TẠP CHÍ KHOA HỌC & CÔNG NGHỆ ĐẠI HỌC DUY TÂN
DTU Journal of Science and Technology 5(54) (2022) 61-68

TRƯỜNG ĐẠI HỌC DUY TÂN
DUYTAN UNIVERSITY

Features of the synthesis of calcium-aluminate phases with the introduction of modifying additives

Một số đặc điểm về tổng hợp các pha canxi-nhôm sử dụng các phụ gia biến tính

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(Ngày nhận bài: 14/4/2022, ngày phản biện xong: 24/4/2022, ngày chấp nhận đăng: 15/8/2022)

Abstract

In this work, the influences of boric acid and high alumina cement used as modifying additives on the formation of $CaO{\cdot}Al_2O_3$ and $CaO{\cdot}2Al_2O_3$ were studied. Herein, commercially available chalk of the M-90 label and technical alumina of the G-0 label were utilized as initial raw materials. Heat treatment of powder mixtures with various concentrations of modifying additives was carried out in the temperature range of 1250-1350ºC with an isothermal exposure times of 1h and 2h. It was found that the addition of additives into the raw mixture affected the ratio of target phases and the temperature interval of the phase formation of calcium-aluminate minerals.

Keywords: Calcium-aluminate phases; heat treatment; boric acid; high alumina cement; modification.

Tóm tắt

Trong nghiên cứu này, ảnh hưởng của các chất phụ gia như axit boric và xi măng alumin cao đến sự hình thành các pha $CaO.Al_2O_3$ và $CaO.2Al_2O_3$ đã được khảo sát. Trong đó, phấn thương mại M-90 và alumin kỹ thuật G-0 được sử dụng làm nguyên liệu ban đầu. Quá trình xử lý nhiệt hỗn hợp bột với các nồng độ phụ gia khác nhau được thực hiện trong khoảng nhiệt độ 1250-1350ºC với thời gian nung là 1 và 2 giờ. Kết quả cho thấy rằng việc bổ sung các chất phụ gia vào hỗn hợp nguyên liệu thô ban đầu đã ảnh hưởng đến tỷ lệ pha của sản phẩm và khoảng nhiệt độ của giai đoạn hình thành khoáng chất canxi-aluminat.

Từ khóa: Pha canxi-aluminat; xử lý nhiệt; axit boric; xi măng alumin cao; biến tính.

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1. Introduction

$CaO·Al_2O_3$ (CA) and $CaO·2Al_2O_3$ (CA_2) are the main phases of calcium aluminate cement, which are widely used in the construction, mining and metallurgical industries [1] and are also considered as promising biomaterials, especially in dentistry and orthopedics [2]. Cement with an aluminum oxide content of more than 70 wt. % are called high alumina cement (HAC). The main ways of producing HAC are complete melting of the raw mix and sintering. In these processes, clinker is produced mainly by solid-phase reactions [3-5]. Highly pure HAC is produced by sintering in rotary kilns (in case of multi-tonnage production) as well as in tunnel or chamber kilns (in medium-tonnage production) [6, 7].

The development of the composition and technology for producing highly pure HAC includes: (i) the study of the synthesis process of clinker minerals; (ii) the identification of factors that determine the conditions of formation and temperature ranges of the target phase CA and CA_2; and (iii) the definition of technological and physical-mechanical characteristics of the finished product [8-13].

The aim of this work was to investigate the effect of some modifying additives on the phase formation processes of CA and CA_2 in the production of high alumina clinker.

2. Methodology

When calculating the content of raw materials in the charge, it was assumed that high alumina clinker with 71-72 wt. % of Al_2O_3 and 27-28 wt. % of CaO would be produced. This mass ratio in the CaO – Al system state diagram suggests the presence of two calcium-aluminate phases CA and CA_2 [14, 15]. The predicted phase composition of the clinker is 64 wt. % CA and 36 wt. % CA_2. Chalk of M-90 and technical alumina of G-0 labels were used as initial raw materials. The chemical composition of the feedstock is shown in Table 1. A more detailed description of the starting materials can be found in [16].

Table 1. Chemical composition of raw materials

Material from	**wt. (%)**						
	Al_2O_3	SiO_2	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**Other**
G-0	98.60	0.02	0.015	tracks	tracks	0.10	1.26
M-90	0.10	0.10	0.08	98.60 ($CaCO_3$)	tracks	tracks	1.12

As is known, initiators for the formation of new phases can be introduced in limited quantities of chemical substances close in nature as “seed”. In our study, HAC (NK-CEM 72) with 70.50 wt. % Al_2O_3 was the source of phase-forming initiator substances. In terms of mineralogical composition, HAC is represented by two phases: CA and CA_2. The content of these phases is 78.5 and 21.5 wt. %, respectively.

