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Calcium aluminate composites with controlled duplex structures: I. Hydration reaction and densification

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Three calcium aluminate (CA) powders were synthesized and added into Al_2O_3 for the preparation of ceramic-based composites by the processes, either dry-pressing (D), colloidal dispersion/filtration (SH), and hydration-gelation (H). The heat evolution, gelation and related hydration processes of the aluminates and the admixtures were investigated. Besides, the green and the sintering properties of the $CaO*Al_2O_3$(CA)-Al_2O_3 admixtures were measured and are reported. The effects of acetic acid and alcohol (retarding agents) on the hydration reaction of the hydrates were studied, and used for the control of the gelation process. The sintering results of the admixtures with CA indicated the formation of CA_6 phase greatly influenced the densification rate and final porosity.

Key words: calcium aluminate, composite, hydration, gelation, densification.

Introduction

Calcium aluminate includes at least seven aluminate compounds in the CaO-Al_2O_3 binary system, which are the important ingredients in high alumina cements (HACs) or high temperature castable refractories for continuous steel casting. Only CA_2 (CaO-$2Al_2O_3$), CA (CaO-Al_2O_3), $C_{12}A_7$ ($12Ca0$-$7Al_2O_3$), and C_3A ($3CaO$-$A1_20_3$) have apparent hydration and gelation reactions in humid and ambient conditions. Those aluminates undergo various rates of hydration, which are mainly controlled by the solid/water (S/W) ratio and the type of impurity. In addition, the reaction produces Al-hydrate (AH_3) and Ca-hydrate are in amorphous state. These hydrates may transfer to other crystalline Ca-Al hydrates, such as CAH_{10} or C_2AH_8, in the curing stage.

The hydration reaction of the calcium aluminates has been extensively studied by several techniques, e.g. NMR [1, 2], to determine the various crystalline Ca-Al hydrate phases at ambient temperatures from 4 °C to 70 °C. The morphologies of the hydrates were reported to be thin plates, needles, hexagonal prisms, or gel type [3]. The amount of these crystalline or amorphous hydrates is responsible for the green strength of cement materials.

One opportunity for the improvement via microstructural design of ceramic composites [4-6] has recently become obvious by introducing new processing concepts. One example given by Lutz and Claussen [4] who prepared a duplex structure in ZrO_2 materials and reported the advantages in the improvements of toughness and thermal shock resistance. Padture and Lawn [5] demonstrated an impact-resistant capability of a new SiC material with a tabular grain microstructure. Moreover, the case of Al_2O_3 reinforced with submicrometric SiC particulates, a so-called nanocomposite, prepared by Niihara and Nakahira [5] performed a several-fold increase in fracture strength and toughness. Unique structures in company with effective mechanisms offer an improvement of mechanical properties of ceramic composites.

This study has used three types of calcium aluminates to produce ceramic composites with different microstructures by means of hydration and gelation reactions. The reactions of the CA powder was characterized in detail in the first part of the study, and compared with that of $C_{12}A_7$ and C_3A powders. The properties, including the viscosity, gelation, green and sintered density of the CA-Al_2O_3 admixtures were measured and evaluated in order to differentiate the effects of the processes, either dry-pressing, hydration-gelation, colloidal dispersion/filtration. Also, a systematic study of the densification and phase formation of the Ca-aluminates, especially the CA_6 phase was conducted in this study. The second part will deal with the microstructural development and the mechanical properties of the composites after the appropriate sintering.

Experimental

Synthesis of calcium aluminates

Three calcium aluminate powders, C_3A, CA and $C_{12}A_7$, were synthesized by a mixing process of Al_2O_3

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Table 1. Properties of the chemicals used in this study

