Perfection of technology for manufacture of heating units on the base of mica and glass

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Abstract. Implementation of energy saving programs, reduction of energy consumption for heating and development of efficient heating systems is a challenge. The use of resistive mica- and glass-based heaters (SKENs) is thought to be a perspective trend in this area. It is a heater of new generation that has no analogues abroad. Objective of the paper is enhancement of technologies for manufacture of resistive heaters on the base of mica and glass for improving heater’s performances. Consideration is given to development of new compositions of charge material and to treatment of its surfaces. Results of study. Technology for manufacture of SKENs with high mechanical strength and low water absorption that are widely used in different areas of building industry has been developed on the base of experimental studies and scientific generalizations.

1. Introduction
Use of heat and power for residential buildings in Russia is currently rather inefficient. The policy of “cheap” energy carriers pursued in Soviet period allowed construction of buildings with low heat insulation level, and absence of heat meters and poor control over heat energy consumption favored its wasteful use. All these factors necessitated development of new technologies for low-temperature heating.

2. Methods and materials
Mixtures of muscovite and phlogopite mica of different percentage were investigated using IR-spectroscopy and thermography methods. Resistive heaters on the base of mica and glass were subjected to mechanical and physico-chemical studies in conformity with GOSTs.

3. Results and discussion
Research workers of INRTU developed a method for manufacture of mica- and glass-based heating elements named SKEN. It is a heater of new generation that has no analogues abroad. A new method for heater manufacture includes the following procedures: a nichrome heating element is placed into a mixture of powdered mica and soft glass to be followed by briquettes production by applying cold pressing method. Briquettes produced are heated to the temperature of 600-700°C. A heated briquette is then hot-pressed and further baked [1-4].

SKEN has good operating performances. It is intended for heating the industrial and residential facilities, cattle-breeding and paltry farms, storehouses, auxiliary premises, car washing premises, as
well as for heating the premises with high humidity. It is also recommended for container-type houses [5, 6].

Present-day heating units shall meet a number of requirements, such as higher insulation resistance, maintenance of mechanical strength at higher temperatures, good thermal conductance, and low water absorption [7].

For enhancing the mechanical strength and for reducing the water absorption the charge for the electric insulation layer of a heater is recommended to have the following percentage of components: muscovite mica - 25-35%, phlogopite mica - 25-35%, and low-melting alumina-borosilicate glass - 35-45%. Addition of phlogopite mica into the electric insulation mixture activates inter-phase interrelations of components during heating and hot pressing. As a result, a dense monolith structure is formed [8-10].

During heating the mica is dehydroxylated. IR-spectroscopy and thermography studies revealed that dehydroxylation process in the mixture with approximately equal percentage of mica and phlogopite is intensified. This factor creates conditions for more intensive subsequent interaction of mica and glass. In the course of interaction in such a system, alumomagnesian spinels and olivine are formed on the mica crystals boundaries along with feldspar, sillimanite and leucite, which additionally strengthen the material [11-14].

Moreover, presence of magnesium oxide and fluorine within phlogopite contributes to formation of low-melting eutectics with glass components, which favors more intensive glass formation. A part of hydroxylic ions of some phlogopites are substituted by fluorine that is not removed during heating, as chemically bound fluorine is less volatile compared to hydroxylic ions. Fluorine during heating can form fluorides interacting with glass components, particularly with quartz. Lower percentage of high-melting (heat resistant) oxide Al₂O₃ in phlogopite as compared to muscovite also contributes to formation of eutectics in the mica and low-melting-glass system.

Flumomagnesium spinel MgAlO₄ makes a major contribution into the structure strengthening. During muscovite dehydroxylation, Al₂O₃ is formed, and MgO is formed during dehydroxylation of phlogopite; their interaction produces spinel [15,16]. Higher mechanical strength and lower water absorption are attained at approximately equal content of the above mentioned mica in the composition of electric insulation material (25-30%). At lower content of phlogopite the output of spinels is negligible, and in case of its absence the spinels are not formed at all as there is magnesium neither in muscovite nor in glass. At low muscovite content the output of spinels drastically falls due to deficiency of Al₂O₃ in the system, which is partially replenished at the expense of glass.

Thus, in the process of resistive heater manufacture, more intensive inter-phase interaction is ensured in the mica-glass system that creates monolith dense material with high mechanical strength and low water absorption. Breaking strength at static bending increases by 40-50%, water absorption decreases fivefold.

Addition of a modifying agent (5% furnace clinker) into the composition of electric insulation charge of a heater allows 50% reduction of water absorption, specific volume resistance in this case increases tenfold [17-19].

Higher water resistance subject to maintenance of insulation resistance during long operation of heaters in humid media is attained owing to surface treatment after baking with 3-5% solutions of organic stillage residues from methylchlorosilane production, that is to be followed by heating at 110-150°C.

