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*A.V. Zaichuk, A.A. Amelina***BLUE-GREEN SPINEL-TYPE CERAMIC PIGMENTS PREPARED FROM THE SLAG OF ALUMINOTHERMAL PRODUCTION OF FERROTITANIUM****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

Directed synthesis of blue-green spinel-type ceramic pigments is theoretically justified and experimentally vindicated using the system $\text{CoO-MgO-CaO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-TiO}_2$. The slag of aluminothermal production of ferrotitanium with a high content of aluminium (III) oxide (71.5 wt.%) is used as a raw material. It is shown that calcium hexaaluminate is a primary phase of slag which takes part in the formation of magnesium and cobalt aluminate spinels. This allows appreciably reducing the temperature of pigments' firing (to 1150–1200°C in the presence of mineralizing additive B_2O_3). The introduction of chromium (III) oxide into the composition of pigment batches in the amount of 0.1–0.5 mol (9.8–32.1 wt.%) provides blue-green coloring of ceramic pigments ($\lambda=467\text{--}487$ nm). The results of physicochemical study shows that the color of the pigments is connected with different ratio between aluminate and chrome spinels in a solid solution $(\text{Co, Mg})(\text{Cr, Al})_2\text{O}_4$; their crystal size is 4–6 μm . The developed spinel pigments exhibit improved chemical stability (water resistance of 99.99%; 1 N HCl acid resistance of 99.97–99.99% and 1 N NaOH alkali resistance of 97.40–99.95%). They can be used to fabricate high-quality glass coatings of a blue-green color range ($\lambda=472\text{--}485$ nm).

Keywords: ceramic pigments, slag of aluminothermal production of ferrotitanium, thermodynamic calculations, mineral composition, spinel, color indices, glass coatings.

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Introduction

Synthesis of ceramic pigments is commonly carried out using crystalline compounds having stable properties towards the exposure to high-temperature corrosive environments (glass melts). Various spinels, as crystal lattice-acceptors with structural features that allow obtaining the most stable pigments, are often used to this end. Their traditional sphere of application is ceramics and glass industries and fabrication of colored glass-enamel coatings for metals [1].

Similarity of structures and parameters of crystal lattices of a number of spinels defines one of their features, i.e. easy formation of substitutional solid solutions. This, in turn, determines the possibility of obtaining ceramic pigments in a wide range of colors on the basis of various aluminates, chromites, ferrites and titanates [2–5]. Spinel formation occurs at high temperatures which sometimes reach 1500°C and more. The use of mineralizers (preferably boric acid) allows reducing the temperature of solid-phase synthesis of spinel type pigments to 1300–1350°C [1].

Spinel pigments are also obtained by co-precipitation method. Although this method is multi-step and complex, it nevertheless permits reducing the firing temperature of these pigments by 200–300°C [6].

Another method to produce spinel type pigments in a wide color range is a self-propagating high-temperature synthesis (SHS). It is based on the use of the heat of exothermal reactions and is faster and more energy efficient than conventional methods [7]. At the same time, the implementation of this method requires the usage of special reagents and specific composition of batches. Furthermore, the process of the pigments' heat treatment is rather complex as well, being a limiting factor in the industrial implementation of the SHS process.

Therefore, ceramic pigments, in particular spinel ones, are mainly produced with the use of solid-phase synthesis according to the traditional ceramic technology. The blue-green pigments are synthesized on the basis of aluminate and chrome spinels. However, the use of expensive raw materials

of the technical pure and high temperatures of firing determine high cost of such pigments and cause the need to find a qualitatively new kind of raw materials, including recycled one.

Consequently, the development of physical and chemical fundamentals of the resource- and energy efficient technology of spinel-type ceramic pigments is a topical problem.

Our previous studies [8,9] showed the feasibility of using open-hearth and blast furnace slag in fabrication of spinel ceramic pigments. The work [10] reports the results of theoretical and experimental study concerning the preparation of blue pigments with the aluminite spinel structure based on the slag of aluminothermal production of ferrotitanium (APF). Among various industrial wastes concentrated in Ukraine, slags of this type are of particular interest for synthesis of spinel ceramic pigments because of high content of aluminum (III) oxide (up to 75 wt.%). The expansion of color range of the pigments synthesized on the basis of APF slag is the subject of research in this paper. Thus the work objective is the establishment of physical-chemical patterns and process parameters for the synthesis of blue-green ceramic pigments of spinel type using APF slag.

