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Interactions between aggressive ions and the surface of a magnesium-yttrium alloy

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***Abstract*—Magnesium alloys possess many desirable properties for biodegradable orthopedic implants. Unfortunately, magnesium degrades too rapidly *in vivo*. This rapid degradation reduces the alloys' mechanical properties and increases the alkalinity of the local environment. Controlling the degradation rate and mode is an essential step in the development of magnesium based biomaterials. Accomplishing this essential step will require an improved understanding of magnesium alloy degradation. Herein, three interacting factors controlling magnesium degradation were investigated; (1) alloy composition, (2) alloy surface, (3) presence of aggressive ions in the immersion media. The magnesium-yttrium alloy was more susceptible to degradation in water than the high purity magnesium alloy. However, the polished surface magnesium-yttrium alloy had the least susceptibility to degradation in phosphate buffered saline (PBS) among all the sample compositions and surfaces.**

Keywords- magnesiun, yttrium, PBS, degradation, aggressive ions, polished surface, oxidized surface, orthopedic implant.

I. INTRODUCTION

Magnesium alloys have attracted great interest as potential biomaterials for degradable orthopedic implants. One of the greatest obstacles preventing the use of magnesium alloys in orthopedic implants is their rapid degradation *in vivo*. Physiological environments contain many ions such as chloride that aggressively attack magnesium. Chloride ions undermine and dissolve the protective degradation layer on the surface of magnesium. Rapid magnesium degradation can result in mechanical failure before the healing tissues regain their strength. Magnesium degradation also produces hydroxide ions and hydrogen gas. The hydroxide ions can significantly increase the local pH, which may be cytotoxic. Therefore, the degradation rate of magnesium must be controlled to alleviate these problems.

One method of controlling magnesium degradation is to add certain alloying elements to magnesium. Yttrium is often added to magnesium alloys in order to increase material strength [1]. WE43, a common magnesium-yttrium alloy, has a 280 MPa ultimate tensile strength [2]. Alloying with yttrium can also improve the degradation resistance of magnesium [3]. Yttrium oxide (Y_2O_3)accumulates in the degradation layer when yttrium migrates to the metal surface and is oxidized [4]. On one hand, yttrium oxide in the degradation layer can slow down magnesium degradation by inhibiting cathodic reactions [5]. On the other hand, yttrium can promote microgalvanic degradation because it can make the β phase behave as a cathode [4]. Yttrium may inhibit magnesium alloy degradation when there is a stable and protective degradation layer, but will promote degradation in the absence of such stable and protective degradation layer [6]. Additionally, the alloy surface created by alloy processing can also play an important role in magnesium degradation [6].

In summary, three key factors are crucial in controlling magnesium degradation: (1) the body fluid composition, (2) the alloy composition, and (3) the alloy surface. The objective of this study was to investigate the roles of these three key factors and their interactions in controlling magnesium degradation.

II. MATERIALS AND METHODS

A. Magnesium and Magnesium Alloy Preparation

Magnesium-4 wt.% yttrium alloy was prepared by melting magnesium with 4 wt.% yttrium in a protected environment and casting as an ingot. The as-cast magnesium-yttrium alloy ingot was cut into 250μm thick discs using a wire electric discharge machine (AgieCharmilles, Agiecut 200 VHP). The as-produced alloy discs had a thermal oxide layer on the surface and were called MgY_O in this study. "O" indicated the oxidized surface. Some of the MgY_O samples were polished using 600, 800, and 1200 grit silicon carbide abrasive papers (PACE Technologies) to remove the oxidized surface, and were referred to as MgY_P in this study. "P" indicated the polished surface. MgY was used to refer to both MgY_O and MgY_P in this manuscript.

High purity (99.9%) magnesium foil (Goodfellow corporation, as-rolled) with a thickness of 250μm was used as a control in this study. The as-rolled magnesium foil had a thermal oxide layer on its surface and was called Mg_O in this study. Some of the Mg_O

samples were polished using 600, 800, and 1200 grit silicon carbide abrasive papers to remove the oxidized surface, and were referred to as Mg_P in this study. Mg was used to refer to both Mg_O and Mg_P in this manuscript.

