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THE STUDY OF CERAMIC PIGMENTS OF SPINEL TYPE WITH THE USE OF SLAG OF ALUMINOTHERMAL PRODUCTION OF FERROTITANIUM

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Abstract. The article deals with the results of theoretical and experimental research on the production of ceramic pigments of blue color with the structure of spinel on the basis of slag of aluminothermal production of ferrotitanium. The sequence of the physical and chemical processes that determine the formation of the set of crystalline phases under drossy pigments burning was established. The influence of the concentration of cobalt oxide and the temperature of researched pigments firing on their optical-color characteristics was studied. The application of the developed pigments for glaze coatings painting was shown.

Keywords: color, IR-spectroscopy, ceramic pigments, phase composition, optical-color indicators, X-ray phase analysis, thermodynamic calculations, slag.

1. Introduction

Ceramic pigments of spinel type are characterized by stability of their properties under the influence of various factors and, therefore, are widely used for painting of glass coatings of various purposes, as well as in overglaze and underglaze decoration. The similarity of structures and parameters of crystal lattice of many spinels causes one of their main features, which is the ability to isomorphic substitution with the formation of solid solutions.

Ceramic pigments of spinel type are synthesized in different systems, using the aluminum oxide as a primary component. In this case, a significant amount of pigments of blue colors are obtained based on cobalt aluminate ($CoAl_2O_4$), which has an intense blue -light blue tint and high melting point (2293 K) [1].

However, the use of expensive technically pure raw materials and high temperatures of baking, which even with the use of mineralizing additives are not lower than 1523–1623 K, predetermine high cost of such pigments and cause the necessity of using for the synthesis of a qualitatively new kind of raw materials, including the recycled ones.

Among the various industrial wastes concentrated in Ukraine, of special interest for the synthesis of ceramic pigments of spinel type are furnace slags of ferrotitanium production in aluminothermal way, which are characterized by a high content of aluminum oxide [2].

Therefore, the aim of this work is directed synthesis and study of ceramic pigments of blue color with the spinel structure with using of slag of aluminothermal production of ferrotitanium (APF) as the main component of the blend.

2. Experimental

For the production of ceramic pigments slag of APF, as well as oxides of magnesium and cobalt of “chp” classification were used. Boric acid of “chp” classification was used as mineralizing additive.

Pigment mixtures were prepared by consistent wet grinding of raw materials in the ball mill to the size of particles which are characterized by the balance on the control sieve No. 0056 of not more than 0.2 %. After drying the obtained raw mixtures were loaded in alumina crucibles and fired in a laboratory electric furnace in the temperature range of 1473–1573 K with exposure to the maximum temperature for 1 h. After the synthesis of the pigments their fine grinding to a particle size of less than 5 microns was carried out.

For colored glaze coatings obtaining, the developed ceramic pigments were injected into the transparent frit glaze in the number of 8 mass parts. Baking of glaze coating was conducted in the laboratory electric furnaces at the temperature of 1373 K with subsequent fast cooling.

In thermodynamic calculations in the system of CoO–CaO–MgO–Al_2O_3–TiO_2 the value of isobaric-isothermal potential of reactions ΔG_T^0 was calculated with the account of the constant of integration [3].

Thermodynamic constants for some compounds participating in the reactions of synthesis of ceramic pigments, which contain raw material mixture of APF slag as a component, are not available in the reference literature. Therefore, the change in the standard isobaric-isothermal potential (ΔG_{298}^0) and formation enthalpies of compounds (ΔH_{298}^0) were calculated according to the method developed by S. Lahzdinya [4], and the values of the coefficients a, b and c in the equation of the dependence of isobaric heat on the temperature was determined by the method of N. Landiya [5].

To establish the impact of the factor of concentration of cobalt oxide in the drossy ceramic pigments, burned out in the temperature range of 1473–1573 K, on their optical-color indicators, full factorial experiment FFE 3^2 was used. Processing of the received experimental data was conducted on a computer with the use of the methods of mathematical statistics [6].

The X-ray phase analysis of APF slag and ceramic pigments, obtained on its basis, was performed on the X-ray machine DRON–3 in Cu–Kα radiation. The identification of crystalline phases was carried out using [7]. The absorption spectra of the research slag and pigments in the infrared region were filmed using the Nicolet IS 10 in the range of 400–1000 cm^{-1}.

Optical-color measurements of ceramic pigments and glaze coating with their introduction were carried out with the help of the comparator color of the CC-3.

3. Results and Discussion

According to chemical analysis data (Table 1) the content of aluminium oxide in the sample of the researched slag is 71.5 wt %. Moreover, the aluminium oxide is mainly represented by the phases of corundum (α-Al_2O_3) and alkaline earth *β*-alumina (calcium hexaaluminate– $CaO{\cdot}6Al_2O_3$) – Fig. 1a. In addition, the initial slag contains a relatively large number of titanium(II) oxide, which in thermal treatment processes in air environment changes to titanium dioxide (Fig. 1b). On the basis of the obtained data on the chemical and mineralogical composition the researched slag as a whole can be attributed to the calciumaluminatitanium system and in terms of 1 mole of a substance contains: CaO – 0.1; Al_2O_3 – 0.65; TiO_2 – 0.25.

