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# Investigation into the Composition of Heat Insulating Coatings on the Basis of Microspheres and Anisotropic Nanostructures.

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## ABSTRACT

The article discusses experimental investigations into obtaining of new heat insulating coating on the basis of microspheres and anisotropic nanostructures, capable to provide operability of equipment at high temperatures. Optimum composition of the heat insulating coating has been determined. The strength of the heat insulating coating is provided by hollow microspheres as binder. Microspheres form supporting frame of heat insulating material, and gas pressure in the microspheres prevents alteration of their shape even at reaching of glass softening point. Heat insulating coatings on the basis of liquid glass binder are characterized with high adhesion to nearly any surface, they are solidified already at ambient temperature, though, total dehydration requires heating to 400°C. In order to improve heat insulating properties of the material it is recommended to select vacuum hollow microspheres or filled with gas (heat conductance lower than that of air). In order to decrease heat conductance of heat insulating coatings the binders should consist of foamed materials on the basis of liquid glass with additive increasing foam expansion ratio of foam agent aqueous solution. The obtained results made it possible to confirm possibility to develop heat insulating coatings of the basis of microspheres.

**Keywords**: heat insulating coating, heat conductance, microspheres, anisotropic nanostructures, binder.

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## INTRODUCTION

Intensive development of technologies and continuous improvement of its results require for creation of structures providing rational use of power resources (Rogalev, 2005; Tsvetkov, Grigor'ev, 2001; Semenov, 2004).

High quality insulation should be characterized with heat conductance coefficient lower than that of air under ambient conditions (Sokolov, 1999). Conventional heat insulating materials consist of foamed and fibrous substances of various composition (Shoikhet et al., 2002).

Recently numerous projects in Russia and abroad have been devoted to development of heat insulating materials with the use of hollow microspheres which are characterized with significantly lower coefficients of heat conductance (Purkhalo et al., 2009; Purkhalo et al., 2010). Moreover, addition of nanostructured materials to such heat insulation provides further decrease in its heat conductance and increase in efficiency of heat insulation at lower thickness of heat insulating layer (Martynov et al., 2006; Askhadullin et al., 2008). In practice heat insulating materials are applied both as items of non-construction purposes (slabs, mats, tubes), and as heat insulating coatings on various structural elements and parts. Herewith, in addition to functional properties strength properties of non-construction heat insulating items are highly important, as well as adhesive properties of heat insulating coatings on structural items. Therefore, various approaches exist with regard to development of highly efficient heat insulating materials applied as heat insulating items of non-construction purposes and heat insulating coatings on structural items.

The work is aimed at development of heat insulating coatings on the basis of hollow microspheres and nanostructures, capable to provide operability of structural items at increased temperatures.

## LITERATURE REVIEW

Analysis of R&D and patent publications demonstrates that in order to obtain heat insulating structures it would be reasonable to apply hollow glass or alumophosphate microspheres with melting point of at least 1000ºC and thin shell. The size of microspheres should be in the range from 50 to 500 µm. Such size range of microspheres is comparable with medium and long wave thermal infrared radiation, excited at the temperatures up to 700°C, which creates conditions for its maximum absorption by microspheres (Purkhalo et al., 2009; Purkhalo et al., 2010; Ryzhenkov et al., 2010).

In order to produce heat insulating coatings on the basis of microspheres it is necessary to apply a binder, as well as additives promoting additional decrease in coating heat conductance. Currently, there is a set of requirements to high temperature heat insulation. It should be mentioned that the major and determining role is played by heat conductance (Sokolov, 1999). Table 1 summarizes the main requirements to high temperature heat insulating coatings.

**Table 1. Technical requirements to high temperature heat insulating coatings**

| Property | Range |
|---|---|
| Operability in temperature range, °C | 0-700 |
| Adhesion to metal substrate, MPa, at least | 1 |
| Ultimate compression strength, MPa, at least | 0.5 |
| Ultimate bending strength, MPa, at least | 0.3 |
| Effective heat conductance, $W \cdot m^{-1} \cdot K^{-1}$ at 20°C, not more than | 0.027 |
| Surface albedo, %, at least | 15 |
| Vapor permeability, $cm^3 \cdot m^{-2} \cdot 24\ h^{-1} \cdot bar^{-1}$, not more than | 1000 |
| Vibration strength, Hz with displacement amplitude of 0.5 mm | up to 100 |
| Thermal moisture resistance, wetting-drying cycles, at least | 30 |

