CaO-Al$_2$O$_3$ System and Possibilities of Sol-Gel Synthesis

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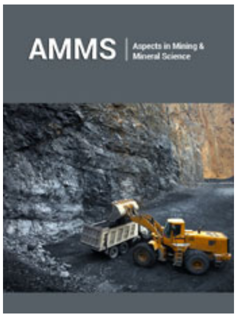

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Abstract

Compounds of calcium monoaluminate were synthesized using the sol-gel method. The effect of soluble aluminum and calcium salts on the synthesis, kinetics, and mechanism of the phase formation reaction during sintering of calcium monoaluminate in the temperature range of 500-1000 °C has been studied. The formation of calcium monoaluminate occurs through an intermediate compound - the mineral maenite.

Keywords: Calcium aluminate; Oxide compounds; Sol-gel method; Dispersed system; Eutectic; Melting point

Introduction

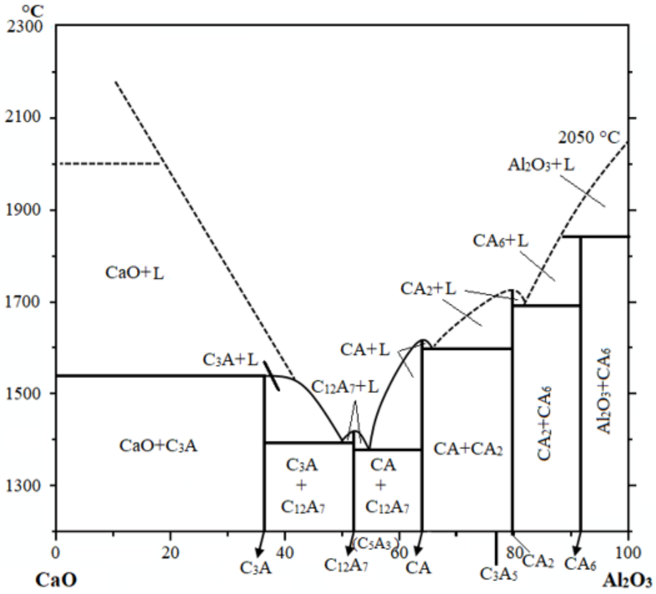

Figure 1: State diagram of the CaO system-Al2O3 built based on the latest data [5].

Calcium aluminates - are among the most widely studied compounds that are part of a number of technical products, such as aluminous cement, portland cement, some special cements, abrasive products, phosphors, etc. Also, they are widely used in ceramics, as a binder in refractory cast products, for the steel industry of detectors, biomaterials and optical devices. They have different crystal structures and are formed during the production of a number of chemical products. They are not found among natural materials, however, as intermediate compounds, they can be formed during the formation of rock eruption [1,2]. Many works [3,4] are devoted to research on the study of the physico-chemical properties of calcium aluminates. The following five individual chemical compounds are mainly formed in the CaO-Al_2O_3 system: $3CaO\cdot Al_2O_3$, $5CaO\cdot 3Al_2O_3$ ($12CaO\cdot 7Al_2O_3$), $CaO\cdot Al2O_3$, $CaO\cdot 2Al_2O_3$, $CaO\cdot 6Al_2O_3$. Calcium aluminate CaO·Al2O3 is one of the most widely studied oxide systems. This is mainly due to the hydraulic properties of some oxide compounds in this system - $CaO\cdot Al_2O_3$ (CA), $CaO\cdot 2Al_2O_3$ (CA_2), $12CaO\cdot 7Al_2O_{33}$ ($C_{12}A_7$) - used during the production of aluminous cement. Two other compounds - $CaO\cdot 6Al_2O_3$ (CA_6) and $3CaO\cdot Al_2O_3$ (C_3A) - are not included in the composition of high alumina cement. For the first time, Rankin and Wright investigated and built a state diagram of the $CaO\cdot Al_2O_3$ compound system (Figure 1) [5]. Subsequently, the composition of some compounds was refined and a new compound $CaO\cdot 6Al_2O_3$ was discovered. Also, some authors believe that the $3CaO\cdot 5Al_2O_3$ compound described in Rankin's works actually corresponds to the formula $CaO\cdot 2Al_2O_3$, which was determined by Tawashi, and this formula is generally accepted.

