UDC 544.31

G.N. Shabanova, A.N. Korohodska, S.V. Levadna, O.A. Gamova

TRIANGULATION AND CHARACTERIZATION OF THE SUBSOLIDUS STRUCTURE IN THE SYSTEMS $CaO-CoO-MoO_3$, $CoO-Al_2O_3-MoO_3$ AND $CaO-Al_2O_3-MoO_3$

National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine

Three-component systems $CaO-CoO-MoO_3$, $CoO-Al_2O_3-MoO_3$ and $CaO-Al_2O_3-MoO_3$ are characterized in this work. The results of the research of the subsolidus structure of the systems under study are given. Diagrams of the systems in the field of the subsolidus are presented. The calculations of the changes of Gibbs free energy are performed at different temperatures for the model reactions. The thermodynamic and geometric topological calculations based on the developed thermodynamic database allow establishing the direction of solid-phase reactions in the three-component systems $CaO-CoO-MoO_3$, $CoO-Al_2O_3-MoO_3$ and $CaO-Al_2O_3-MoO_3$ with the participation of steadily existing compounds; as a result, all conodes in these systems have been determined. The main geometric topological calculations of elementary triangles and phases of systems are performed. Geometric topological system performance is important for the prediction of the accuracy of a dosage of components and the duration of their mixing before synthesis to obtain materials with the specified phase composition. The data on subsolidus structure of the considered three-component systems are essential for further forecasting phase structure of the aluminate cements fabricated with the use of the waste of cobalt catalysts that additionally contain molybdenum oxide.

Introduction

The cement industry is one of the leading sectors in the production of building materials. Among various construction materials and special-purpose products, a large group of them is produced using alumina-containing raw materials. This group includes high-alumina products, corundum and alumina-mullite ceramics, aluminates and expanding cements. Aluminum oxide, depending on the purpose of the material, ensures refractoriness, considerable strength and durability in aggressive environments. Technical alumina or natural bauxite are most often used as starting alumina-containing materials. However, the scarcity of raw materials and high-energy intensity of technology restrain wide production and consumption of these high-quality materials.

At the same time, catalysts based on alumina are used in many processes of the chemical and petrochemical industry. There is a serious problem of reuse of the spent catalysts. The recuperation of the spent catalysts allows reducing the consumption of natural resources, significantly decreasing the cost of cement production and improving the environmental safety due to the waste disposal.

Results and discussion

It is possible to use a catalyst waste containing 86.8% Al_2O_3, 2.5% CoO, 10.7% MoO_3 instead of alumina in the composition of the raw mix for alumina cement. However, the use of molybdenum-containing wastes requires the investigation of the structure of three-component systems containing molybdenum oxide, $CaO-CoO-MoO_3$, $CoO-Al_2O_3-MoO_3$ and $CaO-Al_2O_3-MoO_3$, to create the physicochemical basis for the development of aluminous cement compositions based on the abovementioned waste.

It is advisable to conduct a thermodynamic analysis of the processes that take place, which is possible only if the initial thermodynamic constants are known. We failed to find in the literature all thermodynamic constants concerning cobalt

Initial thermodynamics data

| Compound	$-\Delta H^0_{298}$, kJ/mol	S^0_{298}, J/mol·K	$C_p=a+bT+cT^{-2}$, J/mol·K			Temperature range, K	Ref.
			a	$b \cdot 10^3$	$-c \cdot 10^{-5}$		
MoO_3	745.6	77.74	86.73	21.67	17.49	298–1068	[2]
α-Al_2O_3	1675.6	50.92	114.77	12.8	35.44	298–2323	[3]
CaO	635.55	39.75	48.83	4.52	6.53	298–2000	[3]
CoO	238.9	52.97	48.28	8.535	−1.67	298–2000	[2]
$CaMoO_4$	1542.2	122.6	133.47	29.2	22.3	298–1718	[4]
β-$CoMoO_4$	1031.8	133.9	35.27	4.26	0	298–1453	[2; *]
$CoAl_2O_4$	1948.9	101.7	154.716	22.343	36.905	298–2233	[5]

Note: * − calculated values.

molybdate ($CoMoO_4$) and calcium molybdate ($CaMoO_4$). Therefore, the calculation of the initial thermodynamic values (the coefficients in the equations of heat capacity) was carried out by using the methods described elsewhere [1]. The results of the calculation of the initial thermodynamic data are shown in Table 1.

