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GLASS MICROSPHERES THERMO-DEFORMATION SINTERING PROCESSES IN THE TECHNOLOGIES OF OBTAINING MATERIALS FOR UNDERWATER TECHNICAL EQUIPMENT

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ABSTRACT

In this work, the important scientific and technical problem of creating multifunctional composite materials for shipbuilding and ocean engineering was solved. The work aimed to study the thermal deformation processes of sintering glass microspheres to obtain lightweight glass composites with a cellular structure that provides positive buoyancy and sound insulation properties. For this purpose, glass microspheres of Na_2O–SiO_2 and Na_2O–B_2O_3–SiO_2 composition with a dispersion of 10 to 60 μm were used as raw materials. They were sintered to form a closed, porous structure.
The theoretical substantiation of technological parameters is based on the concepts of solid state and glassy state chemistry and physicochemical concepts of glass softening processes. The process of hot-pressing glass microspheres without plasticisers and additives was investigated. The author's own laboratory equipment was used for the experiments. The sintering intensity was determined from the results of shrinkage processes; the kinetic shrinkage curves were constructed in semilogarithmic coordinates. The glass composite samples were examined by optical and electron microscopy. As a criterion, the storage of spherical microspheres under the influence of simultaneous heating to 700 °C with the application of pressure in the range of 0,5 to 1,5 MPa was chosen. It was established that the formation of a predominantly closed-porous structure of glass composites with a density of 350...600 kg/m^3 occurs by the mechanisms of viscous glass phase flow through liquefaction processes in the walls of microspheres. At the same time, shrinkage processes in the linear direction reach up to 50%.
The acoustic properties were investigated by measuring the differences in sound pressure levels in octave frequency bands using a Kundt pipe. The water absorption of the glass composite samples was determined at hydrostatic pressures up to 20 MPa. The research results were compared with the characteristics of analogue composites, such as syntactic foams and foam glass. The developed materials can be used in the design and manufacture of technical equipment for research and maintenance of underwater infrastructure. The prospects for further research are related to the feasibility study and marketing research on implementing the developed glass composites.

Keywords: temperature, pressing pressure, structure, porosity, sphericity, fiberglass composites, subsea equipment, and infrastructurecharacteristics

INTRODUCTION

The main purpose of creating a network of subsea infrastructure is to service offshore mineral production and the technical equipment for lifting and transporting them [1, 2]. Today, oil and gas exploration are carried out at great depths (from 2 to 6-7 km) [3, 4] and not only in sedimentary basins but also in crystalline Precambrian rocks, both onshore and offshore [5]. Moreover, in recent decades, the world has been successfully developing fundamentally new gas deposits - gas from "tight reservoirs" located in shale, siltstone, and fine-grained sandstones ("shale" and "central basin" gas) [6]. Improving and developing methods for developing subsea deposits is very important for finding new sources of raw materials for energy and industry. This research is being conducted in almost 70 countries and covers the shelves of

all continents. By 2000, more than 3,000 offshore oil and gas fields had been discovered [7]. Products are delivered to land using special product pipelines that are laid on the seabed on special supports or buried in the ground [8]. They are in difficult operating conditions, and in addition to the working pressure of the transported product, they are also loaded with external hydrostatic water pressure. Pipelines can also be affected by waves and currents. They must be insulated to protect against corrosion and lined to protect the coating from mechanical damage [9]. Unlike deep-water drilling, offshore mining takes place at a depth of 100...200 meters. However, the work is complicated due to water surface disturbance, rock washout, and its release into the habitat of marine life, which is a threat to the environment [10]. Most underwater vehicles operating at these depths have a limited carrying capacity, which can be increased by equipping them with buoyancy modules (Fig. 1), which are installed externally in a space free of equipment and supporting structures.

Fig. 1. Buoyancy modulus [10]

They can have a variety of configurations and consist of separate blocks that are not identical in size and shape [11]. They are an integral part of the combined buoyancy systems that are placed in volumes free of load-bearing structures and are subject to hydrostatic pressure during operation.

Problematic issues in their design and operation are the combination of strength characteristics of structures with reduced weight and dimensions and functional capabilities to operate under extreme conditions of wave, hydrostatic, and acoustic loads. Solutions include the development and use of highly specialised and multifunctional composite materials.

