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AFM Observation of Calcite Surface after Reaction with Phosphate

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Cleaved calcite was immersed into phosphoric acid or diammonium hydrogenphosphate under the various conditions. After the immersion, the calcite surface was observed by AFM. In the case of phosphoric acid, calcite was dissolved into phosphoric acid. Many hollows were observed on the calcite surface. These hollows were lined in particular direction. In the case of diammonium hydrogenphosphate, products were observed on the calcite surface. From the XRD results, the products were considered to be hydroxyapatite.

Key words: calcite, AFM, phosphoric acid, diammonium hydrogenphosphate,

1. INTRODUCTION

Calcite ($CaCO_3$; calcium carbonate) is well known for wide distribution as one of ores in the nature. Calcite has also the property to cleave along $(10\bar{1}4)$ plane. The synthesis of hydroxyapatite at low temperatures was studied by some investigators [1-4]. Ueda et al. [1] reported the morphology after reaction between some kinds of calcium carbonates and phosphate. Kasahara et al.[2] reported the reaction between the powder of calcium carbonate and phosphate. However, they did not study the reaction between calcite (single crystal of calcium carbonate) and phosphate, nor did they examine the reaction using AFM. The purpose of this study is to examine the reaction between calcite and phosphate using AFM.

2. EXPERIMENTAL PROCEDURE

We selected two kinds of phosphate. One is a phosphoric acid, and the other one is diammonium hydrogenphosphate. The calcite was cleaved along $(10\bar{1}4)$ plane. The size of cleaved calcite is 5 mm × 4 mm × 3 mm. The cleaved calcite was immersed into a phosphoric acid solution at the concentration of 1～85 mass% for 10～60 s at room temperature. Also, the cleaved calcite was immersed into a phosphoric acid solution at the concentration of 1～10 mass% which was heated to 40℃ ~ 80℃. After reaction, the calcite was washed with deionized water to stop the reaction and subsequently with ethanol to clean the surface.

The cleaved calcite was immersed into a diammonium hydrogenphosphate solution at the concentration of 0.25～2.0 $mol \cdot dm^{-3}$ for 30 s～10 min at the temperature range from room temperature to 80℃. After immersion, the calcite was washed with deionized water and ethanol in a manner similar to the case of phosphoric acid. The surface of these samples was observed using AFM (Seiko Instruments Inc., SPA 300).

3. RESULTS AND DISCUSSION

To confirm that reaction did not occur between cleaved calcite and deionized water or ethanol, the cleaved calcite was immersed into deionized water at 60℃ and ethanol at room temperature. After immersion, the calcite surface was observed using AFM. The result is shown in Fig. 1. The surface of calcite after immersion did not show any evidence of reaction. Consequently any change in surface morphology of cleaved calcite after immersion in phosphate would be due to the reaction with phosphate.

