

Synthesis and sintering behavior of wollastonite fabricated by a polymer solution technique

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Porous wollastonite (CaSiO_3) powders were fabricated by a polymer solution technique. Silica sol and calcium nitrate were dissolved in de-ionized water without any precipitation, and polyvinyl alcohol (PVA) was mixed as a polymer carrier. An explosive exothermic reaction during the calcination process resulted in a porous powder structure. The crystalline development and specific surface areas of the calcined powders were dependant on the polymer content and type of silica sol. The porous powders were crystallized to $\beta\text{-CaSiO}_3$ at a lower temperature of about 900 °C than that of other synthesis methods, and the calcined powders were ball-milled to fine particles and densified at 1200 °C with an uniform grain size of α phase.

Key words: Wollastonite, Powder technology, Polyvinyl alcohol, Porous particles, Ball milling, Sintering.

Introduction

Ceramic processing is evolving in the direction of chemical synthesis of powders [1]. Methods based on soft-solution processing provide powders with desired properties such as high purity and homogeneity. Recently, as one of the soft-solution processing methods, an organic-inorganic solution technique using PVA (polyvinyl alcohol), PEG (polyethylene glycol) or EG (ethylene glycol) as a polymer carrier has been developed to make an easier and highly productive soft-solution processing method [2-10]. The PVA ensures the homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation and/or precipitation from the solution. In the solution involving the polymer and nitrate ions, the long chain polymer, which has $-(\text{OH})$ hydroxyl groups, prevents contact between cations and limits their agglomeration and precipitation. In particular, the amount of polymer and its molecular length can affect the distribution of cations in the solution [6, 9, 10]. The PVA process also produces carbonaceous material that gives heat through its combustion, so that fine and single-phase powders can be formed at a relatively low external temperature [4, 6, 9, 11-13].

Wollastonite (CaSiO_3) is an important material in fine ceramics, and the tile and cement industries. A host of favorable properties such as low shrinkage,

good strength, lack of volatile constituents, body permeability, fluxing characteristics, whiteness, and acicular shape render wollastonite useful in several ceramic and other applications [14]. Wollastonite also has many polymorphic forms and its transformation behavior is dependent on the powder preparation method [15]. The preparation of fine CaSiO_3 powders has been established by a co-precipitation method [16], and recrystallization occurred just at or below the temperature of incongruent melting [17]. In the co-precipitation method using an ethanol solution of calcium nitrate and tetraethyl orthosilicate, $\beta\text{-CaSiO}_3$ was synthesized at 1000 °C for 2 h showing a 1 μm primary particle size and particles agglomerated to several micrometers in diameter. In the sintering behavior of the co-precipitated material, abnormal grain growth was observed at a high sintering temperature of 1400 °C for 1 h. In another study, densification of pure $\beta\text{-CaSiO}_3$ has been attempted using xonotlite, as a pre-material of $\beta\text{-CaSiO}_3$, at a low temperature with long time holding schedule [18].

In this study, porous CaSiO_3 powders are prepared by a polymer solution method employing PVA as a polymeric carrier, and the effects of polymer content on powder characteristics are studied. In addition, the sintering behavior of ball-milled CaSiO_3 powder is also examined.

Experimental Procedure

Powder Synthesis and sintering

Ludox SK colloidal silica (25 wt% suspension in water, pH: 10.0, surface area: 345 m^2/g , Du Pont

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Chemicals, Wilmington, DE) or Ludox AS-40 colloidal silica (40 wt% suspension in water, pH: 9.1, surface area: 135 m²/g, Du Pont Chemicals, Wilmington, DE) and calcium nitrate (Ca(NO₃)₂·4H₂O, reagent grade, Aldrich Chem. Co., Milwaukee, WI), were dissolved in stoichiometric proportions in de-ionized water. After dissolving completely, a polymeric carrier was added, and then the mixture was heated up to 100 °C with stirring. As the polymeric carrier, polyvinyl alcohol (PVA) solution was added to the mixture. The PVA solution was made from 5 wt% PVA (degree of polymerization-1700) dissolved in D.I. water. The amount ratio of the PVA to cation sources in the solution were adjusted in such a way that there were 1 or 4 times more positively charged valences of the cations than the negatively charged -(OH) functional ends of the organics [2, 6]. The water in the solution was evaporated by continuous stirring during heating on a hot plate. The resulting gel-type precursors were completely dried at 100 °C and the dried precursors were calcined or crystallized at various temperatures in an air atmosphere in a box furnace. The inside of the furnace was monitored through a window in the low temperature range (100 °C~300 °C) to observe the explosive, pop-up reaction. The calcined, porous powders were wet, ball-milled to break agglomerates with ϕ 5 mm zirconia media for 2 h. Isopropyl alcohol was used as a solvent for milling. Finally, the ball-milled powder was compacted by uniaxially pressing at 30 MPa, and then sintered at 1200 °C for 2 h in an air atmosphere.

