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The features of the formation of solid solutions in a pseudo-binary section $BaAl_2O_4$–$CoAl_2O_4$

***G.M.Shabanova*[1], *A.M.Korogodska*[1], *S.M.Logvinkov*[2], *O.O.Gamova*[1]**

[1]Department of Ceramics, Refractories, Glass and Enamels Technology, National Technical University "Kharkiv Polytechnic Institute", 2 Kyrpychova Str., 61002 Kharkiv, Ukraine
[2]Department of Technology and Life Safety, Simon Kuznets Kharkiv National University of Economics, 9a Nauki Ave., 61166 Kharkiv, Ukraine.

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The article presents an analysis of qualitative and quantitative phase relations in the temperature range of 900°C–1500°C; the analysis was carried out from the point of view of the limitedness of the formed solid solutions in the pseudo-binary section $BaAl_2O_4$–$CoAl_2O_4$ and made it possible to give an adequate interpretation of the experimental results. The pseudo- binary section $BaAl_2O_4$–$CoAl_2O_4$ is a promising area for creating compositions of refractory binders based on compositions of the BaO–CoO–Al_2O_3 system. It was found that the nonmonotonic change in the amount of the main phases in the material of the samples after firing at different temperatures can be explained by the peculiarities of the formed solid solutions based on cobalt-aluminate and barium-aluminate spinels, saturation of their cation sublattices due to the isovalent isomorphism of Co^{+2} to Co^{+3} and participation in the cationic substitution of Al^{+3} in trivalent sublattices. The results obtained make it possible to predict the phase composition of binders in the BaO–CoO–Al_2O_3 system and regulate their hydration activity.

Keywords: solid solution, phase formation, isovalent isomorphism, cationic sublattices, phase decomposition.

Характер й особливості формування твердих розчинів у псевдобінарному перетині $BaAl_2O_4$–$CoAl_2O_4$. *Г.М.Шабанова, А.М.Корогодська, С.М.Логвінков, О.О.Гамова*

У статті проведено аналіз якісних і кількісних фазових співвідношень в інтервалі температур 900°C–1500°C, що дозволило обірунтувати позиції обмеженого характеру твердих розчинів у псевдобінарному перерізі $BaAl_2O_4$–$CoAl_2O_4$, що утворюються. Псевдобінарний переріз $BaAl_2O_4$–$CoAl_2O_4$ є перспективною областю для створення складів вогнетривких в'яжучих матеріалів на основі композицій системи BaO–CoO–Al_2O_3. Встановлено, що немонотонна зміна кількості основних фаз в матеріалі зразків після випалу при різних температурах обумовлена особливостями утворення твердих розчинів на основі кобальталюмінатної і барійалюмінатної шпінелей, насиченням їх катіонних підрешіток за рахунок ізовалентного ізоморфізму $Co^{+2} \longleftrightarrow Ba^{+2}$, можливістю окислення Co^{+2} до Co^{+3} і участі в катіонному заміщенні Al^{+3} в тривалентних підрешітках. Отримані результати дозволяють прогнозувати фазовий склад в'яжучих матеріалів на основі системи BaO–CoO–Al_2O_3 і регулювати їх гідратну активність.

1. Introduction

The $BaO–CoO–Al_2O_3$ system is of particular importance in the technology of special binders, since it is possible to obtain materials with a set of specified properties (fire resistance, resistance to corrosive environment and ionizing radiation) based on the compositions. The presence of this complex with high operating descriptions at the synthesized materials is ensured by a combination of hydraulically active barium aluminates with compounds having a spinel structure. It is their presence that helps to increase the slag and metal resistance of the finished product. The prospects for the application of this technological solution are confirmed by the results of research by a number of authors, both in the technology of spinel-containing refractory cements and concretes based on them [1–4].

