Developing physical-chemical principles to manufacture effective heating systems when using mica

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Abstract. The organization of effective heating systems in non-industrial, industrial and livestock buildings is an urgent problem. The developing of heating is especially relevant for utilizing in agricultural industry. Energy prices are steadily rising, and as a result, the efficient utilization of energy resources is of great significance for this industry. One of the most prospective lines of development in this area can be the trend to utilize resistive heaters where mica is used as a basic material. The research aim. Developing physical-chemical principles to manufacture effective heating systems when using mica for the construction industry. The possibility of employing composite materials to produce an economically sound, reliable, electro-permissible and stable heater is considered. Finding physical and chemical laws of interaction of mica with the binder element in the technology of micaceous composites.

Research methods. The methods of thermodynamic quantum chemical calculations, as well as kinetic studies that involve a number of advanced techniques of physical and chemical studies (x-ray phase analysis, thermal analysis, and IR spectroscopy). Electro physical and mechanical characteristics of composites and starting materials were determined by the standardized methods to comply with the All Union State Standard.

Research results. The foundations of effective heating systems when utilizing micalex have been worked out by means of scientific generalizations and experimental studies. The developed technology of electric heating elements (mica ceramic electric heating) is employed in various fields of construction industry.

The organization of effective heating systems in non-industrial, industrial and livestock buildings is an urgent problem. The developing of heating is especially relevant for utilizing in agricultural industry. Developing small and medium-sized businesses need modern, safe buildings and structures. The availability of such buildings and structures in sparsely populated areas of Irkutsk region is not more than 5%. The relevance and practical significance of this research involve developing the technology for the needs of consumers to use highly-efficient, electrical safe, low-inertia, resistant to aggressive environments, stable in operation, economically sound and ecologically friendly resistive heaters and heating devices based on them.

Scholarly importance: to develop physical-chemical principles to manufacture effective heating systems when using mica.

Due consideration in this research is paid to the implementation of the program “The national strategy for sustainable development of the Russian Federation”, as well as to the implementation of the resource utilization model. That is the direction focused on meeting human needs while preserving the environment for the present and future generations. The improvement of human well-being and the preservation of the harmony between society and nature, as well as the need for new technologies to solve environmental problems should be paid attention to. This is an extremely important issue for improving the efficiency of the entire national economy and improving the quality of people's life.
In 2009 the government of the Russian Federation adopted the Federal Law “On energy saving and energy efficiency”, making energy saving a priority direction of the state policy. The main reserves of energy saving involve the field of reconstruction of previously built facilities by means of reducing heat losses and efficiency of central heating systems through optimizing the heating control systems and the use of new composite materials [1,2,3].

Mica-based composites that combine high dielectric properties with mechanical, chemical and thermal resistance are considered to be the most efficient among a great number of composite materials created in recent years. Mica-containing composites are widely employed in various spheres of the technical field as electrical insulating materials. Micalex holds the most unique position among this series since its being a high-quality insulating material obtained by means of hot pressing of mica and glass.

There are different structures of heating systems. The main requirements for these structures are reliability in operation, economic justifiability, high electrical and physical properties, resistance to aggressive environments.

The main part of any heating device is the heating element. Flat resistive heaters are widely used. They have found application for the creating of microclimate in the premises, the production of anticing systems. So, they are widely used in industrial fields, in agriculture and have a wide range of applications in other areas. Different materials are used in the structures of these heaters: polymer-based materials, carbon steel, aluminium alloys, and the heaters are placed into the concrete with polyvinylchloride insulation. Most of them have high water absorption capacity, ineffective structure of polyvinylchloride insulation, and they have high energy consumption capacity and short life expectancy. The most promising in this respect is mica-based flat resistive heaters [4 and 5], which are devoid of the above mentioned disadvantages. This is micalex that is used as an insulating layer.

