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Effects of H_2O in EtOH–H_2O Disperse Medium on the Electrophoretic Deposition of $CaSiO_3$ Fine Powder

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Abstract

The effects of H_2O in the EtOH–H_2O disperse medium on the electrophoretic deposition (EPD) of $CaSiO_3$ fine powder were investigated. Fine $CaSiO_3$ powder with average diameter of 1·7 μm was prepared by the coprecipitation method. It was deposited on a stainless steel substrate by EPD in the disperse media with various H_2O concentrations (0–20·2 mass%) under a DC field of 50 V. The amount of the $CaSiO_3$ deposition increased with increasing H_2O up to 11·2 mass% but decreased rapidly beyond this concentration. The surface potential of the powder showed a similar trend as the amount of deposition against H_2O concentration. The effect of H_2O was summarized as follows: (1) the addition of positive charge on the surface of $CaSiO_3$ particles (2) the neutralization of the surface charge by OH^- caused by the dissolution of $CaSiO_3$ in the H_2O.

Keywords: silicate, powders, chemical preparation, electrophoretic deposition, suspensions, shaping

1 Introduction

$CaSiO_3$ (wollastonite) has been traditionally used as a raw material for tiles, pottery, a resin filler, etc. On the other hand, the biocompatibility of the ceramics containing crystalline $CaSiO_3$ (glass ceramics,[1,2] sintered body,[3] etc.) has been reported, so that $CaSiO_3$ ceramics is attracting the attention as a biomaterial. The brittleness of $CaSiO_3$ ceramics, however, may limit the application in the human body. For example, the fracture toughness of glass ceramic Apatite–Wollastonite (A–W), 2·0 MPa $m^{1/2}$, is lower than that of human cortical bone, 6 MPa $m^{1/2}$ at maximum.[4] The coating of a $CaSiO_3$ layer on another material with high toughness, e.g. metal, will solve this problem effectively.

Electrophoretic deposition (EPD) is one of the forming process which has been widely and theoretically studied, and used commercially in ceramic processing;[5,6] it is also a convenient method to prepare a ceramic coating on a metal. EPD is composed of two processes: (1) dispersion of powder in liquid medium and (2) deposition of the powder by electrophoresis. A fine and well-dispersed powder with relatively high surface charge is necessary in this process. For disperse medium, H_2O was used as dispersion medium in many cases, but organic liquid is desirable for some materials. When organic medium is used, H_2O content in the medium may have a large effect on the above two processes. Parfitt *et al.*[7] reported that a small amount of H_2O (ppm level) inverted the surface charge of TiO_2 particles from negative to positive in xylene with AOT (Aerosol OT, dispersant). Cooper *et al.*[8] found the similar tendency on Cu–phthalocyanine in heptane with AOT. In actual ceramic forming process, however, the control of small quantity of H_2O is difficult because the concentration of H_2O is easily changed by the absorption of moisture and/or the evaporation of organic component in the medium. The fluctuation of the small amount of H_2O content will make the dispersion condition unstable. This problem is considered to be avoided by the intentional addition of H_2O over a few percent in the organic dispersion medium because it cancels the slight change of H_2O concentration during the forming process.

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The present paper describes the effect of H_2O (over a few percent) in EtOH–H_2O dispersion medium on the EPD forming of $CaSiO_3$ fine powder prepared by solution method.

2 Experimental Procedures

2.1 Powder preparation

Fine and homogeneous $CaSiO_3$ powder was prepared by the coprecipitation method. Chemicals used were calcium nitrate tetrahydrate and tetraethyl orthosilicate (TEOS). They were dissolved in ethanol and used as a starting solution. The concentration was adjusted to be $0{\cdot}4\,mol\,dm^{-3}$ for $CaSiO_3$. Precipitate was obtained by adding the same amount of 25% NH_4OH to the starting solution. It was dried by a rotary evaporator and an oven at 110°C, and was calcined at 500°C for 2 h and 1000°C for 12 h in air. The powder was ground by a planetary potmill with ethanol for 2 h using Si_3N_4 pot and balls with 2 mm diameter. After grinding, the concentration of the suspension was adjusted to $7\,g/100\,cm^3$ and stored in a polyethylene container.

