Research Article

Controlling the Structure of Hydroxyapatite Ceramics with Dual Pores Prepared Using Freeze-Casting

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A hydrogen peroxide solution in deionized water was used as the pore-forming agent in freeze-casting to fabricate a hydroxyapatite porous ceramic containing both lamellar and spherical macropores. The influence of the volumetric content of H_2O_2 in the mixed solvent on the morphology of the porous ceramic was analyzed, and the effect of the solvent cooling speed on the microstructure and pore morphology of the pore ceramic was also investigated. The results show that H_2O as the sole pore-forming agent led to the formation of a HA scaffold with only lamellar pores. When 3% (v/v) of H_2O_2 solution was used, both lamellar and spherical pores were observed. However, when the concentration of H_2O_2 reached 9% (v/v), only spherical pores were formed in the porous ceramic. The average lamellar spacing and the spherical pore size of the pore ceramic composed of HA decreased with the increase of the cooling speed.

1. Introduction

Porous ceramics are widely used as carriers for catalysts, in sound absorption and insulation, heat preservation, filtering and separation, feedback sensors, and general biology [1]. In 2000, Fukasawa et al. reported the first preparation of porous ceramics by freeze-casting [2]. After this seminal study, most research focused on the development of pore-forming agents used in freeze-casting in order to control the pore structure. Zhang et al. used a water-based slurry as the pore-forming agent to prepare porous ceramics with lamellar pores using the freeze-casting method and achieved a porosity of 94% [3]. Soon et al. used a camphor-based slurry as the pore-forming agent and adopted freeze-casting to obtain a dendritic porous ceramic [4]. Subsequently, Wang et al. conducted research on a tert-butanol-based slurry as the pore-forming agent, obtaining a porous columnar ceramic with cellular morphology [5]. The pore structure of porous ceramics is determined by the pore-forming agent, that is, by the crystal

morphology of the liquid-phase solvents. Thus, the pore structure of porous ceramics is strongly dependent on the size and shape of crystalloids solidified from the liquid-phase solvents. In the freeze-casting process, the liquid-phase slurry should be carefully investigated. Generally, a slurry with a moderate solidification temperature, small rate of volume change during the solidification process, low liquid viscosity, and high vapor pressure in the solid state is optimal for obtaining high-porosity ceramics [6]. To date, only three pure substances, water, camphene, and tertiary butanol, were found to meet those requirements and are commonly used as pore-forming agents [6].

To obtain ceramics with diverse pore structures that meet the requirements of different applications, the development of different kinds of pore-forming agents is very important. Recently, the use of slurries based on solutes such as NaCl, sucrose, and polyethylene glycol mixed with water as pore-forming agents was reported, and porous ceramics with pores of diverse morphologies were obtained [7, 8]. For

example, Mohamed et al. used 1,4-dioxane and glycerin in water as the pore-forming agent. However, the resulting porous ceramics still contained lamellar pores with a morphology similar to those obtained when using a water-based slurry [9]. To date, there are no reports on the manufacture of porous ceramics with spherical and lamellar pores using complex solvents as pore-forming agents.

It is known that hydrogen peroxide can disproportionate to release oxygen gas. The authors believed that if the hydrogen peroxide was mixed with water, spherical holes induced by oxygen and lamellar pores induced by water could be obtained simultaneously, generating spherical and lamellar pores at the same time. Based on this idea, $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixtures with different $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ratios were used as the pore-forming agent to prepare porous ceramics. Finally, the size and shape of the pores were controlled successfully by tuning of the cooling speed.

2. Materials and Methods

2.1. Starting Materials. Hydroxyapatite (HA) powder with a grain size ranging from 0.5 to 1.0 μm ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; Alfa Aesar, USA) was used as the raw material. Hydrogen peroxide (H_2O_2 , Tianjin Bodi Chemical Co., Ltd.) and distilled water in different proportions were used as solvent. Carboxymethyl cellulose (Ningbo Cellulose Derivative Plant, China) and sodium polyacrylate (Mw 8000; Alfa Aesar) were used as a binder and dispersing agent, respectively.