Based on this state diagram, the invariant points of the compounds of the $CaO\cdot Al_2O_3$ system were determined (Table 1). Chemically prepared powders are considered to be the most common type of starting material in the manufacture of ceramics. During the manufacturing process, materials are powdered to obtain ceramic particles of the desired size. Unfortunately, the processing of such powders remains a problem, although the resulting properties, such as high mechanical, electrical and thermal properties of coarse granular ceramics, differ significantly from their traditional homologues. The main steps in the manufacture of nanoceramics are associated with obtaining non-agglomerated nanopowders with a uniform size distribution and sintering to a theoretical density without grain growth. Chemical methods for obtaining the synthesis of ceramic powders can basically be divided into three classifications, depending on the medium in which the physical and chemical process occurs - liquid, gas, plasma [6-10]. Synthesis in a liquid medium: precipitation methods, heterophase synthesis, sol-gel method, hydrothermal method; Synthesis in a gaseous medium: gas-phase synthesis, interaction of a solid body with a gas and processes of decomposition of salts, hydroxides, organoelement compounds; Synthesis with the participation of plasma: Plasma-chemical, electroerosive, self-propagating high-temperature synthesis. Reducing the temperature of synthesis and sintering in the technology of obtaining ceramic materials remains an urgent task, the solution of which leads to savings in fuel and energy resources. Recently, many scientists have paid special attention to the synthesis of the above materials using the sol-gel method [11]. In industry, more than 70-80% of $MgAl_2O_4$ spinel is produced by the solid-phase reaction method. The synthesis of spinel requires homogeneous, highly reactive and non-agglomerated powders of starting components with a firing temperature of more than 1600 °C, which is necessary to complete spinelization through solid-state reactions.

Table 1: Invariant points of the $CaO\cdot Al_2O_3$ system [5].

Dot	Phases	Process	Composition, Weight. %		Temp. °C
			CaO	Al_2O_3	
1	CaO+Liquid (L)	Melting	100	0	2570
2	$CaO+3CaO\cdot Al_2O_3+L$	Melting	57.0	43.0	1535
3	$3CaO\cdot Al2O3+5CaO\cdot 3Al_2O_3+L$	Eutectic	50.0	50.0	1395
4	$5CaO\cdot 3Al_2O_3+L$	Melting	47.8	52.2	1455
5	$5CaO\cdot 3Al_2O_3+CaO\cdot Al_2O_3+L$	Eutectic	47.0	53.0	1400
6	$CaO\cdot Al_2O_3+L$	Melting	35.4	64.6	1600
7	$CaO\cdot Al2O3+CaO\cdot 2Al_2O_3+L$	Eutectic	33.5	66.5	1590
8	$CaO\cdot 2Al_2O_3+L$	Melting	27.0	73.0	1765
9	$CaO\cdot 2Al2O3+CaO\cdot 6Al_2O_3+L$	Eutectic	19.5	80.5	1730
10	$CaO\cdot 6Al_2O_3+Al_2O_3$ + L	Melting	8.0	92.0	1850
11	Al_2O_3+L	Melting	0	100	2050

The sol-gel method has a number of advantages, such as: to form the necessary phase compositions and structure of the material at lower temperatures (several hundred degrees) than those of traditional technologies, the possibility of obtaining powders with a controlled particle size distribution; the possibility of obtaining high purity and dispersion (100-10nm); as well as high homogeneity of the material [12]. The sol-gel method of obtaining glass and ceramics from metal oxides is carried out by chemical hydrolysis to form a sol, and then a gel, which, when dried and pyrolyzed, produces an amorphous oxide [13]. In this work, $CaAl_2O_4$ was synthesized by the sol-gel method. The sol-gel method makes it possible to form the necessary phase compositions and material structure at lower temperatures.

Experiment

For the study, 4-aqueous calcium nitrate ($Ca(NO_3)$ $4H_2O$ grade 99.9) and 9-aqueous aluminum nitrate ($Al(NO_3)_3\cdot 9H_2O$ grade 99.9) as well as citric acid were used as initial components. The phase composition of the materials used and the synthesized calcium aluminate powder was determined on a LABX XRD-6100

SHIMADZU diffractograph using CuKα radiation and a Ni filter with a wavelength of 1.5418 Å. 4-aqueous calcium nitrate ($Ca(NO_3)$ $4H_2O$) and 9-aqueous aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) were dissolved in distilled water at room temperature. After stirring, citric acid was added to the resulting solution. The precursor solution was stirred on a magnetic stirrer at a temperature of 70 °C until a gel-like mass was obtained. The resulting gel-like mass was dried at a temperature of 130 °C in an oven to obtain a xerogel. To determine the formation of the crystal structure, monocalcium aluminate and the influence of the exposure time during heat treatment on the synthesis process and the complete completion of the phase formation of tricalcium aluminate, the dried gel was fired at a temperature range from 500 to 1000 °C with an exposure of 120 minutes in a SNOL 5/1300 muffle furnace.

