-dispersion microanalyzer *Edax*. It is shown in the figure that nearby the interpore partition the silicon concentration is the highest while in the centre it is minimal. This high content of silicon must result in formation of crystal inclusions of SiO_4 in the boundary layer of the interpore partition. The presence of crystal phase in amorphous matrix increases the strength of the interpore partitions. In applying the load to the sample during the compression test process, the partitions collapse.

Fig. 8 Deformation *curve* (by time) of the foam glass-crystal material

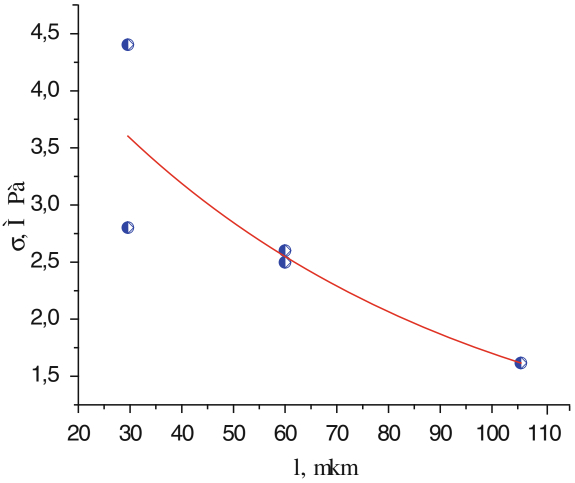


The relation of grain size and strength for non-deformed materials is similar to Hall–Petch relation for the yield strength of ductile metals: if average grain size could be decreased even further to the nanometer length scale the yield strength would increase as well. However, in case of porous materials, this correlation should take place rather between the sizes of interpore partitions than the pores themselves because all mechanical properties of the material depend on the properties of partitions themselves.

Figure 9 illustrates the curve of average size of the interpore partition in the foam glass-crystal material depending on stress. One can see that this dependence is similar to Hall–Petch relation.

The important feature of cellular material affecting the mechanical strength is the porosity character that includes spatial arrangement of pores (packing),

Fig. 9 Dependence of the average size of the interpore partition upon the ultimate strength



distribution of pores by their size (pore combination of various sizes), the form and the thickness of interpore partitions.

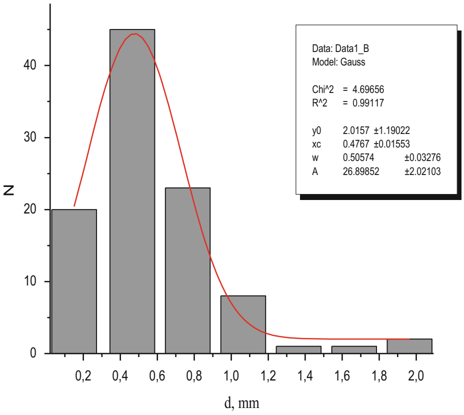
The pore shape is the parameter which characterizes a degree of deformation of spherical pores into regular polyhedrons. One can judge about the degree of pore deformation according to the cellular porosity bulk: the 75–80 % excess indicates the possibility of transition from spherical pores to polyhedrons. The higher porosity the more regular polyhedrons should be. The system tends to such porosity parameters that provide formation of pores with a dense smooth surface. The porosity increase is achieved at various sizes and aspheric shapes of pores. Products with more homogenous honeycomb structure of pores possess higher strength. A polydisperse character of pore distribution by their sizes provides the high probability of uniform location of smaller pores between the larger ones.

It is worth noting, that the pore distribution by sizes in the foam glass-crystal material is similar to that one of the structural elements presented in nanocrystalline materials. This distribution of hierarchically subordinate microvolumes of materials should have an impact on strength properties (Fig. 10).

At the same time, the size and the shape of pores are connected with mechanical properties. Figure 11 presents the diagram of the pore size (average value according to the image) depending on the definite fracture stress. This linear dependence has the high correlation coefficient.

Thus, the defect structure of pore types in cellular materials can characterize the performance of foam glass products. At the load applied to cellular materials the pressure transmits along the partitions of pores which form arches. Due to this, the structure of linearly loaded material always has the bulk stress state. It is known that at big arch sizes high stresses occur. Arch sizes in the structure of cellular articles are in direct relation to the pore sizes. Therefore, cellular materials possess higher strength characteristics when they have pores of smaller sizes, all other conditions being equal.

