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ARTICLE

Corrosion Behavior and Electrochemical Properties of As-cast Mg-2Zn-0.5Ca-Y Series Magnesium Alloys in Hank's Solution and NaCl Solution

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Abstract: Microstructure and bio-corrosion behavior of as-cast Mg-2Zn-0.5Ca-Y series alloys were investigated for biomedical application by optical microscopy, scanning electronic microscopy (SEM), immersion tests and electrochemical measurements in Hank's solution and NaCl solution (3.5wt%). The morphologies of the Mg-2Zn-0.5Ca-Y series magnesium alloys indicate that the corrosion is not uniform and a lot of cracks are formed on the surface of the corrosion layer after immersion tests. The corrosion resistance of as-cast Mg-2Zn-0.5Ca-Y series alloys increases owing to the addition of the rare earth element Y and that of Mg-2Zn-0.5Ca-1.0Y alloy is the best. All of the potentiodynamic polarization curves obtained in the tests in Hank's solution and NaCl solution show current plateaus which are due to the presence of a protective corrosion product film. The electrochemical impedance curves of the alloys in the test solutions have only one capacitive loop. The appearance of a capacitive loop at high frequency is caused by the stable double-layer capacitance. The capacitive loop at low frequency is attributed to diffusion control at film-free areas.

Key words: Mg-2Zn-0.5Ca-Y series alloy; corrosion behavior; potentiodynamic polarization; electrochemical impedance

Magnesium alloys show potential application as biodegradable materials due to their outstanding biological performance. Recently, it has even been reported that the presence of magnesium in the bone system is beneficial to bone strength and growth[1]. Unfortunately, rapid corrosion is an intrinsic response of magnesium alloys to chloride containing solutions[2], including human body fluid or blood plasma. In general, it is accepted that Mg is easily oxidized to form a thick hydroxide film when it is in contact with humid air or water[3,4]. In solutions containing Cl^-, the corrosion resistance of magnesium alloy is much worse. Enhancement of the corrosion resistance of magnesium alloys is one of important issues if their application is to be increased.

The corrosion behavior of magnesium alloys with rare earth (RE) element additions has been investigated during past decades[5,6]. It is well known that the addition of rare earth elements is an effective way to enhance the corrosion resistance of magnesium alloys. The improvement has been attributed primarily to the formation of metastable RE-containing phases along the grain boundaries. Another important effect of RE on the corrosion resistance of these alloys is the so-called “scavenger effect”, i.e. some impurity elements in the alloys, such as Fe, will deteriorate their corrosion resistance significantly. RE additions are reported to cancel the influence of such impurities by the formation of intermetallic compounds[7].

Yttrium (Y) is a particularly interesting alloying element for magnesium alloys because Y has a standard electrochemical potential (–2.372 V) equal to that of magnesium (–2.372 V)[8]. More recently, researchers focused on the effects of Y on magnesium alloys. The corrosion behavior and electrochemical properties of Mg-2Zn-0.5Ca-Y series alloy have been evaluated in Hank's solution and NaCl solution.

In the present study, a new Mg-2Zn-0.5Ca-Y series alloy,

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used as a high performance structural material as well as a biomaterial containing different Y element concentrations, was prepared by casting and was tested to determine the amount of elemental Y that could provide higher corrosion resistance for Mg-2Zn-0.5Ca-Y series alloys.

1 Experiment

The chemical composition of as-cast Mg-2Zn-0.5Ca-Y series alloy used in this work is listed in Table 1. The alloys were prepared by conventional casting methods under the protection of molten salt. The melts were then poured into a steel die with 90 mm×45 mm×12 mm in size at 800 °C. The specimens for the tests were machined to form a cast sheet.

Rectangular samples for the immersion test with a dimension of 10 mm×10 mm×2 mm were cut from the cast alloy directly. Before the immersion tests, the surface of the specimens was polished with 2000 grit emery paper and finely polished with 0.5 μm diamond powder, cleaned with alcohol solution, and then dried in a warm air blast. Then the sample was immersed in 150 mL Hank's solution under ambient conditions at room temperature (the ratio of the volume of the solution to the surface area is 150 mL:2 cm^2)[9] for up to120 and 168 h. The chemical composition of Hank’s solution is listed in Table 2.

