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Short communication

A new approach to the fabrication of porous magnesium with well-controlled 3D pore structure for orthopedic applications

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ABSTRACT

A new approach to the fabrication of porous magnesium by using the titanium wire space holder (TWSH) method has been developed. Since the entangled titanium wire structure is used as the space holder, the porous structure is pipe-like and interconnected, and the pore size is identical and equals to the diameter of the titanium wire. In particular, the pore size, porosity, and porous morphology of the porous magnesium can be exactly and individually controlled. When the porosity is in the range of 54.2–43.2%, the compressive yielding strength is in the range of 4.3–6.2 MPa, and the Young's modulus is in the range of 0.5–1.0 GPa.

1. Introduction

Porous metallic materials have drawn widespread attention in various industrial fields due to their excellent physical and mechanical properties, such as high stiffness at extremely low density, high energy absorption, heat resistance, permeability and so on [1,2]. In particular, porous titanium and magnesium with very good biocompatibility have shown their potentials for the biomedical applications in surgical implants. The open-cellular structure in the porous materials can provide adequate spaces for the living tissue ingrowth and the nutrient transportation [3,4], and most importantly, the Young's modulus of the porous metals can be well controlled by adjusting the porosity, so as to match the stiffness of the natural bone [5]. Except for the above superiority, the porous magnesium also has very good biodegradability, which has been recently recognized as a very promising biomaterial for tissue engineering [6–9].

So far, many methods, such as investment casting [10], powder metallurgy with space holder [11], vacuum foaming [12], thixo casting [13], and directional solidification [14], have been developed to prepare porous magnesium. However, those traditional metallurgical methods are difficult to accurately control the pore morphologies (e.g., open and interconnected pores, 300–500 μm pore size, certain porosity ensuring appropriate stiffness and adequate strength) which are highly important for guaranteeing the biomechanical properties and the biocompatibility [4,15,16]. In recent years, a solid free-form fabrication (SFF) process for producing topologically ordered magnesium (TOPM) structures has been developed [17], which adopt a layer-by-layer fabrication process from computer aided design (CAD) models for manufacturing ordered pore architectures by accurate control of porous topology. This provides a possible route to fabricate the porous magnesium scaffolds with designed 3D pore structure and tailored mechanical properties. The drawback is that the SFF method needs six-steps which are complicated and cost-intensive.

In this study, we report a new approach to the fabrication of porous magnesium with controlled 3D pore structure, which needs only three-steps: (1) the entangled (or woven) 3D structure was prepared by using titanium wire [18], (2) the 3D structure was used as a space holder to fabricate the titanium/magnesium composite by infiltrating cast, and (3) the 3D structure, i.e., titanium wire space holder (TWSH) material, was then removed from the composite by etching off. With this method, it is possible to fabricate the porous magnesium with well-controlled 3D pore structure.

2. Materials and methods

The starting materials are commercially available titanium wire (purity: 99.9%, diameter: 0.27 mm) and magnesium ingot (purity: 99.9%). The 3D entangled titanium wire material with dimensions of Φ10 mm × 20 mm was prepared (details have been described elsewhere [18,19]), which was used as a space holder material. The solid magnesium was melted and kept at 700 °C under the atmosphere of the mixed gas of SF_6 and CO_2. Then the TWSH was soaked in the magnesium melts. In order to improve the melt infiltration into the porous structure in the TWSH material, the supersonic vibration (the source

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frequency: 40 kHz; output: 80 W; the vibration time is 60 s) was applied. After all the voids were completely filled with the magnesium melt, the sample was taken out slowly and cooled down in the protective atmosphere, so as to form titanium/magnesium composite. After that, the composite was immersed in the hydrofluoric acid (HF) solution (analytical reagent with the concentration of 40 wt.%) at room temperature to remove the TWSH material. During the etching, a supersonic vibration was applied on the sample from start to finish so as to quicken the Ti-etching and promote the discharge of the hydrogen gas. The etching time was about 72 h in this situation. When all the titanium wire in the composite was etched off, the sample (already becoming porous magnesium at this step) was taken out and cleaned by immersion in acetone with ultrasonic agitation. After the above steps (as illustrated in Fig. 1), the porous magnesium with well-controlled 3D pore structure could be fabricated.

The porosity of the porous magnesium could be calculated with the following formula:

$$P = \left(1 - \frac{m_1}{\nu\rho_{\mathrm{Mg}}}\right) \times 100\% \tag{1}$$

where ρ_{Mg} is the density of the magnesium which is 1.74 g/cm^3, v is the volume of the sample, and m_1 is the weight of the magnesium in the composite (i.e., the weight of the porous magnesium), which can be directly measured or calculated by following relation:

$$m_1 = m - m_2 \tag{2}$$

where m denotes the weight of the as-prepared Ti/Mg composite, and m_2 denotes the weight of the TWSH. Both could be measured directly. If the measured data (m, m_2 and m_1) could meet the above equation, the TWSH would be confirmed to be removed completely from the composite.