The CaO−CoO−MoO_3 system is poorly investigated, and there is practically no data in the literature on the full subsolidus structure of this system. The binary systems that make up this three-component system, CaO−CoO, CaO−MoO_3 and CoO−MoO_3 are examined in refs. [6,7]. In the CaO−MoO_3 system, there is one stable binary compound $CaMoO_4$. $CaMoO_4$ crystallizes in the scheelite structure, in which the central ion is coordinated by eight simply connected molybdate groups. The form of $CaMoO_4$ crystals is a tetragonal bipyramid, the lattice parameters are as follows: a=5.221 Å and c=11.425 Å [6]. Calcium molybdate melts congruently at 1445⁰C.

The CoO−MoO_3 system implies the formation of $CoMoO_4$, which exists in two polymorphic modifications. Reversible transformation α→β is observed at the temperature of 400⁰C; β-$CoMoO_4$ melts congruently at 1180⁰C. The parameters of the crystal lattice of a low-temperature modification, α-$CoMoO_4$, are as follows: a=9.671 Å, b=8.852 Å and c=7.764 Å. The parameters of the crystal lattice of a high-temperature modification, β-$CoMoO_4$, are as follows: a=10.21 Å, b=9.32 Å and c=7.01 Å [8].

To determine the subsolidus structure of the CaO−CoO−MoO_3 system, the thermodynamic data given in Table 1 were used. The presence of only two binary compounds, calcium and cobalt molybdates, in the CaO−CoO−MoO_3 system suggests the following single exchange solid-phase reaction:

$$CaO+CoMoO_4=CoO+CaMoO_4.$$
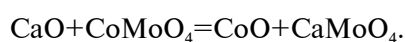
The thermodynamic evaluation of the change in Gibbs energy values was performed for the temperature range of 800−1400 K.

Because the calculated values of the function ΔG vs. T, shown in Table 2, have positive values, one can assert that the coexistence of the starting compounds is thermodynamically preferable, which ensures the presence of CaO−$CoMoO_4$ conodes in the subsolidus structure of this system.

Results of the calculation of the change in the Gibbs free energy for the reaction in the CaO−CoO−MoO_3 system

Temperature, K	Gibbs free energy, kJ/mol
800	327.33
900	314.36
1000	300.01
1100	284.39
1200	267.61
1300	249.75
1400	230.87

Based on the result of the triangulation of the three-component CaO−CoO−MoO_3 system, it was established that it is divided into 3 elementary triangles (Fig. 1), which corresponds to the Kurnakov rule [9].

Thermodynamic data presented in Table 1 were used for the analysis of the exchange reactions in the system CoO−Al_2O_3−MoO_3. The presence of two binary compounds in the three-component CoO−Al_2O_3−MoO_3 system and the absence of any ternary compounds predetermine its splitting according to the results of the calculation of the direction of the following reaction:

$$Al_2O_3+CoMoO_4=MoO_3+CoAl_2O_4.$$
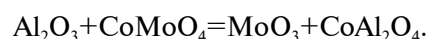
To establish the probable pairs of coexisting phases, the values of the change in the Gibbs energy
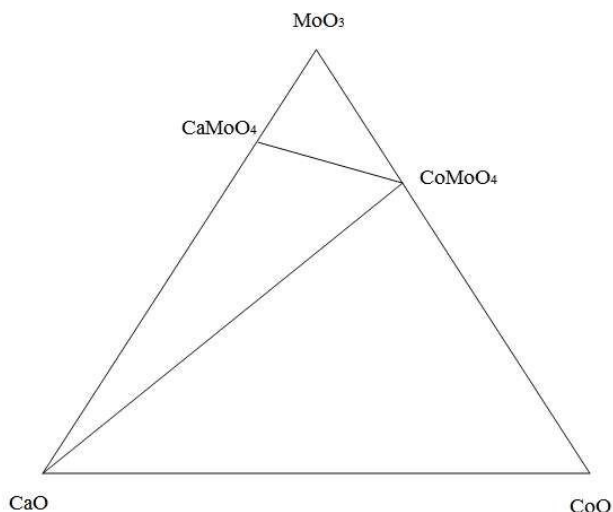
Fig. 1. The structure of the three-component
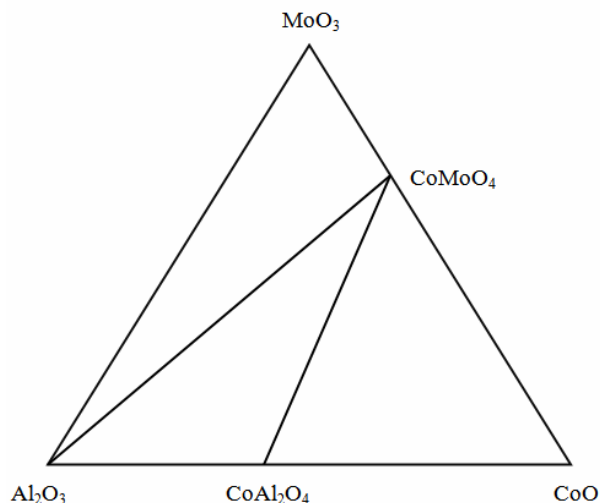$CaO-CoO-MoO_3$ system in the subsolidus region

