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Influence of albumin on *in vitro* degradation behavior of biodegradable Mg-1.5Zn-0.6Zr-0.2Sc alloy

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ABSTRACT

The immersion and electrochemical degradation behaviors of as-extruded Mg-1.5Zn-0.6Zr-0.2Sc (ZK21-0.2Sc) alloy in Hank's solution with and without albumins were investigated and the influencing mechanism was elucidated. The immersion experiment showed that the presence of albumins could inhibit the corrosion of the ZK21-0.2Sc alloy through the adsorption effect at the initial immersion stage. With immersing on, the albumins underwent denaturation and began to show the chelation effect, which accelerated the corrosion of the ZK21-0.2Sc alloy. With increasing albumin concentration, the corrosion potential of the ZK21-0.2Sc alloy increased while the corrosion current density greatly reduced. The electrochemical test showed the presence of albumins had nearly no change to the cathodic Tafel slops, but the anodic Tafel slops increased obviously with increasing albumin concentration.

1. Introduction

Recently, magnesium alloys designed as a new kind of biodegradable implants have attracted much attention due to their fantastic characteristics [1–3]. The degradation behaviors of magnesium alloys have been extensively studied both *in vivo* and *in vitro*. However, the *in vitro* models cannot perfectly mimic the *in vivo* model due to the complex physiological environment *in vivo* [4,5]. For *in vitro* studies, Hank's solution is a representative testing solution. It contains similar inorganic components compared with human blood plasma except for the lack of much amount of proteins [6]. As an important component, protein participates in a variety of biochemical reactions within body. Once been implanted, the implants will inevitably interact with proteins. That directly influences the degradation behaviors of the implants and the associated cell attachment and functional expression. Hence, it is critical to elucidate the influences of proteins on *in vitro* degradation behavior.

So far, it has not yet reached a unified stance as for the influences of proteins on *in vitro* degradation behavior of Mg alloys. Some studies have shown that proteins would be adsorbed on the surface of Mg alloy, forming a passivation layer, which could hinder the further degradation of Mg alloy [7–9]. While some other studies have drawn the opposite conclusion, that is the addition of proteins could accelerate the degradation of Mg alloys [10,11]. The present work aims to compare the degradation behaviors of a newly developed ZK21-0.2Sc alloy in Hank's solution with and without proteins and further elucidate the influencing mechanism so that to provide more accurate evaluation before *in vivo* testing.

2. Experimental

The ZK21-0.2Sc alloy was first casted and then extruded at 310 °C with an extrusion ratio of 36. The samples were cut perpendicular to the extrusion direction. Two solutions were used in immersion tests: the standard Hank's solution and 40 g/L bovine serum albumin modified Hank's solution (Hank's + BSA). Immersion tests were conducted at 37 °C. After immersion tests, the corrosion products were removed from the specimens by chemical cleaning in a solution of 200 g/L CrO_3 and 10 g/L $AgNO_3$ for 1 min at room temperature according to ASTM G1-03 [12]. The mass losses were measured and the degradation rates were calculated. Three specimens were tested for each group. The surface morphologies were

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examined by a SEM (Zeiss Supra 55, Germany). Potentiodynamic polarization (PDP) curves were measured in Hank's solutions with 0, 20 and 40 g/L BSA at 37 °C using an electrochemical workstation (Chenhua CHI660D, China). More details can be referred to Refs. [13,14].

3. Results and discussion

3.1. Immersion degradation behavior

Fig. 1 shows the surface morphologies of ZK21-0.2Sc alloy after immersion. After immersion for 6 h, corrosion has begun to expand on the surface of the alloy in Hank's solution, forming a few corrosion spots. And a continuous corrosion film deposited on the alloy. While for the alloy in Hank's + BSA solution, the surface was smooth with no corrosion spots being found. There attached many albumin crystals on it. Unlike forming a thick corrosion film, it is covered with a passivated translucent film. Furthermore, the corrosion is relatively weak beneath the attached albumin crystal. This revealed that until the first 6 h, the addition of albumin could inhibit alloy corrosion. For alloys in Hank's solution, when immersing for longer time the corrosion was not substantially different from that at 6 h. While for the alloy in Hank's + BSA solution, albumins occurred intensive gathering on alloy surface at 12 h. Relatively severe corrosion happened beside the adsorbed albumins. The albumins have begun to decompose, resulting in a slightly incomplete structure. When immersed for 168 h, the alloy in Hank's + B SA solution was severely corroded. The corrosion film appeared to peel off. Especially, another layer formed outside of the corrosion products layer. Comparatively, the corrosion of the alloy in Hank's solution was far weaker.

Fig. 2 presents the corroded surface morphologies of ZK21-0.2Sc alloy with degradation products removed. When immersed for 6 h, it appeared some distinct corrosion spots on the alloy in Hank's solution, while only few slight corrosion spots were found on the alloy in Hank's + BSA solution. However, the corrosion area had a significant expanding for the alloy in Hank's + BSA solution after 12 h, which was much larger than that of the alloy in Hank's solution. For the following immersions, the alloy corrosions in Hank's + BSA solution were all severer than those in Hank's solution and the gap was more and more significant.

