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Dissolution behavior of hydroxyapatite powder in hydrothermal solution

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Abstract

The dissolution behavior of hydroxyapatite (HA) in a hydrothermal solution was investigated using a Morey-type autoclave over a range of 150–350°C and a pH value range of 5–9. The results showed that the dissolubility of HA powder was determined as a function of temperature and time under constant pressure, and the temperature coefficient for the solubility of HA powder was positive. The rate of dissolution of HA in the hydrothermal aqueous solution was mainly controlled by a polynuclear mechanism. The dissolution behavior of HA was affected mainly by the hydrothermal temperature and the dissolving activation energy. The effect of temperature was obviously more than that of the pH value of the solution. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Hydrothermal; Dissolution; HA

1. Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, hereafter called HA, has many technical applications in prosthetic devices, tooth and bone implants, chromatographic separation catalyses, ion-exchange, etc. Numerous studies have been carried out to investigate the growth and dissolution of HA crystal [1–6]. It is well known that solubility is one of the important basic parameters for crystal growth from solution, and the solubility curve can provide the important basis for selecting the methods and the temperature region of crystal growth. Recently, many reports have been presented concerning the synthesis of HA fiber, whisker and nanograde powder using a hydrothermal methods [7–10], which are required in the development of modern composite materials, particularly in the reinforced composites based upon polymers and ceramics. However, so far, although studies on the solubility, kinetics of dissolution and other research of HA under normal temperature and pressure have been carried out for many years, the fundamental researches of HA under the hydrothermal environment, especially the dissolubility and dissolving behavior of HA, are still unclear. In this paper, a series of tests are described to investigate the dissolution behavior of HA powder in the hydrothermal solution.

2. Materials and methods

2.1. Preparation of raw materials

Hydroxyapatite powder was synthesized by a homogeneous precipitation using analytical grade regents $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ in the molar ratio 1.67:1 according to the following reaction:

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12NH_4NO_3 + 8HNO_3$$

After the reaction, the precipitation was filtered and then washed with distilled water, followed by ethanol treatment to remove the residual ions and water. Finally, HA powders were heat-treated at 800°C for 2 h and ground by an agate grinder. The average size of HA particle is 2.47 μm.

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2.2. Dissolution experiments

The dissolution behavior of HA powder in the hydrothermal solution was conducted using Morey-type titanium autoclave over a range of 150–350°C and a pH value range of 5–9. The filling ratio of autoclave was controlled at 60~70% and the concentration of HA suspension solution at 10~20%. The hydrothermal solution of HA at a chosen pressure–temperature condition was retained for a period of time, and then quenched with cold water to room temperature. The dissolubility of HA was measured by the changes of calcium and phosphorus concentrations in the supercooling solution using an atomic absorption spectrometer (Hitachi 180-70, Hitachi Ltd, Japan) and an infra-red spectra-photometer (751-GW, Shanghai Analytical Instrument Factory, PR China), respectively.

3. Results and discussion

The results presented in Fig. 1, show the dependence of calcium and phosphate ion concentrations in the hydrothermal solution of HA powder at the different temperatures. The concentrations of calcium and phosphate ion increased with the temperature increase at the constant filling ratio of 65% and pH of 7 for the duration of 6 h. The concentrations of calcium and phosphate ion could rise to the level of 620 and 835 μg/ml at 350°C, respectively. The hydrothermal temperature had obvious effects on the dissolution of HA powder. Fig. 2 showed the relationship of PO_4^{3-} concentration in the hydrothermal solution with different time. It can be seen from Figs. 1 and 2 that the dissolubility of HA was determined as a function of temperature and time under a constant filling ratio of autoclave and pH value in the system HA–H_2O, and the HA powder possessed a positive temperature coefficient of solubility. The dissolution equilibrium time could be reached at 300°C after 10 h, and the concentrations of phosphate ion were observed almost unchanged up to 12 h. For the experiment at 200°C, the concentration of phosphate ions tended to increase up to 10 h. The equilibrium time of HA in the hydrothermal solution would be shortened with the increasing of hydrothermal temperature.