Due to a set of valuable physical and mechanical properties, the use of inorganic glass shells, glass, and alumina ceramics is considered universal in deep-water technologies. Theoretical and experimental studies of their strength have shown that, along with lightness and strength, shell structures made of these materials are non-magnetic, radiotransparent, and chemically resistant.

Buoyancy materials are subject to the requirements of low density, optimal buoyancy, ability to withstand hydrostatic loads, high specific strength, corrosion and chemical resistance, and resistance to atmospheric and bacterial action. PVC is used for small depths [12]. Also, polyurethane foams will meet these requirements. Each kilogram of polyurethane foam provides a lifting force of approximately 300 N (density as low as 100 kg/m^3), so its use is effective in raising sunken vessels, removing them from reefs, shoals, and underwater pipeline equipment. Polyurethane foams are also used to make life-saving equipment such as rafts, belts, bibs, lapel pins, and dinghies. They are used as coatings on the sides of heavy ships and on the floors and ceilings of shipboard accommodations [13]. However, their low strength characteristics do not allow them to be used in technologies for manufacturing additional buoyancy blocks for underwater exploration and research vehicles. The maximum immersion depth of polyurethane foam is 350 meters (density 0.4 kg/m^3). In addition, they are flammable, toxic, and unable to operate for a long time at temperatures above 60 °C.

Syntactic foams are considered to be more competitive composite materials. They are synthesised by filling a polymer matrix with glass, ceramic, and carbon microspheres. The existing experience in producing composite materials and coatings based on non-metallic microspheres is based on low-temperature technologies for the preparation of colloidal solutions. Phenolic, polyester, polyamide, and, most often, epoxy matrices are used for the manufacture of composites. They ensure homogeneity of composition, a certain density, and increased adhesion strength. Glass inclusions are evenly distributed in the polymer matrix (Fig. 2a). The use of this material as part of the buoyancy material provides an apparent density in the range of 450...700 kg/m^3 with a possible operating depth to 12,000 m [14]. An important disadvantage of syntactic foams is the impossibility of their long-term operation at temperatures above 110 to 130 °C due to the presence of a polymeric thermosetting binder.

The choice of materials is an important and difficult stage in solving design problems. Most polymer compositions are characterised by increased flammability and toxicity, and they lose their thermal insulation properties with increasing temperature and water absorption. Alternative buoyancy composite materials that combine high hydrostatic strength with thermal insulation capacity are foam glasses with a density of 300...700 kg/m^3 [15]. The technology for their production is based on the sintering of glass powders with a dispersion of 20...150 μm in a particular sodium silicate composition, with a gas-forming agent (Fig. 2b). As a result, a porous structure is formed, making this material indispensable for use in combined buoyancy units of underwater vehicles with a submergence depth of up to 2000 m.

Thus, the analysis of the problems of using modern composite materials in the technologies of designing and manufacturing underwater technical means has shown the prospects of introducing materials with a cellular structure that provides a set of valuable operational properties. The choice of raw materials for their creation is based on the principles of forming cells with a certain geometry. For this purpose, dispersed substances such as glass powders or hollow microspheres are suitable. Reducing the density of the compositions will be facilitated by the choice of high-temperature technologies, such as sintering, which will exclude the use of polymeric binders. However, the influence of technological parameters, in particular temperature and pressure, on the processes of structure formation during the sintering of microspheres without additional impurities remains insufficient.

The aim of the work is to study the thermo-deformation processes of sintering hollow glass microspheres to obtain lightweight glass composites with a cellular structure that provides positive buoyancy and sound insulation properties.

