Developing physical and chemical foundations to manufacture mica phosphate materials for various science-based areas of engineering and construction industry

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Abstract. Intensification of the existing technological processes as well as introduction of innovative technology are not conceivable without applying high-temperature electric heating. There is much concern about new generation materials with increased heat resistance, which can withstand the service temperature of 1200°C for a long period of operation. The research aim: to develop the physical and chemical principles for manufacturing heat-resistant mica-phosphate materials with high performance characteristics. The objects of the research are compositions of powdered mica from various deposits with the aluminum-chromium-phosphate bounding component at the component ratio 1: 1. Research methods: a number of modern physical and chemical methods were used: x-ray phase and thermal analyses, as well as IR spectroscopy method. Research results: as a matter of the experimental studies and scientific generalization, the regularities in the “mica – phosphate bounding component” system are revealed. The parameters that allow obtaining heat-resistant mica-containing materials with high performance characteristics for a wide range of applications in various scientific based areas of engineering and construction industry are determined and improved.

1. Introduction
Technical advancement in many areas of the national economy is aligned with electrothermy. Intensification of the existing mica composites as well as development of innovative mica composites are impossible without applying the high-temperature electric heating process. In electrothermy, a wide range of minerals including mica are utilized as electrical insulation materials, they are used to develop mica composites [1-5]. Distinguished by some qualities are micanite and micaceous laminate [6]. The technical characteristics of the composite depend on both the filler and the bounding component [7]. This research is devoted to the development of physical and chemical foundations to manufacture versatile high-specification mica-phosphate materials, electrothermy is one of those areas.

To achieve the aim, the following objectives were determined:
– Identification of scientific principles of synthesis of mica-phosphate composite materials;
2. Methods and materials
A number of modern physical and chemical methods were used: x-ray phase and thermal analyses, as well as IR spectroscopy method. The objects of the research are the compositions of powdered mica from various deposits with the aluminum-chromium-phosphate bounding components at the component ratio 1: 1.

3. Results and discussions
To develop the technology of heat-resistant mica-phosphate materials, the data about the physical and chemical processes of the "mica-phosphate bounding component" system and about the composition of the resulting products are required. Mica composite formation is a complex physical and chemical process [8-10]. To find out its regularity, a comprehensive analysis of interphase interactions is necessary [11, 12]. When producing a composite at elevated temperatures, it is possible for mica to dissolve, as well as for new phases and compounds to appear at the mica and phosphate material interface [13-16]. Finding out the sequence of interphase interactions allows understanding the essence of the phenomena occurring and determining the key directions for developing technologies for creating new composite materials with a wide range of electrophysical characteristics.

In the process of manufacturing heat-resistant micaceous laminate and other micaceous laminate based materials, phosphoric acid and its salts - aluminium-chromium-phosphate, etc. are used as bounding components. Such compounding materials, having high temperature resistance, can significantly increase the temperature characteristics of composite materials. It can be assumed that the interaction between mica and aluminium-chromium-phosphate can significantly affect the process of mica dehydroxylation. Table 1 shows the results of testing mixtures of mica with an aluminium-chromium-phosphate bounding component when heated to 1000°C.

**Table 1. The stages of weight loss when heating mica mixtures with the bounding component up to 1000°C according to the thermography data.**

| Mixture                           | Stage | Interval, °C | Maximum, °C | Weight loss, % |
|----------------------------------|-------|--------------|-------------|----------------|
| Muscovite + Aluminium-chromium-phosphate | I     | 40-280       | 130         | 17.67          |
|                                   | II    | 120-560      | 220         | 8.67           |
|                                   | III   | 600-1080     | 840         | 2.67           |
| Kovdor phlogopite +               | I     | 20-320       | 110         | 18.17          |
| Aluminium-chromium-phosphate     | II    | 110-620      | 210         | 7.17           |
|                                   | III   | 760-1120     | 1030        | 1.50           |
| Ust-Tungerevsky phlogopite +      | I     | 40-300       | 130         | 18.17          |
| Aluminium-chromium-phosphate     | II    | 120-690      | 220         | 6.67           |
|                                   | III   | 820-1100     | 1040        | 1.33           |
| Aryabilovsky phlogopite +         | I     | 40-320       | 120         | 18.33          |
| Aluminium-chromium-phosphate     | II    | 140-500      | 210         | 7.33           |
|                                   | III   | Getting started at 1000 | - | 1.17 |

The process of weight loss in the compositions of mica with a bounding component, as well as in "pure" micas, can be divided into three stages, but the temperature intervals are significantly shifted.