The corrosion rate was cross-checked by measuring the mass of the specimens before and after the immersion tests. The latter was done after cleaning and removal all of corrosion products in 15%CrO_3+1%$AgNO_3$+400 mL H_2O solution.

The corrosion morphology observation of the alloy before and after immersion was performed using optical microscopy (OM) and scanning electron microscopy (SEM). The phase composition of the alloys was studied using X-ray diffraction (XRD).

A three-electrode test cell was used for electrochemical measurements. The electrochemical impedance spectroscopy (EIS) studies were performed at open circuit potential with amplitude of 10 mV over the frequency range of 10^5~0.01 Hz on specimens. The specimens were exposed to the corrosive electrolytes of NaCl solution (3.5wt%) and Hank's solution to investigate the corrosion mechanism. All the tests were carried out at room temperature.

The electrochemical tests used a ‘Bio-logic’ VSP potentiostat/ frequency response analysis system to evaluate the corrosion behavior of the specimens at room temperature. A saturated Ag/AgCl (saturated with KCl) was used as the reference electrode. A platinum mesh and the investigated specimen were used as the counter electrode and the working electrode, respectively. The electrochemical tests were conducted in solutions at a scan rate of 5 mV/s. The polarization curves were used to estimate corrosion and passivation potentials (E_{corr}, E_{pp}), and corrosion current density (I_{corr}) at the corrosion potential (E_{corr}) by the Tafel extrapolation of the cathodic branch. Five tests were performed on each sample to obtain the average response and the standard deviation.

Table 1 Chemical composition of as-cast Mg-2Zn-0.5Ca-Y series alloy (wt%)

Alloy No.	Zn	Ca	Mg	Y
I	2.0	0.5	Bal.	0
II	2.0	0.5	Bal.	0.5
III	2.0	0.5	Bal.	1.0
IV	2.0	0.5	Bal.	1.5
V	2.0	0.5	Bal.	2.0

Table 2 Chemical composition of Hank’s solution (g/L)

NaCl	$CaCl_2$	$Na_2HPO_4·12H_2O$	KH_2PO_4	$MgSO_4·H_2O$	$C_6H_{12}O_6$
8.00	0.14	0.06	0.06	0.20	1.00

2 Results and Discussion

2.1 Morphology and corrosion products

Fig.1 shows the microstructures of the as-cast Mg-2Zn-0.5Ca-Y series alloys before immersion testing. It can be seen that the structure of alloy I is composed of multiphase structure and has no continuous grain. The structure of the others are composed of many fine equiaxed crystal grains that have been elongated and the second phase precipitates appear at the grain boundaries. After immersion in Hank's solution for 120 h and 168 h, the specimen surface was covered with a film of corrosion products. The samples were cleaned in a solution comprising 15% CrO_3, 1% $AgNO_3$, and 400 mL H_2O for 10 min and then ultrasonically cleaned in alcohol for 7 min. The samples then were dried in a warm air blast. The morphologies of the cleaned Mg-2Zn-0.5Ca-Y series alloys are shown in Fig.2. The surface of Mg-2Zn-0.5Ca alloy is covered by a corrosion layer with many cracks, and some white particles could be found on the corroded surface. Few cracks and white particles could be seen on the surface of alloy II, III, IV, and V, which indicates that the corrosion layers of these alloys are denser than that of alloy I. However, there are many precipitates could be found on the surface of alloy IV and V. Representative XRD patterns from the alloy samples before immersion in the test solutions are shown in Fig.3. Samples are mainly consisted of Mg, Mg_3YZn_6, Mg_2Zn, and MgY for alloy IV and V.

2.2 Immersion tests

During the immersion tests, hydrogen was generated continuously on the surface of the samples and the surface gradually became black corrosion product. After the samples were cleaned, their surface exhibited signs of corrosion attack. It is evident that the corroded areas are uneven and pitting has occurred on the surface. There is evidence of crack formation and some of the surface layer has become detached. The uneven surface originates from the attack by the chloride ions and the dissolution of the Mg. Fig.4a and 4b indicate that the oxygen contents of alloy I and alloy II are significantly higher