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# INORGANIC MATERIALS AND NANOMATERIALS

# Phase Formation Specifics in the High-Alumina Region of the CaO-Al<sub>2</sub>O<sub>3</sub> System

M. A. Trubitsyn<sup>a, \*</sup>, L. V. Furda<sup>a</sup>, M. N. Yapryntsev<sup>a</sup>, and N. A. Volovicheva<sup>a</sup>

<sup>a</sup> Belgorod National Research University, Belgorod, 308015 Russia
 \*e-mail: troubitsin@bsu.edu.ru
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Abstract—Phase formation of calcium monoaluminate and calcium dialuminate in the CaO–Al<sub>2</sub>O<sub>3</sub> system in the range 230–1450°C was studied using a model powder mixture comprising aluminum and calcium hydroxides. The onset of formation of an intermediate phase Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (C<sub>12</sub>A<sub>7</sub>) was observed at 430°C. At 1100°C, the appearance of CaAl<sub>4</sub>O<sub>7</sub> (CA<sub>2</sub>) and the presence of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> were observed. The onset of intense formation of the CaAl<sub>2</sub>O<sub>4</sub> (CA) phase is at 1170°C. In the range 1250–1400°C, the CA amount increases notably, while the CA<sub>2</sub> proportion remains almost unchanged. The final formation of the CA and CA<sub>2</sub> target phases occurs in 2 h at 1450°C. The syntheses of CA and CA<sub>2</sub> is controlled by Ca<sup>2+</sup> diffusion inward the aluminum-enriched cores of spherulites. Energy dispersive X-ray spectroscopy elucidated the CA and CA<sub>2</sub> distribution in the form of concentric layers.

**Keywords:** calcium aluminates, monoaluminate, dialuminate, solid-phase interaction, ion diffusion **DOI:** 10.1134/S0036023622080277

# INTRODUCTION

The CaO–Al<sub>2</sub>O<sub>3</sub> system has been studied in several works [1–3]. Jerebtsov and Mikhailov proposed a revised version of the phase diagram [4]. The following phases can exist in the CaO–Al<sub>2</sub>O<sub>3</sub> system depending on the molar ratio CaO/Al<sub>2</sub>O<sub>3</sub>: Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (C<sub>3</sub>A), Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (C<sub>12</sub>A<sub>7</sub>), CaAl<sub>2</sub>O<sub>4</sub> (CA), CaAl<sub>4</sub>O<sub>7</sub> (CA<sub>2</sub>), and CaAl<sub>12</sub>O<sub>19</sub> (CA<sub>6</sub>). Of these phases, calcium monoaluminate (CA) and calcium dialuminate (CA<sub>2</sub>) are of greatest applied importance.

Calcium aluminates are used in optical ceramics [5] and construction ceramics [6]. Calcium monoaluminate and calcium dialuminate are the major phases of calcium aluminate (aluminous) cements, which are widely used in the construction, mining, and metallurgical industries [7]. In recent years, calcium aluminate cements have been considered as promising biomaterials, primarily for dentistry and orthopedics [8].

As a consequence of the great practical importance of CA and CA<sub>2</sub>, the synthesis of these compounds has become the subject of a number of studies aimed at increasing the yield of target phases and decreasing the process temperature and time [9–18]. Various technological approaches were used in those studies, namely, self-propagating high-temperature synthesis [19, 20], spray drying [21], mechanochemical activation of precursors [22], the Pechini process [23], and the sol–gel method [24, 25]. However, these methods are of little use for the large-scale production of aluminous cements.

Ordinarily, calcium aluminate phases in the largescale production of aluminous cements are synthesized by high-temperature alloying or sintering using raw materials that contain Al<sub>2</sub>O<sub>3</sub> and CaO and some amount of impurities as well [7, 9, 26, 27]. The major impurities are silica and iron, magnesium, titanium, and alkali oxides. Phase transformations and the formation mechanisms of calcium compounds in the  $CaO-Al_2O_3-Na_2O$  system are considered by Yu et al. [28]. When the raw materials used have high amounts of impurities, the sintering range is quite close to the melting temperatures, so alloying technology is used in the mass production of aluminous cements, as a rule. The presence of impurities has a significant impact on the phase composition of aluminous clinker and phase-formation processes; however, these aspects are beyond the scope of this article.

