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THERMODYNAMICS OF THE REACTIVE PHASE FORMATION OF THE BINDER OF THE CoO−BaO−Al₂O₃ SYSTEM FOR ELECTROMAGNETIC RADIATION PROTECTION

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The article discusses the physicochemical basis for the production of barium aluminate binders, supplemented with compounds and solid solutions including cobalt oxide. The results of calculating the temperature dependence of Gibbs free energy are presented for model reactions simulating all possible variants of two-phase equilibria in the CoO−BaO−Al₂O₃ system. Using thermodynamic analysis, the stability of the terminals of the above system is established, which makes it possible to triangulate it. The complete subsolidus structure is presented, as well as the geometric and topological characteristics of the CoO−BaO−Al₂O₃ system and its phases. The presented results of thermodynamic analysis of solid-phase reactions involving barium aluminates and cobalt-containing oxides allow comparing the paths of reaction phase formation of binders from various ingredients. The article substantiates the possibility of effectively modifying barium-aluminum binders with waste cobalt catalysts on corundum supports. These circumstances make it possible to justify the choice of raw materials at a qualitative level, and, in combination with calculated data on the geometrostatistical characteristics of the subsolidus structure of the CoO−BaO−Al₂O₃ system, to obtain technologically important information about the features of dosage and mixing of components when fabricating the binder. The results of this study allow reducing the number of long-duration and labor-intensive experiments to obtain a modified binder with a target set of characteristics.

Keywords: solid-phase reaction, Gibbs energy, thermodynamic stability, connode, system, interaction mechanism, synthesis.

Introduction

The physicochemical basis for the production of barium aluminate binders have always aroused and continue to arouse interest among many researchers [1−4]. Such binders are attributed to hydraulically hardening and refractory and are characterized by an increased ability to absorb X-ray and gamma radiation due to a significant size of the cross section for their capture by the barium atom nucleus. It is supposed to be sensible to expand the range of wavelengths of absorbed radiations for the binder, including the coverage of the microwave and radio frequency electromagnetic waves. It is reasonable to explore additional capabilities of the binder in this field by supplementing the phase composition of barium aluminate cements with compounds and solid solutions including cobalt oxide. Such prospects are opened due to the analysis of obtained research data [5,6]. In this case, the contribution made to the functional characteristics of such specific binding properties by the compounds and phases of the Co−O₂ system should also be taken into account. This system has been studied for a long time and continues to be studied due to its exceptional importance for the

production of pigments, magnetoceramic materials, and special alloys, including ferromagnetic ones [7,8].

The most thermodynamically stable compound in this system is cobalt oxide CoO, which has deviations from stoichiometry due to the presence of cation vacancies in the crystal lattice and is expressed in the formula notation of $Co_{1-x}O$, or more precisely: Co^{2+}_{1+3x}, and $Co^{3+}_{2x}V_xO$, where V is the cation vacancy. The nonstoichiometry parameter (x) nonlinearly depends on the partial pressure of oxygen and temperature, defining the semiconductor properties (p-type conductivity) of this oxide. Information about other oxides of this system and the resulting solid solutions is still controversial. This circumstance is conditioned by the thermodynamic instability of higher Co_2O_3 and CoO_2 oxides in the low-temperature region, and it prevents their production in pure form including those with overall specimen dimensions sufficient for precision studies. The Co_3O_4 oxide has a spinel crystal lattice structure and it is not strictly stoichiometric due to the presence of oxygen vacancies (at room temperatures the formula is close to that of $Co_3O_{3.39}$); it crystallizes to form small cubic octahedra of black color with a unit cell parameter of a=8.4 nm; density of 6.17 g/cm³; at ordinary temperatures, it is a paramagnetic (spatial group O^7_h-Fd3m,)), undergoing an antiferromagnetic transformation at 40 K with a change in the spatial group to T^2_d-F43m peculiar to the antiferromagnetic state [9].