Taking into account the molar contents of the basic oxides in the research slag, and also the fact that during its subsequent thermal treatment calcium dioxide ($CaO{\cdot}2Al_2O_3$) interacts with corundum and forms hexacalcium, it would be logical to expect almost complete absence of α-Al_2O_3 in the final phase composition (Fig. 1b). At the same time, the X-ray of slag baked at 1573 K recorded intense reflections of corundum, which probably indicates the binding of calcium oxide and silicon dioxide, with the total content of 2.89 wt % (Table 1), in the residual glass phase. Ultimately, only about half of CaO, which is contained in the experimental slag may be in the form of $CaO{\cdot}6Al_2O_3$. In the end, only about half of the CaO contained in the experimental slag, can be in the form of $CaO{\cdot}6Al_2O_3$.

Table 1

Data on chemical analysis of the samples of investigated slag of aluminothermal production of ferrotitanium

Name and content (wt %) of components						
SiO_2	Al_2O_3	TiO	CaO	FeO	MgO	Amount
2.89	71.50	17.64	5.74	1.53	0.70	100

Therefore, when compiling the pigment blends in the future for convenience the following content of the main components of the APF slag was taken (mol): CaO – 0.05; Al_2O_3 – 0.65; TiO_2 – 0.25.

As an additional component magnesium oxide was studied. Its efficiency in the composition of ceramic pigments of spinel type was confirmed in the following publications [8-11].

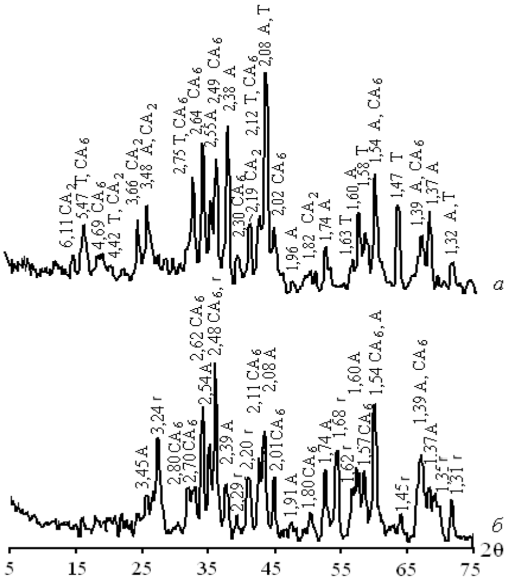


Fig. 1. X-ray phase analysis of researched slag: initial (a) and after thermal processing at 1573 K (b). A – α-Al_2O_3; T – TiO; CA_6 – $CaO{\cdot}6Al_2O_3$; CA_2 – $CaO{\cdot}2Al_2O_3$; r – TiO_2 (rutile)

To obtain the pigments of blue color, equimolecular replacement of magnesium oxide to cobalt oxide in their composition was done. The proximity of ion radii for Mg^{2+} (0,74 Å) and Co^{2+} (0,78 Å) [12] defines the possibility of spinels formation in the form of a continuous series of solid solutions of substitution in the phase composition of the researched pigments and formation of their blue color at a smaller amount of costly cobalt oxide.

At the same time, the complex phase composition of APF slag necessitates the study of the mechanism of mineral formation in systems with its application with a view to make substantiated choice of compositions of the initial composite mixtures.

Therefore, to assess the sequence of the reactions in the system of $CoO–CaO–MgO–Al_2O_3–TiO_2$ and to establish a possible mechanism of formation of drossy ceramic pigments phase composition, thermodynamic calculations of the Gibbs free energy change for a series of chemical reactions, presented below, in the temperatures range of 873–1573 К were conducted.

The values of the calculated and tabular [13, 14] thermodynamic values of individual compounds, both outgoing as well as those formed as intermediate and end products of the process of synthesis of ceramic pigments in the system $CoO–MgO–CaO–Al_2O_3–TiO_2$ at standard temperature are given in Table 2.

The results of thermodynamic calculations are presented in Table 3.

The analysis of the data obtained has shown that the primary products of firing of the researched drossy compositions of the system under consideration will be titanium dioxide and calcium hexaaluminate, as evidenced by the greatest negative values of isobaric-isothermal potential reaction (1 and 2).

Reactions 4–10 were excluded from the further interpretation of the results of thermodynamic analysis, as characterized by predominantly positive values of isobaric–isothermal potential, or occurring with very low energy effect, which testifies to the impossibility of solid–phase interaction between $CaO\cdot 6Al_2O_3$ and TiO_2, as well as formation of aluminum titanate ($Al_2O_3\cdot TiO_2$) in the system in the considered temperature range.

