Study of aluminosilicate waste-based materials

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Abstract: Valuable technical properties of mica have attracted attention of people for a long time. Mica is widely used in various industries, including electrical, radio, paint and varnish production. Two types of mica - muscovite and phlogopite – are applied in modern production. Mica belongs to a large group of minerals characterized by perfect cleavage, i.e. the ability to split into very thin sheets having smooth surfaces. Muscovite and phlogopite are the most important industrial micas. They are easily split into thin sheets. In addition, they have high hardness and mechanical strength. They are thermally and chemically stable, non-hygroscopic, flexible, elastic and transparent. Due to these properties, muscovite and phlogopite are the most important composite materials used for producing electrical insulating materials. Along with these varieties, vermiculite, lepidolite and biotite are used in various industries. Mica has properties that other dielectrics lack (high electrical strength, heat resistance, chemical resistance, moisture resistance, mechanical strength, and flexibility). Muscovite and phlogopite are electrical insulating materials. The mining and processing industries produce a lot of mica waste. Methods for using muscovite and phlogopite waste in combination with aluminosilicate waste and a number of low-melting chemical additives were developed.

1. Introduction and Background
Thermal and chemical properties of mica have parameters which affect micalex properties. In electrical insulating equipment, phlogopite KMg$_3$ [Si$_3$AlO$_{10}$] (OH)$_2$ and muscovite KAl$_2$ [SiAlO$_{10}$] (OH)$_2$ are mainly used. Mica has good electrical characteristics, low dielectric losses, high surface and bulk electrical resistivity and electrical strength. It has high mechanical strength, non-inflammability, and chemical resistance [1,2]. Muscovite is used in the electrical insulation industry: it withstands heating up to 600 °C. Phlogopite is a hygroscopic mica: it is softer and more difficult to split into thin layers compared to muscovite, it is more heat-resistant and can withstand heat up to 800 °C [3-5]. The thermal resistance of phlogopite crystals is higher than that of muscovite by 200–300 °C [6-8]. This is due to the fact that both phlogopite and muscovite emit an equal amount of gases at a temperature of 400 °C. When the temperature rises by 100 °C, gas emission increases due to the water removal. For phlogopite, gas emission does not change at 400 °C [9].

Dehydroxilation of phlogopite [10-12] is associated with the removal of structural water. The dehydroxilation region ranges from 800 to 1000 °C. Taking into account structural features of mica crystals, the authors assume that water is concentrated in the interlayer gap, causing the diffusion resistance of water removed from the interpacket zone. For phlogopites, two processes of water removal occur in the range of 700–900 °C (water is removed in two modes). In the range of 700-800 °C, water is removed in a diffusion mode. At 800 °C, the removal of water is completed, and above 800 °C, dehydroxilation (the removal of chemically bound water) begins. In Katalakh and Kovdor phlogopites, dehydroxilation begins when the separation of interlayer water has not been completed.
whereas in Aryabilov phlogopite, the removal of interlayer water is differentiated. The study of natural phlogopites [13-15] identified that adsorbed water is removed at 40-220°C, interlayer water – at 220-900°C, and constitutional water – at 960°C. Mica with high fluorine content is more heat-resistant. At high temperatures, in muscovite crystals, gas emission increases due to the dehydration of some octahedra. As a result, the crystal cracks and creates favorable conditions for gas emission. In [16], results of the X-ray studies of phlogopites are presented.

2. Materials and Methods
To study the aluminosilicate composition, a thermal analysis was applied. The thermal analysis is used to study chemical reactions and physical transformations occurring in chemical compounds or between individual compounds under the influence of heat. Thermal processes (chemical reactions or phase transformation) are accompanied by changes in the internal heat content of the system. The transformation entails heat absorption (endothermic transformation) or heat release (exothermic transformation). These heat effects can be identified by the differential thermal analysis. The transformation is due to the change in weight which can be determined by the thermogravimetric method.

Thermal transformations of mica occur at high temperatures. An analysis of pure mica showed that heating causes a loss of its weight due to the dehydroxilation which involves three stages.

1. Release of adsorbed water at 120°C.
2. Isolation of interlayer molecular water at 300-500°C.
3. Dehydroxilation at 900°C.

In Muscovite, the third stage occurs in the range of 700-1000°C at a maximum temperature of 900°C. At temperatures of 850-1000°C, the endo-effect is observed on the DTA curve with a maximum of 900°C without changes in the weight corresponding to the disintegration of the muscovite lattice [2]. Thermal transformations of glass N on the heating curves indicate the thermal destruction of glass and the release of gas products. There are two processes - dehydroxylation and decarbonization. These processes correspond to the heating stage in the range of 20-450°C with a maximum at 150°C which is fixed on the DTG curve.

