The rational use of mica as a priority for the mining industry of Irkutsk region

T I Shishelova, V V Fedchishin and M A Khramovskikh

Irkutsk National Research Technical University, Russia

E-mail: i03@istu.edu

Abstract. Mica is one of the most widespread minerals. Muscovite and phlogopite whose large reserves are located in Irkutsk region have various industrial applications. Due to the crisis, a large amount of mica remained unclaimed. There are mining dumps of raw materials and production waste. The use of mica and the disposal of industrial waste are urgent problems. One of the ways to solve them is to produce mica-based composite materials. The use of such materials will improve technical and economic indicators of production processes and contribute to the development of low-waste and non-waste technologies, protection of the environment. The article aims to establish fundamental laws of production of mica-based composite materials. The article provides recommendations on production technologies. Samples of muscovite, phlogopite mica, mine scraps and mica waste were studied. The methods of physicochemical analysis were used to study the samples. Thermodynamic and quantum chemical calculations were made. Based on the experimental studies and scientific generalizations, the theoretical foundations of the production technology for temperature-resistant mica-based materials and effective heating elements based on mica composite materials were developed. They are based on the integrated and rational use of mineral raw materials.

1. Introduction
Mica is one of the most widespread minerals. Muscovite and phlogopite have various industrial applications. Irkutsk region has large reserves of high-quality mica. In the 1980-1990s, mica was used for producing electrical insulating materials. Due to the crisis, many mica mines were mothballed, mica plants were closed [5]. A large number of mica raw materials remained unclaimed. There are dumps of raw materials and production wastes. All this exacerbates the environmental situation. However, previously unclaimed minerals and production waste can be used to produce high-quality products. It is necessary to analyze alternative, non-traditional areas of applications [3, 7]. The article analyzes possibilities and present results of production technology development for mica-based composite materials and production waste using other minerals extracted in Irkutsk region [1]. The possibility of using small-sized mica in the construction industry was described in [2]. A promising area is the development of new radiation-resistant mica materials for the disposal of radioactive waste [11, 13].

2. Methods and materials
Methods of physicochemical analysis (X-ray phase, chemical, thermal, IR spectroscopy, etc.) as well as methods of thermodynamic and quantum-chemical calculation were used. Electrophysical
characteristics were determined in accordance with GOST. The research objects were samples of muscovite, phlogopite mica, mine scraps, and mica waste.

3. Results and discussion
Production of mica composites is a complex physicochemical process. To establish its laws, a comprehensive analysis of interphase interactions is required. In order to identify the mechanism of particle-matrix bonds and determine a product of interphase interactions, the studies were conducted using modern physicochemical methods. The identification of a sequence of interphase interactions and the study of physical properties of composites help understand the nature of the phenomena and determine directions for improving the existing production technologies for new composite materials [4,8].

One of the most famous mica composite materials is mica paper. This material is made from aqueous suspension containing mica particles. Mica particles are located on a plane parallel to each other with the overlap of several tens of layers. Due to the fact that mica has different conductivity values in different directions, such overlapping ensures high dielectric properties of the material [6]. Water plays an important role in the formation of bonds. When the samples are heated to 500 °C, a decrease in the mass is proportional to an increase in the temperature and amounts to 0.2-0.3% (Figure 1) [12.14]. At this temperature, molecular water is released – the dehydration process begins. The water film becomes thinner with an increasing temperature. The dielectric strength of paper remains unchanged.

The IR-spectrum of mica paper in the region of stretching vibrations of the OH bond was studied. The spectrum is represented by a single band with a maximum of 3620 cm\(^{-1}\). When heated to 700 °C, reversible changes in the spectrum are observed; when heated to 800 °C, irreversible changes are observed. Heat treatment of mica paper decreases intensity of the 3620 cm\(^{-1}\) band even for relatively low temperatures (Figure 2); during cooling, the band is completely restored (a reversible process). As a result of heating (up to 800°C for 5 hours), the 3620 cm\(^{-1}\) band disappears and does not appear after cooling (an irreversible process) (Figure 2, b). After the heat treatment, the sample becomes brittle and disperses in water.
During heating, molecular water is removed, the particles move closer, which makes it difficult to disperse them in water. In addition, paper becomes resistant to polar solvents. After being heated at 100 °C for 5-60 minutes, the paper disperses in water for 10-30 seconds and can withstand several immersions into ethyl alcohol. As the temperature rises to 200 °C, the dispersion time increases to 2-3 minutes, and the number of immersions increases to 100. At 300-600 °C, the paper retains water resistance for 2-3 days and can withstand 500-600 immersions. Heating at 700-800 °C makes the paper resistant to water and other polar solvents. In addition, this treatment contributes to the uniform impregnation of thick and thin layers of mica paper with insulating varnish.