Fig. 2. Subsolidus structure of the $CoO-Al_2O_3-MoO_3$ system

vs. the temperature were calculated (Table 3).

Table 3

Results of the calculation of the change in the Gibbs free energy for the reaction in the $CoO-Al_2O_3-MoO_3$ system

Temperature, K	Gibbs free energy, kJ/mol
800	1475.36
900	1463.91
1000	1451.14
1100	1437.16
1200	1422.08
1300	1405.94
1400	1388.83

When analyzing this reaction, the coexistence of MoO_3 and $CoAl_2O_4$ is less thermodynamically advantageous than of Al_2O_3 and $CoMoO_4$ as follows from the positive values of ΔG. The closure of the $Al_2O_3-CoMoO_4$ conode leads to the existence of the $CoMoO_4-CoAl_2O_4$ conodes without any alternatives from the geometric-topological principles of the closure of triangles.

The results of the thermodynamic study allow performing the triangulation of the three-component $CoO-Al_2O_3-MoO_3$ system, the subsolidus structure of which is shown in Fig. 2.

Thus, it was found that the three-component $CoO-Al_2O_3-MoO_3$ system is divided by two stable conodes into 3 elementary triangles, which corresponds to the Kurnakov rule.

Despite some available information about the binary subsystems that make up the three-component system $CaO-Al_2O_3-MoO_3$, there is no information about their full structures. In this regard, the issue of studying the structure of the $CaO-Al_2O_3-MoO_3$

system in the field of subsolidus is very important. For the of the subsolidus structure of this system, the thermodynamic data given in Table 1 were used.

The thermodynamic analysis of the subsolidus structure of the three-component system under study was carried out by analyzing the changes in the Gibbs energy for the temperature range of 800 K to the temperatures of phase transition of the compounds involved in the reactions according to the procedure described in ref. [3] for the following model exchange reactions:

1. $CaAl_{12}O_{19}+MoO_3=CaMoO_4+6Al_2O_3$
2. $CaAl_4O_7+MoO_3=CaMoO_4+2Al_2O_3$
3. $3CaAl_4O_7+2MoO_3=2CaMoO_4+CaAl_{12}O_{19}$
4. $CaAl_2O_4+MoO_3=CaMoO_4+Al_2O_3$
5. $6CaAl_2O_4+5MoO_3=5CaMoO_4+CaAl_{12}O_{19}$
6. $2CaAl_2O_4+MoO_3=CaMoO_4+CaAl_4O_7$
7. $Ca_{12}Al_{14}O_{33}+12MoO_3=12CaMoO_4+7Al_2O_3$
8. $6Ca_{12}Al_{14}O_{33}+65MoO_3=$
   $=65CaMoO_4+7CaAl_{12}O_{19}$
9. $2Ca_{12}Al_{14}O_{33}+17MoO_3=$
   $=17CaMoO_4+7CaAl_4O_7$
10. $Ca_{12}Al_{14}O_{33}+5MoO_3=5CaMoO_4+7CaAl_2O_4$
11. $Ca_3Al_2O_6+3MoO_3=3CaMoO_4+Al_2O_3$
12. $6Ca_3Al_2O_6+17MoO_3=$
   $=17CaMoO_4+CaAl_{12}O_{19}$
13. $2Ca_3Al_2O_6+5MoO_3=5CaMoO_4+CaAl_4O_7$
14. $Ca_3Al_2O_6+2MoO_3=2CaMoO_4+CaAl_2O_4$
15. $7Ca_3Al_2O_6+9MoO_3=9CaMoO_4+Ca_{12}Al_{14}O_{33}$

The results of calculation are given in Table 4.