$CaO\cdot 2Al_2O_3 + 4(\alpha\text{-}Al_2O_3) \rightarrow CaO\cdot 6Al_2O_3$ (1)
$TiO + 0.5O_2 \rightarrow TiO_2$ (rutile) (2)
$CaO\cdot 2Al_2O_3 + TiO_2$ (rutile) $\rightarrow CaO\cdot TiO_2 + 2(\alpha\text{-}Al_2O_3)$ (3)
$CaO\cdot 6Al_2O_3 + TiO_2$ (rutile) $\rightarrow CaO\cdot TiO_2 + 6(\alpha\text{-}Al_2O_3)$ (4)
$\alpha\text{-}Al_2O_3 + TiO_2$ (rutile) $\rightarrow Al_2O_3\cdot TiO_2$ (5)
$CaO\cdot 2Al_2O_3 + TiO_2$ (rutile) $\rightarrow CaO\cdot Al_2O_3 + Al_2O_3\cdot TiO_2$ (6)
$CaO\cdot 6Al_2O_3 + 5TiO_2$ (rutile) $\rightarrow CaO\cdot Al_2O_3 + 5(Al_2O_3\cdot TiO_2)$ (7)
$CaO\cdot 6Al_2O_3 + 4TiO_2$ (rutile) $\rightarrow CaO\cdot 2Al_2O_3 + 4(Al_2O_3\cdot TiO_2)$ (8)
$CaO\cdot 6Al_2O_3 + TiO_2$ (rutile) $\rightarrow CaO\cdot Al_2O_3 + Al_2O_3\cdot TiO_2 + 4(\alpha\text{-}Al_2O_3)$ (9)
$CaO\cdot 6Al_2O_3 + TiO_2$ (rutile) $\rightarrow CaO\cdot 2Al_2O_3 + Al_2O_3\cdot TiO_2 + 3(\alpha\text{-}Al_2O_3)$ (10)
$MgO + \alpha\text{-}Al_2O_3 \rightarrow MgO\cdot Al_2O_3$ (11)
$CoO + \alpha\text{-}Al_2O_3 \rightarrow CoO\cdot Al_2O_3$ (12)
$MgO + 2TiO_2$ (rutile) $\rightarrow MgO\cdot 2TiO_2$ (13)
$CoO + 2TiO_2$ (rutile) $\rightarrow CoO\cdot 2TiO_2$ (14)
$MgO + TiO_2$ (rutile) $\rightarrow MgO\cdot TiO_2$ (15)
$CoO + TiO_2$ (rutile) $\rightarrow CoO\cdot TiO_2$ (16)
$2MgO + TiO_2$ (rutile) $\rightarrow 2MgO\cdot TiO_2$ (17)
$2CoO + TiO_2$ (rutile) $\rightarrow 2CoO\cdot TiO_2$ (18)
$MgO + CaO\cdot 2Al_2O_3 \rightarrow MgO\cdot Al_2O_3 + CaO\cdot Al_2O_3$ (19)
$CoO + CaO\cdot 2Al_2O_3 \rightarrow CoO\cdot Al_2O_3 + CaO\cdot Al_2O_3$ (20)
$4MgO + CaO\cdot 6Al_2O_3 \rightarrow 4(MgO\cdot Al_2O_3) + CaO\cdot 2Al_2O_3$ (21)
$4CoO + CaO\cdot 6Al_2O_3 \rightarrow 4(CoO\cdot Al_2O_3) + CaO\cdot 2Al_2O_3$ (22)
$5MgO + CaO\cdot 6Al_2O_3 \rightarrow 5(MgO\cdot Al_2O_3) + CaO\cdot Al_2O_3$ (23)
$5CoO + CaO\cdot 6Al_2O_3 \rightarrow 5(CoO\cdot Al_2O_3) + CaO\cdot Al_2O_3$ (24)
$CaO\cdot Al_2O_3 + TiO_2$ (rutile) $\rightarrow CaO\cdot TiO_2 + \alpha–Al_2O_3$ (25)
$2MgO\cdot TiO_2 + \alpha\text{-}Al_2O_3 \rightarrow MgO\cdot TiO_2 + MgO\cdot Al_2O_3$ (26)
$2CoO\cdot TiO_2 + \alpha\text{-}Al_2O_3 \rightarrow CoO\cdot TiO_2 + CoO\cdot Al_2O_3$ (27)
$2MgO\cdot TiO_2 + TiO_2$ (rutile) $\rightarrow 2(MgO\cdot TiO_2)$ (28)
$2CoO\cdot TiO_2 + TiO_2$ (rutile) $\rightarrow 2(CoO\cdot TiO_2)$ (29)

Table 2

Source thermodynamic constants of individual compounds

Compound	Condition	$-\Delta H^{0}_{298.15}$, kJ/mol	$-\Delta G^{0}_{298.15}$, kJ/mol	$S^{0}_{298.15}$, J/mol·K	$C_p = a + b \cdot T + c \cdot T^{-2}$, J/mol·K			Temperature range, K
					a	$b \cdot 10^{3}$	$c \cdot 10^{-5}$	
MgO	cr.	601.78	569.53	27.08	42.61	7.28	–6.19	298–2100
CoO	cr.	239.02	215.21	52.74	48.31	8.54	–1.67	298–2000
TiO	cr.	525.93	496.60	34.77	10.57	3.60	–1.86	298–1264
O_2	gas.	0	0	205.04	31.46	3.39	–3.77	298–3000
α-Al_2O_3	cr.	1675.69	1582.27	50.92	114.82	12.81	–35.45	298–1800
TiO_2 (rutile)	cr.	943.87	888.61	50.33	75.20	1.20	–18.20	298–1800
$CaO \cdot Al_2O_3$	cr.	2326.18	2208.67	114.22	150.70	24.95	–33.32	298–1800
$CaO \cdot 2Al_2O_3$	cr.	3994.70	3785.040	177.91	276.65	22.94	–74.51	298–1800
$CaO \cdot 6Al_2O_3$	cr.	10742.84	10160.54	376.56	647.14*	129.77*	0*	473–2206
$MgO \cdot Al_2O_3$	cr.	2300.78	2175.90	80.58	154.05	26.79	–40.94	298–1800
$CoO \cdot Al_2O_3$	cr.	1948.91	1831.69	103.64	154.70*	22.55*	–36.20*	298–2223
$CaO \cdot TiO_2$	cr.	1659.92	1574.61	93.64	127.55	5.69	–28.00	298–1530
$MgO \cdot 2TiO_2$	cr.	2507.89	2367.47	135.56	170.29	38.51	–30.77	298–1800
$MgO \cdot TiO_2$	cr.	1571.93	1483.59	74.56	118.42	13.73	–27.33	298–1800
$2MgO \cdot TiO_2$	cr.	2164.01	2047.44	115.10	150.53	35.75	–28.84	298–1800
$CoO \cdot 2TiO_2$	cr.	2148.26*	2009.99	110.8*	178.26*	26.07*	–47.89*	298–1755
$CoO \cdot TiO_2$	cr.	1210.52	1129.68	97.07	107.78*	22.11*	–17.45*	298–1736
$2CoO \cdot TiO_2$	cr.	1444.31	1344.28	165.27	149.81*	30.95*	–16.25*	298–1835
$Al_2O_3 \cdot TiO_2$	cr.	2607.21	2461.03	109.62	182.63	22.19	–46.92	298–1800

