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Hydration of β-dicalcium silicate at high temperatures under hydrothermal conditions

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Abstract

Hydration of β-dicalcium silicate was carried out under hydrothermal conditions at different temperatures from 50 °C to 400 °C up to 5 days by using two methods to start the reactions at room temperature or at a desired reaction temperature. 9 C-S-H phases with the same Ca/Si ratio as precursor (γ-dicalcium silicate hydrate and α-dicalcium silicate hydrate and dellaite), Ca-rich compositions (jaffeite and reinhardbraunsite), Si-rich compositions ($Ca_8Si_5O_{18}$, kilchoanite and foshagite), and C-S-H gel were obtained at the initial stage of the hydration of β-dicalcium silicate. The reaction products were different in dependence in the hydrothermal processes. It was found that α-dicalcium silicate hydrate was directly formed from β-dicalcium silicate at low temperatures below 220 °C. The products obtained at above 240 °C were different in dependence in the hydrothermal processes, due to the different decomposition route of γ-dicalcium silicate hydrate, the initial product from β-dicalcium silicate. The room temperature mixing method gave reinhardbraunsite and kilchoanite through $Ca_8Si_5O_{18}$. In the case of the high temperature mixing method, γ-dicalcium silicate hydrate decomposed to from $Ca_8Si_5O_{18}$ and reinhardbraunsite with jaffeite, then $Ca_8Si_5O_{18}$ decomposed to from jaffeite and kilchoanite, and final products at 400 °C were reinhardbraunsite and foshagite which was formed from kilchoanite.

Keywords: Hydration; β-Dicalcium silicate; Calcium-silicate-hydrates (C-S-H); Hydrothermal treatment; High temperature mixing method

1. Introduction

β-Dicalcium silicate is one of the most important components of Portland cement. Many researchers [1–5] have studied on hydration activity and hydration process of β-dicalcium silicate. Though Pritts and Daugherty [6] and Shibata et al. [7] showed that the hydration activity of β-dicalcium silicate is high without stabilizers, they did not investigate the hydration behaviors. By using pure β-dicalcium silicate prepared from hillebrandite, Ishida et al. [2,3] investigated its hydration behavior at 25 °C with water/solid (w/s) ratio of 1.0 and 0.5, and showed that hydration of β-dicalcium silicate completed in 14 and 28 days, respectively. Ishida et al. [8] also investigated the effect of curing temperatures (40, 60 and 80 °C) on the hydration of β-dicalcium silicate, and reported that the hydration was completed in 1 day at 80 °C and in 14 days at 40 °C. The hydration product was amorphous in their experiments [2,3,8], and they used ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS NMR) to observe the structural change of C-S-H (calcium silicate hydrate) gel during curing.

Cements used for casing geothermal wells or deep oil-wells are exposed to high temperature and pressure. In geothermal wells, the temperature reaches as high as 400 °C [9]. The hydration of β-dicalcium silicate, however, has not been investigated at high temperatures, and the hydrated phases formed from β-dicalcium silicate at high temperatures have not been identified. Though the current researchers have focused on synthesis and elucidation of structural relationship of the C-S-H compounds [10,11], there still remains a great deal of works to be done to understand the cement systems. In order to provide a basis of designing cements for applications of geothermal wells or deep oil-wells, one must know C-S-H phases and their formation mechanism at high temperatures.

Mitsuda et al. [12] first designed a rapid heating method to investigate the formation of kilchoanite, and also showed hydrothermal formation of γ-dicalcium silicate as an initial phase from lime-silica mixture by this method [13] without formation of C-S-H gel. It is clear that the hydrothermal

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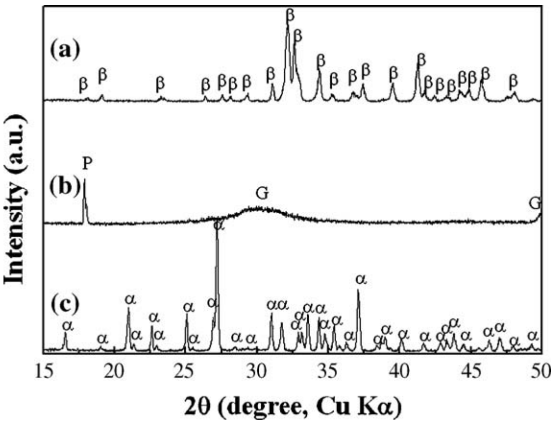

Fig. 1. XRD patterns of β-dicalcium silicate (a) and the products obtained by the room temperature mixing method at 80 °C (b), 150 °C (c) for 1 day.

processing has large effects on formation C-S-H compounds. In the present research, we modified the method and developed the high temperature mixing method to initiate the hydrations of β-dicalcium silicate at high temperatures with a fixed w/s ratio. We investigated the effect of hydrothermal processes of the high temperature and room temperature mixing method on the formation of calcium silicate hydrates from β-dicalcium silicate at high temperatures up to 400 °C.

