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Surface corrosion behavior and reaction product film deposition mechanism of Mg-Zn-Zr-Nd alloys during degradation process in Hank's solution

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ABSTRACT

The surface corrosion behavior and reaction product film deposition mechanism of biodegradable as-extruded Mg-2Zn-0.6Zr-*x*Nd alloys with different Nd addition were investigated using electron backscattered diffraction (EBSD), scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM), X-ray diffraction (XRD), electrochemical test and immersion test. The results showed that 0.2–0.6 wt% Nd addition led to significant grain refinement of the alloys and the formation of fine MgZn and T phases. Excessive Nd addition (1 wt %) significantly resulted in large size Zr-rich precipitates and second phases as cathodes, causing micro-galvanic corrosion acceleration. The electrochemical measurements, immersion tests and corrosion morphologies proved that the alloy with 0.6 wt% Nd addition had the best corrosion resistance and exhibited a uniform corrosion mode, which were attributed to small grain size, fine second phases and formation of compact $CaHPO_4{\cdot}2H_2O$ film. Moreover, corrosion models with different Nd contents were proposed to interpret the corrosion product film deposition mechanism.

1. Introduction

Mg alloys are receiving increasing attention as biodegradable implant materials due to their good biocompatibility, biodegradability and excellent mechanical properties, especially low density (1.7–2.0 g/cm^3) and close elastic modulus (41–45 GPa) to the natural bone [1–3]. Additionally, Mg alloys have excellent machining property as metallic materials and better stiffness than polymers (1–3 GPa), which give them significant advantages as orthopedics implants [4] and cardiovascular stents [5]. However, Mg alloys exhibit unsatisfactory corrosion resistance in body fluids which are rich in chloride concentrations [3,6], leading to premature losses of mechanical integrity [7], thus limiting their practical applications as implant biomaterials [8–10]. Therefore, it is necessary to develop novel Mg alloys with a slow corrosion rate and a uniform corrosion mode, which can provide a good stability in the initial stage of implantation and then gradually degrade in the expected time.

It is well known that the addition of different alloying elements is an efficient way to enhance the properties of Mg alloys. Mg alloys containing Al showed a relatively high strength and good corrosion resistance, however, it has been reported that Al element can cause nerve toxicity and restraining growth to human body [3,11]. For biodegradable Mg alloys, non-toxic alloying elements are essential, so Ca, Zn, Mn, Zr, Sr and low toxicity rare earth (RE) elements such as Y and Nd are suggested as potential alloying elements for biomedical applications [10,12–15]. In recent years, the Mg-Zn-Zr alloys, which were widely applied in automotive industry, have been investigated as potential biomedical materials [4,16,17]. Zn is an essential element in human body, and Zn addition can improve strength and corrosion resistance of Mg alloys at the same time [18,19]. Zr is the best grain refiner in Mg alloys without Al [20] and it has low ionic cytotoxicity [21]. However, commercial Mg-Zn-Zr alloys such as ZK30 [16], ZK40 [17] and ZK60 [4,16] cannot reach certain degradation performance (corrosion rate ≤ 0.5 mm/year) and uniform corrosion mode to be applied as suitable biodegradable materials. Previous works by Li [22] and Wang [23] showed that the addition of Nd in Mg alloys could effectively enhance the corrosion resistance. In addition, a small amount of Nd shows excellent biocompatibility *in vitro* and vivo [11]. Chang [24] investigated the microstructures and corrosion resistance of Mg-5Zn-0.3Zr alloys with different Nd addition. However, recent study showed that the concentration of Zn in Mg-Zn based alloys should be limited up to 3 wt% for good corrosion resistance [18]. Concerning the further application of biodegradable Mg alloys, the dynamic corrosion behavior, corrosion modes and especially the corrosion product film formation mechanism of Mg-(< 3 wt%) Zn-Zr-*x*Nd alloys in physiological media have not been discussed.

In this study, the Mg-2Zn-0.6Zr-*x*Nd alloys with various Nd contents were prepared to investigate the effects of Nd addition on the

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microstructure and corrosion resistance, and then the roles of precipitations and second phases in corrosion process as well as the formation mechanism of corrosion film were investigated.

2. Materials and methods

2.1. Materials preparation

Magnesium alloys with the nominal compositions of Mg-2Zn-0.6Zr with different Nd addition (0–1 wt%) were prepared in a vacuum induction furnace with a graphite crucible, protected by high purity Ar. High purity Mg (99.99 wt%), Zn (99.995 wt%), Mg-30Zr (wt%) and Mg-30Nd (wt%) master alloys were added to prepare these alloys. The melt was held for 30 min at a temperature of 780 °C to ensure that all the required alloying elements were dissolved in the melt alloy, which then was poured into a steel mould at 720 °C. Afterwards, the as-cast ingots were treated with homogenizing annealing at 400 °C for 12 h, and then were machined to remove the oxide skin on the surface. Finally, the ingots were preheated at 350 °C for 2 h and hot extruded into bars with 12.6 mm in diameter under an extrusion ratio of 16:1 and an extrusion rate of 3 mm/s. The chemical compositions were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), as listed in Table 1.

2.2. Microstructure characterization

The as-extruded microstructures were observed using a field emission scanning electron microscope (FE-SEM, Zeiss Merlin VP Compact) equipped with an energy dispersive spectrometer (EDS, Oxford). The grain sizes were measured using an electron backscattered diffraction (EBSD) installed on a scanning auger electron spectroscopy (AES, PHI 710). The samples used for EBSD analysis were mechanically polished with #4000 *SiC* paper and then were electropolished in a solution of 20 vol% nitric acid and 80 vol% methanol at 5 V for 10 s.