In the production of heat-resistant mica, phosphoric acid and its salts are used as a binder. A study on the use of mica from various deposits for the production of heat-resistant mica was conducted. Samples from the Ust-Tungerev and Aryabilov deposits showed the best results. During heating, muscovite interacts with aluminochromophosphate more intensively than with phosphoric acid [15].

One of the mica-based composite materials is micalex produced by pressing and heating mica and glass. Glass is a binder. It was established that the presence of a binder reduces temperature ranges of mica dehydration and dehydroxylation and increases the speed of these processes. A comprehensive study was carried out to identify the structure of micalex. The optical polarization microscopy of micalex samples identified that the smallest mica particles are dissolved in glass, large flakes are deformed, bent along the edges, sometimes have uneven outlines and are arranged unevenly in glass forming clusters. During the formation of the mica-glass boundary, intense physical and chemical changes occur. Mica calcination contributes to a better dissolution in glass. The studies on the use of various glasses as a binder were conducted. In glass 203, mica dissolution was 20%; in glass 15 or glass 35, mica dissolution was 10%. Fractograms of the transverse and longitudinal sections show the structure of the composite.

The mica powder is unevenly distributed, particle sizes vary in a wide range, the edges of mica particles are melted and have traces of dissolution and interaction with glass. In comparison with phlogopite, muscovite dissolves better in glass 203. Preliminary mica annealing contributes to its greater dissolution in glass. The X-ray microanalysis showed that in the sintering zones, there is a mutual diffusion of elements accompanied by mica destruction [9]. The IR spectroscopy showed that during the micalex formation, new chemical bonds and compounds are formed. In general, the IR spectra of the products of calcination of muscovite and glass are determined by the superposition of the spectra of muscovite, microcline, sillimanite and glassy products. The derivatographic analysis
indicates that during the micalex formation, mica dehydration and chemical interaction of mica with glass result in the formation of chemical compounds in the contact zone. To identify the phase composition of interaction products, X-ray diffraction patterns of micalex were studied. An analysis of the phase composition of micalex samples taken at different production stages showed that new phases are formed at the sintering stage. According to the results of the studies, the dissolution of mica in glass is a complex multi-stage process; one of its first stages is dehydroxylation which is limiting. Physical and chemical transformations include a number of successive stages. The scheme of interaction of muscovite with glass 203 is as follows:

\[
\text{Stage I - Dehydroxylation of Mica} \\
\text{KAl}_2[\text{AlSi}_3\text{O}_{10}]\text{(OH)}_2 \rightarrow \text{KAl}_2[\text{AlSi}_3\text{O}_{10}]\text{O}+\text{H}_2\text{O} \\
\text{MUSCovITE DEHYDROXYLATE STEAM} \\
\]

\[
\text{Stage II - Decomposition (dissociation) of dehydroxylate} \\
\text{KAl}_2[\text{AlSi}_3\text{O}_{10}]\text{O} \rightarrow \text{KAlSi}_3\text{O}_8 + \text{Al}_2\text{O}_3 \\
\text{DEHYDROXYLATE SANIDINE ALUMINIC OXIDE} \\
\]

The process of interaction of muscovite with glass 203 can be represented using the following equation

\[
\text{KAl}_2[\text{AlSi}_3\text{O}_{10}]\text{(OH)}_2 + \text{SiO}_2 \rightarrow \text{KAlSi}_3\text{O}_8 + \text{Al}_2\text{SiO}_4 + \text{H}_2\text{O} \\
\text{MUSCovITE GLASS SANIDINE SILLIMANITE STEAM} \\
\]

The result of physicochemical transformations in the system “layered silicate-aluminoborosilicate melt” is new phases [10]: sanidine and sillimanite (in muscovite micalex); sanidine, olivine and enstatite (in phlogopite micalex).

4. Conclusion
As a result of the experimental studies and scientific generalizations, the theoretical foundations of the production technology for mica-based composite materials were established:

- During the production of a mica-based composite, the chemical transformation of components occurs and new phases (sanidine, sillimanite, enstatite, and olivine) are formed. The successive stages of composite formation are as follows: mica dehydroxylation, dehydroxylate decomposition and chemical interaction with a binder.
  - Conditions for producing a high-quality mica-containing composite were identified: selection of a binder, joint use of muscovite and phlogopite, mica termination, use of mine scraps, muscovite schists, volcanic ash, introduction of modifiers into the mixture.
  - New areas of integrated and rational applications of mica-based materials are as follows: electrothermy, radiation protection, construction, nanotechnology.

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