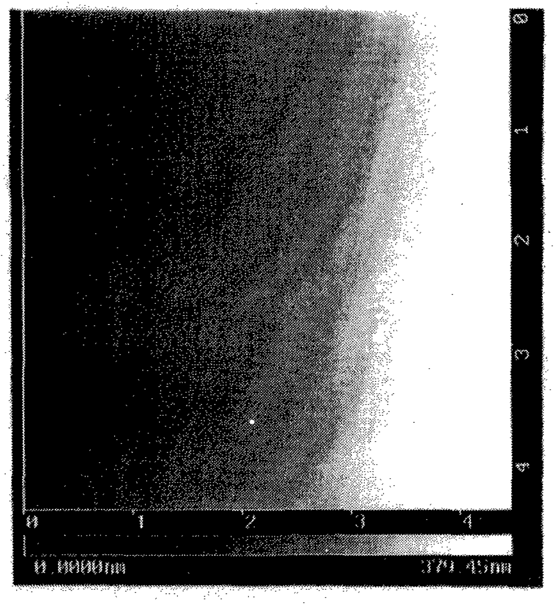
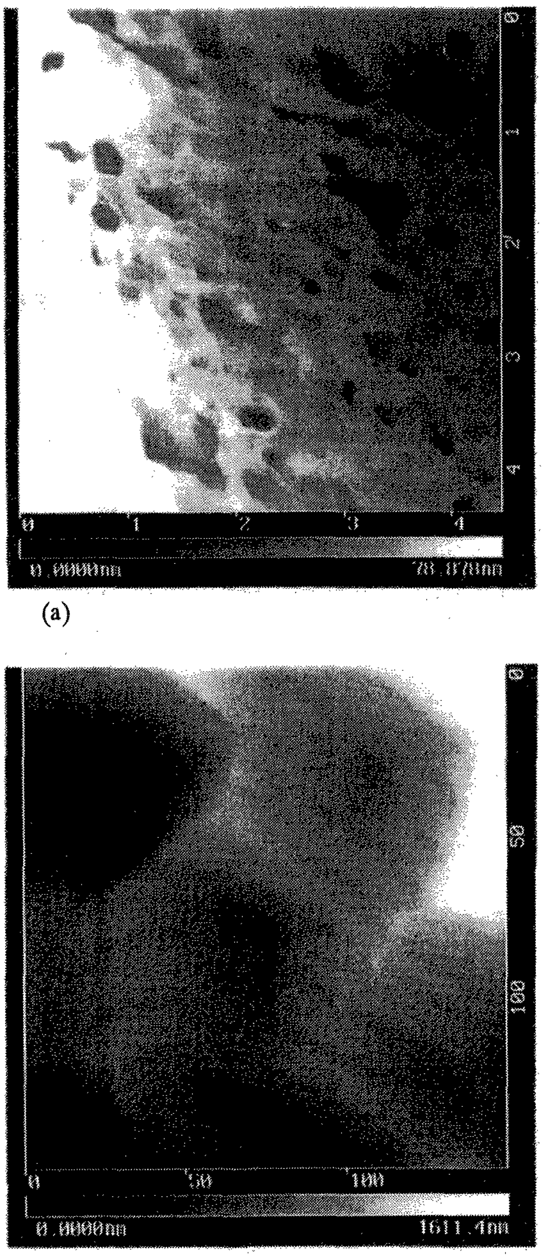


Fig. 1 AFM image of cleaved calcite surface. Scan area was 4.47×4.47 μm.

3.1 Reaction with phosphoric acid

When the cleaved calcite was immersed into a phosphoric acid solution, many bubbles came out from the calcite surface. AFM images of the cleaved calcite surface after immersing into 5 mass% phosphoric acid for 10 and 60 s are shown in Fig. 2. Many hollows were observed on the calcite surface after immersion for 10 s. These hollows on calcite surface were lined in particular direction. With increasing immersion time, the hollows became big and deep (see Fig. 2(b)). After analyzing the gas which came out, we can conclude that the following reaction took place:



(a)

(b)