2. Experimental procedure

The raw materials were calcium carbonate (Wako Pure Chemical Industries, Ltd., >99.9%), amorphous silica powder (Aerosil, Wako Pure Chemical Industries, Ltd., >99.9%). β-Dicalcium silicate was prepared by calcination of the mixture of calcium carbonate and amorphous silica powder with CaO/SiO_2 (Ca/Si) molar ratio of 2.0 at 1000 °C for 3 h. The formation of β-dicalcium silicate was confirmed by powder X-ray diffractions (Fig. 1a). After grinding to get a powder with specific surface area of 7.7 m^2/g, 1 g of β-dicalcium silicate powder was used for each of experiments. The weight ratio of w/s was fixed to be 20.

Hydrothermal treatments were carried out in stainless steel or Hastelloy C autoclaves (inner volume of 50 cm^3) with agitation at temperatures from 50 °C to 400 °C up to 5 days. The temperature was controlled by a thermocouple on the wall of the autoclave and the reaction temperature was monitored by a thermocouple in the autoclave. The temperature controlled on the wall of the autoclave was much higher than the desired reaction temperature, and their relation was determined for each reaction temperature by separate experiments.

In this study, two hydrothermal reaction methods were employed. For the room temperature mixing method, β-dicalcium silicate powder was mixed with the distilled water in the autoclave at room temperature, and then the autoclave was heated to a desired temperature at a rate of 10 °C/min. In the case of the high temperature mixing method, only β-dicalcium silicate powder was placed in the autoclave and hydration reactions started at a desired temperature by injection of heated distilled water into the preheated autoclave. The temperature inside the autoclave increased quickly by injection of heated water and reached higher temperature (about 10 °C) than a desired reaction temperature. In a few minutes, the temperature inside the autoclave decreased to the desired reaction temperature without adjusting the controlling temperature.

After hydrothermal treatments, the autoclave was quenched to room temperature. The products were filtered by using a small amount of distilled water, and dried in vacuum. The crystalline phases of the hydration products were identified by powder X-ray diffractions (XRD, Rigaku RTP-300 RC) with Cu Kα radiation (40 kV and 100 mA). A scanning electron microscope (SEM; Hitachi S-530) was used to observe the morphology of the products.

3. Results and discussion

The hydration products obtained from β-dicalcium silicate and reactant β-dicalcium silicate are shown in Table 1 with their abbreviations. The products were varied by hydrothermal processes and reaction temperatures.

3.1. Hydration products obtained by the room temperature mixing method

Figs. 1 and 2 show the XRD patterns of the hydration products obtained by the room temperature mixing method at various temperatures. Most of the patterns were complicated due to overlapped diffractions of the different hydration products. The SEM observation was helpful to identify the crystalline phases, because each crystalline product has a characteristic appearance, thin rectangular plate for α-dicalcium silicate hydrate [14], prismatic crystals for dellaite [14] and bundles of rod-like crystals for reinhardbraunsite (also named calcio-chondrodite) [15]. SEM photographs of the hydration products are shown in Fig. 3.

Table 1
Phases in this study

Abbreviation	Phase name	Cement notation	Crystallochemical formula	JCPDS card
β	β-dicalcium silicate	β-C_2S	β-Ca_2SiO_4	33-0302
P	portlandite	CH	$Ca(OH)_2$	04-0733
G	low crystalline C-S-H gel	C-S-H gel	–	–
γ	γ-dicalcium silicate hydrate	γ-C_2SH_x	γ-$Ca_2SiO_4 \cdot xH_2O$	[13,17]
α	α-dicalcium silicate hydrate	α-C_2SH	$Ca_2(SiO_3OH)(OH)$	29-0373
C	calcium silicate $Ca_8Si_5O_{18}$	C_8S_5	$Ca_8(SiO_4)_2(Si_3O_{10})$	29-0368
D	dellaite	C_2SH	$Ca_6(SiO_4)(Si_2O_7)(OH)_2$	29-0376
R	reinhardbraunsite (calcio-chondrodite)	C_5S_2H	$Ca_5(SiO_4)_2(OH)_2$	84-0148
K	kilchoanite	C_3S_2	$Ca_6(SiO_4)(Si_3O_{10})$	29-0370
J	jaffeite (tricalcium silicate hydrate)	C_3SH	$Ca_6(Si_2O_7)(OH)_6$	29-0375
F	foshagite	C_4S_3H	$Ca_4(Si_3O_9)(OH)_2$	29-0377

In the cement notation, C = CaO, S = SiO_2, and H = H_2O.