The microspheres applied for production of heat insulating coating are characterized with certain specific properties: spherical shape; free spreadability; low weight; low reactivity; low heat conductance; high melting point. Spherical shape of microspheres makes it possible to apply the lowest content of binder for its wetting than for any other shape of filler. Low density of hollow microspheres assumes low heat conductance, herewith, sufficient strength of structure with heat insulating coating is provided. Microspheres are characterized with very low reactivity. Their chemical composition provides high resistance against acids and alkalis. Their pH is neutral and they do not influence on reactions of materials or items, where they are applied. Heat conductance of the hollow microspheres depends on shell thickens and composition, as well as on pressure of gas filling the cavity. Solid surface of microspheres provides their high resistance against erosion and it is absolutely impermeable for liquids and gases (Fasyura et al., 2013; Bessonov et al., 2011; Ryzhenkov et al., 2015; Ryzhenkov et al., 2009; Ryzhenkov et al., 2010; Ryzhenkov et al., 2010; Ryzhenkov et al., 2012) .

In practice two types of microspheres are widely applied: alumosilicate and sodium borosilicate, their appearance is illustrated in Fig. 1, and their main properties are summarized in Table 2 (Platov, 2012; Ignatov and Shiryanin, 2010). Alumosilicate microspheres are the product of combustion of flare coals at power plants, they contain air and carbon dioxide in hollow space as coal combustion products. These microspheres are of natural origin, thus, they cannot be absolutely tight (in the course of time carbon dioxide escapes from pores, being completely displaced by air) (Danilin et al., 2012; Samorokov et al., 2012; Pimenov et al., 2005).

Sodium borosilicate microspheres are produced in open gas furnaces by air inflation of molten oxides. Despite their low weight (density of about 0.3 g·cm$^{-3}$) such microspheres are sufficiently strong. Herewith, alumosilicate microspheres are by far stronger than various sodium borosilicate microspheres. The melting point of alumosilicate microspheres is 1350ºC, however, their properties are retained up to 1000ºC. The melting point of sodium borosilicate microspheres is about 1000ºC, however, they are softened and adhered without loss of properties at 700ºC.

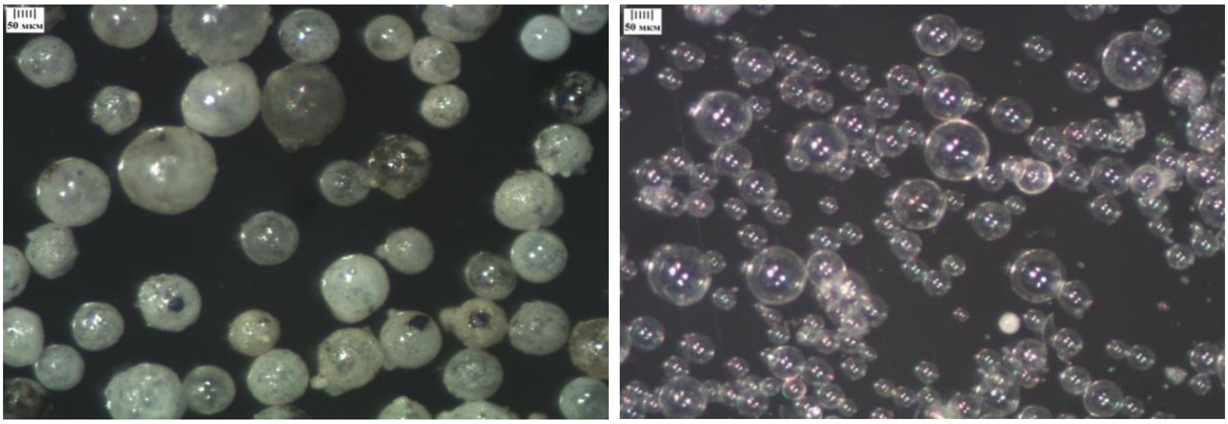

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**Fig. 1. Appearance of microspheres: a -- alumosilicate; b -- sodium borosilicate.**