2.2. Preparation of Scaffold. Firstly, $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solutions with H_2O_2 content of 3, 4, and 9% (v/v) were freshly prepared. Then, add dispersing agent and adhesive to the solutions at 1 and 2% of solute mass, respectively, mixed with HA powder, after which a sizing agent with 25% (v/v) of solid content was prepared. The agent was stirred using a magnetic apparatus for 30 min at 25°C and subsequently ground in a roller-type ball mill (self-made equipment) for 24 h at 25°C.

The ceramic slurry was poured into the mold ($\varnothing 12\text{ mm} \times 30\text{ mm}$), which comprised two sections. The side and top were made of the thermal insulation material, and the bottom was made of metal with high thermal conductivity. This mold design was chosen to ensure that the freeze direction is from the bottom to top, thus guaranteeing an oriented freezing of the ceramic slurry (Figure 1). The electronic probe of a freeze-drier (VFD2000G; Boyikang Co., Ltd., Beijing, China) was used to measure the cryogenic temperature of the sizing agent to obtain the freezing curve. After demolding, the frozen sample was lyophilized at -20 to 0°C for 24 h and subsequently sintered at the temperature of 1250°C for 2 h. The heat preservation period was 2 h.

2.3. Characterization of the HA Scaffold. A JSM-6700 scanning electron microscope (SEM; JEOL, Japan) was used to observe the morphology of the porous ceramic. PCI View software (JEOL, Japan) was used to measure pore size in the electromicrographs. From each group, 5 samples were

FIGURE 1: Schematic diagram of the directional freeze-casting apparatus.

selected, each of which was tested at 2 to 3 points, and the weighted average was used as the result. Fenton's reagent was used to test the disintegration quantity of H_2O_2 in the ceramic slurry [10].

3. Results and Discussion

3.1. Morphology of Porous Ceramics Manufactured Using Solvents with Different H_2O_2 Contents. Figure 2 shows the morphology of the porous HA ceramics obtained through freeze-casting based on different ratios of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (0, 3%, and 9%). As shown, Figures 2(a), 2(c), and 2(e) indicate the macroscopic morphology of the porous ceramic, while Figures 2(b), 2(d), and 2(f) are the corresponding SEM images. The dark zones are the pore channels, and the light zones are the pore walls. Figure 2 shows that pure water produces porous ceramics with lamellar pores. By contrast, when the mixture with 3% of H_2O_2 was used, lamellar pores and spherical pores were obtained. However, a further increase of the H_2O_2 content to 9% results in a porous ceramic with only spherical pores.

Because it is inherently unstable, H_2O_2 easily decomposes when exposed to light, heat, and other physical or chemical factors. Due to this, we measured the content of H_2O_2 before and after ball milling of the slurry. As shown in Table 1, H_2O_2 decomposed, and oxygen was released during the ball milling process. The oxygen accumulated as foam in the ceramic slurry, and thus, spherical pores formed in the porous ceramic. As shown in Figure 2 and Table 1, when a ceramic slurry with 3% (v/v) of H_2O_2 was used, spherical pores formed in the resulting porous ceramic slurry. However, due to the small amount of H_2O_2 , the amount of bubbles or spherical pores formed in the slurry was insufficient to form large pores in the final ceramics. Consequently, the slurry still contained a large amount of water, and lamellar pores formed as the main pores in the porous ceramic after freeze-casting (Figures 2(c) and 2(d)). When the H_2O_2 content in the ceramic slurry was increased to 9% (v/v), the content of oxygen produced by H_2O_2 decomposition also increased. In this case, large pores were formed in the final ceramic, and large numbers of spherical pores were observed (Figures 2(e) and 2(f)).

FIGURE 2: Morphology of HA scaffolds prepared from a 25% (v/v) suspension by freeze-casting: (a) and (b) water-based; (c) and (d) 3% (v/v) H_2O_2 ; (e) and (f) 9% (v/v) H_2O_2 .

TABLE 1: The content of H_2O_2 in the ceramic slurry before and after milling.