The authors carried out theoretical studies of the structure of the system $BaO–CoO–Al_2O_3$, the results of which indicate that in a limited range of concentrations of $CoO–BaAl_2O_4–CoAl_2O_4$ compositions, favorable conditions are fixed for obtaining specific binder materials with high performance characteristics [5]. The phases that make up the elementary triangle of the system have the highest probability of existence, which makes it possible to synthesize special materials without additional methods to ensure the accuracy of dosing of raw materials. However, when developing cement compositions based on a complete analysis of the subsolidus structure of ternary systems, researchers tend to avoid concentration regions that include pure oxides. Therefore, a promising direction in the creation of refractory materials based on the binder compositions of the $BaO–Al_2O_3–CoO$ system is a sectional consideration of the $BaAl_2O_4–CoAl_2O_4$ pseudobinary section.

Both compounds of this section refer to spinels ($MeO{\cdot}Me_2O_3$, where Me is a metal in oxidation states 2+ and 3+, respectively), which usually have a cubic crystal lattice of the type which suggests the possibility of solubility in the solid state. However, these processes have not previously been studied. This fact creates difficulties in predicting the formation of phases during the synthesis of specific binding materials.

The processes involved in the synthesis of refractory materials are predominantly solid-phase. The speed of such processes depends on a number of factors: the chemical nature of the reagents, size, shape and degree of mixing of heterogeneous particles, compaction of the reaction mixture, diffusion rate through the reaction product layer, etc. Thus, the purpose of this work is to analyze and establish the nature and peculiarities of formation of solid solutions in the pseudo-binary cross section of the $BaAl_2O_4–CoAl_2O_4$ system.

The authors of [6] experimentally established the existence polymorphic transitions in barium carbonate, when studying the kinetics and mechanism of $BaCO_3$ thermal decomposition in gas media Ar, CO_2 and air: $1\alpha\rightarrow 808\ C\ \beta\rightarrow 971\ C\ \gamma$. This data is consistent with earlier information on polymorphic transformations of barium carbonate during operation [6]. It is noted that the temperature of the beginning of $BaCO_3$ dissociation with the formation of BaO is the highest (1335°C) in the CO_2 atmosphere, while in the argon atmosphere it is 1283°C, and in the air — 1275°C.

The authors [7] also note that anhydrous alumina has a number of polymorphic transformations. Al_2O_3 exists in three forms — α, β and γ. Under natural conditions, only the hexagonal form $\alpha–Al_2O_3$ occurs. The trigonal modification of $\beta–Al_2O_3$ is transformed into $\alpha–Al_2O_3$ in the range of 1600°C–1700°C. When heated, the cubic modification $\gamma–Al_2O_3$ turns into $\alpha–Al_2O_3$. This transition is irreversible and occurs gradually, starting from 1100°C–1200°C and ending at 1450°C.

According to [8], CoO is able to absorb oxygen already at 18°C–20°C, while changing the stoichiometry almost to the composition of Co_3O_4, but without rearranging the crystal lattice. If the process of oxygen absorption occurs at 120°C–200°C, the crystal lattice of Co_3O_4 spinel is already formed. At 400°C the transformation of CoO into Co_3O_4 occurs very rapidly, but the completeness of the conversion has not been discussed and insufficiently studied.

2. Experimental

The raw mixture was calculated on phase composition: 50 mass % $BaAl_2O_4$ and 50 mass % $CoAl_2O_4$. Technical barium car-

1 Text of Footnote

bonate (DSTU 95-2326-91), cobalt (II) carbon dioxide water base (DSTU 5407-78) and anhydrous aluminum oxide (DSTU 69-12-94) were used as the initial raw materials.

The raw material was grinded and thoroughly mixed in the form of a sludge in a laboratory ball mill (mixture moisture 50 %). The fineness of grinding was controlled by sieve analysis (complete passage through a No. 008 sieve). The obtained raw material was dried at temperature of 105°C–110°C; then, cylindrical samples with a diameter and height of 20 mm were formed on a hydraulic press at a specific pressing pressure of 35 MPa.