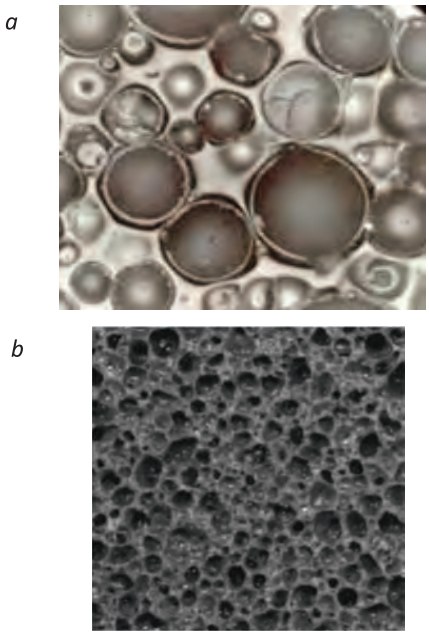

Fig. 2. Optical micrographs of the structure of buoyancy materials: a – syntactic foam (×600); b - foam glass (1:3) [Microphotographs were taken using the BIOLAM optical microscope]

EXPERIMENTAL DETAILS

The experimental work consists of obtaining samples from glass microspheres sintered using hot pressing technology and studying their performance properties.

For sintering, the glass microspheres used were bulk inorganic powders with a dispersion of 10 to 60 μm and a shell thickness of δ = 0.5 to 2.0 μm. They were made of sodium silicate glass from the Na_2O-SiO_2 system (chemical composition (wt. %): SiO_2 – 77.0; Na_2O_3 - 23.0) and sodium borosilicate glass from the Na_2O - B_2O_3 - SiO_2 system (chemical composition (wt. %): SiO_2 - 69.0; B_2O_3 - 7.5; CaO - 6.0; Na_2O_3 - 13.5; ZnO -2.0; F - 2.0). The sintering process was carried out in a hermetically sealed graphite container which was filled with microspheres without additives and plasticisers. The theoretical substantiation of the technological parameters is based on the provisions of solid-state chemistry [16] and glassy-state, physicochemical concepts of glass-softening processes [17].

For the experimental work, the author's own model of the installation for sintering powders in an oxidising environment at temperatures up to 900 °C [18] was used. The peculiarity of the equipment is the presence of a mechanical pressing device (Fig. 3) with an indicator of the movement of the mould punch, which is used to measure shrinkage processes every minute. This allows for careful control of the sintering process and stopping it when the material reaches a certain structure or to prevent distortion of the geometric dimensions of the samples.

The formation of the interface between the microspheres during heating to a temperature of 700 °C with a pressure of 0,5 to 1,5 MPa was studied by optical and electron microscopy (BIOLAM-I and REMMA-102-02 microscopes). The purpose of forming the structure of glass composites is to store microspheres of a spherical shape, which provides hydrostatic strength.

Fig. 3. Pressing device of the sintering setup

The acoustic properties of fibreglass composites with a density of 320...500 kg/m^3 were investigated by measuring the sound pressure level drops in octave frequency bands, for which a Kundt tube wasater absorption of glass composite samples was determined at a hydrostatic pressure of up to 20 MPa. The studies were carried out in a hydrostatic chamber (Fig. 4, a), using distilled water as the working environment.

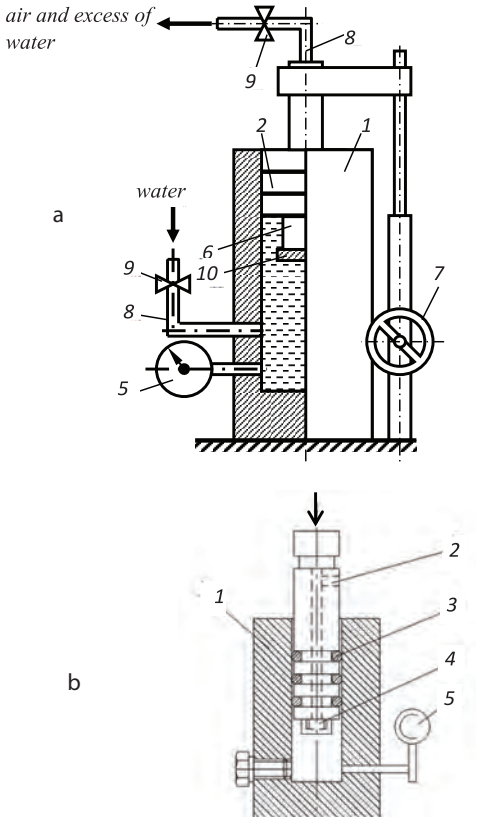

Fig. 4 Scheme of the test chamber for determining the hydrostatic strength of samples.
1 - chamber body; 2 - rod; 3 - sealing ring; 4 - piezoelectric element; 5 - pressure gauge; 6 - syntactic glass sample; 7 - lifting mechanism for controlling the rod; 8 - nozzles; 9 - taps; 10 - ballast.

