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Short communication

A study of hydroxyapatite/calcium sulphate bioceramics

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Abstract

Hydroxyapatite/calcium sulphate anhydrate (HAP/CSA) powders were prepared by the wet precipitation method at pH 10. HAP/CSA ceramics were sintered at 1000 °C, and then degraded in citric buffer solution at 37 °C. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed to study phase composition and microstructure of the ceramics. The results showed that HAP/CSA was a kind of potential in situ pore forming bioceramics.

Keywords: Hydroxyapatite (HAP); Calcium sulphate; Bioceramics; Degradation

1. Introduction

Hydroxyapatite (HAP) has been studied extensively because of its excellent biocompatibility and bioactivity. Many in vivo experiments have confirmed the advantages of a bioceramic with porous structure for tissue ingrowth [1,2]. But the application of the porous HAP ceramics is limited, as the strength of the porous ceramics decreases exponentially with the pore volume ratio [3]. Calcium sulphate anhydrate (CSA) the stable phase of calcium sulphate at high-temperature, is generally called "insoluble anhydrite". It could spontaneously transform into CSD at low-speed and this process could be accelerated by CSD crystals [4].

On the above analysis, sintered HAP/CSA biphasic ceramics might have higher strength than porous HAP, and a porous HAP structure might be gradually formed if the CSA dissolves slowly or transforms into CSD. This paper is a pilot study of HAP/CSA biphasic ceramic.

2. Experiment

Na_2SO_4 solution was added into $Ca(NO_3)_2{\cdot}4H_2O$ solution at 60 °C. The suspension was stirred for 1 h. Then $(NH_4)_2HPO_4$ solution was dropped into the suspension. After total addition of the $(NH_4)_2HPO_4$ solution, the suspension was matured during 2 h. The pH of the suspension was maintained at 10 by adding ammonia solution. The suspension was filtered, washed and dried. The initial Ca/P/S molar ratio was changed from 2/1/1 to 2.5/1/1. As the Ca/S molar ratio of the calcium sulphate was 1/1, the initial Ca/P molar ratio (from 1/1 to 1.5/1) was used to express the reaction systems.

The dried powder was calcined at 800 °C for 1 h, and then pressed into plate with the dimension of ϕ: 20 mm × 2 mm. Sintering was carried out at 1000 °C for 1 h. According to ISO 10993-14, the ceramic plate was immersed in citric buffer solution (20 ml/g) at 37 °C for degradation test. X-ray diffraction (XRD) (Model BDX3300 Peking University China) and scanning electron microscopy (SEM) (XL30 Philips Holland) were performed to study the phase composition and microstructure of the ceramics.

3. Results and discussion

The XRD analysis shows that the ceramic plate was composed of HAP and CSA (Fig. 1). Fig. 2 shows that the aggregated CSA particle was covered by small sized HAP particles. This was consistent with the synthesizing process of the powders.

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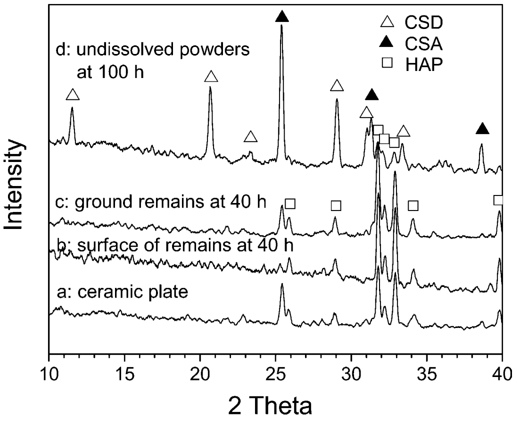

Fig. 1. The XRD patterns of the ceramics.

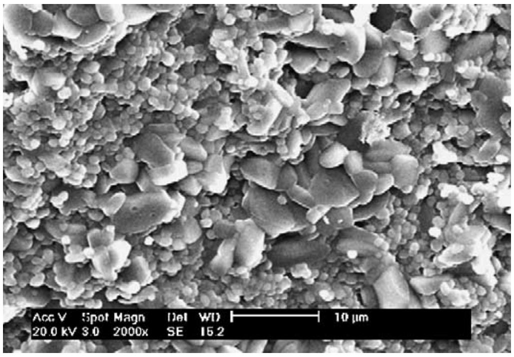

Fig. 2. The image of the fracture surface.

The first step of the precipitation of HAP was to form an amorphous compound, which Ca/P molar ratio was close to 1.5 [5]:

$$9Ca^{2+} + 6PO_4^{3-} \rightarrow Ca_9(PO_4)_6 \quad (1)$$

Then the following reactions took place:

$$Ca_9(PO_4)_6 + yCa^{2+} + 2yOH^- \rightarrow Ca_{9+y}(PO_4)_6(OH)_{2y} \quad (2)$$

$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^- \quad (3)$$

As the solubility of $CaSO_4 \cdot 2H_2O$ is higher than that of HAP, the concentration of Ca^{2+} promoted reaction (2), which increased the Ca/P molar ratio of HAP. At higher pH value reaction (3) was suppressed. So, despite of the initial composition, the Ca/P ratio of the precipitate might reach a value near 1.667 and there was only one kind calcium phosphate phase, HAP, in the ceramics.

Fig. 1 also gives the phase revolution of the ceramics during degradation. At 40 h only HAP was detected at the surface of the remains, but CSA peaks appeared when the remains was ground to powders, which indicated there was CSA inside the remains. At 100 h, the ceramic degraded into powder, in which CSD, CSA and HAP were detected, but the HAP peaks were very weak. Fig. 3 shows a porous structure of HAP at the surface of remains.

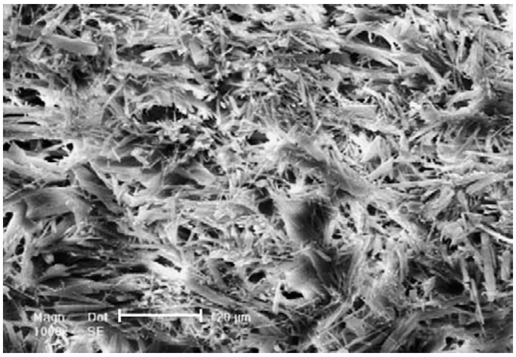

Fig. 3. The surface morphology after 40 h degradation.

As HAP is stable at pH ≥ 4.2, when contacted with the buffer solution (pH < 3), the particles dissolved and recrystallized to needle shape. In the mean time CSA particles separated from the ceramic and a porous surface structure formed. The needle shaped HAP gradually dissolved, so the XRD peaks became very weak after 100 h degradation. As pH has little influence on the stability of calcium sulphate, the undissolved powder was mainly CSA and CSD.

Although the degradation results in citric buffer solution must be very different from that in vivo, the results indicated that HAP/CSA was a potential in situ pore forming bioceramic.

4. Conclusion

HAP/CSA powders were prepared at pH 10 by a wet method. HAP/CSA ceramic was sintered at 1000 °C and was a potential in situ pore forming bioceramic. The initial Ca/P molar ratio did not influence the phase composition of the ceramics.

Acknowledgement

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