* thermodynamic characteristics calculated by the author

Table 3

Summary of the calculated change values of Gibbs free energy for reactions 1–29 in the temperatures interval of 873–1573 K

Reactions number	Value of the Gibbs energy of the reactions (kJ/mol) at the temperature, K							
	873	973	1073	1173	1273	1373	1473	1573
1	2	3	4	5	6	7	8	9
1	–70.43	–75.00	–79.45	–83.81	–88.10	–92.36	–96.60	–100.87
2	–355.99	–351.82	–348.11	–344.80	–341.86	–339.25	–336.96	–334.95
3	–52.30	–50.49	–48.80	–47.23	–45.78	–44.43	–43.19	–42.06
4	18.13	24.51	30.65	36.58	42.33	47.93	53.41	58.81
5	4.92	4.07	3.20	2.32	1.41	0.47	–0.50	–1.50
6	2.90	2.63	2.31	1.93	1.46	0.91	0.25	–0.51
7	93.02	93.91	94.58	95.01	95.20	95.15	94.88	94.38
8	90.12	91.28	92.26	93.08	93.73	94.24	94.63	94.89
9	73.32	77.63	81.77	85.74	89.57	93.27	96.86	100.36
10	75.35	79.07	82.66	86.13	89.51	92.83	96.11	99.38
11	–25.65	–25.99	–26.36	–26.77	–27.21	–27.70	–28.22	–28.80
12	–31.56	–30.73	–29.83	–28.86	–27.84	–26.76	–25.63	–24.45
13	–24.29	–24.90	–25.59	–26.36	–27.24	–28.23	–29.34	–30.60
14	–2.986	0.18	3.41	6.68	9.98	13.3	16.61	19.91
15	–24.31	–24.28	–24.31	–24.39	–24.53	–24.72	–24.97	–25.27
16	–19.29	–17.81	–16.30	–14.77	–13.23	–11.69	–10.15	–8.64
17	–26.00	–27.30	–28.69	–30.19	–31.80	–33.54	–35.41	–37.41
18	–25.97	–25.50	–24.94	–24.30	–23.60	–22.85	–22.08	–21.28
19	–27.68	–27.43	–27.25	–27.15	–27.15	–27.26	–27.48	–27.81
20	–33.59	–32.17	–30.72	–29.25	–27.78	–26.32	–24.88	–23.47

Table 3 (continued)

1	2	3	4	5	6	7	8	9
21	–32.19	–28.96	–25.99	–23.25	–20.74	–18.43	–16.30	–14.32
22	–55.82	–47.93	–39.87	–31.64	–23.24	–14.67	–5.90	3.07
23	–59.86	–56.39	–53.23	–50.41	–47.90	–45.69	–43.77	–42.13
24	–89.40	–80.1	–70.59	–60.89	–51.02	–40.99	–30.78	–20.40
25	–50.28	–49.06	–47.92	–46.85	–45.83	–44.87	–43.94	–43.04
26	–23.96	–22.97	–21.98	–20.97	–19.94	–18.88	–17.79	–16.66
27	–24.88	–23.05	–21.20	–19.34	–17.47	–15.60	–13.70	–11.81
28	–22.61	–21.26	–19.93	–18.59	–17.25	–15.90	–14.53	–13.14
29	–12.61	–10.13	–7.67	–5.24	–2.86	–0.52	1.77	4.00

When magnesium and cobalt oxides are used in the composition of the researched ceramic pigments the primary phase of APF slag, which participates in the formation of corresponding aluminates, according to the conducted calculations, is calcium hexaaluminate. Moreover, up to the temperature of 1173 K formation of cobalt spinel is thermodynamically more probable (Table 3, reaction 24). In the temperature range of 1273–1373 K interaction of MgO and CoO with $CaO{\cdot}6Al_2O_3$ is almost equiprobable. But beginning with the temperature of 1473 K formation of magnesium spinel by reaction 23 is more probable. A by-product at formation of cobalt and magnesium aluminates from calcium hexaaluminate is monocalcium aluminate ($CaO{\cdot}Al_2O_3$), which can further interact with TiO_2 by reaction 25. Titanium dioxide, which remained in the system, is spent on formation of magnesium orthotitanate $2MgO{\cdot}TiO_2$ (reaction 17). Only after that formation of alumomagnesium and alumocobalt spinel with the participation of α-Al_2O_3, is possible, since such reactions (11 and 12) are accompanied by relatively low values of isobaric–isothermal potential

At the same time, as a result of reaction 17, nonstoichiometry of free magnesium oxide in relation to α-Al_2O_3 or TiO_2 (when entering MgO into the blend composition for $MgO{\cdot}TiO_2$ formation) may occur in the system, which determines the possibility of their interaction with magnesium orthotitanate by the reactions 26 or 28, respectively.