Results and Discussion

The results of X-ray phase analysis of fired samples in the temperature range of 500-1000 °C are shown in Figure 2. On the X-ray diffraction patterns of the synthesized samples at a temperature of 500 °C, the beginning of the formation of calcium monoaluminate (d=0.467, 0.297, 0.251, 0.192nm) and the intermediate compound maenite (0.244, 0.152nm) was observed. With an increase in temperature to 800 °C, an intensive increase in the diffraction lines of calcium monoaluminate, as well as the mineral maenite, was observed. However, with an increase in temperature to 1000 °C, an intensive formation of calcium monoaluminate occurs, due to a decrease in the amount of maenite, which precedes the formation of calcium monoaluminate.In this temperature range, no diffraction lines are observed corresponding to calcium and aluminum oxides, which are in an amorphous state as a result of the decomposition of the corresponding nitrate compounds. Hence aluminum nitrate decomposes to γ-Al_2O_3 while $Ca(NO_3)_2$ decomposes in part to form calcium oxide. The resulting CaO reacts intensely with Al_2O_3, forming maenite $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$). It should be noted that the formation of $C_{12}A_7$ via the $CaOAl_2O_3$ reaction is exothermic and has a high negative ΔG (energy). When introducing more energy into the system through increasing temperature, $Ca(NO_3)_2$ decomposes in large quantities and melts them, forming an amorphous form of CaO. In this temperature range, no diffraction lines are observed corresponding to calcium and aluminum oxides, which are in an amorphous state as a result of the decomposition of the corresponding nitrate compounds. Hence aluminum nitrate decomposes to γ-Al_2O_3 while $Ca(NO_3)_2$ decomposes in part to form calcium oxide. The resulting CaO reacts intensely with Al_2O_3, forming maenite $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$).

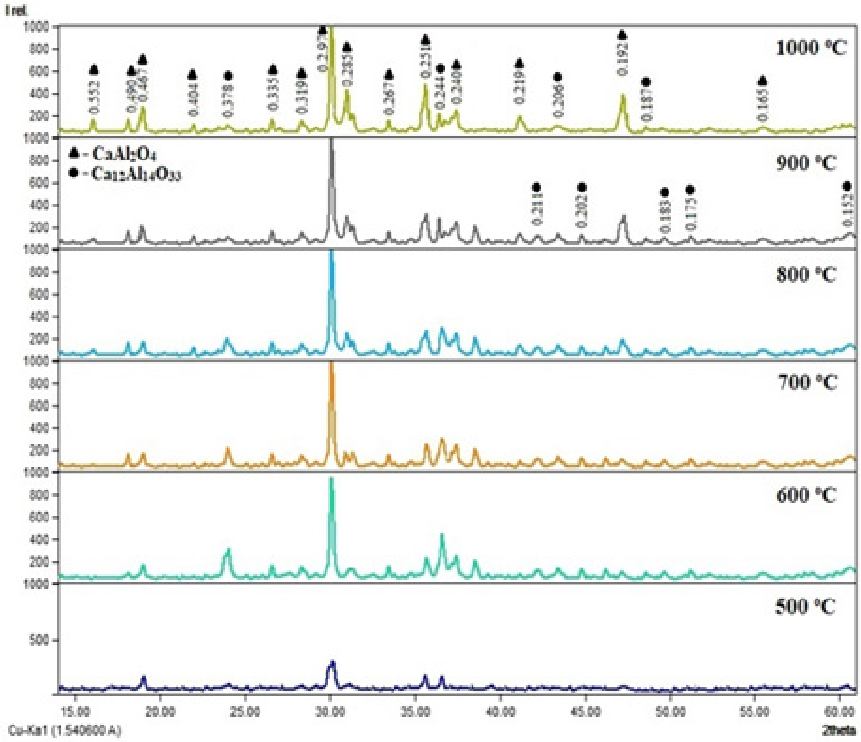

Figure 2: X-ray diffraction patterns of the synthesized samples in the temperature range 500-1000 °C.