All of the Mg and MgY samples in this study were cut into dimensions of 10 mm x 10 mm, cleaned in isopropanol (Sigma-Aldrich, CAS number 67-63-0), and weighed. Both sides of the samples were disinfected under ultraviolet (UV) radiation before degradation experiments.

B. Immersion Degradation

The immersion method was used to investigate Mg and MgY degradation. Briefly, Mg and MgY samples were immersed in two solutions for comparison: deionized (DI) water and phosphate buffered saline (PBS), under standard cell culture conditions (37 ºC, 5% CO_2 / 95% air, humidified, sterile environment). DI water was produced by a Millipore Milli-Q® Biocel System and used as a control. PBS was prepared by dissolving 8 g NaCl, 0.2 g KCl, 1.5 g Na_2HPO_4, and 0.2 g KH_2PO_4 in a 1000 ml of DI water and adjusting the pH to 7.4 (all chemicals from Sigma). PBS was chosen as one of the immersion media to determine the effects of aggressive physiological ions (e.g. Cl^-) on magnesium degradation. Both PBS and DI water were sterilized by autoclave at 120°C.

All Mg and MgY samples were incubated in DI water and PBS according to prescribed sequential time points. The incubation time points were 1 hr, 2hr, 4 hr, 8 hr, 16 hr, 24 hr, 48 hr, and then every 48 hr until the samples were completely dissolved. When the prescribed incubation times ended, the samples were removed from their media and dried in a 37 ºC isotemp oven for 12 hours or until the sample reached a constant mass. Degradation products precipitated on the surface of the Mg and MgY samples were left intact, while soluble degradation products remained in the media. The pH meter was first calibrated with known standards, and then used to measure the pH of the immersion media at the end of every incubation time. The samples were dried, weighed, photographed, sterilized under UV radiation, and then placed in fresh immersion media for the next incubation time. This procedure was repeated for each incubation time. All samples were tested in triplicate.

C. Microstructure Analysis

Mg and MgY were incubated in DI water or PBS for 24 hr under standard cell culture conditions, then dried in vacuum for 48 hr. The surfaces of Mg and MgY samples were characterized before and after degradation using a field emission scanning electron microscope (FESEM; Philips XL-30). Energy dispersive X-ray spectroscopy (EDS) analysis was performed at 2500X magnification with an accelerating voltage of 15 kV.

III. DISCUSSION

A. Effects of Degradation in DI Water

Mg_O and Mg_P developed a more uniform degradation layer on their surfaces in DI water because of their purity and uniform microstructure (figure 1A,B).

Mg gained little mass initially, and lost mass slowly thereafter (figure 2A). The DI water containing Mg_O was initially less alkaline than the DI water containing Mg_P, and then the pH values later became nearly identical after 8 hours of incubation (figure 3A). The initial alkalinity in the DI water holding Mg_P was caused by the formation of the degradation layer. Mg_O already had a protective thermal oxide layer, so its degradation was less prevalent initially.

MgY_O degrading in DI water had an irregular degradation layer and jagged sample edges (figure 1C). MgY_O shed surface fragments during degradation. MgY_P displayed a similar looking degradation layer in DI water (figure 1D). The formation of the degradation layer in DI water did not significantly increase the mass of the MgY

