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BLUE-GREEN CERAMIC PIGMENTS IN THE SYSTEM $CaO-MgO-Al_2O_3-SiO_2-CoO-Cr_2O_3$ BASED ON GRANULATED BLAST-FURNACE SLAG

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The paper establishes the conditions of preparation and patterns of change of the ceramic pigment color indices in the system $CaO-MgO-Al_2O_3-SiO_2-CoO-Cr_2O_3$. Granulated blast-furnace slag was used as a basic component, it is characterized by high content of oxides of calcium, magnesium, aluminium, and silicon(IV) oxide (in total, about 97 wt.%) and chiefly represented by an active vitreous phase. It is shown that the replacement of the part of chromium(III) oxide in the composition of experimental pigments by cobalt(II) oxide contributes to widening their color range. Low-temperature (with a firing temperature of 1200^{0}C) pigments of dark-green (λ=501–502 nm) and turquoise (λ=493–495 nm) coloring were synthesized. The main phases which determine the color of such pigments are calcium-chromium garnet (uvarovite) formed via direct involvement of minerals of the blast-furnace slag and spinel (cobalt chromite). The developed pigments are characterized by high chemical stability (water resistance of 99.62–99.64%; 1 N HCl acid resistance of 92.33–92.38%; and 1 N NaOH alkali resistance of 91.34–91.53%). Their use ensures production of high-quality glass coatings in blue-green color range (λ=492–540 nm).

Keywords: ceramic pigments, granulated blast-furnace slag, mineral composition, spinel, uvarovite, color indices, glass coatings.

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Introduction

Ceramic pigments are top-line coloring agents in the silicate technology owing to a number of their advantages. They are resistant to solvent action of the aggressive glass melts and exhibit high covering power; the use of such pigments allows achieving actually any range of colors of glass coatings.

The system $CoO-Cr_2O_3-Al_2O_3$ is traditionally considered the base of blue-green ceramic pigments. They feature spinel structure, being stable to high temperatures and aggressive impact of the various glasses melts [1–5]. X-ray diffraction studies showed [6–8] that the color of such pigments in the absence of additives is determined by different combination of the following coloring compounds: Cr_2O_3 (dark-green), $CoA1_2O_4$ (blue) and $CoCr_2O_4$ (blue-green) which form the continuous solid solutions. Free $A1_2O_3$ dilutes the color without changing its characteristics. The fabrication of blue-green pigments of spinel type is associated with high temperatures, being not lower than 1250^{0}C even with the use of mineralizing additives (compounds of boron and alkaline metals). As a rule, the temperature of synthesis of these pigments is within the range of 1300–1350^{0}C, and they are prepared with the use of commercially pure raw materials.

Therefore, the studies aimed at developing physical and chemical concepts of the resource- and energy-saving technology of ceramic pigments, in particular, blue-green ones, are of immediate interest.

In previous works [9–11], we have shown that open-hearth slags and slags of alumino-thermal production of ferrotitanium can be effectively used for obtaining spinel ceramic pigments as an equivalent substitute for a number of technical pure raw components.

In work [12] the peculiarities of phase composition (predominant content of glass phase) and chemical composition of granulated blast-furnace slag are taken as a basis for development of the compositions and technology of green ceramic pigments with the structure of calcium-chromium garnet (uvarovite, $3CaO\cdot Cr_2O_3\cdot 3SiO_2$). The use of this slag allows intensifying the reaction behavior in

the solid phase with the formation of the required uvarovite phase in the finished product of thermal treatment. Apart from the uvarovite mineral, free chromium (III) oxide is also present in the finished pigments; it creates prerequisites for expanding their color palette, in particular, due to obtaining of blue-green coloring.

The objective of the work was to establish physical-chemical patterns and process parameters for preparation of low-temperature chromium-cobalt pigments based on granulated blast-furnace slag.

Experimental method

Pigment batches were prepared by the method of joint wet grinding of the initial raw components. Moisture content of prepared suspensions was equal to 35%. Pigment batches dried to residual moisture content of 1% were firing in the electric furnace in the temperature range of 1150–1250^{0}C with the hold time of 1 h. Finished pigments were finely ground with the addition of water to moisture content of 35%. The dispersity of pigments was characterized by the residue on the control sieve No. 0056, which should not exceed 0.4%. Prepared pigments were dried to moisture content of max. 0.8%. To obtain the colored glass coatings, the synthesized pigments were added to the composition transparent fritted glaze intended for application onto ceramic tiles, in an amount of 8 wt.%. Glaze coatings were firing at the temperature of 1100^{0}C.