2.2 Electrophoretic deposition

The $CaSiO_3$ suspension was diluted to $1g/150\,cm^3$ using a mixture of EtOH and H_2O. The concentration of H_2O was adjusted from 0 to 20·2 mass%. It was stored in the beaker ($300\,cm^3$), and a pair of parallel stainless steel plates (austenitic steel containing 19% Cr and 9% Ni, $40\times20\times\,1\,mm^3$, one surface was polished) were dipped as electrodes. The distance between the electrodes was 10 mm. EPD forming was performed by applying a DC electric field of 50 V between them for 3 min. The electrode deposited the powder with was dried in air.

The weight of the deposit per unit area was calculated from the weight measured with a balance and the deposited area measured by an image analysis program on a personal computer (NIH Image Ver. 1·60, written by National Institute of Health, USA) assuming that the thickness was constant at any position of the deposit. The thickness of the deposit was measured with an optical microscope with a microgauge. Before the measurement, the electrode with the deposited powder was molded in epoxy resin, cut, polished and etched with 35% HCl solution to clarify the image. The density of the deposit was calculated from the weight per unit area and the thickness.

2.3 Zeta potential of $CaSiO_3$ particles

Zeta potential of $CaSiO_3$ particles suspended in various EtOH–H_2O solutions was measured by electrophoresis method (Pen-Kem, Lesar Zeemeter 500). For this measurement, the suspension was diluted to $0{\cdot}1\,g/150\,cm^3$ for the observation of particles by laser scattering. For various dispersion medium, dielectric constant and viscosity, which are necessary to calculate zeta potential, were estimated from the interpolation of the data on the literature.[9,10]

2.4 Ca^{2+} ion dissolved into the suspension medium

The concentration of Ca^{2+} ion dissolved from $CaSiO_3$ powder into the dispersion medium was measured by inductive coupled plasma spectroscopy (ICP, Seiko Instruments, SPS-1500VR). Before the measurement, ethanol in the dispersion medium was exchanged to H_2O because ethanol solution cannot be used as a sample for ICP analysis. The procedure was as follows; the $CaSiO_3$ suspension was filtrated with a polypropylene syringe filter ($0{\cdot}2\,\mu m$) and the liquid was dried up in a beaker. The residue was dissolved by HCl solution of 1·8%.

2.5 Firing of the deposited $CaSiO_3$ powder

The $CaSiO_3$ deposit on the substrate was fired in Ar atmosphere with a furnace using a SiC heater at various temperatures ranging from 1100 to 1300°C for 1 h. Heating and cooling rates were 5 and $10°\,min^{-1}$, respectively. The microstructure of the fired samples was observed by scanning electron microscopy (SEM, Hitachi, S-2050).

3 Results and Discussion

3.1 Powder preparation

The particle size distribution and SEM micrograph of $CaSiO_3$ powder after grinding are shown in Figs. 1 and 2 respectively. The morphology of particles were isotropic, and the cumulative diameters of 50 and 90% were 1·7 and $3{\cdot}7\,\mu m$, respectively. This shows that the size of most particles was in the range of micrometers. Powder X-ray diffraction indicated that the crystalline phase was only β-$CaSiO_3$ (wollastonite).

3.2 Electrophoretic deposition of $CaSiO_3$ powder in various mixture-solution of EtOH and H_2O

Figure 3 indicates the amount of deposited $CaSiO_3$ powder on the substrate. The powder deposited on the cathode regardless of the experimental conditions. The amount increased gradually with the H_2O content in the disperse medium up to 11·2 mass%, but decreased rapidly beyond this concentration. In the suspension with a H_2O content higher than 11·2%, $CaSiO_3$ particles agglomerated and sedimented during the EPD process. This caused the decreasing of the amount of deposition. On the other hand, one of the reasons of the

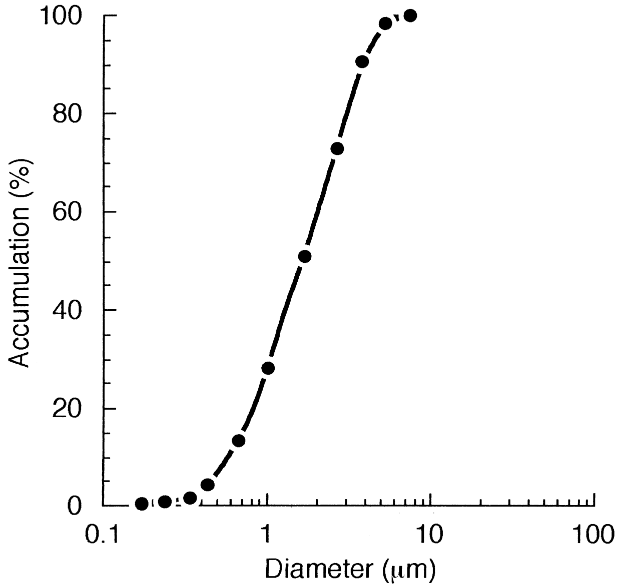

Fig. 1. Cumulative particle size distribution of $CaSiO_3$ powder.