Analysis of the obtained data shows that the $CaMoO_4$ and Al_2O_3 phases coexist in the system (reaction (1)), which determines the presence of this conode in the system under consideration. Analysis

G.N. Shabanova, A.N. Korohodska, S.V. Levadna, O.A. Gamova

Table 4

Results of the calculation of the Gibbs energy change for the corresponding model reactions in the CaO−Al$_2$O$_3$−MoO$_3$ system

No.	Gibbs free energy, kJ/mol					
	800 K	1000 K	1200 K	1400 K	1600 K	1700 K
1	−195.58	−186.13	−172.47	−155.01	−134.04	−122.30
2	−120.02	−115.09	−110.56	−106.44	−102.73	−101.02
3	−164.47	−159.14	−159.22	−164.32	−174.14	−180.76
4	−132,05	−128.87	−125.29	−121.24	−116.66	−114.15
5	−596,72	−587.08	−579.29	−572.44	−565.90	−562.59
6	−144.08	−142.65	−140.02	−136.04	−130.59	−127.28
7	−1784.41	−1772.78	−1761.75	−1750.52	−1738.53	–
8	−9337.43	−9333.78	−9363.20	−9418.02	−9492.91	–
9	−2728.72	−2739.94	−2749.56	−2755.94	−2757.97	–
10	−860.07	−879.71	−884.70	−901.82	−921.94	–
11	−489.20	−485.86	−482.94	−480.49	−478.52	−477.73
12	−2739.60	−2729.03	−2725.19	−2727.92	−2737.10	−2744.08
13	−858.38	−856.63	−855.32	−854.53	−854.32	−854.44
14	−357.15	−356.99	−357.65	−359.25	−361.87	−363.58
15	−1639.96	−1628.24	−1618.86	−1612.90	−1611.13	–

of the reactions (2) and (3) reveals the closure of the CaMoO$_4$ conodes, CaAl$_{12}$O$_{19}$. In connection with the established stability, the CaMoO$_4$−CaAl$_{12}$O$_{19}$ conodes in the analyzed system determine the existence of the following conodes: CaAl$_4$O$_7$−CaMoO$_4$, CaAl$_2$O$_4$−CaMoO$_4$, Ca$_{12}$Al$_{14}$O$_{33}$−CaMoO$_4$ and Ca$_3$Al$_2$O$_6$−CaMoO$_4$ (from the geometric-topological principles of triangulation). The subsolidus structure of the CaO−Al$_2$O$_3$−MoO$_3$ system is depicted in Fig. 3.
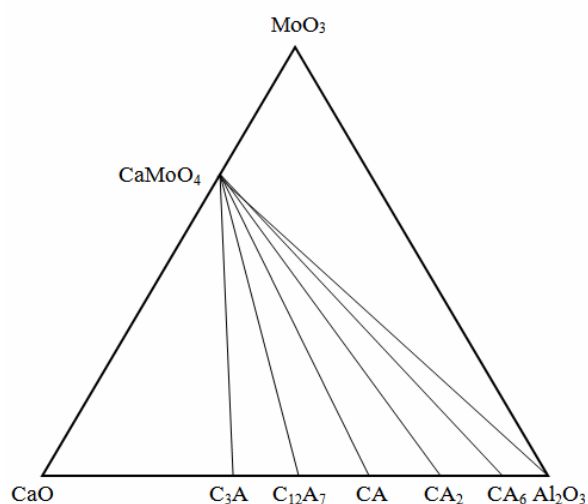
Thus, it was stated that the three-component system CaO−Al$_2$O$_3$−MoO$_3$ is divided by six stable compounds into seven elementary triangles, which corresponds to the Kurnakov rule.

The geometrical-topological characteristics of the CaO−CoO−MoO$_3$, CoO−Al$_2$O$_3$−MoO$_3$ and CaO−Al$_2$O$_3$−MoO$_3$ systems (i.e. the length of tie lines, the area of elementary triangles and the probability of existence of phases) were determined by the procedure given in ref. [9] (Tables 5−7).

