HIGH-TEMPERATURE PHASE TRANSFORMATIONS IN THE COMPOSITION "KAOLIN-DOLOMITE-ALUMINA"

Afzal A. Eminov, Baxtiyor T. Sabirov, Azizjon A. Eminov, Zulayho R. Kadyrova

Institute of General and Inorganic Chemistry
Academy of Sciences of Uzbekistan
77a Mirzo-Ulugbek St., Tashkent 100170, Uzbekistan
E-mail: kad.zulayho@mail.ru

Received 05 July 2023
Accepted 12 August 2023
DOI: 10.59957/jctm.v59.i5.2024.8

ABSTRACT

The article presents the results of a study of phase transformations in sintered compositions "kaolin-dolomite-alumina". It has been established that the nature of the location of melting isotherms on the triple diagram indicates the spread of neoformation processes into the region of the internal compositions of the triangle and the formation of crystalline phases of the mineral's spinel, corundum, mullite. It is shown that based on alumina-containing waste and kaolin, as well as partially introduced dolomite, it is possible to develop compositions of low-temperature sintering ceramic masses for technical materials.

Keywords: *phase transformations, triple diagram, kaolin, dolomite, alumina-containing waste, fusibility, crystalline phase, fusibility, mineralogical composition, spinels, corundum, mullite.*

INTRODUCTION

It is known that the study of phase relations in complex multicomponent aluminosilicate systems is of great practical importance for the technology of technical ceramics with functional properties, including mechanical properties [1 - 3]. Aluminosilicate oxides and the phases formed by them determine the properties and material compositions of several inorganic materials, in particular ceramic products for various purposes. In this regard, the study of phase interactions and solid-phase reactions of the formation of compounds formed at various ratios of kaolin, dolomite and alumina-containing waste minerals makes it possible to evaluate high-temperature phase relations and mechanical strengths of ceramic materials to the impact of various mechanical shocks and forces.

It should be noted that the main operational requirement for grinding media for grinding fine-ceramic masses is their high wear resistance under the abrasive action of silicate raw materials with high hardness [4 - 6]. High wear resistance can be achieved by synthesizing a densely sintered material with significantly higher hardness and density than the ground raw materials.

At the same time, it should be noted that the identification of the concentration regions of the existence of aluminosilicate minerals also allows us to generalize the results of studying the properties of the compositions of the ternary reciprocal system "kaolin-dolomite-alumina-containing waste".

In addition, the phase composition of the high-alumina material of grinding media should include the maximum content of crystalline phases of minerals with increased hardness - corundum and mullite. In this case, the main role is played by the phase of corundum, as a mineral with a hardness index of 9.5 according to the well-known Mohs scale [7, 8]. Obtaining from enriched kaolin and alumina waste a densely sintered corundum-mullite material of the required density and hardness, without mineralizing and smooth-forming additives, is possible with reaching synthesis temperatures of 1700°C and above.

In this regard, to study the possibility of reducing the temperature of synthesis and sintering of corundum-mullite material with the highest content of $A1_2O_3$, compositions containing a sintering additive of dolomite from the Muzbulak deposit, which is an almost monomineral rock with a minimum content of impurities, were studied.

EXPERIMENTAL

Materials

Samples of enriched Alyans kaolin and dolomite of the Muzbulak deposit, as well as the spent catalyst of the Shurtan Gas Chemical Complex (SGCC), which is an alumina-containing component, were used as the initial component for experimental studies.

Methods

To determine the material composition of the initial components and samples of experimental masses, silicate rational chemical analysis was used, the determination of the mineralogical composition was carried out by the X-ray phase analysis method [7, 8]. X-ray phase analysis was carried out by the powder method on a "LABX XRD - 6100 SHIMADZU" X-ray diffractometer with CuKα radiation. X-ray photographs were taken with a step of 0.05, the mode of current and voltage of the tube was 30 mA, 40 kV. The X-ray power was 2 kW. Identification of mineral phases and analysis of the results were carried out using reference books and an international database [9 - 12].