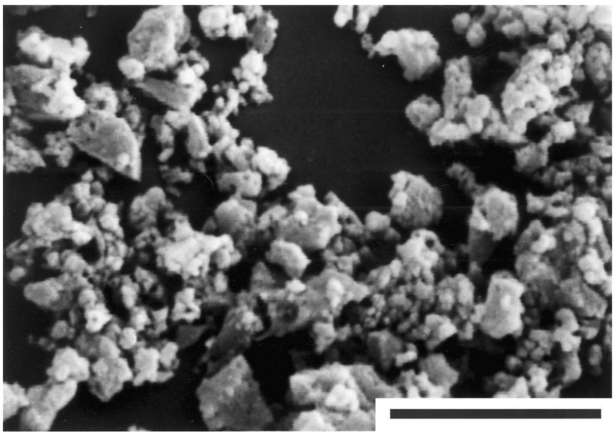

Fig. 2. SEM micrograph of $CaSiO_3$ powder (bar = 5 μm).

increase of the deposition with increasing of H_2O up to 11·2% is considered to be the change of zeta potential of the particles. Figure 4 shows the zeta potential of the particles as a function of H_2O content in the suspension. It increased initially and decreased afterwards with the increasing of H_2O. This trend is similar to that of the amount of deposition, but the H_2O content corresponding to the maximum zeta potential was lower than that for the maximum deposition. It means that the electrophoretic velocity of the particles was not directly proportional to the amount of the deposition. Generally, EPD can be regarded as the 'coagulation' of particles on an electrode. The rate of coagulation is inhibited by repulsive forces between particles caused by zeta potential. That is, when zeta potential is high enough to keep good dispersion, the repulsive force between particles is also large and it can play a suppressive factor for the deposition of powder on the electrode. The highest rate of deposition is achieved by the particles with moderate zeta potential which do not agglomerate in the suspension but easily agglomerate on the substrate. In such a case, the density of the deposit may be lower than that produced by the powder with higher zeta potential; this prediction is derived from the fact that the density of the deposit prepared by the gravitational sedimentation of poorly-dispersed powder is lower than that of well-dispersed powder. Figure 5 shows the density of the deposit as a function of the concentration of H_2O in the suspension. As predicted above, the density decreased with increasing H_2O content. It supports the discussion about the relation between density and zeta potential. There is, however, one discrepancy in the

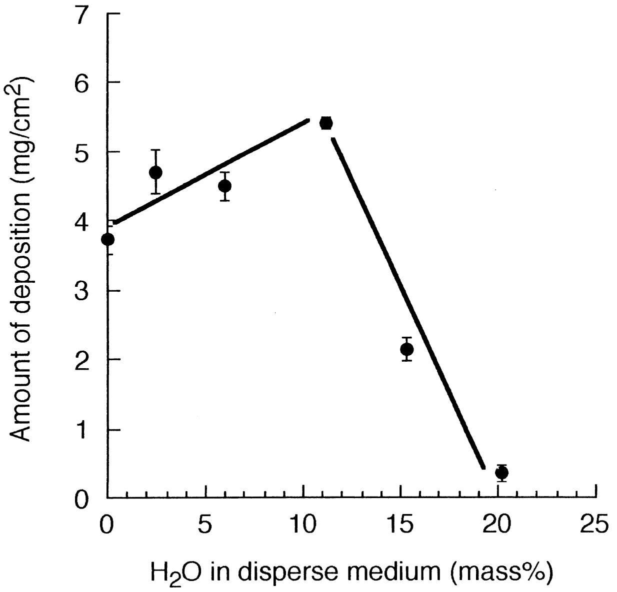

Fig. 3. Effect of H_2O content in disperse medium on the deposition amount of $CaSiO_3$ powder.

