

## Preparation of hydroxyapatite in a reaction between alite and phosphoric acid

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### Abstract

Reactions between alite( $3\text{CaO} \cdot \text{SiO}_2$ ) and phosphoric acid have been carried out at the temperatures from  $30^\circ\text{C}$  to  $80^\circ\text{C}$ . The hydroxyapatite(HA) prepared on the surfaces of alite particles was characterized on the basis of both microstructural and kinetic data. The fraction of reaction was well expressed by the equation of an interfacial reaction rather than by the equation of ion diffusion through a reaction layer. The activation energy of the reaction obtained was 2.78 kcal/mol. Such a small value was related to that of calcium dissolution from alite. The formation mechanisms of HA were discussed.

Key words: Hydroxyapatite, Alite, Phosphoric Acid, Reaction Mechanism

### 1 Introduction

It is well known that HA has good biological compatibility in living tissues. However, the clinical use of HA in a load-bearing part is limited because of its brittle nature. So far various approaches such as HA coatings on metals<sup>1)</sup> and ceramics<sup>2)</sup>, HA sintering with fibers<sup>3)</sup>, and other processes<sup>4-5)</sup> to improve its mechanical properties have been studied.

In this connection, we have interest in cement concrete reinforced with iron wires, since it indicates high strength in comparison with that without wires. So, if we can change the surface of cement concrete reinforced with iron wires to HA, it may be possible to produce a material with high strength for biological applications in a load bearing part. Based on such idea, we have studied about the synthesis of HA in the reaction

of alite, one of the typical cement compounds, with phosphoric acid. In this paper, we intend to clarify the formation mechanisms of HA in reactions between alite and phosphoric acid on the basis of microstructural and kinetic data.

### 2 Experimental

Alite pellets were prepared in the following. Commercial available powders of  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  were mixed during a ball milling for 10 h without binders. The particle size of  $\text{Ca}(\text{OH})_2$  was about  $0.1 \mu\text{m}$  and that of  $\text{SiO}_2$  was also about  $0.1 \mu\text{m}$ . The mixture of  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  powders was pressed to pellets at 10 MPa. The resultant pellets were heated at  $1650^\circ\text{C}$  for 10 h in a platinum crucible in the flow of  $\text{N}_2$ . The pellets obtained were crushed into powders with average particle size of  $0.6 \mu\text{m}$ . The X-ray diffraction pattern of the powders clearly showed

only the peaks of alite.

The resultant powders were dipped into a phosphoric acid solution controlled at a given temperature and pH. The concentrations of the solution were 0.001, 0.01, 0.1, and 1.0 mol/l. The reaction temperatures were 30, 45, 60, and 80 °C. The pH values of the solution were controlled by the addition of ammonium solution from 7.5 to 11 at 0.5 intervals. The reaction times of alite in the solution were for 1 min – 240min. After a reaction, samples were washed with distilled water four times and were dried for 10 h at 100°C in a drier. The resultant samples were characterized by X-ray diffractometry and with a SEM, and were analyzed by EDX.

### 3 Results and discussion

Alite powders used in this experiment were approximately spherical in shape. If we assumed that the average diameter of them was  $r$ , and that the reaction layer at time  $t$  was  $x$ , the fraction of reaction,  $\alpha$ , is expressed in the following equation,

$$\alpha = \{\pi r^3 - \pi(r-x)^3\} / \pi r^3 = 1 - (r-x)^3 / r^3 \quad (1)$$

For interface reaction, the growth rate of reaction layer,  $dx/dt$ , is proportional to the interfacial area, so the growth rate is expressed in the next equation,

$$dx/dt = 4k'\pi(r-x)^2 = K_s(r-x)^2 \quad (2)$$

where  $K_s = 4\pi k'$ . Integrating the equation (2) in considering the equation (1) and the boundary conditions,  $x = 0$  at  $t = 0$ , the following equation can be obtained,

$$\{1 - (1 - \alpha)^{1/3}\} / (1 - \alpha)^{1/3} = rK_s t \quad (3),$$

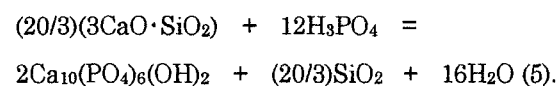
where  $K_s$  is a rate constant for interface reaction.