Experimental

Pigment batches were prepared by the method of joint wet grinding of the initial raw components. The content of moisture in prepared suspensions was equal to 35%. Pigment batches dried to residual moisture content of 1% were fired in the electric furnace in the temperature interval of 800–1300°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 (not more than 0.4%). Prepared pigments were dried to moisture content of max. 0.8%. To obtain the colored glass coatings, synthesized pigments were added for grinding of transparent fritted glaze intended for application onto ceramic tiles, in an amount of 8 wt.%. Glaze coatings were fired at the temperature of 1100°C.

The mineral composition of synthesized pigments was evaluated by X-ray phase analysis using the diffractometer DRON-3.0 in Cu-K α radiation.

Spectral characteristics of the pigments absorption in the infrared region were studied by means of the Fourier IR-spectrometer Nicolet IS 10 in the range of wavenumber of 400–1000 cm⁻¹. Electron microscopic study of ceramic pigments was performed using scanning electron microscope REM-106I. Color characteristics of the developed pigments and glass coatings were investigated by the color comparator CC-3. Density of ceramic pigments was determined by pycnometer method, and chemical resistance was found on their weight loss after boiling in 1 N hydrochloric acid solution and 1 N sodium hydroxide solution.

Thermodynamic probability of chemical reactions in the system CoO–MgO–CaO–Al₂O₃–Cr₂O₃–TiO₂ was evaluated by the calculation of Gibbs energy changes (ΔG_T^0) in the temperature interval of 1073–1573 K.

Results and discussion

The composition of pigment batches is determined by the chemical and mineral composition of APF slag shown in Table 1. It could be referred to system CaO–Al₂O₃–TiO₂ (CAT). In terms of 1 mol of a substance, slag contains: CaO 0.1, Al₂O₃ 0.65 and TiO₂ 0.25.

The analysis of the data given in Table 1 shows that calcium dialuminate (CaO·2Al₂O₃) interacts with corundum (α -Al₂O₃) in the course of heat treatment of APF slag to produce calcium hexaaluminate (CaO·6Al₂O₃). Taking into account the molar ratio of the basic oxides in the slag composition, it would be logical to expect the almost complete absence of α -Al₂O₃ in the resulting phase composition thereof. At the same time, the presence of α -Al₂O₃ in the mineral composition of heat-treated slag may indicate the binding of calcium (II) oxide with silicon (IV) oxide, the total content of which in the residual glass phase being 2.89 wt.% (Table 1). Eventually, only about one half of calcium (II) oxide contained in the APF slag is in the form of CaO·6Al₂O₃ [10]. For convenience, the preparation of the pigment batches was further guided by the content of main components in the experimental slag as stated below, mol: CaO 0.05, Al₂O₃ 0.65 and TiO₂ 0.25.

In order to fabricate the pigments of blue-green color range with the use of APF slag, the oxides of

Table 1

Results of chemical analysis of APF slag sample and its mineral composition [10]

Name and content (wt.%) of components						
SiO ₂	Al ₂ O ₃	TiO	CaO	FeO	MgO	Total amount
2.89	71.50	17.64	5.74	1.53	0.70	100.0
Mineral composition of initial slag sample – α -Al ₂ O ₃ , TiO, CaO·6Al ₂ O ₃ , CaO·2Al ₂ O ₃						
Mineral composition of slag heat treated at 1300°C – α -Al ₂ O ₃ , TiO ₂ (rutile), CaO·6Al ₂ O ₃						

cobalt and chromium were used as coloring components, and magnesium (II) oxide was introduced too. The possibility of isomorphous substitution of the part of Mg^{2+} ions for Co^{2+} ions in the aluminate spinel structure was suggested, because of the proximity of their ionic radii (0.74 Å and 0.78 Å, respectively [11]). At the same time, complex crystal-phase composition of the APF slag necessitates the research of mineral formation in the systems where it is used with a view to reasonably choosing the initial composition mixtures.

In this context, we initially performed the thermodynamic calculations concerning the chemical reactions in the system $CoO-MgO-CaO-Al_2O_3-Cr_2O_3-TiO_2$. The results of ΔG_T^0 calculations for the most probable reactions in the temperature range of 1073–1573 K are shown in Table 2.