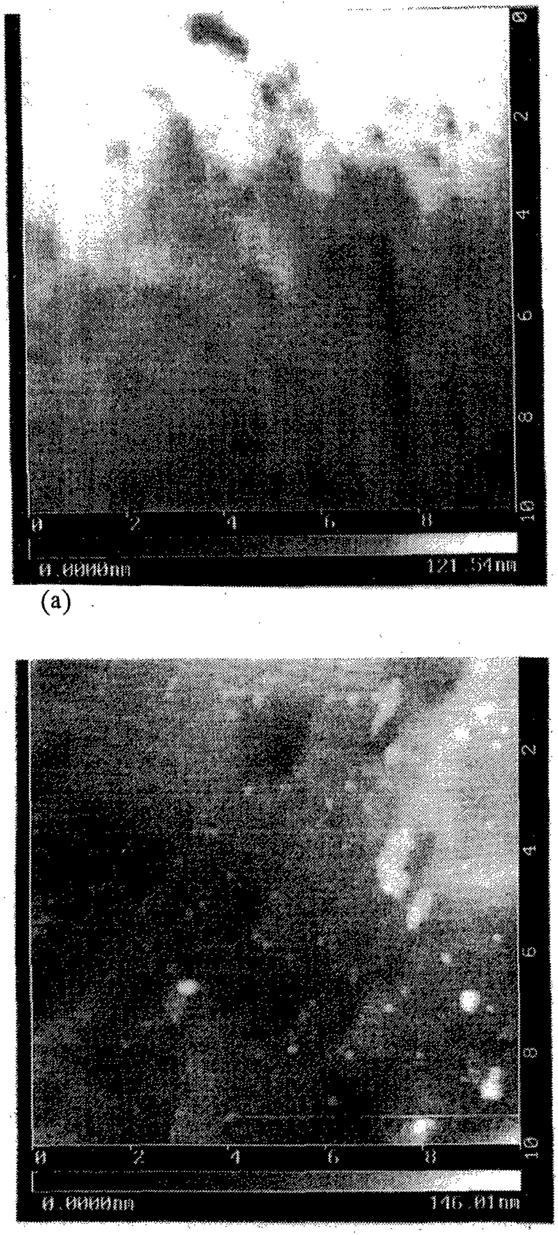
Fig. 2 AFM images of calcite surface after immersion into phosphoric acid for (a) 10 s and (b) 60 s. Scan area was (a) 4.47×4.47 μm and (b) 150×150 μm

$$CaCO_3 \rightarrow CaO + CO_2\ (g) \qquad (1)$$

Therefore, the calcite was just dissolved into acid.

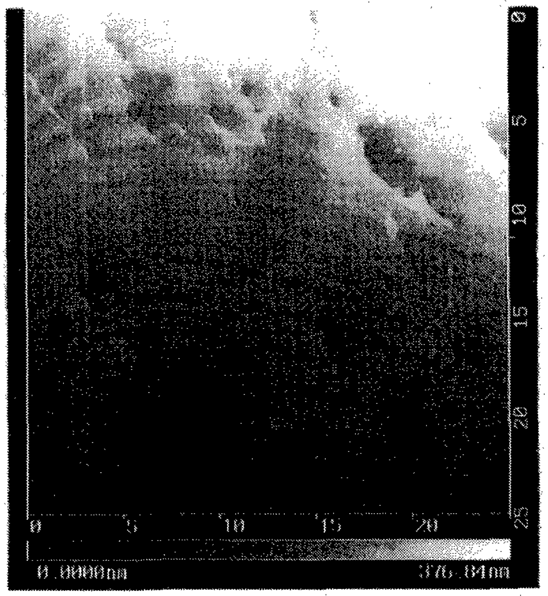
3.2 Reaction with diammonium hydrogenphosphate

AFM images of the cleaved calcite surface after immersion into diammonium hydrogenphosphate are shown in Fig. 3. If the immersion time was short (see Fig. 3(a)), the hollows were observed on the calcite surface. However, for the long immersion time (see Fig. 3(b) and (c)), some products were observed on the calcite surface. The amount of products was increased with increasing immersion (reaction) time.



(a)

(b)



(c)

Fig. 3 AFM images of calcite surface after reaction with diammonium hydrogenphosphate under the condition of 40℃ (a) 1 min, (b) 5 min, and (c) 10 min. Scan area was (a) 10×10 μm, (b) 10×10 μm and (c) 25×25 μm.