**Table 2. Main specification of glass microspheres**

| Specification | Hollow microspheres | |
|---|---|---|
| | alumosilicate | sodium borosilicate |
| Appearance | homogeneous loose powder of gray color | homogeneous loose powder of white color |
| Particle size range, µm | 0-500 | 15-200 |
| Chemical composition | $SiO_2$ (50-60 %); $Al_2O_3$ (25-35 %); $Fe_2O_3$ (1.5-2.5 %); CaO (0.1-1.5 %); MgO (0.1-1.5 %); $K_2O$ (0.2-2.9 %); $Na_2O$ (0.3-1.5 %) | $SiO_2$ (71.7-73.8 %) $Na_2O$ (25.5-28.2 %) $B_2O$ (3.8-4.4 %) $A1_2O_3$ + $Fe_2O_3$ (not more than 0.4 %) |
| Bulk density, g·cm$^{-3}$ | 0.32-0.45 | 0.24-0.32 |
| Melting point, °C | 1350 | 1000 |
| Compression strength, MPa | 15-29 | 6 |
| Mohs hardness | 5-6 | – |
| Wall thickness as a function of diameter | 5-10 | 5-10 |
| Heat conductance | 0.06 | 0.05 |
| Moisture, not more than % | 0.5 | 0.6 |
| Coefficient of space filling, at least, % | 60-80 | 60 |

In addition to numerous advantages of the microspheres for solution of the problem they have significant disadvantage. Microspheres do not comply completely with the requirements to heat insulating coatings in terms of heat conductance. Since the microspheres as filler provide main properties, their coefficient of heat conductance should be not lower than 0.027 $W\cdot m^{-1}\cdot K^{-1}$. Thus, in order to decrease the coefficient of heat conductance of the microspheres their cavity is filled not with air but with gas with lower coefficient of heat conductance. For instance, upon production of sodium borosilicate microspheres carbon dioxide is used instead of air, its heat conductance is 0.010-0.014 $W\cdot m^{-1}\cdot K^{-1}$. In addition, it is possible to produce vacuum microspheres. Currently only vacuum alumosilicate microspheres are produced.

However, production of vacuum microspheres or microspheres filled not with air is rather expensive, thus, the cost of heat insulating coating on their basis would also be high. Therefore, in practice hollow microspheres filled with air are used and liquid glass binder in order to decrease total coefficient of heat conductance. Due to air tightness of the hollow microspheres, the binder cannot penetrate inside.

Heat insulating coatings made of fillers on the basis of microspheres are formed by application of their mixture with various binders onto the surface of structural items or their elements. The main task of the binder is to provide filler adhesion to treated surface and required strength of heat insulating coating. At present two types of high temperature binders are used in practice: liquid sodium glass and various modifications of alumophosphate binders.

Liquid glass has numerous advantages in comparison with alumophosphate binders. Adhesion of mixtures on the basis of liquid glass is several fold better than that of mixtures on the basis of alumophosphate binders. In addition, the mixtures on the basis of liquid glass are solidified already at ambient temperature, and those on the basis of alumophosphate binders only upon heating to about 200°C. At this, heating of solidified at ambient temperature coating on the basis of liquid glass to 250-300ºC results in the fact that the coating becomes in fact insoluble and withstands 30-fold wetting-drying cycle. The mixtures on the basis of alumophosphate binders have higher heat conductance in comparison with the mixtures on the basis of liquid glass, however, they have higher heat resistance (Belyaev and Fedotov, 2007).

Foamed liquid glasses are characterized with cellular porous structure, total porosity is 98-99.6 %, in average. The size of pores in foamed material depends on the amount of bound water and existence of additives in initial alkaline silicate: water leads to increase and additives to decrease in the size of pores. Exceptionally high decrease in pore size occurs in the presence of such active additives in liquid glass, as inorganic acids, acid salts, alcohols and others. Most compounds, resulting in coagulation of liquid glass, or generation of poorly soluble silicates prevent its foaming. Thermal mode of foaming also influences on the size of formed pores. Slow heating of liquid glass is accompanied by significant loss of bound water, which leads to sharp decrease in pore size.

The density of materials made of foamed liquid glass is easily adjusted in wide range (10-200 $kg\cdot m^{-3}$) by variation of additive amount in initial mixture. Heat conductance of materials made of foamed liquid glass does not exceed 0.065 $W\cdot m^{-1}\cdot K^{-1}$ under normal conditions. For the lightest variants of this groups, silipore and steklopore, it equals to 0.028-0.035 $W\cdot m^{-1}\cdot K^{-1}$. With increase in density the heat conductance increases by several folds (Grigor'ev, 2013).