Most of the known studies are devoted to the synthesis of monophasic products, primarily CA [12, 13, 22, 29, 30]. According to Williamson and Glasser [10], the formation of the primary nonequilibrium reaction product for equimolar CaCO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> mixtures heat-treated for 3-120 h at  $1045-1405^{\circ}$ C occurs without a strictly defined sequence.

According to Kuznetsova and Talaber [7], the formation sequence of calcium aluminates can be written as follows:

$$\begin{split} &12\text{CaO} + 7\text{Al}_2\text{O}_3 \rightarrow 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \left(600 - 800^\circ\text{C}\right), \\ & \text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \left(600 - 900^\circ\text{C}\right), \\ & 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 + 5\text{Al}_2\text{O}_3 \rightarrow 12\text{CaO} \cdot \text{Al}_2\text{O}_3 \left(900 - 1200^\circ\text{C}\right), \\ & \text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 2\text{Al}_2\text{O}_3 \left(1000 - 1400^\circ\text{C}\right). \end{split}$$

The above schemes imply that CA and  $C_{12}A_7$  formation occurs in the low-temperature range (600– 900°C). The increasing temperature speeds up the reaction of alumina with CaO, so the amount of CA seriously increases and the amount of  $C_{12}A_7$  decreases. At 1000°C, where a considerable part of CaO is bound into CA, CA<sub>2</sub> formation is due to the reaction of CA and Al<sub>2</sub>O<sub>3</sub>.

Singh et al. [11] studied the formation of calcium aluminates in the range  $1200-1460^{\circ}$ C using CaO and Al<sub>2</sub>O<sub>3</sub> as precursors.

 $C_3A$  and  $C_{12}A_7$  phases were first identified after 1250°C heat treatment, and then their amounts decreased over time. The CA<sub>2</sub> proportion was insignificant. It was concluded that CA in mixtures is formed not as a result of a direct reaction between CaO and Al<sub>2</sub>O<sub>3</sub>, but through the transformation of intermediates.

Mohamed and Sharp [12] considered the kinetics and mechanism of CA synthesis in the range 1250–

1400°C. They verified Singh et al.'s results [10] and showed that the acquisition of phase equilibria is accelerated as the temperature and time of isothermal exposure increase, and  $C_3A$  and  $C_{12}A_7$  should be regarded as intermediates in CA formation.

High-purity calcium monoaluminate CA was prepared in the range 900–1550°C using mixtures of Al<sub>2</sub>O<sub>3</sub> or amorphous Al(OH)<sub>3</sub> with CaCO<sub>3</sub>, pre-milled in a high-energy mill [13]. Powder mixtures after joint milling had a high degree of homogeneity and had the following parameters:  $S_{sp} = 5.6-8 \text{ m}^2/\text{g}$ ;  $d_{50}$  for CaO particles was 2 µm, and  $d_{50}$  for Al<sub>2</sub>O<sub>3</sub> particles was 0.35 µm. At 920°C, a C<sub>12</sub>A<sub>7</sub> phase appeared in the reaction

$$7\mathrm{Al}_{2}\mathrm{O}_{3} + 12\mathrm{CaO} \rightarrow \mathrm{Ca}_{12}\mathrm{Al}_{14}\mathrm{O}_{33}(\mathrm{C}_{12}\mathrm{A}_{7}).$$

At 1100°C, it was the onset of formation of calcium monoaluminate CA. According to Mercury et al. [13], thermodynamically allowed reactions are:

