

COATINGS. ENAMELS

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BEHAVIOR OF COPPER OXIDE IN SILICOBORATE GLAZED GLASSES

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Copper-containing glazed glasses in the $B_2O_5 - SiO_2 - Al_2O_3 - CaO - CuO$ system with a copper oxide molar content of 5 to 25%, added during synthesis of the glasses, was investigated. The glasses with a minimum content of 15% B_2O and 15–25% CuO crystallized during processing with separation of fine-needle CuO crystals. However, all glasses formed a good glaze coating when applied on ceramics at temperatures of 900–1000°C. The CuO crystals totally dissolved in the melt.

The basic application of copper (II) oxide in silicate glasses is to play the role of a pigment. As a function of the concentration and composition of the glass, copper (II) oxide colors the glass light blue or blue-green, providing ionic coloration. Copper (I) oxide does not color glass and is not used as a pigment. In the presence of the reducing agents SnO_2 and $KHC_4H_4O_6$, copper oxide is easily reduced to metallic copper and turns the glass a dark cherry color (colloidal coloration) after induction.

Silicate and silicoborate glasses containing copper oxide are basically used as colored high-quality glasses and glazes in which the CuO content usually does not exceed 5–7%² [1, 2]. The glaze of the following composition can be cited as an example (%): 37.20–43.40 SiO_2 , 15.28–17.74 B_2O_3 , 8.33–12.48 Al_2O_3 , 1.29–1.66 K_2O , 8.43–9.75 CaO , 0.80–2.50 CuO , 3.37–4.40 Na_2O , 4.56–5.65 Bi_2O_3 , 4.70–5.90 ZnO , 5.60–6.80 F (USSR Inventor's Certificate No. 537969) or glaze with a higher CuO content (up to 7%): 10.0–15.0 SiO_2 , 6.0–9.0 Al_2O_3 , 1.6–2.0 MgO , 1.2–4.0 ZnO , 5.0–10.0 pyrite cinder or 7.0 CuO pigment (RF Patent No. 2148037).

Coatings designed to decorate ceramics, ceramic tiles, majolica, and some other articles constitute the group of decorative glazes. A special feature of these glazes is the high decorative value, but they have a limited area of application so that there are few studies of these coatings [3]. Colored coatings are most widely represented in the form of glazes whose color is due to addition of coloring oxides directly to the glazes during melting. In contrast to coloring with pig-

ments, the coatings are transparent and have a more intense luster [4]. When such coatings are used, interesting decorative effects are obtained on the relief surface of ornamental ceramics, where they acquire darker coloring in depressions. Such coating compositions are described in [5] for majolica with copper oxides. However, copper-containing coatings are only suitable for the outer surfaces due to the slight toxicity of CuO. Compositions of melted color glazes with a 2.0 to 6.0 pts. by wt. CuO content are reported in [5]. They are all colored green.

However, glazes in which the copper(II) oxide is incorporated in amounts greater than 20% and practically plays the role of not only a pigment but also a basic component of the glass are stimulating significant interest. First, such glazes ensure an unusual decorative effect — black coloring with a metallic luster, second, they are distinguished by more active reaction with the ceramic (USSR Inventor's Certificate No. 857035) [6]. Such studies were conducted on glazes of the following composition (%) at Riga Polytechnic Institute: 15.0–40.0 B_2O_3 , 7.5–20.0 Al_2O_3 , 18.0–40.0 CuO , 5.0–12.0 P_2O_5 , 10.0–20.0 SrO , 0.5–10.0 K_2O , 2.0–12.0 SiO_2 [6]. The melting temperature was 1200–1300°C and the melting point was 950–1000°C. The glazes are distinguished by elevated thermal stability and weatherproofing due to the strong reaction of the glaze with the ceramic paste made from multi- and low-carbonate hydromica kaolinite clays. In addition, copper-containing borate glazes are characterized by good spreadability and covering properties.