Crystal-phase composition of the ceramic pigments was evaluated by X-ray phase analysis on the diffractometer DRON–3.0 in Cu-K_α radiation. Color indices of the developed pigments and glass coatings with their introduction were studied using the colorimetric instrument CC–3. The density of the ceramic pigments was determined by pycnometer method and chemical stability was estimated by their weight loss after boiling in 1 N hydrochloric acid solution and 1 N sodium hydroxide solution.

Composition of the batches of ceramic pigments under study

Component name	Content, wt.%		
	Number of compositions		
	1u1 [10]	1u2	1u3
Blast-furnace slag	41.21	43.10	45.17
Chromium(III) oxide	51.84	45.18	37.88
Phosphorus(V) oxide*	6.95	7.27	7.62
Cobalt(II) oxide**	–	4.45 (0.257)	9.33 (0.514)

Notes: * Phosphorus(V) oxide was introduced using $NH_4H_2PO_4$.
** The content of cobalt(II) oxide, mol, is stated in brackets.

Results and discussion

To prepare the pigment, granulated blast-furnace slag was used as a basic component (Table). This slag is characterized by high content of calcium, magnesium and aluminium oxides as well as silicon (IV) oxide (in total, about 97 wt.%). The products of its crystallization are solid solution between akermanite and helenite (melilite), as well as calcium meta-silicate and ortho-silicate. The calculated mineral composition of the experimental slag is shown below, mol [12]:

$Ca_2MgSi_2O_7$ (akermanite) 0.235; $Ca_2Al_2SiO_7$ (helenite) 0.136; α-$CaSiO_3$ (pseudowollastonite) 0.417 and γ-Ca_2SiO_4 (shennonite) 0.212.

Chromium (III) oxide was stepwise replaced in the composition of pigments by cobalt (II) oxide in the amount of up to 0.514 mol in increments of 0.257 mol. The withdrawal of a larger amount of Cr_2O_3 from the pigment batches composition inevitably leads to the violation of specified stoichiometry between the initial components. At the same time, uvarovite phase does not form to the full extent.

The process of obtaining of experimental chromium-cobalt pigments can be depicted as follows:

$$0.235Ca_2MgSi_2O_7+0.136Ca_2Al_2SiO_7+$$
$$+0.417CaSiO_3+0.212Ca_2SiO_4+0.443SiO_2+$$
$$+(1.542-x)Cr_2O_3+xCoO=$$
$$=0.514[3(Ca_{0.85}, Mg_{0.15})O\cdot Cr_2O_3\cdot 3SiO_2]+$$
$$+0.136Ca_2Al_2SiO_7+ xCoCr_2O_4+(1.028-2x)Cr_2O_3,$$

where x values vary within the limits from 0.257 to 0.514.

Besides, free SiO_2 in the composition of such pigments, introduced for binding the initial components in the uvarovite phase, was replaced by P_2O_5. We took into account the possibility of equimolecular replacement of the acid radical $[SiO_4]^{4-}$ in the structure of the uvarovite mineral by $[PO_4]^{3-}$, having a positive effect on the purity of green color of the uvarovite slag-containing pigments [12].

Firing of the pigments under study was carried out in the temperature range of 1150–1250^{0}C.

As follows from experimental results, an increase in the content of cobalt(II) oxide in the composition of experimental chromium-cobalt pigments from 0.257 to 0.514 mol causes enhancement of their turquoise coloring, which is consistent with the data for their color indices (Fig. 1). In particular, transition of values of the dominating wavelength (λ) from green (501–505 nm) to a shorter

wave region of spectrum (blue-green at 493–498 nm) is observed. Color purity falls from 8–13 to 6–10%. The temperature of 1200°C is considered to be sufficient for the firing of pigments under study; there is almost no enhancement of their coloring at higher temperatures. It is proved by insignificant changes of the values of color tone (from 495–502 to 493–501 nm). At the same time, a further increase in the temperature of synthesis of such pigments to 1250°C causes certain deterioration of their color purity (a decrease to 6–8%) and an increase in sintering capacity.

X-ray patterns of experimental chromium-cobalt pigments prepared at the temperature of 1200°C are shown in Fig. 2. It can be observed that the amount of chromium-cobalt spinel in the phase composition of these pigments grows with an increase in the content of cobalt (II) oxide, as evidenced by the intensification of its reflexes at $d \cdot 10^{-10}$=4.84; 2.08; 1.60 and 1.47 m. At the same time, displacement and redistribution of the intensity of main diffraction maximums typical of pure $CoCr_2O_4$ ($d \cdot 10^{-10}$=2.95 and 2.51 m) [13] is caused by the presence of calcium-chromium garnet phase and free chromium (III) oxide in the pigment 1u2. An increase in the proportion of cobalt chromite in the synthesized pigments ultimately determines the enhancement of their turquoise coloring.