To study phase transformations during the synthesis of corundum-mullite materials using the addition of dolomite, the traditional method of annealing and hardening of samples was used, followed by phase identification by X-ray phase analysis. The melting points of the compositions were determined by the cone melting method [13, 14]. To obtain correct results, the synthesis of test samples was carried out using calcined raw materials.

A study was carried out on a section of a ternary system formed by compositions prepared from calcined samples of raw materials, which were used as: enriched kaolin of the Alyans deposit; alumina waste of the Shurtan GCC; dolomite of the Muzbulak deposit.

Samples of the original raw materials were subjected to preliminary calcination in a silicate furnace at 1500°C, with a holding time of 3 hours, for the complete decomposition of their constituent original minerals containing crystallization water and carbonates. As a result, hygroscopic and crystallization water was removed from kaolin, and chamotte cake was obtained as a product, the mineralogical composition of which is represented by mullite, β-quartz and glass phase. The product of calcination of waste alumina was a high-temperature form of aluminium oxide α-corundum and a small amount - less than 3 wt.% - impurities of silicates and aluminates of calcium and iron. When calcining dolomite, a solid solution of calcium and magnesium oxides was sintered.

The products of calcination were subjected to fine grinding in an Uralite ball mill, the resulting finely ground powders were sifted through a No. 02 sieve (mesh size 0.2 mm). To prevent the hydration of the solid solution of calcium and magnesium oxides before the preparation of charge mixtures, the ground powder of the solid solution was placed in a desiccator filled with calcium chloride.

For research, experimental mixtures were prepared from the powders obtained, the compositions of which corresponded to the points of the ternary system composed of calcined components: Alyans enriched kaolin - Muzbulak dolomite - Shurtan alumina-containing waste, in the range of compositions limited by the content of dolomite to 40 wt. %. The test mixtures under study were prepared by careful fine grinding of mixtures of the synthesized initial components. Test cones were then pressed into a metal mold to determine the melting points.

The maximum temperature reached in the tube laboratory furnace was 1640°C ± 10°C. The melting points of the experimental compositions were determined visually by the method of falling cones. The cones that withstood the test temperature of 1640°C were then tested in the flame of an oxy-gas burner, which allows the test temperature to be increased to 2000°C. For this purpose, the experimental cones were installed on a highly refractory corundum substrate and introduced into the combustion zone of an oxygen-gas flame. Temperature control was carried out using an optical pyrometer OPPIR - 017E using the "vanishing thread" method at an average heating rate of the test cone in the temperature range of 1600 - 2000°C within 30 - 35°C per minute. The accuracy of melting point determination using an optical pyrometer is ± 20°C. In total, 32 experimental mixtures were prepared, each weighing 100 g, which were subjected to wet grinding in an agate mortar to obtain a fine powder. Using an aqueous solution of CMC glue, the powders were plasticized, then prototypes were molded from glass tubes in the form of rods with a diameter of 8 mm and a length of up to 100 - 120 mm. The resulting prototype rods were dried in an oven at a temperature of 105 - 110°C, and fired in a silicate furnace at a temperature of 1400°C with a three-hour exposure.

RESULTS AND DISCUSSION

The obtained results of the study on the material composition of samples of raw materials samples showed that the content of basic oxides satisfies the requirements for raw materials for obtaining high-alumina mass. The chemical compositions of the initial samples of raw materials, in terms of the calcined substance, are given in the Table 1.

The charge compositions of samples of experimental compositions "kaolin-dolomite-alumina" and the results of determining their melting points are shown in Table 2.

After firing the sintered rods in a melting unit in a voltaic arc, molten pellets were obtained by slowly introducing the end of the sample rod into the voltaic arc combustion zone. The formed molten droplets broke away from the end of the sample and fell onto a metal plate installed under the flame zone. It should be noted that as a result of the rapid cooling of the melt droplets, upon contact with the cold surface of the plate, hardened samples were obtained, melted to the state of a homogeneous melt. With a sharp cooling of the drops, along with the quenched melt, a certain part of the molten sample had time to crystallize, with the formation of a primary crystalline phase, which is in equilibrium with the melt.

