Accelerated Formation of β-Dicalcium Silicate by Solid-state Reaction in Water Vapor Atmosphere

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β-Ca_2SiO_4 powders were prepared from commercially available raw materials, $CaCO_3$ and amorphous SiO_2 (a-SiO_2), by solid-state reactions in water vapor atmosphere. The formation of β-Ca_2SiO_4 was accelerated by water vapor. Water vapor is considered to enhance the thermal decomposition of $CaCO_3$ and to attack surface Si–O–Si bonds in a-SiO_2 to accelerate the formation of β-Ca_2SiO_4. The effect of water vapor atmosphere on the formation of β-Ca_2SiO_4 from a mixture of $CaCO_3$ and a-SiO_2 was stronger than that of mechanochemical processing for 30 min.

Dicalcium silicate (Ca_2SiO_4) is a major component of Portland cement. Recently, Ca_2SiO_4 is reported to be a potential candidate for new biomaterials for hard tissue repair because of its excellent bioactivity.[1–3] Ca_2SiO_4 powders are conventionally prepared by solid-state reactions of $CaCO_3$ and SiO_2. However, the high calcination temperature generally required by solid-state reactions leads to many disadvantages such as large particle size, wide size distribution and high degree of particle agglomeration. In order to overcome the disadvantage of solid-state reactions, mechanochemical effects are known to be quite effective to reduce the calcination temperatures for solid-state reactions.[4]

On the other hand, it has been shown that thermal decomposition of $CaCO_3$ is accelerated by water vapor.[5,6] It is expected that enhanced thermal decomposition of $CaCO_3$ would accelerate the formation of Ca_2SiO_4 by solid-state reactions with SiO_2 in water vapor atmosphere. In addition, the decrease of calcination temperatures would give fine Ca_2SiO_4 powders. In this paper, the influence of water vapor on the formation of Ca_2SiO_4 and on its powder properties was investigated by solid-state reactions of $CaCO_3$ and amorphous SiO_2 (a-SiO_2) in air and water vapor atmosphere. Furthermore, we also observed the mechanochemical effects for the solid-state reactions in both atmospheres.

The starting mixed powder of $CaCO_3$ ($d_{BET} = 0.40\,\mu m$) and a-SiO_2 with Ca/Si molar ratio of 2 was prepared by dry mixing in a stainless ball mill for 6 h at 280 rpm. The starting mixed powder was heated at a rate of $25\,^{\circ}C\,min^{-1}$ and calcined at various temperatures for 2 h in air and water vapor atmosphere by a tubular furnace equipped with a water evaporator. Distilled water was introduced at a flow rate of $2\,mL\,min^{-1}$ into the evaporator to generate water vapor atmosphere in the furnace. Characterization of the calcined powders was conducted by powder X-ray diffraction (XRD, Rigaku Rotaflex RAD-RC), specific surface area measurement (S_{BET}, Yuasa-ionics NOVA-1200) and particle size distribution measurement (PSD, Shimadzu SALD-2200).

Figure 1 shows the XRD patterns of the samples obtained by calcinations at 600–800 °C for 2 h in air and water vapor atmosphere. In air atmosphere, $CaCO_3$ remained in large quantities up to 700 °C and CaO was detected up to 750 °C. Although the formation of β-Ca_2SiO_4 already began at 600 °C, high calcination temperature (800 °C) was required to get single β-Ca_2SiO_4 phase in air in 2 h. In contrast, the solid-state reactions of $CaCO_3$ and a-SiO_2 were accelerated by the injection of water vapor, and single-phase β-Ca_2SiO_4 was obtained at 650 °C in 2 h. $CaCO_3$ was completely decomposed at 650 °C to form β-Ca_2SiO_4 without formation of CaO. Water vapor is considered to enhance the thermal decomposition of $CaCO_3$ and the formation of β-Ca_2SiO_4 at lower temperatures.

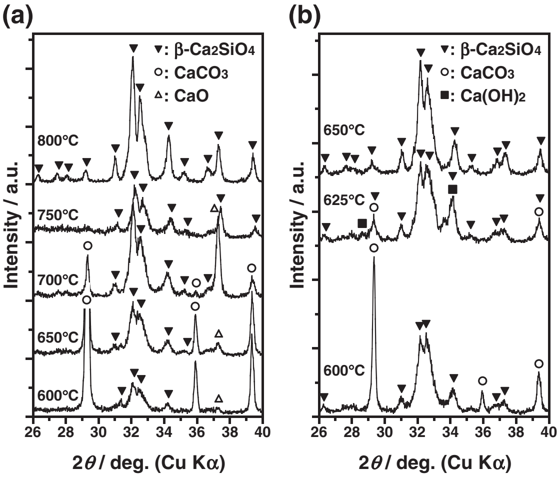

Figure 1. XRD patterns of the samples obtained by calcinations at 600–800 °C for 2 h in (a) air and (b) water vapor atmosphere.

We also investigated the solid-state reactions using a starting mixture prepared by planetary ball milling. Mechanochemical processing for the starting material was conducted for 30 min by planetary ball milling (Fritsch Pulverisette 5) with disc rotation speed of 200 rpm using agate vials and balls. Figure 2 shows the XRD patterns of the samples obtained by calcinations at 600–800 °C for 2 h in air and water vapor atmosphere. The thermal decomposition of $CaCO_3$ in air was promoted and completed at 700 °C by mechanochemical processing, probably because of the decrease of the particle size of $CaCO_3$. Nevertheless, 800 °C was required to get single β-Ca_2SiO_4 phase in air, in the same manner as the calcination of the starting mixture without mechanochemical processing. In water vapor atmosphere, the reaction was completed at 650 °C, at which single β-Ca_2SiO_4 phase was obtained from the mixture without mechanochemical processing. Thus, significant effects by planetary ball milling were not observed, because a-SiO_2 was too fine to get the effect of mechanochemical processing. It is concluded that the effect of water vapor atmosphere on the formation of β-Ca_2SiO_4 by solid-state reactions of $CaCO_3$ and a-SiO_2 is more effective than that of mechanochemical processing for 30 min.

