

Synthesis of Calcium Titanate Films and the Recycle of the Raw Material by Hydrothermal Method

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A calcium titanate film was deposited on a titanium substrate in a mixed solution of calcium salts and potassium hydroxide over 100°C. The amount and the morphology of the deposited films were varied with the kind and the concentrations of calcium salt, the concentration of potassium hydroxide and the reaction temperature. A calcium hydroxide powder was also precipitated with calcium titanate film, when using calcium chloride as the starting material, and it was difficult to reuse this co-product for the starting material. In this study, we used calcium carbonate instead of calcium chloride as the starting material for synthesis of the calcium titanate film. After the syntheses of the calcium titanate film, only calcium carbonate powder co-existed and the morphology of the film varied with the particle size of calcium carbonate.

Key words: hydrothermal treatment, calcium titanate, calcium carbonate, solubility, dissolution rate

1. INTRODUCTION

The hydrothermal process was applied for the fabrication of the single crystals of quartz, the light construction materials and the fine powders, and so on. The film formation of the perovskite-type compounds by the hydrothermal method was reported¹⁾ since the end of 1980's. In this process, the electrochemical reaction enhanced the formation of the film by increasing of the thickness of the reacting layer of the substrate. Usually in the hydrothermal process without using an electrochemical technique, the concentrations of the starting materials were increased in order to increase the amount and the rate of deposition. The powders were also precipitated in the reactor and the yield of the film was very low, though the amount of the deposition of the film was increased by this method. Generally, the produced powders were not reused for the synthesis of the film because they were different from the starting materials. The flow-system was proposed^{2, 3)} when the concentration of the starting materials was not so high.

On the other hand, a calcium titanate film was easy to form on a titanium substrate by hydrothermal method with good adhesion and has no toxicity. In previous study⁴⁾, calcium titanate (CaTiO₃) was applied to the interlayer of the titanium substrate and hydroxyapatite layer as a multilayer for the biomaterial. The calcium titanate was formed on the titanium substrate from the mixed solution of calcium chloride and potassium hydroxide under the hydrothermal condition. A calcium hydroxide powder was also formed with the calcium titanate film. In this study, the calcium titanate film was formed hydrothermally using the various kinds of calcium salt as the starting material, in order to reuse the starting material and improve of the yield.

2. EXPERIMENTAL

Various kinds of calcium salts, calcium chloride dihydrate (CaCl₂·2H₂O; Kanto Chemical Co. Inc., Reagent Grade), calcium nitrate tetrahydrate

(Ca(NO₃)₂·4H₂O; Koso Chemical Industries, Ltd., Reagent Grade), calcium acetate monohydrate (Ca(CH₃COO)₂·H₂O; Wako Pure Chemical Industries, Ltd., Reagent Grade), calcium hydroxide (Ca(OH)₂; Wako Pure Chemical Industries, Ltd., Reagent Grade), calcium sulfate dihydrate (CaSO₄·2H₂O; Wako Pure Chemical Industries, Ltd., Reagent Grade), calcium carbonate (CaCO₃; Wako Pure Chemical Industries, Ltd., Reagent Grade) and calcium fluoride (CaF₂; Wako Pure Chemical Industries, Ltd., Reagent Grade) were used as the starting materials. The solution of potassium hydroxide (KOH; Kanto Chemical co., Reagent Grade) was prepared and the concentration was 1.7 mol·dm⁻³. A titanium plate (Nilaco Co., 10 x 40 x 0.05 mm³) as a substrate was poured into Teflon-lined stainless-steel autoclaves with the KOH solution and the calcium salt and heated to 150°C for 24 h. The charged concentration of the calcium salts was 0.10 mol·dm⁻³. The reacted substrates were separated from the reacting solution and the precipitated powders, and the substrates were rinsed in the distilled water using an ultrasonic wave and dried at 70 °C for 24 h.

The classified calcium carbonate was also used as the starting material. The particle distribution of the calcium carbonate (calcite; SS#30; Nitto Funke K. K.) was measured by particle size analyzer (Microtrac® HRA9320-X100). The powder was classified by the air flow and the classification points were 10 and 30µm. The powder which classified as larger than 30µm was treated in the KOH solution (1.7 mol·dm⁻³) at 150°C for 6h in order to remove fine particles adhered on the surface. The synthesis duration was 1-6 h when using the classified calcium carbonate.

The films and the powders were analyzed by X-ray diffractometry (XRD; MAC Science MXP-3) using Cu radiation to identify the crystalline phases, and the surface morphology of the film was observed by scanning electron microscopy (SEM; JEOL JSM-5310).

