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THERMODYNAMIC ANALYSIS OF THE REACTIONS OF DIOPSIDE PHASE FORMATION DURING SYNTHESIS OF CERAMIC PIGMENTS FROM GRANULATED BLAST-FURNACE SLAG

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The purpose of this study is to perform the thermodynamic analysis of the reactions of diopside phase ($CaO\cdot MgO\cdot 2SiO_2$) formation during the synthesis of ceramic pigments based on the granulated blast-furnace slag. Thermodynamic analysis is of great practical importance in studying solid-phase interactions, which are involved in the pigment technology. At the same time, the scope of energy-intensive experimental studies of ceramic pigments is significantly reduced. When performing thermodynamic calculations, we assessed the fundamental possibility and direction of occurrence of chemical reactions by determining the changes in the Gibbs energy. In order to verify the calculation data, the change in the mineralogy of the diopside compositions was evaluated with the use of X-ray phase analysis at different firing temperatures. It was found that the diopside phase in the $CaO-MgO-Al_2O_3-SiO_2$ system is formed in several stages. The merwinite ($3CaO\cdot MgO\cdot 2SiO_2$) mineral is formed first. Further, merwinite, along with blast-furnace slag minerals, is involved in the diopside formation. The formation of diopside is completed at the temperature of 1200^0C. The findings of the study will provide a reasonable approach to the choice of compositions of ceramic pigments using complex raw materials, including the wastes of various industries.

Keywords: ceramic pigment, blast-furnace slag, thermodynamic analysis, X-ray phase analysis, mineralogical composition, diopside.

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Introduction

Ceramic pigments represent the most effective components for coloring glass coatings and provide a diversity of color palettes. Industrial pigments of the given color are obtained predominantly by solid-phase synthesis using the corresponding chemical systems. Spinel-type ceramic pigments, characterized by the cubic structure, have the most stable color [1,2].

In order to obtain a wide range of stable ceramic pigments characterized by low firing temperature, it is expedient to use the crystal lattice of various silicates. During the synthesis of such pigments, the ions of transition elements and rare earth elements are introduced in the silicate crystal lattice with the formation of color-bearing phases in the reaction products. In this case, the pigment color depends on the chemical nature of the introduced chromophore ion, its coordination environment, and the level of symmetry of coordination polyhedral [3–5].

Ceramic pigments with a wide range of colors based on various mineral raw materials can be synthesized using the crystal lattice of the chain silicate, such as diopside ($CaO\cdot MgO\cdot 2SiO_2$). The diopside structure determines the possibility of processes of isomorphic substitution of Mg^{2+} ions for Co^{2+}, Ni^{2+} and Mn^{2+} ions; Si^{4+} ions for Ti^{4+}, Fe^{3+} ions, and, particularly, for Al^{3+} ions [6].

The substitution of MgO for CoO within the diopside structure causes the formation of $Ca(Co_xMg_{1-x})Si_2O_6$ substitution solid solution (where x=0.05–0.80 mol) and change in the pigment color from pink to purple. The color of these pigments is determined by the presence of Co^{2+} ions in the octahedral coordination [7]. The pigments ensure

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the blue color of glass coatings similar to that provided by the industrial blue pigments. At the same time, the content of CoO in the pigments of diopside structure is 5 wt.% lower than in the traditional cobalt-containing pigments.

Diopside pigments obtained by stepwise introduction of nickel oxide (0.3–0.8 mol) instead of MgO are acquired to the light green color of varying intensity. The substitution of MgO by MnO in diopside changes the color of the pigments from pinkish grey to brown. Color-bearing phases of such pigments, along with the diopside solid solution, are also represented by various spinels and, in part, by coloring oxides not undergoing a reaction.