In the CaO−CoO−MoO$_3$ and CoO−Al$_2$O$_3$−

Fig. 3. Subsolidus structure of the CaO−Al$_2$O$_3$−MoO$_3$ system

Table 5

Lengths of tie lines in the systems CaO−CoO−MoO$_3$, CoO−Al$_2$O$_3$−MoO$_3$ and CaO−Al$_2$O$_3$−MoO$_3$

No.	Length of tie lines	L, relative units
	CaO–CoO–MoO$_3$	
1	CoMoO$_4$–CaO	0.88032
2	CoMoO$_4$–CaMoO$_4$	0.315601
	CoO–Al$_2$O$_3$–MoO$_3$	
1	Al$_2$O$_3$–CoMoO$_4$	0.88032
2	CoMoO$_4$–CoAl$_2$O$_4$	0.6212
	CaO–Al$_2$O$_3$–MoO$_3$	
1	Ca$_3$Al$_2$O$_6$–CaMoO$_4$	0.6238
2	Ca$_{12}$Al$_{14}$O$_{33}$–CaMoO$_4$	0.6424
3	CaAl$_2$O$_4$–CaMoO$_4$	0.6857
4	CaAl$_4$O$_7$–CaMoO$_4$	0.7542
5	CaAl$_{12}$O$_{19}$–CaMoO$_4$	0.8354
6	Al$_2$O$_3$–CaMoO$_4$	0.8935

Table 6

Characteristics of elementary triangles in the systems CaO−CoO−MoO₃, CoO−Al₂O₃−MoO₃ and CaO−Al₂O₃−MoO₃

No.	Elementary triangle	Area, rel. units	Degree of asymmetry
		CaO–CoO–MoO₃	
1	$CaO–CoMoO_4–CoO$	0.6580	1.52
2	$CaO–CoMoO_4–CaMoO_4$	0.2462	2.79
3	$CoMoO_4–CaMoO_4–MoO_3$	0.0958	1.08
Total		1.0000	–
Max		0.6580	2.79
Min		0.0958	1.08
		CoO–Al₂O₃–MoO₃	
1	$CoO–CoAl_2O_4–CoMoO_4$	0.3793	1.14
2	$CoAl_2O_4–CoMoO_4–Al_2O_3$	0.2787	2.08
3	$Al_2O_3–CoMoO_4–MoO_3$	0.3420	2.92
Total		1.0000	–
Max		0.3793	2.92
Min		0.2787	1.14
		CaO–Al₂O₃–MoO₃	
1	$CaO–Ca_3Al_2O_6–CaMoO_4$	0.2717	1.91
2	$Ca_3Al_2O_6–Ca_{12}Al_{14}O_{33}–CaMoO_4$	0.0989	4.68
3	$Ca_{12}Al_{14}O_{33}–CaAl_2O_4–CaMoO_4$	0.0940	5.25
4	$CaAl_2O_4–CaAl_4O_7–CaMoO_4$	0.1001	5.42
5	$CaAl_4O_7–CaAl_{12}O_{19}–CaMoO_4$	0.0948	6.34
6	$CaAl_{12}O_{19}–Al_2O_3–CaMoO_4$	0.0605	10.64
7	$CaMoO_4–Al_2O_3–MoO_3$	0.2800	3.57
Total		1.0000	–
Max		0.2800	10.64
Min		0.2787	1.91

MoO_3 systems, the presence of only two tie lines automatically determines the longest and shortest tie lines. For the $CaO−Al_2O_3−MoO_3$ system, the $Al_2O_3−CaMoO_4$ (0.8935 rel. units) has the greatest length, while $Ca_3Al_2O_6−CaMoO_4$ (0.623 rel. units) has the shortest length.

It can be seen from the obtained results that the elemental area of existence has the largest $CaO−CoMoO_4−CoO$ triangle (0.658 rel. units) in the $CaO−CoO−MoO_3$ system, whereas the $CoMoO_4−CaMoO_4−MoO_3$ triangle is the smallest one (0.0958 rel. units). When analyzing the degree of asymmetry of triangles, it was established that the elementary triangle $CoMoO_4−CaMoO_4−MoO_3$ is distinguished by the least degree of asymmetry in the system. $CoMoO_4$ (0.3333 rel. units), CaO (0.3015 rel. units) and CoO (0.2193 rel. units), which are the parts of the triangle with the largest area, have the highest probability of existence in this system.

