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Porous hydroxyapatite ceramics by ice templating: Freezing characteristics and mechanical properties

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Abstract

Ice templating produces porous hydroxyapatite (HA) scaffolds with a lamellar morphology and aligned channels when using aqueous HA slurries. We investigated the freezing characteristics of HA slurries with regard to the pore structures of the porous HA scaffolds. We found that by increasing the cooling rate, the lamellar spacing decreased. The average lamellar spacing is about 785.7 μm at a cooling rate of 1.3 °C/min. The porous geometry changes from lamella and well aligned channels to a partial dendrite and partially aligned cavities with a decrease in the initial nucleation temperature and an increase in the degree of supercooling. Additionally, we determined the relationship between compressive strength and porosity. The compressive strength of the porous HA scaffolds reach 6.7 MPa at a porosity of 64% and the lamellar spacing is about 124 μm.

Keywords: C. Mechanical properties; Ice templating; Hydroxyapatite; Freezing characteristics

1. Introduction

Hydroxyapatite (HA) is a major inorganic component of hard tissues that are used in the human body, because of its excellent biocompatibility and bone bonding ability [1–3]. Porous HA ceramics have received a great deal of attention in the field of bone regeneration [4–6] since they allow bone cells to penetrate the interconnected pores and to grow on their biocompatible surfaces [7,8]. Controlling the pore structures of the porous scaffold is important for the establishment of channels for histiocytes and nutrients [9,10]. Various manufacturing techniques are available to produce porous HA scaffolds. These methods include the replication of polymer foams [11], the use of pore-forming agents [12] and gel-casting [13]. These methods are suitable for the fabrication of porous scaffolds, but for further investigation, porous ceramics with controllable porosity and open interconnected pores need to be produced.

Recently, ice templating has been used to produce porous HA scaffolds from aqueous HA slurries [14–16]. Among the approaches that use different HA slurry content and a freezing process to control the porosity, the manipulation of interlamellar spacing and compressive strength of the porous HA scaffolds is most promising. Since the pores of the porous HA scaffolds are a replica of the ice structures found after freezing HA slurries [17–19], the freezing characteristics of the HA slurries such as the initial nucleation temperature and supercooling will affect the pore geometry and the interlamellar spacing of the HA scaffolds.

Therefore, in this study we investigated the effects of initial nucleation temperature (T_n) and supercooling (ΔT) to adjust the freezing characteristics of the HA slurries and thus control the pore structures of the porous HA scaffolds. The interlamellar spacing and pore morphologies of the samples were thus investigated. The new results presented here are the temperature curve measurements, clearly showing the supercooling and the nucleation temperature, and the facts that HA samples with very large pores were obtained. We also investigated the quantitative relationship between the porosity and the compressive strength.

2. Experimental procedure

Commercially available hydroxyapatite ($Ca_{10}(PO_4)(OH)_2$, Alfa Aesar Co., Milwaukee, WI) powder and deionized water

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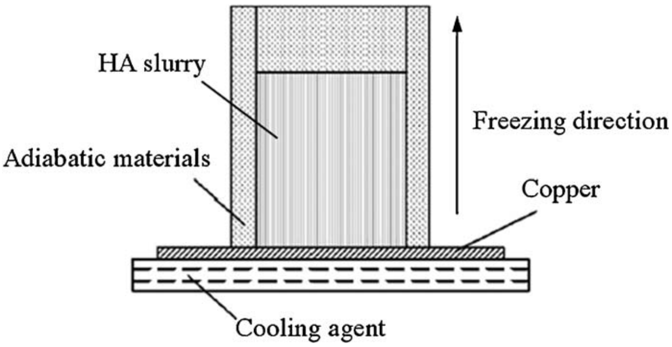

Fig. 1. Brief description of the freezing process.

were used as the ceramic raw material and the freezing vehicle, respectively. In addition, polyvinyl alcohol (PVA, Yakuri Pure Chemicals Co. Ltd., Osaka, Japan) was used as the binder. HA slurries with various initial HA content and 1 wt% PVA were prepared over 4 h by stirring at 60 °C. The slurries were then poured into polyethylene molds with an inner diameter of 15 mm. The molds were placed onto a pre-cooled freeze drier plate (VFD2000G, Boyikang Co. Ltd., Beijing, China) or liquid nitrogen. The samples were frozen by unidirectional freeze casting for 4 h. Since the cooling rate is an important parameter, the temperature of the top and bottom of the samples were determined using an electron thermometric indicator (TH-212, Beijing High-chance High-pech Science Co. Ltd.). The freezing process is shown in Fig. 1. The samples were dried for 48 h to remove the frozen vehicle and then the green bodies were sintered at 1250 °C for 2 h.