It should also be noted that the interaction between the cobalt oxide and titanium dioxide (as in the case with MgO) are more likely with the formation of orthotitanate phase of reaction (18), but only after a complete binding of corundum in cobalt aluminate.

Thus, the carried out thermodynamic calculations have shown a high probability of formation of phases of cobalt and magnesium aluminates during firing of ceramic pigments of the system CoO–CaO–MgO–Al_2O_3–TiO_2, obtained with the use of APF slag as the main component. In addition, based on the given initial conditions, the most likely is the linking of titanium dioxide in magnesium ortho- or metatitanate, the presence of which, obviously, will not cause a significant deterioration in optical-color indicators of the researched pigments. Formation of $2CoO{\cdot}TiO_2$ phase in the above system has become possible only with high concentration of cobalt oxide, which exceeds 0.5 mol.

In view of the above, taking into account pigments cost, entering into their composition of MgO for magnesium metatitanate formation is rational. Thus, in the researched pigments equimolecular substitution of magnesium oxide to CoO in the amount of 0.25–0.5 mol in increments of 0.125 mol was done.

Molecular formulas of the obtained ceramic pigments can be expressed in the following form:

$0.25CoO{\cdot}0.6MgO{\cdot}0.05CaO{\cdot}0.65Al_2O_3{\cdot}0.25TiO_2$ (F-1)

$0.375CoO{\cdot}0.475MgO{\cdot}0.05CaO{\cdot}0.65Al_2O_3{\cdot}0.25TiO_2$ (F-2)

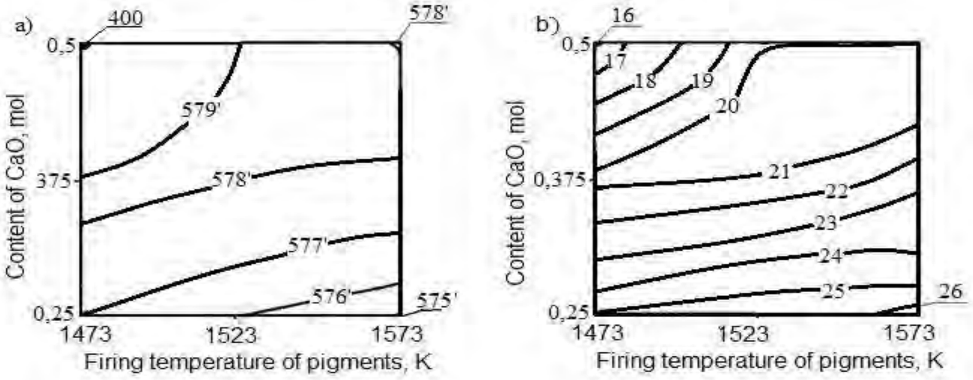
$0.5CoO{\cdot}0.35MgO{\cdot}0.05CaO{\cdot}0.65Al_2O_3{\cdot}0.25TiO_2$ (F-3)

As a result of mathematical processing of experimental data the regression equations, which adequately describe the relationship of optical–color indicators with the concentration of cobalt oxide in the research of ceramic pigments and the temperature of their synthesis have been obtained. Verification of the adequacy of the mathematical model established that with its help λ of ceramic pigments with the accuracy of ± 0.222 nm and CDR – with the accuracy of 0.524 % can be calculated.

Graphical interpretation of the obtained dependencies is illustrated in Fig. 2.

The analysis of the given data shows that two factors are significant. Increase of cobalt oxide concentration in the composition of pigments (F-1 to F-3) from 0.25 to 0.5 mol causes increased intensity of blue color, which is confirmed by the drop of diffuse reflection (CDR), in general from 25–26 up to 16–20 % and increase of the values of wavelength in the purple area of the spectrum to 578'–579' nm with their subsequent transfer to violet part of the spectrum (400 nm).

With increasing firing temperature of such pigments from 1473 to 1573 K the degree of their sintering increases, and color changes from blue with grey-turquoise tint to the blue of varying intensity. Growth of the CSC values from 16–25 to 20–26 % occurs.



$y = 511.222–0.183·x_1+52·x_2–1.119·10^{-11}·x_1x_2–$
$–6.667·10^{-5}·x_1^2–53.333·x_2^2$

$y = –234.61+0.461·x_1–216.247·x_2+0.119·x_1·x_2–$
$–1.933·10^{-4}·x_1^2+53.227·x_2^2$

x_1 – firing temperature of pigments (K); x_2 – content of CoO (mol)

$r = 0.989$ $r = 0.986$

where r – the correlation coefficient

Fig. 2. Effect of the concentration of cobalt oxide and firing temperature of the researched pigments on their optical-color indicators: wavelength (a) and coefficient of diffusion reflection (b)