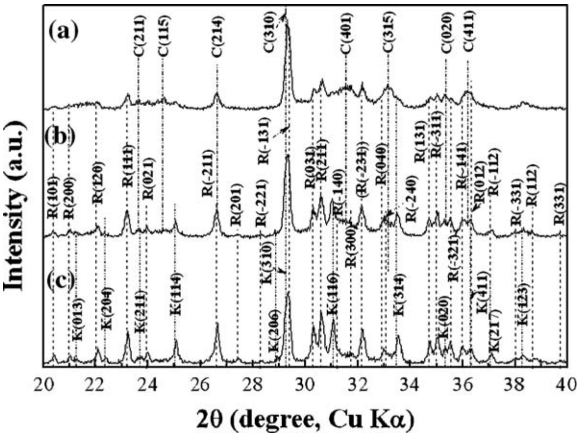

Fig. 2. XRD patterns of the products obtained by the room temperature mixing method at 240 °C (a), 300 °C (b), and 350 °C (c) for 1 day.

Hydration of β-dicalcium silicate was so slow at 50 °C that a small amount of C-S-H gel and portlandite were formed with a large amount of starting β-dicalcium silicate which remained in the product even after the reaction for 1 day. β-dicalcium silicate was completely changed to portlandite and low crystallinity C-S-H gel at 80 °C (Fig. 1b), as shown by Eq. (1).

$$\beta - \mathrm{Ca_2SiO_4}(\beta) + \mathrm{H_2O} \rightarrow \mathrm{C - S - Hgel(G)} + \mathrm{Ca(OH)_2} \qquad (1)$$

This result is different from that given by Ishida et al. [8] who obtained C-S-H gel with Ca/Si ratio of 2.0 by hydration of β-dicalcium silicate with a small amount of water (w/s ratio of 0.5) at temperatures above 60 °C. The difference can be explained by the large w/s ratio of 20 used in this study. C-S-H gel with high Ca content may be unstable in a large amount of water. Further hydrothermal treatment of C-S-H gel and portlandite at 200 °C for 1 d gave α-dicalcium silicate hydrate, which agreed with the result given by Taylor [14].

α-dicalcium silicate hydrate started to crystallize at 130 °C and was obtained as a single phase by the reaction at 150 °C for 1 day (Fig. 1c). The crystals of α-dicalcium silicate hydrate were formed with a characteristic appearance of thin rectangular plates (Fig. 3a,b). At above 160 °C, α-dicalcium silicate hydrate coexisted with a small amount of $\mathrm{Ca_8Si_5O_{18}}$ and reinhardbraunsite after the reaction for 1 day. At 200 °C, their small crystals were observed with large crystals of α-dicalcium silicate hydrate (Fig. 3c).

By the reaction at lower temperatures below 220 °C for 1 day, α-dicalcium silicate hydrate was detected in the products, but at 240 °C the main hydration products were $\mathrm{Ca_8Si_5O_{18}}$ and reinhardbraunsite (Fig. 2a). The small rods (Fig. 3d) must be the mixture of $\mathrm{Ca_8Si_5O_{18}}$ and reinhardbraunsite. $\mathrm{Ca_8Si_5O_{18}}$ phase was first obtained along with other phases by Bennett et al. [16] over a wide range of conditions and was reported to crystallize best from starting materials of bulk Ca/Si ratio of 1.5–1.75 under conditions ranging 180–600 °C. $\mathrm{Ca_8Si_5O_{18}}$ phase was also obtained by Speakman et al. [17] by hydration of γ-dicalcium silicate unhydrate prepared by solid state reaction, with or without the addition of portlandite at 180–250 °C, and they showed that $\mathrm{Ca_8Si_5O_{18}}$ was imperfect crystalline and was not an equilibrium product. Thus, the X-ray diffraction peaks assigned to $\mathrm{Ca_8Si_5O_{18}}$ phase obtained in this study were always broad peak.

Reinhardbraunsite and kilchoanite were detected as main phases at 300 °C as shown in Fig. 2b. It was confirmed that the metastable phase of $\mathrm{Ca_8Si_5O_{18}}$ was hydrated to form kilchoanite and reinhardbraunsite by long time reactions at higher temperatures than 200 °C. After reaction time of 1 day at 350 °C, $\mathrm{Ca_8Si_5O_{18}}$ was completely decomposed to kilchoanite and reinhardbraunsite(Fig. 2c). Kilchoanite and reinhardbraunsite (long needle crystals and bulky crystals, respectively, as shown in Fig. 3e) were formed even at 400 °C for 1 day. When β-dicalcium silicate was treated at 400 °C up to 5 days, dellaite was detected together with kilchoanite and reinhardbraunsite. Dellaite was crystallized to large bulky crystals shown in Fig. 3f.

