Studies on contact interaction of mica and glass

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Abstract. The issue of waste-free use of mineral raw materials is crucial for the national economy. Mica- and glass-based composites combining high dielectric properties with chemical, thermal and mechanical strength are of special significance. For about fifty years, domestic composite materials have been based on aluminum borosilicate glass containing fluoride compounds which are harmful substances polluting the environment and worsening working conditions. The paper presents data on the uses of glass production waste and mica deposit waste for producing new composite materials which have better ecological characteristics and require lower production costs. It was identified that mica wetting depends on the chemical composition of the crystalline substance. The quantitative content of acidic oxides and the difference between the content of acidic and basic oxides have the greatest impact on the temperature interval of wetting.

1. Introduction
Environmental protection, complex and rational use of natural resources, waste recycling are crucial issues. They can be solved by maximizing the extraction of minerals, complex processing of raw materials, implementation of technological advances in the mining industry, development of high economic low-waste and waste-free production technologies, recycling of industrial waste. The mechanism of interphase interaction in the mica-glass system is difficult to explain [1].
The first attempt to dissolve mica in glass during the production of the micalex was made by Fedoseev. However, his method was imperfect. The newly formed phase was not described. No interphase interaction products were identified. It is reasonable to believe that dielectric properties, chemical, thermal stability, and mechanical strength depend on the mica-glass interface and its composition [2].

2. Materials and methods
The research aims to study contact interaction at the mica-glass interface. To study this phenomenon, 33 types of mica from various deposits were selected. These are phlogopites of the Aldan, Elkonka, Timpton, Slyudyansky, Kovdor and Aryabilov mica deposits. Aluminum borosilicate glass was used as wetting fluid.

Chemical composition of glass and phlogopites was studied. The experiments were conducted at room and mica decomposition temperatures. For phlogopites, the latter one is 800°C. For the temperature dependence of the wetting angle on temperature intervals \( t_f - t_i = \Delta t \) corresponding to angles \( \theta_i = 90^\circ \) and \( \theta_i = 90^\circ \) were identified. They varied in the range of \( -\Delta t, t_i \) and \( t_f \) depending on
the chemical composition of the mica support. The samples with the largest values were studied to analyze the mica-glass composition production technology. [3].

According to the literature data, the acidic oxides $SiO_2, TiO_2, Fe_2O_3$ are easier to wet with sodium borosilicate glass than the basic oxides $CaO, MgO, Al_2O_3$ [4]. It can be assumed that the use of aluminum borosilicate glass for mica wetting is similar. Since mica and glass have ionic conductivity, an increase in temperature causes chemical wetting and mica dissolution in glass associated with structural transformations which lead to glass-ceramic composition formation. The mica-glass relationship depends on [5]. To identify the influence of oxides on the wetting temperature range, phlogopites from Slyudyanka (S - 3, S - 8, S - 11), Ust-Tyungere (U-T-1), Elkonka (E - 22, E - 24), Kovdor (K - 28) with the largest temperature range $\Delta t$ were selected. The statistical mathematical model was developed. The percentage content of acidic $SiO_2, TiO_2, Fe_2O_3$ oxides were summed up similar to the basic $CaO, MgO, Al_2O_3$ oxides.

3. Results and analysis

Table 1. The chemical composition of phlogopites with the largest temperature range of glass softening on their surface.