It should be noted that CoO is also paramagnetic, its Curie temperature is close to 293 K and the transition to the antiferromagnetic state is accompanied by a slight compressive deformation of one of the cubic axes of the crystalline cell with a transition to the tetragonal syngony. The parameter of the cubic lattice of CoO, determined using the specimens with different production histories, is varied from a=4.2596±0.0004 to 4.270±0.002 Å [9]. Accordingly, the density of CoO, as shown in various studies, is in the range of 6.45−6.47 g/cm³. It is possible that the reason for the deviations is the ability of CoO to absorb oxygen at temperatures of 291 to 293 K up to a composition corresponding to the Co_3O_4 formula with no change in the crystal lattice; and at 673 K the transformation of CoO into Co_3O_4 occurs very quickly. In addition, it is possible that CoO and Co_3O_4 are capable of forming solid solutions with intermediate synthesis of compounds of variable composition that are disproportionating when heated in the temperature range of 1173 to 1233 K.

The circumstances noted above justify the prospects of modifying the phase composition of the binder with cobalt oxide CoO and compounds containing it. It is obvious that the binder base should be composed of hydraulically active barium aluminates

$Ba_3Al_2O_6$ and $BaAl_2O_4$. Accordingly, it is necessary to establish the thermodynamic stability of the noted aluminates in two- and three-phase combinations of barium with CoO, $BaCoO_2$ and $CoAl_2O_4$ (the last two compounds are the only ones in the corresponding pair systems of BaO−CoO and CoO−CoO−Al$_2$O$_3$).

In addition, the results of thermodynamic analysis of solid-phase reactions involving barium aluminates and cobalt-containing oxides allow comparing the paths of reactive phase formation of binders using various ingredients. These circumstances make it possible to qualitatively justify the choice of raw materials, and, in combination with calculated data on the geometrostatistical characteristics of the subsolidus structure of the CoO−BaO−Al$_2$O$_3$ system, to obtain technologically important information on specific features of the dosage and mixing of components when obtaining the binder. Particularly these goals are to be achieved in this study.

Experimental

Methods of thermodynamic calculations and analysis of solid-phase reactions are described elsewhere [10]. The initial thermodynamic data used for calculations are summarized in Table 1.

Determination of geometrostatistical characteristics of the subsolidus structure of the system was performed according to the procedure described in ref. [11]. All the calculations were done with an accuracy of 1 J/mol, and then rounded off to 1 kJ/mol. For clarity, the formulae of compounds were written in oxide form and with the following abbreviations: C, B, and A stand for CoO, BaO, and Al_2O_3, respectively.

Results and discussion

Solid-phase exchange reactions involving barium aluminates and cobalt-containing oxides were modeled and the values of changes in the Gibbs energy (ΔG) at certain temperatures (T) were calculated for them. The calculation data are presented in Table 2.

The analysis of the phase relationships in the subsolidus of the CoO−BaO−Al$_2$O$_3$ system done according to the calculation data (Table 2) shows that the pair combination of $BaAl_{12}O_{19}$ and $CoAl_2O_4$ is thermodynamically stable due to the positive sign of the ΔG values in the analyzed temperature range for reaction 1. Solid-phase reaction 2 (Table 2) can proceed in a thermodynamically favorable direction; from left to right, which is indicated by the negative value of ΔG and which determines the stability of the pair combination of cobalt and barium spinels ($CoAl_2O_4$ and $BaAl_2O_4$, respectively). The thermodynamic preference of the pair combination of CoO and $BaAl_2O_4$ was established by analyzing the results of calculations of ΔG values for reactions 3−5 (Table 2). The thermodynamic stability of the pair

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combination $BaCoO_2$ and $BaAl_2O_4$ is more difficult to establish, since by reaction 6 the coexistence of the interaction products (CoO and $Ba_3Al_2O_6$, Table 2) is more favorable. However, a more significant contribution to the stability of $BaCoO_2$ and $BaAl_2O_4$ is made by reaction 7, due to which, in the total interaction of reactions 6 and 7, the coexistence of the noted pair combination is more thermodynamically favorable due to the positive sign of ΔG for reaction 8; and the formation of CoO and $Ba_3Al_2O_6$ in the ternary combination with $Ba_3Al_2O_6$ is thermodynamically unfavorable (reaction 8, Table 2). The established thermodynamic stability of paired combinations makes it possible to express them by appropriate connodes in the subsolidus structure of the $CoO-BaO-Al_2O_3$ system: $CoAl_2O_4-BaAl_{12}O_{19}$, $CoAl_2O_4-BaAl_2O_4$, $CoO-BaAl_2O_4$, and $BaCoO_2-BaAl_2O_4$ (Figure).