The concentration of phosphate ions (Cp) against time curves derived from Fig. 2 were approximate to the classical parabolic behavior before achieving the dissolution equilibrium, and could be expressed by the equation:

$$Cp^2 = Kt + b \approx Kt$$

where K is the parabolic rate constant and b is a constant which accounts for the effect of a possible non-parabolic initial stage, i.e. for the uncertainty of the exact definition of beginning of the parabolic process. Plots of the square of phosphate ion concentration, Cp^2, as a function of time were reported in Fig. 3. The slope, K, was the dissolution rate constant, which was independent of the concentration, but dependent on the temperature by the Arrhenius equation [11], $K = Ae^{-Ea/RT}$, where A is the pre-exponential factor, Ea is the activation energy and R is a constant.

The dissolution rate constant at different temperature, K, determined from a mathematical interpolation of plots in Fig. 3 were 152.7, 556.5, 1387.7 $\mu g^2\ ml^{-2}\ min^{-1}$, respectively. The activation energy, Ea, for the dissolving of HA in the hydrothermal solution was calculated as 49 kJ mol^{-1}, which corresponded to the literature source for HA dissolution, $Ea = 45$ kJ/mol in normal

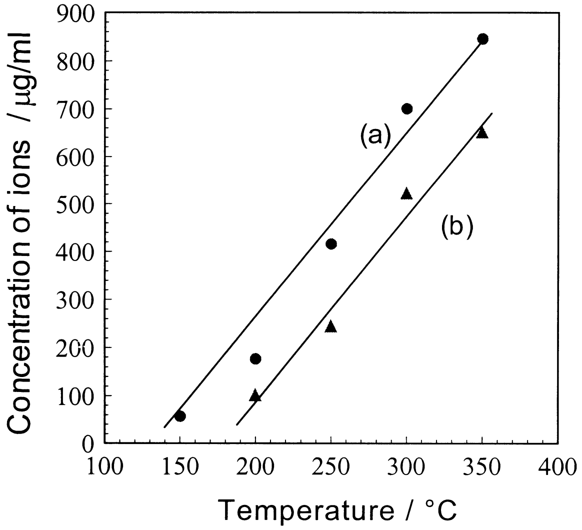

Fig. 1. Relationship of calcium and phosphate ions concentration in the hydrothermal solution of HA powder with different temperature: (a) PO_4^{3-} ions; (b) Ca^{2+} ions.

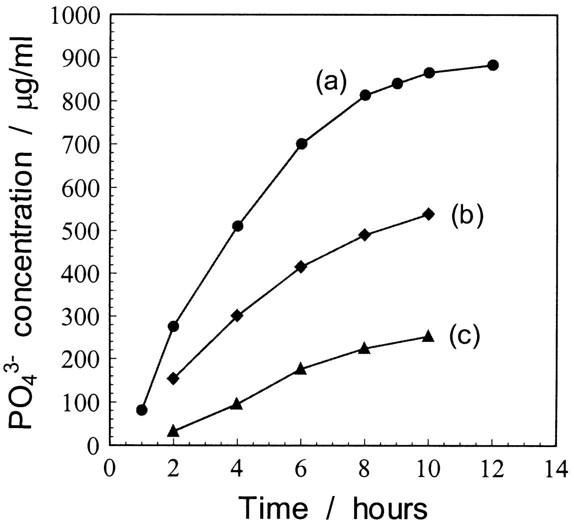

Fig. 2. Dependence of phosphate ions concentration in the hydrothermal solution of HA powder on different temperature: (a): 300°C, (b) 250°C, (c) 200°C.

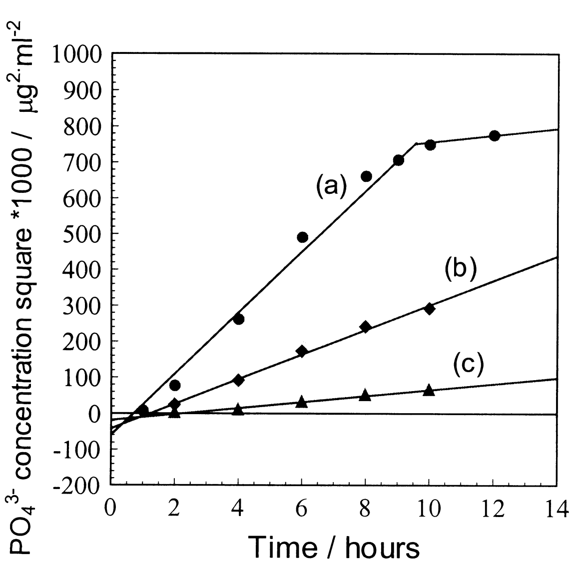

Fig. 3. Dependence of PO_4^{3-} concentration square on time at different temperature in hydrothermal solution: (a) 300°C, (b) 250°C, (c) 200°C.