|            | Slyudyanka S - 5 | Ust-Tyungere U - T - 1 | Slyudyanka S - 11 | Slyudyanka S - 3 | Elkonka E - 22 | Kovdor K - 28 | Slyudyanka S - 8 | Elkonka E - 24 |
|------------|------------------|------------------------|-------------------|-----------------|----------------|---------------|------------------|----------------|
| $SiO_2$    | 39,80            | 39,43                  | 38,70             | 38,86           | 37,71          | 38,79         | 38,70            | 37,79          |
| $TiO_2$    | 0,84             | 0,44                   | 0,86              | 1,30            | 0,69           | 0,72          | 1,83             | 0,63           |
| $Al_2O_3$  | 15,75            | 15,80                  | 16,47             | 17,2            | 16,95          | 14,90         | 15,45            | 17,0           |
| $Fe_2O_3$  | 0,89             | 1,90                   | 1,00              | 0,13            | 2,80           | 3,07          | 1,23             | 3,41           |
| $FeO$      | 1,40             | 0,73                   | 4,09              | 1,58            | 4,30           | 3,67          | 5,04             | 3,86           |
| $MnO$      | 0,04             | 0,05                   | 0,66              | 0,07            | 0,07           | 0,05          | 0,05             | 0,07           |
| $MgO$      | 25,70            | 25,14                  | 23,83             | 24,61           | 22,20          | 24,37         | 22,51            | 21,95          |
| $CaO$      | -                | 0,17                   | -                 | -               | 0,20           | 0,09          | -                | 0,13           |
| $Na_2O$    | 0,37             | 0,75                   | 0,42              | 0,52            | 0,75           | 0,61          | 0,31             | 0,65           |
| $K_2O$     | 10,33            | 9,78                   | 9,90              | 9,71            | 9,89           | 9,51          | 9,93             | 9,68           |
| $H_2O^-$   | -                | 0,02                   | 0,15              | 0,01            | 0,02           | 0,02          | 0,8              | 0,07           |
| $H_2O^+$   | 2,70             | 2,60                   | 2,79              | 1,98            | 2,65           | 3,55          | 2,95             | 2,90           |
| $BaO$      | 0,70             | 0,93                   | 0,60              | 2,80            | 0,74           | 0,66          | 0,66             | 0,72           |
| $F$        | 2,33             | 3,30                   | 2,41              | 2,4             | 1,25           | 0,34          | 2,07             | 1,35           |
| $t_i - t_f$| 200              | 200                    | 185               | 180             | 180            | 175           | 175              | 170           |
### Table 2. The number of acidic and basic oxides in phlogopites from different deposits.

| Deposit          | Slyudyanka | Slyudyanka | Ust-Tuyngere | Slyudyanka | Elkonka | Elkonka | Elkonka | Elkonka | Kovdor |
|------------------|------------|------------|--------------|------------|---------|---------|---------|---------|--------|
|                  |            |            |              |            | E = 22  | E = 24  | E = 24  | E = 24  | K = 28  |
| **The total content of acidic oxides** | 41,53      | 40,56      | 41,71        | 41,81      | 41,20   | 41,76   | 41,81   | 40,60   |         |
| **The total content of acidic oxides** | 41,45      | 40,30      | 41,11        | 40,29      | 39,25   | 38,96   | 39,08   | 38,11   |         |

To derive the regularity of the influence of the content of oxides on the temperature range of phlogopites, a second-order mathematical model was developed. It takes into account both individual and complex effects of the content of basic and acidic oxides:

$$ T = A_1 + A_2 X_k + A_3 X_o + A_4 X_k X_o + A_5 X_k^2 + A_6 X_o^2 + A_7 X_k X_o^2 + A_8 X_k^2 X_o $$  (1)

where $T$ – the temperature range for phlogopites, $X_k, X_o$ – the number of oxidic and basic oxides, $A_1 - A_8$ - polynomial coefficients.

To determine the polynomial coefficient $A$, the following system of equations was developed:

$$ T_i = A_1 + A_2 X_{ki} + A_3 X_{oi} + A_4 X_{ki}X_{oi} + A_5 X_{ki}^2 + A_6 X_{oi}^2 + A_7 X_{ki}X_{oi}^2 + A_8 X_{ki}^2 X_{oi} $$  (2)

where $1, 2, ..., 8$ - the number of the phlogopite deposit, $T_i$ – the temperature range for phlogopite from the first deposit, $X_{ki}, X_{oi}$ - the number of acidic and basic oxides in phlogopites from the $i$-th deposit, $A_1 - A_8$ - polynomial coefficients.

After the substitution of the experimental data from Table 2, the system of equations is as follows:

$$ A_1 + A_2 41,53 + A_3 41,45 + A_4 41,53 · 41,45 + A_5 41,53^2 + A_6 41,45^2 + A_7 41,53 · 41,45 + A_8 41,53 · 41,45^2 = 200 $$

$$ A_1 + A_2 40,56 + A_3 40,30 + A_4 40,56 · 40,31 + A_5 40,56^2 + A_6 40,30^2 + A_7 40,56 · 40,30 + A_8 40,56 · 40,30^2 = 200 $$

$$ A_1 + A_2 41,71 + A_3 41,11 + A_4 41,11 + A_5 41,71^2 + A_6 41,11^2 + A_7 41,71 · 41,11 + A_8 41,71 · 41,11^2 = 185 $$

$$ A_1 + A_2 41,81 + A_3 40,29 + A_4 41,81 · 40,29 + A_5 41,81^2 + A_6 40,29^2 + A_7 40,29 · 40,29 + A_8 41,81 · 40,29^2 = 180 $$

