TECHNICAL REPORT

Growth of calcium carbonate crystal on various substrates from a saturated calcium carbonate solution utilizing difference in solubility

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Crystalline calcium carbonate was deposited on various substrates (substrate temperature of 80 °C) from a saturated calcium hydrogen carbonate solution (solution temperature of 10 °C). A single aragonite phase deposited on the Al substrate, whereas a mixed phase of aragonite and calcite grew on the soda lime glass, borosilicate glass, silica glass, and polycarbonate substrates. With increasing deposition time, the crystal size and the proportion of calcite on the soda lime silicate glass substrate increased. Furthermore, calcite crystals were preferentially deposited on an Al substrate with a thin film of Au as a buffer layer (Au/Al substrate).

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1. Introduction

Calcium ions present in various solutions deposit on available surfaces as calcium carbonate (CaCO_3) by reacting with atmospheric carbon dioxide gas. These calcium scales not only block pipes, pumps, and other equipment of various machineries in chemical plants, but also decrease the thermal conductivity.^{1)–3)} Therefore, the prevention and control of scale deposition is crucial in industrial facilities.⁴⁾ In recent years, extensive research has been conducted on the development of inhibitors for suppressing CaCO_3 formation.⁵⁾ Kojima et al. studied the morphology of CaCO_3 deposited by the decarboxylation of a saturated calcium hydrogen carbonate [$\text{Ca}(\text{HCO}_3)_2$] solution at various temperatures.⁶⁾ In a previous work, we deposited calcite from a saturated aqueous CaCO_3 solution by mimicking the formation of stalagmites in nature.⁷⁾ Importantly, because Ca ions present in a solution can react with CO_2 and immobilize as CaCO_3 , the investigation of the deposition of CaCO_3 from solutions is expected to provide a useful technique for reducing the amount of CO_2 ,⁸⁾ a greenhouse gas, in atmosphere. The investigation of the deposition of CaCO_3 on various solid surfaces can provide useful insights for not only the removal and controlled deposition of scales, but also the immobilization of atmospheric CO_2 gas.

CaCO_3 exhibits a negative temperature dependence of solubility, that is, its solubility in water increases with decreasing temperature and vice versa.^{6),9),10)} We have

previously reported Hydroxyapatite (HAp) deposition from a saturated calcium phosphate solution,¹¹⁾ in which HAp exhibits a negative solubility coefficient similar to that of CaCO_3 . In the previous experiment, a heated substrate was placed on the surface of a cooled saturated HAp aqueous solution; the contact of the heated substrate with the cooled solution reduced the HAp solubility near the substrate, thereby facilitating the deposition of HAp on the substrate. In this study, we deposited CaCO_3 by the same process¹¹⁾ utilizing the negative solubility difference of the CaCO_3 aqueous solution. CaCO_3 is highly soluble in saturated aqueous CO_2 solutions.¹²⁾ Hence, CO_2 was bubbled on the solution during deposition. Using this solution, CaCO_3 was deposited on various substrates.

2. Experimental

CaCO_3 powder (Wako Pure Chemical Industries, Ltd., Japan) was dissolved in 1 L of ion-exchanged water with a CaCO_3 concentration of 0.2 wt % (highly saturated solution). The obtained solution was stirred at 10 °C for 0.5 h with the simultaneous bubbling of CO_2 at 0.02 MPa at a rate of 2 L/min. The resulting solution was filtered to remove undissolved CaCO_3 powder to obtain a saturated $\text{Ca}(\text{HCO}_3)_2$ solution. For deposition, metallic aluminum (as a common metal), polycarbonate (as a common resin), soda lime silicate glass (as a common glass), borosilicate glass (as a common non-alkaline glass), and silica glass (pure silicate glass) substrates were used. Hereinafter, soda lime silicate glass is denoted as “glass”. Furthermore, we prepared a substrate by sputtering a gold buffer layer onto a metallic Al substrate using an ion coater (Eiko Engineering Co., Ltd., Japan). **Figure 1** shows a schematic of the

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Fig. 1. Schematic illustration of the apparatus used for depositing calcium carbonate on substrates.

Fig. 2. XRD spectra of the samples grown on various substrates at a substrate temperature of 80 °C for 5 h.

apparatus used for depositing CaCO_3 on various substrates. The substrates were placed on the surface of a heater and placed in contact with the surface of a saturated $\text{Ca}(\text{HCO}_3)_2$ solution for 1–7 h. The substrate was heated to a temperature of 80 °C. The substrate temperature was measured using a radiation thermometer (TMHX-CN, Japan Sensor Co., Ltd., Japan). After deposition, the substrate with the deposited specimen was removed from the solution. The crystallographic structures of the prepared films were analyzed by X-ray diffraction (XRD, Rigaku Miniflex, Japan) analysis with $\text{Cu K}\alpha$ radiation (30 kV, 15 mA). The microstructures of the resulting films were analyzed by scanning electron microscopy (SEM, JEOL JCM-6000 Plus, Japan).