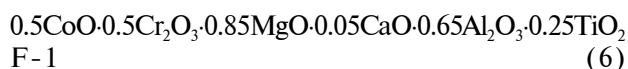
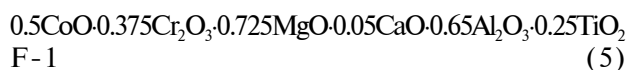
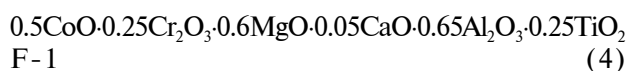
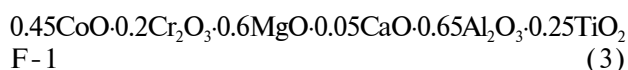
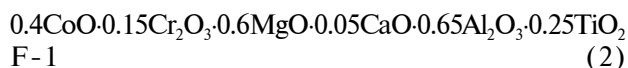
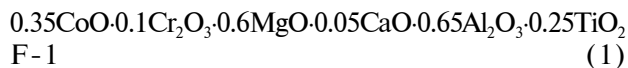
Thermodynamic analysis revealed that regardless of the composition of slag-containing batches of the considered system the most preferable primary products of their firing are titanium (IV) oxide and calcium hexaaluminate, as evidenced by the highest negative values of ΔG_T^0 (reactions no. 1 and 2).

The formation of spinel phases most probably begins from cobalt chromite which is indicated by the ΔG_T^0 values of the reaction no. 3 in the entire temperature interval under study. Besides, a high probability of the formation of cobalt aluminates (in case of an excess content of CoO with regard to stoichiometric one in the compound $CoO \cdot Cr_2O_3$) and magnesium is shown. Calcium hexaaluminate performs the role of primary phase of slag which takes part in the formation of magnesium and cobalt aluminate spinels. Furthermore, based on specified initial conditions, the most preferred variant is binding of titanium (IV) oxide into magnesium ortho- or

metatitanate and calcium metatitanate, the presence of which, obviously, cannot cause any noticeable deterioration of the color indices of the pigments.

In consideration of the foregoing, the ratio CoO/Cr_2O_3 in their composition was varied within 1.0–3.5 in order to obtain slag-containing pigments with a wide range of blue-green coloring. Magnesium (II) oxide together with titanium (IV) oxide was introduced to form magnesium metatitanate.

The molecular formulas of the obtained pigments are given below:



Experimental pigments were fired in the temperature interval of 1200–1300°C with the hold time of 1 hour.

To verify the data of calculations, we conducted X-ray phase study of the experimental ceramic pigment F-1 (6) which were fired in the temperature interval of 800–1300°C, and collected the data on

Table 2

Summary of calculated values of ΔG_T^0 for the most probable reactions

No.	Reactions	ΔG_T^0 (kJ/mol)					
		1073 K	1173 K	1273 K	1373 K	1473 K	1573 K
1	$CaO \cdot 2Al_2O_3 + 4(\alpha-Al_2O_3) \rightarrow CaO \cdot 6Al_2O_3$	-79.45	-83.81	-88.10	-92.36	-96.60	-100.87
2	$TiO + 0.5O_2 \rightarrow TiO_2(\text{rutile})$	-348.11	-344.80	-341.86	-	-	-
3	$CoO + Cr_2O_3 \rightarrow CoO \cdot Cr_2O_3$	-77.54	-77.70	-77.86	-78.02	-78.18	-78.34
4	$5CoO + CaO \cdot 6Al_2O_3 \rightarrow 5(CoO \cdot Al_2O_3) + CaO \cdot Al_2O_3$	-70.59	-60.89	-51.02	-40.99	-30.78	-20.40
5	$5MgO + CaO \cdot 6Al_2O_3 \rightarrow 5(MgO \cdot Al_2O_3) + CaO \cdot Al_2O_3$	-53.23	-50.41	-47.90	-45.69	-43.77	-42.13
6	$CaO \cdot Al_2O_3 + TiO_2(\text{rutile}) \rightarrow CaO \cdot TiO_2 + \alpha-Al_2O_3$	-47.92	-46.85	-45.83	-44.87	-43.94	-43.04
7	$2MgO + TiO_2(\text{rutile}) \rightarrow 2MgO \cdot TiO_2$	-28.69	-30.19	-31.80	-33.54	-35.41	-37.41
8	$MgO + \alpha-Al_2O_3 \rightarrow MgO \cdot Al_2O_3$	-26.36	-26.77	-27.21	-27.70	-28.22	-28.80
9	$CoO + \alpha-Al_2O_3 \rightarrow CoO \cdot Al_2O_3$	-29.83	-28.86	-27.84	-26.76	-25.63	-24.45
10	$2MgO \cdot TiO_2 + \alpha-Al_2O_3 \rightarrow MgO \cdot TiO_2 + MgO \cdot Al_2O_3$	-21.98	-20.97	-19.94	-18.88	-17.79	-16.66
11	$2MgO \cdot TiO_2 + TiO_2(\text{rutile}) \rightarrow 2(MgO \cdot TiO_2)$	-19.93	-18.59	-17.25	-15.90	-14.53	-13.14