The samples were fired in a laboratory cryptol furnace in the temperature range of 900–1500°C in steps of 100°C. The rate of temperature rise in the furnace was 50–70°C/min; temperature measurements were made using an optical pyrometer "Smotrich". The isothermal exposure of the samples at maximum temperature was 180 min.

The formation process of basic phases from the raw mixtures was controlled by X-ray phase analysis on a DRON-3M diffractometer (copper anode, nickel filter, anode voltage — 35 kV, anode current — 20 mA).

3. Results and discussion

On the diffraction patterns of all the studied samples, crystalline phases were identified, the interplanar distances (d) of which are close to the standard values [9] of $BaAl_2O_4$ and $CoAl_2O_4$. Both compounds belong to the class of spinels. Their crystal lattices have unit cells of hexagonal and cubic type. The perfection of crystal lattices is an essential prerequisite for the formation of substitutional solid solutions. At the same time, comparison of cationic radii of Ba^{+2} and Co^{+2} (1.43 and 0.82 nm respectively) indicates a limited character of solid solutions, since, according to Goldsmidt's rule [10], a continuous series of solid solutions can be observed if the cation radii differ less than 15 %. In our case, the difference between the cation radii of Ba^{+2} and Co^{+2} is more than 42.7 %. This fact is the cause of mechanical stresses in the crystal lattice at a certain critical concentration of substituting cations. In this regard, the formation of solid solutions in the synthesized material is expected both on the basis of the $BaAl_2O_4$ crystal lattice, where part of Ba^{+2} will be replaced by Co^{+2}, and on the basis of $CoAl_2O_4$, where part of Co^{+2} will be replaced by Ba^{+2}. The degree of relevance of the X-ray phase analysis results of the sample material was high. This was indicated by the nonmonotonic nature of the change in the intensity of the diffraction peaks and the deviation from the standard values of the interplanar distances (d) for $BaAl_2O_4$ and $CoAl_2O_4$.

To establish the phase changes occurring in the studied material, the following characteristic interplanar distances were identified on diffraction patterns: $BaAl_2O_4$ (d = 3.149 Å); $CoAl_2O_4$ (d = 2.4407 Å); $BaCo_3$ (d = 3.7199 Å).

The corresponding diffraction peaks in the presence of other phases in the sample material were well resolved and did not overlap with the diffraction peaks of the accompanying phases, which made it possible to take them as characteristic ones. The highest values of intensities of characteristic peaks for each phase were measured in millimeters on diffraction patterns and taken as 100 %. The relative contents of these phases in the material at different temperatures were then calculated (Table 1). In this case, barium carbonate is taken into account as a precursor of BaO in order to be able to control the course of the phase formation process.

It should be noted that with an increase in the firing temperature of the samples, the relative content of $BaCO_3$ changes unevenly. At initial temperatures, it decreases and reaches a minimum, and above 1200°C it increases. A logical explanation for this behavior is the formation of free BaO at firing temperatures above 1300°C due to the phase decomposition of the resulting solid solutions. At the same time, the fast cooling rate of the samples prevents the reabsorption of the formed barium oxide, which is subsequently easily carbonized by carbon dioxide contained in the gaseous air medium.

For better visualization of the results obtained, graphic dependences of the change in the relative content of $BaAl_2O_4$, $CoAl_2O_4$ and $BaCO_3$ in the sample material are plotted depending on the firing temperature (ig. 1). The analysis of Fig. 1 shows that the initial decarbonization of $BaCo_3$ occurs already at 900°C, and due to the formed BaO, a certain amount of spinels is synthesized, not only $CoAl_2O_4$, but also $BaAl_2O_4$ spinels. In our opinion, partial oxidation of Co^{+2} to Co^{+3} occurs, and homogeneous solid solutions are formed based on both spinels. Both spinels are identified on diffraction patterns of the investigated samples. Values

