STUDYING OF THE STRUCTURE OF Al_2O_3–SiO_2–CaO–P_2O_5 SYSTEM AND ITS SIGNIFICANCE IN THE TECHNOLOGY OF REFRACTORIES

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Abstract

The paper shows that presence of such phases as mullite, corundum is required in order to obtain high quality refractories that are able to work effectively under the conditions of the simultaneous effects of corrosive environments, high temperatures and pressure, sudden changes in temperature. The structures of Al_2O_3–SiO_2–CaO–P_2O_5 system are examined in the materials in which the formation of defined phases is probably. Based on data it is carried out partitioning of the system on the elementary tetrahedrons. The data on the lengths of tie lines, volumes, the asymmetry degree and the eutectic temperature of elementary tetrahedrons are given. The geometric-topological characteristic of the phases of this system are presented. The choice of oxides compositions areas for the production of refractories is justified based on the obtained results.

Keywords: geometric-topological characteristics, mullite, corundum, phase, refractories, elementary tetrahedrons, system.

DOI: 10.21303/2461-4262.2017.00367

1. Introduction

Systems comprising refractory oxides, and compounds as well as phosphates of the composition are of great interest for the study of the kinetics and mechanism for determining the hardening of phosphate tangles composed refractory like at normal temperature or under heating. It is important because the processes of hardening and the products of formation occur in different ways [1–4]. One of such system is the Al_2O_3–SiO_2–CaO–P_2O_5 system. This system has practical value in the technology of refractory non-metallic materials. Especially it is necessary in considering the life of refractories in thermal units of construction industry [5–7]. The first version of the partition of this system into elementary tetrahedral is given [5].

The aim of research is determination of the geometric-topological characteristics of the phases of the system, taking into account new data on the coexistence of phases and structure of the system.

According to the classification [1], Al_2O_3–SiO_2–CaO–P_2O_5 system is the system of high complexity (43 elementary tetrahedrons, 32 compounds). Absence of the thermodynamic data about this system will not allow to clarify the processes of phase formation that occur in the material at high temperatures, as well as to solve important problems associated with the scientifically grounded choice of compositions and development of rational technological methods. The study of this system will be continued due to its great value for the construction and metallurgical areas. Also it is necessary to be studied by the authors in a form such as described in [8–10].

2. Materials and Methods

The geometric-topological characteristics of phase of the system consist of: number of the tetrahedrons where this phase is in, number of phases with which coexist, the volume of existence (ΣV_i, the total volume of all elementary tetrahedrons where this phase is in), probability of existence (ω).

The calculating formula of probability existence of phases in this concentration tetrahedron is presented (1):

$$\omega_i = \frac{\sum V_i}{n \times V_0}, \quad (1)$$

where $\sum V_i$ – total volume of elementary tetrahedrons in which there is this phase, V_0 – the volume of concentration tetrahedron, n – the number of components in the system, in this case n = 4.

The relative volume of the elementary tetrahedron is calculated using the determinant by the formula (2):

$$V_i = \begin{vmatrix} X_1 & Y_1 & Z_1 & 1 \\ X_2 & Y_2 & Z_2 & 1 \\ X_3 & Y_3 & Z_3 & 1 \\ X_4 & Y_4 & Z_4 & 1 \end{vmatrix}, \quad (2)$$

where X_i, Y_i, Z_i – content of oxides Al_2O_3, SiO_2, CaO, P_2O_5 in the compounds constituting the elementary tetrahedron.