To study the phase compositions of crystalline phases and melting points, the prototypes were subjected to crushing and grinding. Samples were taken from crushed pieces to determine the melting point. Sample powders were used for qualitative X-ray phase analysis.

The resulting hardened samples were subjected to X-ray phase analysis to identify the phases of minerals that initially crystallize from the melt and are in equilibrium with the melt. The establishment of such phases is necessary to identify compositions, the final stage of sintering of which is the crystallization of the corundum phase. The calculated chemical compositions of the test points are shown in Table 3.

The figure shows the fusibility diagram of a ternary system based on the studied raw materials - kaolin, alumina-containing waste and dolomite [15 - 17]. Based on the results of determining the melting points of the samples, liquidus lines are plotted on the polythermal sections of the triple diagram. The area of compositions with the highest possible content of corundum and dolomite phases has been determined for the development of experimental compositions for the production of technical ceramics, in the form of high alumina grinding media.

On the basis of the experimental studies carried out and taking into account the known rules for the crystallization of melts in ternary systems, it has been established that the compositions of points 13, 20, 27, 28, 29, 30 will form increased contents of corundum and mullite phases, with relatively low contents of smoothly forming dolomite, which is necessary for sufficient sinter ability, and these compositions should be used for the synthesis of prototypes of high-alumina grinding media from used raw materials.

Table 1. Chemical compositions of raw materials, in terms of the calcined substance.

Name calcined component	Contents per air-dry substance, wt. %								
	SiO_2	Al_2O_3	$Fe_2O_{3\ tot.}$	TiO_2	MgO	CaO	Na_2O	K_2O	P_2O_5
Enriched Kaolin Alliance	57.30	38.92	0.57	0.36	0.43	0.53	0.27	1.59	0.03
Dolomite Muzbulak	2.34	1.23	0.73	0.06	39.59	55.79	0.07	0.15	0.04
Alumina waste	1.35	96.11	0.90	0.34	0.68	0.35	0.20	0.05	0.02

Table 2. Charge compositions and melting temperatures of the points of the triple diagram “kaolin - dolomite - alumina containing waste (ACW)”, phases of melt crystallization.

№ composition	Components, wt.%			T_{melt}, °C	Primary crystallization phase
	Kaolin	Dolomite	ACW		
1	60	30	10	1650	spinel
2	50	30	20	1660	spinel
3	40	30	30	1670	spinel
4	30	30	40	1680	spinel
5	20	30	50	1680	spinel
6	10	30	60	1720	spinel
7	70	20	10	1560	spinel
8	60	20	20	1620	spinel
9	50	20	30	1660	spinel
10	40	20	40	1680	spinel
11	30	20	50	1710	spinel
12	20	20	60	1730	spinel
13	10	20	70	1770	spinel
14	80	10	10	1670	mullite
15	70	10	20	1720	mullite
16	60	10	30	1760	mullite
17	50	10	40	1780	mullite
18	40	10	50	1790	mullite
19	30	10	60	1780	corundum
20	20	10	70	1820	corundum
21	10	10	80	1860	corundum
22	85	5	10	1720	mullite
23	75	5	20	1750	mullite
24	65	5	30	1770	mullite
25	55	5	40	1790	mullite
26	45	5	50	1810	mullite
27	35	5	60	1820	mullite
28	25	5	70	1800	corundum
29	15	5	80	1880	corundum
30	5	5	90	1920	corundum
31	10	50	40	1720	spinel
32	20	40	40	1690	spinel

Table 3. Estimated chemical compositions of the experimental points of the triple diagram.