Table 1. Relative contents of main phases in the sample material at different temperatures

Firing temperatures, °C	$BaAl_2O_4$ $d \cdot 10^{-10}$ = 3.149 nm		$CoAl_2O_4$ $d \cdot 10^{-10}$ = 2.4407 nm		$BaCO_3$ $d \cdot 10^{-10}$ = 3.7199 nm	
	mm	relative %	mm	relative %	mm	relative %
900	79	51.0	67	88.2	8	72.7
1000	120	77.4	41	53.9	3	27.3
1100	104	67.1	72	94.7	0	0
1200	121	78.1	58	76.3	0	0
1300	155	100	76	100	3	27.3
1400	133	85.8	35	35.5	9	81.8
1500	119	76.4	27	32,9	11	100

of interplanar distances differ slightly from the standard ones [9].

In the temperature range of 900°C–1000°C, there is an increase in the relative $BaAl_2O_4$ content with a simultaneous decrease in the relative $CoAl_2O_4$ content. Obviously, solid solutions based on $BaAl_2O_4$ are formed at a higher rate due to the dissolution of $CoAl_2O_4$ in the solid phase by isomorphic replacement of a certain part of the Ba^{+2} cations by Co^{+2}; in general, solid solutions of partial substitution of cations are denoted by non-stoichiometric parameters, in this case x: $(Ba_{1-x}, Co_x)\ Al_2O_4$. Solid solutions based on $CoAl_2O_4$ are also formed in this temperature range, but in much smaller quantities, and the parameter of their non-stoichiometry z is significantly lower than x: $(Ba_z, Co_{1-z})\ Al_2O_4$. The formation of solid solutions on the basis of both spinels is subject to general regularities of the formation of crystallization nuclei with a change in their type as the non-stoichiometry parameters increase from homogeneous to saturated, supersaturated, and followed by phase decomposition. An increase in the values of the non-stoichiometry parameters causes distortions in the structure of the bivalent sublattice sublayers of spinels and, accordingly, deviations of the values of interplanar distances from the nominal ones were recorded on the diffraction patterns.

The relative content of solid solutions on the basis of $CoAl_2O_4$ crystal lattice increases in the temperature range of 1000°C–1100°C. A synchronous decrease of the relative content of $BaAl_2O_4$ based solid solutions and initial $BaCo_3$ to the minimum value is also observed in this temperature range (Fig. 1). In fact, the tendencies of physico-

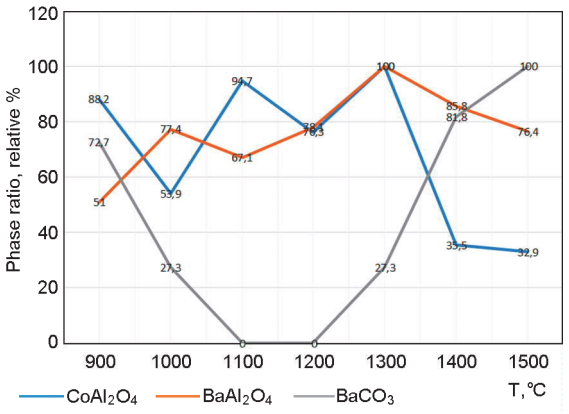

Fig. 1. Phase changes in samples of the pseudo-binary section $BaAl_2O_4$–$CoAl_2O_4$ as a function of temperature.

chemical processes change in relation to similar processes in the temperature range 900°C–1000°C, which indicates the predominant formation of solid solutions based on cobalt spinel. The nonstoichiometry parameter z increases more significantly than x, since $BaAl_2O_4$ dissolves rapidly in the solid state in $CoAl_2O_4$. In addition, it can be assumed that the formation of mixed-type metastable solid solutions is possible, including due to the introduction of cobalt cations not only into the divalent sublattices of spinel solid solutions, but also into their trivalent sublattices. Not only isomorphic substitution of Ba^{+2} for Co^{+2}, but also Al^{+3} for Co^{+3} one takes place. Trivalent cobalt cations are most likely formed during the oxidation of the initial cobalt oxide CoO, which, for kinetic reasons, did not have time to fully enter into the formation of spinel solid solutions.