Micalex as a dielectric material appeared in the world embracing market long ago. It competes favourably with ceramics and plastics. Micalex is a composite material that is produced by means of hot pressing of a mixture of finely crystalline powdered natural muscovite mica, or a mixture of phlogopite and fine-grained low-melting glass.

Ground mica and fine-grained glass are mixed at the mass ratio of 3:2 for 1 hour in a humid state. The resulting mixture is sieved and pressed into bricks at the specific pressure of 20-40 millipascal and then dried for 1 day at the room temperature. Then the bricks are heated in a tunnel oven to 700-750 °C. The process is followed by hot pressing and annealing. The product (micalex plates) are sent for machining and goes through the technical control [6].

The physical properties of micalex are determined by the quality of the starting materials, by their microstructure, as well as by the technology of manufacturing.

The formation of micaceous composites is a complicated physical-chemical process. A comprehensive analysis of interphase interactions is necessary to clarify its regularities.

Research aim: To find out the fundamental principles of producing mica-composite materials as a scientific basis for the development of new mica-composites and the development of efficient heating systems based on them.

When producing mica in circumstances of elevated temperatures and high pressure at the interface boundary of mica and glass, it is possible both the dissolution of mica and the formation of new phases and intermediate compounds. Being aware of the mechanism of these phenomena makes it possible to create composites with certain technical characteristics. Advanced studies using modern physical-chemical methods [7,8,9] were conducted in order to clarify the linkage mechanism of the elements with the matrix and to identify the products of inter-phase interactions. The targets of the research are the starting mixture of ground mica and the binder element, as well as standard reference materials.
Research methods

The methods of thermodynamic quantum chemical calculations, as well as kinetic studies that involve a number of advanced techniques of physical and chemical studies (x-ray phase analysis, thermal analysis, and IR spectroscopy) are employed. Electro physical and mechanical characteristics of composites and starting materials are determined by the standardized methods to comply with the All Union State Standard.

The phase identification was carried out according to microstructural, x-ray and IR spectroscopic studies.

As a result of the research, the mechanism of interaction of mica with glass while producing micalex is analysed. It is understood that the destruction of the crystal structure of mica in the grained glass begins with the dehydroxylation of mica. The mechanism of interaction of muscovite mica and mica amber with aluminoborosilicate glass 203 and the structure of the resulting composite material are revealed.

It has been found out that in the process of the interaction of mica (mica amber, muscovite mica) with glass №203 the following processes take place: dissolution of mica in molten glass in the contact zone, mutual diffusion of mica and glass components; crystallization of supersaturated solution components in the transition zone when cooling.

It is shown that in the transition zone of muscovite – glass 203 the following elements are formed: potassium feldspar, sillimanite, mica amber-glass 203-spinel, olivine, enstatite. Glass in the transition zone has a composition that is different from the starting composition.

The structure of the composite is layered; mica flakes are located in an inhomogeneous way; their shape is mainly ellipsoidal; large flakes are deformed with their fused edges. In the cross sections, there are closed pores up to 0.01 mm in size in the glass.

The possibility of using different minerals in the process of manufacturing composites is largely determined by their thermal stability. From this point of view, aluminosilicates are particularly appealing. There is mica, amphiboles, clay minerals, etc. in the group of aluminosilicates. The common characteristic of these minerals is that they include hydroxyl, which is a major part of their structure. These substances when being exposed to heating, lose physically adsorbed water – interlayer water first. At high temperatures, the process of dehydroxylation occurs, which is accompanied by changing in the physical properties of minerals. This process precedes the stage where new amorphous and crystalline phases appear. [10]

Dehydroxylation is a very important point. It occurs at temperatures that depend both on the nature of the mineral and also on the degree of crystallinity, as well as on the size of the particles. It is necessary to know how the mechanism of dehydroxylation happens to determine the thermal stability of mica, to understand the mechanism of inter-phase interactions, as well as to improve the technology of composite materials based on mica.