Characterization

The crystallization behavior of the gel-type precursor powders was examined as functions of calcination temperature and PVA content, using an X-ray diffractometer (Dmax 2200, Rigaku/USA, Danvers, MA) with CuK α radiation (40 kV, 30 mA). The measurements were made with a scanning speed of 10°/minute and a sampling interval of 0.02°. Five-point BET analysis from nitrogen gas absorption (Model Autosorb-1, Boynton Beach, FL) was conducted to obtain BET-specific surface areas of the crystalline powders. The morphologies of the porous, crystallized powders and sintered sample were examined by scanning electron microscopy (SEM, Hitachi S3500N, Hitachi, Japan). For the SEM observations, the powders were sprayed and the sintered specimens were mounted on aluminum stubs, and then the samples were Au-Pd sputtered at 15 mA for 40 s. The density of sintered wollastonite was measured by the Archimedes' method, using distilled water as a displacement liquid.

Results and Discussion

The CaSiO₃ precursors showed a distinct calcination behavior. The dried precursor gels were quite hydrophilic and showed a vigorous exothermic reaction at

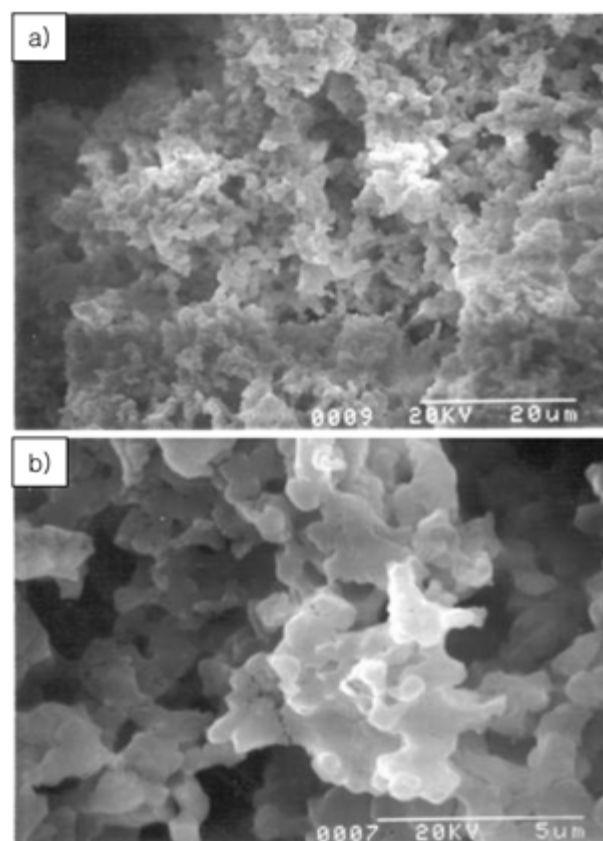


Fig. 1. SEM micrographs of (a) porous, calcined CaSiO₃ powder (calcined at 900 °C) employing PVA polymer of 1:1 ratio and (b) enlargement of (a).

about 300 °C during the calcination process. The exothermic reaction was accompanied with an abrupt volume expansion. This reaction occurred regardless of the polymer content. However, the reaction occurred more vigorously as the amount of polymer increased. After the reaction, the precursor gel changed to a soft and porous powder having a significant volume expansion. In the precursor derived from the PVA content of 1:1 ratio, the porous morphology of the calcined powder is shown in Fig. 1. The powders containing less PVA content (1:4 ratio) and no PVA also had porous structures, however, the porosities were lower than that of the powder derived from the 1:1 ratio. In the enlargement of the microstructure (Fig. 1(b)), the particle size was in the range of sub-micrometer to 1.5 μm with some agglomeration. In the calcination process, the reason for the volume expansion may be speculated that an abrupt oxidation of calcium cations occurred in elevating the temperature with a vigorous exothermic reaction, and simultaneously the reaction made extensive voids in the powder structure by the volume expansion, which results from the pyrolysis of organic substances during the exothermic reaction [9]. For these reason, it may be explained that the volume expansion occurs more extensively in the powder employing a larger PVA

Table 1. Observed crystalline phases of the precursor prepared by employing PVA polymer of 1:1 ratio, at each heating temperature

600 °C~800 °C	900 °C	1000 °C~1100 °C	1200 °C~1400 °C
amorphous	wollastonite (2 M) [§]	pseudo-wollastonite [§] + wollastonite	pseudo-wollastonite

[§]wollastonite (2 M) = β -CaSiO₃

[§]pseudo-wollastonite = α -CaSiO₃

Table 2. Observed crystalline phases of the precursor prepared without polymer, at each heating temperature

600 °C~800 °C	900 °C	1000 °C~1100 °C	1200 °C~1400 °C
amorphous	amorphous + wollastonite (2 M) [§]	(pseudo-wollastonite) [§] + wollastonite	pseudo-wollastonite

[§]wollastonite (2 M) = β -CaSiO₃

[§]pseudo-wollastonite = α -CaSiO₃

() : minor phase

content.