The degrees of asymmetry of elementary tetrahedrons are estimated as the ratio of the maximum (L_{max}) to a minimum edge length (L_{min}) by the formula (3):

$$K = \frac{L_{max}}{L_{min}}. \quad (3)$$

The conode length of elementary tetrahedrons is calculated using the barycentric coordinates and elements of Euclidean geometry by the formula (4):

$$\begin{aligned} L^2 = {} & (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 + \\ & + (T_2 - T_1)^2 + (x_2 - x_1)(y_2 - y_1) + (x_2 - x_1)(z_2 - z_1) + \\ & + (x_2 - x_1)(T_2 - T_1) + (y_2 - y_1)(z_2 - z_1) + \\ & + (y_2 - y_1)(T_2 - T_1) + (z_2 - z_1)(T_2 - T_1), \end{aligned} \quad (4)$$

where x_1, y_1, z_1, x_2, y_2, z_2 – the coordinates (component concentration) of coexisting vapor phase.

To illustrate the relationship of elementary tetrahedrons of system it is necessary to use the method of topological graphs, as described in [11]. The number of edges (R) is calculated according to Euler's formula (5):

$$R = \frac{Z_1 + 2Z_2 + 3Z_3 + 4Z_4}{2}. \quad (5)$$

Taking into account that the eutectic temperature of the liquid curves for all components of the system are equal, the calculation of the temperature and eutectic composition for the four-systems are produced by the decision of the system of equations (6) given in [11]:

$$\begin{cases} T_i = \dfrac{T_{пл.i}}{1 - \dfrac{\ln(X_i)}{N_i}} = T_2 = T_{пл.2} \Big/ \left(1 - \dfrac{\ln(X_2)}{N_2}\right), \\ T_2 = \dfrac{T_{пл.2}}{1 - \dfrac{\ln(X_2)}{N_2}} = T_3 = T_{пл.3} \Big/ \left(1 - \dfrac{\ln(X_3)}{N_3}\right), \\ T_3 = \dfrac{T_{пл.3}}{1 - \dfrac{\ln(X_3)}{N_3}} = T_4 = T_{пл.4} \Big/ \left(1 - \dfrac{\ln(X_4)}{N_4}\right), \\ X_1 + X_2 + X_3 + X_4 = 1. \end{cases} \quad (6)$$

Calculation of geometric-topological characteristics of the phases of the system is carried out using programs developed at the department of technology of ceramics, refractories, glass and enamels of NTU "KPI".

3. Research results of the Al_2O_3–SiO_2–CaO–P_2O_5 system

To analyze the probability of formation reactions of the crystalline phases, the calculation of the free Gibbs energy are made from the equations given by [12, 13].

It is established the possibility of the occurrence of conjugate reactions by considering the structure of the Al_2O_3–SiO_2–CaO–P_2O_5 system:

1) $AP+3C_3P+2S \rightarrow 3C_2P+C_3APS_2$;
2) $AP+A_3S_2+C_3P \rightarrow C_3APS_2+A_3P$;
3) $S+C_3P+CAS_2 \rightarrow C_3APS_2+CS$;
4) $2C_3P+3CS+C_2AS \rightarrow CAS_2+2C_5SP$;
5) $C_3P+CA+C_2AS \rightarrow CA_2+C_5SP$;
6) $A_3S_2+C_3P \rightarrow C_3APS_2+2A$.

The temperature dependence of the free Gibbs energy for which is determined (**Fig. 1**).

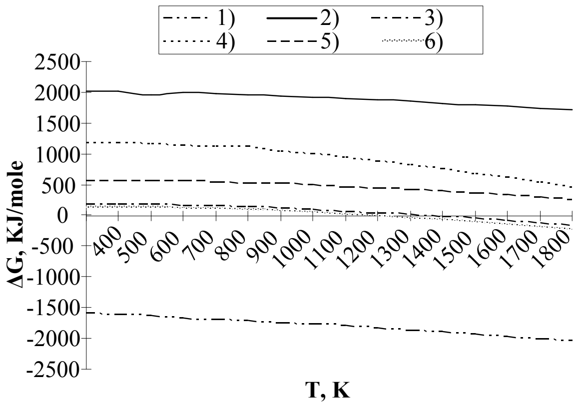

Fig. 1. The dependence ΔGт = f (T) for the reactions in the system: 1 – reaction 1; 2 – reaction 2; 3 – reaction 3; 4 – reaction 4; 5 – reaction 5; 6 – reaction 6