Sedel'nikova and Pogrebenkov [8] studied the ceramic pigments of diopside structure with the use of the natural silicate raw materials, in particular, wollastonite, talc and tremolite. The firing was carried out in the temperature range of 1100–1300^{0}C. With the increase in the content of oxide-chromophores from 0.1 to 1.0 mol in the pigment composition, their color intensifies: it turns to lilac, to green and to brown for cobalt-containing pigments, chromium-containing pigments and iron-containing pigments, respectively. When the considered chromophores are introduced instead of magnesium oxide, cristobalite and spinels ($MgO{\cdot}Fe_2O_3$, $MgO{\cdot}Cr_2O_3$) are also identified in the phase composition of diopside pigments. Cobalt oxide is not recorded at any concentration under study. Chromium and iron oxides are observed in the free form at the content of 0.5 mol (about 28 wt.% in the batch) and above.

In order to expand the raw material base of pigment technology and reduce the synthesis temperature, it is advisable to use secondary raw materials, including in the form of slags from various metallurgical industries. The use of metallurgical slags can significantly reduce the material and energy costs for the production of ceramic pigments.

The expediency of using open-hearth slags in the production of spinel pigments is shown in the literature [9]. Open-hearth slags feature high content of ferric oxide (up to 30 wt.%). The additional introduction of chromium and nickel oxides (jointly and separately) allows obtaining the pigments with a wide range of brown colors. The use of $ZrO_2{\cdot}SiO_2$ as an opacifying component and the additional introduction of CoO provide the grey color of pigments [10]. For spinel pigments of the blue-green series, granulated blast-furnace slag [11] and slag of the alumino-thermic production of ferrotitanium [12] were used as the main raw materials. Cobalt and chromium oxides were used as the coloring components. When the metallurgical slags are used, the firing temperature of spinel pigments is reduced to 1150–1250^{0}C.

The granulated blast-furnace slag has found an effective application in the preparation of pigments of the orthosilicate structure (tin sphene). The developed chromium-containing pigments have a stable pink color [13].

Calcium oxide, magnesium oxide and silicon dioxide are the basic components of blast-furnace slag. In view of the above, it is expedient to use blast furnace slag as the main component in the production of ceramic pigments with a diopside structure.

To date, the waste from alumina production, nepheline sludge, is known as the only material used for production of diopside pigments among the secondary materials [14]. CaO and SiO_2 are its main components at a molar ratio of 2:1 and total content of 85–88 wt.%. When nepheline sludge is used, wollastonite, akermanite, and coloring oxides are identified in the phase composition of pigments, along with diopside. This fact indicates the complexity and gradation of processes of diopside phase formation in pigments.

The multistage nature of the diopside phase formation is also evidenced by X-ray phase studies of ceramic pigments obtained based on natural wollastonite. In the first stage, forsterite and a small amount of magnesium metasilicate are formed, and then diopside appears.

The processes occurring during the synthesis of ceramic pigments can be studied quite effectively using the modern physicochemical methods of analysis. However, these studies are possible only under the condition of obtaining specific practical results in the form of a finished product. On the other hand, thermodynamic analysis is a rather fruitful method of preliminary assessment of the probable conditions and sequence of the chemical and physical-chemical processes. It is of high practical significance in the study of solid-phase interactions typical of the pigment technology and in explaining their various features.

The purpose of this study is to perform the thermodynamic analysis of the reactions of diopside phase formation during the synthesis of ceramic pigments based on the granulated blast-furnace slag. The study provides a reasonable approach to the choice of compositions of ceramic pigments using complex raw materials, including secondary ones.

Experimental

Thermodynamic calculations were performed to identify the sequence of chemical reactions in the $CaO{-}MgO{-}Al_2O_3{-}SiO_2$ system using the granulated blast-furnace slag as a basic component.

The mineralogy of diopside compositions after firing was evaluated using X-ray phase analysis (XPA) on the diffractometer Philips APD-15 in the Cu-K_α radiation.

