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A novel approach to fabricate Zn coating on Mg foam through a modified thermal evaporation technique

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ABSTRACT

Zn enriched coatings with distinct microstructures and properties were fabricated on Mg foams by a modified thermal evaporation technique using a tubular resistance furnace. As the temperature and kinetic energy of Zn vapor varied along the tubular system, a spatial variation of preparation conditions was created and the obtained coatings were found to follow two growth mechanisms: a thermal diffusion pattern in high-temperature zone and the a relatively low-temperature deposition model. A Zn-based deposition coating with dense texture and nearly uniform structure was acquired while Mg foam was placed 20 cm far from the evaporation source, where the Zn vapor deposition model dominated the coating growth. Mechanical properties and bio-corrosion behaviors of the samples were investigated. Results showed that the Zn coatings brought dramatic improvements in compression strength, but exhibited differently in biodegradation performance. It was confirmed that the diffusion layer accelerated corrosion of Mg foam due to the galvanic effect, while the Zn-based deposition coating displayed excellent anti-corrosion performance, showing great potential as bone implant materials. This technique provides a novel and convenient approach to tailor the biodegradability of Mg foams for biomedical applications.

1. Introduction

In recent years, Mg foam with open-celled pore structures has received growing attentions as bone implant materials [1–4], as it can degrade in biological environments and promote tissue cells ingrowth into open pores [1,5]. Moreover, Mg foam exhibits good biocompatibility, favorable bioresorbability and suitable mechanical properties close to those of natural bones, being recognized as a promising biomaterial for bone tissue engineering scaffolds [1,5,6]. However, Mg and Mg alloys usually degrade rapidly in biological environments, which grievously hampers their biomedical applications [2,5–7].

Surface coating technique is an effect way to protect Mg and its alloys against corrosion. Many coatings have been employed for the purpose, such as HA coating [2], bioceramic coating [8], chemical conversion layer [9] and metallic coatings [10–17]. Among these, Ti and Zn metallic coatings can provide Mg substrates with excellent mechanical properties, wear and corrosion resistance to suit their clinical applications, enabling the service life of the implant materials to be well matched with the bone tissue regeneration [10–14,16].

Recently, interests for Zn-based biodegradable metals with moderate degradation rate between Mg and Fe-based materials have grown [18–20]. Similar to the biocompatible Mg element, Zn is an essential matter in human nutrition and is the second most abundant transition metal element in the human body, playing a crucial role in cell proliferation of the immune and nervous systems [19]. Nevertheless, Zn implants usually suffer from inferior mechanical properties because of their low ductility and relatively high density compared to Mg-based biomaterials [20]. Thus, it is of great value to fabricate Zn coating on Mg foam to take full advantage of these two metals. However, the general surface treatments used to coat Zn layer on Mg blocks, such as electrodeposition, ion implantation or thermal diffusion are hardly applied to porous samples. As for electrodeposition, it is limited due to the fluctuant electric field distribution along the foam skeleton, which would lead to inhomogeneous coating or no coating growth within the inner pores [15,16]. Also, the diffusion layer through pack cementation process by embedding Mg blocks into Zn powders followed by annealing is not applicable to Mg foam because of the serious channel blockage [13,14]. Coating prepared by PVD process [17] usually requires expensive and sophisticated equipment, which constrains

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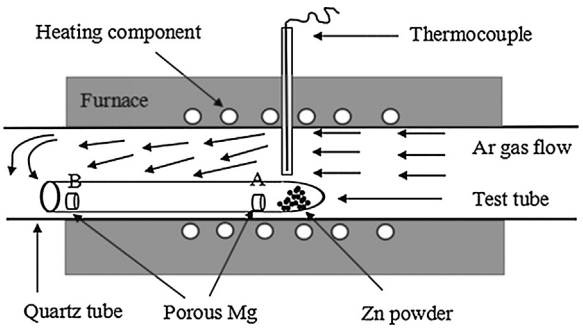

Fig 1. Schematic diagram of thermal evaporation apparatus.

its widespread use. Hence, a novel and suitable approach to obtain Zn coating on Mg foam substrate is urgently needed.

In the present study, a thermal evaporation technique using a simple tubular resistance furnace has ever been employed to synthesis some novel nanostructures of functional oxides before [21,22] was introduced, as it is favorable for the substrate materials with complex shapes and has a high degree of flexibility in experiment adjustment. Very recently, a Zn enriched diffusion coating on open-celled Al foam was fabricated through a thermal evaporation technique by our group due to the gaseous thermal diffusion reaction, showing great advantages over other methods in regulating the mechanical properties of metal foams [16]. Based on these, a long quartz test tube was designed and applied in the tubular resistance furnace system to create different reaction conditions and a gaseous environment with super-saturated Zn vapor. The influences of spatial variation of the substrates on microstructures, mechanical properties and bio-corrosion behaviors of Zn coated foam composites were examined. The results are expected to provide useful information for further studies on the development of Mg foam scaffolds for the applications in the bone implant fields.