These results for the formation of $\mathrm{Ca_8Si_5O_{18}}$, reinhardbraunsite and kilchoanite were similar to those reported by Speakman et al. [17], who used γ-dicalcium silicate unhydrate as a starting material. Speakman et al. summarized the hydration results of γ-dicalcium silicate unhydrate under

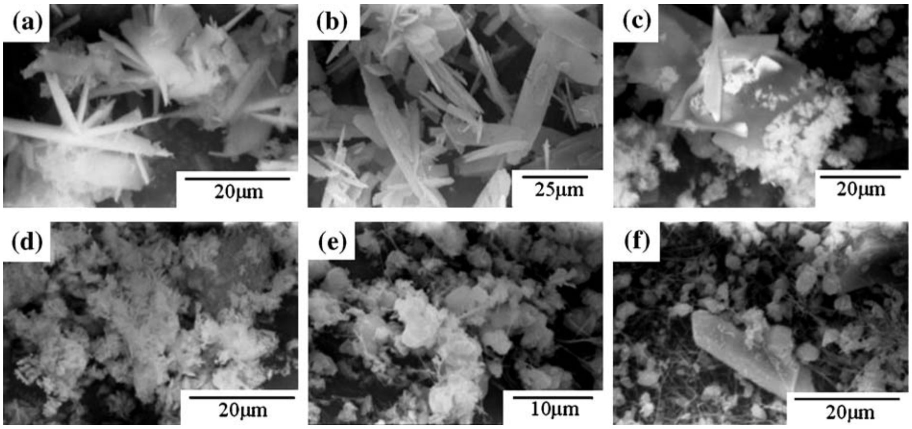

Fig. 3. SEM photographs of the products obtained by the room temperature mixing method at 130 °C (a), 150 °C (b), 200 °C (c), 240 °C (d), 400 °C (e), for 1 day and 400 °C for 5 days (f).

hydrothermal conditions at 150–600 °C by using following sequence of reactions.

$$9\gamma - \mathrm{Ca_2SiO_4}(\gamma) + 2\mathrm{H_2O} \rightarrow \mathrm{Ca_8(SiO_4)_2(Si_3O_{10})(C)} + 2\mathrm{Ca_5(SiO_4)_2(OH)_2(R)} \qquad (2)$$

$$8\mathrm{Ca_8(SiO_4)_2(Si_3O_{10})(C)} + 2\mathrm{H_2O} \rightarrow 9\mathrm{Ca_6(SiO_4)(Si_3O_{10})(K)} + 2\mathrm{Ca_5(SiO_4)_2(OH)_2(R)} \qquad (3)$$

$$3\mathrm{Ca_6(SiO_4)(Si_3O_{10})(K)} + 6\mathrm{Ca_5(SiO_4)_2(OH)_2(R)} + 2\mathrm{H_2O} \rightarrow 8\mathrm{Ca_6(SiO_4)(Si_2O_7)(OH)_2(D)} \qquad (4)$$

Reaction (2) is slow at 150 °C, but is completed in 3 days at 180 °C. The $\mathrm{Ca_8Si_5O_{18}}$ phase is initially of higher Ca/Si ratio. Reaction (3) is slow at 180 °C, but approaches completion after 7 days at 250 °C. Reaction (4) is slow at 400 °C, but is completed in 3 days at 600 °C. Assarsson [18] pointed out that the formation of a high-temperature phase from metastable phases formed at an initial stage should be taken place at higher temperature than their highest formation temperature. This is true for the formation of dellaite. Dellaite could be formed from α-dicalcium silicate hydrate by a short time reaction of 1 day at 350 °C under saturated vapor pressure [19], though the formation of dellaite from γ-dicalcium silicate unhydrate or β-dicalcium silicate needed long time reactions at higher temperatures.

Mitsuda [20] showed γ-dicalcium silicate hydrate released water by heating at high temperatures, but was rehydrated quickly. It should be noted that the starting materials used by Speakman et al. [17] must be γ-dicalcium silicate hydrate. The similarity in our results and those obtained by Speakman et al. [17] can be explained by formation of γ-dicalcium silicate hydrate as an initial phase from β-dicalcium silicate. Mitsuda [20] reported that pure γ-dicalcium silicate hydrate can be formed from β-dicalcium silicate at 180 °C for 4 h without stirring. In order to confirm the formation of γ-dicalcium silicate hydrate from β-dicalcium silicate, short time reactions were carried out. Fig. 4 shows the hydration process of β-dicalcium silicate at the initial stage by the room temperature mixing method. After 1 h at 180 °C, γ-dicalcium silicate hydrate was formed with a large amount of unreacted β-dicalcium silicate (Fig. 4a), and after 4 h α-dicalcium silicate hydrate was formed as a main hydration product along with a very small amount of $\mathrm{Ca_8Si_5O_{18}}$ which was formed by decomposition of γ-dicalcium silicate hydrate (Fig. 4b). This result is inconsistent with that given by Mitsuda [20] who obtained pure γ-dicalcium silicate hydrate at 180 °C for 4 h. The contradiction may be explained by difference of the starting material and hydrothermal processing with or without stirring. Mitsuda [20] used high reactive β-dicalcium silicate prepared by heating synthetic hillebrandite, but we used low reactive β-dicalcium silicate prepared by solid state reaction. Thus, a large amount of unreacted β-dicalcium silicate remained in our case. We used stirring system, so that the decomposition of γ-dicalcium silicate hydrate was accelerated. Thus β-dicalcium silicate changed to γ-dicalcium silicate hydrate at the initial stage of the hydration as shown by Eq. (5).