Property	Alumina	Calcia	Acidic acid	Semicarbazide hydrochloride
Chemical formulation	Al_2O_3	CaO	CH_3COOH	$CH_5ON_3{\cdot}HCl$
Purity	99.7%	98.0%	Regent grade	Regent grade
Impurities	Na_2O (800 ppm) SiO_2 (800 ppm) Fe_2O_3 (100 ppm) MgO (500 ppm)	Fe_2O_3 (150 ppm) MgO (1.98%) Cl (500 ppm) SO_4 (800 ppm)	–	–
Appearance	White powder	White powder	Transparent liquid	White powder

powder (A16-SG, Alcoa Chemical Co., USA) and CaO powder (98% pure, Nacalai Tesque Co., Jpn) in an iso-propanol solution. The CaO was pre-calcined at 750 °C for 2 h in order to dehydrate the $Ca(OH)_2$. After the suspension was dried at 85 °C for 2 h and calcined at 650 °C for 4 h, the powder mixture was re-calcined at 1300 °C for 5 h. The calcined powder was then pulverized and sieved through a 400 mesh screen. The specific surface area and crystalline phases of the aluminate powders were determined by the BET method and X-ray diffractometry (XRD), respectively. C_3A and $C_{12}A_7$ powders show a pure single phase without CaO and Al_2O_3 residues. The CA powder still had a little CA_2 and C_3A phases.

Hydration reaction/dispersion/filtration process

There were three routes to produce calcium aluminate/Al_2O_3 composites. Briefly, one is by a hydration/gelation reaction process which mixed Ca-aluminate powder in an Al_2O_3 aqueous solution, then the slurry was cast into a polyacrylic mold with the dimensions of 2 × 6 × 8 cm^3, curing at 50 °C until gelling. The sample was assigned "HCA_x". If the slurry was further turbo-mixing and pressure-filtered, the sample was assigned "$SHCA_x$". The third route used die-pressing of a powder mixture of the calcium aluminates and Al_2O_3 powder. The sample was assigned as "DCA_x". In order to control the gelation time of the calcium aluminate in solution, several additives were used, including semicarbazide hydrochloride (SHCl) as the dispersant for the Al_2O_3 suspension and acidic acid (Ac) as the gelation retarding agent for the composite in solution. The S/W ratio and the amount of the additive used for the suspension are assigned as the abbreviation of $H_xCA3S1Ac_y$, where H_x means that the water content is x vol% with respect to solid phases, CA3 means 3 wt% CA added in 97 wt% Al_2O_3 powder, S1 represents 1 wt% SHCl added in Al_2O_3 suspension, and Ac_y means that y wt% acetic acid is added based on the mass of the CA powder. Detailed information of the chemicals used in this study is shown in Table 1.

Characterization

The heat emission of calcium aluminate powders or the mixtures during hydration was measured by a thermal measurement device with a reaction batch controlled from 0 °C to 50 °C. The viscosity of the suspension was measured by a viscometer (Model DVII, Brookfield Eng. Lab. Inc., USA). The dried and sintered composite bodies were also characterized by a thermal mechanical test (TMA, Theta Co. USA) for sintering shrinkage, and microstructural observation by environmental scanning electron microscopy (ESEM, Cambridge, England). The

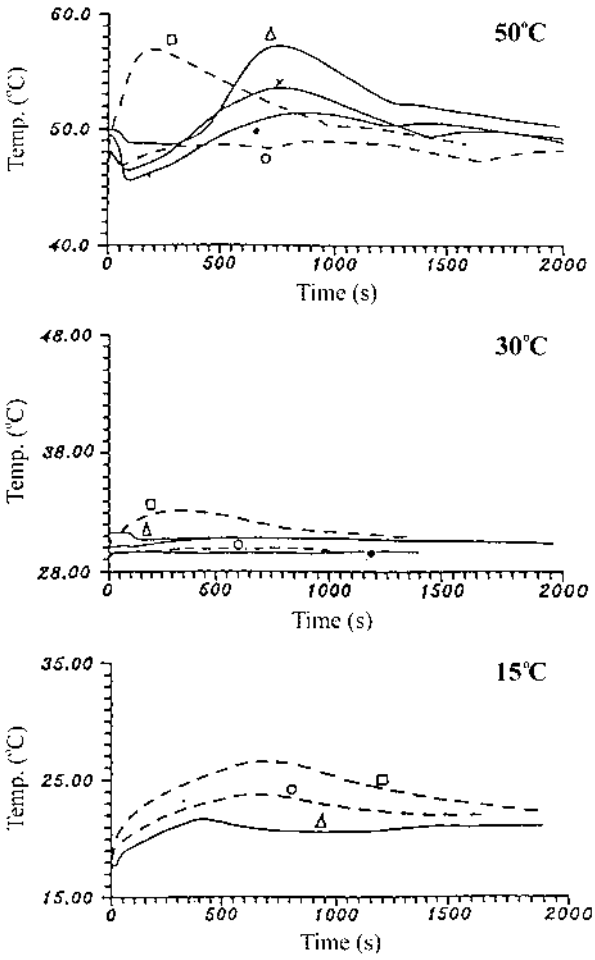

Fig. 1. Hydration reaction of CA, $C_{12}A_7$, C_3A at various processing temperatures or with the addition of ethanol. Triangle: CA+H_2O, square: $C_{12}A_7$ + H_2O, circle: C_3A + H_2O, cross: CA + (20% ethanol + 80% H_2O), full circle: CA + (40% ethanol + 60% H_2O).

crystalline phases of calcined samples were analyzed by X-ray diffractometry (PW1792, Philips, Netherlands).

Results and Discussion

Hydration reaction

The temperature curves of C_3A, CA and $C_{12}A_7$ samples in a solid/water (S/W) ratio 5.0/1.5 are shown in Fig. 1, which indicates that the reactions are exothermic and the heat emission gradually declines over 30 min. The samples tested at 30 °C underwent relatively milder reaction than the others. The batches with $C_{12}A_7 + H_2O$ emitted their hydration heat faster and more apparently than the other aluminates.

The reaction was slower for the CA hydration. The CA powder needed a longer incubation period than C_3A and $C_{12}A_7$. Although the CA has a slow reaction rate at 30 °C, the processing requires a longer time to achieve a will dispersed condition if mixing with Al_2O_3 powder. The fastest consolidation by the hydration-gelation was obtained at 50 °C in 10 min. Another result showed that the reactions could be retarded by the addition of ethanol in water. It is believed that a methyl (-OCH_3) group occupies surface sites of calcium aluminate, resulting in a slow hydration reaction on the surface.

Figure 2 is the heat evolution of the CA powder in S/W ratio of 5.0/3.0 tested at 30, 40 or 50 °C. The curves revealed that the hydration reaction of CA could reach a maximum heat emission in 15 min, and totally decayed in 10 min, but took longer for the reaction held at 40 °C. The reaction at 30 °C took a very long time to get the heat emission, taking almost 9 h and vanishing in 1 h. The possible reasons for causing the dramatic change at various temperatures are the volumetric expansion of the newly-formed hydrates [6, 7]. CAH_{10} and C_2AH_8 were detected with the CA/water mixture curing for 9 h at 30 °C. But, additional C_3AH_6 and gibbsite phases were found after curing for 24 h. This means that the formation rate of the hydrates (CAH_{10} and C_2AH_8) on the surface of the CA particles is slow, and consequently less volume expansion resulted.

One set of the cured samples (a mixture of 20 wt% CA with Al_2O_3) was observed by ESEM. Only the one cured for 1 day is shown in Fig. 3. The microstructure of the fracture surface changes from granular (1 d) to uniform, then to crystalline (30 d). Figure 3(a) reveals two basic features, one as marked as "A" is Al_2O_3 particles, which have been bridged by gel material (Fig. 3(b). The bridging material can be a precipitate of amorphous $Al(OH)_3$ [1]. A larger feature, as marked as "B", is a partially hydrated CA particle. This surface morphology corresponds to the formation of very fine C_xAH_y hydrates mixed with Al-hydrate gel material. The thickness of the C_xAH_y hydrate layer is of the order of nm, [1, 2] and is amorphous in the initial stage. After the end of the incubation period, a

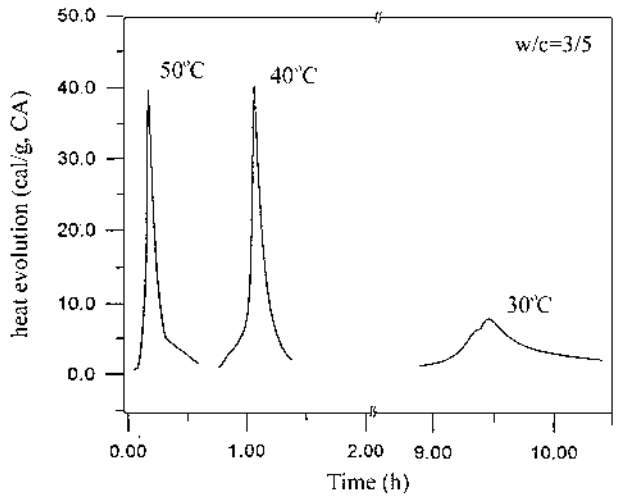

Fig. 2. Heat evolution of the hydration reaction of CA in a water/solid (W/S) ratio of 3/5 processed at (a) various temperatures, or (b) in different W/S ratios.

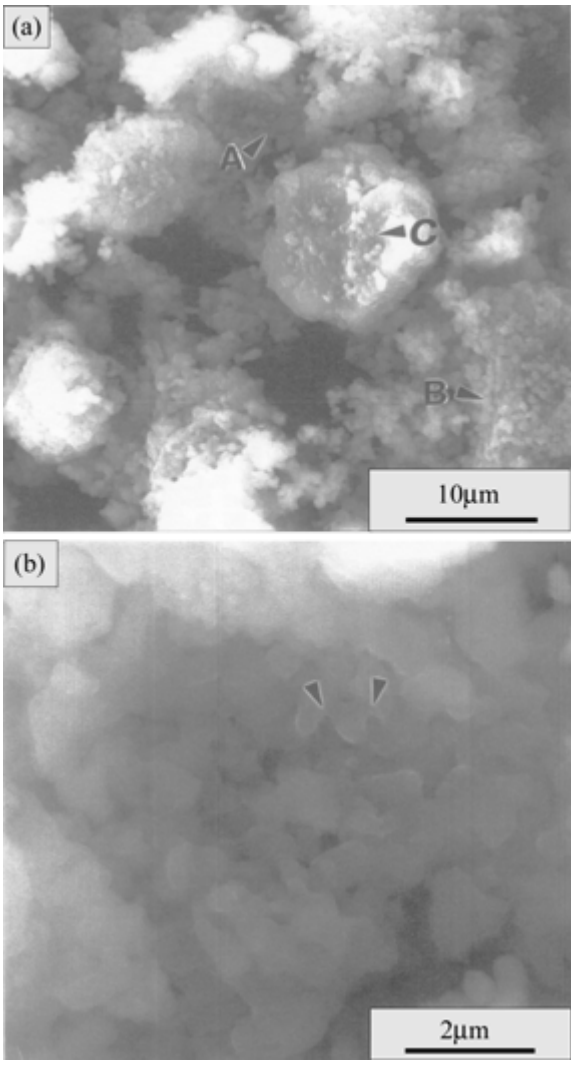

Fig. 3. ESEM micrographs of hydrated 20 wt% CA-Al_2O_3 admixture cured for 1 day.

protective hydrated layer on CA surface is destroyed. Crystal ripening from the amorphous C_xAH_y hydrates on CA continuously grown by a dissolution-crystallization mechanism cause an increase in viscosity.

Effect of acetic acid on gelation

The gelation of a CA-Al_2O_3-water mixture is defined as the point when the viscosity increases dramatically. Rodger and Double [8] have reported the effects of various chemicals on the hydration reaction of calcium aluminates. Citric acid retarded the reaction by precipitation of a passive gel on the surface of CA. As a result, the hydrates were not growing regularly. But cation species, e.g. Li^+, Cs^+, Mg^{2+} ions, tends to form aluminate phases, which enhance the nucleation of Ca-Al hydrate crystals. Therefore, the cation impurities have the opposite effect, making the growth of Ca-Al hydrate faster.

Figure 4 gives the apparent viscosities of the admixtures with different amounts of acidic acid (Ac) from 0 to 10 wt% based on CA content. The admixture of $H_{70}CA3S_1Ac_0$ will gel in 2 min if held at 70 °C, but becomes a gel in 50 min at 25 °C. As compared to $H_{70}CA3S_1Ac_{10}$ (Fig. 4(d)), the addition of the acid effectively reduces the gelation time.

The gelation time (t_g), in fact, is a function of temperature, revealing a thermal activation process. The plot of logarithmic t_g versus the reciprocal of curing temperature (T) is shown in Fig. 5. The slope of the best fitting lines represents the activation energy (Q) of the hydration reaction. The Arrihenius relationship of the 3 wt% Ca in Al_2O_3 suspension with the additives is shown as below.

$$\ln(t_g) = \ln(A) - \frac{Q}{R}\left(\frac{1}{T}\right) \quad (1)$$

Where A is a constant, and R is the gas constant. The admixtures without or with 2.5 wt% acetic acid showed

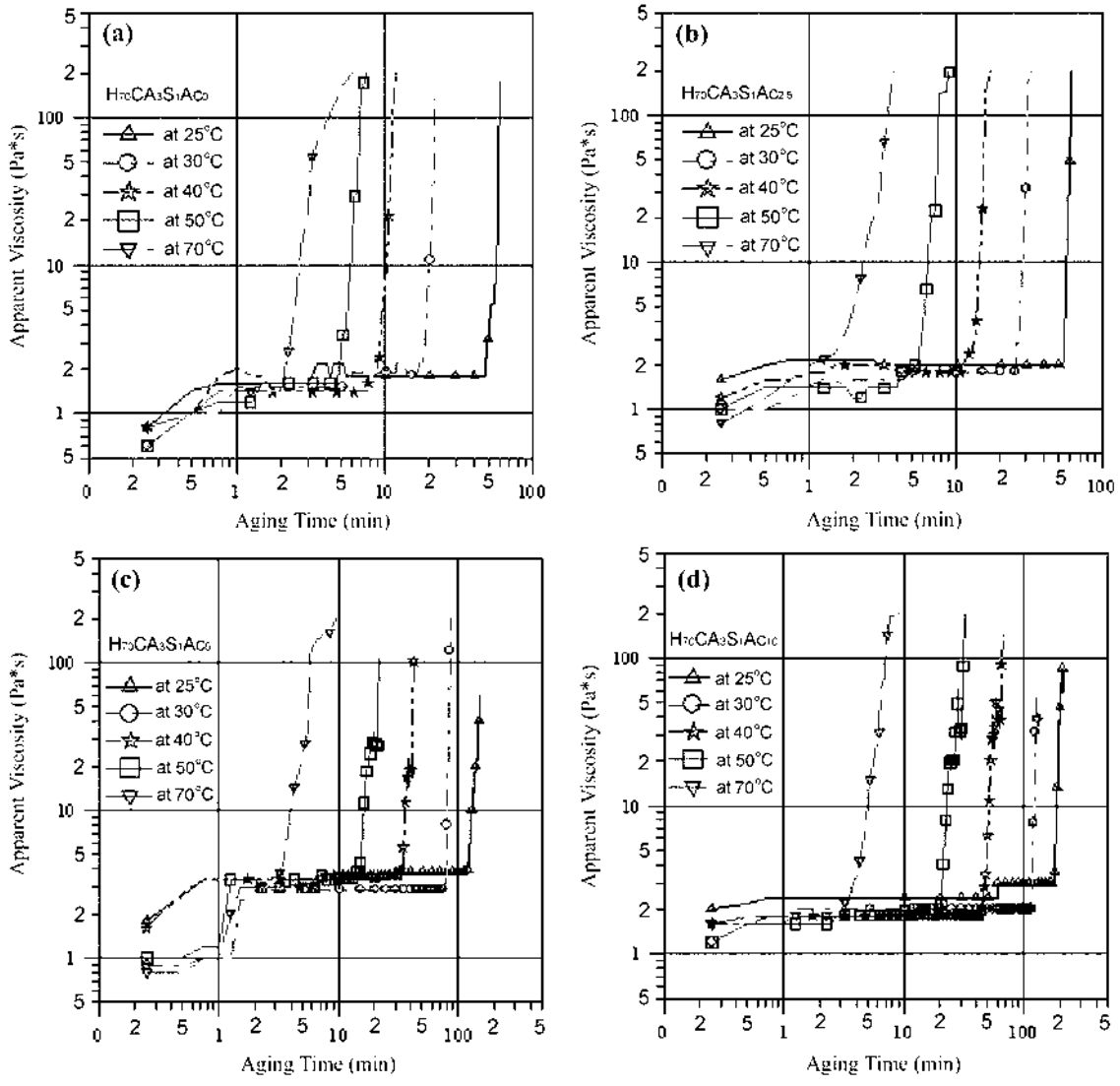

Fig. 4. Apparent viscosity of admixtures with various amounts of retarding agent plotted against aging time at different temperatures (shear rate 0.084 s^{-1}) (a) $H_{70}CA_3S_1Ac_0$, (b) $H_{70}CA_3S_1Ac_{2.5}$, (c) $H_{70}CA_3S_1Ac_5$, (d) $H_{70}CA_3S_1Ac_{10}$.

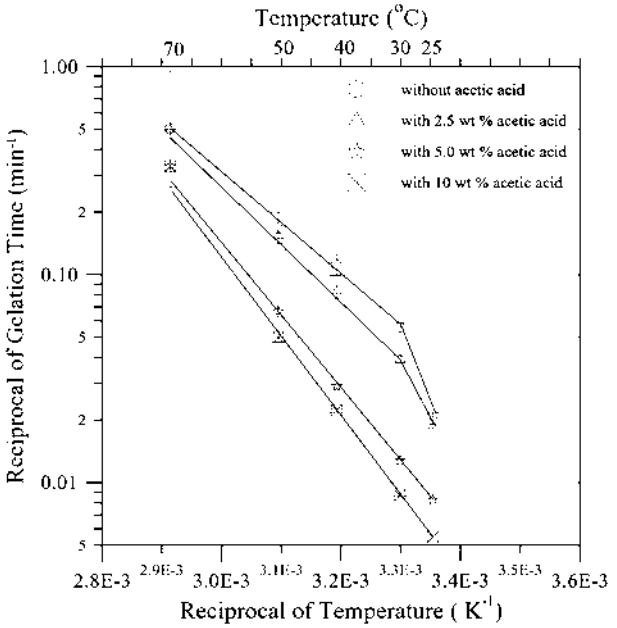

Fig. 5. Gelation time in logarithmic scale of admixtures with various amounts of retarding agent plotted against 1/T.

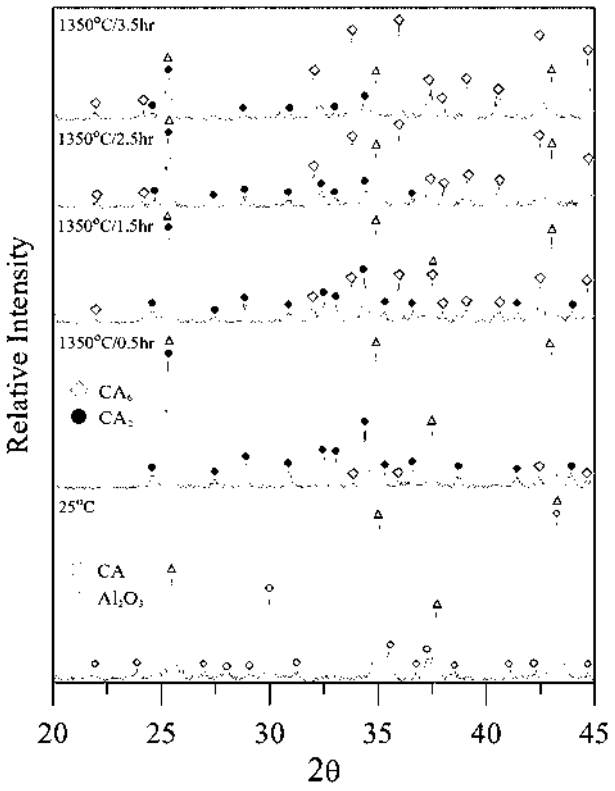

Fig. 6. XRD patterns of powder mixtures held at 1350 °C and soaked for various periods. Note that CA_6 phase can be observed when sintered at 1350 °C for 0.5 h.

a two-stage dependence. At low temperatures (25-30 °C), the value of the activation energy is around 113-147 kJ/g·mol (Table 2), which is much higher than those processed at higher temperatures or with more acetic acid. Two admixtures with acetic acid at 5 or 10 wt% had a temperature dependence with one activation energy of about 67-72 kJ/g·mol, as shown in Table 2. Our XRD data revealed that the CA particles slowly transformed to crystalline C_2AH_8 in contact with H_2O at 25-30 °C. But the nucleation of the hydrate became easier as the temperature increased. Based on the data of activation energy and gelation time, we chose 5 wt% acetic acid added into the formulation to prepare the green aluminate composites.