$$\begin{aligned} &7Al_2O_3 + 12CaO \rightarrow Ca_{12}Al_{14}O_{33} \ (\Delta G = -275 \ \text{kJ/mol}), \\ &Al_2O_3 + CaO \rightarrow CaAl_2O_4 \ (\Delta G = -38 \ \text{kJ/mol}), \\ &2\alpha - Al_2O_3 + CaO \rightarrow CaAl_4O_7 \ (\Delta G = -51 \ \text{kJ/mol}), \\ &7CaAl_2O_4 + 5CaO \rightarrow Ca_{12}Al_{14}O_{33} \ (\Delta G = -30 \ \text{kJ/mol}), \\ &5Al_2O_3 + Ca_{12}Al_{14}O_{33} \rightarrow 12CaAl_2O_4 \ (\Delta G = -172 \ \text{kJ/mol}), \\ &17Al_2O_3 + Ca_{12}Al_{14}O_{33} \rightarrow 12CaAl_4O_7 \ (\Delta G = -308 \ \text{kJ/mol}), \\ &5CaAl_4O_7 + Ca_{12}Al_{14}O_{33} \rightarrow 17CaAl_2O_4 \ (\Delta G = -122 \ \text{kJ/mol}). \end{aligned}$$

Mercury et al. infer that the pre-milling of precursors reduces the onset temperature of CA phase formation. When  $Al_2O_3$  was used, the lowest  $C_{12}A_7$  and CA formation temperature was 900 and 1100°C, respectively; when  $Al(OH)_3$  was used, both phases started forming at 900°C.

Iftekhar et al. [14], prior to the synthesis, mixed the reagent mixtures in a drum using  $Al_2O_3$  grinding media in isopropanol, and then additionally manually triturated them with hexane. The initial grain size of CaCO<sub>3</sub> and  $Al_2O_3$  was <10 µm and <1 µm, respectively. Heat treatment was carried out at 1300, 1400, and 1500°C and with various isothermal exposure times. Iftekhar et al.'s results do not support the opinion that calcium-rich phases  $C_{12}A_7$  and  $C_3A$  are formed as intermediates, while CA<sub>2</sub> is formed in the initial side reaction. Local areas with low calcium con-

tents yield  $CA_2$  in equilibrium with  $Al_2O_3$ . CA is the only calcium aluminate phase that is formed at 900°C.

In recent decades, there has been an increase in the production of extra-pure high-alumina cements where  $Al_2O_3$  70%. Such cements are widely used as a hydraulic binder in the technology of new-generation low-cement castable refractory composite masses [15].

The stability of the characteristics of high-alumina cements is of great importance to achieve high technological and operational properties of these refractory composites. The industrial production of ultra-pure calcium aluminate cements with 70-80% Al<sub>2</sub>O<sub>3</sub> is currently carried out by solid-phase sintering in rotary, tunnel, or chamber kilns [7].

According to the CaO–Al<sub>2</sub>O<sub>3</sub> phase diagram, the preparation of a high-alumina clinker containing 70% alumina or more, suggests two target phases: CaO·

Al<sub>2</sub>O<sub>3</sub> (CA) and CaO·2Al<sub>2</sub>O<sub>3</sub> (CA<sub>2</sub>). In the settings of real production, as a rule, phase formation proceeds under non-steady-state conditions. As a result, heterogeneous products of variable phase composition are formed, containing various amounts of CA and CA<sub>2</sub> as the major phases, and C<sub>12</sub>A<sub>7</sub> and unreacted  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as side phases. However, there are only a few contemporary works devoted to the theoretical and practical aspects of the preparation of ultra-pure highalumina clinkers [16–18].

In some articles, researchers refer to the fact that the CA/CA<sub>2</sub> phase ratio changes at high temperatures, while there are no unreacted Al<sub>2</sub>O<sub>3</sub> and CaO precursors and no the C<sub>12</sub>A<sub>7</sub> intermediate in the system. Kuznetsova and Talaber [7], for example, noted that the phase composition of the clinker changed in response to even small fluctuations in isothermal exposure temperature within the range 1420–1480°C. Our preliminary studies gave similar results. However, there are currently no satisfactory explanations to the above facts.

In this paper, we present the results of our studies of the factors that provide a targeted flow of calcium monoaluminate and calcium dialuminate phase formation in the high-alumina region of the  $CaO-Al_2O_3$ system.

## **EXPERIMENTAL**

CA and CA<sub>2</sub> phase formation in the CaO–Al<sub>2</sub>O<sub>3</sub> system were studied in a model powder mixture containing the corresponding precursors. The Al<sub>2</sub>O<sub>3</sub> precursor was aluminum hydroxide Al(OH)<sub>3</sub> (chemically pure grade); the CaO precursor was calcium hydroxide Ca(OH)<sub>2</sub> (chemically pure grade).