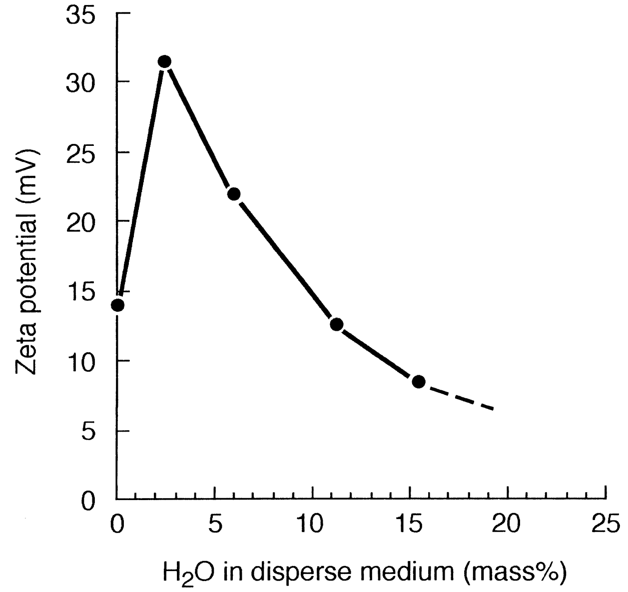

Fig. 4. Effect of H_2O content in disperse medium on the zeta potential of $CaSiO_3$ powder.

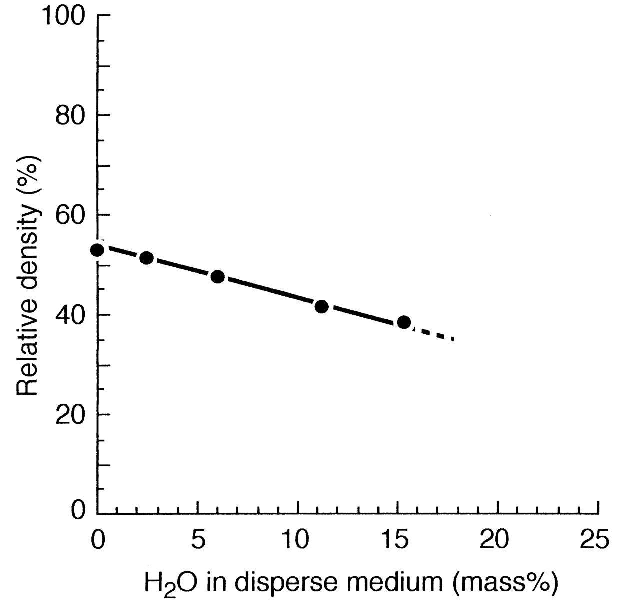

Fig. 5. Effect of H_2O content in disperse medium on the relative density of the deposit of $CaSiO_3$ powder.

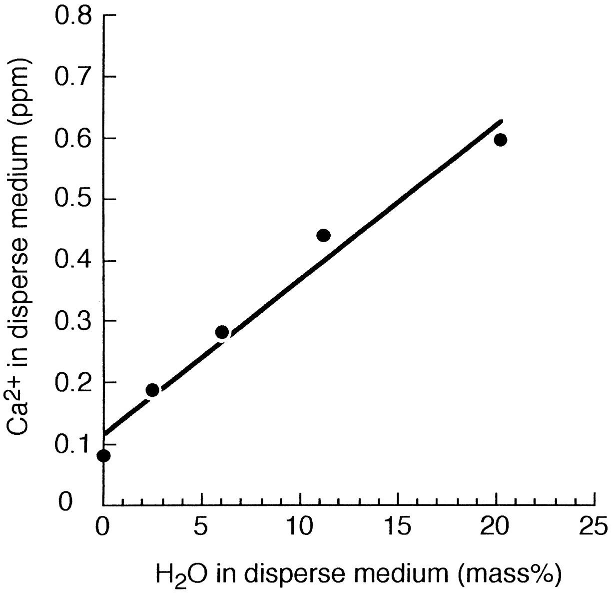

Fig. 6. Effect of H_2O content in disperse medium on the concentration of Ca^{2+} ion in disperse medium.

discussion; the density of 0% H_2O was larger than that of 2·5% H_2O although the zeta potential of the former is lower than that of the latter. The reason is, however, not clear at this stage.