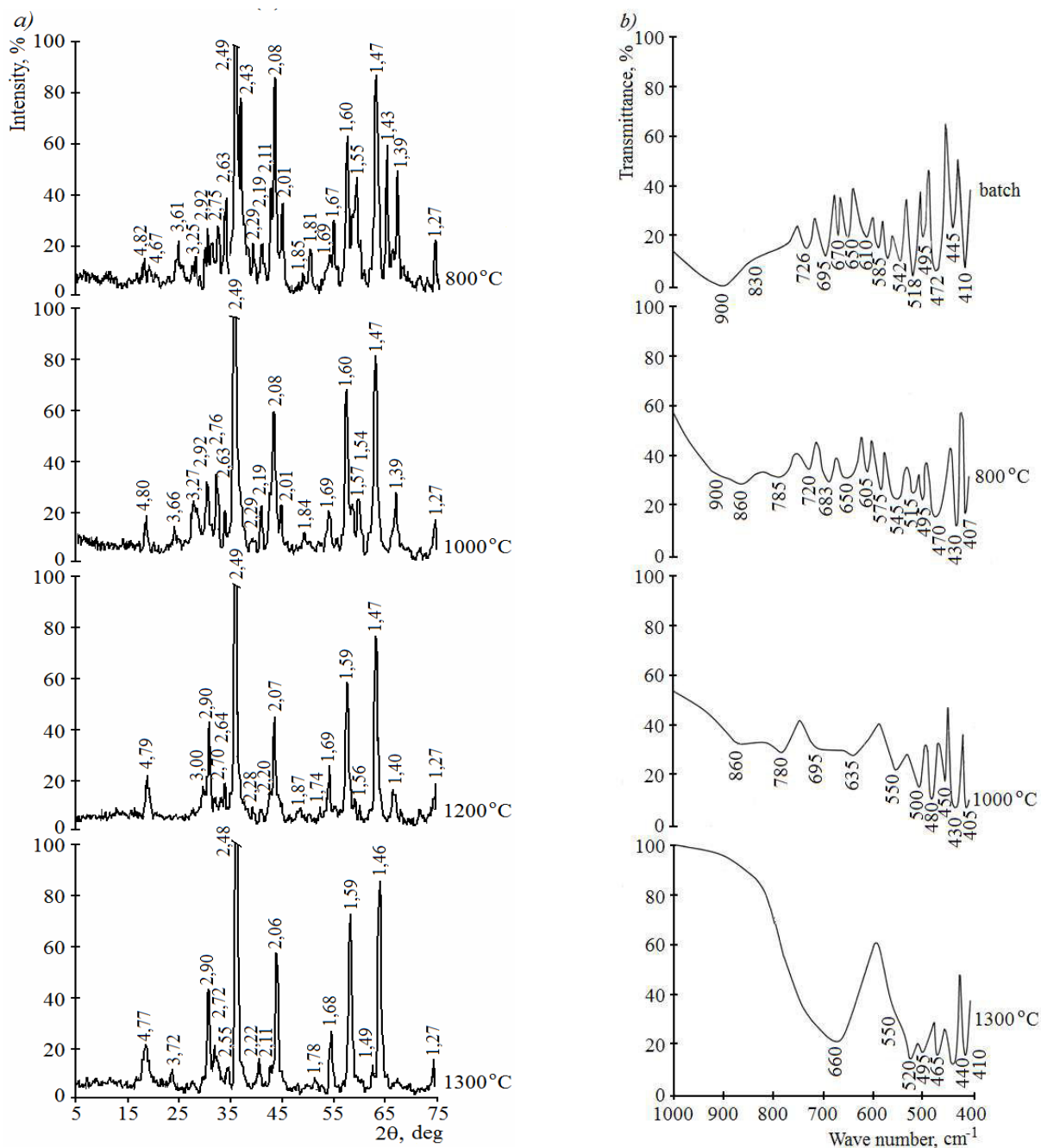


Fig. 1. X-ray diffraction patterns (a) and IR-spectra (b) of ceramic pigment F-1 (6) fired at various temperatures

its spectra of absorption in IR-region (Fig. 1).