3. RESULTS AND DISCUSSION

3.1 Morphology of the film and the precipitated powder

The SEM photographs of the films are shown in Fig. 1. The deposition amount of the film and the phases of the precipitated powder are shown in Table I. The synthesized film was CaTiO_3 regardless of the kind of calcium salts in this study. Calcium hydroxide powder was produced after the formation of CaTiO_3 film, when using calcium nitrate, chloride, acetate and hydroxide as the starting material. The stepped surface was observed and the deposition of the film was small when synthesized from these calcium salts.

The amount of the deposition on the substrate was relatively large and the euhedral cubic grains were formed when using calcium sulfate and calcium carbonate. This morphology was also observed when calcium chloride was used for the starting material with small concentration or at high KOH concentration⁴). In these cases, the phases of the precipitated powders were same as those of the starting calcium salts.

A calcium fluoride was also remained as the precipitation powder after the formation of calcium titanate film. The grain was round and was not euhedral cube, and the fine particles seemed to adhere on the surface of the film, though the amount of the film deposition of the film was medium in Table I.

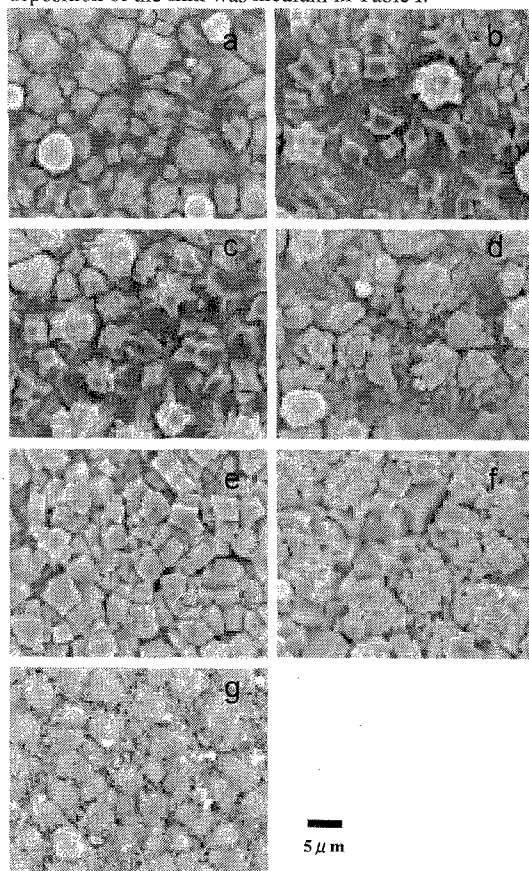


Fig. 1. SEM photographs of CaTiO_3 films synthesized at 150°C for 24 h from various kinds of calcium salt. The charged concentrations of KOH and calcium salts were 1.7 and $0.10 \text{ mol}\cdot\text{dm}^{-3}$, respectively. The starting materials are a) nitrate, b) chloride, c) acetate, d) hydroxide, e) sulfate, f) carbonate and g) fluoride.

Table I. The amount of the film and the phases of the film and of the precipitated powder

Starting material*	amount**	film	powder
$\text{Ca}(\text{NO}_3)_2$	0.221	CaTiO_3	$\text{Ca}(\text{OH})_2$
CaCl_2	0.130	CaTiO_3	$\text{Ca}(\text{OH})_2$
$\text{Ca}(\text{CH}_3\text{COO})_2$	0.186	CaTiO_3	$\text{Ca}(\text{OH})_2$
$\text{Ca}(\text{OH})_2$	0.235	CaTiO_3	$\text{Ca}(\text{OH})_2$
CaSO_4	0.377	CaTiO_3	CaSO_4
CaCO_3	0.712	CaTiO_3	CaCO_3
CaF_2	0.259	CaTiO_3	CaF_2

* Described as anhydrides

** mg/cm^2 (substrate)

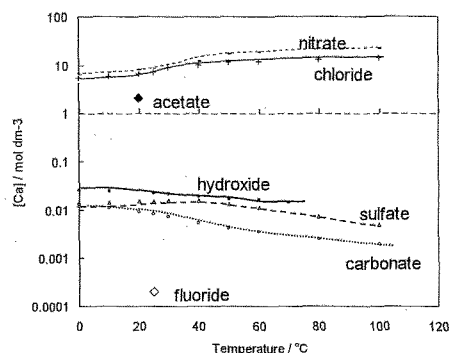


Fig. 2. The solubility curves of the calcium salts to the water (revised from ref.5).

The yield of the calcium salts as the film was only 1 %, when the carbonate used as the starting material. Most of the calcium existed in the aqueous solution and as the precipitated powder after the formation of the CaTiO_3 film.