Granulated blast-furnace slag produced by «ArcelorMittal Kryvyi Rih», Avdiivka quartz sand (Ukraine) and chemically pure magnesium oxide (MgO content ≥98.0 wt.%) were used as the raw materials to obtain diopside compositions. Diopside compositions were prepared by joint wet grinding of the initial raw materials. The firing was carried out in the temperature range of 800–1200°C.

Results and discussion

To obtain the diopside compositions, we consider the granulated blast-furnace slag as a basic component; it is characterized by a high content of calcium oxide, magnesium oxide, aluminum oxide and silicon dioxide (about 97 wt.% in total). Blast-furnace slag is characterized by low iron oxides content (up to 0.5 wt.%), which is of great importance in the synthesis of ceramic pigments of high color purity. The products of crystallization of the granulated blast-furnace slag are the solid solution (melilite) between akermanite ($2CaO\cdot MgO\cdot 2SiO_2$) and gehlenite ($2CaO\cdot Al_2O_3\cdot SiO_2$), as well as calcium meta- and orthosilicates [13]. In addition, calcite ($CaCO_3$) is formed during the storage of solid slag wastes in dumps. X-ray phase analysis and differential thermal studies confirm the presence of the above-mentioned crystalline phase in the blast-furnace slag.

The ultimate goal of thermodynamic calculations is to find the change in the Gibbs energy $\left(\Delta G_T^0\right)$ of the reaction. The fundamental possibility and probable direction of occurrence of any physicochemical process is determined by the magnitude and sign of change in the Gibbs energy. The reaction is fundamentally possible if $\Delta G_T^0 < 0$. Among various processes occurring in the system, the process accompanied by the highest decrease in the Gibbs energy change is the most favourable from the thermodynamic point of view.

There are no thermodynamic constants for blast-furnace slag minerals in the glassy state in the literature, so we used the thermodynamic data for crystalline compounds. A slight difference between the thermodynamic constants for various silicates in the crystalline and glassy states does not cause any noticeable distortion of the final result. When performing thermodynamic calculations, we took into account the polymorphic transformations of α-quartz→α-tridymite and $\gamma\text{-}Ca_2SiO_4\rightarrow\alpha'\text{-}Ca_2SiO_4$.

X-ray phase analysis of heat-treated blast-furnace slag showed no direct interaction between its minerals [13]. Therefore, we did not consider these reactions in our thermodynamic calculations. At the same time, we considered the molar ratio of the main crystalline phases in the heat-treated blast-furnace slag. Thus, individual slag minerals could simultaneously act as the basic substances in several solid-phase reactions. Charge-adjusting components (MgO and SiO_2) could also be involved in several reactions.

Thermodynamic calculations for slag-containing compositions of the $CaO-MgO-Al_2O_3-SiO_2$ system were performed for the chemical reactions in the temperature range of 1073–1473 K.

The reactions characterized by the highest decrease in the values of ΔG_T^0 of all reactions under study are listed below:

$$2MgO+SiO_2\rightarrow 2MgO\cdot SiO_2; \quad (1)$$

$$2CaO\cdot MgO\cdot 2SiO_2+MgO+2SiO_2\rightarrow \rightarrow 2(CaO\cdot MgO\cdot 2SiO_2); \quad (2)$$

$$2CaO\cdot MgO\cdot 2SiO_2+MgO+2CaO\cdot SiO_2\rightarrow \rightarrow 3CaO\cdot MgO\cdot 2SiO_2+CaO\cdot MgO\cdot SiO_2; \quad (3)$$

$$2(2CaO\cdot MgO\cdot 2SiO_2)+2MgO\cdot SiO_2+3SiO_2\rightarrow \rightarrow 4(CaO\cdot MgO\cdot 2SiO_2); \quad (4)$$

$$2CaO\cdot SiO_2+MgO+SiO_2\rightarrow \rightarrow 2CaO\cdot MgO\cdot 2SiO_2; \quad (5)$$

$$2CaO\cdot SiO_2+MgO+CaO\cdot SiO_2\rightarrow \rightarrow 3CaO\cdot MgO\cdot 2SiO_2; \quad (6)$$