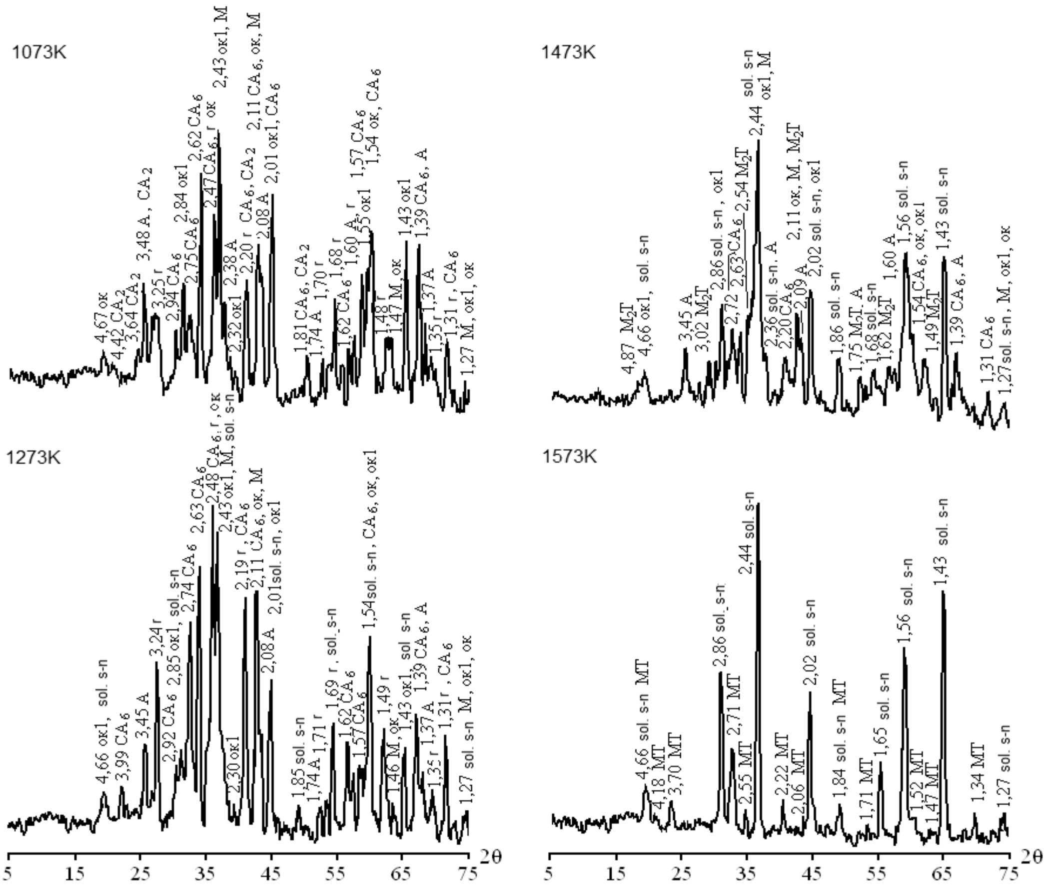


Fig. 3. Diffractograms of ceramic pigment F-1, baked in the temperature range of 1073–1573 K: A – α-Al_2O_3; CA_6 – $CaO·6Al_2O_3$; CA_2 – $CaO·2Al_2O_3$; r – TiO_2 (rutile); sol. s-n – solid solution between $CoAl_2O_4$ and $MgAl_2O_4$; M_2T – Mg_2TiO_4; MT – $MgTiO_3$; ок – CoO; ок1 – Co_3O_4; M – MgO

To identify the dynamics of the phase composition formation of ceramic pigments received in the system CoO–CaO–MgO–Al_2O_3–TiO_2, their X-ray and IR-spectroscopic studies were performed (Figs. 3 and 4).

The data of physico–chemical studies correlate well with the results of thermodynamic calculations (Table 3) and optical-colorimetric measurements (Fig. 2).

By the X-ray analysis it was found that up to 1273 K inclusive the formation of rutile phase takes place in the investigated pigment F-1, and increase in the content of calcium hexaaluminate according to the reactions 1 and 2 (see data Table 3) occurs, as confirmed by a substantial increase in the intensity of the main diffraction peaks corresponding to these compositions. Formation of magnesium and cobalt aluminates starts with the temperature of 1273 K, and actively flows only at 1473 K. The primary phase of slag, which participates in the formation of these spinels, is calcium hexaaluminate, because for this compound strong drop in the intensity of its basic reflexes at $d\cdot10^{-10}$ = 2.72; 2.63; 2.47 and 2.20 m is observed.

It should be noted that oxides of magnesium and cobalt are almost equally spent on interaction with $CaO\cdot6Al_2O_3$, and further with α-Al_2O_3. Phase composition of the pigment, which is synthesized at the temperature of 1473 K, is also characterized by the presence of magnesium orthotitanate ($d\cdot10^{-10}$ = 4.87; 3.02; 2.54 and 1.49 m).

The completion of the process of mineralization in the investigated pigment takes place only at the temperature of 1573 K, and its final phase composition is mainly represented by a solid solution between cobalt and magnesium aluminates (Co, Mg)Al_2O_4, which is confirmed by the high level of reflexes at $d\cdot10^{-10}$ = 4.66; 2.86; 2.44; 2.02; 1.65; 1.56 and 1.43 m. In addition, magnesium metatitanate was identified ($d\cdot10^{-10}$ = 3.70; 2.71; 2.55 and 2.22 m). Calcium metatitanate, which obviously is also present in the composition of the pigment, cannot be identified separately due to the proximity of its basic diffraction maxima to $MgTiO_3$, as well as due to its small content.

Heat treatment of pigment composition of the batch F-1 also causes a change of the position and the nature of the high-frequency bands of infrared spectrum (Fig. 4) in the field of 700–1000 cm^{-1}, which are responsible for the valence vibrations of the AlO_4-tetrahedra, which are the main structural elements of the dialuminate and, partially, hexaaluminate of calcium (in β-forms Al_2O_3 cations of aluminum also occupy octahedral voids [15]). In particular, there has been a gradual shift of the main maximum of absorption to low frequencies (900 → 785 cm^{-1}) and the decrease in intensity of a broad frequency band in whole, with the increase of the investigated pigment firing temperature to 1273 K. Moreover, already at 1073 K a sufficiently intensive single band 720 cm^{-1} is transformed into the shoulder with the frequency of absorption of 705 cm^{-1}. The above mentioned indicates a decrease in the system of the number of ions of Al^{3+}, tetrahedrally coordinated by oxygen, which is caused by the interaction of crystalline phases of slag (calcium dialuminate and aluminum oxide) with the formation of calcium hexaaluminate and is consistent with the X-ray analysis data (Figs. 1 and 3).