Thermodynamic analysis of the reactions in Al_2O_3 – SiO_2 – CaO – P_2O_5 system (accepted conventions of Al_2O_3–A, SiO_2–S, CaO–C, P_2O_5–P) has allowed to establish the following co-existing phases of the pair (conodes taking place in three-dimensional space): C_3P–CAS_2; C_3APS_2–C_3P; C_3APS_2–C_2P; S–C_3APS_2; A_3S_2–C_3APS_2; A_3P–C_3APS_2; A_3S_2–C_3P; C_3APS_2–CS; C_3APS_2–CAS_2; AP–C_3APS_2; C_3P–C_2AS; CAS_2–C_5SP; C_5SP–CA; C_5SP–C_2AS; C_7S_2P–CA; C_7S_2P–C_2AS; C_7S_2P–$C_{12}A_7$; C_7S_2P – C_3A; C_5SP – $C_{12}A_7$; C_3A – C_5SP.

32 phases, 4 oxides constituting the system, 23 according to the number of binary oxides of simple compounds, 4 ternary compounds, 1 four-component are taken in determining the structure of the system. The system is partitioned on 45 elementary tetrahedrons in the subsolidus. The characteristics (data volume V_i, the temperature T_i of occurrence and degree of asymmetry of the melt) are shown in **Table 1.**

It is evident (from **Table 1** data) that the minimum temperature of the melt in the appearance of Al_2O_3–SiO_2–CaO–P_2O_5 system is equal to 854 K, and corresponding composition is located in elementary tetrahedron No. 7 (AP–CP–S_5P_3–S). The maximum temperature is equal to 1781 K (C_7S_2P–C_2S–C_3A–C_3S) at which the solid phase still persists in the system.

The tetrahedrons AP–A_3S_2–S–C_3APS_2 (V_i=133,95 ‰, T_i=1552 K), A–A_3S_2–C_3P–A_3P (V_i= =49,22 ‰, T_i=1742 K), C_3APS_2–A_3S_2–S–CAS_2(V_i=39,27 ‰, T_i=1573 K) are the most technologically considering the volume of the elementary tetrahedron, the degree of asymmetry and minimal occurrence of melt temperature of the composition. The compositions of elementary tetrahedrons including mullite, corundum are the most appropriate for the technology of refractory materials (**Table 1**, tetrahedron number 15).