$$2CaO\cdot SiO_2+2MgO+3SiO_2\rightarrow \rightarrow 2(CaO\cdot MgO\cdot 2SiO_2); \quad (7)$$

$$2CaO\cdot SiO_2+2MgO\cdot SiO_2+2SiO_2\rightarrow \rightarrow 2(CaO\cdot MgO\cdot 2SiO_2); \quad (8)$$

$$2CaO\cdot SiO_2+2MgO+SiO_2\rightarrow \rightarrow 2(CaO\cdot MgO\cdot SiO_2); \quad (9)$$

$$CaO\cdot SiO_2+MgO+SiO_2\rightarrow \rightarrow CaO\cdot MgO\cdot 2SiO_2; \quad (10)$$

$$2CaO\cdot Al_2O_3\cdot SiO_2+MgO+2SiO_2\rightarrow \rightarrow CaO\cdot Al_2O_3\cdot 2SiO_2+CaO\cdot MgO\cdot SiO_2; \quad (11)$$

$$2CaO\cdot Al_2O_3\cdot SiO_2+MgO+3SiO_2\rightarrow \rightarrow CaO\cdot Al_2O_3\cdot 2SiO_2+CaO\cdot MgO\cdot 2SiO_2; \quad (12)$$

$$2(2CaO\cdot Al_2O_3\cdot SiO_2)+MgO+4SiO_2\rightarrow \rightarrow 2(CaO\cdot Al_2O_3\cdot 2SiO_2)+2CaO\cdot MgO\cdot 2SiO_2; \quad (13)$$

Table 1

Initial thermodynamic constants of individual compounds [15]

Compound	State *	$-\Delta H^0_{298,15}$, kJ/mol	$-\Delta G^0_{298,15}$, kJ/mol	$S^0_{298,15}$, kJ/mol·K	$C_p = a + b \cdot T + c \cdot T^{-2}$, kJ/mol·K			Temperature rang K
					a	$b \cdot 10^3$	$c \cdot 10^{-5}$	
$2CaO \cdot Al_2O_3 \cdot SiO_2$	cr.	4007.85	3809.12	209.78	266.81	33.49	–63.29	298–1600
$2CaO \cdot MgO \cdot 2SiO_2$	cr.	3877.14	3679.79	209.20	251.54	47.72	–47.72	298–1700
α-$CaO \cdot SiO_2$	cr.	1628.73	1544.68	86.23	108.21	16.49	–23.65	298–1700
γ-$2CaO \cdot SiO_2$	cr.	2316.68	2200.02	120.79	133.37	51.57	–19.42	298–1120
α'-$2CaO \cdot SiO_2$	cr.	2308.58	2194.00	127.67	134.62	46.13	0	970–1710
$CaO \cdot Al_2O_3 \cdot 2SiO_2$	cr.	4243.41	4017.77	199.28	269.66	57.35	–70.70	298–1600
$CaO \cdot MgO \cdot 2SiO_2$	cr.	3202.68	3028.53	142.92	221.31	32.82	–65.89	298–1600
$CaO \cdot MgO \cdot SiO_2$	cr.	2263.04	2145.45	108.78	144.52	38.53	–28.49	298–1600
$3CaO \cdot MgO \cdot 2SiO_2$	cr.	4567.42	4340.20	253.13	305.45	50.06	–60.44	298–1600
$2MgO \cdot SiO_2$	cr.	2171.91	2052.93	95.19	149.90	27.38	–35.66	298–1800
α-quartz	cr.	911.50	857.08	41.86	60.32	8.13	0	848–2000
α-tridymite	cr.	905.98	852.19	43.53	57.10	11.05	0	390–2000
$CaCO_3$ (calcite)	cr.	1206.83	1128.35	91.71	104.52	21.92	–25.94	298–1200
CO_2	gas.	393.51	394.37	213.66	44.14	9.04	–8.54	298–2500