$$ A_1 + A_2 41,20 + A_3 39,25 + A_4 41,20 · 39,25 + A_5 41,20^2 + A_6 39,25^2 + A_7 41,20 · 39,25 + A_8 41,20 · 39,25^2 = 180 $$

$$ A_1 + A_2 41,76 + A_3 38,96 + A_4 41,76 · 38,96 + A_5 41,76^2 + A_6 38,96^2 + A_7 41,76 · 38,96 + A_8 41,76 · 38,96 = 175 $$

$$ A_1 + A_2 41,81 + A_3 39,08 + A_4 41,81 · 39,08 + A_5 41,81^2 + A_6 39,08^2 + A_7 41,81 · 39,08 + A_8 41,81 · 39,08 = 170 $$

$$ A_1 + A_2 40,60 + A_3 38,11 + A_4 40,60 · 38,11 + A_5 40,60^2 + A_6 38,11^2 + A_7 40,60 · 38,11 + A_8 40,60 · 38,11 = 170 $$

IBM-oriented Turbo-Pascal software was developed to solve the system of equations [6]. Calculation errors and simulation accuracy checks can be set [7]. The software implements the Newton method for solving non-linear systems of equations [8].

The mathematical model can be written as

$$ T = 3,64X_o^3X_k + 5,88 · 10^4X_o - 7,02 · 10^3X_kX_o - $$

$$ -5,38 · 10^5X_k^2 + 2,16 · 10^3X_o^2X_k + 134X_kX_o^2 - 5,82 · 10^6 $$  (3)

After the transformations, the formula can be written as
4. Discussion

Formula (3) shows that the quantitative content of acidic and basic oxides $X_k$ has the greatest influence on the temperature interval $\Delta t$, the influence of the difference between the content of acidic and basic oxides is less significant. The influence of the square terms of formula (4) is even less significant. Thus, an increase in the content of acidic oxides in phlogopites significantly increases the temperature range. The difference between the content of acidic and basic oxides is significant as well. For example, a decrease in $X_k - X_o$ increases $\Delta t$, while an increase in the difference between the percentage content of acidic and basic oxides decrease the temperature range $\Delta t$ which confirms the suggested hypothesis.

A method for waste-free use of cullet has been developed. It can be applied in the production of micaceous composite. The use of a technology for producing glass-based composites was justified. The composite materials are used for producing shells of Sicoma ceramic heaters. In order to utilize industrial waste of the glass industry, the authors developed a method for producing economical heaters. Their component is glass produced on the basis of glass production wastes with the addition of boric acid, $H_3BO_3$, barium nitrate $H_3BO_3$, and sodium silicate fluoride $Na_2SiF_6$, potassium nitrate $KNO_3$, small-sized mica muscovite. Waste was crushed by a jaw crusher in order to obtain uniform pieces of glass waste.

The crushing process occurred in the with a movable cheek and a vertical connecting rod. It ensured uninterrupted yield of crushed glass. It was determined that crushing can be completed after the first crushing stage, since at the end of the process it was possible to obtain glass with a size of up to 30 mm. Glass is a brittle material, its amorphous structure has microscopic cracks[9]. With a relatively small increase in external influences, density of microcracks increases. The cracks and pores increase in size, combine into one or several large conglomirates and tear the pieces of glass apart breaking the structure. During the expansion of cracks, stresses become concentrated. As a result, glass is destroyed at a small medium voltage value. Explosion-like destruction of the form is caused by bulk stresses. SHDP 1,6x2,5 was used [10].

Crushed glass waste was supplied to the vibrating screen for segregation of the material. The accelerations vary from zero to maximum according to the sinusoidal law. The size of the screened material was 30 mm. The product was separated in order to eliminate metallic inclusions. For magnetic separation, a hanging magnet installed above the conveyor belt was used. After crushing, screening and magnetic separation, the glass waste was mixed with chemical additives (40% glass and 60% additives) [11]. The mixing process was carried out in a pot rotating glass furnace, with a capacity of 150 liters. The glass flow is a component that contributes to the liquid phase which “absorbs” chemical additives. These additives were selected according to their effect on the properties of glass [12]. Boric acid and barium nitrate were used to improve electrical characteristics, namely: a dielectric constant and dielectric loss angle. Boric acid $H_3BO_3$ introduced into glass, decomposes into boric anhydride, which is an accelerator of glass melting. Sodium silicofluoride $Na_2SiF_6$ causes a liquid phase at lower temperatures. In this regard, silica formation and electrical conductivity of the charge increase. Nitric acid $KNO_3$ is introduced into the glass to reduce crystallization. All compounds introduced reduce the glass softening temperature [13]. The table shows the chemical composition of the cullet of silicate glass used in the experiment. Percentage ratios were selected taking into account $SiO_2$ as the most high-temperature oxide. The calculation was carried out for 100% of the mass [14].