$$\beta - \mathrm{Ca_2SiO_4}(\beta) + \chi\mathrm{H_2O} \rightarrow \gamma - \mathrm{Ca_2SiO_4}\chi\cdot\mathrm{H_2O}(\gamma). \qquad (5)$$

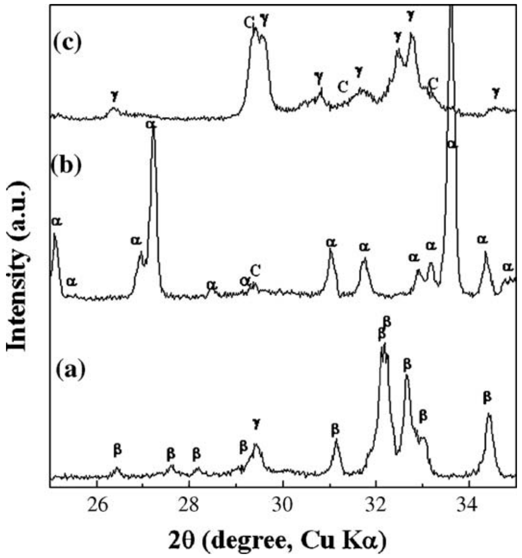

Fig. 4. XRD patterns of the products obtained for a short reaction time by the room temperature mixing method, (a) 1 h and (b) 4 h at 180 °C, (c) 1 h at 250 °C.

The formation of γ-dicalcium silicate hydrate from β-dicalcium silicate was accelerated with the increase in reaction temperature, so that γ-dicalcium silicate hydrate was formed as a main phase along with $\mathrm{Ca_8Si_5O_{18}}$ at 250 °C for 1 h (Fig. 4c). By the longer time reaction, γ-dicalcium silicate hydrate decomposed to form $\mathrm{Ca_8Si_5O_{18}}$, reinhardbraunsite, and kilchoanite, as shown before. Thus, these results well agreed with those given by Speakman et al. [17], because they were all given by decomposition of γ-dicalcium silicate hydrate under hydrothermal conditions.

The difference of our results from those given by Speakman et al. [17] was the formation of α-dicalcium silicate hydrate at low temperatures below 220 °C. It is believed that the unreacted β-dicalcium silicate directly changed to α-dicalcium silicate hydrate as shown by Eq. (6). The direct formation of α-dicalcium silicate hydrate from β-dicalcium silicate will be shown later.

$$\beta - \mathrm{Ca_2SiO_4}(\beta) + \mathrm{H_2O} \rightarrow \alpha - \mathrm{Ca_2(SiO_3OH)(OH)}(\alpha) \qquad (6)$$

It has been shown that α-dicalcium silicate hydrate is not stable at high temperatures above 230 °C and changes to reinhardbraunsite and jaffeite but the reaction rate is very slow at low temperatures below 220 °C [19]. Thus, α-dicalcium silicate hydrate was formed at low temperatures below 220 °C in this study. At above 240 °C, the initial hydration phase must be γ-dicalcium silicate hydrate.

3.2. *Hydration products obtained by the high temperature mixing method*

XRD patterns and SEM photographs of the hydration products obtained by the high temperature mixing method

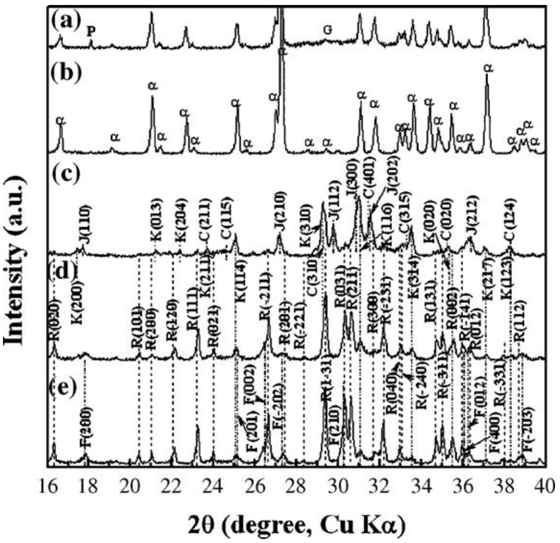

Fig. 5. XRD patterns of the products obtained by the high temperature mixing method at different temperatures, (a) 100 °C, (b) 150 °C, (c) 240 °C, (d) 300 °C, and (e) 400 °C for 1 day.