The sample was subjected to hydrostatic pressures of 2, 5, 15, and 20 MPa, and the exposure of the pressure time was 3 - 5 min at a rate of 0.01 MPa/s. The water absorption was determined by hydrostatic weighing after each loading; the relative error in the measurements did not exceed ± 5 %. The number of destroyed microspheres was determined by a method based on the readings of thermal sensors with piezoelectric elements (Fig. 4, b). The method is based on registering acoustic emission waves caused by the destruction of microspheres [19].

RESULTS

The sintering kinetics of the glass composite samples was analysed (influence of temperature and pressure). Changes in the material structure are shown in Fig. 5. The microstructure was investigated for the glass-microspheres of the Na_2O-SiO_2 system (Fig. 5a) and Na_2O-B_2O_3-SiO_2 system (Fig. 5b). The sintering temperature was 650 °C.

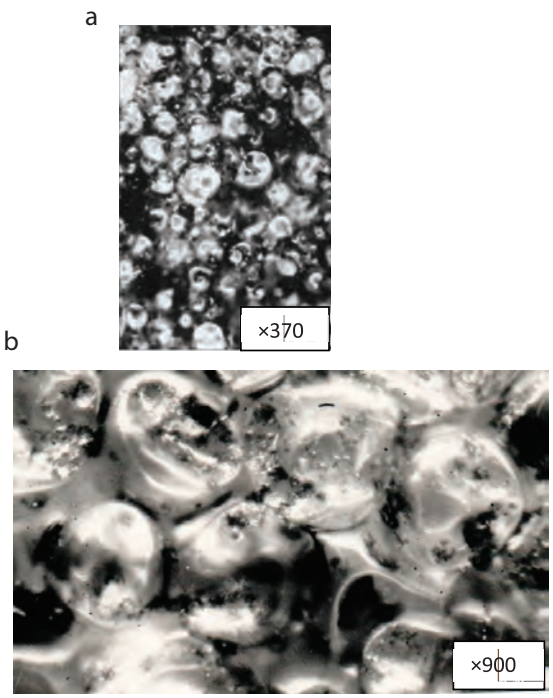

Fig. 5 Changes in the glass-microspheres' structure during sintering

The pressure was applied to the heated container with microspheres. The heating temperature was controlled by a chromium-aluminium thermocouple inserted directly into the microsphere mixtureThe density of the material at the stage of its formation is 250 – 270 kg/m^3. Heating to a temperature of 650 °C with a pressure of 0.5 – 1.5 MPa contributes to their compaction by the mechanism of contact cauterisation with the shells deforming by 20 to 25% of their original size, as shown in the microstructure (Fig. 5b). The physicochemical processes in the formation of a contact area (perimeter of 30 - 50 μm) are explained by the chemical composition of the glasses. The deformation criterion of glass microspheres is the change in their shape factor as the ratio of the minimum particle size to the maximum (from 1.0 to 0.75). The more complex chemical composition of the sodium boron silicate glass microspheres determines the presence of fusible components that contribute to forming the liquid phase and more intensive sintering of microspheres, as shown in Fig. 6b.

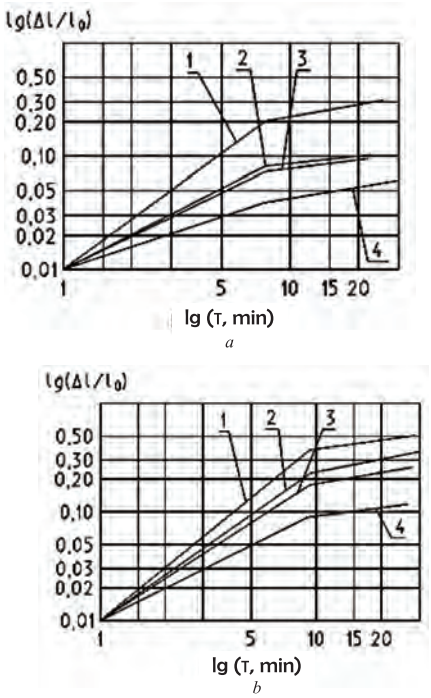

Fig. 6. Sintering kinetics of microspheres from glass systems: a - Na_2O-SiO_2-glass system; b - Na_2O-B_2O_3-SiO_2-glass system; 1 – p = 1,5 MPa; 2 – 1,2 MPa; 3 – 1,0 MPa; 4 – 0,5 MPa