X-ray phase study revealed (Fig. 1,a) that the rutile phase ($d \cdot 10^{10} = 3.27; 2.49; 2.19$ and 1.69 m) was formed in the obtained material at the temperature of up to 1000°C inclusive. A marked increase in the content of calcium hexaaluminate ($d \cdot 10^{10} = 2.76; 2.49$ and 2.19 m) is observed according to reactions no. 1 and 2 (see data of Table 2). Furthermore, the diffraction maxima of cobalt chromite ($d \cdot 10^{10} = 4.82; 2.92$ and 2.49 m) are clearly

identified at the temperature of 800°C , which agrees well with the results of thermodynamic calculations. Processes connected with the formation of the above spinel are actually completed at the temperature of 1200°C , after which free oxides of cobalt and chromium are no longer recorded in the products firing of pigment. At the same time, the final crystal-phase composition of such a pigment is formed only at the temperature of 1300°C . It is necessary to state the fact of the formation of the solid solution between

magnesium aluminate and cobalt chromite (both are crystallized in cubic system). It can explain the impossibility of separate identification of MgAl_2O_4 phase using the characteristic diffraction maximums ($d \cdot 10^{10} = 4.66; 2.86; 2.44; 2.02; 1.55$ and 1.43 m), because of redistribution of their intensity and shift towards chrome-cobalt spinel for which $d \cdot 10^{10} = 4.82; 2.95; 2.51; 2.08; 1.60$ and 1.47 m [12].

Our findings are also consistent with the results of infrared spectroscopic studies (Fig. 1,b). For example, heat treatment of the pigment blend F-1 (6) causes the change in the position and nature of high-frequency bands in the region of $700\text{--}1000\text{ cm}^{-1}$, responsible for valence vibrations in AlO_4 -tetrahedra. They are the main structural elements in calcium

dialuminate and, partially, calcium hexaaluminate (aluminium cations in β -form of Al_2O_3 also occupy the octahedral voids [13]). In particular, there is a gradual shift of the principal absorption maximum towards low frequencies ($900 \rightarrow 780\text{ cm}^{-1}$) and a decrease in its intensity as a whole, with the growth of temperature of experimental pigment firing to 1000°C . The above indicates the decrease in number of Al^{3+} ions, tetrahedrally coordinated on oxygen, in the system. It is caused by the interaction of crystal phases of the slag (calcium dialuminate and corundum) to produce calcium hexaaluminate. An increase in the temperature of synthesis of the considered pigment F-1 (6) to 1000°C also causes significant transformations in the middle part of