Note: * – cr. – crystalline; gas. – gaseous.

$$2CaO \cdot Al_2O_3 \cdot SiO_2 + 2MgO + SiO_2 \rightarrow \rightarrow 2[CaO \cdot MgO \cdot 2((Si_{0.5}, Al_{0.5})O_{1.75})]; \quad (14)$$

$$CaCO_3 + 2CaO \cdot MgO \cdot 2SiO_2 \rightarrow \rightarrow 3CaO \cdot MgO \cdot 2SiO_2 + CO_2; \quad (15)$$

$$CaCO_3 + MgO + 2CaO \cdot SiO_2 + SiO_2 \rightarrow \rightarrow 3CaO \cdot MgO \cdot 2SiO_2 + CO_2; \quad (16)$$

$$CaCO_3 + MgO + 2(CaO \cdot SiO_2) \rightarrow \rightarrow 3CaO \cdot MgO \cdot 2SiO_2 + CO_2; \quad (17)$$

$$3CaCO_3 + MgO + 2SiO_2 \rightarrow \rightarrow 3CaO \cdot MgO \cdot 2SiO_2 + 3CO_2; \quad (18)$$

$$CaCO_3 + MgO + 2SiO_2 \rightarrow \rightarrow CaO \cdot MgO \cdot 2SiO_2 + CO_2; \quad (19)$$

$$2CaCO_3 + MgO + 2SiO_2 \rightarrow \rightarrow 2CaO \cdot MgO \cdot 2SiO_2 + 2CO_2; \quad (20)$$

$$CaCO_3 + MgO + SiO_2 \rightarrow \rightarrow CaO \cdot MgO \cdot SiO_2 + CO_2; \quad (21)$$

$$3CaO \cdot MgO \cdot 2SiO_2 + 2MgO + 4SiO_2 \rightarrow \rightarrow 3(CaO \cdot MgO \cdot 2SiO_2). \quad (22)$$

Thermodynamic constants of the substances involved in the above reactions are presented in Table 1 [15]. Table 2 includes the results of thermodynamic calculations for reactions (1)–(22).

Table 2

Summary of calculated values of ΔG^0_T for reactions (1)–(22)

Reaction number	Reaction ΔG^0_T values (kJ/mol) at different temperatures				
	1073 K	1173 K	1273 K	1373 K	1473 K
1	–53.32	–57.33	–57.10	–56.93	–56.83
2	–58.40	–62.80	–58.72	–54.76	–50.91
3	–43.23	–38.33	–38.10	–37.89	–37.70
4	–63.47	–68.27	–60.35	–52.59	–44.98
5	–65.10	–64.60	–64.38	–64.11	–63.78
6	–42.53	–38.55	–39.15	–39.69	–40.16
7	–123.49	–127.40	–123.10	–118.87	–114.68
8	–70.17	–70.08	–66.01	–61.94	–57.85
9	–94.76	–93.37	–92.44	–91.63	–90.94
10	–43.33	–46.00	–44.43	–42.93	–41.50
11	–54.32	–61.28	–59.86	–58.68	–57.76
12	–68.69	–78.30	–75.20	–72.31	–69.63
13	–78.98	–93.80	–91.66	–89.84	–88.34
14	–175.40	–171.25	–163.12	–155.28	–147.74
15	–49.52	–64.63	–	–	–
16	–114.61	–129.24	–	–	–
17	–77.78	–93.83	–	–	–
18	–221.95	–275.21	–	–	–
19	–115.41	–136.69	–	–	–
20	–172.43	–210.57	–	–	–
21	–101.05	–119.67	–	–	–
22	–124.30	–134.85	–128.39	–122.12	–116.02

The calculations of ΔG^0_T of the chemical reactions showed (Table 2) that merwinite mineral