The most heat resistant are the materials on the basis of high-modulus liquid sodium glass with certain additives. In average, for most foamed liquid glass materials the working temperature is in the range from –200°C to +760°C.

In addition to microspheres upon development of heat insulating coating it would be reasonable to add nanostructured materials into the mixture. Aerogel with nanosized anisotropic structure was used in this work. Two types of aerogels are most widely applied: xerogels on the basis of $SiO_2$ and aerogels on the basis of AlOOH. In this work the aerogel on the basis of AlOOH was selected, which retains its properties up to 1000ºC. As for now, this aerogel is the lightest solid material, providing the best heat insulating properties stipulated by nanoporous structure (1-100 nm) and low density (3-250 $kg\cdot m^{-3}$) (Martynov et al., 2006; Askhadullin et al., 2008). The appearance of AlOOH aerogel is illustrated in Fig. 2, and its properties are summarized in Table 3.

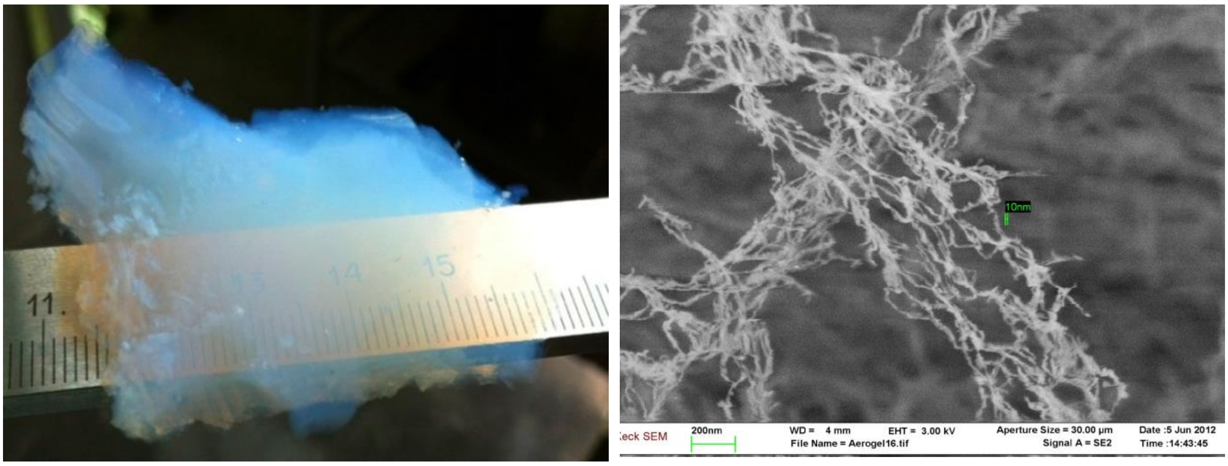

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**Fig. 2. Appearance and structure of AlOOH aerogel: a -- appearance of AlOOH aerogel sample with the size of 40×25×8 mm; b -- microstructure of AlOOH aerogel, 4000× magnification.**

**Table 3. Main properties of AlOOH aerogel**

| Properties | Value |
|---|---|
| Pore size, nm | 1-100 |
| Pore content, % | 95-99 % |
| Density, g·cm$^{-3}$ | 0.005-0.5 |
| Heat conductance, W·m$^{-1}$·K$^{-1}$ | 0.01-0.03 |
| Maximum working temperature, ºC | 1000 |
| Specific surface area, m$^{2}$ | 1000 |
| Limiting wetting angle, ° | > 99 |

Aerogels are comprised of 3D cross linked chain of spherical primary particles, the size of which is in nanosized range. Total heat conductance of aerogels is determined by three factors: heat conductance of gas, radiation heat conductance and heat conductance of solids. Since aerogels are completely transparent for infrared radiation, then the heat transfer due to radiation exactly at high temperatures cannot be neglected. By means of addition or infiltration of opacifying components (pigments), or by application of coatings with lower radiating capability (coatings with low emission) it is possible to reduce significantly the contribution of this type of heat transfer. Generally aerogels are characterized with high optical transparency.