To examine the product formed on the calcite surface, the sample was examined by X-ray diffraction before and after reaction. However, the X-ray pattern showed the existence of only calcite after reaction at 40 ℃. To enhance reaction rate, the experimental temperature was increased to 60℃. Since the calcite sample was a single crystal, the sample before the reaction had to be exposed to low power x-ray to protect the x-ray detector. Still very strong peaks were observed. On the other hand, the sample after the reaction at 60℃ could be exposed to high power x-ray and most of the peaks were assigned to calcite (sharp peaks in Fig. 4). There was broad peak in Fig. 4 that was not assigned to calcite. This must be originated from the product. To confirm this, the powder of calcite (ground calcite) was reacted with diammonium hydrogenphosphate and studied by

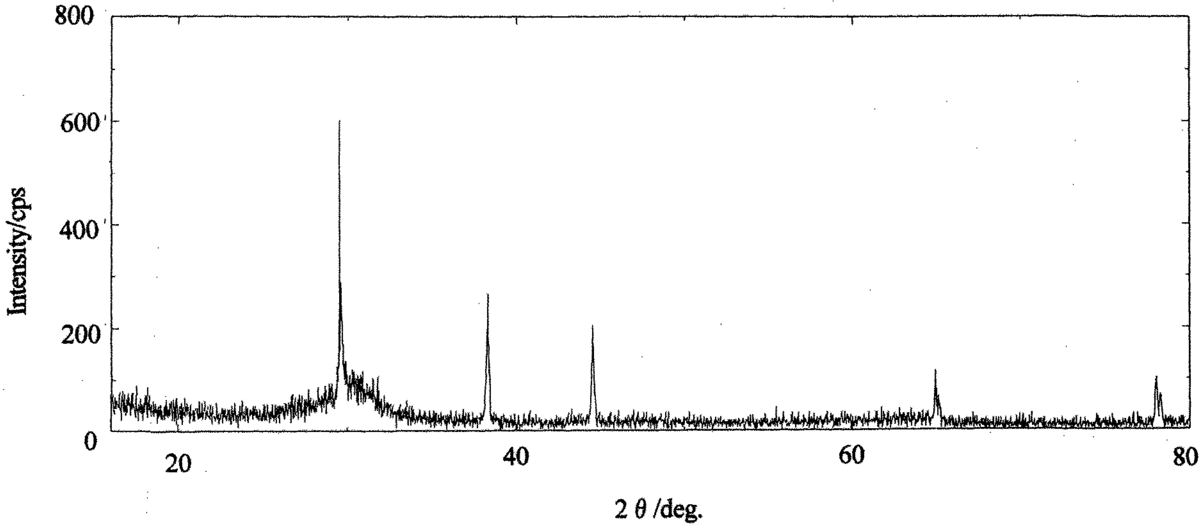


Fig. 4 X-ray diffraction pattern of calcite after reaction with diammonium hydrogenphosphate under the condition of 60℃ for 24 hrs.

X-RD. The x-ray diffraction peaks of hydroxyapatite were observed. Therefore, it was considered that the product on the calcite surface shown in Fig. 3 was hydroxyapatite.

4. CONCLUSIONS

The reaction between cleaved calcite and phosphoric acid or diammonium hydrogenphosphate was performed under the various conditions. In the case of phosphoric acid, the calcite was dissolved into phosphoric acid resulting in many hollows at the surface. In the case of diammonium hydrogenphosphate, the calcite was dissolved at first step. In the next step, the products were formed on the calcite surface. From the results of X-ray diffraction, the products were considered to be hydroxyapatite.

5. REFERENCES

[1] Y. Ueda, K. Nitta, T. Nakajima, Y. Hirohama, H. Kasahara, M. Hanazaki, and S. Minayoshi, Inorganic Material, **5**, 28-35 (1998).

[2] H. Kasahara, S. Minayoshi, T. Fujita, and Y. Ueda, Inorganic Material, **6**, 53-66 (1999).

[3] M. A. Araiza, J. Gomes-Morales, R. Rodriguez Clemente, V. M. Castano, J. Mater. Synthesis and Proc., 7[4], 211-219 (1999).

[4] H. Morgan, R. M. Wilson, J. C. Elliott, S. E. P. Dowker, and P. Anderson, Biomaterials, **21**, 617-627 (2000).

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