Line 1 characterises the pressure of 1.5 MPa, 2 – 1.2 MPa, 3 – 1.0 MPa, 4 – 0.5 MPa.

The sintering intensity of glass microspheres was determined by the results of the shrinkage processes. The kinetic shrinkage curves were plotted in semilogarithmic coordinates. The results of studies of the acoustic characteristics of glass composites are shown in Fig. 7.Curve 1 characterises the sound signal for octave frequency bands without samples in the Kundt tube. Curves 3 and 5 determine the sound pressure level for glass composites obtained by sintering microspheres of Na_2O-SiO_2 glass (curve 3) and microspheres of Na_2O-B_2O_3-SiO_2 glass (curve 5). For a qualitative assessment, the acoustic characteristics of foam rubber (curve 2) [20] and foam plastic (curve 4) samples were investigated [21].

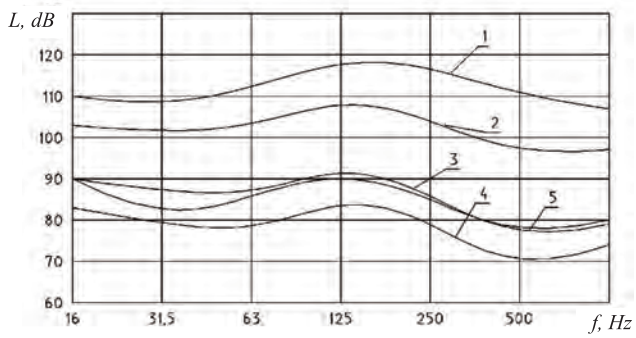

Fig. 7. Sound pressure levels in octave frequency bands

Figure 8 shows the graphical dependence of the water absorption values of samples with densities of 320 kg/m^3 (curve 1), 400 kg/m^3 (curve 2), and 500 kg/m^3 (curve 3) under conditions of gradual loading with all-round hydrostatic pressure.

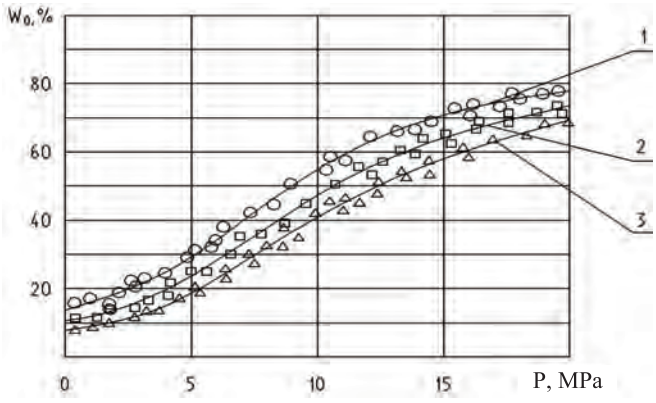

Fig. 8. Water absorption of samples under hydrostatic pressure

The local destruction of microspheres in the sintered composite material was determined by experimental studies of loading samples with hydrostatic pressures from 5 to 45 MPa, where the criterion was the number of destroyed microspheres, Np, expressed in per cent. The quantitative destruction of microspheres for glass microspheres of the Na_2O-SiO_2 system (curve 1) and glass microspheres of the Na_2O-B_2O_3-SiO_2 system (curve 2) is shown graphically in Fig. 9.

