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The article discusses the physicochemical principles for the production of alumina cements based on nickel and cobalt spinel. The results of tetrahedration of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO system, which undergoes changes due to solid-state exchange reactions in the high-temperature region of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO subsystem at a calculated temperature of 1439 K, as well as the decomposition of the Ca<sub>3</sub>CoAl<sub>4</sub>O<sub>10</sub> ternary compound near 1530 K, are presented. Thermodynamic analysis establishes the stability of the conodes of the above system, allowing for its triangulation. Modifications of the subsolidus structure are combined and given for the temperature of 1530 K. All binary, ternary, and quaternary combinations thermodynamically stable in the subsolidus region of the system under study are presented. Topological graphs depicting the interconnection of elementary tetrahedrons, which allow the prediction of solid-state processes in multi-component systems, have been constructed. Based on the study of the structure of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO system, the possibility of technological forecasting of heterophase materials with high-performance characteristics is substantiated.

**Keywords:** multi-component system, solid-state exchange reaction, tetrahedron, ternary compound, topological graphs, prediction.

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**Introduction**

The unchanging task of the cement industry, even in times of military conflicts and exacerbated environmental contamination, is the enhancement of cement quality, improvement of its properties, and an increase in the production efficiency. Special attention is paid in this context to the development of novel types and compositions of refractory cements and materials based on them. Additionally, the exploration of potential applications of resource-efficient technologies is a topical issue. Most frequently, refractory materials utilize aluminous and high-alumina cements as binders, which constitute an integral component of refractories, providing strength post-hardening and forming a wear-resistant structure. The primary drawback of such binding systems is a significant heat evolution during the setting process

and a reduction in strength during solidification. Avoiding this can be achieved by varying the phase composition of the cement, providing the resulting material with increased strength, low porosity, refractoriness, heat resistance, and resistance to the influence of aggressive environments. Within the composition of calcium aluminates, which form the basis of aluminous cements, it is expedient to substitute calcium oxide with other oxides of elements having higher melting temperatures. Additionally, partial replacement of aluminum oxide can be considered, allowing the resulting binding materials to acquire unique properties.

A promising system for obtaining modified aluminous cements and heterophase materials with a complex of magnetic properties is the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO system (the following abbreviations are

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*Physicochemical principles of creating alumina cements based on nickel and cobalt spinel*

further used: «A», «C», «Co» and «Ni» stands for  $\text{Al}_2\text{O}_3$ , CaO, CoO, and NiO, respectively). Materials based on subsystems of the above system have practical applications in various industrial sectors, including lime production, production of lime binders and refractories, production of enamels incorporating classic «bonding» oxides, CoO and NiO; aluminum production; corundum abrasive materials and refractories; high-temperature catalysts; structural and functional ceramics with specific electromagnetic properties [1–3].

At the same time, information about the structure of the four-component phase diagram of the CaO– $\text{Al}_2\text{O}_3$ –CoO–NiO system is absent in reference literature and scientific articles. Therefore, preparation of such materials is complicated by insufficient knowledge of the regularities in the determined multicomponent system, which does not allow predicting the phase composition of spinel-containing aluminous materials. Thus, theoretical and practical research into the structure of the CaO– $\text{Al}_2\text{O}_3$ –CoO–NiO system is a relevant task.

#### *Theoretical analysis*

Binary and ternary subsystems of the experimental system have been investigated with varying degrees of reliability of the obtained experimental and computational results. The phase diagram of  $\text{Al}_2\text{O}_3$ –CaO has been studied most comprehensively, and its modern representation is outlined in ref. [4]. In this system, the following binary oxide compounds have been reliably identified:  $\text{Ca}_3\text{Al}_2\text{O}_6$ ,  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ,  $\text{CaAl}_2\text{O}_4$ ,  $\text{CaAl}_4\text{O}_7$  and  $\text{CaAl}_{12}\text{O}_{19}$ .