The indices of chemical resistance determined for chromium-cobalt pigments prepared at the temperature of 1200°C were as follows: water resistance of 99.62–99.64%; 1 N HCl acid resistance of 92.33–92.38% and 1 N NaOH alkali resistance of 91.34–91.53%. The values of density obtained by

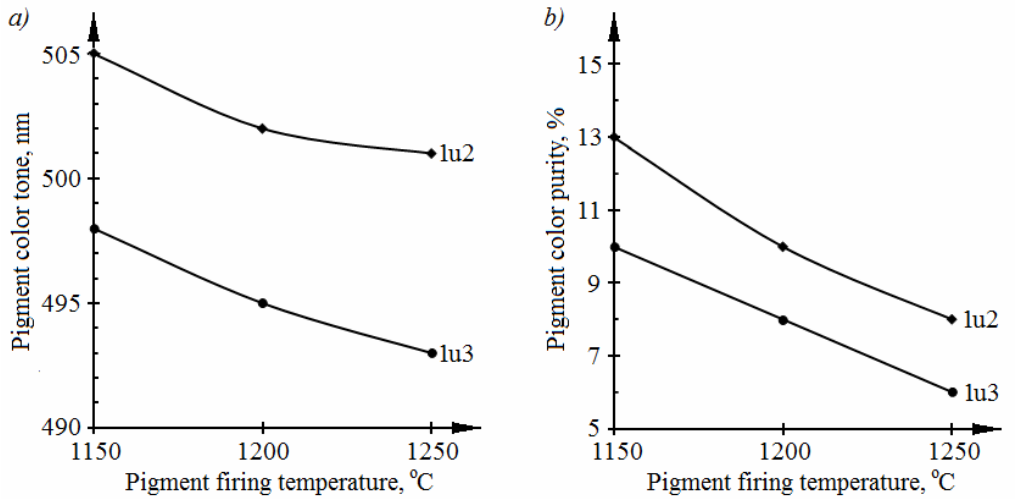

Fig. 1. Effect of the temperature of firing of experimental chromium-cobalt pigments on their color tone (a) and color purity (b)

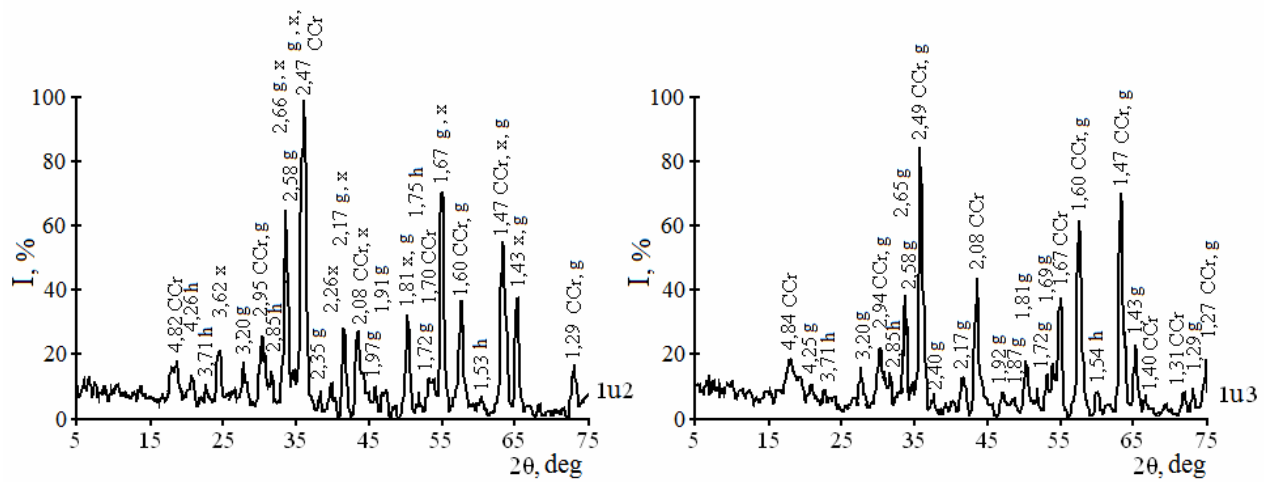

Fig. 2. X-ray patterns of chromium-cobalt ceramic pigments synthesized at 1200°C:
g – solid garnet solution; CCr – $CoCr_2O_4$; x – Cr_2O_3; h – $2CaO \cdot Al_2O_3 \cdot SiO_2$