For a diffusion process, similarly the following equation can be obtained from the parabolic law,

$$\{1 - (1 - \alpha)^{1/3}\}^2 = (K_d/r^2)t \quad (4),$$

where  $K_d$  is a rate constant for diffusion. From the plots of equations (3) and (4),  $K_s$  and  $K_d$  can be obtained, respectively. The fraction of reaction can be determined from weight change between before and after the reaction of alite with phosphoric acid.

As the net reaction was considered to be in the following equation,



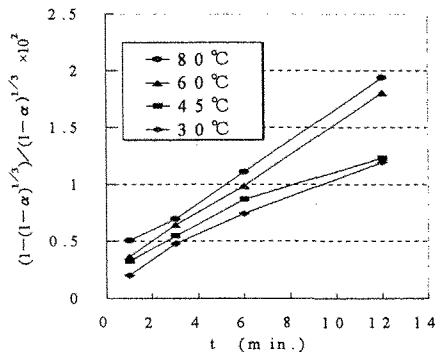
if  $W_g$  of alite reacted perfectly with  $\text{H}_3\text{PO}_4$ , the theoretical increase of weight is  $0.315W_g$ . Therefore, the fraction of reaction can be calculated by the following equation using experimental data,

$$\alpha = X/0.315W \quad (6),$$

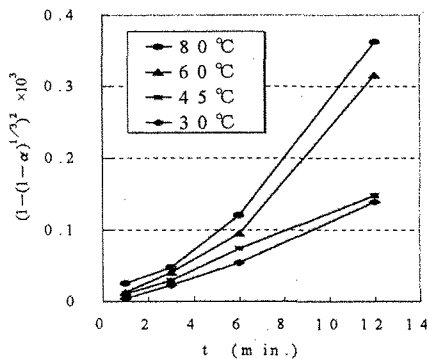
where  $X$  is the weight increase at time  $t$  due to the production of HA at a given temperature.

The relationship between the fraction of reaction and reaction time  $t$  indicated that  $\alpha$  increased rapidly at initial stage, but after 10 min increased gradually. The plots of  $\alpha$  by equations (3) and (4) as shown in Fig. 1 indicated that the data were well expressed by an equation (3) rather than by an equation (4). This would suggest that the reaction proceeded in an interface process. The activation energy obtained from the Arrhenius plots of reaction

constants  $K_s$  obtained was 2.78 kcal/mol. The value is very small but it is in common in a liquid phase reaction.



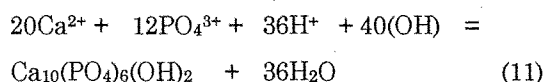
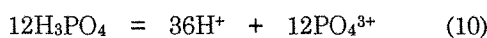
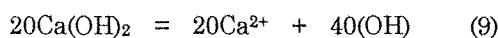
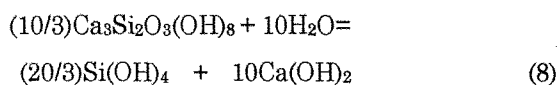
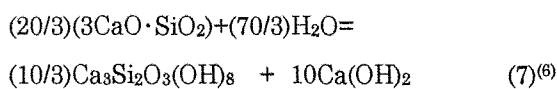
(a)



(b)

Fig. 1 The reaction data are plotted (a) by an interfacial equation(3) and (b) by a diffusion equation(4).

The reaction mechanisms of alite with phosphoric acid would be speculated in the following.



Among these reactions, reactions from (9) to (11) are considered to be very rapid because of ion reactions<sup>7)</sup>. So, the dissolution of calcium ions from alite expressed by equation (7) or from calcium silicate hydroxide expressed by equation (8) would be a rate-determining step for the HA formation reaction. However, the pH measurement during the reactions showed two step processes. This would suggested that the HA formation reactions took place firstly by an equation (7) and thereafter by an equation (8) as shown in Fig. 2. So, if we used reaction data for first 12 min, only the reaction of  $Ca(OH)_2$  originated from the hydration of alite with  $H_3PO_4$  would proceed dominantly.