2. Experimental

2.1. Preparation of Mg foam samples

Mg foam was prepared by an infiltration process based on weakly corrosive and highly flexible space holder materials as proposed in our previous study [3]. Two kinds of cylindrical samples with dimensions of Φ20 mm × 20 mm and Φ10 mm × 8 mm were cut from the foam block by wire-cutting, and then cleaned with acetone, etched with 1 M hydrochloric acid solution followed by ultrasonic cleaning in distilled water. Finally, the samples were air-dried before use.

2.2. Thermal evaporation process

Fig. 1 schematically shows the thermal evaporation apparatus employed in the study. Zn powder (Alfa Aesar, 99.9%) was used as source material and placed in the bottom of the test tube (Φ22 mm × 200 mm) and Mg foam samples were located in zones A and B as marked in Fig. 1, respectively. The quartz tube was evacuated to 10^{-3} Torr first, and then purged with argon gas until an atmospheric pressure was established. Subsequently, the furnace was fast heated to 600 °C holding for 60 min, with a stable argon gas flow of 90 sccm. To create a super-saturated Zn vapor environment, a graphite sheet (Φ20 mm × 10 mm) fabricated by cold pressing carbon powders was placed at the open end of the test tube, which also played a role in residual oxygen removal. Finally, Zn coated foams (marked as Samples A and B, respectively) were cooled down naturally to room temperature in the furnace.

2.3. Characterization and mechanical tests

Macroscopic morphologies and cross-section images of the samples were observed by optical microscopy (Zeiss, A10X) and field-emission scanning electron microscopy (FE-SEM, SU8020). Chemical compositions of cross-section of the samples were analyzed by EDS microanalysis system equipped to FE-SEM. Phase analysis was performed at X-ray diffraction (XRD, X'Pert ProMPD) with Cu$K\alpha$ radiation. Mechanical properties of bare and Zn coated Mg foams were evaluated by compression tests on rally to room temperature in Φ20 mm × 20 mm using a universal testing machine (Instron 3369) at a cross-head speed of 2 mm/min. Minimum three replicate tests were conducted for each group for reproducibility. Apparent density of samples was calculated by measured weight and dimensions. The elastic modulus of Mg foams was calculated on the basis of curves fitted to the linear elastic regions of the stress-strain curves and the compressive yield strength value was determined using the 0.2%-offset method. Vickers microhardness of the samples was measured at a load of 0.98 N and holding time of 15 s.

2.4. Bio-corrosion measurements

Bio-corrosion behavior of bare and Zn coated Mg foams was investigated by monitoring the variation of pH values of the simulated body fluid (SBF) solutions and weight loss of the soaked samples. Each sample with size of Φ10 mm × 8 mm was immersed into 30 mL SBF solution at 37 °C and SBF was refreshed every two days according to the description in literature [23]. Prior to weight measurement, the soaked samples were rapidly washed in a chromic solution (200 g/L CrO_3 + 10 g/L $AgNO_3$) to remove the corrosion products, ultrasonically cleaned in distilled water, and dried in air and weighed. Three parallel measurements were employed for each group.

3. Results and discussion

3.1. Microstructures of the samples

As shown in Fig. 2(a), Mg foam features two types of pores: spherical cells gained by dissolution of salt particles and micropores derived from inter-particle contacts. The later generates connection tunnels among spherical cells, making a high open porosity containing about 99% open cells [3], which could facilitate nutrients transmission and bone tissue ingrowth [1,5]. Moreover, Mg foam exhibits a rough surface texture, this may be attributed to the slight oxidation in ambient environment, as confirmed by XRD analysis (Fig. 3), in which the diffraction peak originated from MgO phase appeared at 2θ of 44.37°.

It is seen from Fig. 2(b) and (c) that the Zn coated foams present similar morphology compared to Mg foam, in particular, the original cell shape and open porosity of the sample remain after thermal evaporation process. It should be noted that the cross-sectional image of Sample A inserted in Fig. 2(b) reveals that no obvious deposition coating was formed on Mg foam skeleton, whilst the samples developed a diffusion layer composed of two-phase structure (α-phase + intermetallic phase). According to the XRD pattern in Fig. 3, the diffraction peaks of Sample A were almost originated from α-Mg and $MgZn_2$ phase, which is in agreement with the results of metallographic analysis. In contrast, Sample B presents an obvious interface between the deposition coating and substrate (refer to the cross-sectional image inserted in Fig. 2(c)), and the Zn coating with a thickness of 16–25 μm shows a smooth surface texture, which could be clearly observed from Fig. 2(d). As shown in Fig. 3, the XRD pattern of Sample B presents relatively weak diffraction

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