($3CaO{\cdot}MgO{\cdot}2SiO_2$) was the most preferred product of the interaction of the blast-furnace slag minerals with silicon dioxide and magnesium oxide at the first stage. The merwinite formation following reaction 18 is characterized by the highest negative values of . Subsequently, reactions of the diopside phase formation are likely to occur. In this case, diopside is formed in several stages. In the temperature range under study, the highest negative values of the Gibbs energy (−175.4...−147.74 kJ/mol) were stated for the reaction of diopside formation from gehlenite (reaction (14)). Apparently, the isomorphic substitution of Si^{4+} ions for tetrahedrally coordinated Al^{3+} ions may occur in the diopside structure. Subsequently, the formation of diopside with the involvement of shennonite (γ-$2CaO{\cdot}SiO_2$), blast-furnace slag mineral (reaction (7)), and previously formed merwinite (reaction (22)) is possible. Considering the close values of for reactions (7) and (22), their occurrence is equally probable. Close values of for the reaction of formation of magnesium orthosilicate $2MgO{\cdot}SiO_2$ (reaction (1)) and the reaction of diopside formation with akermanite mineral (reaction (2)) in the temperature range of 1073−1473 K should also be noted. This fact indicates the energetic equiprobability of reactions (1) and (2). In the formation of magnesium orthosilicate, its interaction with akermanite and silicon dioxide following reaction (4) is energetically favorable. After that, pseudo-wollastonite mineral (α-$CaO{\cdot}SiO_2$) can be involved in the formation of diopside (reaction (10)).

Therefore, the results of thermodynamic calculations indicate a high probability of the diopside formation in the $CaO-MgO-Al_2O_3-SiO_2$ system. It allows us to state that it is the diopside phase, which is the final product of the reactions of silicate formation in the pigment mixtures obtained based on the granulated blast-furnace slag. The only difference is in the occurrence of processes of isomorphic substitution in the diopside structure of a part of Mg^{2+} ions for coloring ions (Co^{2+}, Ni^{2+} and Mn^{2+}), which have close ionic radii.

To confirm the data of thermodynamic calculations, we have made a composition based on blast-furnace slag. The resulting process of formation of the diopside phase can presumably be presented as follows:

$$\begin{aligned}&0.205Ca_2MgSi_2O_7+0.118Ca_2Al_2SiO_7+\\&+0.492\alpha\text{-}CaSiO_3+0.059\gamma\text{-}Ca_2SiO_4+\\&+0.126CaCO_3+1.177MgO+1.45SiO_2=\\&=1.382[CaMg(Si_{0.915},Al_{0.085})_2O_{5.91})]+0.126CO_2. \quad (23)\end{aligned}$$

The composition obtained by reaction (23) was fired in the temperature range of $800-1200^0$C, followed by X-ray phase analysis of the resulting products (Figure).

X-ray phase studies confirmed the results of thermodynamic calculations. It is recorded that merwinite is formed first. This mineral is found already after firing at 800^0C by the characteristic lines on the diffraction pattern ($d{\cdot}10^{10}$=4.70; 2.66; 2.44; and 1.89 m). With an increase in the firing temperature, previously formed merwinite, along with blast-furnace slag minerals, participates in the formation of diopside. The diopside phase in sufficient quantities is registered on X-ray patterns starting from the temperature of 1000^0C ($d{\cdot}10^{10}$=3.21; 2.99; 2.50; and 2.12 m). Formation of diopside is completed at the temperature of 1200^0C. It is evidenced by the absence of lines from the initial and intermediate compounds on the diffraction pattern (Figure).

Conclusions

The thermodynamic analysis of the reactions of formation of the diopside phase in the $CaO-MgO-Al_2O_3-SiO_2$ system was carried out using blast-furnace slag as the initial component. It was established that diopside mineral was the final product of silicate formation reactions in the considered system. The diopside phase is formed in several stages. The merwinite formed first. Subsequently, merwinite, along with blast-furnace slag minerals, participates in the formation of diopside. X-ray phase studies confirmed the sequence of chemical reactions established by thermodynamic calculations. The formation of diopside is completed at the temperature of 1200^0C. A similar sequence of solid-phase interactions will likely be observed in the direct synthesis of diopside ceramic pigments. The only difference is the occurrence of processes of isomorphic substitution in the diopside structure of a part of Mg^{2+} ions for coloring ions with the close ionic radii.