Another possible factor to affect the density of the deposit is the gas evolution at the electrodes caused by the electrolysis of H_2O. Since the electric current during the deposition increased from 11·3 to 101·5 μA cm^{-2} with increasing water content from 0 to 20·2 mass%, it may be possible to consider gas evolution on the electrode and it inhibits the packing of the electrophoretically deposited particles. However, this may not be a dominant factor; if the decreasing of the density occurs mainly by the gas evolution, the amount of the deposit may also decrease with increasing H_2O. This is incompatible with the experimental result shown in Fig. 3.

As discussed above, zeta potential of the $CaSiO_3$ particles changed with the H_2O content in the suspension. It was caused by the addition and the removal of positive charge on the surface of the particles. The former reason may be due to the proton generated by the dissociation of H_2O while the latter one can be explained by the dissolution of Ca^{2+} ion from the particle. That is,

$$CaSiO_3 + H_2O \rightarrow Ca^{2+} + SiO_2 + 2OH^-$$

The OH^- ions formed in this reaction may neutralize the surface charge of the particles and lower the zeta potential. The concentration of Ca^{2+} ion in the dispersion medium is shown in Fig. 6. The above discussion is supported by the increase of Ca^{2+} with increasing H_2O content. When $CaSiO_3$ powder was ground with H_2O, the slurry showed relatively high alkalinity (pH~9), and high viscosity by agglomeration. This fact also supports the above consideration. In addition, Ca^{2+} ions themselves also seemed to promote the agglomeration due to the decreasing of thickness of diffuse double layer by increasing of the ionic strength in the suspension. This occurred parallelly with neutralization of the surface charge by the OH^- ions.

3.3 Firing of the powder deposit formed by EPD

The samples of 0% H_2O were fired at temperatures ranging from 1000 to 1300°C in Ar atmosphere for 1 h to avoid the oxidation of the substrates. The powder deposit did not peel off from the substrates by firing at 1000 and 1100°C. The SEM micrograph of the sample fired at 1100°C is exhibited in Fig. 7. The layer of $CaSiO_3$ was very porous after firing in this condition but it was not broken and removed by the scratching in parallel crosses with a craft knife (this method is used as a test of adhesion of

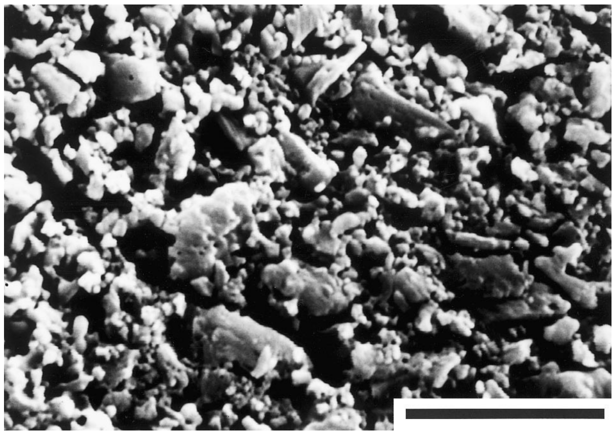

Fig. 7. SEM micrograph of the surface of deposited $CaSiO_3$ powder fired at 1100°C for 1 h (bar = 5 μm).

paint in Japanese Industrial Standard, K-5400). On the other hand, the powder deposit fired at 1200 and 1300°C were largely peeled off from the substrates. For the densification of $CaSiO_3$ layer, it will be necessary to optimize the firing schedule and/or to form an intermediate layer between the $CaSiO_3$ layer and the substrate, which compensates the shrinkage by sintering and minimizes the difference of thermal expansion.

4 Conclusions

The effects of H_2O (over a few percents) in the EtOH–H_2O disperse medium on the electrophoretic deposition of $CaSiO_3$ fine powder were investigated and the following conclusions were obtained.

1. The amount of the deposition increased with increasing H_2O content in the suspension up to 11·2 mass% but decreased above this concentration.
2. The H_2O in the suspension showed two effects; when the concentration was lower than 11·2% it added positive charge to the surface of the powder, but when the concentration was higher than 11·2%, it lowered the surface positive charge by the formation of OH^- ions.
3. The H_2O amount which brought about the maximum deposition rate did not agree with that with the highest zeta potential; the rate of deposition was determined not only by the rate of electrophoresis but also by that of deposition process.
4. Porous $CaSiO_3$ thick film was prepared by firing the powder deposit lower than 1100°C.

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