The temperature of the first maximum is approximately the same for all compositions.

The second stage - the removal of sorbed water is shifted towards lower temperatures and is obviously explained by the fact that aluminium-chromium-phosphate interacts with molecular water
(hydrolysis), which is well subjected to further dehydration. The removal of sorbed water in the compositions with aluminium-chromium-phosphate is shifted, in comparison with pure mica, from 320°C to 210°C (Aryabilovsky phlogopite), from 340 to 220°C (Ust-Tyungerevsky phlogopite), 320 to 210°C (Kovdor phlogopite), 440 to 220°C (muscovite). The found temperature limit for the removal of sorbed water with aluminium-chromium-phosphate determines the technological mode of composite manufacturing.

The third stage – mica dehydroxylation - is also slightly shifted towards lower temperatures.

On the curves of differential thermal analysis (DTA), a number of endoeffects can be seen: 1 - dehydration, 2 – interaction of components, 3 – dehydroxylation, 4 - decay of the mica structure. Studies conducted by means of IR spectroscopy method have shown that the yield of OH groups in muscovite decreases with aluminium phosphates, as well as explaining the reason for the less intense interaction of aluminium with aluminium-phosphate, whereas in mixtures of Kovdor phlogopite, dehydroxylation begins at 700°C, in the mixtures of Aryabilovsky phlogopite it starts after 900°C.

Thus, it was found that the presence of aluminium-chromium-phosphate significantly reduces the temperature intervals of dehydration and dehydroxylation of mica and depends on the genesis of mica.

Interphase interactions in the "mica-phosphates" system were studied through x-ray, IR spectroscopy, and thermography methods [17, 18]. The mixtures were preheated at 200-900°C for an hour, then the spectrogram and x-ray images of the initial and heated samples were taken.

Thermograms of muscovite mixtures and mixtures with Kovdor phlogopite within the studied temperature range show the presence of a high-temperature effect characterized by the decay of the mica structure, whereas in mixtures with Ust-Tyungerevsky and Aryabilovsky phlogopites, even when heated to 1100 °C, this effect is not observed. In addition, the differential thermal analysis (DTA) curves show a number of effects in the temperature range 540-810°C for the muscovite mixtures and 540-1000°C for the phlogopite mixtures corresponding to the interaction of the components.

The IR spectrum of the initial mixture of muscovite with phosphoric acid is represented by the muscovite spectrum. When the mixture is heated to 300°C, the bands 735 cm⁻¹ (microcline or aluminum phosphate) and 930 cm⁻¹(leucite) appear. With further heating, the bonds in the mica structure are weakened, and aluminum passes from six-point coordination to five-point coordination.

According to the conducted analysis of the research results, it can be assumed that muscovite interacts with aluminium-chromium-phosphate more intensively than with phosphoric acid.

The study of the phase composition of the products of mica interaction with phosphates shows that when the mixture of muscovite and phosphoric acid is heated to 700°C, new phases appear: microcline, leucite, potassium and aluminum phosphates.

The scheme of interaction of muscovite with phosphoric acid can be represented by the following stages. First the dehydroxylation of mica to form muscovite phosphate takes place:

\[ 3\text{KAI}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2 + 2\text{H}_3\text{PO}_4 \rightarrow (\text{KAI}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 + 6\text{H}_2\text{O} \]

Muscovite phosphate breaks down into microcline, aluminum phosphate, and aluminum oxide:

\[ (\text{KAI}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 \rightarrow 3\text{KAlSi}_3\text{O}_8 + 2\text{AlPO}_4 + 2\text{Al}_2\text{O}_3 \]

Microcline dissociates into leucite and amorphous silica:

\[ \text{KAlSi}_3\text{O}_8 \rightarrow \text{KAlSi}_2\text{O}_6 + \text{SiO}_2 \]

The newly formed silicate reacts with phosphoric acid, forming, along with potassium phosphate, a number of amorphous decomposition products:

\[ 3\text{KAlSi}_3\text{O}_6 + 2\text{H}_3\text{PO}_4 \rightarrow \text{K}_3\text{PO}_4 + 6\text{SiO}_2 + \text{Al}_2\text{O}_3 + 2\text{AlPO}_4 + 3\text{H}_2\text{O} \]