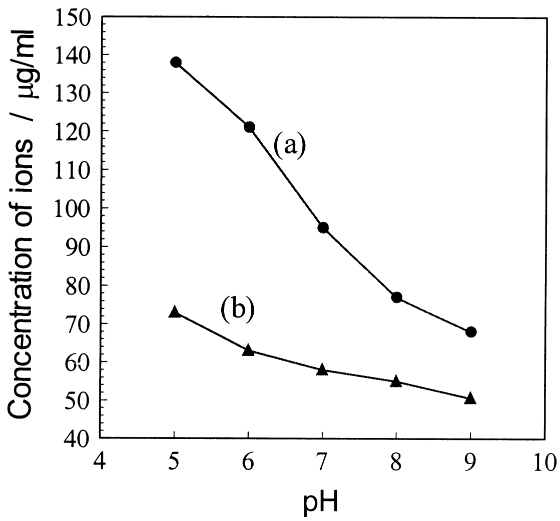

Fig. 4. Relationship of phosphate ions concentration in the hydrothermal solution of HA with pH value at 200°C for 4 h. (a) PO_4^{3-} ions; (b) Ca^{2+} ions.

conditions [4,5]. In the course of the dissolving of HA, the rate of dissolution was not only affected by the activation energy, *Ea*, but also by the hydrothermal temperature. So the concentration of calcium and phosphate ions increased with the temperature for a constant hydrothermal time, and HA had higher dissolubility under the hydrothermal environment than the normal pressure and temperature.

Christoffersen's studies on the rate of dissolution of HA crystal in water [4,5] showed that transport of substance between the volume adjacent to the crystal surface and the bulk always took place, which associated with the dissolving of HA crystals and the sedimentation by the convective diffusion. The rate of dissolution in water with pH≈7 could be explained by a polynuclear mechanism together with a surface free energy. During the dissolving of HA in the hydrothermal solution, the reaction may be expressed as follows:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 10Ca^{2+} + 6PO_4^{3-} + 2OH^- \quad (1)$$

The concentrations of calcium and phosphate ion dissolved from the surface of HA crystals increased with time and rose rapidly higher valve for less than 1 h. On the other hand, HA nuclei produced by the inverse reaction of Eq. (1) could be formed on the HA crystal surface and spread over the surface with a finite lateral velocity, and eventually sedimentated to the surface of the HA powder by convective diffusion. With the increasing and growing of HA nuclei, the concentrations of calcium and phosphate ion were scarcely changed when the equilibrium between dissolving and sedimentating was achieved. So the rate of dissolution of HA powder in hydrothermal solution was controlled mainly by the polynuclear mechanism.

It has been proved that the pH value of the solution has the effect on the solubility of calcium phosphate, and the solubility of the mineral HA depends on the pH [12]. With the increasing of pH value, the inverse reaction of Eq. (1) would be accelerated, re-crystallizing to $Ca_{10}(PO_4)_6(OH)_2$. In the mean time, for the solution with a low pH value, hydrogen ions could react with hydroxide ions or phosphate ions to form the H_2O and hydrogen phosphate group, and the equation proceed in a positive direction. So the dissolution of HA decreased with the increasing of pH value (as shown in Fig. 4). This was similar to the dissolution of HA under normal pressure and temperature and confirmed in the conclusion of Van Raemdonck [12], but the effects of pH values of the hydrothermal solution on the solubility of HA were much weaker than that of the temperature.

4. Conclusion

The dissolubility of HA powder was measured as a function of temperature and time under constant filling ratio of autoclave in the hydrothermal system HA–H_2O, and HA powder possessed a positive temperature coefficient of solubility. The dissolution behavior of HA powder was affected by the hydrothermal temperature and time, pH value of solution and the activation energy, and also the hydrothermal temperature. The rate of dissolving of the HA powder in the hydrothermal solution was controlled mainly by the polynuclear mechanism. Therefore, HA powder had a higher dissolubility under the hydrothermal condition than under normal pressure and temperature. The effect of hydrothermal temperature on the dissolubility of HA powder was much more intense than that of the pH value of the hydrothermal solution and other factors. The solubility of HA decreased with the increasing pH value.

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