One of the technological ways to reduce the operating temperature of phase formation is the introduction of additives that ensure the early emergence of micro-melts. This process intensifies the diffusion of cations and anions into the reaction zone. As an additive of this type, we chose boric acid of the chemically purified label.

The phase composition of materials was determined by X-ray diffraction analysis (XRD) conducted on an Ultima IV diffractometer (Rigaku Japan) using CuKα radiation (λ = 1.54056 Å), Bragg-Brendano imaging scheme, with a scanning speed of 2 deg/min in the 2θ angle range of 10-70˚ at 0.02˚ scanning steps. The peak identification was

performed using the PDF-2 database. Experimental diffractograms were processed using PDXL software (Rigaku Corporation) with Rietveld refinement. The phase ratio was calculated using the corundum number method.

The synthesis of clinker minerals was carried out as follows. Dosing of raw materials and modifying additives was carried out by the weight method on laboratory technical scales. The homogenization of the raw mix was performed by mixing in a drum of a laboratory ball mill with a working volume of 2L for 60 min. The prepared powder mixture was moistened with distilled water to a pasty state and homogenized with an overhead paddle mixer. The resulting mass was then placed in polypropylene molds with a diameter of 40 min and a height of ~ 30 mm, followed by vibration compaction for 10 – 20 seconds. The moulded samples were pre-conditioned at room temperature for 8h and then incubated in a forced convection drying oven at 120ºC for 2h. The dried briquettes were placed in a Nabertherm LHT 02/17 high-temperature furnace on a corundum substrate and heated as follows: heating rate 250ºC per hour, the first isothermal holding at 900ºC for 30 min, the second isothermal holding at the given maximum temperatures for 1 or 2 hours.

3. Results and discussion

At the initial stage of the study, the effect of the addition of boric acid on the formation of the clinker phases was evaluated. For this purpose, the samples were prepared with the addition H_3BO_3 in the initial mixture, equal to 0.5 and 1.0 wt. % according to the procedure mentioned above. The heat treatment was carried out at 1250, 1300 and 1350ºC with isothermal exposure for 1 and 2h. The obtained samples were investigated by the XRD technology. The results of the influence of additive H_3BO_3 in the initial charge on the phase formation processes are shown in Figures 1, 2 and Tables 2, 3.