The marked connodes completely triangulate the system under study, since the missing connodes in its concentration region, limited by the compositions of the $BaCoO_2-BaO-BaAl_2O_4$ compounds, are precisely defined by the only option for the topological closure of elementary triangles due to the coexistence of $BaCoO_2$ with barium aluminates: $Ba_{10}Al_2O_{13}$, $Ba_8Al_2O_{11}$, $Ba_7Al_2O_{10}$, $Ba_5Al_2O_8$, $Ba_4Al_2O_7$ and $Ba_3Al_2O_6$. Accordingly, all thermodynamically stable three-phase combinations have also been established, since they correspond to compounds whose composition points are the vertices of elementary triangles (Figure). The topological graph of the relationship of elementary triangles is a straight line, and therefore it requires no additional plotting.

Taking into account the above analysis data, we will consider the feasibility of modifying barium-aluminum binders with cobalt-containing compounds. First, we would like to note that the basis for the hydraulic activity of barium-aluminum binders is

Table 1

Initial thermodynamic data of the compound constants of the $CoO-BaO-Al_2O_3$ system

| Compound formula	$-\Delta H^0_{298}$, kJ/mol	S^0_{298}, J/mol·K	$C_p=a+bT+cT^{-2}$, J/mol·K		
			a	$b \cdot 10^3$	$-c \cdot 10^{-5}$
CoO	238.9	52.97	48.28	8.535	1.67
BaO	558.15	70.29	53.30	4.35	8.3
α-Al_2O_3	1675.61	50.92	114.77	12.08	35.44
$CoAl_2O_4$	1948.9	101.7	161.17	32.97*	30.32
$BaCoO_2$	837.13	123.08	78.99	38.34	4.49
$BaAl_2O_4$	2334.17	123.43	148.32	35.44	29.25
$Ba_3Al_2O_6$	3537.91	267.78	247.86	48.53	17.41
$BaAl_{12}O_{19}$	10740.33	376.56	738.22	70.50	221.75
$Ba_4Al_2O_7$	4014.49	329.99	275.85	56.89	23.33
$Ba_5Al_2O_8$	4569.03	427.82	298.73	123.87	15.51
$Ba_7Al_2O_{10}$	5689.5	567.66	374.18	164.90	14.03
$Ba_8Al_2O_{11}$	6238.10	611.68	441.99	96.23	25.31
$Ba_{10}Al_2O_{13}$	7350.52	778.85	478.25	226.40	12.24

Table 2

Values of change in Gibbs free energy as a function of temperature for model reactions in the $CoO-BaO-Al_2O_3$ system

Reaction number	Reaction*	ΔG, kJ/mol at different temperatures				
		1000 K	1200 K	1400 K	1600 K	1800 K
1	$BA_6+CoA=7A+BCo$	125	126	127	128	129
2	$BA_6+5Co=5CoA+BA$	−129	−130	−132	−138	−146
3	$BA_6+5BCo=5Co+6BA$	−268	−262	−257	−251	−244
4	$BCo+CoA=2Co+BA$	−28	−27	−25	−23	−20
5	$2Co+3BA=2CoA+B_3A$	41	37	33	28	23
6	$2BCo+BA=2Co+B_3A$	−14	−16	−17	−17	−16
7	$3BCo+BA=3Co+B_4A$	121	125	130	138	147
8	$5BCo+2BA=5Co+B_3A+B_4A$	107	109	113	121	131