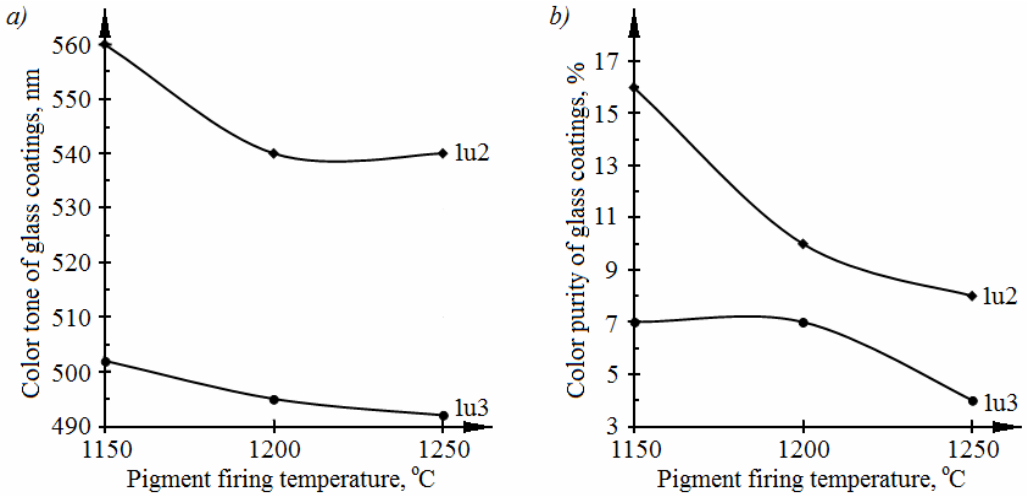

Fig. 3. Effects of the temperature of firing of chromium-cobalt pigments on the color tone (a) and color purity (b) of glaze coatings obtained with their introduction

pycnometer method for powders of the pigments were 3.60–3.65 g/cm^3 with the average particle size in the range of 3.6–4.0 mm.

The dependence of color indices of glaze coatings obtained with the introduction of chromium-cobalt pigments under study on the temperature of firing is shown in Fig. 3.

Our findings show that the dynamics of color indices' change of the obtained glaze coatings was similar to chromium-cobalt pigments themselves. In particular, quantitative increase of cobalt (II) oxide in the experimental compositions, firing at 1150^{0}C, caused glass coatings color change from green to turquoise-green and the relevant transition of values l from yellow-green (540–560 nm) to a shorter wave region of spectrum (green at 502 nm).

With an increase in the temperature of pigment synthesis to 1200–1250^{0}C, the fabricated glass coatings gain blue-green coloring (λ=492–495 nm), color purity being reduced from 8–16 to 4–7%. Besides, it is confirmed that the synthesis of the experimental pigments is inexpedient at the temperature exceeding 1200^{0}C, which does not lead to any significant enhancement of the coloring of glaze coatings with their introduction, as evidenced by minor variations of color indices (Fig. 3).

Conclusions

As a result of experimental studies, it was found that the replacement of the part of chromium (III) oxide in the composition of developed uvarovite-containing pigments by cobalt (II) oxide causes widening their color palette. Low-temperature (with the firing temperature of 1200^{0}C) pigments of dark-green (λ=501–502 nm) and turquoise (λ=493–495 nm) coloring were obtained. Spinel phase (cobalt chromite) acts as a carrier of color in such pigments along with calcium-chromium garnet.

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СИНЬО-ЗЕЛЕНІ КЕРАМІЧНІ ПІГМЕНТИ В СИСТЕМІ $CaO–MgO–Al_2O_3–SiO_2–CoO–Cr_2O_3$ НА ОСНОВІ ГРАНУЛЬОВАНОГО ДОМЕННОГО ШЛАКУ

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У роботі встановлені умови отримання і закономірності зміни колірних показників керамічних пігментів у системі $CaO–MgO–Al_2O_3–SiO_2–CoO–Cr_2O_3$. Як базовий компонент застосовувався гранульований доменний шлак, який характеризується високим вмістом оксидів кальцію, магнію, алюмінію, кремнію діоксиду (сумарно близько 97 мас.%) і переважно наданий активною склоподібною фазою. Показано, що заміна в складі дослідних пігментів частини хром(III) оксиду на кобальт(II) оксид сприяє розширенню їх колірної гами. При цьому синтезовані низькотемпературні (температура випалу 1200°С) пігменти мають темно-зелене (λ=501–502 нм) і бірюзове (λ=493–495 нм) забарвлення. Основними фазами, що зумовлюють колір таких пігментів, є хромовий гранат (уваровіт), що утворюється при безпосередній участі мінералів доменного шлаку, і шпінель (кобальту хроміт). Розроблені пігменти характеризуються високими показниками хімічної стійкості (водостійкість 99,62–99,64%; кислотостійкість до 1 н. HCl 92,33–92,38%; лугостійкість до 1 н. NaOH 91,34–91,53%). Їх застосування забезпечує одержання високоякісних склопокриттів синьо-зеленої колірної гами (λ=492–540 нм).

Ключові слова: керамічні пігменти, гранульований доменний шлак, мінералогічний склад, шпінель, уваровіт, колірні показники, склопокриття.

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