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Formation mechanism of calcium aluminate compounds based on high-temperature solid-state reaction

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ABSTRACT

Calcium aluminate compounds were synthesized through the sintering process within the temperature ranges of 1100–1400 °C. The obtained compounds were characterized using XRD, FT-IR, SEM, EDS and DSC methods. The results show that the calcium aluminate compounds include $Ca_3Al_2O_6$, $Ca_5Al_6O_{14}$, $Ca_{12}Al_{14}O_{33}$, $CaAl_2O_4$, $CaAl_4O_7$ and $CaAl_{12}O_{19}$ in the sintered products with different molar ratios of CaO to Al_2O_3. The calcium aluminates present as a layered distribution. The outer layer calcium aluminate contains more CaO, and Al_2O_3 is in the core. CaO gradually diffuses into the distribution of Al_2O_3 during the solidstate reactions, and $Ca_3Al_2O_6$ and $Ca_5Al_6O_{14}$ are formed in the initial reaction stage. The variation in the molar ratios of CaO to Al_2O_3 in the mixtures has no effect on the phase constitutions of calcium aluminates in the initial stage of the reactions. All the calcium aluminates play roles as the intermediate phases to the final equilibrium phases and the molar ratios of equilibrium phases are similar with those of the sintered products. As the sintering process proceeds, the unit cell volumes of $Ca_3Al_2O_6$, $CaAl_2O_4$ and mayenite decrease, and the chemical formula of mayenite transforms from $Ca_{11.3}Al_{14}O_{32.3}$ to $Ca_{12}Al_{14}O_{33}$.

1. Introduction

Calcium aluminates are the main constituents of calcium aluminate cements, which are widely used in the construction industry [1,2]. Calcium aluminates can be used as persistent luminescence materials [3] when doped with Eu^{2+} ions and as potential candidates for optical information storage devices because of their photosensitive property [4,5]. Calcium aluminates are also used in the alumina production industry [6,7] as $CaAl_2O_4$ (CA) and $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) are the main constituents of clinkers during the lime sinter process, which are suitable for the alumina extraction from low-grade bauxites and non-bauxite resources such as nepheline, fly ash and red mud. Calcium aluminates are mostly produced by sintering over 1350 °C with mixtures of suitable proportions of aluminates and calcareous materials. However, it is difficult to obtain a target calcium aluminate through the sintering process, even though no un-reacted reactants are present in the final products [8–10]. When the molar ratio of CaO to Al_2O_3 (C/A) is 1, the calcium aluminates in the final products mainly include CA, $CaAl_4O_7$ (CA_2), $C_{12}A_7$ and a trace amount of un-reacted Al_2O_3 when the durations are between 1 h and 40 h and the temperatures are between 1300 °C and 1500 °C [11–13]. $C_{12}A_7$ and CA were observed as reaction intermediates during the formation of $Ca_3Al_2O_6$ (C_3A) when the C/A ratio is 3 with the materials of calcite and α-alumina (α-Al_2O_3) or gibbsite [14]. However, it was reported that the intermediate phases during the mayenite synthesis process involve CA, C_3A and C_5A_3 [15] when the C/A ratio is 1.7. Almost pure compounds of $C_{12}A_7$, CA and CA_2 can be formed with the matrix compositions, but the formation of C_3A is incomplete, indicating that the formation kinetics of C_3A is slower than other calcium aluminates [16].

Previous reports mainly studied the transformation processes of calcium aluminates when the C/A ratio is the specific stoichiometry of calcium aluminates such as CA, $C_{12}A_7$ and C_3A. In this paper, samples with different C/A ratios were synthesized through solid-state reactions to study the phase transformations and structural characteristics of calcium aluminates during the sintering process. The phase constitutions and distributions in the micro-regions as well as the thermal characteristics of the CaO–Al_2O_3 system were also investigated.