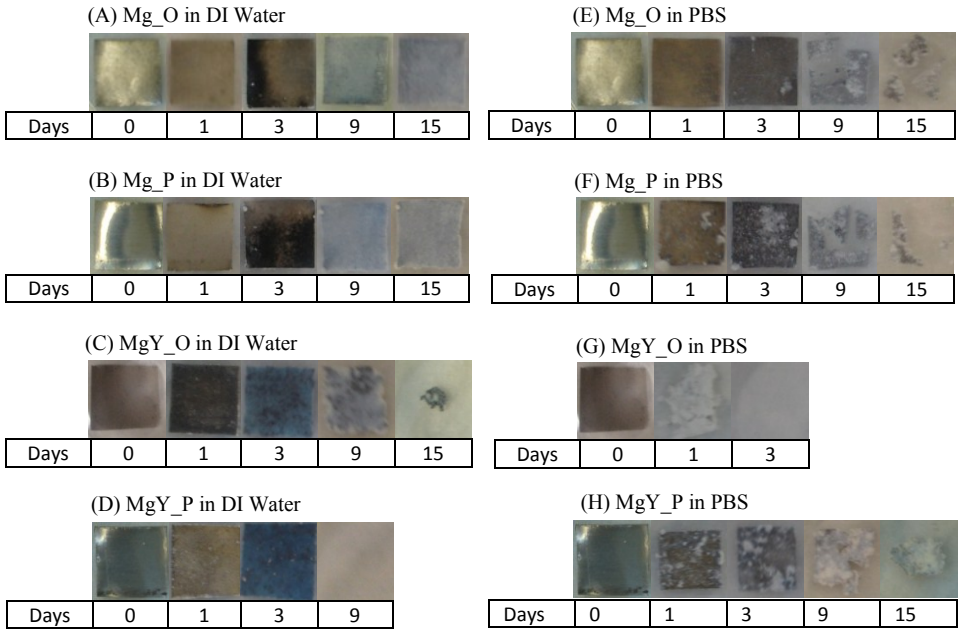

Figure 1: Photographs of Mg and MgY after incubation in DI water and PBS under standard cell culture conditions.

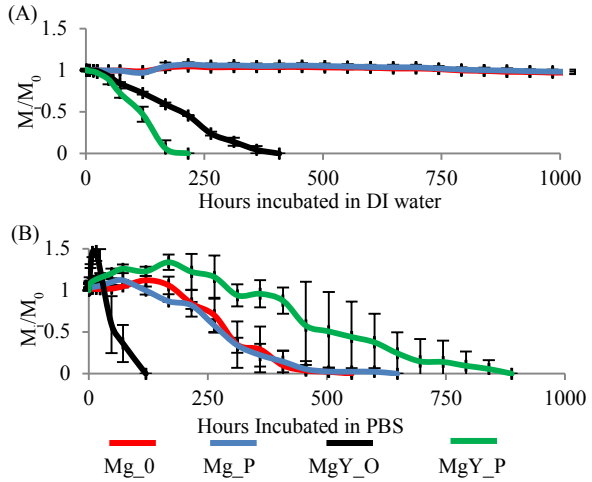

Figure 2: The mass loss of Mg and MgY samples during their incubation in immersion media:
(A) DI water; (B) PBS. M_i was the mass after incubation and M_0 was the initial mass.

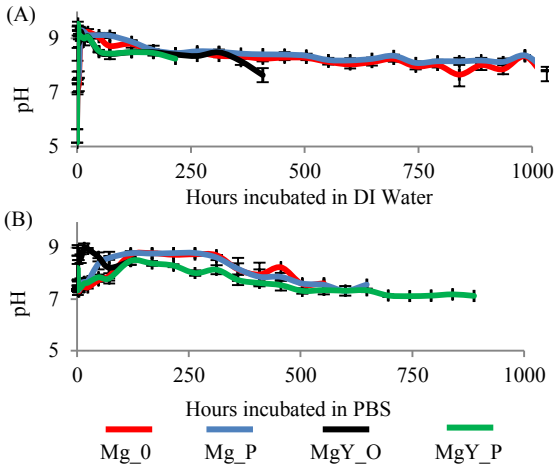

Figure 3: The pH change of the immersion media over time during incubation of Mg and MgY samples.
(A) DI water was used as the immersion media.
(B) PBS was used as the immersion media.

samples. MgY lost mass much more rapidly in DI water than Mg, and MgY_P lost mass more rapidly than MgY_O (figure 2A). The pH for the DI water holding MgY_O and MgY_P was similar to the pH for the DI water holding Mg_O and Mg_P (figure 3A).

Yttrium has both degradation inhibiting and promoting behaviors in magnesium alloys. Yttrium inhibits degradation by passivating the surface of magnesium. If a stable degradation layer is not formed, then the degradation promoting activities of yttrium will become dominant. