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ARTICLE

Degradation Mechanism of the Biomedical Mg-3Zn-0.5Zr Alloy in a Simulated Physiological Environment Containing Different Anions

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Abstract: The interaction and synergetic effects of four corrosive anions (Cl^-, HPO_4^{2-}, HCO_3^-, and SO_4^{2-}) on the degradation behavior of a Mg-3wt%Zn-0.5wt%Zr (Mg-3Zn-0.5Zr) alloy were investigated using electrochemical tests, such as potentiodynamic polarization, open circuit potential evolution, and electrochemical impedance spectroscopy (EIS). We find that chloride ions induce porous pitting corrosion on the alloy. The corrosion pits expand on the surface and become much deeper. Hydrogen phosphate ions decrease the degradation rate and restrain the pitting corrosion. However, the degradation rate of the Mg-3Zn-0.5Zr alloy is accelerated at early time points during immersion in solutions containing hydrogen carbonate ions; never the less, precipitation of the magnesium carbonate results in passivation, and the corrosion products totally inhibit the pitting corrosion. In addition sulfate ions could also corrode the Mg-3Zn-0.5Zr alloy; due to its low concentration in the physiological environment, however, the effects of sulfate on the degradation rate and corrosion morphology are limited.

Key words: Mg-3Zn-0.5Zr alloy; biomaterial; corrosive anions; degradation mechanism

As a potential biodegradable material, magnesium alloys have received increasing research attention in recent years due to their desirable mechanical properties and good biocompatibility. However, the poor corrosion resistance of magnesium and its alloys restrict their application. In addition, pure magnesium and its alloys corrode too quickly in the physiological environment, as well as in solutions containing the same aggressive ions as human body fluids [1]. These aggressive ions, such as chlorides, hydrogen phosphates, hydrogen carbonates, and sulfates, are generally considered to be the reason for the fast degradation rates of pure magnesium and its alloys.

The influence of aggressive ions on the degradation rate of commercial magnesium alloys has been studied[2]. For instance, the corrosive behavior of Mg alloys in solutions that contain chloride ions has been investigated[3]. Chloride ions can transform the protective corrosion products MgO and $Mg(OH)_2$ into soluble $MgCl_2$[4].

In the present work, we prepared Mg-3wt%Zn-0.5wt%Zr (Mg-3Zn-0.5Zr) alloy as the test material. In our previous research[5], we found that this alloy displays better biocompatibility and proper mechanical properties. Research on the degradation behavior of Mg-3Zn-0.5Zr alloy in Simulated Body Fluid (SBF) indicates that the degradation rate is fast. However, the synergistic effect and mutual influence of aggressive anions on the degradation of Mg-3Zn-0.5Zr alloy has not been understood. Thus, investigation of the influence of aggressive anions on this Mg alloy may offer more information about the corrosion mechanism and may reveal appropriate ways to improve the corrosion resistance of the alloy.

Four solutions containing different corrosive ions (chloride ions, hydrogen phosphate ions, hydrogen carbonate ions, and sulfate ions) with concentrations as that of the human body fluids were designed to test the degradation behavior of the

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Mg-3Zn-0.5Zr alloy. Our results may provide knowledge on the degradation mechanism of Mg-3Zn-0.5Zr alloy in a physiological environment.

1 Experiment

Samples with a size of *Φ*8 mm×3 mm were cut from the extruded and aged bars of Mg-3Zn-0.5Zr alloy that was prepared in a vacuum induction melting furnace. The four types of solutions were prepared with NaCl, $K_2HPO_4·3H_2O$, $NaHCO_3$, and Na_2SO_4, which were denoted as solution 1#, 2#, 3# and 4#, respectively. The concentration of the Cl^-, HPO_4^{2-}, HCO_3^-, and SO_4^{2-} in the four solutions simulated that in human body fluids[2].

The immersion tests were performed in four solutions at 37 °C without de-aeration using an immersion oscillator according to ASTM-G13-72. The samples were removed from the solutions, after different immersion periods (30 min to 7 d). The pH values of the four test solutions at different immersion periods (30 min to 7 d) were tested after samples were removed from the solutions at 37 °C. Field emission scanning electron microscopy (FE-SEM, JOEL6700F, Japan) was used to characterize the surface morphology of the samples after immersion for 7 d. Glancing angle X-ray diffraction (GAXRD) was employed to identify the corrosion products on the samples after immersion for 7 d. Subsequently, the corrosion rates were calculated by mass loss according to the equation:

$$CR = (w_0 - w_1)/(At) \tag{1}$$

The electrochemical corrosion behavior of the Mg-3Zn-0.5Zr alloy was investigated in the four test solutions using potentiodynamic polarization tests, open circuit potential evolution (E_{corr}-t), and EIS using Zennium (Germany) [6].

2 Results and Discussion

2.1 Corrosion products and morphology

Fig.1 shows the XRD patterns of the Mg-3Zn-0.5Zr alloy immersed in the four anion solutions for 7 d. Based on the XRD pattern of the Mg alloy immersed in solution 1# (Fig.1a), we observed the narrow and high intensity peaks of $Mg(OH)_2$, which reveal the high crystallinity of the corrosion product. In Fig.1b, diffraction peaks of $Mg_2PO_4(OH)$ appear at 18.6° and 36.98°. Meanwhile, the $Mg(OH)_2$ still exists on the surface of the samples, with very little decrease in $Mg(OH)_2$ peak intensity, indicating that only a small amount of $Mg(OH)_2$ is substituted for $Mg_2PO_4(OH)$. The corrosion products of the alloy immersed in solution 2# are composed of $Mg(OH)_2$ and $Mg_2PO_4(OH)$. The corrosion products change significantly in solution 3# (Fig.1c). The diffraction intensity of the $Mg(OH)_2$ is much lower, but the diffraction peaks of $MgCO_3·3H_2O$ are present at 30.1° and 38.1°. This indicates that the HCO_3^- has a large effect on the corrosion behavior of the alloy. $Mg(OH)_2$ and $MgCO_3·3H_2O$ are the main components of the corrosion layer. The XRD pattern of the sample immersed in solution 4# (Fig.1d) is similar to that of solution 3# for the concentration of SO_4^{2-} is quite low in solution 4#.

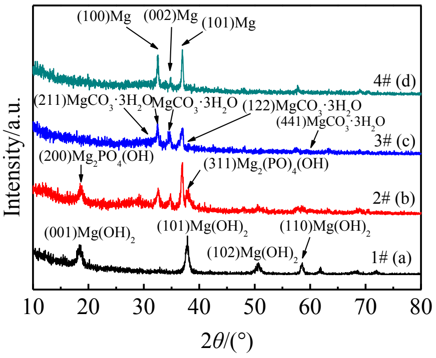

Fig.1 XRD patterns of the Mg-3Zn-0.5Zr alloy after immersion in the four test solutions for 7 days

The surface morphology of the Mg-3Zn-0.5Zr alloy soaked in the four test solutions displays significant differences in different solutions depending on the immersion time. After immersion for 12 h, many corrosion pits are found on the surface of samples in solution 1#, where non-uniform corrosion apparently occurs (Fig.2a). The corrosion pitting is observed at fewer locations, and the surface of the alloy remains flat in solution 2# (Fig.2b), indicating that the corrosion is less serious than samples incubated in solution 1#. As shown in Fig.2c and 2d, the corrosive pitting is not obvious on the surface of the alloy. Some cracks are clearly visible in Fig.2c and 2d, but these cracks may be attributed to the dehydration of the corrosion products in the corrosion layer. With increasing of the soaking time, the corrosion pits in solutions 1# and 2# increase in depth after 2 d (Fig.3a and 3b). Many serious corrosion pits are observed in the macroscopic figures, and many corrosion pits merge together in solution 1#. On the contrary, the corrosion layers of samples in solutions 3# and 4# are dense and uniform. Fig.4 presents the corrosion morphology of the alloy after immersion in the solutions for 7 d. Although the corrosion products also peel off from the samples immersed in solutions 3# and 4#, the corrosion in these solutions is uniform without serious corrosion pits[7].

With the degradation of the Mg-3Zn-0.5Zr alloy, OH^- promotes the precipitation of $Mg(OH)_2$, and thus, the $Mg(OH)_2$ layer is too loose to provide enough protection. The Cl^- in solutions can react with $Mg(OH)_2$ to form the soluble $MgCl_2$, and this reaction accelerates the degradation rate of the alloy[8]. The propagation and spread of the pits lead to porous corrosion morphology (Fig.4a). The early corrosion product of the alloy immersed in solution 2#, *i.e.*, the insoluble Mg_2PO_4-(OH), partially protects the alloy. Due to the low content of HPO_4^{3-}, the product layer could not completely prevent the alloy from pitting (Fig.4b). However, no porous pitting corrosion is visually observed on the entire surface of the samples soaked in solutions 3# and 4#. The degradation of the alloy results in increasing pH. The existence of HCO_3^- enables