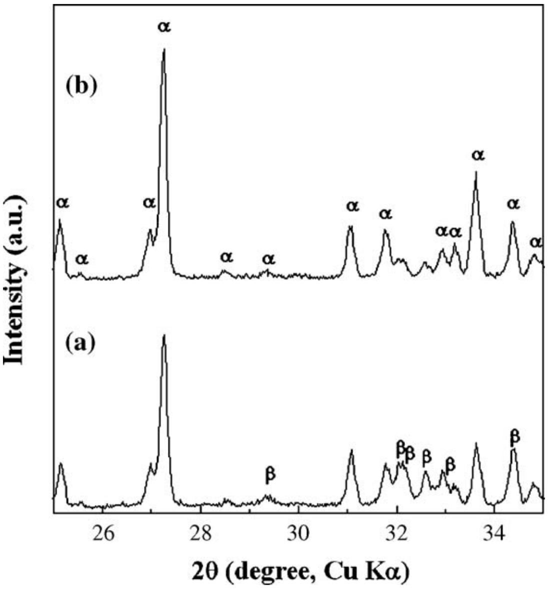

Fig. 7. XRD patterns of hydration products of β-dicalcium silicate for a short reaction time at 180 °C by the high temperature mixing method, (a) 0.5 h and (b) 1 h.

at different temperatures are shown in Figs. 5 and 6, respectively.

α-dicalcium silicate hydrate was crystallized even at 100 °C by the high temperature mixing method along with low crystalline C-S-H gel and portlandite (Fig. 5a). Small thin plate crystals of α-dicalcium silicate hydrate were observed in aggregated fine particles (Fig. 6b). Pure α-dicalcium silicate hydrate was obtained at temperatures between 150 and 200 °C. The purity of α-dicalcium silicate hydrate was confirmed by TG-DTA analysis, which showed only one endothermic peak at 450 °C with large weight loss, as shown by Ishida et al. [21].

Fig. 7 shows the hydration processes of β-dicalcium silicate at 180 °C by the high temperature mixing methods. α-dicalcium silicate hydrate was formed only by a short time reaction for 0.5 h along with unreacted β-dicalcium silicate; and after 1 h, the amount of α-dicalcium silicate hydrate increased with the decrease of the amount of β-dicalcium silicate. The formation of γ-dicalcium silicate hydrate was not detected. Even if γ-dicalcium silicate hydrate was formed, its amount must be very small. Thus, it is concluded that α-dicalcium silicate hydrate is directly formed from β-dicalcium silicate in the stable region of α-dicalcium silicate hydrate as shown by Eq. (6).

By the room temperature mixing method, a small amount of γ-dicalcium silicate hydrate was formed from β-dicalcium silicate at 180 °C and the formation of α-dicalcium silicate hydrate was slow in comparison with the high temperature mixing method. This result suggested that γ-dicalcium silicate hydrate was formed during heating to 180 °C to cover β-dicalcium silicate particles, which inhibited the hydration of β-dicalcium silicate to form α-dicalcium silicate hydrate. The formation rate of α-dicalcium silicate hydrate must be faster than that of γ-dicalcium silicate hydrate at 180 °C. In other words, the high temperature mixing method is helpful to obtain pure α-dicalcium silicate hydrate without formation of γ-dicalcium silicate hydrate at temperatures below 200 °C.

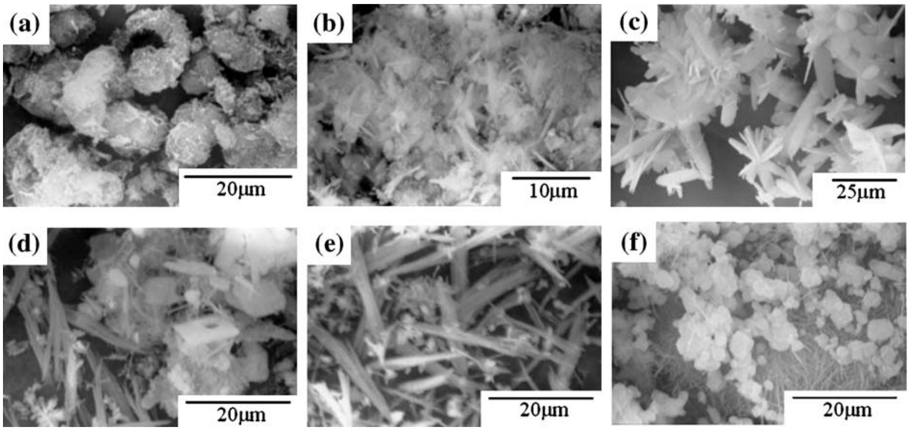

Fig. 6. SEM photographs of the products obtained by the high temperature mixing method at different temperatures, (a) 80 °C, (b) 100 °C, (c) 150 °C, (d) 220 °C, (e) 250 °C, and (f) 350 °C for 1 day.