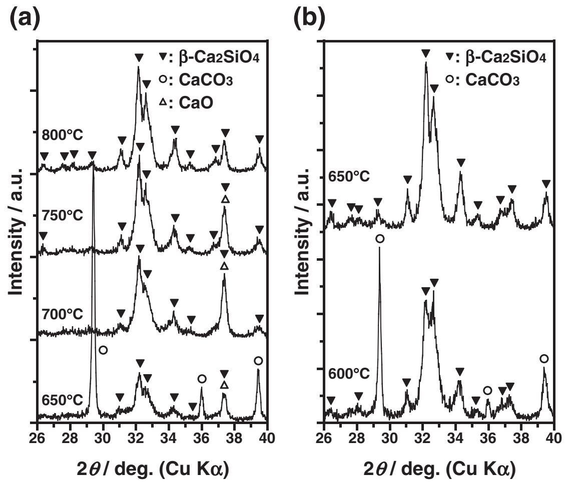

Figure 2. XRD patterns of the samples obtained by calcinations at 600–800 °C for 2 h in (a) air and (b) water vapor atmosphere using planetary ball milling mixtures.

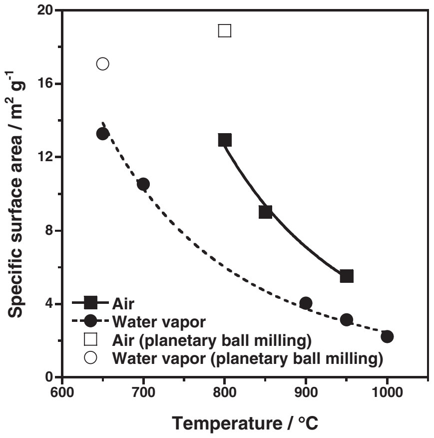

Figure 3. Specific surface area of the β-Ca_2SiO_4 powders obtained by calcinations at 650–1000 °C for 2 h in air and water vapor atmosphere using simple and planetary ball milling mixtures.

Figure 3 shows the S_{BET} of β-Ca_2SiO_4 powders prepared by calcinations for 2 h. By using planetary ball milling mixtures, β-Ca_2SiO_4 powders with high S_{BET} in comparison with that obtained from the simple ball milling mixtures were prepared in both atmospheres. Table 1 shows the powder properties of single β-Ca_2SiO_4 phase. The particle size was estimated from S_{BET} (d_{BET}) and PSD measurement (d_{50}) (Supporting Information).[7] The span of PSD, defined as $(d_{90} - d_{10})/d_{50}$, shows the order of size distribution. β-Ca_2SiO_4 powders with smaller particle size (d_{50}) were prepared at lower temperatures in water vapor atmosphere from both starting mixtures, in comparison with those obtained in air. In addition, the calcination in water vapor atmosphere gave the powders with the same or narrow particle size distribution compared that in air.

Wang and Thomson[6] regarded that water vapor adsorbed on $CaCO_3$ weakened CaO–CO_2 bonds and that the thermal decomposition of $CaCO_3$ was accelerated by water vapor. In addition, Hayashi et al.[8] showed that calcinations in water vapor atmosphere accelerated the crystallization of amorphous silicate precursors prepared by coprecipitation and considered that water vapor attacked surface Si–O–Si bonds in a-SiO_2 to cause the powder active state. In this study, synergistic effects in water vapor atmosphere are expected for decomposition of $CaCO_3$ and formation of β-Ca_2SiO_4. The accelerated formation mechanism of β-Ca_2SiO_4 in water vapor atmosphere is considered as follows: Water vapor attacks Si–O–Si bonds in a-SiO_2 and generates Si–OH bonds to promote rotation and movement of SiO_4 tetrahedra. Ca^{2+} ions which have already formed by accelerated decomposition of $CaCO_3$ in water vapor atmosphere easily react with SiO_4 tetrahedra. The formed hydroxy groups are eliminated by the rearrangement of SiO_4 tetrahedra to the nesosilicate structure of β-Ca_2SiO_4.

Table 1. Powder properties of the β-Ca_2SiO_4 powders obtained by calcinations for 2 h

Calcination conditions	Starting mixtures	d_{BET}/μm	d_{50}/μm (Span of PSD)
800 °C in air	Simple	0.14	0.77 (2.7)
650 °C in water vapor	Simple	0.14	0.67 (3.1)
800 °C in air	Planetary	0.10	0.73 (5.9)
650 °C in water vapor	Planetary	0.11	0.63 (3.0)

In summary, the solid-state preparation of β-Ca_2SiO_4 from commercially available raw materials, $CaCO_3$ and a-SiO_2, was accelerated by water vapor. β-Ca_2SiO_4 powders with the smaller particle size than that obtained in air were prepared by calcinations in water vapor atmosphere at lower temperatures than in air. Planetary ball milling of the starting material for 30 min had effects to decrease the particle size of the products but not to decrease the calcination temperature to complete the reactions. The solid-state reactions in water vapor atmosphere should be effective to prepare other ceramic powders consisting of oxygen polyhedra at low temperatures.

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