Analysing data resources about the mechanism of dehydroxylation of various minerals, and mica among them, it is assumed that there are two types of the dehydroxylation process: homogeneous (when hydroxyl ions are the elements that change their location) and heterogeneous (inhomogeneous), where it is the proton that moves. The homogeneous mechanism has a number of disadvantages. Therefore, the heterogeneous mechanism seems to be more real. To understand the mechanism of dihydroxylation, it is necessary to take into account the behaviour of the proton of hydroxyl groups. The behaviour of the proton provides conditions when the expected reaction is possible. The degree of dehydroxylation can be assessed by various methods: physical, thermographic, x-ray phase analysis, etc. The simultaneous use of all these methods makes it possible to adequately describe the thermal decomposition of mica. Moreover, additional information can be obtained by studying the isotopic exchange of hydrogen and deuterium.

The isotopic exchange of hydrogen and deuterium. To determine the behaviour of hydrogen during dehydroxylation, the isotopic exchange have been carried out for samples of muscovite, phlogopite when using heavy water. In the process it is possible to estimate the speed and diffusion
coefficient of hydrogen and deuterium, as well as the degree of participation in their exchange reactions.

The experiments have shown that the sum of the absorption coefficients remains constant over time. This indicates that the amount of protons and deuterons is almost unchangeable in the process of deuterization. It is understood that the diffusion coefficients of the isotopic exchange are of the same order for muscovite and phlogopite.

There are several models of dehydroxylation process. It is also assumed that one isolated proton diffuses. In this case, the speed of dehydroxylation will be determined by the value of the energy barrier that depends on the nature of mica. This means that each mica has its own activation energy of the dehydroxylation process and it occurs at different temperatures for different mica.

The structure of anhydrous muscovite that was proposed by Eberhart (1963) [11] requires that oxygen during dehydroxylation should not change its location. Since isolated oxygen cannot diffuse as an isolated proton, this hypothesis assumes interacting the proton with oxygen during its transition.

The thermodynamics of the process of dehydroxylation of mica. Based on the analysis of the resource data and on the research experimental data, it can be assumed that when natural mica is heated, its composition changes. They are dependent on the removal of both molecular water (dehydration) and hydroxyl ions (dehydroxylation) from the interlayer space. [12, 13]

The total process of removal of various forms of water can be represented by a set of individual stages. As for muscovite, these stages are:

1. The stage of molecular water removal
   \[ KAl_2\left[ AlSi_3O_{10}\right](OH)_2\cdot nH_2O \rightarrow KAl_2\left[ AlSi_3O_{10}\right](OH)_2 + H_2O \]  
   hydromica mica water

2. The stage of structural water removal
   \[ KAl_2\left[ AlSi_3O_{10}\right](OH)_2 \rightarrow KAl_2\left[ AlSi_3O_{10}\right] \cdot O + H_2O \]  
   mica dehydroxylate water

It is quite obvious that the balance between hydrated mica and mica (equation 1) is determined by the laws of getter phenomena. Their detailed aspects for mineral layered materials were considered in the research [14]. In this regard, we will focus only on the following points.

It is known [14] that the adsorption speed \( Q_{aqc} \) is determined by the pressure (P) and the degree of filling the surface with the sorbed substance \( Q \), i.e.:
\[ Q_{aqc} = k_1(1-Q)P \]  
(3),

where \( Q \) is the degree of the surface filling in the proportion of unit.

The speed of water desorption \( Q_{dec} \) is directly proportional to the degree of filling, i.e.:
\[ Q_{dec} = k_2Q \]  
(4),

Under the conditions of balance considered by thermodynamics, the velocities of these two mutually opposite processes become the same, i.e.
\[ Q_{aqc} = Q_{dec} \]  
(5).

The balance position of the reaction (2) is characterized by the value of the balance constant and depends on the temperature (Van’t Hoff equation):
\[ \frac{d\ln k_P}{dT} = \frac{\Delta H}{RT^2} \]  
(6),
where $k_P$ is the balance constant; $\Delta H$ is enthalpy of the reaction; $R$ is the universal gas constant. Thus, the amount of hydroxylate, as well as the amount of water formed from hydroxyl ions (included in the structure of aluminum-silicon tetrahedra) is also a function of temperature.