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2. Experimental

Analytically pure reagents of $CaCO_3$ and amorphous Al_2O_3 were used in the current work. The molar ratios of $CaCO_3$ to Al_2O_3 are from 0.60 to 3.00. The mixtures were mixed by zirconia beads with the diameter of 10 mm for 3 h. The mixtures were sintered from room temperature to 1400 °C in a $MoSi_2$ resistance furnace (KSL-1700-A2). The sintered products were ground to 100 μm after sintering. The formation processes of calcium aluminate compounds were investigated through air quenching from different temperatures. The crystal structure of mayenite was researched when the samples were sintered at 1350 °C and 1400 °C for different durations.

The X-ray diffraction (XRD) data were collected by a PHILIPS PW3050/60 with CuKα1 radiation ($\lambda_{Cu} = 1.54056$ Å) operated at 40 kV and 40 mA. Data were recorded in the 2θ ranges of 10–75° with the resolution of 0.026°. XRD patterns were resolved by Rietveld analysis using MDI Jade software. The phases in samples were confirmed by the PDF2-2004 database [17]. High-purity SiO_2 was used to reduce the parameter errors of the XRD instrument. The sintered products were mixed with MgO with a mass percentage of 10% to confirm the phase content variation according to the relative intensity of the characteristic peaks of MgO and the target phase. The fractions of the observed phases were determined by the refined scale factors in the Rietveld refinements. The crystallographic data for the analysis were taken from the Inorganic Crystal Structure Database (ICSD) [18]. The pseudo-Voigt function was used during the fitting processes of spectra, and nearly 40 parameters were fitted for each XRD spectrum. The parameters include scale factors and unit cell parameters of phases, atomic coordinates, isotropic value, occupancy of atoms, a 0 point error, two profile shape parameters (eta value for pseudo-Voigt), and two profile asymmetry parameters. The weight fraction of phase α with good crystallization was calculated according to Formula (1),

$$\omega_\alpha = \frac{S_\alpha Z_\alpha M_\alpha V_\alpha}{\sum_{\alpha=1}^{n} S_\alpha Z_\alpha M_\alpha V_\alpha} \tag{1}$$

where ω_α is the fraction of phase α, S is the scale factor, Z is the number of formula units in the unit cell, M is the formula unit mass, and V is the unit cell volume.

The microstructural analyses were carried out by a scanning electron microscopy (SEM, SHIMADZU SSX-550) with an energy-dispersive X-ray spectroscopy (EDS, DX-4). The samples were polished in water-free ethylene glycol using SiC papers and cleaned by ultra-sound method in water-free ethylene glycol. The differential scanning calorimetry (DSC) was performed on a NETZSCH STA409C/CD with the heating and cooling rates of 10 °C/min. The absorption spectra of Fourier transform infrared spectroscopy (FTIR) of the sintered samples were obtained by a SHIMADZU IR Prestige-21 apparatus with the matrix material of KBr.

3. Results and discussion

3.1. Structural transformation of calculate aluminates

The transformations of calcium aluminates were firstly investigated though XRD and FT-IR methods with the sintered products by air quenching to room temperature. The products were taken out from the furnace immediately when the temperature increases to 1100 °C, 1150 °C, 1325 °C, 1350 °C, 1375 °C and 1400 °C, respectively. Mixtures with the C/A ratios of 0.60, 1.70 and 3.00 were heated to 1100 °C or 1150 °C. As shown in Fig. 1, no $CaCO_3$ was observed suggesting that $CaCO_3$ decomposes entirely when the temperature increases from 825 °C to 1100 °C. Hence, most of the calcium aluminates are formed by CaO and Al_2O_3. The Al_2O_3 used is amorphous, so none of the characteristic peaks of Al_2O_3 were observed. However, trace amounts of α-Al_2O_3 are present when the temperature increases to 1150 °C, as given in Fig. 2. The calcium aluminates include C_3A, C_5A_3 and a trace amount of CA. The characteristic peaks of C_5A_3 in Figs. 1 and 2 are almost the same with the results of Ruszak [15]. The contents of the Ca-rich phases C_5A_3 and C_3A increase with the increasing C/A ratio. The constitutions of calcium aluminates in the samples show no significant difference, indicating that varying the C/A ratio has little effect on the phase fractions during the initial stage of the solid-state reactions.