Compared with α-dicalcium silicate hydrate crystals obtained by the room temperature mixing method (Fig. 2b), the size of α-dicalcium silicate hydrate crystals obtained by the high temperature mixing method (Fig. 6c) was smaller. This result also suggested that in comparison with the room temperature mixing method, the high temperature mixing method gave higher hydration rate and produced a larger number of nuclei which resulted in the formation of smaller crystals of α-dicalcium silicate hydrate.

By the reaction for 1 day, $Ca_8Si_5O_{18}$, reinhardbraunsite, jaffeite and kilchoanite were formed as minor phases along with major α-dicalcium silicate hydrate phase at 220 °C. At above 240 °C, α-dicalcium silicate hydrate was not detected (Fig. 5c). With the increase in reaction temperature, the amount of $Ca_8Si_5O_{18}$ increased up to 240 °C, and the amount of jaffeite and kilchoanite increased up to 260 °C. The aggregates of fine fibrous and bulk crystals with length of 2 μm and bunchy aggregates of long fibrous crystals with length of 20 μm were observed in Fig. 6d,e. The bunchy aggregates of long fibrous crystals were characterized by jaffeite [14]. The aggregates belonged to mixture of kilchoanite, $Ca_8Si_5O_{18}$ and reinhardbraunsite because they usually are randomly intergrown on a unit-cell scale [20]. Foshagite started to crystallize at 280 °C. At 300 °C, reinhardbraunsite and foshagite were formed as main phases (Fig. 5d), and these amount increased with the increase in temperature up to 400 °C (Fig. 5e). Fig. 6f clearly showed bulky crystals of reinhardbraunsite and aggregates of long fibers with length of over 20 μm of foshagite were formed at 350 °C for 1 day.

The hydration products obtained at high temperatures by the high temperature mixing method were different from those obtained by the room temperature mixing method. The difference might be explained by the different reaction route which is shown in Fig. 8 by short time reactions at 250 °C. By the high temperature mixing method, β-dicalcium silicate was more quickly hydrated to form γ-dicalcium silicate hydrate than by the room temperature mixing method. The main product obtained by the reaction for 0.5 h was γ-dicalcium silicate hydrate with a small amount of $Ca_8Si_5O_{18}$ (Fig. 8a). After 1 h, γ-dicalcium silicate hydrate decomposed to form $Ca_8Si_5O_{18}$ with a small amount of reinhardbraunsite, following the reaction (2). At this stage, a small amount of jaffeite was also formed (Fig. 8b). By the high temperature mixing method, the hydration started at high temperature at which solubility of portlandite is low, so that jaffeite, the Ca rich phase, is preferentially formed during the transformation of γ-dicalcium silicate hydrate to $Ca_8Si_5O_{18}$. By the long time reactions, $Ca_8Si_5O_{18}$ decomposed to jaffeite and kilchoanite as shown in Eq. (7), because nuclei of jaffeite had been already produced in the products. Thus jaffeite and kilchoanite was formed as main phases, and reinhardbraunsite was a minor phase (Fig. 8c,d).

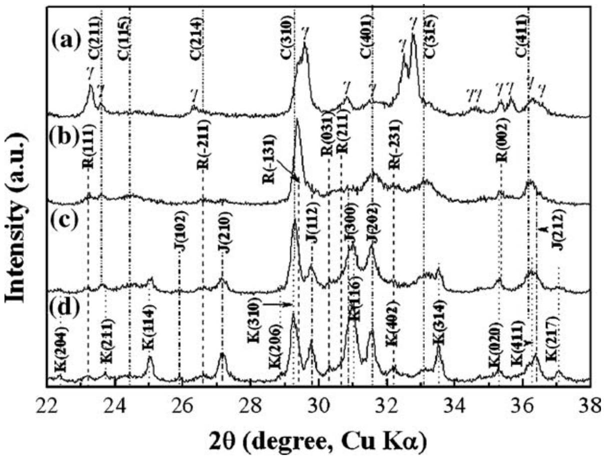

Fig. 8. XRD patterns of hydration products of β-dicalcium silicate for a short reaction time at 250 °C by the high temperature mixing method, (a) 0.5 h, (b) 1 h, (c) 10 h and (d) 1 day.