The morphology of the porous HA scaffolds was determined by scanning electron microscopy (SEM, 1000B, AMRAY, Cambridge, United States) and binocular stereomicroscopy (SZ61, OLYMPUS, Tokyo, Japan). The lamellar spacing was determined by measuring the cross section of the samples using a digital imaging tool and eight samples were tested to obtain an average value. The porosity of the scaffolds was measured using Archimedes principle. The compressive strength of the scaffolds was measured on cylindrical samples of Φ10 mm × 10 mm using a computer servo to control the material testing machine (HT-2402-100KN, Hungta, Taiwan) with a crosshead speed of 0.5 mm/min. Ten samples were tested to obtain an average value.

3. Results and discussion

Fig. 2(a) shows the morphology of the sintered porous HA scaffold made by a 40 wt% HA content in the initial slurry with the freezing rate of 2.0 °C/min. The HA scaffold with unidirectional aligned channels is lamellar. Macroscopic aligned pores of the HA scaffold are formed almost uniformly over the entire sample. The pore structure of the porous HA scaffold is a replica of the ice structure obtained when freezing HA slurries. These pores were generated during sublimation of the ice and sintering. A dendritic structure is present on the internal walls of the lamellae, as shown in Fig. 2(b). These features reach the adjacent pore walls and, therefore, connecting struts are produced. The aligned channels and the dendritic structure on the internal surface might act as a guiding pattern for cell growth, which will improve the osteoconduction characteristics [20].

The lamellar spacing of the porous HA scaffolds was measured at various freezing rates (1.3, 1.7, 2.0, 2.4, 3.0, 7.0 and 10.0 °C/min), as shown in Table 1. The average lamellar spacing of the porous HA scaffold decreases as the freezing rate increases. The pores are parallel to the direction of heat transfer during solvent crystallization. Aligned channels are produced when the ice crystals are forced to sublimate by adequate drying. At a freeze rate of 10 °C/min, the water in the slurry rapidly reaches a supercooled state and then large quantities of ice crystals are formed. Ice crystal growth is suppressed and they are small in size because of the short freezing time. A porous HA scaffold with a narrow lamellar spacing is thus obtained. At a freeze rate of 1.3 °C/min, a small amount of ice crystals are formed in the HA slurry. Porous HA scaffolds with wide lamellar spacings are obtained since the ice crystals grow over longer freezing times.

Ice crystal growth is dependent on the freezing parameters such as the initial nucleation temperature (T_n) and supercooling (ΔT, the discrepancy between the actual initial nucleation temperature T_n and the equilibrium freezing temperature T_m). The temperature of the slurry was measured periodically when

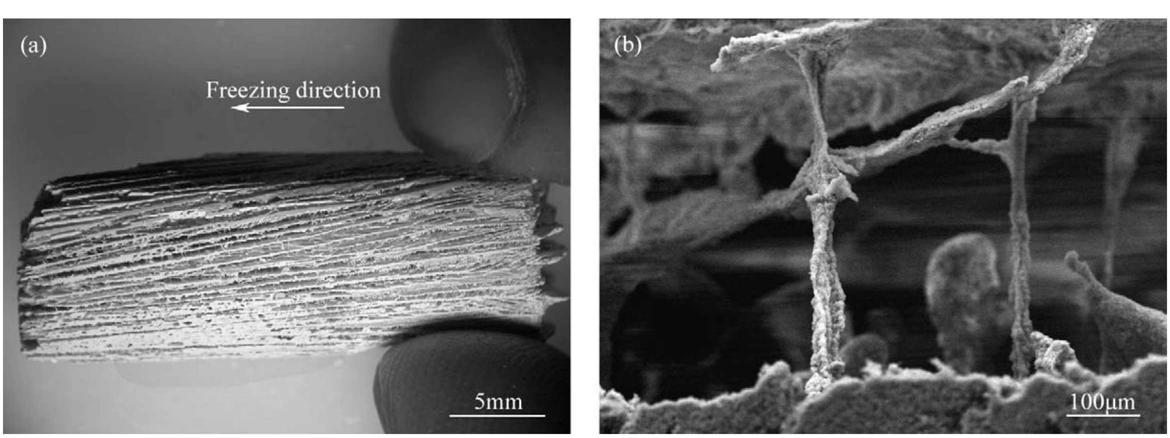

Fig. 2. Morphology of the sintered porous HA scaffolds. (a) Macro morphology and (b) dendritic morphology in the internal walls of the lamellae.