3. Results and discussion

3.1 Deposition of CaCO_3 on various substrates at 80 °C for 5 h

CaCO_3 was deposited at 80 °C for 5 h on Al, polycarbonate, and glass substrates, which were used as representatives of metals, organic substances (resins), and ceramics (glass), respectively. **Figure 2** shows the XRD spectra of the prepared samples. XRD analysis revealed that only aragonite CaCO_3 formed on the Al substrate, whereas both

Fig. 3. SEM images of the samples grown on various substrates at a substrate temperature of 80 °C for 5 h. Rhombohedral like crystals are observed in the solid circle.

aragonite CaCO_3 and calcite CaCO_3 formed on the glass and polycarbonate substrates. **Figure 3** shows the SEM images of the deposited samples. As can be seen, needle-like crystals formed as a main phase on the Al substrate, whereas both needle-like (upper surface) and rhombohedral like crystals (bottom of the deposition, close to the substrate) formed on the glass and polycarbonate substrates. It has been reported that needle-like CaCO_3 crystals are aragonite CaCO_3 ,¹³⁾ while rhombohedral crystals are calcite CaCO_3 .¹⁴⁾ XRD and SEM analyses confirmed that a single aragonite phase deposited onto the Al substrate, while a mixed phase of calcite and aragonite grew on the glass and polycarbonate substrates. Kojima et al. reported that the single aragonite phase forms by the decarboxylation of the $\text{Ca}(\text{HCO}_3)_2$ solution at a temperature of 50 °C or higher.⁶⁾ Because deposition (decarboxylation) on the Al substrate was carried out at a substrate temperature of 80 °C, only a single aragonite phase was deposited. However, calcite also deposited on glass and polycarbonate substrates, which is different from the findings of a previous report.⁶⁾ To understand the growth of calcite/aragonite on the glass substrate, the presence of Na in soda lime glass was considered. Thus, we further studied the change in the precipitation phase with precipitation time (discussed in Section 3.2) and investigated the deposition of CaCO_3 on quartz glass and borosilicate glass (non-alkali glass) substrates (discussed in Section 3.4). Furthermore, it has been reported that the presence of organic compounds produces calcite and vaterite when CaCO_3 is precipitated from an aqueous solution of CaCO_3 .¹⁵⁾ We found that not only aragonite, which is stable at the deposition temperature,⁶⁾ but also calcite deposited on the polycarbonate

Fig. 4. XRD spectra of the samples grown on a glass substrate at a substrate temperature of 80 °C for 1–7 h.

substrate. This implies that a single calcite phase deposited on all the substrates at a substrate temperature of 50 °C or lower under the present experimental conditions.

3.2 Effect of deposition time on the phase and quantity of CaCO_3 deposited on a glass substrate at 80 °C for 1–7 h

CaCO_3 was deposited on a glass substrate at 80 °C for 1–7 h. **Figures 4** and **5** show the XRD spectra and SEM images of the prepared samples, respectively. XRD peaks corresponding to calcite and aragonite were observed for all the samples. With increasing deposition time, the peak intensity of calcite increased, while that of aragonite did not significantly change. As can be seen from the SEM images in Fig. 5, all the samples exhibit needle-like crystals and rhombohedral crystals; however, the rhombohedral crystals (calcite) are deposited close to the substrate surface. With increasing deposition time, rhombohedral crystals (calcite) grew close to the substrate surface. Based on these results, the mechanism of CaCO_3 crystal growth is considered to be as follows: 1) Aragonite and calcite nucleated onto the substrate, 2) Aragonite grew rapidly, and 3) Calcite grew slowly and densely. Here, no growth of aragonite was observed at longer deposition times. This is because when the needle-like crystals of aragonite grew, the heat from the substrate was not sufficiently conducted to the tips of the needle-like crystals because of the low thermal conductivity of aragonite.¹⁶⁾ Therefore, the growth of aragonite crystals was limited because the decarboxylation of the $\text{Ca}(\text{HCO}_3)_2$ solution did not occur at the tips of the aragonite crystals. Further, we evaluated the amount of deposited CaCO_3 . The amounts of deposited CaCO_3 (aragonite and calcite) were 1.13, 2.47, 5.38, and 6.53 mg/cm^2 at deposition times of 1, 3, 5, and 7 h, respectively. The result suggests that the CaCO_3 deposition amount is proportional to the deposition time in the present

Fig. 5. SEM images of the samples grown on a glass substrate at a substrate temperature of 80 °C for 1–7 h. Rhombohedral like crystals are observed in the solid circle.

experiment. Moreover, only calcite crystals grew with increasing deposition time (Fig. 5). Therefore, we studied on the growing rate of calcite. The growth of calcite crystals was incomplete and inhomogeneous in the normal direction to the substrate; however, the deposition of calcite crystals depended on the deposition time, as determined from the cross-sectional image in Fig. 5. The calcite growth rate calculated from the cross-sectional SEM image in Fig. 5 was 1.3 $\mu\text{m}/\text{h}$. In the previous study,⁷⁾ in which calcite was grown by dropping a saturated CaCO_3 solution onto a substrate, the calcite growth rate was 0.7 $\mu\text{m}/\text{day}$; however, the substrate temperature was different. We found that the growth rate of the present growth method is considerably higher than that of the solution dropping method mimicking the formation of calcite stalagmites.⁷⁾

For up to 7 h of deposition, the amount of deposited calcite was proportional to the deposition time. Similar to aragonite, the thermal conductivity of calcite is low.¹⁷⁾ If the deposition time is longer than that employed in the present study, the temperature of the crystal surface may decrease (because the heat conduction from the heated substrate becomes insufficient due to the low thermal conductivity of calcite), thereby decreasing the calcite growth rate.

Fig. 6. XRD spectra of the samples grown on Au/Al substrate at 80 °C for 5 h.

Fig. 7. SEM images of the samples grown on Au/Al substrate at 80 °C for 5 h. Rhombohedral like crystals are observed in the solid circle.

3.3 CaCO_3 deposition on Au/Al substrate at 80 °C for 5 h

Teghidet et al. reported that calcite grows epitaxially on Au substrates when CaCO_3 is deposited by the solution method.¹⁸⁾ Although only aragonite grew on the Al substrate, we considered that calcite can be grown using a Au buffer layer onto the Al substrate. A Au buffer layer was thus sputter coated on an Al substrate (hereinafter denoted as Au/Al), and CaCO_3 was deposited onto the Au/Al substrate at 80 °C for 5 h. **Figures 6 and 7** show the XRD spectra and SEM images of the obtained sample, respectively. XRD analysis revealed the deposition of both calcite [(104) peak] and aragonite on the Au/Al substrate. This is consistent with the SEM analysis, which shows the presence of both rhombohedral crystals (calcite) and

Fig. 8. XRD spectra of the samples grown on soda lime silicate glass, borosilicate glass, and silica glass at 80 °C for 5 h.

needle-like crystals (aragonite) on the Au/Al substrate. Although aragonite grows preferentially at a substrate temperature of 80 °C (CaCO_3 deposition temperature),⁶⁾ the Au buffer layer promoted the growth of calcite under the same deposition conditions. This indicates that the CaCO_3 phase growing on a substrate can be controlled using a buffer layer. In previous reports,¹⁸⁾ calcite was deposited from CaCO_3 solution by an electrochemical method. In this investigation, calcite nuclei were generated by epitaxial growth on gold substrates, and calcite crystals were grown onto the generated calcite nuclei. Under the conditions of the present study, aragonite was expected to deposit, but it was considered that calcite nuclei were preferentially generated on the gold buffer layer and the growth of calcite crystals was observed similar to the previous studies.¹⁸⁾

3.4 CaCO_3 deposition on soda lime silicate glass, borosilicate glass, and silica glass at 80 °C for 5 h

CaCO_3 was deposited on soda lime silicate glass (glass), borosilicate glass, and silica glass at 80 °C for 5 h to determine the effect of the glass substrate on crystal growth. **Figures 8 and 9** show the XRD spectra and SEM images of the prepared samples, respectively. XRD analysis revealed that both calcite and aragonite grew on borosilicate glass and silica glass substrates. The SEM images show rhombohedral calcite and needle-like aragonite crystals on both the borosilicate glass and silicate glass substrates. The crystal growth on borosilicate and silica glass substrates was similar to that on the soda lime silicate glass. The results imply that the growth of calcite on the soda lime glass substrate was not caused by the alkaline component

Fig. 9. SEM images of the samples grown on soda lime silicate glass, borosilicate glass, and silica glass at 80 °C for 5 h.

such as Na, but by the presence of SiO_2 in the silicate glasses.

4. Conclusion

A saturated aqueous solution of $\text{Ca}(\text{HCO}_3)_2$ was prepared by bubbling CO_2 and subsequently cooled. The cooled solution was then used to deposit CaCO_3 crystals on various substrates at a high substrate temperature. We successfully deposited CaCO_3 crystals onto various substrates by utilizing its temperature-dependent solubility. A single aragonite phase deposited on the Al substrate, whereas a mixed phase of aragonite and calcite grew on the soda lime silicate glass, borosilicate glass, silica glass, and polycarbonate substrates. The growth of a mixed phase of calcite and aragonite on the glass substrates were attributed to the presence of SiO_2 in the silicate substrates. The deposition of CaCO_3 on a soda lime silicate glass substrate for a long time led to the preferential growth of calcite, with the growth of a small amount of aragonite. Furthermore, calcite crystals preferentially deposited on an Au/Al (Au buffer layer on Al) substrate, which indicates

that the growth of calcite crystals can be controlled using an Au buffer layer.

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