At the next stage, the congruent melting of glass, i.e. formation of a liquid phase, occurs. This stage corresponds to the interval of 450-1000°C with a maximum value at 900°C. The total weight loss is 10.6%; only 0.6% of weight is lost during dehydroxylation and decarbonization. An analysis of the composition showed that during the heating process, several thermal stages are recorded on the DTG curve. The first stage is represented by an asymmetric curve with a maximum at 150°C. The interval corresponds to 20-200°C. Other four stages were identified: 200-300°C with a maximum at 250°C; 300-370°C with a maximum at 350°C; 370-500°C with a maximum at 400°C and the largest asymmetric interval of 500-1000°C with a maximum at 850°C. At 20-500°C, gas products are released from mica and glass; as a result of dehydration, decarbonization and dihydroxylation, constitutional water is released. Glass and mineral are interacted at the next stage. Polymorphic enantiotropic transformation occurs when mica interacts with glass; the incongruent melting forms liquid solid phases at 500-1000°C with a maximum at 850°C. The total mass loss is 18%. On the DTA curve, two endo-effects are recorded: 20-650°C with a maximum at 600°C and 650-1000°C with a maximum at 900°C. The endo-effect with a maximum at 600°C corresponds to the wetting of mica with glass. The second endo-effect is an amorphous-crystalline phase.

3. Experimental Section
Based on results of the study on physicochemical processes occurring during the heating of muscovite, this heat-resistant composition can be used for producing electric heaters. The manufacturing process involves the following stages: preparation of pressed powder, briquetting, heating, hot pressing, annealing. Pressed powder consists of a mixture of mica powder and glass powder (60% of mica and 40% of glass). Glass is mixed with mica in a rod mill for an hour, the mixture is moistened with 10% H₂O and mixed for 40-45 minutes; then, the mixture is sieved through a sieve with a 2x2 mm cell; the
mixture is dosed. The dosed mass is briquetted under 300-50 kg/cm. Briquettes are heated to the softening temperature in order to fuse glass with mica. A cold briquette is placed on a special embossed baking sheet powdered with ground mica; it enters the upper tunnel of the electric furnace where it is dried and warmed. The briquette is loaded strictly on time. Briquettes are moved when the furnace is turned off using a special engine. There are 15 briquettes in the tunnel. When the first briquettes are at the exit of the first tunnel, they are moved to the middle tunnel for further heating.

The X-ray phase analysis of the micalex composition with a new binder. The following materials were used: a) muscovite fine-crystalline mica, b) mica mixed with glass N in powder (40% of glass and 60% of mica), c) longitudinal and perpendicular sections of the sintered composition. Diffractograms of pure muscovite and thin sections of longitudinal and perpendicular cuts of glass 203-based micalex were used. Boric acid was used as a component fixing the materials in the cuvette. An analysis of the phase composition of sintered samples studied in the longitudinal and perpendicular planes showed that during the sintering of mica with glass, silicate phases are formed. Two polytypes of muscovite 2M and ZT were found in the sintered and pressed glass-mica compositions. In the perpendicular section of the sintered composition, the following substances were observed: microcline K[AlSi3O10] and disthen A12O3 [Si2O5]; microcline, kyanite and sillimanite A12O3 [Si2O5]; mullite A12Si2O10. Intensities of peaks of newly formed phases of longitudinal and perpendicular sections are different.

The results showed that during the formation of a composition at the interphase mica-glass boundary, silicates are formed. Formation of new phases is associated with a mica structure. Varieties of muscovite polytypes are distinguished by interlayer cation and colonization with elements of tetrahedral and octahedral networks. The prevailing orientation of powder increases the intensity of basal reflexes. Mica particles are formed when pressing by the cleavage plane, and probability of reflecting the crystallographic plane of the general position decreases; therefore, intensity of reflections of the general position decreases. The interaction between mica and glass can be represented as follows: after glass has been melted, mica grains are redistributed. Between the two closely spaced grains of the sintered substance, a layer of wetting glass is formed. It has a shape of a lens with a concave meniscus at the boundary with the air medium.

Surface tension forces create an overpressure directed towards the meniscus curvature center. This pressure moves the liquid from the contact zone due to which solid particles converge, accompanied by a denser packing of particles and filling the pores with glass. At the same time, the solid phase of mica dissolves in liquid glass and a new phase recrystallizes. Dissolution occurs at the points of contact. As a result, crystals are converged. Small crystals can dissolve, however, larger ones grow: recrystallization occurs. Composite recrystallization of a mica solution in glass stops. A hard frame is formed. Formation of new phases is influenced by pressure which reaches 300 kg/cm; the temperature is about 750 °C. Application of pressure to the heated fine glass mica briquette causes plastic deformations of mica crystals. Grains are mutually redistributed, the number of contacts increases, voids are filled. As a result, density of the sintered material increases.