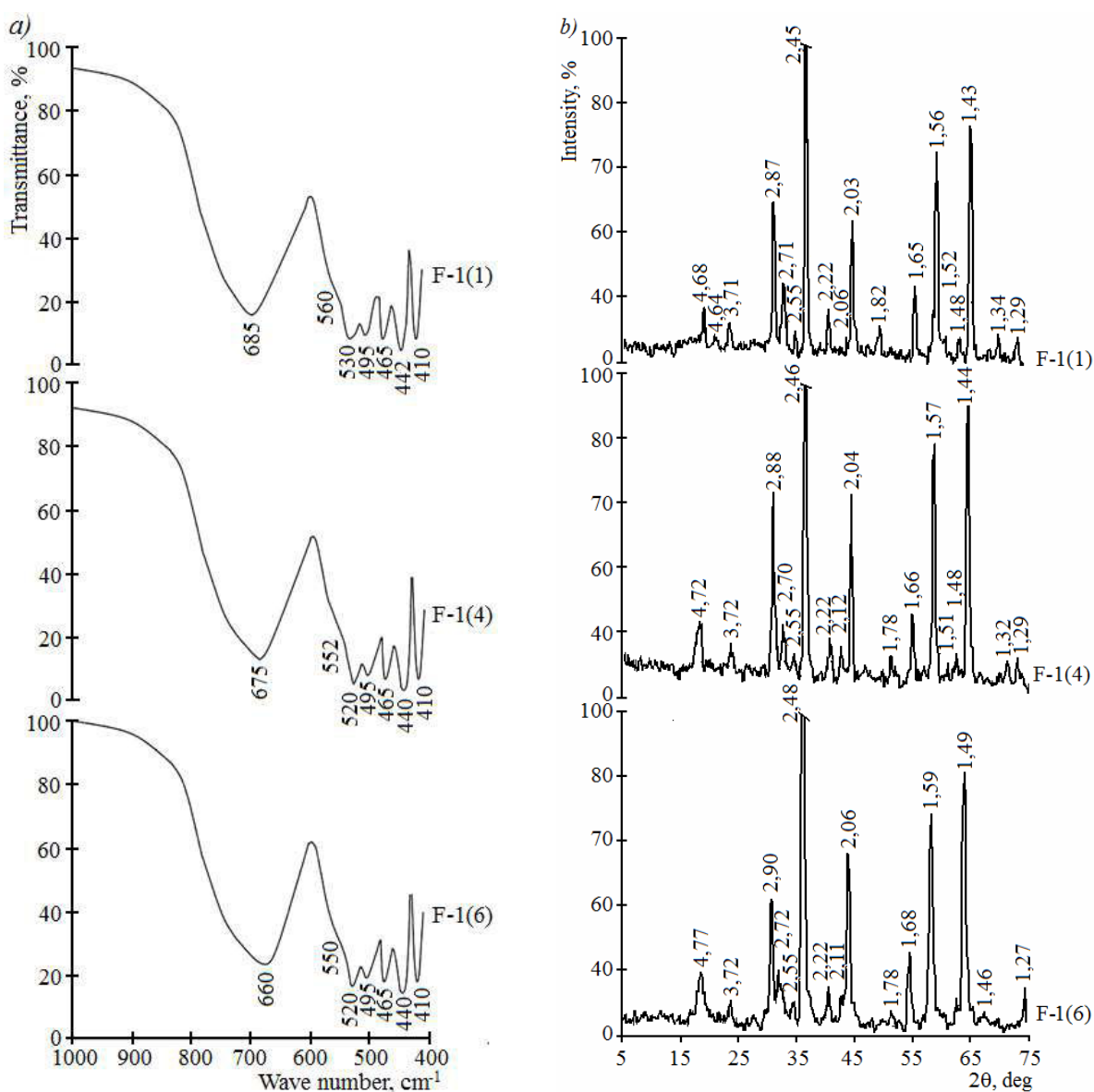


Fig. 2. IR-spectra (a) and X-ray diffraction patterns (b) of experimental ceramic pigments synthesized at the temperature of 1300°C

spectrum in the frequency range of 570–700 cm^{-1} . The number of absorption bands gradually decreases with the formation of double wide band with strongly pronounced maximum at 635 cm^{-1} . This difference in spectra can be mainly explained by the reduction of the share of free oxides of cobalt and chromium in the system under study, the presence of which is manifested by lines 695, 670 and 640, 570 cm^{-1} , respectively. As a result, a spinel phase (cobalt chromite) is actively formed, where Co^{2+} ions are in tetrahedral coordination.

At the temperature of 1300°C, we observed the IR-spectrum typical of the structure of spinel which obviously represents a solid solution between magnesium aluminate and cobalt chromite. It is confirmed by the shift of the characteristic absorption bands towards lower frequencies of 660 and 520 cm^{-1} (Fig. 2,a) with the substitution of the part of Mg^{2+} ions in the tetrahedral position and the part of Al^{3+} ions in the octahedral position by larger and heavier Co^{2+} and Cr^{3+} ions, respectively. Such changes in the IR-spectra agree with the data given in works [14,15].

It is also necessary to mention more complex pattern of absorption of the experimental pigments in a low-wave region of IR-spectra as compared with typical spinels, which is obviously due to the superposition of frequencies of valence vibrations of TiO_6 -octahedrons (450–500 cm^{-1}). These groups are the main structural elements of metatitanates [13]. Apparently, the appearance of the lines in the region of 400–450 cm^{-1} should be due to the vibrations of Me–O in the polyhedrons of $[\text{MgO}_6]$ and $[\text{CaO}_6]$ magnesium and calcium metatitanates.

The formation of solid solution between CoCr_2O_4 and MgAl_2O_4 is also shown by the results of X-ray phase analysis of ceramic pigments synthesized at 1300°C (Fig. 2.b).

An increase in the content of chromium oxide in the composition of experimental pigments from 0.1 to 0.5 mol results in a gradual shift of the principal diffraction maximums on X-ray patterns ($d \cdot 10^{10} = 4.68; 2.87; 2.45; 2.03; 1.56$ and 1.43 m) towards the larger interplanar spacing ($d \cdot 10^{10} = 4.77; 2.90; 2.48; 2.06; 1.59$ and 1.46 m). It is the evidence of formation of a single solid solution between aluminate and chrome spinels, $(\text{Co,Mg})(\text{Cr,Al})_2\text{O}_4$. The share

of cobalt chromite in the above solid solution features an expectable increase with the growth of Cr_2O_3 content when F-1(1) turns to F-1(6). Besides, magnesium metatitanate ($d \cdot 10^{10} = 3.72; 2.72; 2.55$ and 2.22 m) are fixed as a final product of the firing of these pigments. Calcium metatitanate, which apparently is also present in the pigment composition, cannot be identified separately because of low content and similarity of its principal diffraction maximums to MgTiO_3 .

Microstructure of the fired sample of F-1(6) pigment in the point of fracture is characterized by a high degree of agglomeration of crystal phase particles. Spinel crystals are elongated in their shape with the length in the range of ca. 4–6 μm (Fig. 3).