The particle size of the precursor powders was determined by laser diffraction on a Microtrac s3500 analyzer. The test sample was immersed in the analyzer cell filled with distilled water (for  $Al(OH)_3$ ) or ethanol (for  $Ca(OH)_2$ ), and then dispersed by ultrasonication for 60 s. The particle size was determined from three replica measurements.

For Al(OH)<sub>3</sub>, the median particle size was determined as 114  $\mu$ m. For Ca(OH)<sub>2</sub> powders, there was bimodal particle size distribution. The first mode corresponds to ca. 3  $\mu$ m, and the second to ca. 30  $\mu$ m. The median size is 5.0  $\mu$ m.

Taking into account the required content of  $Al_2O_3$ in the range of 70–71 wt %, the  $Al(OH)_3$  and  $Ca(OH)_2$ in the model mixture were taken in the molar ratio  $CaO : Al_2O_3 = 1 : 1.36$ . Given the solid-phase processes are steady-state, this ratio should provide the tailored percentages of the CA and CA<sub>2</sub> target phases of 65 and 35 wt %, respectively.

The dry powder mixture was moistened with distilled water to a paste-like state and then homogenized using an overhead paddle mixer. The thus-prepared mass was placed in polypropylene molds with a diameter of 40 mm and a height of ~30 mm, followed by vibrocompaction for 10-20 s. The molded samples were first kept at room temperature for 8 h and then in a forced convection oven at  $120^{\circ}$ C for 2 h.

At the first stage of the experiment, a dried sample of the model mixtures was studied by TGA/DSC using an SDT Q600 simultaneous thermal analyzer in order to determine the parameters of further heat treatment. The parameters of the thermoanalytical experiment were as follows: temperature range, 20–1400°C; heating rate, 10 K/min; and an argon inert atmosphere. The results of the experiment were processed in the OriginPro2021 software.

The heat treatment of samples was in a Nabertherm LHT 02/17 high-temperature furnace in the following mode: heating at 250 K/h and isothermal exposure at the highest temperature for 60 and 120 min.

An X-ray powder diffraction (XRD) experiment was fulfilled on an Ultima IV (Rigaku) diffractometer using Cu $K_{\alpha}$  radiation ( $\lambda = 1.54056$  Å, the Bragg– Brentano geometry, scan rate: 2 deg/min,  $2\theta = 10^{\circ}$ –  $70^{\circ}$ , scan step: 0.02°). Peak identification was with reference to the PDF-2 database. The measured X-ray diffraction patterns were processed in the PDXL (Rigaku) program.

Morphological studies of materials were on an FEI Nova NanoSEM 450 scanning electron microscope. Images were obtained using a back-scattered electron detector in a low-vacuum mode at a chamber pressure of 80 Pa and an accelerating voltage of 30 kV. For operation in the scanning mode, the samples were glued onto a copper substrate using a conductive carbon adhesive. The secondary electrons emitted by the sample at magnification up to 20000 times were recorded by a recording system, the signal from which was fed to the processing system and recorded in a digitized form.

## **RESULTS AND DISCUSSION**

The thermogravimetric and diffential thermoanalytical curves for model samples are shown in Fig. 1. The weight change during heating appears on the TG curve, the weight loss rate change on the DTG curve, and the heats of processes on the HF and DTA curves. The TG and DTG curves feature five extremes, which correspond to the highest weight loss change of the test sample during heating. The positions of extremes on the TG, DTG, HF, and DTA are the same, so to avoid complicating the figures with unnecessary information, the positions of peaks are marked only on the HF curve.

The TG and HF curves in the range 90–200°C feature an insigniciant weight loss and a temperature-dif-



Fig. 1. Thermogravimetric and differential thermoanalytic curves for model samples: (a) TG and DTG curves; and (b) DTA and HF curves.

fused endotherm corresponding to removal of physically bound water.