The binary  $\text{Al}_2\text{O}_3$ –NiO system has been investigated, and the results are summarized in ref. [5]. There is one compound in the system, nickel aluminate spinel  $\text{NiAl}_2\text{O}_4$ , which melts congruently at  $2110^\circ\text{C}$ , with a cubic crystal lattice parameter of  $0.80461(3)$  nm [6]. This spinel does not form solid solutions with nickel oxide, but it does with  $\text{Al}_2\text{O}_3$ , starting at  $1300^\circ\text{C}$ . At  $1800^\circ\text{C}$ , it contains up to 65 mol.% of  $\text{Al}_2\text{O}_3$  due to isomorphic substitution, where three bivalent nickel cations are replaced by two trivalent aluminum cations, leading to the formation of a cationic vacancy in the crystal lattice. The noted phase  $\delta$ -NiO· $13\text{Al}_2\text{O}_3$  is a solid solution with a limited homogeneity range, existing only above  $2000^\circ\text{C}$ . It belongs to the tetragonal crystal system ( $a=0.7958$  nm,  $c=11.768$  nm). In addition,  $j$ - and  $\varphi$ -phases are mentioned, these should be considered metastable, forming during the decomposition of spinel solid solutions [5].

The CaO–CoO system belongs to the type of simple eutectic systems (eutectic near  $1400^\circ\text{C}$ ) with

the presence of solid solutions based on CoO (up to 30 mol.% CaO) and based on CaO (up to 18 mol.% CoO) [5].

The CaO–NiO system is analogous to the CaO–CoO system. In this system, double oxide compounds also do not form, and the eutectic point is at  $1720^\circ\text{C}$  (the melting temperatures of individual NiO and CaO oxides are reported to be  $1960$  and  $2580^\circ\text{C}$ , respectively). Solid solutions based on NiO achieve CaO concentrations of up to 23 mol.% at the eutectic temperature, while those based on CaO reach up to 42 mol.% NiO [5].

The binary system  $\text{Al}_2\text{O}_3$ –CoO is analogous to the  $\text{Al}_2\text{O}_3$ –NiO one; it also contains one double oxide compound, cobalt aluminate spinel, with a melting temperature around  $1960\pm 10^\circ\text{C}$  and a cubic crystal lattice parameter of  $0.8086$  nm [6]. The similarity of the mentioned subsystems is reflected in the common nature of the structure of more complex systems involving them, for example,  $\text{Al}_2\text{O}_3$ –NiO– $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ –CoO– $\text{SiO}_2$  [7].

Oxides of nickel and cobalt, similar in structure, form a continuous series of solid solutions, which is particularly characteristic of phase diagrams in binary systems of alkaline earth oxides [4].

Information on the study of the phase diagram of the CaO–CoO–NiO system is not found in literary sources. Given that limited and unlimited series of solid solutions are formed in the mentioned binary subsystems and that there are no double oxide compounds, the nature of the structure of the specified ternary system is determined by these circumstances: it is simple and not triangulated.

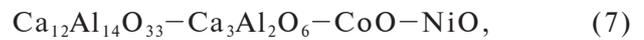
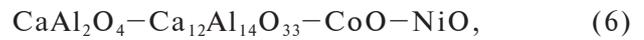
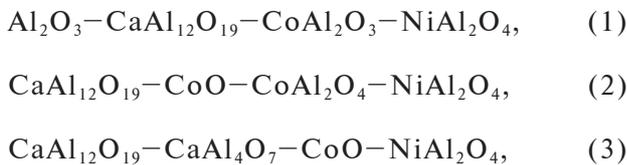
The ternary subsystem CaO– $\text{Al}_2\text{O}_3$ –NiO has been triangulated elsewhere [8], by using the results of thermodynamic calculations for phase equilibria and experimental studies on samples with controlled compositions of synthesized materials.

The subsolidus structure of the CaO– $\text{Al}_2\text{O}_3$ –CoO subsystem has been investigated using known experimental data and computational methods based on the fundamental laws of equilibrium thermodynamics [9]. The thermodynamic analysis of the solid-phase reaction involving cobalt aluminate and nickel aluminate spinels in the  $\text{Al}_2\text{O}_3$ –CoO–NiO subsystem resulted in establishing the stability of binary combinations of the system compounds: NiO and  $\text{CoAl}_2\text{O}_4$ ,  $\text{CoAl}_4\text{O}_7$  and  $\text{NiAlO}_4$ . Considering these conditions, the subsolidus structure of this system has been determined and its characteristics have been provided [10].

#### *Results and discussion*

The triangulated subsystems of the investigated system CaO– $\text{Al}_2\text{O}_3$ –CoO–NiO are shown in Fig. 1.