Note: * − C, B and A stand for CoO, BaO and Al_2O_3, respectively.
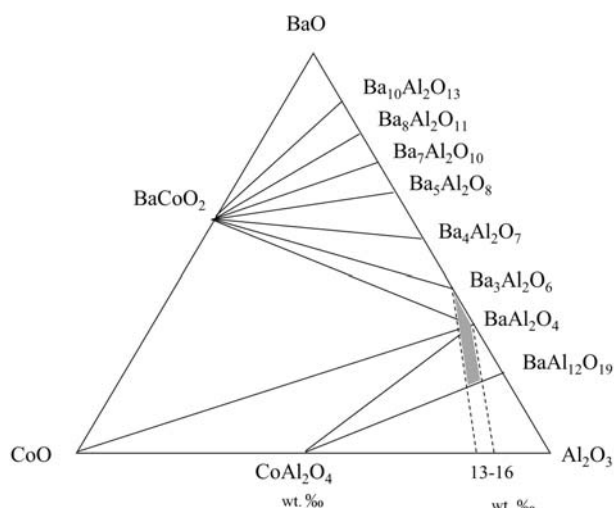
Phase relationships of the CoO−BaO−Al₂O₃ system with the indicated trend of the analyzed reactive phase formation (shown by the dotted line). The concentration region of the target combinations of binder phases is grayed out

provided by the combination of $Ba_3Al_2O_6$ and $BaAl_2O_4$. Obviously, these compounds, in pair combination or separately, must be present in the modified binder. Therefore, the phase composition of the modified binder must be in the concentration region of one of the four elementary triangles: $BaCoO_2$−$Ba_3Al_2O_6$−$BaAl_2O_4$, $BaCoO_2$−$BaAl_2O_4$−CoO, $BaAl_2O_4$−CoO−$CoAl_2O_4$, and $BaAl_2O_4$−$CoAl_2O_4$−$BaAl_{12}O_{19}$. Note that the $Ba_4Al_2O_7$ content should be limited due to a sudden deterioration in the manufacturability of the binder [12].

When preparing a charge for a binder based on the precursors of individual oxides, it is impossible to ensure a sufficiently high yield of the target phases during a single firing due to a significant number of side solid-phase reactions. This statement is substantiated and becomes clear based on consideration of the path of shift of the initial oxides to a point of a given phase composition, belonging to one of the four elementary triangles above. In particular, the path from BaO to the elementary triangle of Ba-CoO_2−$Ba_3Al_2O_6$−$BaAl_2O_4$ crosses six connodes, and it corresponds to the behavior of solid-phase exchange reactions with the formation of $BaCoO_2$ in combinations with appropriate barium aluminates. The resulting barium aluminates are by-products and must also shift to the specified phase composition of the binder during the firing process. Thus, the paths of their intersection with connodes will also correspond to the behavior of the solid-phase exchange reactions, whose mechanisms differ from each other. That is why the process of binder formation is multi-stage

and the resulting clinker will contain a significant amount of intermediately formed phases.

Modifying the barium-aluminum cement by adding $BaCoO_2$ to it with calculation of the composition of the charge in the concentration region of the elementary triangle of $BaCoO_2$−$Ba_3Al_2O_6$−$BaAl_2O_4$ also has disadvantages. Firstly, $BaCoO_2$ coexists with hydraulically active compounds of barium-aluminum cement, and it eliminates the reactive nature of phase formation during sintering. Accordingly, it is possible to predict only partial dissolution of $BaCoO_2$ in aluminum-barium cement, an increase in the amount of glass phase and encapsulation of the remaining $BaCoO_2$ particles, the dispersion of which will be close to the original, and participation in the processes of hydration hardening will actually be reduced to the role of inert filler. In addition, $BaCoO_2$ should be synthesized in advance and finely dispersed powder for the charge should also be prepared in advance, since the sources of such raw materials in finished form are unknown to us. Similar reasons are also peculiar for predicting the phase composition of the binder in the concentration region of the elementary triangle of $BaCoO_2$−$BaAl_2O_4$−CoO. Reactive phase formation can efficiently be arranged using $BaCoO_2$ during predicting the phase composition of the binder in the concentration regions of the elementary triangles $BaAl_2O_4$−CoO−$CoAl_2O_4$ and $BaAl_2O_4$−$CoAl_2O_4$−$BaAl_{12}O_{19}$ (Figure). However, such modification removes no questions about the preliminary synthesis of $BaCoO_2$ and its dispersion.