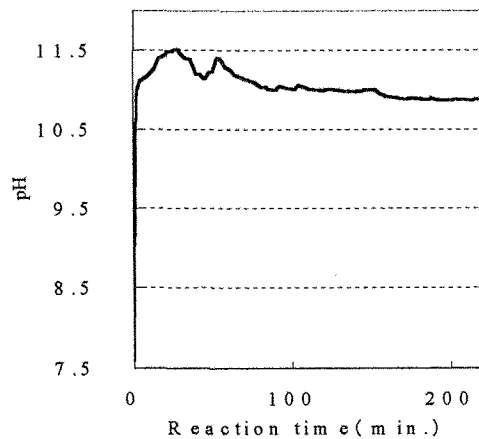


Fig. 2 The relationship between pH values and reaction time in a reaction carried out at 60°C at pH = 8.5.

Figure 3 shows SEM micrographs of HA on alite surfaces prepared at 60°C for various time at pH = 7.5. As can be seen in the figures, the surfaces were covered with scaly particles of HA. The thickness of the scaly particles is very thin, less than a few hundred nm. The dependency of pH values on shape and size is not so large in higher pH values than 7.5. Also the effect of temperatures on the microstructures of HA are very small in the temperature region from 30 to

80 °C. The solubility of HA is very low in comparison with that of  $\text{Ca}(\text{OH})_2$ . Consequently, immediately after  $\text{Ca}^{2+}$  ions dissolved into  $(\text{NH}_4)_3\text{PO}_4$  solution from  $\text{Ca}(\text{OH})_2$  originated from the hydration of alite react very rapidly with  $\text{PO}_4^{3-}$  ions to form HA at the interface between hydrated alite and HA particles. This allows the growth of HA particles at their roots. As SEM observation usually provides information of surfaces, the resultant size of HA particles observed would seem as if it was very small.

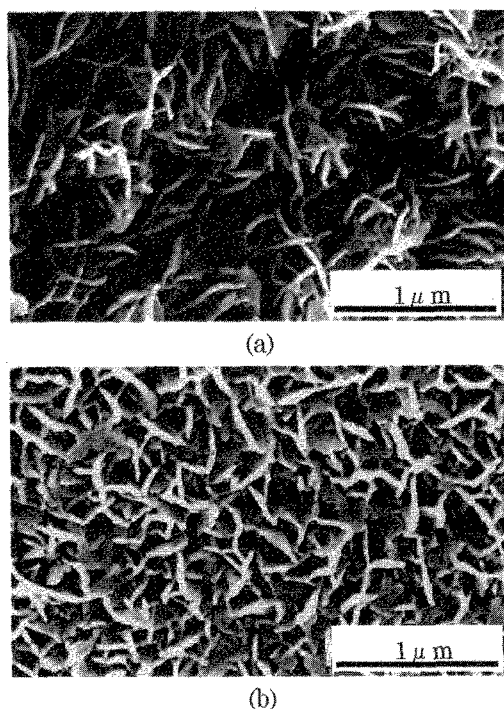


Fig. 3 SEM micrographs of HA prepared (a) at 60°C for 0.5h at pH = 7.5 (b) at 60°C for 4h at pH = 7.5

The effect of phosphoric acid concentration on HA shape is not clear under the experimental conditions.

In comparison of the solubility of alite with that of HA, the solubility of HA is very low. This makes very high supersaturation of calcium ions against HA. As a result, very fast reaction

between calcium ions and phosphoric acid to produce HA took place. This would make HA particles prepared on the surfaces of alite similar, irrespective of pH values, phosphoric acid concentration, and temperatures.

#### 4 Summary

HA prepared by a reaction between alite and phosphoric acid at 30 to 80°C was characterized with a SEM and by EDX and by X-ray diffractometry. The HA particles obtained were scaly with a few micron area and about 100 nm thickness, which were considered to generate under the conditions of very high supersaturation of calcium ions. The fraction of reaction was well expressed by the equation of an interfacial reaction rather than diffusion equations. The activation energy obtained was 2.78 kcal/mol. The value was related to be that of dissolution process of calcium from alite, which process was a rate-determining step in the reaction.

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