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BUILDING MATERIALS TECHNOLOGY USING WASTE

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Abstract: The present paper is devoted to the synthesis of metastable glasses and glass-crystalline materials based on Angren (TPP) ash and slag from fluorite enrichment plants (FEP) are. Composition and technological parameters are shown.

Keywords: glass, glass phase, sintering process, melt, crystallization.

Expansion of industrial and civil construction in our country causes the need to create new and improve the technological and operational properties of existing building materials, including slag-cells.

Slags from Angren TPP are characterized by rather high content of aluminum, calcium and iron oxides. By chemical composition they can be referred to the triple system $CaO-Al_2O_3-SiO_2$. The use of oxide crystallization catalysts for the synthesized compositions of slags is of undoubted practical interest, which is determined by the possibility not only to expand the range of residues with different physical and chemical

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properties but also to increase the stability of the process and cheapen the production of such materials. Besides, it will allow not only to expand the raw material base but also to dispose of wastes, which is of considerable ecological importance/1/.

The purpose of this work is to study the peculiarities of synthesis of glass crystalline materials based on slags from Angren TPP and also to study their technological properties depending on the content of fundamental components and cooking temperature regime.

Chemical composition of Angren TPP slags is as follows (here and hereinafter mass content %): SiO_2 45,07; Al_2O_3 19,84; Fe_2O_3 11,25; CaO 6,51; MgO 0,97; $SO_3$1,27; Na_2O 0,70, K_2O 1,15;, p.p. 7,20.

At present, it is proved practical possibility and economic expediency to use wastes from fluorite enrichment plant (FEP) and ash and slag from TPPs for manufacturing of decorative - facing glass crystal materials in manufacture of which deficient raw materials and expensive glass silencers are usually used.

The choice of these materials is caused by the fact that ashes and slags contain on the average 8-10 % of fuel residues that allows to a lower temperature and accelerates glass transition.

Flotation waste is a finely dispersed silica material formed during processing of fluorite ore by the flotation method. In terms of basic characteristics, the flotation waste is close to natural raw materials used in the production of glass for glass crystalline materials.

During processing, the ore material is affected by flotation agents, which are surface-active substances. As a result, the surface of flotation waste becomes activated /2-3/. This promotes better charge mixing in mixers, ensures high quality of the prepared charge and increases the glass cooking characteristics.

The main stages of the glass-forming process are silicate formation and dissolution of residual silica. The speed of these processes can be significantly increased by replacing quartz sand with flotation waste.

For the synthesis of glasses were prepared blends, varying the content of the initial substances through 10% (here and then the mass content).

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The technology of obtaining glass crystalline materials based on the wastes, as mentioned above, completely corresponds to the generally accepted technological regulations of decorative-facing glass crystalline plates production.

An attempt has been made to use slag as much as possible to obtain glass with satisfactory cooking and production and crystallization properties. Glasses of nine series of compositions of glasses containing 10-90 forests, 90-10 ash and slag were studied. All compositions were boiled in the same conditions at temperature 1200-1250^{0}C. The synthesized glasses had dark brown and black colors that are explained by the content of iron oxides in Fe_2O_3 glass mass 4,56-11,25 %. When glasses with high slag content are boiled, melt viscosity increases. Compositions with 40-60% slag content were well boiled and quickly drained at 1200^{0}C. Crystallization ability of glasses was studied in the temperature range of 800-900^{0}C.

The synthesis of glass crystalline materials is based on a controlled process of glass crystallization. By experimentally setting the temperature dependence of the stationary rate of nucleation, it is possible either to avoid crystallization or to stimulate it purposefully by keeping glass samples in the temperature range near the maximum temperature of nucleation rate.

It is established that all the glasses are boiled at the temperature of 1250-1300^{0}C with a dwell time of 1-2 hours.

The given composition of the glasses corresponded to mass.%: 69 SiO_2; 7,8 Al_2O_3; 0,35-1,56 Fe_2O_3; 3,65 CaO; 0,10 MgO; 12,17,0 Na_2O; 1,85 K_2O; 4,50 CaF_2; 4,00 cryolite.

At the same time, quartz sand was completely excluded from the traditional factory composition and the number of glass crystallization initiators was significantly reduced.

Analysis of the blend showed that the vaporization of glass using fleet waste is more intensive.

To determine crystallization properties, glass samples were heat-treated in an electric furnace at 860^{0}C for 30 minutes.

As per scientists' opinion [1; 2;] propensity of glasses of volume crystallization without deformation at heat treatment, to the formation of glass crystallite structure, is defined by the chemical composition of initial raw materials and introduction of initiators of crystallization.

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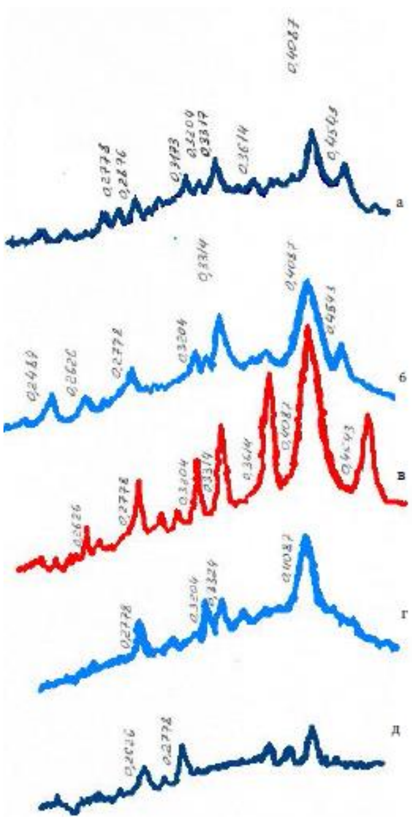
Liquidation phenomena contribute to obtaining glass crystalline structures, and glass crystals can be obtained without the additional introduction of crystallization initiators. As the latter, metals are introduced into the glass composition. Metal catalysts in the melt in atomic state form aggregates. Catalysts such as titanium oxide and fluorides promote the development of metastable liquation during heat treatment. The introduction of Fe_2O_3 in the alloys forms magnetite Fe_2O_4 which promotes the development of metastable liquation during heat treatment.

The phase composition of crystallized glasses was investigated by the methods of differential thermal analysis, X-ray phase analysis (XPA).



X-ray crystallography of crystallized glasses showed that the main crystallized phase of these glasses is β-crystobolite, the difference only in intensity and rate of formation of crystalline phases (Fig-1). The X-ray crystallogram of crystalline samples containing 50-70% of the floatation waste, at 850ºC, showed intensive diffraction maxima corresponding to anorthite, which, judging by their intensity, is the predominant crystalline phase.

Fig. 1. X-ray diffraction diagram of glass crystals.

a - at 700^0C

b - at 750^0C

c - at 850^0C

d - at 900^0C

e - at 950^0C

It is characteristic that as the temperature rises above 900ºC, the crystalline phases decrease. This is evidenced by the reduction of diffraction peaks on X-ray samples.

In connection with the appearance of the liquid phase above 900^0C, the intensity of lines of all compounds decreases, which indicates their dissolution in the liquid phase formed at high temperature.

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Glass crystallites based on the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system are highly wear-resistant. The main crystalline phases of this system are anorthite $CaOAl_2O_32SiO_2$ and bollastonite CaO-SiO2, magnetite Fe_2O_4 (Fig.1). The significant advantage of glass-crystalline materials produced on the basis of these systems is the possibility of using slags, industrial wastes of Angren TPP.

The results of X-ray phase analysis were confirmed by petrographic analysis data. The petrographic examination of crystallized glasses at 850^0C showed that the microstructure is not homogeneous. (Fig.2).

Needle grains of waveastonite with $n_g = 1.589$, n_p +1.576 are often found among the main mass formed by β-crystalline glass and anorthite with refractive index $n_g = 1.65$, n_p +1.63. In Fig. 2, the areas corresponding to the above-mentioned crystal phases are seen.