Given the non-triangulatability of the CaO–CoO–NiO subsystem, the presence of only one double oxide compound in the binary Al<sub>2</sub>O<sub>3</sub>–CoO and Al<sub>2</sub>O<sub>3</sub>–NiO subsystems, as well as the relatively simple nature of the subsolidus structure of the ternary subsystems (Fig. 1), the tetrahedrization of the investigated system poses no difficulties and does not require labor-intensive calculations. The consolidation of ternary subsystems in the high-temperature range (greater than 1439 K) into a concentration tetrahedron of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO system automatically tetrahedrizes it without the involvement of «internal» connodes passing through the concentration space. The subsolidus structure of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO system is presented in Fig. 2,a, and the constructed topological graph characterizing the interrelation of all elementary tetrahedral (1)–(8) are shown in Fig. 2,b.



It can be observed from Fig. 2,a that all elementary tetrahedra in the subsolidus structure of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO system at the temperature above 1439 K are sequentially connected through common faces, which determines the linear nature of the topological graph (Fig. 2,b). There are no embedded elementary tetrahedra in the subsolidus structure (none of the faces extends to the faces of the concentration tetrahedron of the system), which is due to the relatively simple triangulation of the ternary subsystems. Each of the elementary tetrahedra, except for No. 1 and No. 8, shares two faces with its adjacent

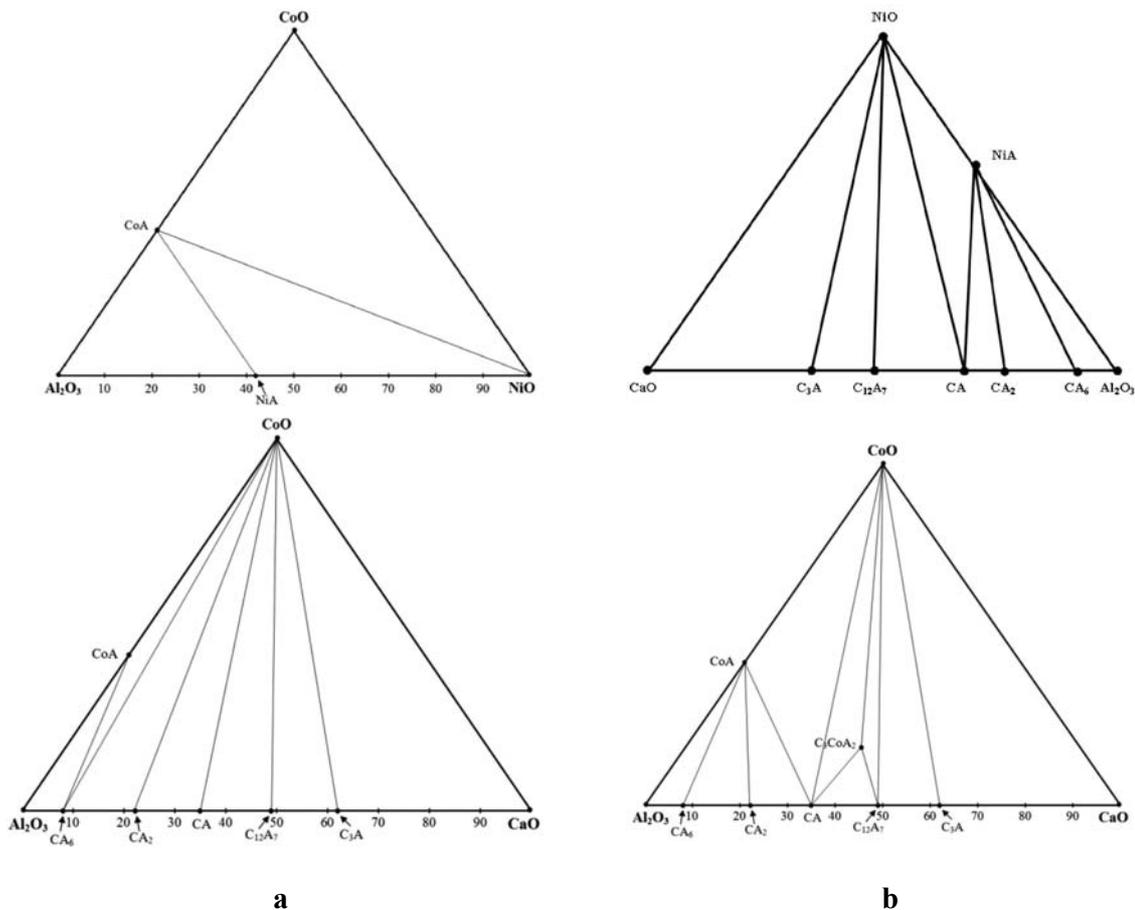


Fig. 1. Triangulated subsystems of the system CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO: a – above 1439 K; b – below 1439 K