The use of precursors or pure cobalt oxide as a binder modifier with prediction of the phase composition in the concentration regions of the elementary triangles $BaCoO_2$−$BaAl_2O_4$−CoO and $BaAl_2O_4$−$CoAl_2O_4$−CoO fails to ensure the reactive nature of phase formation due to the existence of cobalt oxide with hydraulically active aluminum-barium spinel and, accordingly, with $BaCoO_2$ in the first marked elementary triangle and with $CoAl_2O_4$ in the other. Efficient reactive phase formation can be provided by CoO when predicting the phase composition of the binder in the concentration regions of the elementary triangles of $BaCoO_2$−$Ba_3Al_2O_6$−$BaAl_2O_4$ and $CoAl_2O_4$−$BaAl_2O_4$−$BaAl_{12}O_{19}$ (the conventional path of the phase formation in Figure will intersect the $BaCoO_2$−$Ba_3Al_2O_6$−$BaAl_2O_4$ and $CoAl_2O_4$−$BaAl_2O_4$ connodes, respectively). However, the reaction interaction seems to be ensured by reaction 6 (Table 2), but it is thermodynamically unfavorable and it is necessary to take additional technological measures to ensure the presence of the $Ba_4Al_2O_7$ impurity phase in the phase composition of barium-aluminum cement for the development of

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thermodynamically favorable reaction 8 in the opposite direction (Table 2). On the other hand, the presence of $BaAl_{12}O_{19}$ in the phase composition of the binder is necessary, which ensures the development of reaction 2 in the forward direction of behavior (Table 2). This circumstance also requires technological adjustment of the phase composition of the barium-aluminum binder.

The use of $CoAl_2O_4$ as a modifier for barium-aluminum binder also has certain limitations and disadvantages. In particular, $CoAl_2O_4$ coexists with $BaAl_{12}O_{19}$ and $BaAl_2O_4$, and it will not ensure the reactionary nature of phase formation in the concentration regions of the elementary triangles of $CoAl_2O_4-BaAl_2O_4-BaAl_{12}O_{19}$ and $CoAl_2O_4-CoO-BaAl_2O_4$, respectively. At the same time, such a modifier does not seem to be very efficient in predicting the phase composition of the binder in the concentration region of the elementary triangle of $BaCoO_2-BaAl_2O_4-CoO$ (Figure), since for the development of the reactive phase formation (according to reaction 4, Table 2) the presence of $BaCoO_2$ in the charge composition is necessary, which is not technologically advanced for the reasons already discussed. However, a more complicated mechanism of the solid-phase interaction is thermodynamically possible:

$$3\ CoA+2B_3A=BCo+2Co+5BA. \qquad (1)$$
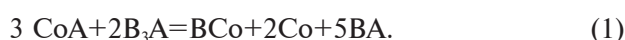
The changes in Gibbs energy for such a reaction will be equal to $\Delta G_{1000\ K}=-54$ kJ/mol, and $\Delta G_{1500\ K}=-31$ kJ/mol.

Accordingly, $CoAl_2O_4$ can ensure the reactive phase formation of the binder with a simultaneous reduction in the amount of $Ba_3Al_2O_6$ in its composition that greatly reduces the hardening onset time and limits the time of use of the binder during hydration. In addition, under conditions of incomplete behavior of the above solid-phase exchange reaction, the remaining $CoAl_2O_4$ particles will be significantly dispersed in the phase composition of the binder due to chemical interaction and cobalt will be evenly distributed throughout the volume of the binder due to the synthesis of other cobalt-containing oxides, in particular CoO and $BaCoO_2$. Moreover, the reaction 5 (Table 2) can be considered as one of the elementary stages in the above reaction and the following reaction:

$$CoA+B_3A=BCo+2BA. \qquad (2)$$

The changes in Gibbs energy for the reaction (2) will be equal to $\Delta G_{1000\ K}=-13$ kJ/mol, and $\Delta G_{1500\ K}=-7$ kJ/mol.