Sintering and phase formation

Figure 6 are the XRD patterns of CA-Al_2O_3 mixtures (1 : 5 molar ratio) sintered to 1350 °C for various periods. Two phases, CA_2 and minor CA_6, can be obtained in 0.5 h. As the treatment extended to 3.5 h, only Al_2O_3 and CA_6 phases could be identified, and CA_2 was hardly observed. Our DTA results also indicated that one endothermic peak could be detected at 1320 °C, implying the formation of CA_6 phase. More detailed phase identification of the admixture CA-Al_2O_3 was conducted [9], and revealed that the crystalline $C_{12}A_7$ was first detected at 800 °C. Then CA, CA_2 and CA_6 were found at 1050 °C, 1260 °C, and 1350 °C, respectively. Only CA_6 in equilibrium with Al_2O_3 was found in the alumina-rich admixture if sintered at 1660 °C for longer than 8 h.

The dilatometric and differential curves of three CA-Al_2O_3 samples are shown in Fig. 7, of the samples prepared by the three specified processes. The green densities of the samples are 2.5 g/ml ($SHCA_3$), 2.2 g/ml (DCA_3), and 2.0 g/ml (HCA_3), respectively. The shrinkage started from 1100 °C, and the maximum sintering rate varied from 1300-1400 °C. It was noted that the turning point of the sintering rate of a DCA_3 sample was 24 °C lower than that of the HCA_3. The sintering rate was reduced due to the formation of CA_6. Tze [9] has proven that the CA ingredient was distributed more uniformly in DCA_3 than in HCA_3. The final density of the HCA_3 showed the most extensive shrinkage partially due to the lowest green density. Nearly a 19% linear shrinkage was detected if treated at 1500 °C.

Table 2. Activation energy of hydration reaction doped with different amounts of acetic acid

Temperature range (°C)	Acetic acid (wt%, based on CA)			
	0.0	2.5	5.0	10.0
25-30	147 kJ/g·mol	113 kJ/g·mol	67 kJ/g·mol	72 kJ/g·mol
30-70	47 kJ/g·mol	55 kJ/g·mol	67 kJ/g·mol	72 kJ/g·mol

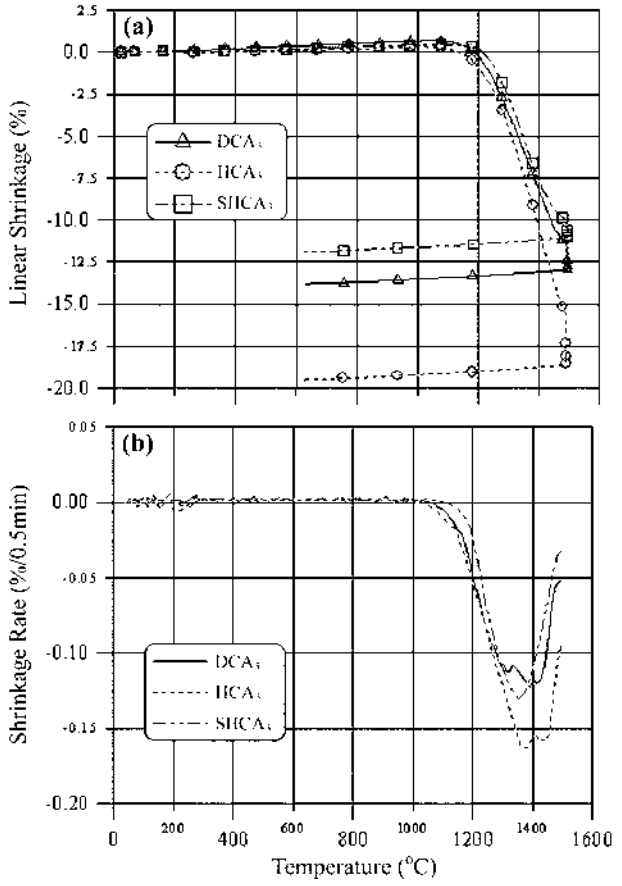

Fig. 7. Dilatometric and differential curves of green bodies of DCA_3, HCA_3 and $SHCA_3$, sintered at a rate of 5 K/min. (a) Linear shrinkage (%) of samples, and (b) shrinkage rate (%/0.5 min) plotted as a function of temperature.