In the $CoO−Al_2O_3−MoO_3$ three-component system, the $CoO−CoAl_2O_4−CoMoO_4$ triangle (0.3793 rel. units) has a maximum area, while the $CoAl_2O_4−CoMoO_4−Al_2O_3$ triangle (0.2787 rel. units)

has a minimum area. The $CoMoO_4$ phase (0.3333 rel. units) has the highest probability of existence, and the MoO_3 phase has the lowest one (0.114 rel. units).

In the $CaO−Al_2O_3−MoO_3$ system, the largest area is occupied by the triangle $CaMoO_4−Al_2O_3−MoO_3$ (0.28 rel. units), whereas the smallest area is occupied by the triangle $CaAl_{12}O_{19}−Al_2O_3 − CaMoO_4$ (0.0605 rel. units). The greatest degree of asymmetry shows the triangle $CaAl_{12}O_{19}−Al_2O_3−CaMoO_4$ (10.64), the smallest degree of asymmetry is revealed for the triangle $CaO−Ca_3Al_2O_6−CaMoO_4$ (1.91). The highest probability of existence is determined for $CaMoO_4$ (0.3333 rel. units), while the smallest one is observed for $CaAl_{12}O_{19}$ (0.0518 rel. units).

Conclusions

According to the results of the thermodynamic and geometrical-topological analysis of the three-component systems, it was established that the molybdenum compounds, $CaMoO_4$ and $CoMoO_4$, have the highest probabilities of the formation, and therefore they are characterized by the highest thermodynamic stability. The coexistence of these

G.N. Shabanova, A.N. Korohodska, S.V. Levadna, O.A. Gamova

Table 7

Geometric-topological characteristics of the phases in the systems CaO−CoO−MoO₃, CoO−Al₂O₃−MoO₃ and CaO−Al₂O₃−MoO₃

Compound	Number of phases with which it coexists	Number of triangles in which it is present	Area of existence, rel. units	Probability of existence, rel. units
CaO–CoO–MoO₃				
MoO_3	2	1	0.0958	0.0319
CaO	3	2	0.9042	0.3015
CoO	2	1	0.6580	0.2193
$CaMoO_4$	3	2	0.3420	0.1140
$CoMoO_4$	4	3	1.0000	0.3333
Total			3.0000	1.0000
Max			1.0000	0.3333
Min			0.0958	0.0319
CoO–Al₂O₃–MoO₃				
MoO_3	2	1	0.3420	0.114
Al_2O_3	3	2	0.6207	0.2069
CoO	2	1	0.3793	0.1264
$CoAl_2O_4$	3	2	0.6580	0.2194
$CoMoO_4$	4	3	1.0000	0.3333
Total			3.0000	1.0000
Max			1.0000	0.3333
Min			0.3420	0.1140
CaO–Al₂O₃–MoO₃				
MoO_3	2	1	0.28	0.0906
Al_2O_3	3	2	0.3405	0.1135
CaO	2	1	0.2717	0.1264
$Ca_3Al_2O_6$	3	2	0.3706	0.1235
$Ca_{12}Al_{14}O_{33}$	3	2	0.1928	0.0643
$CaAl_2O_4$	3	2	0.1941	0.0647
$CaAl_4O_7$	3	2	0.1950	0.0650
$CaAl_{12}O_{19}$	3	2	0.1553	0.0518
$CaMoO_4$	8	7	1.0000	0.3333
Total			3.0000	1.0000
Max			1.0000	0.3333
Min			0.1553	0.0518

compounds with refractory cobalt spinel ($CoAl_2O_4$) and calcium aluminates ($Ca_3Al_2O_6$, $Ca_{12}Al_{14}O_{33}$ and $CaAl_2O_4$) allows fabricating refractory cements based on spent cobalt-molybdenum catalysts and creating resource-saving technologies for their production.

The determination of the subsolidus structure of the considered three-component systems is important for the further prediction of the phase composition of aluminate cements obtained using waste cobalt catalysts that additionally contain molybdenum oxide.