With respect to the above reaction, this reaction is characterized by a reduced CoA/B3A ratio, which makes it possible to exclude cobalt oxide from the reaction products and predict the reactive phase formation in the concentration region of the elementary triangle of $BaCoO_2-Ba_3Al_2O_6-BaAl_2O_4$. Moreover, there are precursors with a significant content of $CoAl_2O_4$, i.e. a multi-tonnage waste, in particular cobalt catalysts on corundum carriers used for the hydrogenation of aromatic compounds of sulfur-containing petroleum products, for example, grade GPS-4Sh. On expiry of their service life, such catalysts are subjected to chemical extraction of cobalt; however, in the case of high-temperature processes, part of the metallic cobalt reacts with corundum to form cobalt spinel $CoAl_2O_4$ and it remains unextracted (13 to 16 wt.% in CoO content [12]). This additional advantage may allow for the effective modification of aluminum barium binders. Figure shows the concentration range of the compositions of such waste catalysts, and the trend of reactive phase formation in the «corridor» of the corresponding paths of development of solid-phase interactions, covering concentration areas in promising elementary triangles (shaded) from the extreme points of the marked range of compositions, the dotted line.

Further analysis of the feasibility of using waste cobalt catalyst on a corundum carrier takes into account the calculated geometric and topological characteristics of the phases and the subsolidus structure of the $CoO-BaO-Al_2O_3$ system (Tables 3 and 4).

In Table 3, the promising concentration regions of the $CoO-BaO-Al_2O_3$ system (the corresponding elementary triangles are written under numbers 7−10) cover the major part of it (total 0.76639‰).

Table 3

Areas of elementary triangles of the $CoO-BaO-Al_2O_3$ system

Item No	Elementary triangle	Area ‰
1	$BaO-BaCoO_2-Ba_{10}Al_2O_{13}$	0.020453
2	$BaCoO_2-Ba_{10}Al_2O_{13}-Ba_8Al_2O_{11}$	0.009602
3	$BaCoO_2-Ba_8Al_2O_{11}-Ba_7Al_2O_{10}$	0.003315
4	$BaCoO_2-Ba_7Al_2O_{10}-Ba_5Al_2O_8$	0.010045
5	$BaCoO_2-Ba_5Al_2O_8-Ba_4Al_2O_7$	0.00824
6	$BaCoO_2-Ba_4Al_2O_7-Ba_3Al_2O_6$	0.01277
7	$BaCoO_2-Ba_3Al_2O_6-BaAl_2O_4$	0.06156
8	$BaCoO_2-BaAl_2O_4-CoO$	0.225272
9	$CoO-BaAl_2O_4-CoAl_2O_4$	0.30518
10	$CoO-BaAl_2O_4-BaAl_{12}O_{19}$	0.153523
11	$CoAl_2O_4-BaAl_{12}O_{19}-Al_2O_3$	0.19004
Total		1
Max		0.30518
Min		0.003315

The reaction formation of the binder in the concentration region of the elementary triangle of $BaCoO_2-Ba_3Al_2O_6-CoO$ due to the modifier in the form of waste of cobalt catalysts can only be predicted through additional technological measures and taking into account the rapid setting of $Ba_3Al_2O_6$ during hydration hardening. The concentration region of the elementary triangle $CoO-Ba_3Al_2O_6-BaAl_2O_4$ has no such restrictions, and stoichiometric relationships of the solid-phase reaction (2) can be used to predict the basic composition of the modified binder. This elementary triangle is 1.7 times larger in area in comparison to the previous one (No. 7 in Table 3), which is positive for more rough restrictions on the accuracy of the dosage of the initial components and for reducing the time of their mixing. In addition, an overdose of the modifier when predicting the phase composition of the binder in the concentration region of this elementary triangle near the $CoO-BaAl_2O_4$ connode can only shift the phase composition to elementary triangle No. 9 due to the synthesis of $CoAl_2O_4$ (Figure), which can provide additional benefits and requires experimental verification. The above situation may occur due to fluctuations in the CoO content in the composition of the cobalt catalyst waste and a relatively high degree of asymmetry of the elementary triangle No. 8 (Table 3). However, all cobalt-containing compounds have a high probability of existing in the subsolidus of the analyzed system (Table 4), which is favorable for reducing the technological risks of random deviations in their dosage.

