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Kinetics of the Formation and Transformation of Alkoxy-derived Calcium Metasilicate

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Wollastonite(β-$CaSiO_3$) was formed directly from the mixed powder prepared by simultaneous hydrolysis of calcium and silicon alkoxides. Crystallization isotherms were described by the Avrami equation $\ln(1-\alpha)=-kt^n$ with $n=3$ and the activation energy was determined as 284.5 kJ/mol. The kinetics of transformation of β- into α-$CaSiO_3$ was best interpreted by the contracting cube equation $1-(1-\alpha)^{1/3}=kt$. The value of the activation energy was 983.2 kJ/mol.

Calcium metasilicate($CaSiO_3$) exists in three polymorphic modifications; wollastonite(triclinic, β-$CaSiO_3$), pseudowollastonite(triclinic, α-$CaSiO_3$), and parawollastonite (monoclinic). Parawollastonite has been recognized as a mineral. Many investigations[1–7] have been made on the solid state reaction of an equimolar mixture of silica and either calcium carbonate or calcium oxide. It is shown that calcium orthosilicate (Ca_2SiO_4) is always one of the first products at any reaction temperature. For example, Jander and Hoffmann[3] reported that Ca_2SiO_4 and $Ca_3Si_2O_5$ are the first-formed products and gradually convert into $CaSiO_3$, the final product. They observed also a strong effect of grinding on the formation of $CaSiO_3$. This indicates that the contact of reactants in the powder mixture plays an important role. On the other hand, though it has been reported that β-$CaSiO_3$ transforms into α-$CaSiO_3$ at 1125±10 °C,[8] 1180 °C,[5] or 1190 °C,[9] no kinetic study has been carried out.

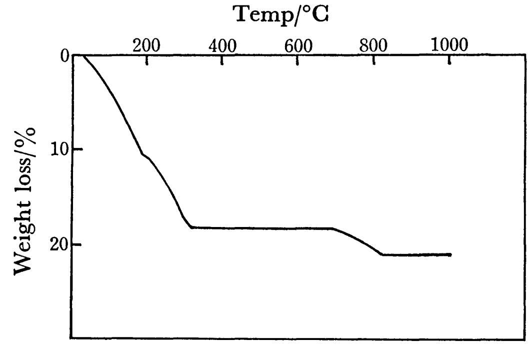

Fig. 1. TG curve of the starting powder.
Sample weight: 20 mg.

In the present study, it was found that β-$CaSiO_3$ is formed directly from the mixed powder prepared by simultaneous hydrolysis of calcium and silicon alkoxides. On the basis of this result, kinetic studies have been made on the formation of β-$CaSiO_3$ and the transformation of β- into α-$CaSiO_3$. The kinetic data were analyzed with available solid state models.

Experimental

Materials and Procedure. Silicon ethoxide used was of guaranteed purity. Calcium methoxide was synthesized by heating calcium metal in an excessive amount of dehydrated methanol at 65 °C for 5 h. The purity of calcium metal was 99.9%. A mixture of these alkoxides with the mole ratio of $Ca^{2+}/Si^{4+}=1:1$ was prepared, and then poured into aqueous ammonia solution at 30 °C. The temperature was slowly raised up to 85 °C while being stirred. The resulting mixed powder was washed repeatedly with hot water and dried at 60 °C under reduced pressure. The mixed powder, in the description below, is termed starting powder. The average particle size of the starting powder is *ca.* 400 Å.

Measurement. Thermal analyses (TG, DTA) were carried out in air at a heating rate of 10 °C/min. Alpha-alumina was used as a standard material in DTA. On

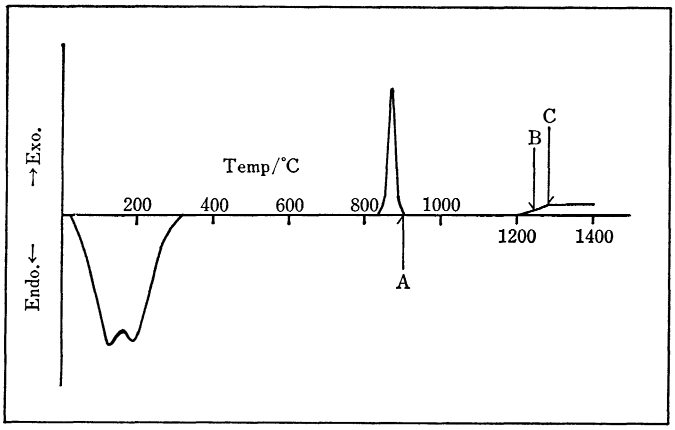

Fig. 2. DTA curve of the starting powder.
Sample weight: 20 mg.
Arrows show the temperatures at which the starting powder was heated in order to obtain several specimens for X-ray diffraction.