tetrahedra, while the remaining two faces belong to the corresponding faces of the concentration tetrahedron of the system (for elementary tetrahedra No. 1 and No. 8, three faces extend to the faces of the system's tetrahedron); these elementary tetrahedra form the outer, so-called «hanging» vertices in the topological graph.

The subsolidus structure of the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$  above 1439 K and topological graph depicting the interrelation of elementary tetrahedra of the system are presented in Fig. 2.

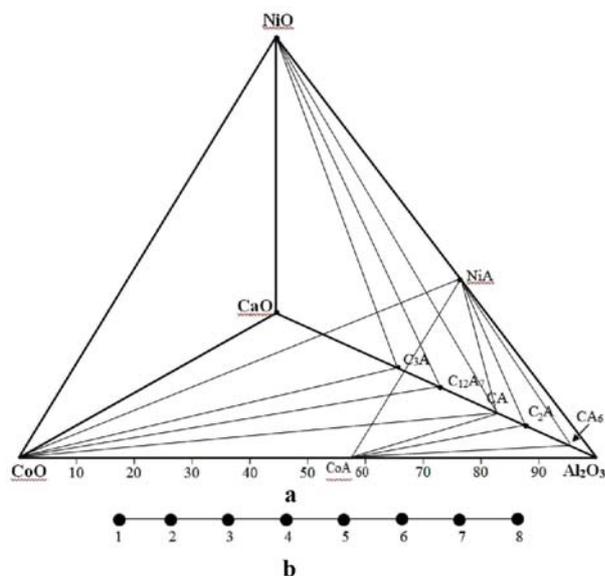


Fig. 2. a – Subsolidus structure of the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$  above 1439 K; b – Topological graph depicting the interrelation of elementary tetrahedra of the system

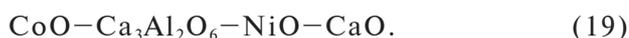
Verification of the correctness of tetrahedrization according to Euler's formula leads to an identity (9) when compared to the number of edges in the graph (R) in Fig. 2,a:

$$R = \frac{\sum n_i z_i}{2} = \frac{1 \cdot 2 + 2 \cdot 6}{2} = 7, \quad (9)$$

where  $z_i$  is the number of vertices in the graph with degree  $i$ , determined by the number of edges at the corresponding vertex; and  $n_i=1, 2, 3, 4$  according to the degree of vertices in the graph.

The low-temperature (less than 1439 K) tetrahedrization of the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$  system takes into account the presence of the triple compound  $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$  and also does not pose difficulties due to the unambiguous closure of all tetrahedra and the unique arrangement of the «internal» connode  $\text{NiO} - \text{Ca}_3\text{CoAl}_4\text{O}_{10}$  (Fig. 3,a, dotted line). The

following elementary tetrahedra are present in the low-temperature range (10)–(19):



The interrelation of elementary tetrahedra is represented by a topological graph (Fig. 3,b), which is also not complex. No embedded tetrahedra are still observed in the low-temperature subsolidus structure, and the topological graph also has two hanging vertices. The topological graph is planar, without false edge intersections, and passes the adequacy check according to Euler's formula (20), providing a calculated value of the number of edges in the graph equal to 10.

$$R = \frac{1 \cdot 2 + 2 \cdot 6 + 3 \cdot 2}{2} = 10. \quad (20)$$

The subsolidus structure of the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$  below 1439 K (a) and topological graph depicting the interrelation of elementary tetrahedra of the system (b) are presented in Fig. 3.