Prediction of reactive phase formation in the concentration region of the elementary triangle $CoO-BaAl_2O_4-CoAl_2O_4$ is possible taking into account the stoichiometry of reaction 5 in the opposite direction of the reaction (Table 2). This elementary triangle has a maximum area (Table 3), but the reactive phase formation will take place in a narrow concentration region (the acute angle of the elementary triangle, Figure) and high-precision dosing of the charge components with careful subsequent mixing will be required. Fluctuations in the CoO content in the composition of cobalt catalyst waste can shift to the region of elementary triangle No. 10 (Table 3), in addition to the above-discussed shift of the phase composition of the binder into the concentration region of elementary triangle No. 8 (Table 3). A priori, we have no opportunity to compare the feasibility of the presence of CoO and $BaAl_{12}O_{19}$ in the phase composition of the modified binder (elementary triangles No. 9 and No. 10, respectively, Figure).

In the case of predicting the phase composition of the modified binder in the concentration region of the elementary triangle of $CoAl_2O_4-BaAl_2O_4-BaAl_{12}O_{19}$ (No. 10, Table 3), the technological risks when dosing and mixing the initial components are minimal (a wide range of promising compositions, Figure). Only a significant overdose of the modifier can shift the phase composition to the concentration region of elementary triangle No. 11 (Table 3), which will be accompanied by a loss of binding abilities, since none of the compounds ($CoAl_2O_4$, CoO, and $BaAl_{12}O_{19}$) has technologically expressed hydraulic activity. Accordingly, the material obtained in this case can only serve as hydraulically inert filler,

Table 4

Geometric and topological characteristics of the phases of the $CoO-BaO-Al_2O_3$ system

Compound	The number of triangles with its existence	The number of phases for its coexistence	Total area of existence S, ‰	Probability of existence, ω, ‰
BaO	1	2	0.021453	0.007151
CoO	2	3	0.540452	0.180151
Al_2O_3	1	2	0.19084	0.063613
$BaCoO_2$	8	9	0.351341	0.117114
$CoAl_2O_4$	3	4	0.65894	0.219647
$BaAl_{12}O_{19}$	2	3	0.36352	0.121173
$BaAl_2O_4$	4	5	0.69397	0.231323
$Ba_3Al_2O_6$	2	3	0.07783	0.025943
$Ba_4Al_2O_7$	2	3	0.02351	0.007837
$Ba_5Al_2O_8$	2	3	0.018795	0.006265
$Ba_7Al_2O_{10}$	2	3	0.01535	0.005117
$Ba_8Al_2O_{11}$	2	3	0.013914	0.004638
$Ba_{10}Al_2O_{13}$	2	3	0.030085	0.010028
Total			3	1
Max			0.69397	0.231323
Min			0.013914	0.004638

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assumingly possessing a certain range of the electromagnetic radiation protection characteristics.

Conclusions

An analysis of literary data allowed us to substantiate the prospects of using cobalt and cobalt oxides for modifying materials in order to improve their ability to absorb electromagnetic radiation in a wide frequency range. To modify barium aluminate binders, the equations of solid-phase exchange reactions were made, for which the dependences of changes in the Gibbs energy on temperature were calculated and the most preferable ones were identified to determine all thermodynamically stable pair and ternary combinations of phases in the $CoO-BaO-Al_2O_3$ system. By analyzing the paths of reactive phase formation with the participation of the main phases of barium aluminate binders ($Ba_3Al_2O_6$ and $BaAl_2O_4$) and cobalt-containing oxides ($BaCoO_2$, CoO and $CoAl_2O_4$), positive and negative factors determining the mechanism of solid-phase interactions were identified. The use of $CoAl_2O_4$ as an effective modifier of barium aluminate binders has been substantiated and consideration was given to the paths of the reactive phase formation and reaction mechanisms when using a raw material component in the form of catalyst waste, the phase composition of which is represented by corundum and cobalt spinel (Al_2O_3 and $CoAl_2O_4$, respectively).