According to the data in USSR Inventor's Certificate No. 765224, the CuO content in a glaze can also be higher than 40%. A glaze composition containing the following (%)

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² Here and below, unless otherwise stated, the weight content.

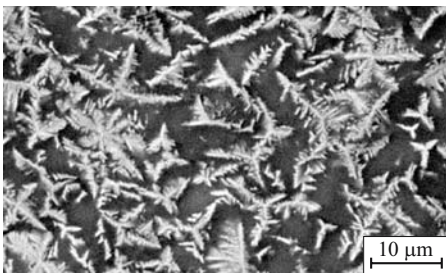


Fig. 1. Electron-microscopic photograph of the structure of glass containing 15% CuO and partially crystallized during processing.

has been patented: 20.0–50.0 B₂O₃, 5.0–8.5 Al₂O₃, 25.0–60.0 CuO, 8.0–20.0 P₂O₅, 5.0–15.0 BaO or SrO. All of these glazes basically provide black coloring. Copper-containing borate glazes have high reactivity and intensively react with the ceramic paste.

Moreover, our studies showed that glazes with a high copper oxide content have a high tendency to crystallize and have a comparatively low CLTE: $(35 - 58) \times 10^{-7} \text{ K}^{-1}$ [5]. Such glazes were not suitable for decorative and ornamental ceramics that have a CLTE of $(57 - 60) \times 10^{-7} \text{ K}^{-1}$. In addition, there are no data on production of glazes from silicoborate systems with a copper oxide content within the limits of 5–20%.

We selected the B₂O₃–SiO₂–Al₂O₃–CaO–K₂O–CuO system in which the CuO content varied from 5 to 20% and the B₂O₃ content varied from 15 to 30%. The initial frits were melted at 1300–1350°C in a gas furnace with holding at the final temperature for 1 h.

All glass compositions melted satisfactorily and exhibited the required fluidity. The glasses containing 5–10% CuO were green or dark green in color and those with 15–20% CuO were black. However, for the minimum amount of B₂O₃ (15%), the glasses containing more than 10% CuO turned yellow-orange in the bulk during pouring while remaining dark green or black in the surface layer. However, the glassy character of the fracture was preserved, which indicated predominance of a glassy phase.

To elucidate the cause of the change in development of the color of glasses containing more than 10% CuO and 15% B₂O₃, their structure was investigated in a JOEL JSM-5610 LV scanning electron microscope (Fig. 1). Separation of fine-needle branched crystals uniformly distributed in the glass. X-ray phase analysis of the crystallized glass clearly showed formation of one type of crystals — copper oxide (Fig. 2). It was clear that the glasses were partially crystallized, but the content of glass phase was much higher than the content of crystalline phase, so that a glassy luster and glass-like character of breaking were preserved when the crystallized glass broke.

Since the initial melts were homogeneous and crystallization only appeared in molding, we can conclude that at a melting temperature of 1300°C, at a content higher than 10%

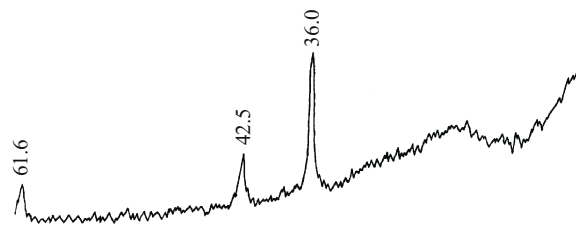


Fig. 2. X-ray diffraction pattern of glass with a 15% CuO content.