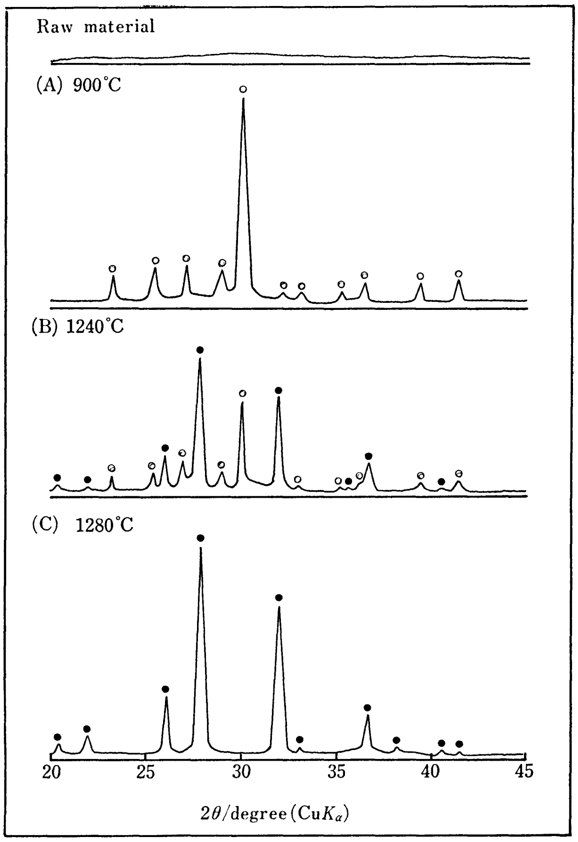

Fig. 3. X-ray diffraction patterns of specimens with increasing temperature.
○: β-$CaSiO_3$, ●: α-$CaSiO_3$.

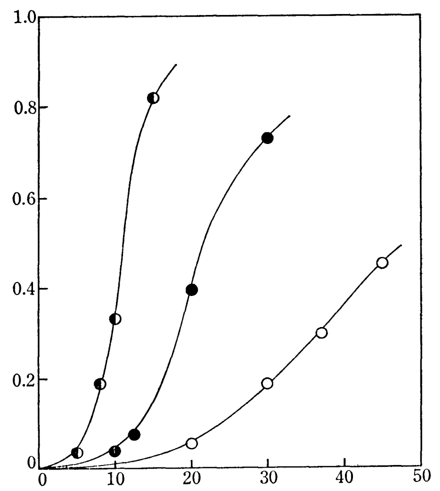

Fig. 4. Formation of β-$CaSiO_3$ as a function of time at different temperatures.
○: 820 °C, ●: 840 °C, ◐: 870 °C.

the basis of the DTA data, the starting powder was heated in an electric furnace up to a desired temperature at a heating rate of 10 °C/min, and then cooled rapidly to room temperature. The specimens were examined by means of X-ray diffractometer using nickel filtered copper K_α. The fractional transformation was determined from the heights of the main peaks characteristics of α-(d=3.20 Å) and β-$CaSiO_3$ (d=2.97 Å), using the calibration curve prepared with known compositions.

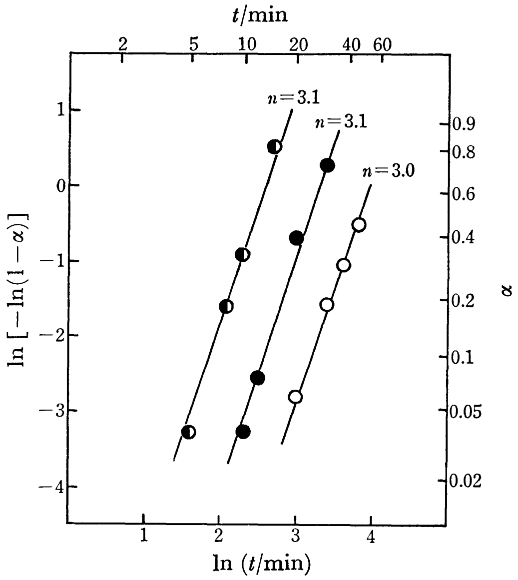

Fig. 5. Plots of ln (1−α) *vs.* time t of the data shown in Fig. 4.
○: 820 °C, ●: 840 °C, ◐: 870 °C.

Results and Discussion

Thermal Analysis. Figure 1 shows a TG curve of the starting powder. The weight loss of 18.2% up to 320 °C is attributed to the loss of ammonia, surface-absorbed methanol and ethanol, absorbed water, and hydrated water. Continued weight loss, 2.8%, was observed between 690 and 820 °C. The specimens heated in this temperature range were grayish. This may be due to the alcoholic hydrocarbon occluded in powders and/or free carbon produced by heating, which reacts with oxygen of bulk at the surface, resulting in the evolution of the decomposition products such as carbon monoxide, carbon dioxide, and water vapor.[10–11)]

A DTA curve of the starting powder is shown in Fig. 2. Two exothermic reactions were observed at 830—900 °C and 1200—1280 °C. From the results of X-ray diffraction, the reactions were found to be the crystallization of β-$CaSiO_3$ from an amorphous phase and the transformation of β- into α-$CaSiO_3$, respectively.