For a correct assessment of phase formation in the  $CaO-Al_2O_3$  system under model conditions, the experimental samples were treated in an electric furnace at temperatures corresponding to the DTA events. In addition, heat treatment was carried out at the temperatures chosen to study the effect of anneal-

ing modes on the synthesis of calcium aluminate phases.

Figure 2 shows X-ray powder diffraction patterns for the initial sample and for samples treated at the temperatures at which thermal events occurred.

X-ray powder diffraction showed that the endotherm at  $235^{\circ}$ C on the DTA curve might correspond to the destruction of aluminum hydroxide to form alumi-



Fig. 2. X-ray powder diffraction patterns of the initial sample and samples heat-treated at 235, 308, 430, 535, and 716°C with 1-h exposure.

num metahydroxide AlO(OH), and when 308°C is reached, the complete decomposition of the aluminum hydroxide occurs with a considerable weight loss.

As temperature increases to  $430^{\circ}$ C, the AlO(OH) reflections in the powder pattern are reduced in intensity (Fig. 2) with a simultaneous broadening of the Ca(OH)<sub>2</sub> reflections.

The X-ray diffraction pattern at this temperature also features reflections due to  $C_{12}A_7$ . In this way, the endotherm on the DTA curve, likely, corresponds to  $C_{12}A_7$  phase formation due to the reaction of the decomposition products of calcium and aluminum hydroxides.

A rise in temperature to  $535^{\circ}$ C leads to the complete decomposition of AlO(OH) and to an increase in the percentage of the calcium aluminate phase C<sub>12</sub>A<sub>7</sub>, as probed by XRD.

The endotherm on the DTA curve at 716°C corresponds to calcium hydroxide decomposition, which is verified by the highest weight loss rate observed on the TG and DTG curves and by a considerable broadening of Ca(OH)<sub>2</sub> reflections on the X-ray powder diffraction pattern.

The HF curve (Fig. 1b) in the range from ~1100 to 1400°C features a broad endotherm due to processes in which the sample weight does not change. This type of thermal event may be assigned to crystallization processes (destruction of the crystal lattice of the starting compounds and the formation of new reaction

products, kinetically controlled by the diffusion of individual components).

For a more detailed assessment of the phase formation processes in the model system, the heat treatment of the studied samples was carried out over the entire range of this endotherm (at 1100, 1170, 1250, 1300, 1350, 1400, and 1450°C).

At 1100°C, calcium oxide crystallizes (Fig. 3a). The major phases are CaO (~48 wt %) and  $C_{12}A_7$  (~21 wt %). CA<sub>2</sub> (~13 wt %) and  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> (~23 wt %) are also detected at this temperature.

At 1170°C (Fig. 3b), the CaO percentage decreases to ~16 wt % with a simultaneous increase in CA<sub>2</sub> percentage (~17 wt %). CA (~31 wt %) is also actively forming in the sample. Meanwhile, the alumina percentage remains almost unchanged (~22 wt %). Likely, this is possible only in the case where crystal lattices inherent in nonstoichiometric compounds CA and CA<sub>2</sub> are formed with vacancies in aluminum ion positions. The phase transition  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>  $\rightarrow \alpha$ -Al<sub>2</sub>O<sub>3</sub> also occurs 1170°C.

Further, the samples were annealed at 1250, 1300, 1350 1400, and 1450°C in order to elucidate the dependence of the phase composition on the heat treatment mode. The XRD results are shown as bar diagrams in Figs. 4 and 5.

At 1250°C with 1-h exposure (Fig. 4), the phase composition is represented by CA,  $CA_2 C_{12}A_7$ ,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and CaO. In the samples heat-treated at temperatures in



Fig. 3. X-ray powder diffraction patterns of samples heat-treated at (a) 1100 and (b) 1170°C with 1-h exposure.

the range  $1300-1400^{\circ}$ C, CaO is unobserved. Quantitative changes associated with a decrease in the amounts of Al<sub>2</sub>O<sub>3</sub>, C<sub>12</sub>A<sub>7</sub>, and CA phases occur in this range of temperatures. So, the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> percentage decreases from 20.3 to 10.0 wt % upon 1-h isothermal exposure, and the C<sub>12</sub>A<sub>7</sub> percentage decreases from 12.6 to 5.0 wt %. At the same time, the share of CA increases from 42.7 to 69.0 wt %. The isothermal exposure time has a significant effect on the changes in CA,  $C_{12}A_7$ , and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> percentages in the sample (Figs. 4 and 5). A significant increase in CA percentage with a peak at 1400°C is observed for the samples heat-treated at 1250–1400°C for 2 h (Fig. 5). At the same time, the CA<sub>2</sub> percentage in the range 1250–1400°C remains virtually at the same level (19–21 wt %). The final and almost equi-



Fig. 4. Phase composition of samples heat-treated at 1250, 1300, and 1350°C with 1-h exposure.



