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Pore structures and mechanical properties of porous titanium scaffolds by bidirectional freeze casting

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ABSTRACT

Porous titanium scaffolds with long-range lamellar structure were fabricated using a novel bidirectional freeze casting method. Compared with the ordinarily porous titanium materials made by traditional freeze casting, the titanium walls can offer the structure of ordered arrays with parallel to each other in the transverse cross-sections. And titanium scaffolds with different pore width, wall size and porosity can be synthesized in terms of adjusting the fabrication parameters. As the titanium content was increased from 15 vol.% to 25 vol.%, the porosity and pore width decreased from 67 ± 3% to 50 ± 2% and 80 ± 10 μm to 67 ± 7 μm, respectively. On the contrary, as the wall size was increased from 18 ± 2 μm to 30 ± 3 μm, the compressive strength and stiffness were increased from 58 ± 8 MPa to 162 ± 10 MPa and from 2.5 ± 0.7 GPa to 6.5 ± 0.9 GPa, respectively. The porous titanium scaffolds with long-range lamellar structure and controllable pore structure produced in present work will be capable of having potential application as bone tissue scaffold materials.

1. Introduction

As a kind of low density and modulus, high strength and good chemical resistance material, titanium is quite suitable for medical implants and other technological applications [1,2]. For example, when porous titanium is used as a bone substitute material, the elastic modulus of porous titanium with a proper level (1– 30 GPa) was adjusted to avoid bone resorption and the loosening of the implant [3,4]. The increase of porosity is an effective method to reduce the elastic modulus of materials and promotes osteocyte proliferate inside the porous titanium block [5]. The mechanical properties of the materials can be controlled by the porosity, pore size and pore morphology through a variety of manufacturing methods [6]. So far, many manufacturing techniques have been reported to produce porous titanium such as bubble generation [7,8], replication of polymeric sponge [9,10], rapid prototyping method [11,12], space holder method [13,14] and freeze casting [15,16].

Freeze casting is a promising method to prepare porous materials with unique aligned and elongated pore structure by driving particles of the slurry to self-assemble along the ice growth direction [6,17]. The pore morphologies are mainly determined by matrix powder kinds, solvent types and frozen temperature gradient [18]. Generally, matrix powder is divided into two categories: one is ceramic powder, and the other is metal powder. Currently, most of investigations are focused on the ceramic powders, because they can keep stable in the slurry and form obvious layered structure easily compared with metal powders [19]. To get porous metal with uniform layer structure, a certain amount of dispersant and binder were added into slurry to ensure the stable suspension of particles [20]. But the introduction of additives is still difficult to achieve homogeneous distribution for the relatively large titanium particles in the slurry during freeze casting [21]. Currently, the common choice of the solvent to carry powder particles is deionized water and liquid camphene. In the case of camphene-base freeze casting, the highly aligned porous structures with pore sizes over 100 μm could be achieved [22], which can provide enough space for bone ingrowth. However, the metal powder in the slurry is difficult to disperse uniformly during the stage of camphene-based freezing, because it exhibits a tendency to precipitate due to its higher density and larger particle size compared with ceramic powder [23]. Besides, it is difficult to improve the length of the aligned camphene dendrites, because the freezing rate of camphene is slow and the dendrites do not have enough space to grow up [8]. By contrast, when water was used as the freezing vehicle, highly aligned porous structure throughout the entire sample could be achieved [24,25], and the porous structure can be easily regulated by controlling the freezing conditions [6,26]. In addition, water is more suitable as a solvent than liquid camphene, due to its non-toxicity, ordinary and good biocompatibility [27]. Temperature gradient is another important factor for the freeze casting method because it directly controls the process of ice growth. For instance, Yasumasa Chino and Dunand [26] produced porous titanium material by putting the slurry in a unidirectional temperature gradient field successively to control the directional growth of ice crystal and

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got long-range aligned pore structure. More importantly, they found the strength and pore morphology of the material was more suitable for implant materials compared with non-directional. The microstructure of the pores can be precisely controlled by this method, however, in particular the lamellar orientation over larger than centimeter dimensions has proven to be difficult. Recently, Robert O. Ritchie et al. [28,29] have developed a bidirectional freeze casting technique, which was capable of assembling small building blocks into large-sized, single domain, porous lamellar structure, and it displayed an excellent mechanical properties. However, the reported bidirectional freeze casting technique was just restricted to prepare porous ceramic materials.

Traditional freeze methods are difficult to precisely control the architectural features of porous materials with large-size and single-domain. In present study, we established the possibility of using bidirectional freeze casting method to produce long-range lamellar structure of porous titanium scaffolds. The pore morphology, chemical composition and crystalline structure of the fabricated porous titanium were characterized. Furthermore, we investigated the effects of sintering condition and initial solid content (15, 20, 25 vol.%) on the material structural and mechanical properties.

2. Experimental procedure

The porous titanium scaffolds were produced by controlled freezing of suspension of minute titanium particles. The slurries were prepared by mixing distilled water with a small amount (0.3 wt.% of water) of Xanthan gum dispersant, an organic binder (polyvinyl alcohol, 2 wt.% of the powder) and the commercially available titanium powder (15 μm, 99.9%, China) in various content, depending on the total porosity. Slurries were ball-milled at the rate of 90 rad/min for 24 h with alumina balls, and then de-aired by string in a vacuum desiccator until air bubbles were completely removed.