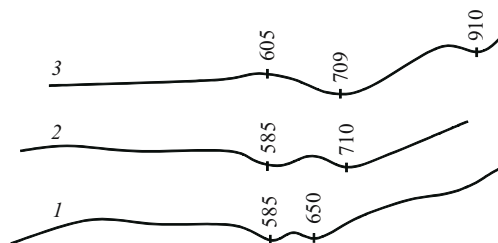


Fig. 3. Differential thermal curves of glasses containing 5% (1), 10% (2), and 15% CuO (3).

and reduced B₂O₃ content (15%), copper oxide was totally dissolved in the melt and on cooling, it separated due to reaching the solubility limit, perhaps in one of the glassy phases. Increasing the B₂O₃ content in the glasses increased the degree of solubility of the copper oxide, so that crystallization was not observed in production in glasses with 25–30% B₂O₃.

The behavior of the glasses on repeated heat treatment in the 600–1000°C temperature range was somewhat unexpected. At temperatures from 700 to 800–850°C, the glasses exhibited signs of crystallization with a change in color from green to weak yellow-orange in the bulk. However, absolute all of the glasses, including those partially crystallized in production, completely melted in the 850–1000°C temperature range. On cooling, the glasses were dark green (including in the volume) with surface signs of opacification. These data confirmed the possibility of using the experimental glasses to manufacture glasses with an application temperature of 900–1000°C.

The DTA curves were taken to study the phase transitions in glasses with different CuO contents (Fig. 3). Two endothermic effects in the softening region are clearly seen on curves 1 and 2, indicating the tendency of the glasses to liquate and caused by the difference in the softening points of the two liquating phases. One phase has a softening point of 585°C (the composition is probably the same for both glasses — with 5 and 10% CuO) and the second, higher-temperature, differs in composition from both glasses and has a softening point of 650 and 700°C.

One endothermic effect in the high-temperature softening region at 710°C was observed in partially crystallized glass containing 15% CuO and 15% B₂O₃ (curve 3). The phase with the low softening point probably crystallized on

cooling of the melt. The next endothermic effect at 910°C was due to melting of this phase. The DTA data in this case explain why the partially crystallized glass totally melted on repeated heat treatment at 850–900°C.

The CLTE of the experimental glasses varied within the limits of $(58.5 - 65.0) \times 10^{-7} \text{ K}^{-1}$, which corresponded to the goals of the research and the initial melting point (with the rod impression method) ranged from 640 to 700°C. The last values indicate that they basically correspond to a high-temperature liquating phase which probably has a much larger volume than the low-temperature phase.

Based on all of the frits obtained, including partially crystallized frits, glaze suspensions with 7% fireclay were prepared. The suspensions were applied on ceramic tiles after firing once, made from a paste designed for fabrication of decorative and ornamental items. After drying, the coated tiles were placed in a gradient furnace for 30 min. All compositions, including those partially crystallized during manufacture, formed good coatings in the 850–1000°C temperature range with a color scale from bright green to bright turquoise and dark green. The coatings were semitransparent and partially opacified.

The copper oxide crystals separated on cooling of glass melts with a CuO content higher than 10% and 15% B₂O₃ thus totally dissolved on repeated heat treatment in the 850–1000°C range, including in formation of the glaze coating.

Boron oxide increases the solubility of CuO in borosilicate glass. With a B₂O₃ content greater than 20%, the glasses did not exhibit any tendency to crystallize during manufacture.

Determining the structural role of CuO as a fundamental component in these glasses requires further studies. No individual absorption bands appeared in the IR spectra of the glasses in the 300–1500 cm⁻¹ region when the CuO content increased. The copper cation can exist in glasses both in four-coordination and in six-coordination. Our calculation of a possible absorption band in the IR spectrum for Cu(IV) and Cu(VI) cations with the Dehill–Roy equation gives the following wavenumbers: 188.7 and 153.8 cm⁻¹, respectively, which are below the limits of ordinary IR spectroscopy (from 300 cm⁻¹ and higher).

Based on the ion radius of Cu²⁺, equal to 0.08 nm, and the $r_{\text{Cu}} : r_{\text{O}}$ ratio, equal to 0.59, the most stable coordination number should be 6, which is responsible for the role of Cu²⁺ in glass as a modifier.

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