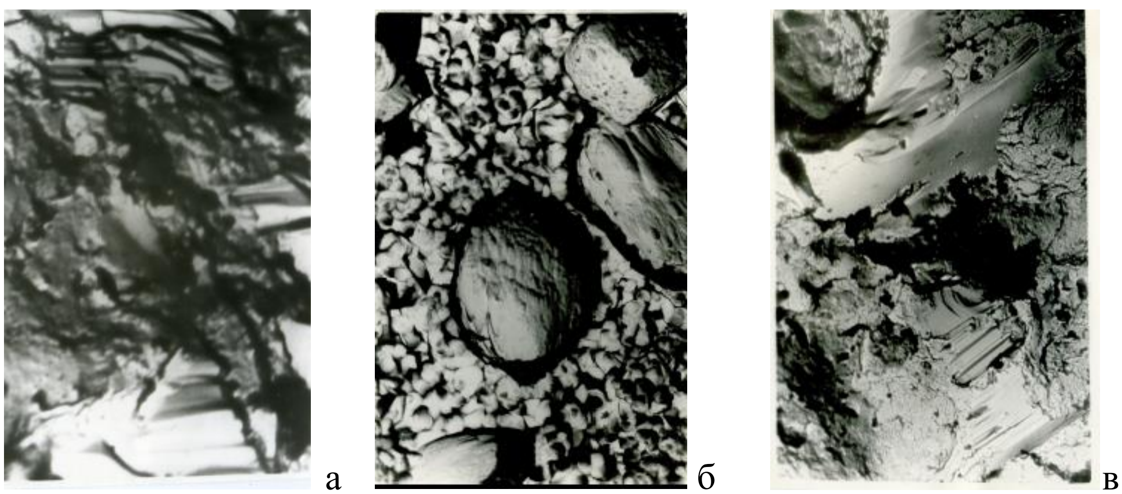

Fig.2. Electron-microscopic images of samples (x3400);

a) T-750^0S; b) T-850^0S; c) T-900^0S.

The practice of using fluoride compounds shows a significant influence on the glass melting processes, glass formation and structure of the finished products. Due to the positive effect of fluorine ions, the volume crystallization of glasses occurs when the content of float waste (which contains up to 5% CaF_2) increases. The crystallization abilities of glasses depending on temperature are given below.

Also reactions, silicate formation in case of use of floatwastes end at lower temperatures (temperature decrease on the average on 100^oC) that leads to the earlier appearance of a liquid phase and the further dissolution of quartz. In general, this speeds up the glass-forming process.

The resulting glass crystallites have a smooth surface. The structure of crystallized materials of the vitreous phase, on the surface of which the formation of droplet-shaped phases is observed, is CaF_2.

Increased crystallization of anorite from the amorphous phase (β-crystalline-bolite, wollastonite) contributes to the creation of a robust structural framework that provides sufficient strength of glass crystallite.

Solidification Temperature T 0C							
650	**700**	**750**	**800**	**850**	**900**	**950**	**100**
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**

Fig.3. Crystallization ability of glasses depending on temperature.

1 - no crystallization;
2 - surface opalescence;
3 - crystalline thin film;
4 - crystalline crust;
5 - bulk crystallization;
6 - the beginning of crystals melting;
7 - the meltdown of crystals;
8 - the complete meltdown of crystals.

In terms of essential properties, the obtained products were not inferior to the production ones and had higher density indices, thermal coefficient of linear expansion, and low water absorption values.

Chemical resistance of crushed crystallized materials was determined in boiling solutions of sulfuric acid of different concentrations (25 and 75%) within 2 hours. It was established that the relative masses of samples after the test were 99.1 and 99.5% respectively at the initial 50g hinge.

The stability in relation to alkaline media (2 n. NaOH solution) was investigated. The choice of alkaline reagents is explained by the fact that most known ashes and slags

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have increased chemical resistance to acidic media. Therefore, resistance to alkaline aggressive media is the most indicative.

It is established that crystallized materials in comparison with initial glasses differ in the increased chemical firmness to the accepted reagents. The mass loss of material after boiling in 2 n. NaOH solution did not exceed 0.8 - 1%. It is natural that increased chemical resistance of crystallized materials is the result of formation of a crystalline phase in them. At the same time, chemical resistance depends on the total amount of the crystalline phase. For example, for a material containing more ash and slag and heat-treated at 850^0C, weight loss in 2 n. NaOH solution is 0,86 %, and for a material with less ash and slag content and heat-treated at the same temperature - 1,05 %.

Thus, waste from the fluorite processing plant and ash and slag can be used for the synthesis of glass and glass crystalline materials.

This will allow not only to expand the raw material base but also to dispose of waste, which is of great economic and environmental importance.

Thus, reactions of silicate formation in case of use of floatation waste ends at lower temperatures (temperature decrease on the average by 100ºC) that leads to the earlier appearance of a liquid phase and further dissolution of quartz. In general, this speeds up the glass-forming process.

The main stages of the glass-formation process are silicate formation and dissolution of residual silica. The speed of these processes can be significantly increased by replacing quartz sand with floatation waste.

Thus, the possibility of application of ash and slag from TPPs and float waste (FW) for glass silica production without changing technological modes of production is established.

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