Fig. 5. Phase composition of samples heat-treated at 1250, 1300, 1350, 1400, and 1450°C with 2-h exposure.

librium formation of the target phases CA and CA<sub>2</sub> (67.9 and 32.1 wt %, respectively) occurs within 2 h at 1450°C. Noteworthy, the CA percentage at this temperature is reduced toward CA<sub>2</sub> formation.

In our opinion, the results of our study of the effect of heat-treatment modes on the synthesis of calcium aluminate phases in the selected model system can be interpreted as follows (Fig. 6). In the range 500– 800°C, where Al(OH)<sub>3</sub> and Ca(OH)<sub>2</sub> decompose to yield submicron-sized reactive species of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> and CaO (Fig. 6b), in the contact zone there occurs C<sub>12</sub>A<sub>7</sub> synthesis reaction:

$$7\text{Al}_2\text{O}_3 + 12\text{CaO} \rightarrow \text{Ca}_{12}\text{Al}_{14}\text{O}_{33} \ (\Delta G = -275 \text{ kJ/mol}).$$

At 1000–1170°C, the presence of reactive  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> species make possible the occurrence of the forward reaction:

$$2\kappa$$
-Al<sub>2</sub>O<sub>3</sub> + CaO  $\rightarrow$  CaAl<sub>4</sub>O<sub>7</sub>.

Above 1200°C (Fig. 6c), the probability of the above reaction will be very low due to the transition of  $\kappa$ -Al2O3 to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, a stable and, accordingly, chemically inert species. Therefore, in the range 1200–1400°C the following reactions will start prevailing:



Fig. 6. Schematic flowsheet for the synthesis of calcium aluminate phases.

$$5Al_2O_3 + Ca_{12}Al_{14}O_{33} \rightarrow 12CaAl_2O_4 \ (\Delta G = -172 \text{ kJ/mol}),$$
  
 $5CaAl_4O_7 + Ca_{12}Al_{14}O_{33} \rightarrow 17CaAl_2O_4 \ (\Delta G = -122 \text{ kJ/mol}).$ 

The occurrence of these reactions causes a significant increase in CA phase concentration with a simultaneous decrease in the amounts of  $Ca_{12}Al_{14}O_{33}$  and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phases. Mass transfer of the material to the reaction zone occurs via the predominant diffusion of

 $Ca^{2+}$  and, to a lesser extent,  $AlO_4^{5-}$ .

Our suggested phase formation scheme is verified by scanning electron microscopy (Fig. 7). The micrographs of the sample (T = 1250°C) feature two types of particles: ultrafine calcium-containing rounded platelets ranging in size from 1 µm to a split micron and larger isometric grains of a cellular structure ~10–25 µm in size, identified as a mixture of aluminum oxide and the CA<sub>2</sub> phase (Figs. 7a and 7b). The consolidation of calcium-enriched submicron-sized particles around nascent spherulites with a high aluminum concentration is observed clearly at this temperature.

Spherulites ~70 µm in size (Figs. 7c and 7d), which are close-packed globules of prismatic particles of composition  $CA_2 + Al_2O_3$ , are well distinguishable on SEM images (T = 1350°C). The surfaces of spherulites are fragmentarily covered with a thin layer of micromelt of calcium-enriched CA and  $C_{12}A_7$  phases. At 1350°C, thin necks appear between spherulites due to sintering of submicron-sized particles, which leads to the formation of a cellular pore space.

