GLASS CRYSTAL MATERIALS MADE FROM MINERAL AND TECHNOCENIC FEEDSTOCK FROM KARELIA

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Facing and decorative glass crystal materials were developed from mineral feedstock and technogenic wastes. The effect of the components present in the mineral feedstock in liquidation and crystallization of the glasses was investigated. The materials obtained can be used in construction for facing walls.

Silicate rocks and industrial technogenic wastes are widely used to make opacified glass and glass crystal facing and decorative articles. Such raw materials usually have a heterogeneous composition with predominance of one or two components that will significantly affect crystallization and the physicomechanical properties of the articles. Such components include the iron, sodium, and potassium oxides present in wastes from concentration of feldspar rocks. In addition, such components as chromium, manganese, etc., present in small amounts in chromite or manganese ore wastes, and phosphoric anhydride and fluorine contained in apatite concentrate initiate crystallization of glass in production of glass crystal materials [1]. The compositions of the glasses obtained from mining industry wastes have been investigated very little.

We studied the effect of the components present in mineral and technogenic feedstock on liquidation and crystallization processes and consequently on the structure and properties of glass crystal materials.

Glass crystal materials were made from local readily available feedstock: Tikshozerskoe carbonatite, quartz-feldspar rock concentration wastes — Kostomuksha hällefintas, apatite concentrate, wastes from concentration of Aganozerskoe chromite (Pudozhsky Region). The chemical composition of the raw materials is shown in Table 1.

The mineral composition of the Tikshozerskoe carbonatites was (%): 70 – 75 calcite, 9 – 11 apatite, 4 – 8 micas, 4 – 5 magnetite. The maximum fluctuations of the P2O5 content were 0.5 – 12.6%. The average P2O5 content by deposit was 4.3%. The variations in the calcium content, established with the value of CO2, varied from 4 to 35% (30% on aver-

### TABLE 1

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>P2O5</th>
<th>MgO</th>
<th>CaO</th>
<th>MnO</th>
<th>Na,O</th>
<th>K2O</th>
<th>Calcination loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonatite</td>
<td>4.41</td>
<td>0.13</td>
<td>0.85</td>
<td>5.82</td>
<td>4.15</td>
<td>3.37</td>
<td>47.00</td>
<td>0.18</td>
<td>0.15</td>
<td>0.49</td>
<td>33.45</td>
</tr>
<tr>
<td>Hällefintas concentration wastes</td>
<td>61.20</td>
<td>0.28</td>
<td>16.60</td>
<td>8.70</td>
<td>–</td>
<td>2.50</td>
<td>2.80</td>
<td>0.14</td>
<td>3.82</td>
<td>1.55</td>
<td>2.10</td>
</tr>
<tr>
<td>Apatite concentrate*</td>
<td>0.54</td>
<td>–</td>
<td>0.09</td>
<td>0.02</td>
<td>39.10</td>
<td>0.01</td>
<td>50.90</td>
<td>–</td>
<td>1.25</td>
<td>–</td>
<td>5.61</td>
</tr>
<tr>
<td>Chromite ore wastes</td>
<td>31.90</td>
<td>&lt; 0.01</td>
<td>0.39</td>
<td>15.25</td>
<td>18.50</td>
<td>22.60</td>
<td>5.72</td>
<td>0.10</td>
<td>0.18</td>
<td>0.01</td>
<td>3.82</td>
</tr>
</tbody>
</table>

* The apatite concentrate contained 2.48% F.

** Cr2O3.
The wastest from concentration of hälleflinta are formed with the following ratio of components (%): 61.50 – 66.00 SiO2, 0.05 – 0.15 TiO2, 14.50 – 17.00 Al2O3, 0.50 – 2.00 Fe2O3, 0.50 – 2.00 FeO, 2.50 – 8.00 MgO, 5.00 – 8.00 CaO, 4.00 – 5.50 Na2O, 0.35 – 1.00 K2O, 0.05 – 3.00 MnO, 0.50 – 2.00 Cr2O3 [3].

The effect of the components present in the mineral feedstock: P2O5, F, Cr2O3, MnO, and Fe2O3, was investigated to stimulate bulk crystallization and liqation of the glasses. The combined effect of Cr2O3, MnO, and Fe2O3 in addition to chromite and manganese ore wastes was effective for microcrystallization of the glasses based on hälleflinta concentration wastes. These glasses crystallized in bulk during firing, since crystal growth took place at a relatively large number of crystallization centers uniformly distributed over the entire volume of the glass. A large amount of iron oxide in the wastes increased the crystallization temperature range (800 – 1000°C) and ensured formation of a more homogeneous fine crystal structure. The chromium oxide present in chromite ore wastes played the role of an initiating additive that caused formation of chromium-oxide groups which separated from the glass in the form of a crystalline phase.

According to the findings of x-ray phase analysis, the crystalline phase of glass made from hälleflinta concentration wastes is represented by the spinel (Mn, Fe) · (Cr, Al)2O4. The mineral composition of hälleflinta intensifies glass formation due to the low-melting eutectics formed by finely dispersed quartz and albite, decreasing the crystallization temperature of the glasses.

The heat treatment regime for the glasses was selected based on the DTA data. The temperature of the first stage of heat treatment (possible formation of crystallization centers) was equal to 600°C with holding for 1 h. Heat treatment in the second stage (crystallization of the basic mineral phase) was conducted at 850 and 950°C with holding for 1–2 h. Tiles made from this glass had a monochromatic shiny surface and after second-stage heat treatment, a glass crystal material with a surface simulating natural stone of the granite type was obtained.

Glasses with carbonatite and apatite concentrate consist of a crystalline phase represented by β-wollastonite and a phosphate-silicate glass phase. Tiles made of opacified glass based on carbonatite have a variable color scale: navy blue and dark blue overflows on a light beige-light blue background.

The studies of the microstructure of these glass crystal materials by small-angle x-ray scattering (Guignet method) were conducted at the Kuusinen Petrozavodsk State University. Three size fractions of inhomogeneities — pores — were found in glasses with different initiating additives (Å): (150 – 200) ± 10, 50 ± 5, and 6 ± 2. Oblique pictures of the samples with respect to the primary beam showed that the form of the electron density inhomogeneities changed from equiaxial in the initial glasses to nonequiaxial in the glasses undergoing heat treatment. This type of change in the morphology of the glasses in heat treatment took place as a result of their crystallization and formation of β-wollastonite phases in glasses of the carbonatite and (Mn, Fe) · (Cr, Al)2O4 spinel type based on hälleflinta concentration wastes, which appeared as a result of annealing at 600 – 650°C. The reflections from β-wollastonite and the spinel were characterized by a significant integral half-width, which indicates their fine dispersion.