During methylchlorosilane synthesis the stillage residue contains considerable amount of hydroxyans, particularly, methylidichlorosilane, trichlorosilane, and methyltrichlorosilane. The proposed oligomethyl-chlor-silane, when interacting with the surface of mica-ceramic material, forms a dense hydrophobial electric insulation layer on the heater surface by substituting the mica hydroxyle ions for chlorine ions. Chemical reaction is given in equation (1).

\[
\text{KAlSi}_3\text{O}_{10}+(\text{OH})_2+(\text{CH}_3)_n\text{SiCl}_n \rightarrow \text{KAlSi}_3\text{O}_{10}\text{Cl}_n+(\text{CH}_3)_n+20\text{H}
\]

(1)

It is the presence of hydroxyans and multi-functional organochlorosilanes that causes efficient substitution of hydroxyl groups on the mica surface, creates steric difficulties for moisture penetration.
to its surface due to formation of branched structures of products of multi-functional organochloropolysilanes interaction. This fact predetermines higher efficiency of treatment with stillage residues as compared to the use of common hydrophobisators.

Use of phosphate glass and other compositions in heaters demonstrates good results.

For enhancing the compression resistance and thermal resistance of a composite, the 0.04-0.07 mm glass should be used, rather than previously used 0.10-0.16 mm glass. Baking temperature in this case can be lowered down to 600-700°C, and, consequently, energy intensity of the technological process can be lowered accordingly.

Temperature required for the composite baking is conditioned by physical and chemical interaction of mica particles with softened glass. The smaller the particles, the more intensive and active the interaction at lower temperatures.

Softened glass most actively interacts with mica at glass size of 0.10-0.16 mm at temperatures of 700-800°C. If glass size reduces down to 0.04-0.07 mm, the interaction starts at temperatures close to the temperature of glass softening, i.e., at about 500°C. In this case, for formation of mechanically resistant material, the heating up to 650-700°C is sufficient. Moreover, owing to increased surface of bonding material the interaction between glass and mica is intensified, it is more complete and material obtained has better thermo-chemical performances.

Composites with better dielectric properties can be produced using certain temperature mode of charge treatment for phlogopite heater [20-22].

Micalex formation process is closely related to mica dehydroxylation process. In the course of mica and glass briquette heating the process of mica decomposition in the softened glass medium occurs. Mica decomposition products interact with glass forming new constituents. These processes condition formation of cementing layer on the surface of mica crystals thus ensuring high dielectric and mechanical properties of composite. It was found out that removal of inter-layer water in phlogopite was terminated at a temperature of 800°C. At a temperature of about 850°C the dehydroxylation process started that precedes the micalex formation process. Preliminary thermal treatment of phlogopite at 850-950°C creates conditions for its more complete interaction with softened glass, which ensures high electric insulation properties of the composite. 50-80 minute thermal treatment is due to low rate of dehydroxylation. Table 1 presents properties of composite produced from phlogopite-based charge

| Filler | Tangent of dielectric losses angle \( \tan \delta \) | Elasticity module \( E \) | Specific volume resistance \( \rho_v, \text{Ohm}\cdot\text{m} \) | Specific surface resistance \( \rho_s, \text{Ohm} \) | Electric resistance \( E_{str}, \text{MW/m} \) |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Phlogopite after thermal treatment at 850-950°C (for 50-60 min.) | 0.0005 | 6.3-7.5 | 1\( \times \)10\(^{11} \) | 1\( \times \)10\(^{11} \) | 22-31 |
| Thermally non-treated phlogopite | 0.005 | 8 | 5.2\( \times \)10\(^{11} \) | 1.4\( \times \)10\(^{11} \) | 20 |

It is obvious that thermal treatment of phlogopite as filler produces composite with enhanced dielectric properties. Such a thermal treatment is most advisable for off-grade phlogopites.

Use of fluoric phlogopites demonstrated the advisability of using natural fluorine-containing phlogopites in composites with higher heat resistance. For raising the heater’s efficiency (in case of production of a panel-type heater) and reliability it was proposed to use phlogopite with hydroxyllic groups partially substituted for fluorine, its content being 3.0-6.5%. The proposed technical solution allows manufacture of a panel-type electric heaters designed for the temperature of 850-1000°C.
4. Conclusion
Studies on selection of the optimum composition of charge for electric insulation layer of a heater were conducted. Addition of phlogopite mica into the electric insulation mixture intensifies inter-phase interrelations of components during heating. At approximately equal percentage of muscovite and phlogopite mica the interaction of mica with glass is more intensive, which enhances the mechanical strength of a heater. Addition of a modifying agent into the charge considerably reduces water absorption, and increases specific volume resistance. Demonstrated is the reaction of chemical interaction of oligomethyl-chlorine-silane with the surface of mica-ceramic materials, which reduces water absorption. Optimum glass size has been selected the use of which results in higher breaking strength towards compression and higher heat resistance. It was found out that for enhancing the electric insulation properties of mica-ceramic material, plogopite mica should be subjected to preliminary thermal treatment. Advisability of using natural fluorine-containing phlogopites for enhancing the composite heat resistance has been demonstrated.

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