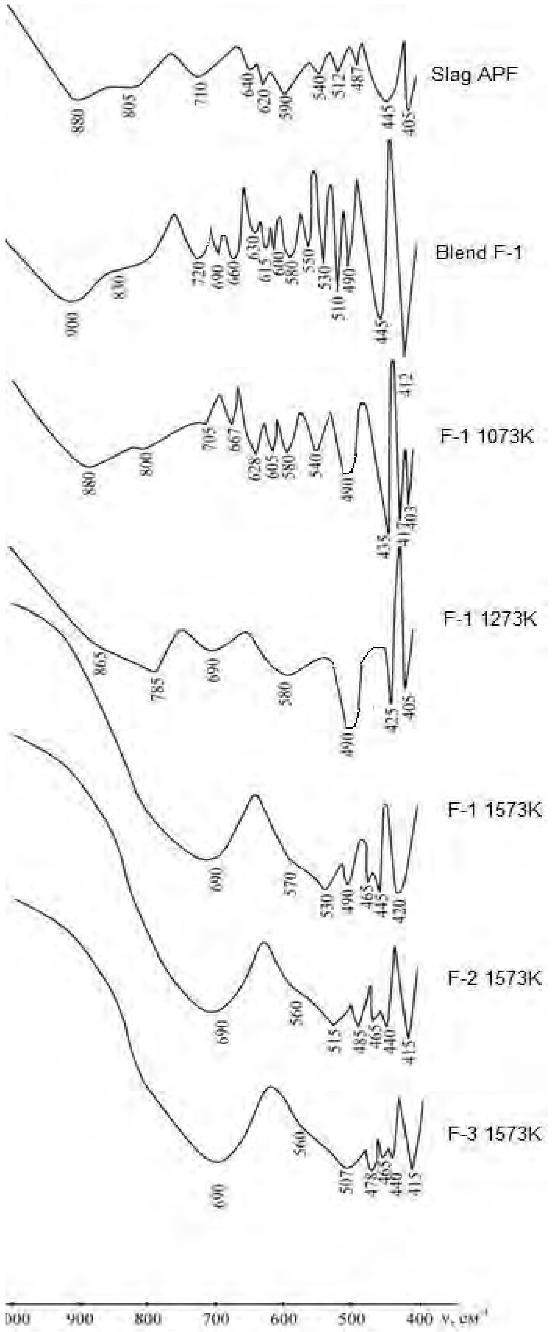


Fig. 4. IR-spectra of ceramic pigments (F-1)–(F-3), obtained at different temperatures

The spectrogram of the studied composition, heat–treated at 1273 K, shows a fairly intensive absorption maximum with the frequency of 690 cm^{-1}, which can be associated with the entry of a part of Mg^{2+} and Co^{2+} ions into the positions of tetrahedral coordination, which is characteristic of the spinel structure [1, 16-19]. After firing at the temperature of 1573 K intensive characteristic absorption bands of spinels in the frequency range of 650–850 cm^{-1} and 500–600 cm^{-1} are observed [16-19]. High-frequency band of the spectrum with a maximum 690 cm^{-1} corresponds to the valence vibrations of the links in tetrahedra [MgO_4] and [CoO_4], while the low-frequency one with shoulder at 570 cm^{-1} and intense absorption at 530 cm^{-1}, is a band of AlO_6-octahedral fluctuations. More complex absorption in low-wave part of the infrared spectrum, in comparison with the typical spinels, obviously, is defined by the imposition of frequencies of valent oscillations of TiO_6-octahedra (490 cm^{-1}), which are the main structural elements of metatitanate [1, 20]. The appearance of the lines of relatively low intensity in the range from 400 to 450 cm^{-1} should probably be attributed to the fluctuations of Me–O bonds in polyhedra [MgO_6] and [CaO_6] magnesium and calcium metatitanates.

Spectroscopic studies also established the fact of the formation of a single solid solution between cobalt and magnesium aluminate in these pigments. This is evidenced by the gradual shift of intensive band (530 cm^{-1}), which is responsible for the fluctuations of the AlO_6-octahedra, in more low wave region (507 cm^{-1}) with the content of CoO in pigments from 0.25 to 0.5 mol, which is characteristic of the transition from $MgAl_2O_4$ to $CoAl_2O_4$ spectrum [15, 18].