REFERENCES

1. *Khimichna* tekhnologiya tugoplavkykh nemetalevykh i sylikatnykh materialiv u prykladakh i zadachakh / Fedorenko O.Yu., Pitak Ya.M., Ryshchenko M.I., et al. − Kharkiv: Pidruchnyk NTU «KhPI», 2013. − Ch. 2. Fizyko-khimichni systemy, fazovi rivnovagy, termodynamika, resurso- ta energozberezhennya v tekhnologiyi TNSM. − 326 p.

2. *JANAF* thermochemical tables. Third Edition / Chase Jr.M.W., Davies C.A., Downey J.R., Frurip D.J., McDonald R.A., Syverud A.N. − Washington: American Chemical Society, 1986. − 1856 p.

3. *Logvinkov S.M.* Tverdofaznye reaktsii obmena v tekhnologii keramiki. − Hharkov: Izd. HNEU, 2013. − 248 p.

4. *Binnewies M., Milke E.* Thermochemical data of elements and compounds, 2rd Edition. − Weinheim: Wiley-VCH Verlag GmbH, 2002. − 928 p.

5. *Termodinamicheskie* konstanty nekotorykh soedinenii sistemy CaO−Al₂O₃−CoO / A.N. Korohodskaya, G.N.

Shabanova, S.V. Levadnaya, T.V. Shkolnikova // Visnyk Nats. tekhn. un-ta «KhPI». − 2017. − No. 48(1269). − P.98-101.

6. *Ropp R.C.* Encyclopedia of the alkaline earth compounds. − Amsterdam: Elsevier, 2013. − 1187 p.

7. *Nanostructured* materials for advanced technological applications / J.P. Reithmaier, P. Petkov, W. Kulisch, C. Popov. − Dordrecht (Netherland): Springer, 2009. − 546 p.

8. *Crystal* structure of cobalt molybdate hydrate CoMoO₄·nH₂O / Eda K., Uno Y., Nagai N., Sotani N., Whittingham M.S // J. Solid State Chem. − 2005. − Vol.178. − P.2791-2797.

9. *Fizikokhimicheskie* sistemy tugoplavkikh nemetallicheskikh i silikatnykh materialov / A.S. Berezhnoj, Ya.N. Pitak, A.D. Ponomarenko, N.P. Sobol'. − Kyiv: UMK VO Publ., 1992. − 172 p.

ТРІАНГУЛЯЦІЯ І ХАРАКТЕРИСТИКА СУБСОЛІДУСНОЇ БУДОВИ СИСТЕМ CaO−CoO−MoO₃, CoO−Al₂O₃−MoO₃ ТА CaO−Al₂O₃−MoO₃

Г.М. Шабанова, А.М. Корогодська, С.В. Левадна, О.О. Гамова

У статті наведені характеристики трикомпонентних систем CaO−CoO−MoO₃, CoO−Al₂O₃−MoO₃ та CaO−Al₂O₃−MoO₃. Надані результати дослідження субсолідусної будови цих систем. Розроблені графічні зображення систем в області субсолідуса. Наведено результати розрахунку зміни вільної енергії Гіббса при різних температурах для модельних реакцій. В результаті виконаних термодинамічних і геометро-топологічних розрахунків на основі сформованої термодинамічної бази даних встановлена спрямованість протікання твердофазних реакцій в трикомпонентних системах CaO−CoO−MoO₃, CoO−Al₂O₃−MoO₃, CaO−Al₂O₃−MoO₃ за участю стабільно існуючих сполук, що дозволило визначити всі коноди даних систем. Розраховані основні геометро-топологічні характеристики елементарних трикутників і фаз систем. Геометро-топологічні характеристики системи важливі для прогнозування ступеня точності дозування компонентів, а також необхідного часу їх змішування перед синтезом матеріалів із заданим фазовим складом. Субсолідусна будова розглянутих трикомпонентних систем має значення для подальшого прогнозування фазового складу алюмінатних цементів, які одержують з використанням відходів кобальтових каталізаторів, що містять додатково оксид молібдену.

Ключові слова: енергія Гіббса, термодинамічна стабільність, комбінація фаз, тріангуляція, субсолідусна будова, геометро-топологічні характеристики.