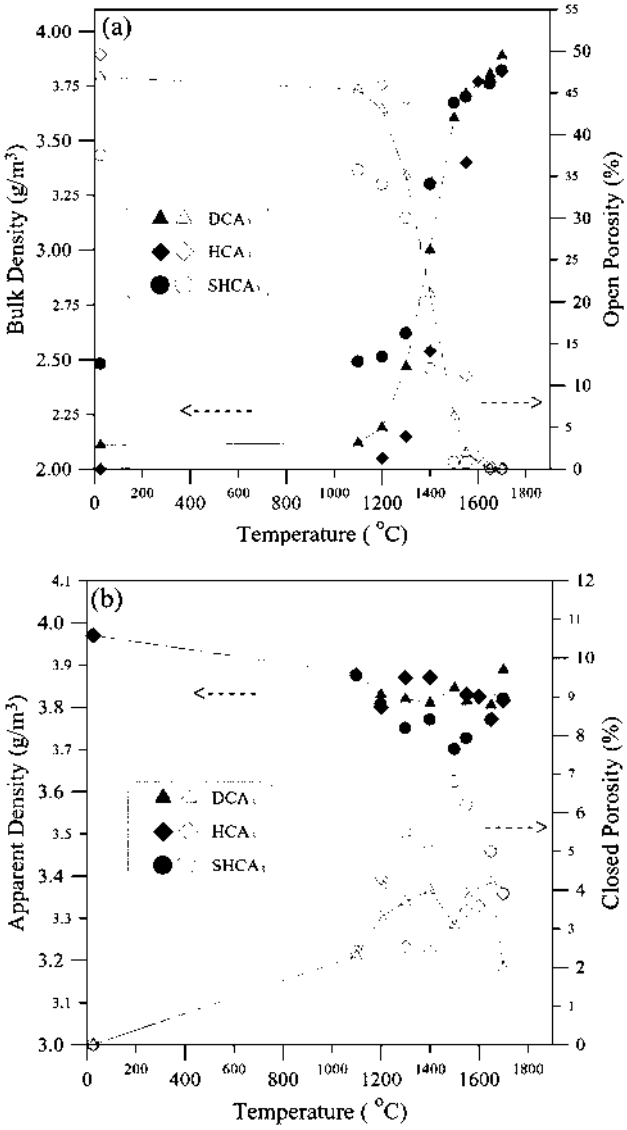

Fig. 8. Density and porosity of DCA_3, HCA_3 and $SHCA_3$ green bodies as a function of temperature. (a) bulk density and open porosity (b) apparent density and closed porosity changed with temperature.

The densities, open and closed porosities, of the samples treated at various temperature are shown in Fig. 8. The ramping rate of the sintering above 1200 °C was 2 K/min. The density results generally showed an increase above 1200 °C, and slow down accordingly to the trend of linear shrinkage reported in the previous Figure. Almost no open porosity was left at the sintering temperature of 1500 °C, but 3% to 6% closed porosity was detected, when sintering between 1300 °C and 1700 °C.

Conclusions

The hydration and sintering behaviors of several calcium aluminates mixed with Al_2O_3 powders were investigated. The CA powder had the slowest hydration rate at 30 °C, especially dispersed in a (water + ethanol) solution. Acetic acid was an effective retarding agent to extend the gelation of the aluminates, and 5 wt% of the acid was able to change the hydration reaction of CA to one stage, revealing an activation energy of 67 kJ/g·mol at ambient temperatures. The CA in 3 wt% was able to consolidate the CA-Al_2O_3 admixture by an appropriate hydration reaction.

The green density of the composites by the processes, either dry-pressing (D), colloidal dispersion/filtration (SH) was better than the samples produced by hydration-gelation (H). However, the distribution of the CA ingredient in the green sample affected the sintering kinetics of the CA-Al_2O_3 admixture. This is because of the growth of the CA_6 phase above 1320 °C, strongly influencing the densification kinetics of the admixture. The retardation due to the CA_6 phase formation made the samples have a few percent of closed porosity (ca. 5%) and various microstructures, which will be reported later.

Acknowledgement

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