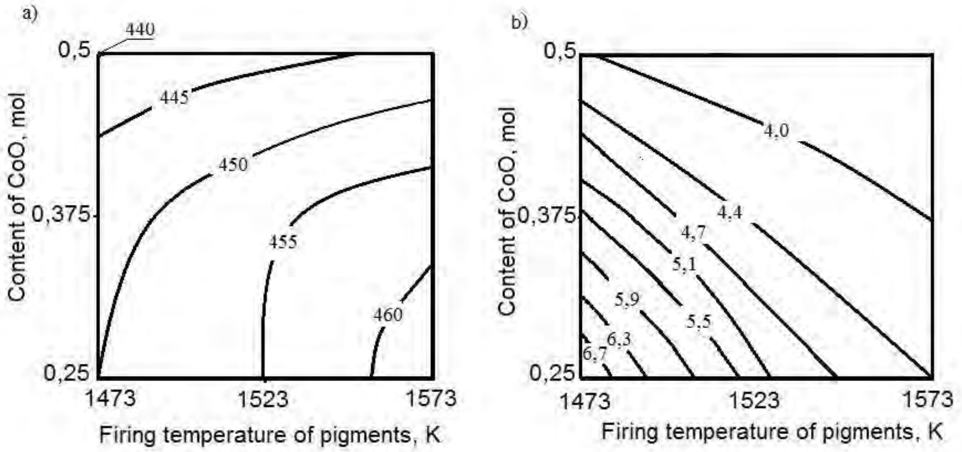
Thus, the results of the physico-chemical studies have identified the formation of cobalt and magnesium aluminates phases, among which solid solutions of substitution are formed, as well as full binding of titanium dioxide in magnesium and calcium metatitanate in the investigates drossy pigments, which confirms the calculated thermodynamic data.

Thin grind powders of the developed ceramic pigments were further introduced into the transparent frit glaze composition.

Mathematical processing of the experimental data allowed to obtain regression equations which adequately describe the correlation of optical–color indicators of scorched glaze coatings with the concentration of cobalt oxide in the composition of the researched ceramic pigments and their temperature synthesis. By the verification of the adequacy of the mathematical model it was established, that with its help λ glaze coatings with the accuracy of ± 0.683 nm and CDR – with the accuracy of ± 0.094 % can be calculated.

The obtained regression equations of the second order were used for the construction of isolines of optical-color characteristics of pigment containing glazed coatings in the investigated factor space (Fig. 5).

Analysis of the data of optical-color indicators allowed to establish that the increase of the temperature of synthesis of magnesium–containing ceramic pigments, in whose structure the concentration of CoO is in the range of 0.25–0.375 mol, to 1573 K causes significant growth of intensity and share of blue painting glaze coating with their introduction. This fact is confirmed by the shift of λ values (447–450 nm) in a more long-wave part of the blue



$y = –18.028+0.532 \cdot x_1+482 \cdot x_2–0.28 \cdot x_1 \cdot x_2–$
$–1.333 \cdot 10^{–4} \cdot x_1^2–245.333 \cdot x_2^2$

$y = 266.832–0.368 \cdot x_1–114.493 \cdot x_2+0.085 \cdot x_1 \cdot x_2+$
$+1.287 \cdot 10^{–4} \cdot x_1^2+2.667 \cdot x_2^2$

x_1 – firing temperature pigments (K); x_2 – content CoO (mol)

$r = 0.995$ $r = 0.995$

where r – the correlation coefficient

Fig. 5. Influence of the temperature of firing and concentration of cobalt oxide in the research of ceramic pigments on the length of wave (a) and the ratio of diffuse reflection (b) glaze of the coatings obtained with their introduction

region of the spectrum (458–462 nm), as well as by the reduction in diffuse reflection from 5.60–6.92 to 4.01–4.40 %. Moreover, an improvement of quality indicators of glaze coating (absence of defects in the form of injections) takes place. Optical-color indicators of glaze coatings obtained with the introduction of pigment F-3 (the contents of CoO is 0.5 mol) and their painting in whole, demonstrate little dependence on the temperature of the pigment synthesis. The values of the color tone are ranging within 440–445 nm, and CDR – 3.70–4.10 %.

Additional introduction of boric acid into the composition of ceramic pigments (2 mass parts in terms of the B_2O_3) allowed to lower the temperature of their synthesis to 1423 K. Burnt pigment–containing glaze coating were characterized by a steady blue (λ = 450–466 nm, CDR = 3.82–4.48 %) and the absence of defects.

4. Conclusions

Using the thermodynamic calculations, which were confirmed by the X-ray study and infrared spectroscopy, the fundamental possibility of using slag of aluminothermal production of ferrotitanium for the production of ceramic pigments containing as the main crystalline phase solid solution between magnesium and cobalt aluminate spinel was established. It was shown that the primary phase of the slag, which participates in the formation of these spinels, is calcium hexaaluminate, which, ultimately, can significantly reduce the temperature of pigments firing (in the presence of mineralizator to 1423 K). The optimal concentration of cobalt oxide in the drossy pigments (0.25–0.375 mol, which is 14.2–20.6 wt %), which allows to obtain an intense blue color of glaze layer (λ = 464–466 nm, CDR = 4.11–4.48 %) and high quality of the surface was established.

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ВИВЧЕННЯ КЕРАМІЧНИХ ПІГМЕНТІВ ШПІНЕЛЬНОГО ТИПУ З ВИКОРИСТАННЯМ ШЛАКУ АЛЮМІНОТЕРМІЧНОГО ВИРОБНИЦТВА ФЕРОТИТАНУ

Анотація. *У статті розглянуті результати теоретичних і експериментальних досліджень з отримання керамічних пігментів синьої колірної гами зі структурою шпінелі на основі шлаку алюмінотермічного виробництва феротитану. Встановлена послідовність протікання фізико-хімічних процесів, які обумовлюють формування заданих кристалічних фаз при випалі шлаковмісних пігментів. Вивчений вплив концентрації оксиду кобальту і температури випалу дослідних пігментів на їх оптико-колірні показники. Показана перспективність використання розроблених пігментів для забарвлення глазурних покриттів.*

Ключові слова: *забарвлення, ІЧ-спектроскопія, керамічні пігменти, кристалофазовий склад, оптико-колірні показники, рентгенофазовий аналіз, термодинамічні розрахунки, шлак.*