Figure 2 shows the solubility of the calcium salts to the water. The solubility of the nitrate, the chloride and the acetate was considerably higher than that of hydroxide around the room temperature. On the contrary, the solubility of the sulfate, the carbonate and the fluoride was smaller than that of the hydroxide. The hydroxide precipitated when using the calcium salts of which the solubility was higher than the hydroxide. And the starting calcium salts remained and the precipitation of the hydroxide did not form at room temperature after the reaction, when using the salts of which the solubility was lower than the hydroxide.

The concentration of OH^- was lowered by the formation of calcium hydroxide when the starting calcium salts were calcium nitrate, chloride and acetate. Therefore, the dissolution of the titanium substrate was suppressed and the deposition of the calcium titanate film was also suppressed. The reaction was occurred in $1.7 \text{ mol}\cdot\text{dm}^{-3}$ KOH solution, not in the pure water like Fig.2. It is considered, that the calcium concentration in the reacting solution was extremely lower than the case of calcium hydroxide in Fig.2. And the calcium sulfate and carbonate might be dissolved in the reacting solution though the rate of the dissolution was not so rapid.

It was not easy to estimate the accurate hydroxide ion concentration, because the hydroxide ion was consumed by the reaction with the titanium substrate from at the low temperature. The concentration of hydroxide ion decreased with the increase of the temperature by the

decrease of the solubility of calcium hydroxide and by the formation of CaTiO_3 ⁶⁾. The solubility of the calcium hydroxide, sulfate and the carbonate tends to lower with the increase of the temperature.

3.2 Effect of the particle size of CaCO_3 on the film formation

The classified calcium carbonate powders were also used for the synthesis of the CaTiO_3 film in order to control the ratio of the dissolution. The particle size distribution and the SEM photograph of the powder before the classification are shown in Figs. 3 and 4a, respectively. The maximum frequencies of the particle size were around 1 and 20 μm . Based on the particle size distribution, the CaCO_3 powder was classified at 10 and 30 μm . The SEM photographs of the classified powders are shown in Fig. 4 b, c. The fine particles adhered on the surface of the large particles even after the classification. The fine particles were removed from the surface of the large particles by the dissolution in the KOH solution at 150°C for 6 h (Fig. 4d). Two kinds of powder 'fine' and 'coarse', shown in Fig. 4 b and d, respectively, were used in this section.

The change in the weight of the substrate with the reaction time at 150°C is shown in Fig. 5. The amount of the deposition was increased rapidly between 1 and 2 h, when synthesized from the coarse CaCO_3 . The rapid increase of the deposition was observed after 2 h, when the fine CaCO_3 was used. The deposition amount of the film synthesized from the fine CaCO_3 was more than that from the coarse CaCO_3 after 6 h.

Figure 6 shows the SEM photographs of the substrates with various synthesis durations using the fine and the coarse CaCO_3 . When the fine CaCO_3 was used, the grain grew rather than nucleated further on the substrate after the first nucleation on the substrate. On the contrary, the further nucleation on the substrate was observed rather than the grain growth, when the coarse CaCO_3 was used.

The dissolution rate of CaCO_3 might be rapid and the hydroxide ion was consumed by the formation of $[\text{Ca}(\text{OH})]^+$ and $\text{Ca}(\text{OH})_2$ when using fine CaCO_3 powder. Then the dissolution of the titanium substrate was delayed, and the nucleation number on the substrate might be few. The nucleation was suppressed because of the limited supply of the titanium ions. Then the stepped surface was improved (Fig.6 e).

When using the coarse CaCO_3 , the dissolution of the particles was slow, and the decrease of the concentration of the hydroxide ion was low. The concentration of the calcium ion in the solution was not enough to nucleate CaTiO_3 on the substrate at 1 h, though the dissolution of the titanium substrate enhanced. After the progress in the dissolution of CaCO_3 , the concentration of the calcium ion in the solution increased to nucleate on the substrate rapidly around at 2 h. There were many nucleation, the fine grains were covered the substrate.

Figure 7 shows the change in the deposition of the CaTiO_3 film with the charged concentration of calcium salts. When using calcium chloride, the deposition of the film decreased with the charged concentration of the calcium salts because of the consumption of the

hydroxide ions. The dissolution of the titanium was suppressed and the formation of the CaTiO_3 film was also suppressed. When using calcium carbonate as the starting material, there was small effect on the decrease in the deposition of the film with the increase of the starting material. After the synthesis of the CaTiO_3 film, the morphology of the precipitated powder was similar to that in Fig. 4 d, when using the coarse CaCO_3 powder. From above results, by using the calcium carbonate as a starting material, the easy control of the synthesis condition and the reuse of the starting material were seemed to be possible.