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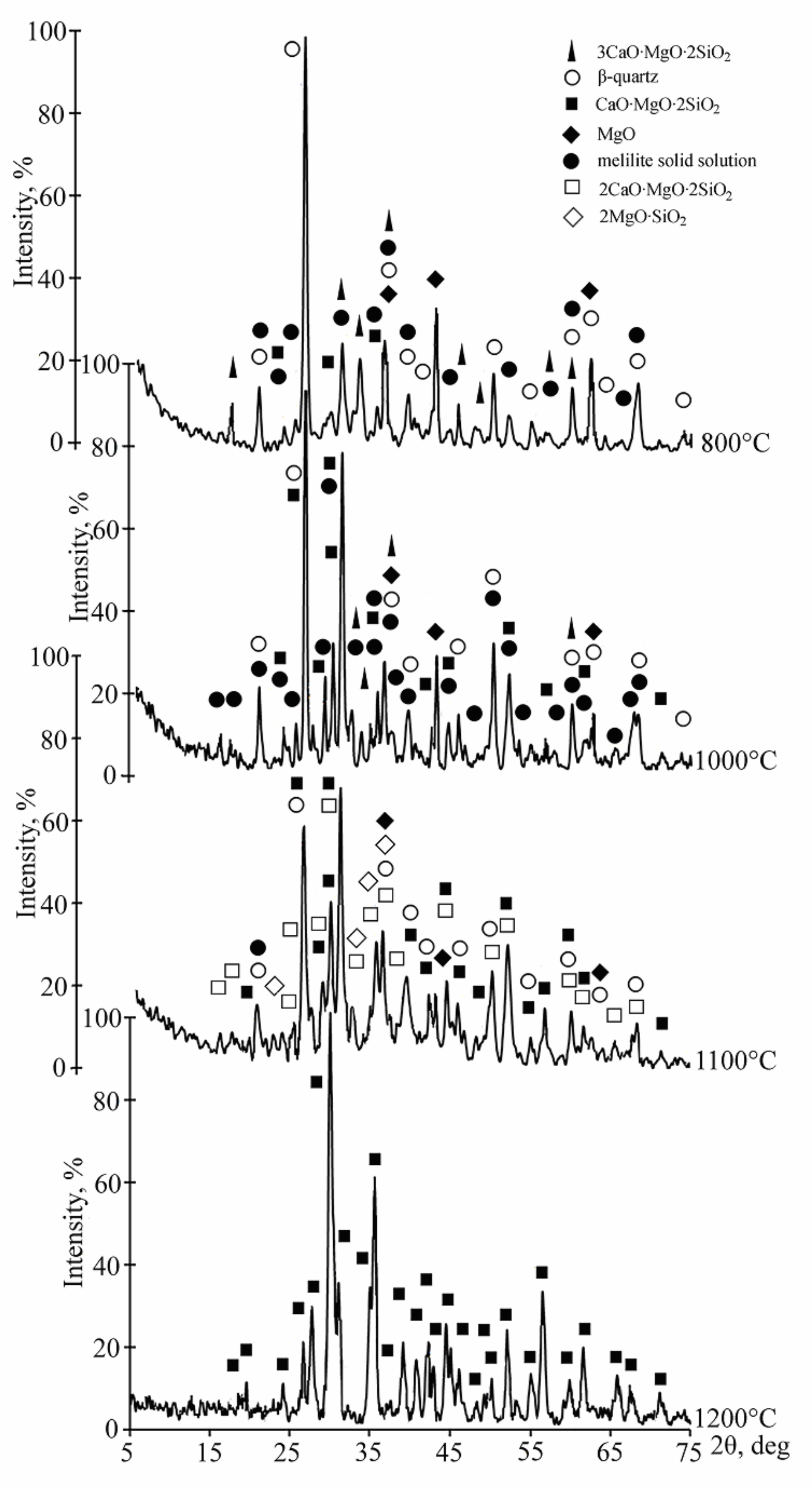