At 1450°C (Figs. 7e and 7f), one can notice a thick homogeneous shell, predominantly of the CA phase, around the spherulites. The size of necks connecting distorted spherulites into a single frame becomes noticeably larger. The formation of pore channels is clearly visible. The solid framework and pore space are interconnected and represent a single morphological system as a result of intense sintering. The SEM micrographs of particles illustrate their morphological specifics; in particular, a clear boundary between the cellular structure constituting the core of spherulites and a dense homogeneous shell is clearly visible.

In view of the foregoing, the formation of the target products CA and CA<sub>2</sub>, in our opinion, is a consequence of the diffusion of more mobile  $Ca^{2+}$  ions released during the destruction of the  $C_{12}A_7$  phase in the region of aluminum-rich spherulites.

This assumption is confirmed by the energy dispersive X-ray spectra (EDX) of a sample annealed for 2 h at 1450°C. The results of EDX processed by the line scanning method, as well as by mapping, are shown in Fig. 8.

Despite the inability of this type of analysis to provide accurate quantitative estimates of the percent contents of elements, their relative changes make it possible to design a well-defined pattern to characterize the dynamics of changes in the calcium and aluminum percentages when moving from the periphery (shell) to the center of the spherulite (core). It can be seen when moving along the line from the center to the periphery that the calcium content increases with a simultaneous decrease in the aluminum concentration (Fig. 8a). A sharp increase in the calcium content occurs at the transition through the boundary between the core and the shell, which indicates the presence of a clear interface between phases with different calcium contents. Analysis of the element distribution map (Fig. 8b) confirms a clear zonal distribution of calcium, aluminum, and, accordingly, calcium aluminate compounds at the final phase formation stage. A high concentration of calcium is observed on the surface of a spherulite (CA phase), and the core is formed by an aluminum-rich phase  $(CA_2)$ . The data obtained are in good agreement with Gakia et al.' conclusions [31].



Fig. 7. SEM images of samples heat-treated at (a, b) 1250, (c, d), 1350, and (e, f) 1450°C with 2-h exposure.

Different concentrations of reactants and reaction products are acquired as a result of the chemical reaction at different points in the reaction space. The concentration gradient of the most mobile reagent is the trigger of diffusion, which is a spontaneous process of material transfer as a result of the movement of molecules until an equilibrium distribution of concentrations is acquired. The chaotic thermal motion of particles causes the ordered, directed transfer of the material to areas where concentration gradients arise or where the distribution of concentrations differs from the equilibrium state. The diffusion rate depends on the density and viscosity of the medium, temperature, the nature of the diffusing species, the influence of external forces, etc.

Taking into account the fact that at the least temperature and exposure time of the studied samples, the main phases are the target calcium aluminate phases (CA and CA<sub>2</sub>), it can be assumed that the rate of their formation reaction under the experimental conditions exceeds the rate of diffusion stages; this case corresponds to the diffusion control region of the chemical reaction.



**Fig. 8.** SEM images with EDX results: (a) the distributions of elements across the spherulite cross-section; and (b) element distribution map (Al in green, and Ca in red).

# CONCLUSIONS

The phase formation of calcium aluminate compounds in the high-alumina region of the  $CaO-Al_2O_3$ system has been studied using model mixtures of calcium hydroxide and alumina. The onset formation temperature of the  $C_{12}A_7$  intermediate is 430°C. At 1100°C, CaO and  $C_{12}A_7$  are the major phases.  $CA_2$ appears at this temperature, and  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is present. Intense CA phase formation starts at 1170°C. In the range 1250-1400°C, the amount of CA increases notably, while the CA<sub>2</sub> proportion remains almost unchanged. In our opinion, this is due to the transition of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> into the stable and, accordingly, chemically inert  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. As a consequence, reactions involving the Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> intermediate prevail in the range 1200-1400°C to provide the considerable rise in CA percentage. The mass transfer of the material to the reaction zone occurs via dominant Ca<sup>2+</sup> diffusion.

The formation of target phases CA and CA<sub>2</sub> ends in 2 h at 1450°C. At the final stage of phase formation, we found the zonal distribution of the target phases, namely, the formation of CA<sub>2</sub> in the cores of spherulite

grains and a dense shell on their surfaces, predominantly of the CA phase.

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### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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