Freezing of the slurries was done by pouring them into a square PMMA mould (58 × 58 × 50 mm), which bottom was sealed by a PDMS wedge (the slope angle of PDMS wedge is 25°). Thereafter, the mould filled with slurry was placed on the copper cold finger for bidirectional freezing. The slurries with different solid concentrations were frozen under the same experimental temperature (−30 °C) for 6 h to ensure a complete freeze of the slurries. Once freezing was completed, the samples were freeze dried for at least 48 h to ensure a complete removal of the ice crystals in the machine (Pilot2-4M). The rough samples were finally sintered in a vacuum furnace with a digital temperature control system and Mo heating element under a pressure of 1.0×10^{-3} Pa. The green bodies were first heated to 600 °C and held for at least 2 h to make sure a completely removal of the organics. The green bodies were then densified by a high-temperature sintering treatment at a rate of 10 °C/min up to 1200 °C, a steady stage of 2 h at 1200 °C, and keep a cooling rate of 5 °C/min to room temperature.

The structure parameters (pore size, pore shape, size of the titanium walls and degree of pore alignment) and chemical compositions of the sintered bodies were characterized by scanning electron microscopy (Nova Nano230, FEI) with energy dispersive spectroscopy (EDS). The phase of the samples was also characterized by X-ray diffraction (D/MAX-RA, Rigaku). The total porosity and open porosity of porous titanium scaffold were determined by the Archimedes method. Compression test have been performed on cube (6 × 6 × 6 mm) on an electric servo-hydraulic material Test system (INSTRON 3369), at a constant displacement rate of 2 mm/min. All specimens were used for each experimental condition. The elastic modulus and compressive strength of the samples were measured from the compressive stress-strain curves.

3. Results and discussion

A schematic diagram of the preparation process is shown in Fig. 1. Firstly, the freezing of slurry was poured into a mould, which is placed on top of the copper cold finger covered by a PDMS wedge. Owing to the addition of the wedge, a horizontal temperature gradient was generated during freezing process, which is perpendicular to the vertical temperature gradient. Subsequently, as the slurries began to freeze, the ice crystals formed at the bottom and then began to grow along the dual temperature gradients, and titanium particles were simultaneously pushed by ice crystals into the space between the layers of ice crystals, forming an ice layer alternating with titanium layer structure. Finally, the lamellar ice crystals were then sublimated out, leaving behind a porous titanium scaffold with homogeneous aligned pores. So the porous lamellar titanium structure scaffold with large-sized (centimeter-scale) and single domain were created by the bidirectional freeze casting.

Fig. 2 shows typical SEM images of three directional cross-sections of the unsintered porous titanium scaffold. Fig. 2a shows the morphology of transverse cross-sections perpendicular to the direction of the temperature gradient. It is indicated that bidirectional freeze casting can be used to prepare porous titanium scaffold with a long-range aligned lamellar structure. However, it is very difficult to succeed by conventional freeze casting due to the fact that the growth of ice crystals only subject to unidirectional temperature [24]. Also, it can be seen that there are strong similarity between the as-prepared porous titanium scaffold and lamellar bone in humans [30], which is very important for medical implants. Because the porous titanium scaffolds have 3D feature structure, the complete information of porous titanium scaffolds is limited just from one cross-sectional image. To possess an overall understanding for the structure of porous materials, Fig. 2b and Fig. 2c present the morphology of mutually perpendicular longitudinal cross-sections of the sample, which is significantly different. The surface of the titanium walls is not absolutely smooth in practice, but has long edge aligned distribution on it throughout the whole sample along the temperature gradient, as shown in Fig. 2b. The reason why the surface morphology was rough could be attributed to directional growth of ice dendrites that drive titanium particles directional movement. These sheet-like ice dendrites which ranked neatly on the surface of titanium walls continue to grow, and pushed titanium powders together slowly. That led to the formation of long ledge between the two ice dendrites. We can also call the long edge as "titanium bridges" that connects between the layers. The lamellar structure also can be clearly seen from Fig. 2c, which was parallel to the temperature gradient and perpendicular to the titanium walls.

In the process of sintering, the porous titanium scaffolds may change the structure morphology with increasing temperature, and it can also form a new phase due to pure titanium with high chemical activity, which easily reacts with other elements(C, O, etc.) at high temperature.

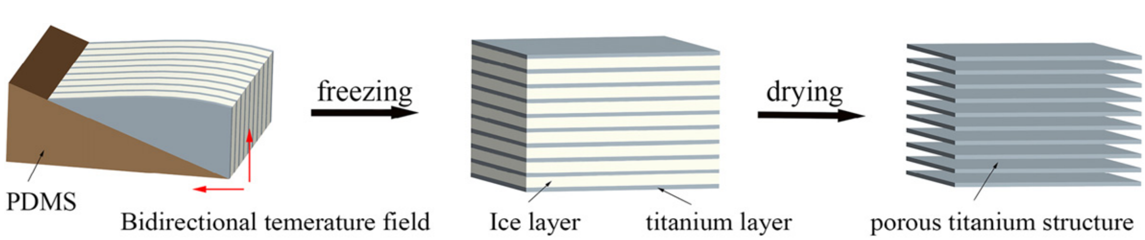

Fig. 1. Schematic diagram showing the creation of long-range lamellar structure of porous titanium scaffolds using bidirectional freeze casting.