Complex research of molybdenum ore tailings

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Abstract. The paper considers the processes of plasma chemical synthesis of silicate melts produced from quartz-feldspar raw materials with a view to obtain new construction materials having the advanced functional performance. Presented results illustrate physicochemical research findings (X-ray diffraction analysis, infrared spectroscopy, thermal analysis) related to quartz-feldspar raw materials and melts produced from them.

1. Introduction
Plasma technologies used in production of high-temperature silicate melts provide consistently high temperatures converting initial silicate materials to a liquefied state. Presently, plasma treatment is widely used for high-temperature melts obtained from bottom ash waste generated by thermal power plants. A silica modulus of these wastes is notably higher than that of raw materials (basalt) which are traditionally used to obtain silicate melts in producing mineral fibers. A subsequent research carried out in this field implies using raw materials obtained from beneficiation of different kinds of ores such as feldspar tailings, a chemical composition of which allows converting them into silicate melt using low-temperature plasma (LTP).

A content of quartz-feldspar raw materials obtained from molybdenum ore beneficiation ranges from 90 to 99%. A great deal of raw materials is accumulated in waste dumps of ore mining and processing enterprises [1-3]. A chemical composition of the raw material under study contains 62% of SiO₂ that corresponds to that of industrial glass and can be used to synthesize silicate melts including those obtained in production of mineral fiber [4-5]. In order to produce high-quality mineral fiber, the melt should possess a uniform chemical composition. Traditional high-temperature melt technologies result in increased energy consumption due to a long-term thermal effect the raw materials are exposed to.

2. Experimental procedure
In existing electric-plasma installations fine particle top feeding is used to supply raw materials to plasma jet projected in a melting furnace [6]. However, according to experiments, in this case many fine particles do not participate in the process of melting. To avoid this problem, an electro-plasma apparatus with side feeding was invented which includes a worm feeder for raw material to be supplied to a zone of silicate melt formation.

Figure 1 presents color photography and a schematic view of this experimental electro-plasma apparatus intended for mineral fiber production using refractory silicate-based materials. This apparatus comprises such principal components as plasma torch, melting furnace, worm feeder, and forming hood.
Operation of the electric-plasma apparatus is based on the interaction between highly concentrated plasma flows and a raw material. Plasma torch is placed in melting furnace equipped with pouring hole. Graphite electrode is installed in the bottom of melting furnace and connected with the positive pole of DC power supply (anode), while the plasma torch is connected with its negative pole (cathode).

Once silicate melt reaches the level of the pouring hole, it will be discharged through it into forming hood. By means of batcher mounted into worm feeder driven by electric drive, powder raw material is fed to the melting furnace. Plasma jet is projecting between plasma torch and graphite electrode. A raw material starts to melt and homogenize under a strong thermal effect (3000-5000 °C). The raw material particles are then mixed with a high-temperature silicate melt and melted uniformly. The melt formed in the forming hood is converted into mineral fibers. Furthermore, this method of feeding of raw materials makes possible to avoid a loss of fine particles blowing by a LTP jet. This method provides a uniformity and viscosity of low melt within the whole volume of the melting furnace [7].

3. Results and discussion
In order to study processes which occur at high-temperature melt synthesis, physicochemical research included X-ray diffraction (XRD) analysis and infrared spectroscopy.

XRD analysis was carried out by DRON-4-07 diffractometer which was modified for digital signal processing. Measurements were conducted using copper radiation ($K_{\alpha}$) and Bragg-Brentano X-ray optical scheme. Specifications for the DRON-4-07 included 0.02° scanning step; 20 – 92° range for angles to be scanned; 30 kV voltage; and 25 mA current. Powder tailing wastes were studied in the initial and amorphous states. Amorphous state was achieved as a result of the LTP flows.

Figures 2 and 3 show theoretical and experimental diffraction patterns for different states of ore tailings. As shown in these Figures, a good agreement between theoretical and experimental diffraction patterns is observed.
Figure 2. Numerical phase analysis of tailing wastes in initial state:

a) experimental (1); theoretical XRD pattern (2); difference between theoretical and experimental XRD patterns (3);
b) theoretical XRD patterns for phases: O$_2$Si (1); O$_{22}$Al$_{20}$ (2); O$_6$Si$_6$ (3).

Figure 3. Numerical phase analysis of tailing wastes in amorphous state:

a) theoretical (1); experimental XRD pattern (2); difference between theoretical and experimental XRD patterns (3);
b) phases: O$_2$Si (1); O$_{22}$Al$_{20}$ (2); O$_{192}$Si$_{96}$ (3).

As shown in Figure 2a, the main phases for molybdenum ore tailings are silica and feldspar. XRD analysis has shown that the melt product has no spikes typical for Figure 3a that indicates the absence of a crystalline structure, i.e. the melt becomes X-ray amorphous upon its cooling.

Infrared spectroscopy of ore mining wastes was conducted before and after plasma chemical synthesis. Fourier transform infrared (FTIR) spectra were detected with Nicolet 6700 infrared spectroscopy manufactured by Thermo Nicolet Corporation (USA). Results of spectroscopy are presented in Figure 4 for silica alumina raw materials and aluminosilicate glass.

Figure 4. FTIR spectra: 1 – molybdenum ore tailings; 2 – melt product.
The main base unit of feldspar is a tetrahedral alumina-silicon-oxygen framework comprising \([\text{SiO}_4]^{4-}\) and \([\text{AlO}_4]^{5-}\). These tetrahedrons are transformed into chains which then form polyhedrons whose cavities are filled with metal cations (K, Na, Ca, etc.) and H\(_2\)O molecules, and neutralize a negative charge of the framework occurring at substitution of Si\(^{4+}\) by Al\(^{3+}\). Infrared spectrum typical for feldspars (Figure 4, curve 1) is sharply changed after plasma treatment. The structure-sensitive band maximum displacement is observed towards ordering of the silicon-oxygen framework. The maximum 1008.1 cm\(^{-1}\) of the antisymmetric stretching absorption band shows a shift to the red resulting in 1061.7 cm\(^{-1}\) maximum. At the same time, the maximum 762.5 cm\(^{-1}\) of the symmetric stretching absorption band shows a shift to the blue resulting in 787.5 cm\(^{-1}\) maximum. A clear deformation band is then observed with 456.9 cm\(^{-1}\) maximum. Discrete stretching absorption bands lying between 400 and 700 cm\(^{-1}\) almost completely vanish due to the intensive vaporization of low melting components and aluminosilicates. As a result, O\(_2\)Si concentration in the melt increases that leads, in its turn, to a structural ordering of the silicon-oxygen framework (Figure 4, curve 2).

The thermal gravimetric analysis/differential thermal analysis (TGA/DTA) was carried out by Simultaneous Thermal Analyzer Netzsch STA 449 C Jupiter (Germany) at heating rate of 10 °C/min in air atmosphere.

Being a natural material, feldspar contains components comprising hydroxyl and carbonate groups. Thermal analysis has shown the presence of these thermally unstable compounds. TGA/DTA measurements (Figure 5) show that the initial feldspar sample has a gradual weight loss within the temperature range of 25–1000 °C.

Figure 5. TGA curves of the initial feldspar sample.

DTA measurement as shown in Figure 1, gives grounds to suppose that the initial feldspar sample has up to 0.16 wt.% crystallization water with dehydration temperature of 117.7 °C.

Thermal analysis of plasma-treated feldspar shows its stability as shown in Figure 6. The insignificant weight growth is observed (0.35 wt.%) within the indicated temperature range. The feldspar sample is characterized by a thermodynamic stability represented by the differential scanning calorimetry (DSC) curve and a chemical inertness in air atmosphere within the temperature range of 25–1000 °C. Plasma treatment results in decay of thermally unstable impurities in the feldspar sample.
4. Conclusions
Thus, physicochemical research findings have shown that plasma chemical synthesis of silicate melts produced from quartz-feldspar raw materials using low-temperature plasma allows obtaining an ordered system of aluminosilicate glass. Melt products are characterized by homogeneity and ordering, i.e. the process of melting has provided a complete melt homogenization. Therefore, it is possible to produce glass-based construction materials by plasma chemical technique employed for melting aluminasilicates, including mineral fibers possessing the improved service properties (chemical, thermal, and water resistant), mechanical-and-physical and thermal properties, and durability. This is connected with the amount of aluminosilicate glasses $\text{SiO}_2$ (62%) and $\text{Al}_2\text{O}_3$ (15%) when the index of mineral fiber acidity has range between 9 ~ 12.

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Figure 6. TGA curves of the plasma-treated feldspar sample.