2.3. Immersion test

The immersion tests consisted of weight loss test and pH value variation test, and they were carried out in Hank's solution (Table 2) at 37 °C. The specimen used was circular (φ 11 mm × 5 mm), and the ratio of solution volume to surface area was 30 mL/cm^2 according to ASTM G31-12a [25]. The initial pH was adjusted to 7.4 with 1 mol/L HCl and NaOH solution. The solution for weight loss test was renewed every 24 h in order to maintain a relatively stable immersion environment. The soaked specimens were removed from Hank's solution after 240 h, gently rinsed in deionized water and dried with cool air. The corrosion surface morphologies and the phases of the specimens after immersion were characterized by FE-SEM equipped with EDS and X-ray diffraction (XRD, Rigaku D/Max 2500 PC) with Cu Kα radiation at a voltage of 40 kV, respectively. The weight losses of the specimens were measured after cleaning with chromate acid (200 g/L CrO_3 + 10 g/L $AgNO_3$). Three samples were measured for each alloy. Then three-dimensional profiles of the corroded surface were observed by a confocal laser scanning microscopy (CLSM, Olympus LEXT OLS4100). The corrosion rate was calculated through following equation [25]:

$$\text{Corrosion rate} = \frac{8.76 \times 10^4 \times W}{A \times T \times D} \quad (1)$$

where W is the weight loss (g), A is the area of the sample exposed to the solution (cm^2), T is the exposure time (h) and D is the density of the material (g/cm^3).

For the pH value variation test, the Hank's solution was not renewed. The samples were soaked in sealed jars of Hank's solution to prevent moisture evaporation for 240 h at 37 °C. The pH values of the solution during immersion were recorded at various time points using a pH meter (HM Digital PH-200).

Table 1
Chemical compositions of experimental alloys (wt%).

Alloy	Zn	Zr	Nd	Fe	Ni	Cu	Mg
#1 (Mg-2Zn-0.6Zr)	1.87	0.54	/	< 0.01	< 0.002	< 0.005	Bal.
#2 (Mg-2Zn-0.6Zr-0.2Nd)	1.91	0.55	0.18	< 0.01	< 0.002	< 0.005	Bal.
#3 (Mg-2Zn-0.6Zr-0.6Nd)	1.94	0.52	0.56	< 0.01	< 0.002	< 0.005	Bal.
#4 (Mg-2Zn-0.6Zr-1Nd)	1.90	0.58	0.91	< 0.01	< 0.002	< 0.005	Bal.

2.4. Electrochemical test

The electrochemical tests were carried out using an electrochemical workstation (Princeton VersaSTAT MC) at 37 °C. The electrochemical tests in 8.0 g/L NaCl solution were used as a comparison of the tests in Hank's solution. In order to study the corrosion protection properties of the corrosion product film, the tests of the samples after 240 h immersion in Hank's solution were carried out. Samples for electrochemical tests were cut from the extruded bar along the cross-section direction. The exposed area for working electrode was 1 cm^2 and the electrolyte volume was 300 mL. Platinum gauze and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The open circuit potential (OCP) was measured for 1 h to establish an approximate steady state before each measurement. Then the electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 100 kHz to 10 mHz with a perturbation amplitude of 10 mV. The polarization curve measurement was subsequently conducted with a scan rate of 1 mV/s. Three tests were performed for each sample condition to investigate the reproducibility of the results.

3. Results and discussion

3.1. Microstructure characterization

The microstructures of as-extruded Mg-2Zn-0.6Zr-*x*Nd alloys measured by EBSD are shown in Fig. 1. Typical equiaxial grains and elongated grains formed due to the phenomenon of dynamic recrystallization during the extrusion process were observed. The non-uniform distribution of plastic deformation energy resulted in the inhomogeneous grains. With increasing Nd addition, the grain refinement was obvious and the average grain sizes of #1–#4 alloys were about 24 μm, 17 μm, 11 μm and 9 μm, respectively.

The SEM micrographs along the cross-section of as-extruded Mg-2Zn-0.6Zr-*x*Nd alloys are shown in Fig. 2. Few white particles were observed in the #1 alloy (Fig. 2(a)). With increasing Nd addition, more white particles gathered at the grain boundaries. The elemental compositions of the white particles (point A in Fig. 2) and the α-Mg matrix (area B in Fig. 2) of the alloys were analyzed by EDS, as shown in Table 3. It was indicated that the white particles in the #1 alloy were composed of Mg, Zn and Zr elements. The white particles in #2, #3 and #4 alloys (Fig. 2(b)–(d)) were composed of Mg, Zn, Nd and Zr (minor) elements. Li [15] and Wei [26] have reported that some Mg-Zn phases were changed to Mg-Zn-Nd phase (T phase) by the addition of Nd. Take the atomic ratio in this study into consideration, the white particles in #2–#4 alloys were suggested to be T phase. With increasing Nd addition, the volume fraction of T phase increased. Except for Mg and Zn elements, extremely low contents of Zr and Nd were detected in area B. It revealed that although the maximum solubility of Zr and Nd in magnesium were 3.8 and 3.6 wt%, they could hardly dissolve in α-Mg matrix due to the decrease of solubility caused by multielement addition.

In order to investigate the effect of Nd addition on the distribution