Diffraction patterns of diopside composition fired in the temperature range of 800–1200°C

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ТЕРМОДИНАМІЧНИЙ АНАЛІЗ РЕАКЦІЙ ФОРМУВАННЯ ФАЗИ ДІОПСИДУ ПРИ СИНТЕЗІ КЕРАМІЧНИХ ПІГМЕНТІВ З ГРАНУЛЬОВАНОГО ДОМЕННОГО ШЛАКУ

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Метою даного дослідження є проведення термодинамічного аналізу реакцій утворення діопсидової фази ($CaO{\cdot}MgO{\cdot}2SiO_2$) при синтезі керамічних пігментів на основі гранульованого доменного шлаку. Термодинамічний аналіз має велике практичне значення при вивченні твердофазних реакцій, які характерні для пігментної технології. При цьому значно скорочуються обсяг енергоємних експериментальних досліджень керамічних пігментів. При виконанні термодинамічних розрахунків оцінювали принципову можливість і напрямок протікання хімічних реакцій шляхом обчислення зміни енергії Гіббса. Для перевірки розрахункових даних із застосуванням рентгенофазового аналізу оцінювали зміну мінералогічного складу діопсидових композицій в залежності від температури випалу. Встановлено, що діопсидова фаза в системі $CaO{-}MgO{-}Al_2O_3{-}SiO_2$ формується в декілька стадій. Першим утворюється мінерал мервініт ($3CaO{\cdot}MgO{\cdot}2SiO_2$). В подальшому, мервініт поряд з мінералами доменного шлаку бере участь в утворенні діопсиду. Утворення діопсиду завершується при температурі 1200^{0}C. Використання отриманих результатів дозволить обґрунтовано підходити до вибору складів керамічних пігментів з використанням комплексної сировини, у тому числі і відходів різних виробництв.

Ключові слова: керамічні пігменти, доменний шлак, термодинамічний аналіз, рентгенофазовий аналіз, мінералогічний склад, діопсид.

THERMODYNAMIC ANALYSIS OF THE REACTIONS OF DIOPSIDE PHASE FORMATION DURING SYNTHESIS OF CERAMIC PIGMENTS FROM GRANULATED BLAST-FURNACE SLAG

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The purpose of this study is to perform the thermodynamic analysis of the reactions of diopside phase ($CaO{\cdot}MgO{\cdot}2SiO_2$) formation during the synthesis of ceramic pigments based on the granulated blast-furnace slag. Thermodynamic analysis is of great practical importance in studying solid-phase interactions, which are involved in the pigment technology. At the same time, the scope of energy-intensive experimental studies of ceramic pigments is significantly reduced. When performing thermodynamic calculations, we assessed the fundamental possibility and direction of occurrence of chemical reactions by determining the changes in the Gibbs energy. In order to verify the calculation data, the change in the mineralogy of the diopside compositions was evaluated with the use of X-ray phase analysis at different firing temperatures. It was found that the diopside phase in the $CaO{-}MgO{-}Al_2O_3{-}SiO_2$ system is formed in several stages. The merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$) mineral is formed first. Further, merwinite, along with blast-furnace slag minerals, is involved in the diopside formation. The formation of diopside is completed at the temperature of 1200^{0}C. The findings of the study will provide a reasonable approach to the choice of compositions of ceramic pigments using complex raw materials, including the wastes of various industries.

Keywords: ceramic pigment, blast-furnace slag, thermodynamic analysis, X-ray phase analysis, mineralogical composition, diopside.

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