In the subsolidus of the $CoO-BaO-Al_2O_3$ system, the most promising concentration regions for the reaction formation of target combinations of modified binder phases have been identified. Using the calculated geometric and topological characteristics of the established subsolidus structure of the analyzed system, technological risks are shown in the accuracy of the dosage and mixing time of the components of the modified binder charge when predicting its phase composition for various options of concentration regions. The obtained research data make it possible to reduce the number of time-consuming and labor-intensive experiments to obtain a modified binder with a specified set of characteristics.

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ТЕРМОДИНАМІКА РЕАКЦІЙНОГО ФАЗОУТВОРЕННЯ В'ЯЖУЧОГО СИСТЕМИ CoO−BaO−Al$_2$O$_3$ ДЛЯ ЗАХИСТУ ВІД ЕЛЕКТРОМАГНІТНОГО ВИПРОМІНЮВАННЯ

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У статті розглянуто фізико-хімічні основи одержання алюмінатбарієвих в'яжучих, доповнених сполуками та твердими розчинами, що включають оксид кобальту. Наведені результати розрахунку температурної залежності зміни вільної енергії Гіббса для модельних реакцій, що моделюють усі можливі варіанти двофазних рівноваг у системі CoO−BaO−Al$_2$O$_3$. За допомогою термодинамічного аналізу встановлена стабільність конод вищенаведеної системи, що дозволяє провести її тріангуляцію. Наведена повна субсолідусна будова, а також геометро-топологічна характеристика системи CoO−BaO−Al$_2$O$_3$ та її фаз. Результати термодинамічного аналізу твердофазних реакцій за участю алюмінатів барію та кобальтвмісних оксидів дозволяють порівняти шляхи реакційного фазоутворення в'яжучого з різних інгредієнтів. У статті обґрунтовано можливість ефективно модифікувати алюмобарієві в'яжучі відходами кобальтових каталізаторів на корундових носіях. Дані обставини на якісному рівні дозволяють обґрунтувати вибір сировини, а у поєднанні з розрахунковими даними про геометростатистичні характеристики субсолідусної будови системи CoO−BaO−Al$_2$O$_3$ також отримати технологічно важливу інформацію про особливості дозування та змішування компонентів при одержанні в'яжучого. Результати дослідження дозволяють зменшити кількість тривалих і трудомістких експериментів щодо одержання модифікованого в'яжучого з цільовим комплексом характеристик.

Ключові слова: твердофазні реакції, енергія Гіббса, термодинамічна стабільність, коннода, система, механізм взаємодії, синтез.

THERMODYNAMICS OF THE REACTIVE PHASE FORMATION OF THE BINDER OF THE CoO−BaO−Al$_2$O$_3$ SYSTEM FOR ELECTROMAGNETIC RADIATION PROTECTION

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The article discusses the physicochemical basis for the production of barium aluminate binders, supplemented with compounds and solid solutions including cobalt oxide. The results of calculating the temperature dependence of Gibbs free energy are presented for model reactions simulating all possible variants of two-phase equilibria in the CoO−BaO−Al$_2$O$_3$ system. Using thermodynamic analysis, the stability of the terminals of the above system is established, which makes it possible to triangulate it. The complete subsolidus structure is presented, as well as the geometric and topological characteristics of the CoO−BaO−Al$_2$O$_3$ system and its phases. The presented results of thermodynamic analysis of solid-phase reactions involving barium aluminates and cobalt-containing oxides allow comparing the paths of reaction phase formation of binders from various ingredients. The article substantiates the possibility of effectively modifying barium-aluminum binders with waste cobalt catalysts on corundum supports. These circumstances make it possible to justify the choice of raw materials at a qualitative level, and, in combination with calculated data on the geometrostatistical characteristics of the subsolidus structure of the CoO−BaO−Al$_2$O$_3$ system, to obtain technologically important information about the features of dosage and mixing of components when fabricating the binder. The results of this study allow reducing the number of long-duration and labor-intensive experiments to obtain a modified binder with a target set of characteristics.

Keywords: solid-phase reaction; Gibbs energy; thermodynamic stability; connode; system; interaction mechanism; synthesis.

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