Spatial structure of materials on the basis of aerogels provides excellent thermal stability of heat insulators, thus maintaining the coefficient of heat conductance at constant level. Nearly complete water impermeability in combination with sufficient vapor permeability of heat insulating materials on the basis of aerogel enables protection of tubes against corrosion, thus making this material ideal for heat insulating application. Heat insulating materials on the basis of aerogel have good flexibility, tensile strength, compression strength, they exhibit no shrinkage in the course of time, they are resistant against deformation. The main issue upon application of aerogel is that during mixing with binder its pores are clogged and air inside the pores is displaced by binder, as a consequence aerogel loses its unique properties. Thus, it is required preliminary to coat (to clog) the aerogel with auxiliary agent.

## EXPERIMENTAL

Hollow glass and alumosilicate microspheres as filler (OAO Novgorod Plant of Fiberglass) and aerogel according to RF Patent No. 81490 (Askhadullin et al., 2008) were used in the work. Liquid sodium glass was used as binder. Surfactants were used as additives.

The heat insulating coating was produced of slurry composed of filler and binder. Weight ratio of the slurry components was 30-40 % of filler and 60-70 % of liquid sodium glass.

The slurry of binder and filler was prepared directly before application as follows. The filler was added in increments to the binder during continuous agitation. Upon addition of the filler the slurry viscosity was monitored by visual observation of slurry droplet placed onto flat surface. The slurry preparation is considered to be completed when the slurry droplet on flat surface retains its shape in 1 min.

The prepared slurry was placed into collecting tank of experimental assembly, which is illustrated in Fig. 3. The main units of the assembly are as follows: 3-axial positioning system (Fig. 3, pos. 1) and its control unit (Fig. 3, pos. 5), slurry collector with meter (Fig. 3, pos. 2) and unit for application of multilayer coatings (Fig. 3, pos. 6). The assembly is also equipped with air cleaning system comprised of dust proof chamber (Fig. 3, pos. 3) and air duct (Fig. 3, pos. 4).

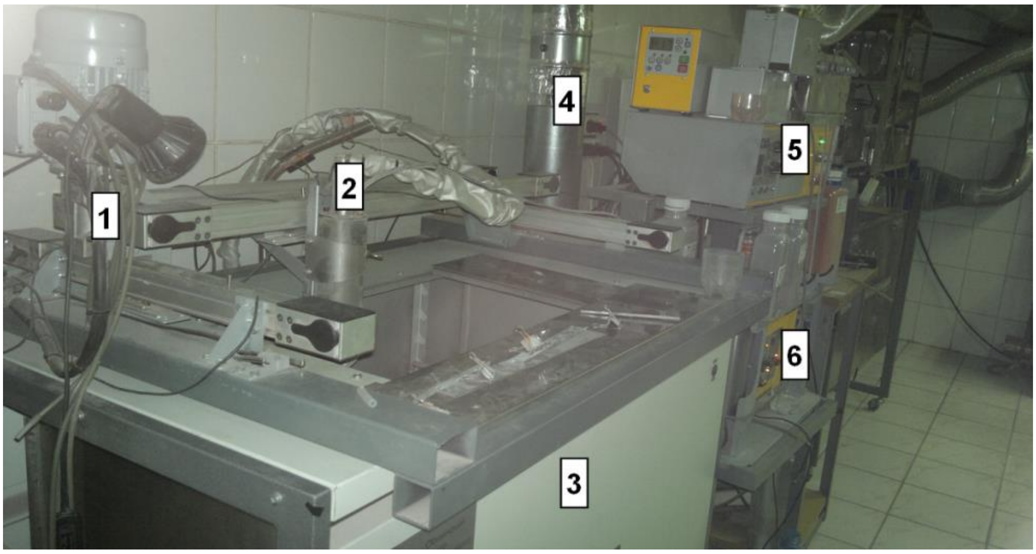

**Fig. 3. Assembly for application of heat insulating coatings on the basis of microspheres and anisotropic nanostructures: 1 - 3-axial positioning system; 2 – meter; 3 – dust proof chamber; 4 – air removal and cleaning duct; 5 – control unit of positioning system; 6 – unit for application of multilayer coatings.**