Similarly, the interaction of muscovite with aluminium-chromium-phosphate can be represented:

\[ \text{KAI}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2 + 2\text{AlCr}(\text{PO}_4)_2 \rightarrow 2(\text{KAI}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 + \text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + 6\text{H}_2\text{O} \]

\[ (\text{KAI}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 \rightarrow 3\text{KAlSi}_3\text{O}_8 + 2\text{AlPO}_4 + 2\text{Al}_2\text{O}_3 \]

\[ \text{KAlSi}_3\text{O}_8 \rightarrow \text{KAlSi}_2\text{O}_6 + \text{SiO}_2 \]

The proposed scheme, being an approximate model, allows justifying the formation of the observed products, as well as explaining the reason for the less intense interaction of aluminium-chromium-phosphate with mica compared to phosphoric acid. Obviously, the key reason is the formation of strong interactions...
chromium compounds such as spinel, which prevent mica from further interaction with phosphoric compounds. When interacting with aluminium-chromium-phosphate, Kovdor phlogopite decomposes not as much as in the mixture with phosphoric acid.

It is difficult to detect potassium phosphate in the heat treatment products at 500, 700 and 900°C. The gradual crystallization of aluminum phosphate only can be traced. It can be assumed that the remaining products of the interaction of phlogopite with aluminium-chromium-phosphate are strongly amorphous and their amount is insignificant. Therefore, they are not found on radiographs.

The scheme of interaction of phlogopite with phosphoric acid can be presented as the follows:

$$3\text{AlMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2 + 2\text{H}_3\text{PO}_4 \rightarrow (\text{KMg}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 + 6\text{H}_2\text{O}$$

$$(\text{KMg}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 \rightarrow 3\text{KAISi}_2\text{O}_5 + \text{Mg}_3(\text{PO}_4)_2 + 6\text{MgO}$$

$$(\text{KMg}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 \rightarrow \text{K}_3\text{PO}_4 + \text{AlPO}_4 + 3\text{SiO}_2 + \text{Al}_2\text{O}_3 + 9\text{MgO}$$

$$\text{KAISi}_2\text{O}_5 \rightarrow \text{KAISi}_2\text{O}_5 + \text{SiO}_2$$

$$\text{Al}_2\text{O}_3 + \text{SiO}_2 \rightarrow \text{Al}_2\text{Si}_3\text{O}_7$$

The sequence of phase formation during the interaction of phlogopite with aluminium-chromium-phosphate corresponds to the equations:

$$6\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2 + 2\text{AlCr}(\text{PO}_4)_2 \rightarrow 2(\text{KMg}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 + 6\text{H}_2\text{O} + \text{Al}_2\text{O}_3$$

$$(\text{KMg}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 \rightarrow 3\text{KMgSi}_2\text{O}_5 + \text{Mg}_3(\text{PO}_4)_2 + 6\text{MgO}$$

$$(\text{KMg}_3[\text{AlSi}_3\text{O}_{10}])_3(\text{PO}_4)_2 \rightarrow \text{K}_3\text{PO}_4 + \text{AlPO}_4 + 3\text{SiO}_2 + \text{Al}_2\text{O}_3 + 9\text{MgO}$$

$$\text{KAISi}_2\text{O}_5 \rightarrow \text{KAISi}_2\text{O}_5 + \text{SiO}_2$$

According to the results of studying the interaction with phosphates, the following conclusions can be drawn:

- Muscovite interacts with aluminium-chromium-phosphate in a more intensive way compared to phosphoric acid.
- According to the indicators showing the degree of interaction with phosphoric acid and aluminium-chromium-phosphate the phlogopites can be arranged in the decreasing order as follows: Kovdor, Ust-Tyungerevsky, Aryabiblovsky.
- All varieties of phlogopite interact more intensively with phosphoric acid than with aluminium-chromium-phosphate.

4. Conclusion

Within the experimental studies of the physical and chemical processes of formation of mica-phosphate materials, new scientific results have been obtained. They are expressed through determining the experimental and theoretical base of physical and chemical data of the "mica-phosphate bounding component" systems for various micas.

The regularities and features of the interaction processes in these systems are determined to develop the technology for heat-resistant composite mica-phosphate materials to be applied in modern scientific-based engineering areas, including electrothermy and construction industry.

It is found that dioctahedral micas (muscovite) interact better with aluminium-chromium-phosphate compared to phosphoric acid. Aluminium-chromium-phosphate reduces the temperature of mica dehyration and dehydroxylation. The products of interphase interactions of micas with phosphates are determined.

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