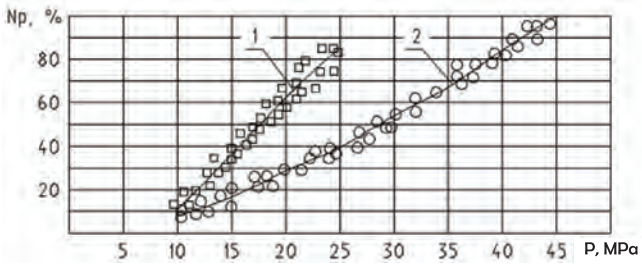

Fig. 9. Dependence of the number of destroyed microspheres on the hydrostatic pressure.

DISCUSSION

The glass composites obtained by sintering glass microspheres are new competitive analogues of syntactic foams in terms of their structure and properties - composite materials consisting of a polymer matrix and hollow spherical particles made of glass, ceramics, polymer, etc. The absence of a polymeric binder helps to obtain lightweight compositions whose density is 20% lower than syntactic foams with glass microspheres. The possibility of obtaining such materials will help to improve the design of subsea equipment for offshore development and research. Their hydrostatic strength is due to the spherical shape of the closed-loop cells. This structure (Fig. 5) is formed during the sintering of glass microspheres under selected temperature and strain conditions. The graphical interpretation of the kinetic shrinkage curves (Fig. 6) indicates the identity of the thermo-deformation processes of sintering microspheres from sodium silicate and sodium borosilicate glasses. From the angle of inclination of the curves to the abscissa axis, it can be established that during isothermal heating at 650 °C, the sintering process of microspheres lasts 25 - 30 min and is most intense in the first 8 min. However, the results of thermometric control showed that shrinkage begins long before reaching the isothermal holding mode: for Na_2O - SiO_2 glasses at 550 °C and Na_2O - B_2O_3 - SiO_2 glasses at 500 °C. This is due to the liquefaction softening processes that occur in the walls of glass microspheres, which is confirmed by comparing the results with the state diagrams of the corresponding silicate systems [22, 23]. The strength of the obtained glass composites is formed through contact curing of glass microspheres by the mechanisms of viscous glass phase flow. The formation of the contact area between the microspheres (Fig. 2b) occurs due to the application of a small pressure (up to 1.5 MPa) to the heated mixture (mass, weight), an increase which will contribute to a more intense sintering process. As shown in Fig. 6, the value of linear shrinkage can reach 50%. However, the results of experimental studies have shown that exceeding the selected temperature and strain modes of sintering leads to a violation of the spherical shape of the particles, which will negatively affect the performance properties of glass composites.

Experimental studies of the acoustic characteristics of the obtained glass composite samples (Fig. 7) showed the prospects of their use as sound insulation. The sound pressure level in the octave frequency bands is lower than that of foam samples. This effect can be explained by the peculiarities of the porous structure of the prototypes. During sintering, closed and open pores are formed between the glass microspheres. The shape and size of the pores depend on the thermo-deformation parameters of sintering, mainly on pressure. The open porosity of glass composites has a positive effect on their soundproofing properties, while the closed porosity reduces water absorption and increases buoyancy.

The results of hydrostatic tests (Fig. 8) showed the ability of glass composites to operate under conditions of comprehensive hydrostatic loading up to 20 MPa and

characterised the dynamics of their damage. The increase in volumetric water absorption is associated with the filling of micropores formed between the microspheres during sintering with water. The analysis of the experimentally obtained results on the destruction of microspheres under higher hydrostatic pressure (Fig. 9) confirms the theoretical ideas about the mechanisms of sintering without binders of Na_2O-SiO_2 and Na_2O-B_2O_3-SiO_2 glasses' microspheres and indicates the possibility of using the developed materials. In this regard, using the developed materials as a filler in combined shell structures is recommended.

Prospects for further research are related to computer modelling of fracture under hydrostatic loads, a feasibility study, and marketing research on the implementation of the developed glass composites.

CONCLUSIONS

The article solves an important scientific and technical problem of creating polyfunctional composite materials for shipbuilding and deep-sea engineering.

The thermal deformation processes of sintering sodium silicate and sodium borosilicate microspheres, which will directly affect the structure formation of glass composites with sound insulation properties and hydrostatic strength, were investigated.

The developed materials can be used in the design and manufacture of technical equipment for research and the maintenance of underwater infrastructures.

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