\[
T = 4,23 \cdot 10^5 X_k - 5,88 \cdot 10^4 (X_k - X_o) - 7,02 \cdot 10^4 X_k X_o - 5,38 \cdot 10^3 X_o^2 + \\
+ 2,16 \cdot 10^3 X_o^2 - 52 X_k^2 X_o + 134 X_k X_o^2 - 5,82 \cdot 10^6
\]
### Table 3. Chemical composition of broken glass.

| Oxides | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Na₂O | B₂O | SiO₂ |
|--------|------|-------|-------|-----|-----|------|-----|------|
| %      | 74   | 0,5   | 0,01  | 6,5 | 2   | 14   | 2,5 | 0,5  |

As a percentage, it was 40% cullet, 14.4% potassium nitrate $KNO_3$, 16.8% barium nitrate $Ba(NO_3)_2$, 19.2% boric acid $H_3BO_3$, and 9.6% sodium silicofluoride $Na_2SiF_6$.

The process of glass production can be divided into the following stages:

**Stage 1 - silicate formation.**

Cullet with additives underwent a number of physical and chemical changes; in the charge, the main reactions in the solid state ended, most of the gaseous products evaporated. By the end of this stage, the charge turned into a caked mass. Silicate is formed at a temperature of 800-900 °C.

**Stage 2 - glass formation.**

With further heating, the sintered mass begins to melt. Silicates and silica are melting simultaneously. By the end of this stage, the mass becomes transparent and heterogeneous. Glass is formed at a temperature of 1150-1200 °C. The following reactions occur at these two stages:

\[
2KNO_3 \rightarrow K_2O + 2NO_2 + \frac{1}{2}O_2 \quad (5)
\]

\[
Ba(NO_3)_2 \rightarrow BaO + NO_2 \quad (6)
\]

\[
4H_3BO_3 \rightarrow 3H_2O + 2BaO_3 \quad (7)
\]

\[
Na_2SiF_6 + \frac{1}{2}O_2 \rightarrow Na_2O + SiF_4 + F_2 \quad (8)
\]

**Stage 3 - homogenization.**

The glass mass was kept at high temperatures (1400-1500°C) to equalize its chemical composition.

**Stage 4 - studs cooling**

The temperature of the glass melt was reduced by 200-300 °C to make glass homogenous.

The purpose of calculation of the crushing scheme is to determine the mass and yield of the products obtained the size of the product. Wastes of the glass industry were used [15]. To calculate the size, it is necessary to know the increment of the calculation class based on the assumption that grains whose size is larger than the width of the crusher are the same, regardless of the presence of grains which are smaller than the width of the feed gap [16]. The largest grain size is larger than or equal to the width of the crusher's discharge gap $d \geq i$ [17]. The increment in the class under consideration will be

\[
\Delta P_{w-d} = P_{n, b}m^{-d} \quad (at d \geq 1) \quad (9)
\]

where $b$ is the content of the design class, mm; $n$ is the index showing the number of the product entering the crusher; $m$ is the index indicating the number of the crushing operation [18].

### 5. Conclusion

The mica wetting mechanism using glass was developed. It explains the flow of a glass layer over the crystal surface and indicates the wetting process.

The wetting of phlogopites from various deposits using aluminosilicate glass was studied. It was revealed that not all micas are equally wetted with the same glass. There are differences in wetting intervals and initial temperatures of interaction.

It has been identified that the mica wetting depends on the chemical composition of the crystalline substance. The quantitative content of acidic oxides and the difference between the content of acidic and basic oxides have the greatest influence on the temperature interval of wetting.
As a result of the research, glass of a new chemical composition has been produced. Due to the neutralization of silicon oxide, it has a lower softening temperature. The maximum yield of the particle size of -0.2 + 0.1 equal to 89.9% was found for the minimum grinding time (1.5 hours). The specific surface of the particles approaches the specific surface of the ground glass powder.

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