However, the case of "intramolecular" oxidation of Co^{+2} to Co^{+3} directly in the

previously formed crystal lattices of spinel solid solutions is not excluded. In this case, the divalent cationic sublattice of the solid solution will be "depleted" due to the transition of part of cations of cobalt to the trivalent sublattice, which will be "enriched" accordingly.

At 1100°C–1200°C all $BaCo_3$ in the sample material is spent on the formation of spinel solid solutions (Fig. 1); and in this temperature range, the increase in the relative content of solid solutions based on barium-aluminate spinel is carried out due to the solid phase dissolution of the still unreacted stoichiometric cobalt aluminate spinel, the relative content of which decreases:

$$(Ba_{1-x},Co_x) \cdot Al_2O_4 + qCoAl_2O_4 = (Ba_{1-x},Co_{x+q}) \cdot Al_{2(1+q)}O_{4(1+q)}, \quad (1)$$

where q is the dissolved part of $CoAl_2O_4$, which is equivalent to changing the non-stoichiometry parameters of the resulting metastable solid solution.

To analyze processes in the crystal lattices of solid solutions, it is more convenient to separate their divalent and trivalent sublattices in formulas, in particular: $BaAl_2O_4 \equiv BaO \cdot Al_2O_3$, $CoAl_2O_4 \equiv CoO \cdot Al_2O_3$. Then, the above equation (1) has the form:

$$(Ba_{1-x},Co_x)O \cdot Al_2O_3 + q[CoO \cdot Al_2O_3] = (Ba_{1-x},Co_{x+q})O \cdot Al_{2(1+q)}O_{3(1+q)}. \quad (2)$$

Obviously, a similar process of solid-phase dissolution of stoichiometric barium aluminate spinel in a solid solution based on cobalt spinel takes place. However, the rate of this process (3) is significantly lower and it is dominated by the solid-phase dissolution according to the reaction (1)≡(2):

$$(Ba_z,Co_{1-z})O \cdot Al_2O_3 + p[BaO \cdot Al_2O_3] = (Ba_{z+p},Co_{1-z})O \cdot Al_{2(1+p)}O_{3(1+3p)}, \quad (3)$$

where p is the dissolved part of $BaAl_2O_4$.

In the same temperature range, all the prerequisites are created for the formation of metastable solid solutions of a mixed type. Cobalt cations are in both divalent and trivalent sublattices. We believe that the gaseous combustion medium in the cryptol furnace at 1100°C – 1200°C creates certain conditions for a more probable "intramolecular" oxidation:

$$CoO + 0.5O \rightarrow CoO_{1.5}. \quad (4)$$

To simplify the notation, we will assume that the same amount of cobalt oxide (δ) isomorphically replaces Al_2O_3 in the trivalent sublattices of spinel solid solutions. Accordingly, cobalt-aluminate solid solutions with a higher cobalt content will be formed:

$$(Ba_{1-x},Co_{x+q})O \cdot Al_{2(1+q)}O_{3(1+q)} \rightarrow (Ba_{1-x},Co_{x+q-\delta})O_{1-0.5\delta} \cdot (Al_{(1+q-0.5\delta)}Co_{0.5\delta})_2O_{3(1+q+0.5\delta)}. \quad (5)$$

$$(Ba_{z+p},Co_{1-z})O \cdot Al_{2(1+p)}O_{3(1+p)} \rightarrow (Ba_{z+p},Co_{1-z-\delta})O_{1-0.5\delta} \cdot (Al_{(1+p-0.5\delta)}Co_{0.5\delta})_2O_{3(1+p+0.5\delta)}. \quad (6)$$