Fig. 3 shows the time-dependent weight loss of ZK21-0.2Sc alloy. Within the first 6 h, the weight loss of the alloy in Hank's + BSA solution was lower. That's because the albumins adsorption can provide an effective corrosive shielding effect. Furthermore, the albumin macromolecules can reduce the mobilities of aggressive ions such as Cl^-. As immersion continued to 12 h, the albumins underwent denaturation, exposing the negatively charged molecular groups. That could chelate with Mg^{2+} to produce organometallic complexes, which promoting the corrosion and the weight loss was thus suddenly accelerated. With immersion went on, the chelation effect of the albumins was getting stronger and stronger, and the difference of weight loss was accordingly becoming bigger and bigger.

3.2. Electrochemical degradation behavior

Fig. 4(a) shows the PDP curves of ZK21-0.2Sc alloy in different solutions. It shows that the corrosion potential of the alloy increased while the corrosion current density greatly reduced with increasing albumin concentration in the solution. It indicated that the addition of albumin can reduce the corrosion sensitivity of the

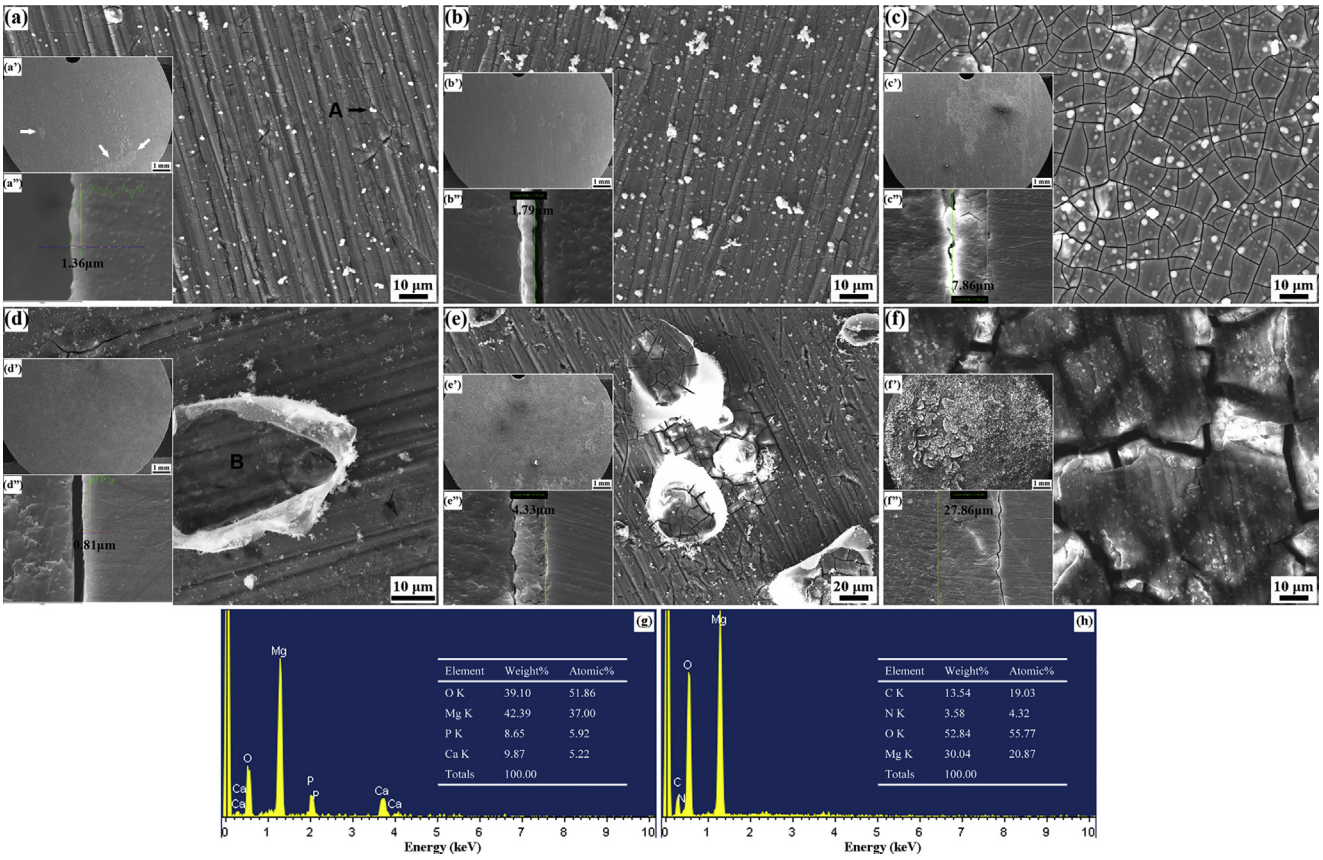

Fig. 1. Surface morphologies of ZK21-0.2Sc alloy after immersion: (a–c) Hank's, (d–f) Hank's + BSA; (a, d) 6 h, (b, e) 12 h, (c, f) 168 h and (g) EDS results for compounds A in (a), (h) EDS results for structures B in (d).