X-Ray Analysis. Figure 3 shows the variation of X-ray diffraction patterns of $CaSiO_3$ with increasing temperature. The starting powder was amorphous, and no significant changes were observed up to 800 °C. The peaks corresponding to β-$CaSiO_3$ appeared after heating at 820 °C for 10 min, and the intensity increased rapidly up to 900 °C. No other peaks were identified except for the β-$CaSiO_3$ spectrum up to 1170 °C. The peaks of α-$CaSiO_3$ began to appear when heated at 1180 °C for 20 min, and the specimen heated at 1280 °C showed an X-ray diffraction pattern characteristic of α-$CaSiO_3$.

Kinetics of the Formation of β-$CaSiO_3$. Figure 4 shows the fraction of the crystallized β-$CaSiO_3$ at 820, 840, and 870 °C. The starting powder was preheated at 500 °C for 1 h. The fractional crystallization of each specimen was determined from the height

Fig. 6. Electron micrograph of the β-$CaSiO_3$ powder.

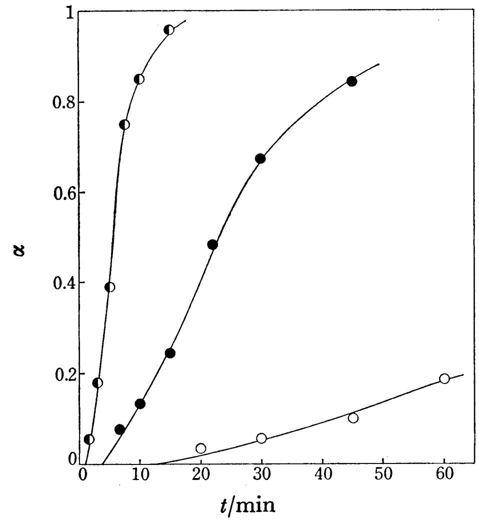

Fig. 7. Phase transformation from β- into α-$CaSiO_3$ as a function of time at different temperatures.
○: 1180 °C, ●: 1210 °C, ◐: 1240 °C.

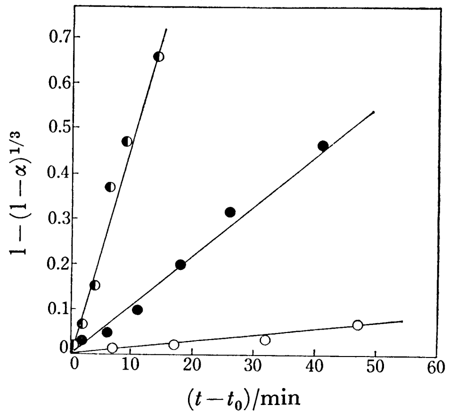

Fig. 8. Plots of $1-(1-\alpha)^{1/3}$ *vs.* time $t-t_0$ of the data shown in Fig. 7.
○: 1180 °C, ●: 1210 °C, ◐: 1240 °C.

of d=2.97 Å which is the strongest peak of the β-$CaSiO_3$ spectrum. A well-crystallized specimen was obtained by heating the starting powder at 1150 °C for 20 min. Quartz was used as an internal standard material. Crystallization isotherms were characterized by sigmoidal shape (Fig. 4), the kinetics being best described by the Avrami equation[12] (Fig. 5),

$$\ln(1-\alpha) = -kt^n \qquad (n=3\text{—}3.1\fallingdotseq 3) \qquad (1)$$

where α, t, k, and n are the fractional crystallization, time, rate constant and a constant related to the reaction mechanism, respectively. Electron micrograph of the β-$CaSiO_3$ powder consisting of nearly spherical particles is shown in Fig. 6. In view of this fact and also the fact that the Avrami equation with $n=3$ was fitted over the whole range of crystallization curves, three-dimensional growth of β-$CaSiO_3$ with site-saturation for nucleation is probably the rate-determining step. The activation energy calculated from the Arrhenius plot was 284.5 kJ/mol.

Kinetics of the Transformation of β- into α-$CaSiO_3$. Figure 7 shows the fractional transformation of β- into α-$CaSiO_3$ as a function of time at different temperatures. The specimens heated at 1150 °C for 20 min were used as a starting material. Induction periods were observed, attempts being made to fit the results to kinetic laws by considering the induction periods. As shown in Fig. 8, transformation isotherms are best described by the contracting cube equation,[13]

$$1-(1-\alpha)^{1/3} = k(t-t_0) \qquad (2)$$

where α is the fractional transformation, t time and t_0 induction period. This indicates that the transformation is controlled by the rate of advance of the reaction interface. The rate constants were determined from the slopes of the straight lines and the activation energy was determined as 983.2 kJ/mol.

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