When introducing more energy into the system through increasing temperature, $Ca(NO_3)_2$ decomposes in large quantities and melts them, forming an amorphous form of CaO. Transition phases begin to crystallize, as $Ca_{12}Al_{14}O_{33}$ passes to $CaA^{12}O_4$ with an increase in the amount of energy. Figure 3 shows the kinetic parameters of $CaA_{12}O_4$ phase formation at a sintering temperature of 1000 °C using precursors. It is known that in solid-phase synthesis, a temperature above 1500 °C is required for the complete formation of calcium monoaluminate. Consequently, during solid-phase synthesis in the composition γ-Al_2O_3+$CaCO_3$ at a temperature of 1000 °C, crystalline phases of calcium monoaluminate are formed in a smaller amount, compared with the synthesis of samples by the sol-gel method. The obtained results of SEM and EMF analyzes of the synthesized calcium monoaluminate by the sol-gel method are shown in Figure 4. The obtained results of SEM analysis show that the calcium monoaluminate synthesized by the sol-gel method also has a nanoporous structure, in which clearly formed particles of the rhombic structure of calcium monoaluminate are found. The presented EMF spectra confirm that in each sample of calcium monoaluminate, only the chemical elements Ca, Al and O are found on the surface.

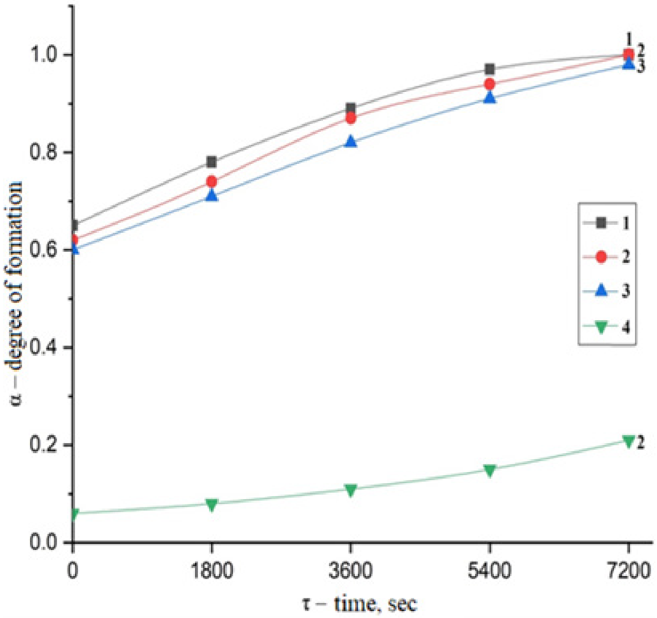

Figure 3: Kinetic parameters of sintering at 1000 °C of $CaAl_2O_4$ phase formation using precursors: 1 – $Al(NO_3)_3$+$Ca(NO_3)_2$; 2 – $AlCl_3$+$Ca(NO_3)_2$; 3 – $Al(OH)_3$+$Ca(NO_3)_2$; 4 – γ-Al_2O_3 CaCO.

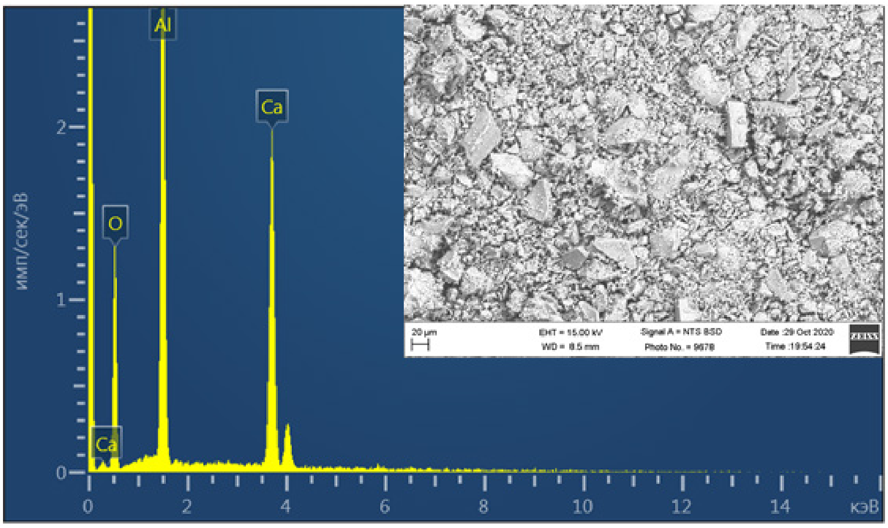

Figure 4: SEM and EMF images of $CaAl_2O_4$ synthesized at 1000 °C.

Conclusion

Thus, calcium monoaluminate compounds were synthesized using the sol-gel method. The effect of soluble aluminum and calcium salts on the synthesis, kinetics, and mechanism of the phase formation reaction during sintering of calcium monoaluminate in the temperature range of 500-1000 °C was studied. It has been established that the formation of calcium monoaluminate occurs through an intermediate compound - the mineral maenite. When the temperature rises to 1000 °C, maenite precedes the formation of calcium monoaluminate.

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