Reaction (3) is intensified in the temperature range of 1200°C–1300°C, and solid-phase interaction (2) continues, which leads to complete consumption of the initial charge components up to 1300°C. Accordingly, Fig. 1 shows a mutual growth of relative content of spinel solid solutions both on the basis of $BaAl_2O_4$ crystal lattice and on the basis of $CoAl_2O_4$ crystal lattice. The content of $BaCO_3$ should also be considered zero in this temperature range, since its low-intensity diffraction peaks are identified only after firing at 1300°C (Table 1). The final compositions of the solid solutions formed by 1300°C correspond to formulas (5) and (6), where the corresponding parameters of non-stoichiometry reach the limit values (recall that the initial raw mixture in the ideal case of unlimited solid-phase solubility of spinels made it possible to form a solid solution $(Ba_{0.5}, Co_{0.5})O \cdot Al_2O_3$.

Starting with 1300°C firing temperatures and above, a decrease in the relative content of solid solutions of both types (5) and (6) with different intensity is observed in the samples (Fig. 1). This process is due to the phase decomposition of supersaturated metastable solutions. In the solid solutions of types (5) and (6) we observe: oxygen "depletion" of divalent sublattices (by — 0.5δ); enrichment with Ba^{+2} cations and "depletion" with Co^{+2} cations of bivalent sublattices in (5) and (6) (by $+p$ and by $-(z+\delta)$), respectively; oxygen "enrichment" of trivalent sublattices (by $3(p+0.5\delta)$); "enrichment" of aluminum sublattices with Co^{+3} cations (by $+0.5\delta$); the presence of competitive processes during isomorphic substitutions in aluminum cationic sublattices and in cationic sublattices of cobalt (II) in solid solutions of type (5), which is evident from the formulas for the alternation of signs in front of the corresponding nonstoichiometry parameters.

The noted concentration changes are realized with the participation of different size cations, cause significant structural distortions accompanied by mechanical stresses exceeding the forces of chemical bonds in the crystal lattices of supersaturated solid solutions. As a result, a radical transformation of the crystal lattice occurs with the segregation of individual crystalline phases, in particular, BaO and, possibly, stoichiometric spinels $BaAl_2O_4$ and $CoAl_2O_4$ or their solid solutions. The detailed phase decomposition mechanism can be very complex and requires additional experiments in further research.

4. Conclusions

As a result of the research, it was established that there is no unlimited solubility in the solid phase between barium-aluminate and cobalt-aluminate spinels. The analysis of the qualitative and quantitative phase relationships in the temperature range of 900°C–1500°C, suggesting limited solubility of the resulting solid solutions in the $BaAl_2O_4$–$CoAl_2O_4$ pseudobinary section, made it possible to give an adequate interpretation of the experimental results. It is shown that the nonmonotonic change in the number of main phases in the sample material after firing at different temperatures is due to the peculiarities of the formation of solid solutions based on cobalt-aluminate and barium-aluminate spinels: saturation of their cationic lattices due to $Co^{+2}\leftarrow\rightarrow Ba^{+2}$ isovalent isomorphism, the possibility of oxidation Co^{+2} to Co^{+3} and participation in the cationic substitution of Al^{+3} in trivalent lattices. The results of the experiments point to the achievement of the limiting solubility of solid solutions of spinel below 1300°C. If the temperature is higher, than 1300°C, phase decomposition is observed with the release of simpler, concentrated unsaturated crystalline phases, in particular BaO, which does not have time to re-integrate into the solid phase interaction during rapid cooling of the sample material, but then carbonizes with carbon dioxide from the air. The results of the research are relevant for predicting the phase composition of materials with binder properties in the system $BaO–CoO–Al_2O_3$ and regulating their hydration activity, which significantly depends on the imperfection of the crystal lattices of the clinker phases.

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