Equation (6) shows that:

1. The system under consideration is monovariant at a constant temperature. This means that each given temperature corresponds to a certain value of the balanced pressure.

2. The lower partial pressure of the water vapour and the higher temperature of the process are, the more complete the reaction is.

3. Molecular water is retained in the interlayer space of mica as long as undecomposed mica is retained. This means that the interlayer water is removed throughout the dehydroxylation process, but its amount depends on the temperature.

4. The balanced position of the reaction (2) and the amount of water and dehydroxylate formed can be judged by the volume of the balance constant.

5. Partial water pressure and its change in time can serve as one of the controlling parameters when studying the kinetics of the dehydroxylation process.

6. The conditions (temperature and pressure) of dehydroxylation of muscovite and phlogopite are determined.

The results of thermodynamic calculations are in good agreement with the experimental data of the authors [15, 16], who studied the decomposition of muscovite at elevated temperatures. The data obtained indicate that the dehydroxylation of muscovite begins at a temperature exceeding $400^\circ$ C. As a result of further temperature increase, the degree of dehydration increases very quickly. This means that the heating of mica up to $400^\circ$ C leads to the removal of molecular water, including sorbed water, while chemically bound water, represented by hydroxyl ions, remains almost unchanged in muscovite.

The fact that each temperature value corresponds to a well-defined balance value of the partial pressure of water suggests that any factors leading to a decrease in the partial pressure of water vapour will inevitably cause a decrease in the temperature of muscovite hydroxylation.

Similar calculations of phlogopite dehydroxylation by equation

$$KM g_3 [AlSi_3O_{10}](OH)_3 \rightarrow KM g_3 [AlSi_3O_{10}]O + H_2O$$

Comparing the obtained data on phlogopite dehydroxylation with the data for muscovite, it becomes clear that phlogopite is a higher temperature mineral. Its noticeable dehydroxylation happens at about $180^\circ - 220^\circ$ C higher than muscovite dehydroxylation. The fact which is in agreement with the experimental data of other authors [7, 10, 16], including NMR data.

The results of thermodynamic calculations allow making the following conclusions:

- Conditions of dehydroxylation of phlogopite and muscovite at elevated temperatures were determined.
- It is shown that the process of phlogopite dehydroxylation occurs at a temperature $180-220^\circ$ higher than that of muscovite.

**Discussions and conclusions**

Thus, the new scientific results related to the processes of mica dehydroxylation and dehydration have been obtained. It has been found out that the process of dehydroxylation includes 3 successive stages. The limiting stages of the dehydroxylation process are either diffusion of water molecules in the interlayer space or rearrangement of hydroxyl ions to form water.
The presence of the binder element in the initial load of micalex reduces the temperature intervals of dehydration and dehydroxylation significantly, and increases the speed of these processes.

The principles of producing mica-containing composite materials have been identified. They consist in determining the nature of the bond between mica and binder element, the sequence of processes of chemical interaction of mica with the binder element, the factors regulating the operating temperature and other technical characteristics.

Conclusions

The theoretical basis of the technology of new temperature-resistant mica-containing materials and efficient heaters based on mica-containing composite materials have been developed on the basis of scientific generalizations. The experimental studies of physical and chemical laws of forming mica-containing composite materials and identifying the nature of the relationship between mica and binders, on the basis of the sequence of their interaction and clarification of the most important factors determine the technical characteristics of the composite. All the data contribute to the expansion of the raw material base, as well as to integrated and rational use of mineral raw materials.

The new field of application of composite materials based on mica and glass in electrothermy has been analysed.

The technology of mica-ceramic heating elements (mica ceramic electric heating) used in various fields of the national economy has been developed.

Physical and chemical principles of effective heating systems based on mica and widely used in construction industry has been explained.

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