The slurry was applied onto preliminary prepared surface by means of the meter. The 3-axial positioning system made it possible to apply the working slurry in horizontal plane along scanning path with varied velocity and step. A layer of slurry with the thickness of not more than 5 mm was applied and the sample was held at 20-25ºC in 24 h. Then, the solidified slurry surface was wetted with liquid glass by means of a brush, placed into muffle furnace, the temperature increased to 100-120ºC, the sample was hold at this temperature in 2 h. Then the slurry surface was again wetted with liquid glass, the temperature increased to 250-300ºC, the sample was hold in 2 h. Upon obtaining of heat insulating coating during heating the slurry layer was increased in volume, and as a consequence of re-hydrolysis water was extracted which then was removed in the form of vapor. Wetting of slurry layer by solution of liquid glass during thermal treatment leads to softening of surface layer, and then to decrease in stress upon solidification of slurry layer, thus facilitating production of heat insulating coating without cracks and other mechanical failures.

## RESULTS AND DISCUSSION

The first experiments on production of heat insulating coatings produced unexpected results. Upon slurry drying at 100ºC and above the slurry layer was heaved as a consequence of water generation during solidification of liquid glass and its removal in the form of vapor. Heaved samples of heat insulating materials were very brittle. The heaving is probably related with generation of dense gas- and vapor-impermeable slurry film on air-tight surface of hollow glass microspheres, preventing removal of generated water vapors. Fig. 4 illustrates photos of these samples, where foamed structure of heat insulating coating with large pores can be seen.

**Fig. 4. Samples of heat insulating coatings on the basis of hollow glass microspheres and foamed liquid glass.**

In order to prevent slurry heaving upon obtaining of heat insulating coating it is necessary to eliminate water vapor by means of generation of pore channels. It can be realized by addition of porous material to hollow glass microspheres into the slurry. Foamed glass and aerogel were used as porous material. Addition of aerogel decreases the coefficient of heat conductance as well. Herewith, addition of foamed glass in high amounts is undesirable due to increase in density and coefficient of heat conductance of heat insulating coating. Porous material was added to the slurry when it became viscous. It was necessary not to allow liquid binder to penetrate into pores and to close gas- and vapor-removing channels. Foamed glass was added to the slurry in amount up to 5 wt % of slurry weight and aerogel up 10 wt % of filler weight. Fig. 5 illustrates images of heat insulating coatings on the basis of hollow glass microspheres with foamed glass and liquid sodium glass as binder. Weight ratio of the slurry components was as follows: 25-35 wt % of hollow glass microspheres, 5 wt % of foamed glass and 60-70 wt % of liquid sodium glass.

**Fig. 5. Samples of heat insulating coatings on the basis of hollow glass microspheres with addition of foamed glass and liquid sodium glass as binder.**

Increase in porosity of heat insulating coating can be achieved by binder foaming. Foamed binder was obtained by addition of distilled water and synthetic surfactant to liquid glass, agitation of the mixture by mechanic mixer. Agitation was performed up to increase in initial volume of the mixture by 4-5 times. As a consequence, foamed binder on the basis of liquid glass was produced. Fig. 6 illustrates samples obtained of 70 wt % of foamed binder: liquid glass, and 30 wt % of filler: hollow glass microspheres with addition of 10 wt % of aerogel. The use of foamed binder resulted in decreased specific density of heat insulating coating and increased volumetric portion of gas pores in the coating. The obtained samples of heat insulating material had sufficient mechanical strength.

**Fig. 6. Sample of heat insulating coating containing 70 wt % of foamed binder and 30 wt. % of filler.**

## CONCLUSIONS

The obtained results made it possible to confirm possibility to develop heat insulating coatings of the basis of microspheres.

The strength of heat insulating coating is provided by the use of hollow microspheres as filler. Microspheres form supporting frame of heat insulating material, and gas pressure in the microspheres prevents alteration of their shape even at reaching of glass softening point.

Heat insulating coatings on the basis of liquid glass binder are characterized with high adhesion to nearly any surface, they are solidified already at ambient temperature, though, total dehydration requires heating to 400°C.

In order to improve heat insulating properties of the material it is recommended to select vacuum hollow microspheres or filled with gas (heat conductance lower than that of air: carbon dioxide, argon).

In order to decrease heat conductance of heat insulating coatings the binders should consist of foamed materials on the basis of liquid glass with additive increasing foam expansion ratio of foam agent aqueous solution.

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