№ composition	Content of oxides, wt.%									Amount
	SiO_2	Al_2O_3	$Fe_2O_{3\ total}$	TiO_2	MgO	CaO	Na_2O	K_2O	P_2O_5	
1	35.22	33.33	0.65	0.27	12.20	17.09	0.20	1.00	0.03	100
2	29.62	39.05	0.68	0.27	12.23	17.07	0.20	0.85	0.03	100
3	23.89	35.16	0.63	0.23	12.19	17.02	0.17	0.69	0.03	100
4	18.43	50.49	0.75	0.26	12.28	17.04	0.18	0.54	0.03	100
5	12.84	56.21	0.78	0.26	12.30	17.02	0.18	0.39	0.03	100
6	7.24	61.93	0.82	0.26	12.33	17.00	0.17	0.23	0.03	100
7	40.71	37.10	0.64	0.30	8.29	11.56	0.22	1.15	0.03	100
8	35.12	42.82	0.67	0.30	8.31	11.55	0.22	0.99	0.03	100
9	29.52	48.54	0.70	0.29	8.34	11.53	0.21	0.84	0.03	100
10	23.93	54.26	0.73	0.29	8.36	11.51	0.20	0.69	0.03	100
11	18.33	59.98	0.77	0.29	8.39	11.49	0.20	0.53	0.03	100
12	12.74	65.70	0.80	0.29	8.41	11.47	0.19	0.38	0.03	100
13	7.14	71.42	0.83	0.29	8.44	11.46	0.18	0.22	0.03	100
14	46.21	40.87	0.62	0.33	4.37	6.04	0.24	1.29	0.03	100
15	40.61	46.59	0.65	0.33	4.40	6.02	0.24	1.14	0.03	100
16	35.02	52.31	0.69	0.32	4.42	6.00	0.23	0.98	0.03	100
17	29.42	58.03	0.72	0.32	4.45	5.98	0.22	0.83	0.03	100
18	23.83	63.75	0.75	0.32	4.47	5.97	0.22	0.68	0.03	100
19	18.23	69.47	0.78	0.32	4.50	5.95	0.21	0.52	0.03	100
20	12.64	75.18	0.82	0.32	4.52	5.93	0.20	0.37	0.02	100
21	7.04	80.90	0.85	0.31	4.55	5.91	0.19	0.21	0.02	100
22	48.96	42.75	0.61	0.34	2.41	3.28	0.25	1.36	0.03	100
23	43.36	48.47	0.64	0.34	2.44	3.26	0.25	1.21	0.03	100
24	37.77	54.19	0.68	0.34	2.46	3.24	0.24	1.06	0.03	100
25	32.17	59.91	0.71	0.34	2.49	3.22	0.23	0.90	0.03	100
26	26.58	65.63	0.74	0.34	2.51	3.20	0.23	0.75	0.03	100
27	20.98	71.35	0.78	0.33	2.54	3.19	0.22	0.59	0.02	100
28	15.39	77.07	0.81	0.33	2.56	3.17	0.21	0.44	0.02	100
29	9.79	82.79	0.84	0.33	2.59	3.15	0.20	0.29	0.02	100
30	4.20	88.51	0.88	0.33	2.61	3.13	0.20	0.13	0.02	100
31	7.44	42.95	0.78	0.20	20.11	28.09	0.14	0.25	0.03	100
32	12.94	46.72	0.77	0.23	16.19	22.56	0.16	0.40	0.03	100

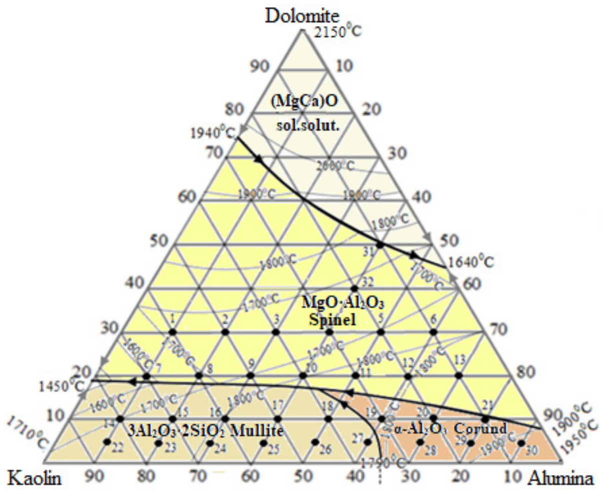

Fig.1. Diagram fusibility of the ternary system “kaolin - dolomite - alumina containing waste (ACW)”.