4. Results and Discussion

Formation of new phases can be represented as a reaction equation. The micalex sample was cut perpendicular to the cleavage plane of 2KAl2SiO5O10 micalex. - KAl3Si1O8 + Al2O3 [Si2O5] + 2H2O + 2K2O + A12O3 + SiO2 microcline disthen. The micalex is cut along the cleavage of muscovite. 2KAl2SiO5O10 - KAl3Si1O8 + Al2O3SiO2 + 2H2O + K2O + A12O3 + SiO2 microcline, sillimanite, kyanite, mullite. The region of isomorphic substitution during the nucleation of new phases was studied using the infrared spectroscopy. The studies showed that depending on the conditions of the technological process, the spectrum of muscovite combined with glass changes. In the IR spectra, it is possible to distinguish a group of intense bands in the frequency range of 400-1200 s⁻¹. These bands are caused by vibrations of Si and O atoms along the connecting line, i.e. by vibrations of the Si – O bond in the SiO₄ tetrahedron. All absorption bands corresponding to silicates are located in a wide spectral range due to the complex structure and a large variety of atomic groups which include Si, O and other atoms. The
nature of surrounding atoms, in particular those associated with oxygen, influences the frequency of oscillations of the Si-O bond. The absorption spectrum of glass N is represented by wide absorption bands characteristic of amorphous substances [8].

In the frequency range of 400–600 cm$^{-1}$, the asymmetric band corresponds to deformation vibrations of distorted silicon-oxygen tetrahedra; the absorption bands with a frequency of 1000 cm$^{-1}$ correspond to stretching vibrations. Deformation vibrations of the O-B-O group occur at a frequency of 740 cm$^{-1}$, and stretching vibrations – at a frequency of -1400 cm$^{-1}$. The absorption band with a maximum of 3420 cm$^{-1}$ refers to the vibration of hydroxyl groups. Due to the fact that chemical compositions of mica and glass used for the production of mica-complex are close, their separate bands in the spectrum of the mechanical mica-complex mixture are combined. In the frequency range of 400–1100 cm$^{-1}$, KBG IR spectra of the mechanical mica-band mass have two fixed maxima - 480 and 535 cm$^{-1}$ characteristic of deformation vibrations of Si $-$ O. In the region of 650–4000 cm$^{-1}$ fixed by a spectral prism from NaCl, the spectrum has intense lines with maxima at 760 cm$^{-1}$ [17-19]; at a frequency of 1000 cm$^{-1}$, a broad intense band is characteristic of Si-O oscillations; at 1400 cm$^{-1}$, a weak pronounced absorption band corresponds to (O $-$ B $-$ O).

The maximum of 1630 cm$^{-1}$ indicates deformation vibrations of the bond (H $-$ O $-$ H). Absorption at frequencies of 3420 and 3620 cm$^{-1}$ is characteristic of structural OH groups. The study of the IR spectrum of the mechanical micalex mass before and after the cold pressing showed that it is represented by the position of the spectra of glass and mica; no new bands were observed. Significant changes were observed after the heat treatment at temperatures of 700-750 °C. Intensity of stretching vibrations of OH groups decreases at a frequency of 3620 cm$^{-1}$ which indicates the dehydroxilation in mica particles and formation of water molecules. In muscovite, a part of Si is replaced by Al in the tetrahedral position; during the heat treatment, the bond is broken (Si-O-Al$_{IV}$). The absorption band has a maximum frequency of 760 cm$^{-1}$ due to the distortion of tetrahedra, while the band 720 cm$^{-1}$ sharply increases which is characteristic of the Al$_{IV}$-O bond. It can be assumed that during the heat treatment and sintering at a temperature of 700–750 °C, the correspondence between octahedral and tetrahedral layers is broken. The structural changes occur in mica crystals heated up to 1000-1200 °C [14-16]. Since mica is in a finely dispersed state, a new amorphous-crystalline bond can be formed at lower temperatures. During the dissolution of mica in glass, elements are mutually diffused, oxygen is redistributed between silicon, aluminum and alkali metals. In the region of 400–900 cm$^{-1}$, these phenomena can be explained by the disintegration of the muscovite structure, formation of new phases of microcline and sillimanite, and increasing intensity of the 1400 cm$^{-1}$ band. Based on the experimental data, we developed a method for controlling the quality of the mica-glass composition [10-23].

5. Summary and Conclusion
The thermography identified temperature ranges for the emission of gas products: removal of capillary water, dehydration, decarbonization, and incongruent melting corresponding to polymorphic enantiotropic transformations of the micalex composed of mica and glass. Using the X-ray phase analysis, new compounds (potassium spar, sillimanite, mullite, disthen, two polytypes of muscovite 2M$_1$ and 2T) were identified in the mica-glass composition. The IR spectroscopy revealed a region of isomorphic replacement of Si by Al in the tetrahedral position and a band with a maximum of 720 cm$^{-1}$ characteristic of the Al$-$O bond; in the region with this maximum, new crystalline phases are formed between amorphous and crystalline bodies.

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