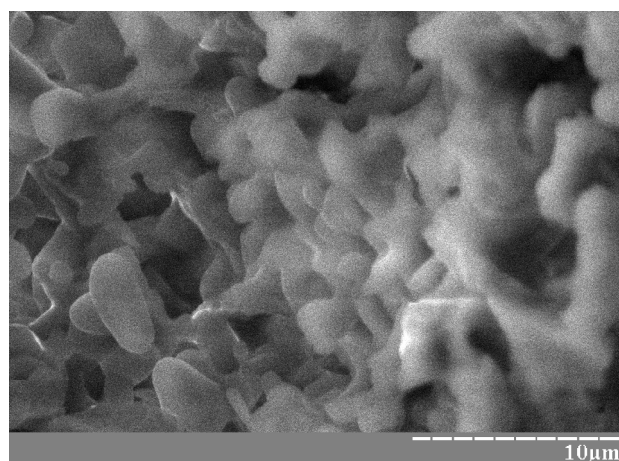


Fig. 3. REM micrograph of the structure of F-1(6) pigment fired at 1300°C

We tested the developed pigments for their chemical stability and determined their density (Table 3).

The developed spinel pigments are distinguished by high chemical stability which also indicates the predominant content of spinel phases. Pycnometric density of pigment powders is within the range of 3.60–3.93 g/cm^3 .

In the course of experimental study, we also performed color measurements in synthesized pigments and glaze coatings with their introduction. As a basis, transparent fritted glaze for application

Table 3

Physical and chemical characteristics of developed ceramic pigments

Pigment name	Water resistance, %	Acid resistance, %	Alkali resistance, %	Density, g/cm^3
F-1(1)	99.99	99.97	97.40	3.60
F-1(4)	99.99	99.99	98.80	3.76
F-1(6)	99.99	99.99	99.95	3.93

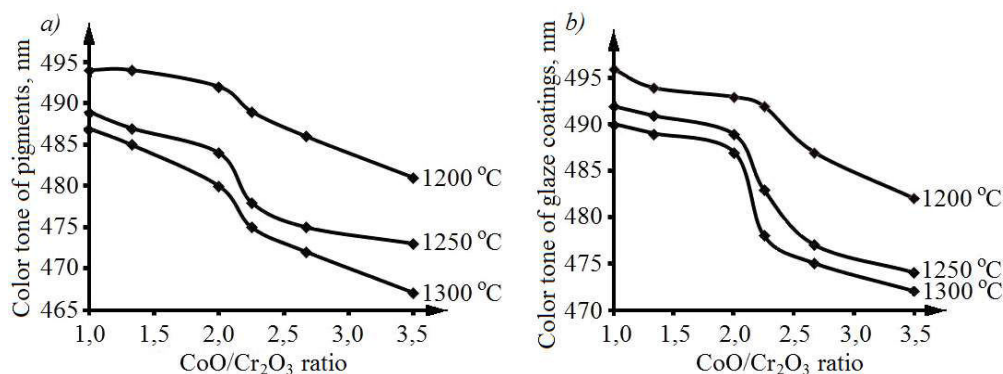


Fig. 4. Effect of CoO/Cr₂O₃ ratio in the composition of experimental pigment batches on the color tone of ceramic pigments and glaze coatings

onto ceramic tiles was used. The dependence of the color tone of experimental pigments and resulting glaze coatings on the CoO/Cr₂O₃ ratio in the composition of pigment batches is shown in Fig. 4.

Experiments proved that slag-containing pigments synthesized in the temperature interval of 1200–1300°C are characterized by a wide color range from blue with the turquoise tint to the turquoise-green. An increase in quantitative ratio of CoO/Cr₂O₃ from 1.0 to 2.0 in the experimental composition causes an insignificant change in color of both pigments themselves and pigment-containing glaze coatings. It is proved by small variations in the values of color tone (Fig. 4).

An increase in the ratio of the above coloring oxides in the experimental batches to 3.5 and firing temperature to 1300°C determines a gradual increase in the share of blue component of the coloring of ceramic pigments and glaze coatings obtained. As a consequence, the transition from the turquoise to blue tones occurs. In particular, the transition of values of the dominating wavelength (λ) of ceramic pigments from blue-green (480–487 nm) to the shorter wave region of spectrum, blue region (467–475 nm) is observed. The values of λ decrease from 487–490 nm to 472–478 nm for the pigment-containing glaze coatings.

An additional introduction of boric acid (2.0 wt.% with the respect to B₂O₃) into experimental ceramic pigments allows reducing the temperature of their synthesis from 1300 to 1150–1200°C. The fired pigment-containing glass coatings are also characterized by stable blue-green coloring (λ =472–485 nm) and absence of defects.