CONCLUSIONS

Thus, on the basis of the conducted studies, it has been established that the nature of the arrangement of melting isotherms on a triple diagram based on kaolin, alumina-containing waste and dolomite indicates the spread of neoformation processes into the area of the internal compositions of the triangle and the formation of crystalline phases of minerals mullite, corundum, spinel based on Alyans kaolin, alumina-containing waste of the Shurtan GCC and Muzbulak dolomite.

REFERENCES

1. A.M. Salakhov, Modern ceramic materials, Educational settlement Kazan, KFU, 2016, 410.
2. N.T. Andrianov, V.L. Balkevich, A.V. Belyakov, A.S. Vlasov, I.Ya. Guzman, E.S. Lukin, Yu.M. Mosin, B.S. Skidan, Chemical technology of ceramics, Educational settlement under the editorship of I.Ya. Guzman, M., LLC RIF, Building materials, 2012, 496.
3. I.A. Pavlova, K.G. Zemlyanoy, E.P. Farafontova, Fundamentals of technology of non-metallic and silicate materials, Yekaterinburg, Ural University Publishing House, 2020, 192.
4. M.W. Barsoum, Fundamentals of Ceramics, Institute of Physics Publishing Ltd., Bristol and Philadelphia, 2003, ISBN 070509024.
5. R. Anorov, O. Rakhmonov, D. Salikhanova, F. Khomidov, A. Abdurakhimov, Justification of the opportunities of obtaining silicate materials based on clay waste adsorbents, E3S Web of Conferences, 2023, 376, 01076.
6. A.V. Knotko, I.A. Presnyakov, Solid State Chemistry, M., Ed. Center “Academy”, 2006, 304.
7. E.S.Lukin, N.T.Andrianov, Technical analysis and control of ceramic production, M., Stroyizdat, 1986, 86-94.
8. O.K. Botvinkin, G.I. Klikovsky, L.A. Manuilov, Laboratory workshop on the general technology of silicates and technical analysis of building materials, M., Stroyizdat, 1966, 76-93.
9. L.M. Kovba, V.K. Trunov, X-ray phase analysis, M., Moscow University Publishing House, 1969, 160.
10. S.S. Tolkachev, Tables of interplanar distances, Chemistry, 1968, 100.
11. L.I. Mirkin, Handbook of X-ray diffraction analysis of polycrystals, M., Phys. Mat. Literature, 1961, 640.
12. ASTM Standards Part 17, Refractories, Glass, Ceramic Materials, Carbon and Graphite Products, ASTM, Philadelphia, 2005, 7-9, 51-61.
13. I.A. Pavlova, K.G. Zemlyanoy, E.P. Farafontova, Fundamentals of technology of non-metallic and silicate materials, Yekaterinburg, Ural University Publishing House, 2020, 192.
14. T.V. Vakalova, T.A. Khabas, I.B. Reva, Workshop on the basics of technology of refractory non-metallic and silicate materials, Publishing house Tomsk PU, 2013, 176.
15. B.T. Sabirov, Z.R. Kadyrova, S.S. Tairov, Development of optimal compositions of ceramic tiles using dune sand, Glass and Ceramics, 2019, 75, 363-365.
16. Al.A. Eminov, Z.R. Kadyrova, M.I. Iskandarova, Gas processing waste: Promising raw material for designing the composition of ceramic grinding bodies, Glass and Ceramics. 2021, 78, 35-39.
17. A.M. Eminov, Z.R. Kadyrova, A.A. Eminov, Al.A, Eminov, I.R. Bayzhanov, Study of synthesis kinetics and features of mullite solid-phase formation, Refractories and Industrial Ceramics, 2021, 62, 394-398.