Fig. 10 Pore distribution by the sizes in the foam glass-crystal material



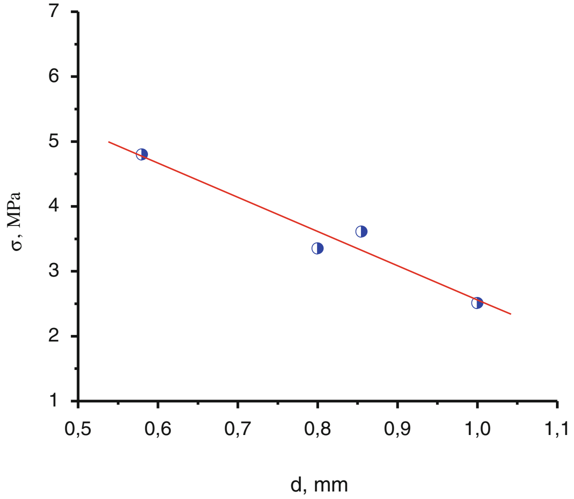


Fig. 11 Dependence of the average pore size on the ultimate strength of the foam glass-crystal material

However, the analysis of micrographs illustrating the foam glass-crystal materials obtained from mixtures of diverse compositions makes obvious the advantage of location of spherical pores of two different diameters, the so-called two-modal filling manner. This layout implies filling of the free space between the spherical pores of larger sizes with those ones of smaller sizes. It can be seen well in Fig. 12 which represents the microstructure of various foam glass-crystal materials.

Moreover, modification of pore shapes, i.e. the tendency to a honeycomb distribution of hexagonal pores can considerably increase the mechanical properties of cellular material. Figure 13 illustrates two pictures of materials with different pores and different ultimate strengths.

According to the research findings in relation to the fracture process of foam glass-crystal samples obtained in vitro it has been stated:

- foamglass-crystal samples have higher strength as compared to the foamglass obtained from cullet;

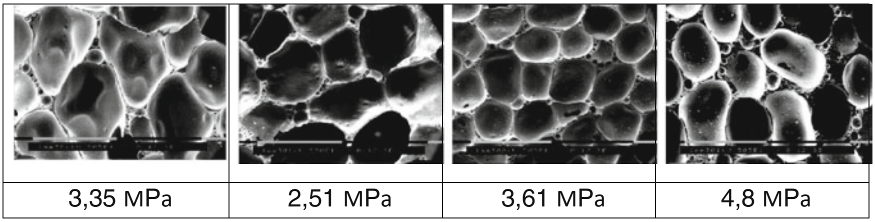
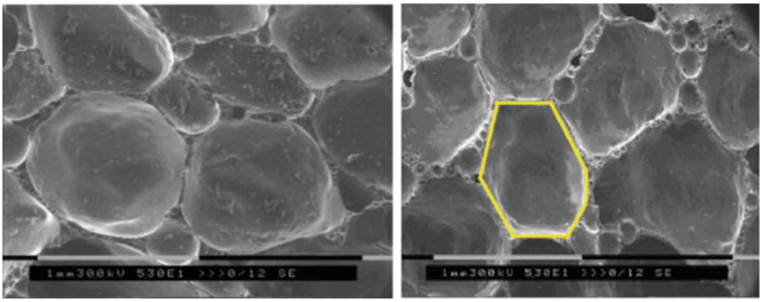


Fig. 12 Sizes and shapes of pores belong to various foam glass-crystal materials and the corresponding strength



3,41 MPa 3,67 MPa

Fig. 13 Hexagonal shape of pores of the foam glass-crystal materials and their strength

- the fracture mechanism for foamglass-crystal samples is well described by the synergetic models of deformation of a quasi-viscous (amorphous) solid;
- the relation between the interpore partitions of foamglass-crystal material and the ultimate strength is similar to Hall–Petch relation;
- the fracture stress is in direct proportion to the pore size whose diminishing raises the strength of cellular materials.

5 Conclusion

The scientific principles of controlled formation of FGCM macrostructure and technological aspects of its production have been formulated in this chapter. A novelty of research findings is consisted in the development of physic-chemical principles of obtaining materials by a formation of nano and microcrystalline phase in a vitrified matrix of the silicate system. This method allows using a wide range of natural and industrial raw materials without glass melting unlike the traditional foam glass production. At this, the strength of foamed materials exceeds the strength of the foam glass 3–4 times as much due to the effect of nanoscale crystals in a vitrified matrix.

It has been shown that the physical and mechanical properties of foam glass ceramic material depend on the number and the size of a crystalline phase. The increase of mechanical strength as compared to the foam glass can be provided by the particle sizes of a crystalline phase of less than 1 μm. Maximum strength depending on the volume rating of the residual crystalline phase accounts for 25 % for less than 1 μm size, and 5–7 % at a size decrease down to 300 nm. With the increase of the crystalline phase size up to 10 μm and higher, the compressive strength of material decreases.

The FGC technology can be recommended as a safe technology for a large-scale industrial introduction. The research of this technology justifies both the safety of methods and high quality of products. At the same time, the problem of energy efficiency of technology have been solved (lowering energy costs by 1.3 times) and decrease of hazardous emissions to the atmosphere at the production stage (by 2 times on average).

Production of materials using this technology is supposed to be carried out at temperatures 850–900 °C what is significantly lower as compared to keramzit technology (1,150–1,200 °C) and traditional cullet-based foam glass (1,400–1,500 °C).

The development of compositions and technology of FGC which combines heat-insulating and constructive properties widens the nomenclature of construction products and facilitates the problem solving of heat-insulating material production which meet the requirements of fire and environmental safety.

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