### Conclusions

To sum up, the analysis and the complex of studies of the sub-solidus structure of the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$  allow us to theoretically predict various thermodynamically stable combinations of compounds, control the synthesis processes and form a given set of properties in the materials of this system. The subsolidus structure of the investigated system has been established over the entire temperature range, both below the melting temperature of the triple oxide compound  $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$  at 1439 K and in the higher-temperature region. The coexistence of phases, united by connodes, elementary triangles, and tetrahedra, forms the basis for technological design of

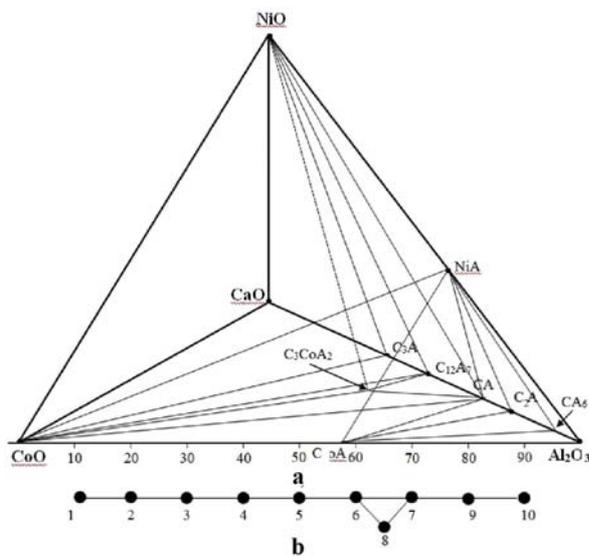


Fig. 3. a – Subsolidus structure of the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$  system below 1439 K; b – Topological graph depicting the interrelation of elementary tetrahedra

heterophase materials in the investigated system. Results of the structural study of the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$  system allows using the compositions of the rational domain to produce materials with an elevated operating temperature, which can be used in various industries for protective areas of thermal units or for the manufacture of heat-resistant structures, as well as in the production of refractories, enamels, high-temperature catalysts, and structural and functional ceramics.

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## ФІЗИКО-ХІМІЧНІ ПРИНЦИПИ СТВОРЕННЯ ГЛИНОЗЕМНИХ ЦЕМЕНТІВ НА ОСНОВІ НІКЕЛЕВОЇ ТА КОБАЛЬТОВОЇ ШПІНЕЛІ

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У статті розглянуто фізико-хімічні принципи одержання глиноземних цементів на основі нікелевої та кобальтової шпінелі. Наводяться результати тетраедрації системи  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$ , яка зазнає змін у результаті протікання твердофазних реакцій обміну у високотемпературній ділянці підсистеми  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}$  при розрахунковій температурі 1439 K, а також в результаті розкладання потрійної сполуки  $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$  поблизу 1530 K. За допомогою термодинамічного аналізу встановлена стабільність конод вищенаведеної системи, що дозволяє провести її триангуляцію. Зміни субсолідусної будови поєднані та наведені для температури 1530 K. Наведені всі бінарні, потрійні та четверні комбінації, термодинамічно стабільні у субсолідусній ділянці досліджуваної системи. Побудовано топологічні графи, що показують взаємозв'язок елементарних тетраедрів і дозволяють прогнозувати твердофазні процеси у багатокомпонентних системах. На підставі здійснених досліджень будови системи  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CoO}-\text{NiO}$  обгрунтовано можливість технологічного прогнозування гетерофазних матеріалів з високими експлуатаційними характеристиками.

**Ключові слова:** багатокомпонентна система, твердофазні реакції обміну, тетраедрація, потрійна сполука, топологічний граф, прогнозування.

**PHYSICOCHEMICAL PRINCIPLES OF CREATING ALUMINA CEMENTS BASED ON NICKEL AND COBALT SPINEL**

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The article discusses the physicochemical principles for the production of alumina cements based on nickel and cobalt spinel. The results of tetrahedration of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO system, which undergoes changes due to solid-state exchange reactions in the high-temperature region of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO subsystem at a calculated temperature of 1439 K, as well as the decomposition of the Ca<sub>3</sub>CoAl<sub>4</sub>O<sub>10</sub> ternary compound near 1530 K, are presented. Thermodynamic analysis establishes the stability of the conodes of the above system, allowing for its triangulation. Modifications of the subsolidus structure are combined and given for the temperature of 1530 K. All binary, ternary, and quaternary combinations thermodynamically stable in the subsolidus region of the system under study are presented. Topological graphs depicting the interconnection of elementary tetrahedrons, which allow the prediction of solid-state processes in multi-component systems, have been constructed. Based on the study of the structure of the CaO–Al<sub>2</sub>O<sub>3</sub>–CoO–NiO system, the possibility of technological forecasting of heterophase materials with high-performance characteristics is substantiated.

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