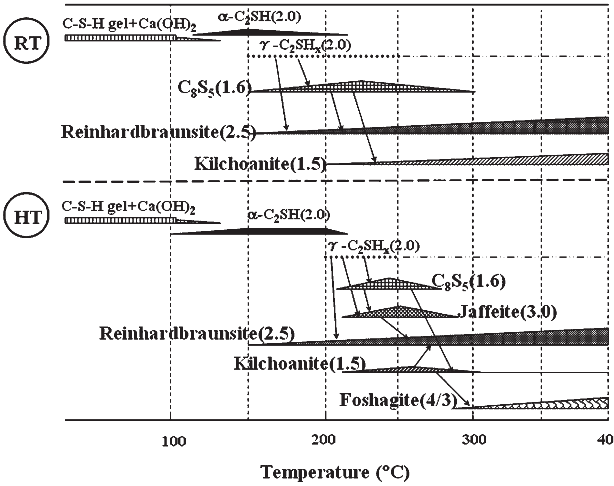

Fig. 9. Schematic diagram for initial hydration products of β-dicalcium silicate against temperature. RT: room temperature mixing method; HT: high temperature mixing method.

$$\begin{aligned}&6Ca_8(SiO_4)_2(Si_3O_{10})(C)\\&\quad+3H_2O\rightarrow 7Ca_6(SiO_4)(Si_3O_{10})(K)\\&\quad+Ca_6(Si_2O_7)(OH)_6(J).\end{aligned}\tag{7}$$

Jaffeite has been prepared with long, fibrous morphology by hydrothermal treatments of starting materials with Ca/Si ratio of 3.0 at 180–450 °C [14,22,23]. It is not stable and changes to reinhardbraunsite and portlandite at about 450 °C [14]. Under the present conditions with the Ca/Si ratio of 2.0, jaffeite must be unstable even at lower temperatures. At above 280 °C jaffeite decomposed to form reinhardbraunsite and portlandite, meanwhile kilchoanite and portlandite reacted to form foshagite and reinhardbraunsite as shown by Eqs. (8) and (9).

$$\begin{aligned}&Ca_6(Si_2O_7)(OH)_6(J)\rightarrow Ca_5(SiO_4)_2(OH)_2(R)\\&\quad+Ca(OH)_2+H_2O\end{aligned}\tag{8}$$

$$\begin{aligned}&2Ca_6(SiO_4)(Si_3O_{10})(K)\\&\quad+Ca(OH)_2\rightarrow 2Ca_4(Si_3O_9)(OH)_2(F)\\&\quad+2Ca_5(SiO_4)_2(OH)_2(R).\end{aligned}\tag{9}$$

4. Conclusions

Nine C-S-H phases with the same Ca/Si ratio as precursor (γ-dicalcium silicate hydrate, α-dicalcium silicate hydrate and dellaite), Ca-rich compositions (jaffeite and reinhardbraunsite), Si-rich compositions ($Ca_8Si_5O_{18}$, kilchoanite and foshagite), and C-S-H gel were obtained at the initial stage of the hydration of β-dicalcium silicate by the room and high temperature mixing method. The hydrothermal processes and reaction temperatures had effects on the formation of reaction products. The results are schematically summarized in Fig. 9.

At lower temperatures than 100 °C, β-dicalcium silicate hydrated to form low crystalline C-S-H gel and portlandite. α-dicalcium silicate hydrate was formed directly from β-dicalcium silicate in the temperature range between 130 and 220 °C. γ-dicalcium silicate hydrate was formed as an initial phase by short time reactions at higher temperatures above 160 °C and 220 °C by the room and high temperature mixing method, respectively. The formation rate of γ-dicalcium silicate hydrate was slow at low temperatures in comparison with that of α-dicalcium silicate hydrate, but increased at high temperatures, especially above 230 °C, at which α-dicalcium silicate hydrate was not stable.

By room temperature mixing method, γ-dicalcium silicate hydrate decomposed to form $Ca_8Si_5O_{18}$ and reinhardbraunsite, and $Ca_8Si_5O_{18}$ decomposed to form reinhardbraunsite and kilchoanite at high temperatures. The reaction products at 400 °C for 1d were reinhardbraunsite and kilchoanite.

In the case of the high temperature mixing method, Ca-rich compound, jaffeite, was formed together with $Ca_8Si_5O_{18}$ and reinhardbraunsite by decomposition of γ-dicalcium silicate hydrate formed as an initial phase at above 220 °C, and $Ca_8Si_5O_{18}$ was decomposed to form jaffeite and kilchoanite at temperatures between 220 °C and 280 °C. At high temperatures over 280 °C, jaffeite and kilchoanite were replaced by foshagite and reinhardbraunsite by further hydrothermal reaction.

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