The FT-IR spectra of samples heated to 1100 °C when the C/A ratios are 0.60, 1.70 and 3.00 are shown in Fig. 3. The spectrum of CA contains a whole set of weaker absorption bands in the lower-frequency part of 420–730 cm^{-1} [19,20]. Therefore, the absorption bands of 420 cm^{-1}, 455 cm^{-1}, 520 cm^{-1}, 643 cm^{-1} and 686 cm^{-1} belong to CA. The bands of 420 cm^{-1} and 455 cm^{-1} can be assigned to bending vibrations [19,20]. The intensities of the absorption peaks are the highest when the C/A ratio is 0.60 indicating that the CA content is the highest. The striking absorption band of $C_{12}A_7$ spectrum is at 850 cm^{-1} corresponding to the vibrations of a bonded tetrahedral [19]. A weak absorption band exists at 843 cm^{-1} when the C/A ratio is 3.00 suggesting that a trace amount of $C_{12}A_7$ is formed. The absorption bands at 817 cm^{-1} and 744 cm^{-1} corresponds to C_3A, which was reported at 811 cm^{-1} and 738 cm^{-1} [21]. The intensities of the both absorption bands are highest in samples with the C/A ratio is 3.00 suggesting that the content of $C_{12}A_7$ is the highest. The bands of 898 cm^{-1} and 866 cm^{-1} are the absorption peaks of C_5A_3, which were also confirmed by Kokhman et al [22]. The intensities of the both absorption bands gradually increase when the C/A ratio increases from 0.60 to 3.00, which shows the increasing content of C_5A_3 in the samples.

The XRD patterns of the sintered products sintered from 1325 °C to 1400 °C are shown in Fig. 4. The phases mainly include CA, CA_2, C_3A, C_5A_3 and $C_{12}A_7$. A trace amount of $C_{12}A_7$ is formed before 1400 °C. The phase diagram of CaO and Al_2O_3 was determined by Nurse, Hallatedt, and Eriksson et al. [23–25], but it does not contain C_5A_3 which can be formed in the dry air [26]. Moreover, it has been reported that C_5A_3 is the precursor of $C_{12}A_7$ [15]. None of the characteristic peaks of C_5A_3 were observed in samples sintered at 1400 °C indicating that C_5A_3 is a metastable phase during the sintering process of calcium aluminates. Peaks of CaO are not present after sintering to 1325 °C or higher temperatures, and a part of Al_2O_3 exists as α-Al_2O_3. The XRD patterns have small changes when the temperature increases from 1325 °C to 1375 °C. The phase fractions of the samples can be calculated according to Formula (2). The phase content of the sintered products can be calculated according to Formulae (3) and (4) when 10% MgO was added, as given in Table 1. The RIR values of CA, CA_2, C_3A and Al_2O_3 are 0.61, 1.17, 3.27 and 1.00, respectively. The content of C_3A is the highest, and the contents of CA and CA_2 increase slightly with decrease of the Al_2O_3 content. The fractions of calcium aluminates do not experience significant changes when the sintering temperature increases from 1325 °C to 1375 °C. Comparing the phase contents of calcium aluminates formed at 1375 °C and 1400 °C, C_5A_3, C_3A and CA_2 transform to other calcium aluminates and the samples mainly include $C_{12}A_7$ with small amounts of CA and C_3A when the sintering temperature increases to 1400 °C (see Fig. 5).

$$\omega_i = \frac{I_i/\mathrm{RIR}_i}{\sum_{i=1}^{n} I_i/\mathrm{RIR}_i} \tag{2}$$