Table 1

Elementary tetrahedrons of Al_2O_3–SiO_2–CaO–P_2O_5 system

#	Elementary tetrahedrons	The degree of asymmetry	T_i, K	V_i, ‰
1	2	3	4	5
1	AP_3–CP_2–SP–P	1,8	858	9,64
2	AP_3–C_2P_3–SP–CP_2	5,99	1020	2,54
3	AP_3–CP–SP–C_2P_3	3,87	1017	4,36
4	AP_3–CP–SP–A_2P_3	2,38	no data	11,16
5	AP–CP–SP–A_2P_3	4,01	no data	8,02
6	AP–CP–SP–S_5P_3	1,90	855	39,37
7	AP–CP–S_5P_3–S	2,42	854	45,01
8	AP–CP–C_7P_5–S	12,23	1208	30,95
9	AP–C_7P_5–C_2P–S	10,33	1251	36,13
10	AP–C_3P–C_2P–C_3APS_2	4,87	1512	9,64
11	AP–C_3APS_2–C_2P–S	2,83	1469	74,99
12	AP–A_3S_2–A_3P–C_3APS_2	2,78	1589	23,95
13	AP–A_3S_2–S–C_3APS_2	1,85	1552	133,95
14	AP–A_3S_2–C_3P–A_3P	2,78	1669	41,09
15	A–A_3S_2–C_3P–A_3P	2,88	1742	49,22
16	C_3APS_2–S–C_3P–CS	2,93	1526	43,13
17	C_3APS_2–A_3S_2–C_3P–CAS_2	2,64	1611	10,15
18	C_3APS_2–A_3S_2–S–CAS_2	2,56	1573	39,27
19	C_3P–A_3S_2–A–CAS_2	3,07	1759	26,49
20	C_3P–CA_6–A–CAS_2	10,32	1761	16,85
21	C_3P–CA_6–C_2AS–CAS_2	3,78	1721	53,28
22	C_3P–CS–C_2AS–CAS_2	2,71	1620	35,92
23	S–CAS_2–C_3APS_2–CS	2,62	1523	43,33
24	C_3P–CA_6–CA_2–C_2AS	6,01	1778	13,39
25	C_3P–CA_2–CA–C_2AS	4,91	1691	14,21
26	C_3P–C_5SP–CA–C_2AS	3,89	1703	7,61
27	C_7S_2P–C_5SP–CA–C_2AS	7,59	1721	3,65
28	C_3P–C_5SP–CS–C_2AS	3,85	1661	10,39
29	C_7S_2P – C_5SP – CS – C_2AS	5,17	1676	4,87
30	C_7S_2P–CA–C_2S–C_2AS	2,85	1717	10,15
31	C_7S_2P–C_3S_2–CS–C_2AS	3,41	1591	8,22
32	C_7S_2P–C_2S–C_3S_2–C_2AS	4,91	1674	5,58
33	C_7S_2P–C_2S–CA–$C_{12}A_7$	4,30	1652	10,05
34	C_7S_2P–C_2S–$C_{12}A_7$–C_3A	3,30	1654	10,55
35	C_7S_2P–C_2S–C_3A–C_3S	4,23	1781	7,10
36	C_7S_2P–C_5SP–CA–$C_{12}A_7$	7,59	1654	3,55
37	C_7S_2P–C_3A–$C_{12}A_7$–C_5SP	6,17	1665	3,75
38	C_7S_2P–C_3A–C_4P–C_3S	2,15	1748	10,05
39	C_7S_2P–C_3A–C_4P–C_5SP	5,44	1747	1,62
40	C_5SP–C_3A–C_4P–C_3P	6,05	1729	3,35
41	C_5SP–C_3A–C_3P–$C_{12}A_7$	4,45	1652	8,02
42	C_5SP–C_3P–$C_{12}A_7$–CA	4,84	1651	7,51
43	C–C_3S–C_3A–C_4P	1,48	1707	39,07
44	C_3P–S–C_2P–C_3APS_2	8,59	1487	19,69
45	C_3P–CAS_2–C_3APS_2–CS	2,03	1568	9,18
	The total volume		1000	

The tie lines rearrangement in the ternary subsystem Al_2O_3–SiO_2–CaO–P_2O_5 is shown in **Fig. 2**.

The geometric-topological characteristics of phases of the system are presented (**Table 2**) [14–17].

Table 2

Geometric-typological characteristics of phases of Al_2O_3–SiO_2–CaO–P_2O_5 system