TRIANGULATION AND CHARACTERIZATION OF THE SUBSOLIDUS STRUCTURE IN THE SYSTEMS CaO−CoO−MoO₃, CoO−Al₂O₃−MoO₃ AND CaO−Al₂O₃−MoO₃

G.N. Shabanova *, A.N. Korohodska, S.V. Levadna, O.A. Gamova

National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine

* e-mail: gala-shabanova@ukr.net

Three-component systems CaO−CoO−MoO₃, CoO−Al₂O₃−MoO₃ and CaO−Al₂O₃−MoO₃ are characterized in this work. The results of the research of the subsolidus structure of the systems under study are given. Diagrams of the systems in the field of the subsolidus are presented. The calculations of the changes of Gibbs free energy are performed at different temperatures for the model reactions. The thermodynamic and geometric topological calculations based on the developed thermodynamic database allow establishing the direction of solid-phase reactions in the three-component systems CaO−CoO−MoO₃, CoO−Al₂O₃−MoO₃ and CaO−Al₂O₃−MoO₃ with the participation of steadily existing compounds; as a result, all conodes in these systems have been determined. The main geometric topological calculations of elementary triangles and phases of systems are performed. Geometric topological system performance is important for the prediction of the accuracy of a dosage of components and the duration of their mixing before synthesis to obtain materials with the specified phase composition. The data on subsolidus structure of the considered three-component systems are essential for further forecasting phase structure of the aluminate cements fabricated with the use of the waste of cobalt catalysts that additionally contain molybdenum oxide.

Keywords: Gibbs energy; thermodynamic stability; combination of phases; triangulation; subsolidus structure; geometric topological calculations.

REFERENCES

1. Fedorenko O.Yu., Pitak Ya.M., Ryshchenko M.I. Shhukina L.P., Bragina L.L., Lisachuk G.V., Taranenkova V.V., Shabanova G.M., Korogods'ka A.M., Savvova O.V., Sobol' Yu.O., Voronov G.K., Shalygina O.V., *Khimichna tekhnologiya tugoplavkykh nemetalevykh i sylikatnykh materialiv u prykladakh i zadachakh* [Chemical technology of refractory nonmetallic and silicate materials in examples and tasks]. NTU «KhPI» Publishers, Kharkiv, 2013. 326 p. (*in Ukrainian*).

2. Chase Jr.M.W., Davies C.A., Downey J.R., Frurip D.J., McDonald R.A., Syverud A.N., *JANAF Thermochemical tables. Third Edition*. American Chemical Society, Washington, 1986. 1856 p.

3. Logvinkov S.M., *Tverdofaznye reaktsii obmena v tekhnologii keramiki* [Solid-phase exchange reactions in ceramic technology]. HNEU Publishers, Kharkiv, 2013. 248 p. (*in Russian*).

4. Binnewies M., Milke E., *Thermochemical data of elements and compounds, 2nd Edition*. Wiley-VCH Verlag GmbH, Weinheim, 2002. 928 p.

5. Korohodska A.N., Shabanova G.N., Levadnaya S.V., Shkolnikova T.V. Termodinamicheskie konstanty nekotorykh soedinenii sistemy CaO−Al₂O₃−CoO [Thermodynamic constants of some compounds of the CaO−Al₂O₃−CoO system]. *Visnyk Natsional'nogo Tekhnichnogo Universyteta NTU «KhPI»*, 2017, no. 48 (1269), pp. 98-101. (*in Russian*).

6. Ropp R.C., *Encyclopedia of the alkaline earth compounds*. Elsevier, Amsterdam, 2013. 1187 p.

7. Reithmaier J.P., Petkov P., Kulisch W., Popov C. *Nanostructured materials for advanced technological applications*. Springer, Dordrecht, 2009. 546 p.

8. Eda K., Uno Y., Nagai N., Sotani N., Whittingham M.S. Crystal structure of cobalt molybdate hydrate CoMoO₄·nH₂O. *Journal of Solid State Chemistry*, 2005, vol. 178, pp. 2791-2797.

9. Berezhnoj A.S., Pitak Ya.N., Ponomarenko A.D., Sobol' N.P., *Fizikokhimicheskie sistemy tugoplavkikh nemetallicheskikh i silikatnykh materialov* [Physicochemical systems of refractory, nonmetallic and silicate materials]. UMK VO Publishers, Kyiv, 1992. 172 p. (*in Russian*).