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Mechanical degradation of porous titanium with entangled structure filled with biodegradable magnesium in Hanks' solution

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ABSTRACT

The degradation behavior of the porous titanium with entangled structure filled with biodegradable magnesium (p-Ti/Mg) in Hanks' solution was investigated. It was found that the p-Ti/Mg composite had higher strength than pure magnesium and porous titanium with entangled structure (p-Ti). Although the magnesium in p-Ti/Mg was completely dissolved in Hanks' solution after immersion for 104 h, the rest of the sample still maintained strength of about 86 MPa. Moreover, the produced porousness (due to magnesium-degradation) could provide channels for the ingrowth and transportation of bone cells. However, the high corrosion rate of p-Ti/Mg is still a problem when used as a candidate biomedical material, which needs further improvement.

1. Introduction

Magnesium is one of the biocompatible metals. It not only plays a role in genomic stability and DNA repair [1–3], but is also biodegradable in physiological environment [4–6]. When magnesium or its alloys are used for orthopedic implants, they are expected to provide adequate mechanical properties and low stress shielding effects [7]. Due to these prospects, the potential medical applications of magnesium have aroused growing interests recently [8–10]. However, the magnesium implant will lose its strength rapidly when the magnesium is degraded. If the mechanical degradation cannot be compensated by the new bone ingrowth [6], the implant may lose its biomechanical function, leading to complete failure. Generally the growth rate of new bone is relatively constant, so the key to the problem is how to maintain the strength of the magnesium implant in the healing period. One way is to prevent rapid corrosion of magnesium. At present the common methods to prevent rapid corrosion and the decay of magnesium in vivo are alloying [11,12] and surface treatments or coating [13–16]. Brar et al. [11] studied the corrosion behavior of three binary Mg–x(wt.%)Sr (x = 0.5, 1.0, 1.5) alloys and three ternary Mg–x(wt.%)Zn–0.5(wt.%)Sr (x = 2.0, 4.0, 6.0) alloys in Hanks' solution, and found that Mg–6.0Zn–0.5Sr alloy had a high degradation rate, while Mg–2.0Zn–0.5Sr alloy had low degradation rate. Berglund et al. [12] studied the corrosion behavior of five alloys in the Mg–xCa–ySr system (x = 0.5–7.0 wt.%; y = 0.5–3.5 wt.%) in Hanks' solution. They found that Mg–7.0Ca–3.5Sr and Mg–1.0Ca–2.0Sr alloys completely dissolved within 24 h of immersion, while Mg–1.0Ca–0.5Sr alloy had low degradation rate. Gu et al. [14] studied the corrosion behavior of alkaline heat treated Mg–Ca alloy in simulated body fluid, and found that the degradation rate of the Na_2HPO_4 heated, Na_2CO_3 heated and $NaHCO_3$ heated samples increased slowly with immersion time in the first 200 h. The treated samples were obviously better than the untreated sample. According to their study, the average corrosion rate could be ranked in the following order: untreated > Na_2CO_3 heated > Na_2HPO_4 heated > $NaHCO_3$ heated. Liu et al. [16] studied the corrosion behavior of magnesium alloy treated by cathodic plasma electrolysis (CPE) in simulated body fluid. They found that at the initial 96 h the corrosion resistance of CPE treated substrate was obviously improved. The achievements of these methods are demonstrable, but still did not reach the level of application of magnesium for orthopedic implants. Combinations of magnesium with non-degradable and other degradable biomaterials may provide hybrid implant solutions with dedicated functionality [17]. Inspired by this, we are exploring new ways to keep the strength of the magnesium implant in vivo. Titanium–magnesium composite is one of the choices [18], in which titanium provides a long-term biomechanical function, but magnesium can be degraded and replaced by new bone, forming stable fixture of the implantation. It is well known that titanium is the closest metal to magnesium in the electrochemical series [19]. When titanium and magnesium are in contact in the presence of an electrolyte, the electrochemical effect between them is minimal. Therefore, the titanium–magnesium composite is expected to have lower galvanic corrosion rate than other metal/Mg composites. In this paper, the new biomaterial — porous titanium

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with entangled structure filled with biodegradable magnesium (p-Ti/Mg) [18] was investigated in terms of the corrosion behavior in Hanks' solution and the degradation of its compressive strength due to the progress of corrosion. The results indicated that the magnesium was completely dissolved within 172 h of immersion in Hanks' solution, resulting in the complete disappearance of the strength. The magnesium in p-Ti/Mg was completely dissolved after immersion for 104 h, but the rest of the sample still maintained strength of about 86 MPa. The titanium did not reduce the degradation rate of p-Ti/Mg but kept the strength when magnesium in it was completely dissolved. This work will reveal the corrosion mechanism of such bimodal composite in vitro, and provide a basis for further research on the corrosion controlling methods of the p-Ti/Mg biomaterials.