Tables 1 and 2 summarize the crystalline development of the precursors derived from Ludox SK at each heating temperature. In the precursors prepared employing PVA, fully crystallized β -CaSiO₃ was observed at 900 °C. By contrast, the precursors prepared without PVA showed some amorphous phase at this temperature. This implies that the PVA polymer affects the crystallization behavior and the β -CaSiO₃ phase can be formed at a relatively low external temperature by the production of carbonaceous material from PVA that gives heat through its combustion [11-13]. In general, α -CaSiO₃ is crystallized at about 1100 °C or above in the normal solid state powder synthesis route. However, using the PVA polymer solution technique, the crystallization temperature was about 100 °C lower as shown in Table 1.

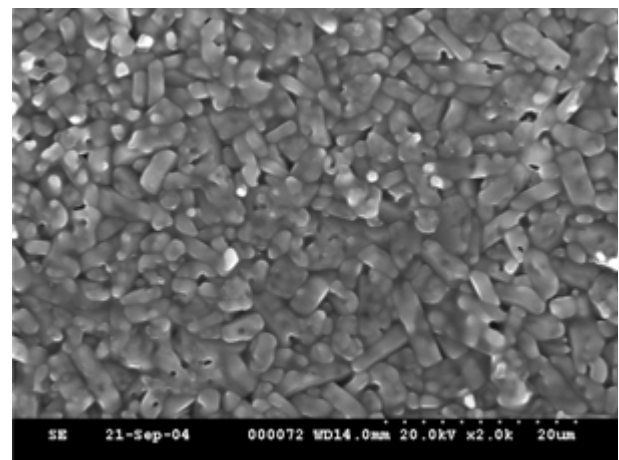
The specific surface areas of the calcined CaSiO₃ powders with the different polymer contents and type of silica sols are listed in Tables 3 and 4. The surface area increased as the PVA content increased. The BET measurements of calcined powder prepared from 1:1 PVA content ratio had the highest specific surface area of 23.2 m²/g in comparison with the no PVA and 1:4 cases (Table 3). These results mean that insufficient polymer gave agglomeration of metal cations in the precursor, and resulted in an increase of the crystalli-

Table 3. Specific surface areas of CaSiO₃ powders calcined at 900 °C, as a function of PVA content (silica sol: Ludox SK)

Polymer content	Specific surface area (m ² /g)
No PVA	5.6
1:4	18.9
1:1	23.2

Table 4. Specific surface areas of CaSiO₃ powders calcined at 900 °C, as a function of type of silica sol (PVA content: 1:1)

Type of silica sol	Specific surface area (m ² /g)
Ludox AS-40	16.8
Ludox-SK	23.2

**Fig. 2.** SEM micrograph for the surface of densified CaSiO₃ sintered at 1200 °C for 2 h.

zation temperature and a low specific surface area. In addition, the larger volume expansion during the exothermic reaction with a high content of PVA indicates a more porous powder structure having a higher specific surface area. The effect of silica sol type was that Ludox SK showed a higher specific surface area. It may be speculated that the colloidal size of silica also affects the specific surface area of synthesized powders. With a constant PVA content, however, the crystalline development was not changed according to the type of silica sol.

The calcined powder prepared from a 1:1 ratio was ball-milled for 2 h to break up agglomerates and densified in an air atmosphere. The ball-milled powder had an average particle size of 0.8 μ m. After sintering at 1200 °C for 2 h, the powder compact was densified with linear shrinkage of 17.2% and to a relative density of 97% (theoretical density of α -CaSiO₃: 2.9 g/cm³) showing pure α phase. A SEM micrograph for the surface of densified CaSiO₃ is given in Fig. 2. The microstructure showed some elongated grains, which are small in size in comparison with those produced by conventional methods, and a relatively uniform grain size was observed without any abnormal grain growth.

Conclusions

The PVA solution method was successfully applied to the fabrication of porous CaSiO_3 powders and densified to CaSiO_3 with a small grain size. The crystallization of β - CaSiO_3 from the simple and processable precursors employing PVA occurred at a relatively low temperature of 900°C . In particular, an exothermic reaction accompanying the volume expansion in the calcination process contributed to form a soft and porous powder structure and highly sinterable fine powders after simple ball milling. The porous powder was sub-micrometer to $1.5\ \mu\text{m}$ in size and had a high specific surface area of $23.2\ \text{m}^2/\text{g}$. The densified CaSiO_3 showed a fine and uniform microstructure of pure α phase.

Finally, the polymer solution method is expected to be applicable to the synthesis of many CaO-based other porous powders because of its special merits, such as expanded powder structure by a distinct exothermic reaction and a simple process, and a relatively low crystallization temperature.

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