No.	Phase	Number of the tetrahedrons where this phase is in	Number of phases with which coexist	The volume of existence, $\sum V_i$, ‰	Probability of the existence, ω_i
1	C	1	3	39,05	0,00976
2	A	3	5	92,54	0,0231
3	S	9	10	466,28	0,116
4	P	1	3	9,65	0,00241
5	C_3A	8	8	83,48	0,0208
6	$C_{12}A_7$	6	6	43,42	0,0109
7	CA	6	7	49,20	0,0123
8	CA_2	2	4	27,58	0,00690
9	CA_6	3	5	83,49	0,0208
10	C_3S	3	5	56,20	0,0141
11	C_2S	5	7	43,42	0,0109
12	C_3S_2	2	4	13,79	0,00345
13	CS	7	8	154,98	0,0387
14	C_4P	4	6	54,07	0,0135
15	C_3P	18	17	378,97	0,0948
16	C_2P	4	5	140,40	0,0351
17	C_7P_5	2	4	67,06	0,0168
18	CP	6	8	138,82	0,0347
19	C_2P_3	2	4	6,89	0,00173
20	CP_2	2	4	12,18	0,00305
21	A_3S_2	7	7	323,99	0,0810
22	A_3P	3	5	114,21	0,0286
23	AP	10	11	442,94	0,111
24	A_2P_3	2	4	19,18	0,00480
25	AP_3	4	6	27,69	0,00692
26	S_5P_3	2	4	84,35	0,0211
27	SP	6	8	75,05	0,0188
28	C_2AS	11	10	167,20	0,0418
29	CAS_2	8	8	243,38	0,0608
30	C_7S_2P	12	10	79,12	0,0198
31	C_5SP	10	8	54,30	0,0136
32	C_3APS_2	10	8	407,12	0,102
33	The total volume Maximum Minimum	179 18 1	212 17 3	4000,0 466,28 6,89	1,0000 0,116 0,00173

C_3P, AP, C_5SP, C_2AS, S phases (respectively – No. 15, 23, 31, 28, 3) have the largest number of coexisting phases (**Table 2**). C_3P phase presents in 18 elementary tetrahedron and has a maximum amount of existence – 424,6 ‰. Significant volumes of existence in this system have a phase: S (481,5), AP (414,2), C_3APS_2 (396,0), A_3S (287,5).

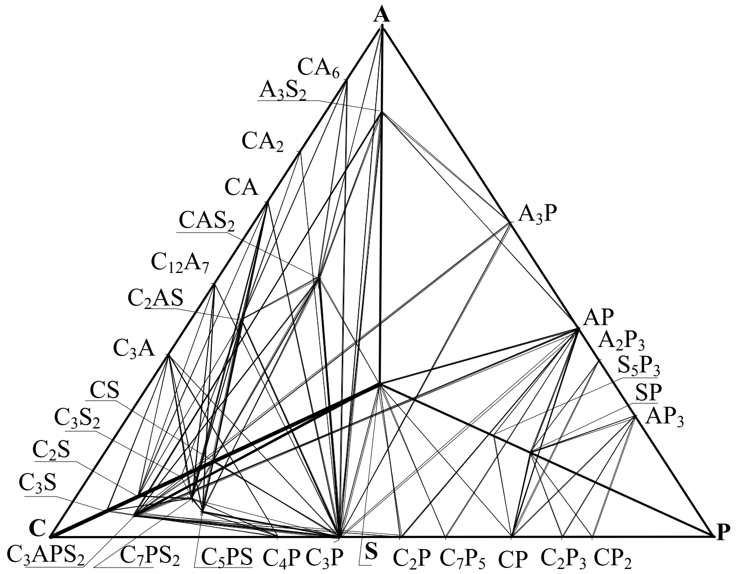

Fig. 2. The state of elementary tetrahedrons of Al_2O_3–SiO_2–CaO–P_2O_5 system in the concentration tetrahedron

4. Discussing of research results

Comparative analysis of the data is revealed the most technological range of compositions for the production of refractory products. They are located in the immediate vicinity to the edges of elementary tetrahedrons AP–A_3S_2–S–C_3APS_2; A–A_3S_2–C_3P–A_3P; C_3APS_2–A_3S_2–S–CAS_2.

To the basis of the structure of the system data it is of interest to modeling changes the phase structure in the compositions of mullite refractory – slag in the future. It will allow coming nearly to explain the reasons for the destruction of refractories in service when the ratio of the components and their interaction temperature are changing [18].

5. Conclusions

The geometric-topological characteristics of the phases of Al_2O_3–SiO_2–CaO–P_2O_5 system are defined; there are identified the elementary volume, the degree of asymmetry and the eutectic temperature of the elementary tetrahedrons.

The results of studies on the structure of the four-component system (Al_2O_3–SiO_2–CaO–P_2O_5) serve as a theoretical basis for further developments in the field of new technology of refractory non-metallic materials.