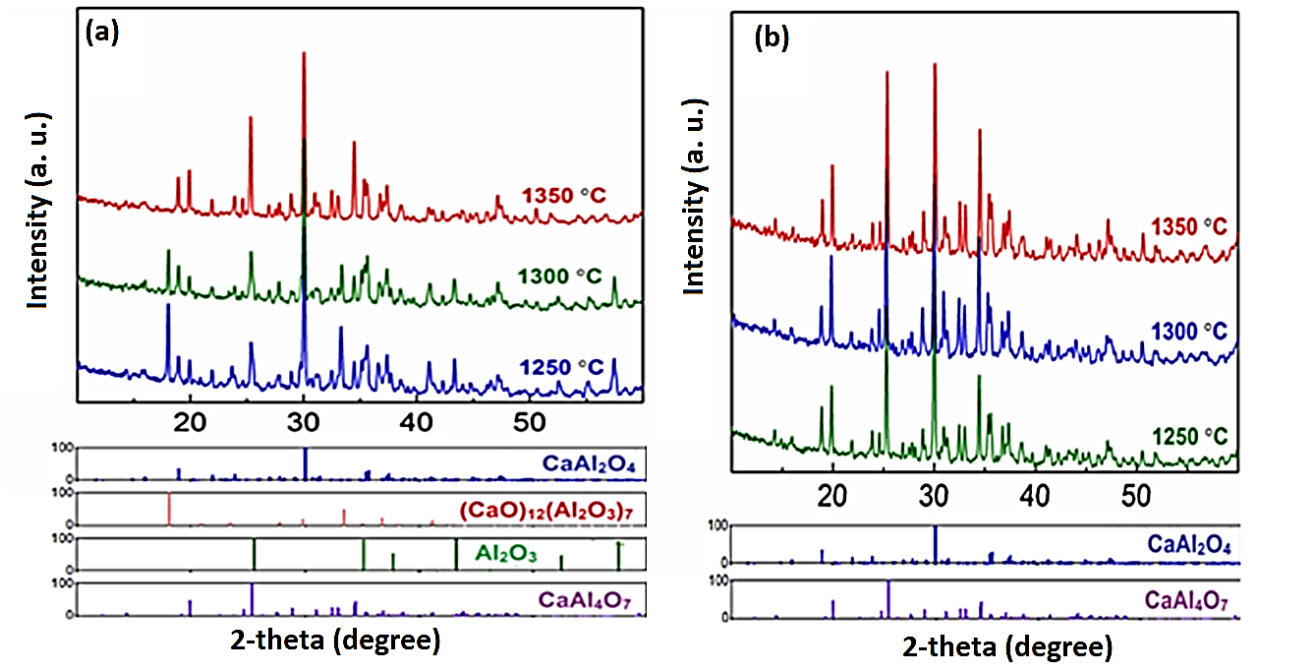

Figure 1. XRD patterns of heat-treated samples with 0.5 wt.% H_3BO_3, isothermal exposure time of 1h (a) and 2h (b).

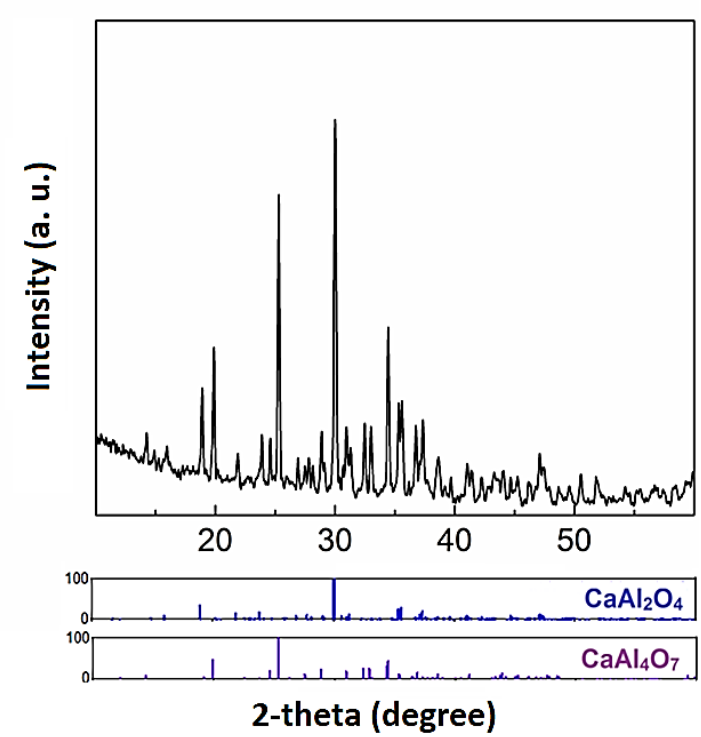

Figure 2. XRD diffractograms of the sample containing 1 wt. % H_3BO_3 with isothermal exposure time of 1 hour at 1250ºC

Table 2. Influence of heat treatment modes on the phase composition of samples with the addition of H_3BO_3 0.5%

Phases	**Maximum temperature (ºC)**					
	1250		1300		1350	
	Isothermal exposure time (h)					
	1	2	1	2	1	2
	wt (%)					
α-Al_2O_3	15.5	-	14.8	-	-	-
$C_{12}A_{77}$	16.2	-	7.6	-	-	-
CA	64.1	76.6	54.1	70.7	78.8	68.7
CA_2	13.5	24.4	14.1	29.3	21.2	31.3

Table 3. Influence of heat treatment modes on the phase composition of samples with the addition of H_3BO_3 1.0%

Phases	**Maximum temperature (ºC)**					
	1250		1300		1350	
	Isothermal exposure time (h)					
	1	2	1	2	1	2
	wt. %					
CA	67.7	62.1	67.6	66.3	68.0	66.0
CA_2	32.3	27.9	32.4	33.7	32.0	34.0

It can be seen from Figure 1a and Table 2, after heat treatment at 1250ºC with isothermal soaking for 1h, the target phases CA and CA_2, as well as α- Al_2O_3 and the intermediate phase $C_{12}A_{77}$ were detected. Increasing the temperature up to 1300ºC did not lead to a

change in concentration of alpha aluminum oxide (~15 wt. %), while the content of phase $C_{12}A_7$ reduced from 16 to 8 wt. %. At the same time, an increase of the isothermal exposure up to 2h allowed obtaining only two target phases – CA and CA_2, regardless of the maximum firing temperature (Figure 1b and Table 2). In the case of firing at 1350ºC, the contents of CA and CA_2 phases in the clinker were close to the design value.