Conclusions

The results of theoretical and experimental studies showed that the slag of aluminothermal production of ferrotitanium can be used as a basic component in fabrication of ceramic pigments of

blue-green color range. Their coloring is determined by different ratios between aluminate and chrome spinels in the solid solution (Co, Mg)(Cr, Al)₂O₄ with the crystal size within the range of 4–6 μ m. Taking into account the features of mineral formation processes in the system under study, it is advisable to adhere to the required stoichiometric ratio of initial components in order to achieve the given crystal-phase composition of pigments with enhanced physicochemical characteristics. These pigments synthesized at low temperatures of 1150–1200°C in the presence of mineralizing additive B₂O₃ allows preparing high-quality blue-green glass coatings (λ =472–485 nm).

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СИНЬО-ЗЕЛЕНІ ШПІНЕЛЬНІ КЕРАМІЧНІ ПІГМЕНТИ, ВИГОТОВЛЕНІ ЗІ ШЛАКУ АЛЮМІНОТЕРМІЧНОГО ВИРОБНИЦТВА ФЕРРОТИТАНУ

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В роботі теоретично обґрунтована і експериментально доведена можливість спрямованого синтезу синьо-зелених шпінельних керамічних пігментів системи $\text{CoO-MgO-CaO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-TiO}_2$. Як базовий компонент застосовувався шлак алюмінотермічного виробництва ферротитану, який характеризується високим вмістом алюмінію(III) оксиду (71,5 мас. %). Показано, що в ролі первинної фази шлаку, що бере участь у формуванні магнієвої і кобальтової алюмошпінелей, виступає кальцій гексаалюмінат. Це дозволяє істотно знизити температуру випалу пігментів (у присутності мінералізуючої добавки V_2O_5 до 1150–1200°C). Введення до складу пігментних шихт хром(III) оксиду в кількості 0,1–0,5 моль (9,8–32,1 мас. %) забезпечує формування синьо-зеленого забарвлення керамічних пігментів ($\lambda=467\text{--}487$ нм). Результати фізико-хімічних досліджень показали, що колір пігментів обумовлений різним співвідношенням між алюмо- і хромошпінелями в твердому розчині (Co, Mg)(Cr, Al) $_2\text{O}_4$, розмір їх кристалів знаходиться в межах 4–6 мкм. Розроблені шпінельні пігменти характеризуються високими показниками хімічної стійкості (водостійкість 99,99%; кислотостійкість до 1 н. HCl 99,97–99,99%; лу-

гостійкість до 1 н. NaOH 97,40–99,95%). Їх застосування забезпечує одержання якісних склопокриттів синьо-зеленої колірної гами ($\lambda=472\text{--}485$ нм).

Ключові слова: керамічні пігменти, шлак алюмінотермічного виробництва ферротитану, термодинамічні розрахунки, мінералогічний склад, шпінель, колірні показники, склопокриття.

BLUE-GREEN SPINEL-TYPE CERAMIC PIGMENTS PREPARED FROM THE SLAG OF ALUMINOTHERMAL PRODUCTION OF FERROTITANIUM

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Directed synthesis of blue-green spinel-type ceramic pigments is theoretically justified and experimentally vindicated using the system $\text{CoO-MgO-CaO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-TiO}_2$. The slag of aluminothermal production of ferrotitanium with a high content of aluminium (III) oxide (71.5 wt.%) is used as a raw material. It is shown that calcium hexaaluminate is a primary phase of slag which takes part in the formation of magnesium and cobalt aluminate spinels. This allows appreciably reducing the temperature of pigments' firing (to 1150–1200°C in the presence of mineralizing additive V_2O_5). The introduction of chromium (III) oxide into the composition of pigment batches in the amount of 0.1–0.5 mol (9.8–32.1 wt.%) provides blue-green coloring of ceramic pigments ($\lambda=467\text{--}487$ nm). The results of physicochemical study shows that the color of the pigments is connected with different ratio between aluminate and chrome spinels in a solid solution (Co, Mg)(Cr, Al) $_2\text{O}_4$; their crystal size is 4–6 μm . The developed spinel pigments exhibit improved chemical stability (water resistance of 99.99%; 1 N HCl acid resistance of 99.97–99.99% and 1 N NaOH alkali resistance of 97.40–99.95%). They can be used to fabricate high-quality glass coatings of a blue-green color range ($\lambda=472\text{--}485$ nm).

Keywords: ceramic pigments; slag of aluminothermal production of ferrotitanium; thermodynamic calculations; mineral composition; spinel; color indices; glass coatings.

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