2. Materials and methods

2.1. Materials

A commercial pure titanium wire (99.9% purity, 0.265 mm in diameter) and a commercial pure magnesium ingot (99.9% purity) were used as raw materials in this study. The titanium wire was wound into a spiral-shape, and then stretched and woven into a 2D mesh. The mesh was rolled into 3D material and pressed in a mold, forming the cylindrical porous titanium (p-Ti) preform. The porosity of the p-Ti preform could be simply determined by direct mass–volume calculation method with the following formula:

$$P = \left(1 - \frac{M}{V\rho_{Ti}}\right) \times 100\% \quad (1)$$

where M is the weight of the preform; V is the volume of the preform; ρ_{Ti} is the density of the solid titanium wire. Thus, the volume fraction of the titanium in the preform is:

$$P_{Ti} = (1 - P) \times 100\%. \quad (2)$$

The p-Ti/Mg composite was fabricated by infiltration casting. To this end, the magnesium was melted and kept at 700 °C under the protective atmosphere of SF_6 and CO_2 mixture. The as-prepared p-Ti preform held with a clamping device was soaked in the magnesium melts. After filled with magnesium melts it was taken out, and quickly cooled down to the room temperature under the SF_6 and CO_2 mixed atmosphere, forming the p-Ti/Mg composite. This processing route could be intuitively illustrated in Fig. 1. In this way, the samples with two dimensions, Ø10 × 20 mm and Ø10 × 3 mm, were prepared for compression and corrosion tests, respectively. Before the tests, the samples were ground with SiC emery paper (up to 1200 grit), and then ultrasonically cleansed in ethanol. In this study, the porosity of the p-Ti preform was controlled to be about 70%, thus the volume fractions of the titanium and magnesium in the p-Ti/Mg composite were about 30% and 70%, respectively.

Table 1
Chemical composition of Hanks' solution (g/L).

NaCl	$NaHCO_3$	$Na_2HPO_4 \cdot 12H_2O$	KCl	KH_2PO_4	$MgCl_2 \cdot 6H_2O$	$MgSO_4 \cdot 7H_2O$	$CaCl_2$	$C_6H_6O_6$
8.0	0.35	0.06	0.4	0.06	0.1	0.06	0.14	1

2.2. Immersion tests

The immersion tests in Hanks' solution (PH = 7.4, its composition was listed in Table 1) were carried out at 37 ± 1 °C. The volume of solution was calculated based on a volume-to-sample area ratio of 100 mL/cm^2. The evolved hydrogen was collected by an upside down funnel covered on the sample, which could be directly measured from the upper burette as shown in Fig. 2. The volumes of hydrogen in the burette were recorded every two hours. All the tests were performed in triplicate. For comparison, the same tests were also conducted with the pure magnesium. The corrosion products formed on the surface of the samples were removed by dipping the samples in a solution of 20% CrO_3 for one hour and then washed in acetone. The surface morphology of the corroded samples was observed by using a Zeiss Stemi2000-C stereo microscope. The weight loss was measured by weighting the sample before and after the corrosion test.

2.3. Compression tests

The compressive properties of the materials investigated were evaluated by using Zwick AG-100KN testing machine. The tests were conducted under displacement control with a cross-head speed of 1 mm/min. The average of three measurements was taken as the value.

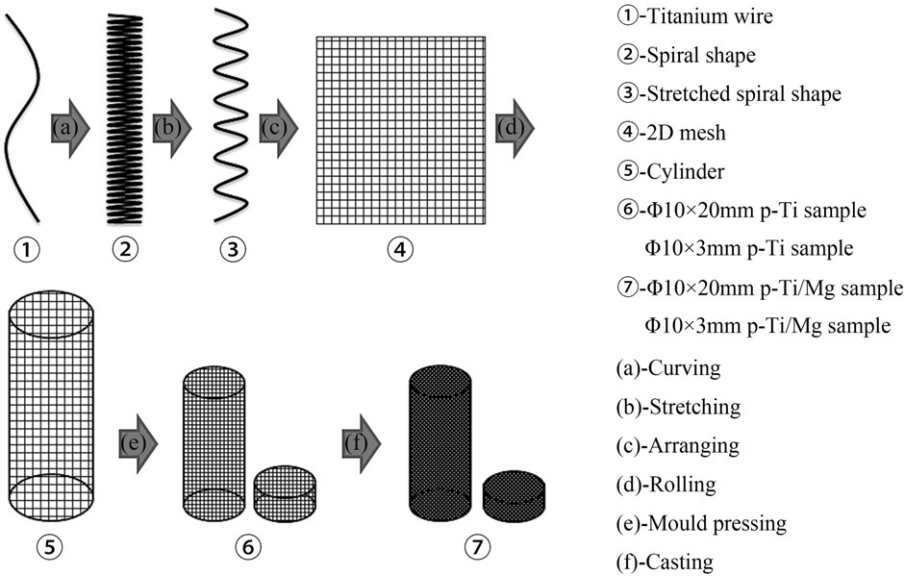

Fig. 1. Schematic illustration of the procedures for the preparation of the p-Ti/Mg composite.