The increase of H_3BO_3 concentration in the initial charge up to 1.0 % made it possible to obtain samples with the designed ratio of CA and CA_2 already at 1250ºC and the exposure time of 1 hour (Figure 2, Table 3). A further increase in temperature and duration of isothermal exposure did not lead to a change in the qualitative and quantitative phase composition.

In the next phase of research, the effect of the HAC additive on the synthesis of clinker phases was evaluated. The phase formation processes of CA and CA_2 from the $CaCO_3$-Al_2O_3 powder mixtures with the addition of HAC 5% in the temperature range of 1250 - 1450ºC were previously studied [16]. According to the data obtained after heat treatment at 1300ºC, the samples did not contain appreciate amounts of calcium oxide; but at the same time, there was a decrease in aluminum oxide content and formation of $C_{12}A_7$. It was shown that an increase of the heat treatment temperature in the range of 1300 - 1350ºC did not result in a significant change in the phase composition of the samples.

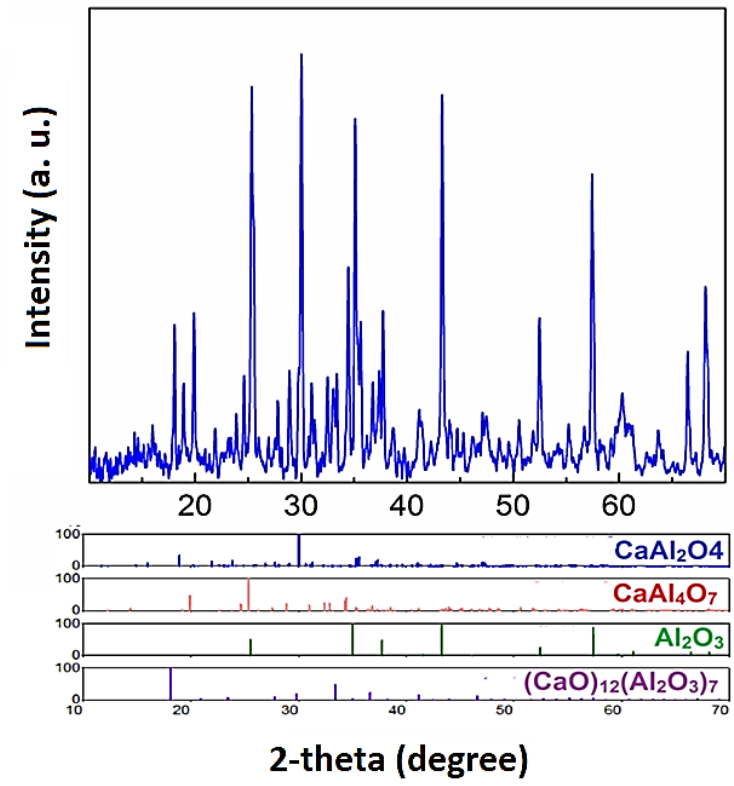

Figure 3. XRD pattern of reference sample with isothermal exposure for 1h at 1350ºC.

Considering the above information, in the present study, the heat treatment of powder mixtures with HAC additive of 5; 7.5 and 10 wt. % was carried out at 1350ºC with exposure times of 1 and 2h, respectively. A reference sample without HAC additive synthesized under the same conditions was used for comparison. The obtained materials were studied by X-ray diffraction analysis. Since all samples had a comparable phase composition, a

powder X-ray diffractogram of the reference sample is shown in Figure 3 as an example, according to which the main components of the obtained clinkers are the target phases CA and CA_2, as well as α- aluminum oxide and $C_{12}A_7$.

The nature of the change in the phase composition of the samples at different concentrations of HAC in the experimental charge is shown in Table 4 and Figure 4.

Table 4. Effect of HAC additive on clinker content after firing at 1350ºC

Phases	**Amount of additive (mass %)**							
	Without a supplement		5		7.5		10	
	Isothermal exposure time (h)							
	1	2	1	2	1	2	1	2
	wt, %							
α-Al_2O_3	32.6	12.7	17.4	15.3	9.1	-	7.2	4.0
$C_{12}A_7$	35.2	66.6	60.1	57.5	62.5	75.1	68.5	62.8
CA	27.1	13.7	17.3	21.2	21.5	22.2	20.2	17.2
CA_2	5.1	8.0	5.6	5.9	6.9	3.6	4.4	17.5

As can be seen from Table 4, the addition of HAC had a significant effect on the change in aluminum oxide content during the 1-hour isothermal soak. The α-Al_2O_3 content in the reference sample was 32.6%; and in the HAC concentration range of 5 – 10%, the aluminum oxide content decreased from 17.4 to 7.2%. Correspondingly, the content of calcium monoaluminate increased from 35.2% (reference) to 60.1 – 68.5%. A similar pattern of change in α-Al_2O_3 was also observed when the isothermal exposure time was increased to 2h.