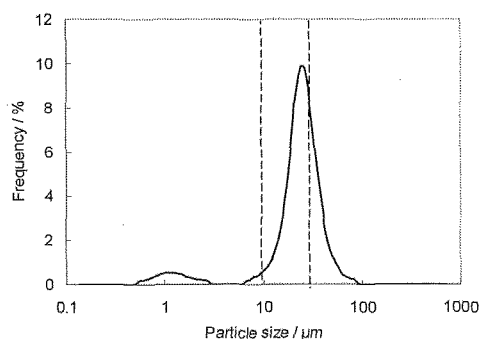


Fig. 3. Particle size distribution of CaCO_3 powder (SS#30) before the classification

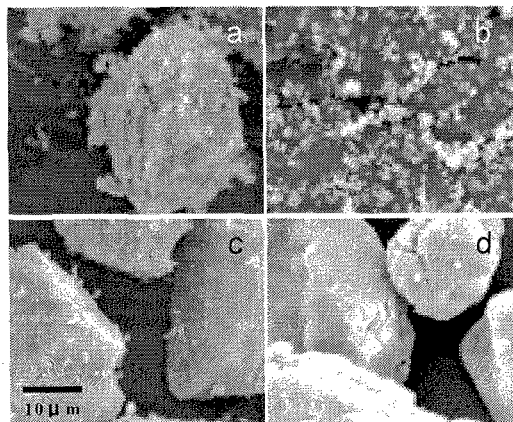


Fig. 4. SEM photographs of calcium carbonate powders; (a) before the classification, (b) classified under 10 μm , (c) classified over 30 μm and (d) classified over 30 μm and treated in KOH solution at 150°C for 6h.

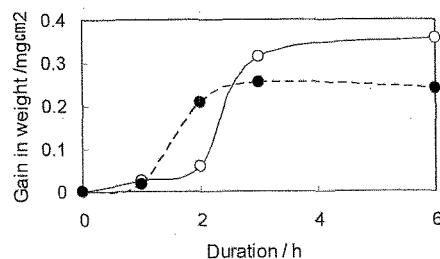


Fig. 5. Change in weight of the substrate after the hydrothermal syntheses from, fine (O) and coarse (●) CaCO_3 .

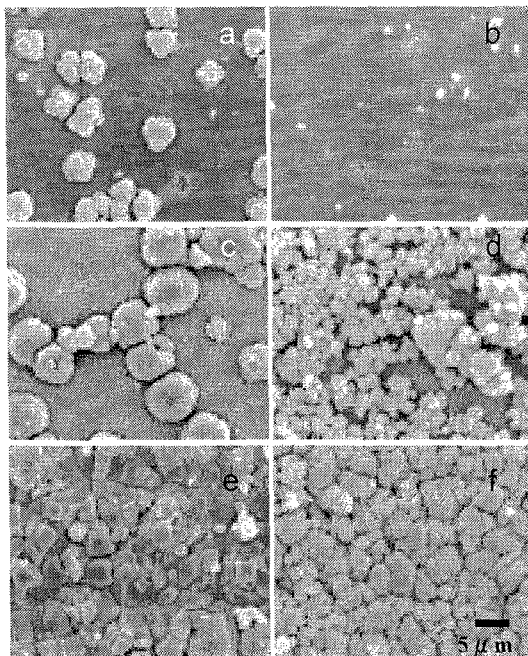


Fig. 6. SEM photographs of the film synthesized from the fine (a, c, e) and the coarse CaCO_3 (b, d, f), treated at 150°C for 1h (a, b), 2 h (c, d) and 3 h (e, f).

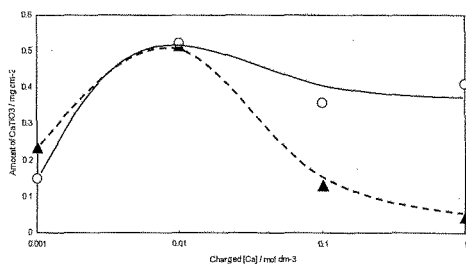


Fig. 7. Change in the deposition of the film with the concentration of calcium salts. \circ : fine CaCO_3 and \blacktriangle : CaCl_2 .

4. CONCLUSION

The film of CaTiO_3 was formed on the titanium substrate by the hydrothermal process using KOH and the various kinds of calcium salt. The calcium salts of which solubility was lower than that of calcium hydroxide seemed to be reused in this process.

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