References

[1] Launch, J., Buhr, A. (1999). Synthetic alumina raw materials – key elements for refrectories innovations. Progressing of the Unified International Conference on Refrectories, Unitecr – 99. Berlin, 348–355.

[2] Ma, W., Brown, P. W. (2004). Mechanisms of Reaction of Hydratable Aluminas. Journal of the American Ceramic Society, 82 (2), 453–456. doi: 10.1111/j.1551-2916.1999.tb20085.x

[3] Keush, D., Lutiy, R., Guria, I. (2015). Strengthening core mixtures with phosphoric acid and metal salts. Foundry Production, 7, 27–29.

[4] Schacht, C. (Ed.) (2004). Refractories Handbook. CRS Press, New York. doi: 10.1201/9780203026328

[5] Berezhnoy, A. (1988). Multi-alkaline oxide systems. Kyiv: Naukova Dumka, 200.

[6] Berezhnoy, A. (1970). Multicomponent oxide system. Kyiv: Naukova Dumka, 544.

[7] Berezhnoy, A., Pitak, Ya., Ponomarenko, A., Sobol, N. (1992). The physico-chemical system of refractory, non-metal and silicate materials. Kyiv: UMK VO, 172.

[8] Krebs, R. (1999). Modern solution of refractory problems with unshaped refractories. Proceeding of the Unified International Conference on Refrectories, Unitecr – 99. Berlin, 1–5.

[9] Bondar, I., Malyshikov, A. (1992). Phosphates elements of the fourth group. Sankr-Peterburg: Science, 112.

[10] Kopeikin, V., Klementeva, V. Krasniy, B. (1986). Refractory solutions on phosphate binders. Moscow: Metallurgy, 102.

[11] Rischenko, M., Fedorenko, O., Pitak, Ya. (2013). Chemical technology of refractory non-metal and silicate materials in the examples and problems. Part II. Physical and chemical systems, phase equilibrium, thermodynamics, resource and energy saving technology TNSM. Kharkiv: NTU «KPI», 326.

[12] Kharybina, Yu. (2016). Thermodynamic analysis of reactions in the system Al_2O_3–SiO_2–CaO–P_2O_5. Technology Audit and Production Reserves, 5 (3 (31)), 7–11. doi: 10.15587/2312-8372.2016.80422

[13] Kharybina, Yu., Pitak, Ya. (2016). Research coexistence of phases in the system Al_2O_3 – SiO_2 – CaO – P_2O_5. Modern trends in production and silicate materials. Lviv: Rastr – 7, 52–54.

[14] Pitak, Ya., Shabanova, G., Nagorny, A. (1995). Geometric-topological characteristics of CaO – Al_2O_3 – SiO_2 – P_2O_5 system using computers. Information technology: science, technology, education, health. Kharkiv, Miskolc: KhSPU, 58.

[15] Pitak, Y. N., Nagornyi, A. O., Shabanova, G. N. (1997). Subsolidus structure of the CaO−Al_2O_3−SiO_2−P_2O_5 system. Refractories and Industrial Ceramics, 38 (9-10), 351–353. doi: 10.1007/bf02767890

[16] Pitak, Ya., Taranenkova, V. (2004). Application of topological graphs for studying the quaternary oxide systems. Geometric Topology: Infinite – Dimensional Topology, Absolute Extensors, Applications. Lviv: Ivan Franko National University, 49–50.

[17] Nagorny, A., Shabanova, G., Pitak, Ya. (1997). Using of Mechanic-chemical Method the Phosphates Containing Binders Obtaining for. 13th International Conference on Building Materials. «13.ibausil». Weimar, 2, 445–450.

[18] Keush, D., Lutiy, R. (2015). Thermodynamics of processes of binding components in mixtures for foundry cores. Special Metals: yesterday, today and tomorrow. Kyiv, 543–548.