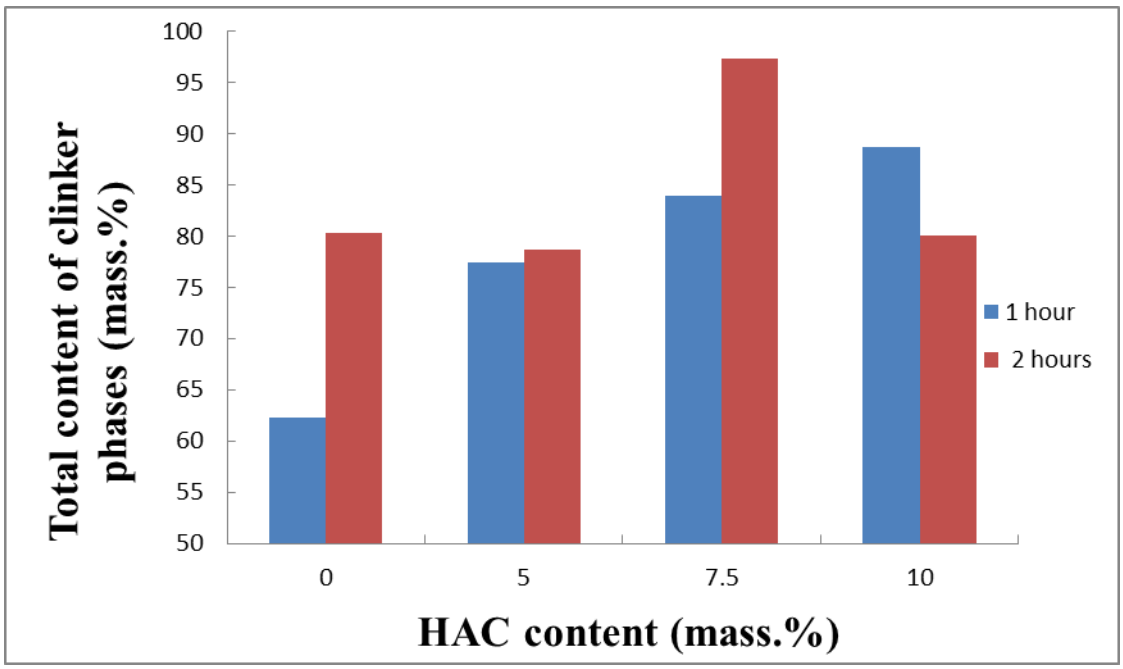

Figure 4. Dependence of total content of target clinker phases CA and CA_2 on HAC concentration; isothermal exposure time of 1h and 2h at 1350ºC

Figure 4 shows that with an increase in the proportion of added HAC, there was also a distinctive tendency to an increase in the total content of the largest phases CA and CA_2 at an

isothermal exposure time of 1h. In case of an increase in the duration of heat treatment up to 2h, the similar dependence was absent. At the same time, an extremum of total CA and CA_2 fraction was recorded, corresponding to HAC content of 7.5%.

4. Conclusions

It has been established that with the introduction of 0.5% H_3BO_3 into the charge, the design parity of CA and CA_2 phases was reached after heat treatment at 1350ºC for 2h. An increase in the content of the boric acid content to 1.0% allowed obtaining clinker phase composition to the designed one at 1250ºC and the exposure time of 1h. A further increase in processing temperature and exposure time did not lead to a change in the qualitative and quantitative phase composition of high alumina clinker. It was shown that the introduction of HAC additive into the charge affected the quantitative phase composition of the investigated products. The correlation was found between the amount of added HAC and the reduction of unreacted α-aluminum oxide content in the samples heat-treated at 1350ºC for 1h. The total content of the target phases CA and CA_2 tended to increase with an increasing proportion of the added HAC. The maximum of the total fraction of CA and CA_2 was recorded as increasing the heat treatment duration up to 2h.

Acknowledgement

The work was carried out at BSU with the financial support of the Ministry of Science and Higher Education of the Russian Federation under the agreement dated 14.12.2020 № 075-11-2020-038 on the implementation of the complex project "Development of import-substituting production of matrix systems components and thermal composite materials of new generation on their basis" in accordance with the Russian Federation Government Decree of 09.04.2010 №218.

The work was carried out using the scientific equipment of Belgorod State University's Technology and Materials Collaboration Centre.

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