% H_2O_2 (v/v)	The content of H_2O_2 before milling (ml)	The content of H_2O_2 after milling (ml)	The content of decomposed H_2O_2 during milling (ml)
3	6.75	4.13	2.62
9	22.5	15.19	7.31

3.2. Influence of Cooling Speed on the Morphology of the Porous Ceramic. To further adjust the size of the spherical and lamellar pores, we set the solid content and the $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ratio in the ceramic slurry to 25 and 4% (v/v), respectively, and attempted to tune the pore structure of the HA ceramic by controlling the cooling speed during the freeze-drying process. Figure 3 shows SEM images of the porous HA ceramics with two kinds of pores obtained at different cooling speeds. As can be seen, the average diameter of

lamellar spacing and the spherical pores inside the ceramics decreased with the increase of cooling speed.

The influence of the cooling speed on pore size can be explained using the Deville model [11], as shown in Figure 4. The blue pores in Figure 4(a) represent ceramic particles, while the gray solvent represents the liquid phase of the slurry. Firstly, under conditions of local undercooling, minute ice crystals formed in the solvent (Figure 4(b)) and subsequently grew gradually. When the solidification speed

FIGURE 3: SEM images of porous HA scaffolds prepared at different cooling speeds: (a) 1.3°C/min; (b) 2.2°C/min; (c) 4.8°C/min; (d) 5.5°C/min.

FIGURE 4: Lamellar pore-forming process in the aqueous slurry.

was lower than the critical speed, ceramic particles were easily repelled and the space was occupied by the liquid phase, thus forming the pore structure (Figure 4(c)). At lower temperatures, the cooling speed was so rapid that ice crystallization was finished before the ceramic particles could be repelled by the frontier of the liquid-phase solidification. Hence, at rapid cooling speeds, the average lamellar spacing was small. On the contrary, an increase of the freezing speed reduced the expansion of O_2 bubbles, and mutual integration of the oxygen pores was also prevented to some degree. Consequently, the spherical pore spacing of the HA ceramic was decreased.

Figure 5 shows the relation between the cooling speed, lamellar spacing, and spherical pore spacing of the two kinds

of ceramic pores. At a cooling speed of 1.3°C/min (Figure 4(a)), the cooling rate of the ceramic slurry and the solvent nucleation speed were low. Consequently, the ice crystals were able to repel the ceramic particles, and the interspersed space was occupied by liquid-phase solidification. Hence, the average lamellar spacing was large.

As the cooling speed increased, the consolidation speed of the slurry also increased. In this case, the ice crystals were not able to repel the ceramic particles, and the spherical pore spacing of the ceramic decreased, as shown in Figures 4(b) and 4(c). As shown in Figure 5, as the cooling speed increased, the average lamellar spacing of the porous ceramics decreased from 405 to 161 μm, and the spherical pore size increased from 59.6 to 121.5 μm.

FIGURE 5: Influence of cooling speed on the average lamellar spacing and the spherical pore size.

After fitting the data, (1) and (2) were obtained as follows:

$$L_M = -158.65 \ln(C_R) + 438.07, \quad R^2 = 0.9863, \quad (1)$$

$$L_S = -167 \ln(C_R) + 414.48, \quad R^2 = 0.9872, \quad (2)$$

where L_M and L_S represent the average lamellar spacing and spherical pore size of the porous ceramic, respectively, and C_R represents the cooling speed.

Equations (1) and (2) can be used to adjust the cooling speed to achieve an accurate average lamellar spacing and spherical pore sizes of the porous ceramic.

4. Conclusions

In this paper, a novel hydroxyapatite scaffold with lamellar and spherical pores was prepared by freeze-casting using an aqueous H_2O_2 solution as the pore-forming agent, and the influence of H_2O_2 content in the aqueous phase on features of the HA porous ceramic was investigated. In addition to the lamellar pores induced by ice crystal formation, spherical pores were also formed in the HA scaffold due to the release of oxygen gas during the decomposition of H_2O_2 . When 3% (v/v) of H_2O_2 solution was used, a highly porous HA scaffold containing both lamellar and spherical pores was obtained. However, when the H_2O_2 volume fraction was 9%, only spherical pores were observed. The average lamellar spacing and spherical pore sizes of the HA porous ceramic decreased as the cooling speed increased.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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