The as-prepared porous structure was directly characterized by using the optical microscopy and the scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The pore size was evaluated by quantitative image analysis using the commercially available software Image-Pro Plus. The mechanical properties of the porous magnesium were evaluated by the uniaxial compressive tests that were performed by using Zwick AG-100KN testing machine at room temperature. The tests were conducted on the specimens with dimensions of Φ10 mm × 20 mm under displacement control with the crosshead speed of 1 mm/min.

Since the porous magnesium deforms easily under a much lower loading, the elastic deformation occurs at relatively low stress levels. The elastic modulus evaluated from the stress–strain curve could be significantly influenced by the test machine compliance. Thus the compliance corrections were conducted by using the known pure magnesium (its Young's modulus is 45 GPa) in this study (the details regarding the compliance correction were described in ref. [20]). Therefore, all the elastic moduli of the porous magnesium reported in this paper had been calibrated accordingly.

3. Results and discussion

The appearance of the as-prepared porous magnesium was shown in Fig. 2a. Its porosity was evaluated to be about 51% according to the 49% porosity of the initial TWSH material. In order to verify the homogeneity of the porous structure, the sample was cut along the axial direction and shown in Fig. 2b. The porous structure was roughly homogenous, indicating that the infiltration of the magnesium melts into the porous TWSH material was well proceeded. Only one shrinkage cavity-like 'large' pore was found in the center of the cylindrical sample as indicated by the black arrow in Fig. 2b, suggesting that the local underfill occurred during the infiltrating cast. This perhaps could be attributed to the local high dense entangled titanium wire structure where the pores were too small to be filled with the magnesium melts. It also showed, as expected, that all the pores in the porous magnesium were pipe-like channels with the diameter of about 270 μm (approximately equivalent to the diameter of the titanium wire, used in this study). Fig. 2c–e showed the sectioned view of these channels, on which some flow lines were clearly shown on the 'channel' inner surface as indicated by the white arrows in Fig. 2c–e. These flow lines were reversely replicated from the surface plastic flowing deformation vestiges of the titanium wire. This just indicated that the titanium wire could be completely wetted by the magnesium melts at the infiltration temperature as reported in ref. [21].

The removal of the titanium wire from the titanium/magnesium composite could be achieved based on the different responses between titanium and magnesium in the HF solution. The titanium wire could be gradually eroded by the following chemical reactions [22]:

$$2\mathrm{Ti} + 6\mathrm{HF} = 2\mathrm{TiF_3} + 3\mathrm{H_2}\uparrow \tag{3}$$

$$\mathrm{Ti} + 4\mathrm{HF} = \mathrm{TiF_4} + 2\mathrm{H_2}\uparrow \tag{4}$$

$$\mathrm{TiF_4} + 2\mathrm{F^-} = [\mathrm{TiF_6}]^{2-}. \tag{5}$$

The dissolution of titanium in the HF solution was suggested to occur via the electrochemical process [22] in which the solid state titanium was converted to ionized state $[\mathrm{TiF_6}]^{2-}$. This process would be continually in progress until all the titanium wire was completely consumed. The release of hydrogen during the dissolution of titanium was just the sign indicating the titanium dissolving.

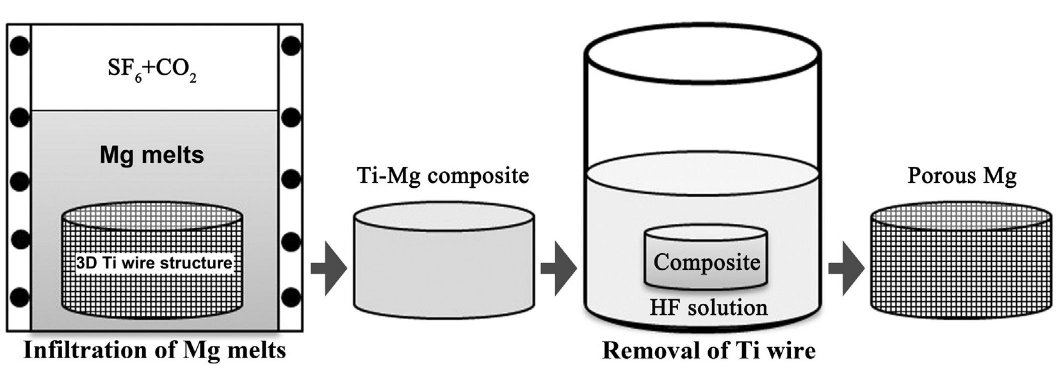

Fig. 1. Schematic illustration of the TWSH method for the fabrication of porous magnesium.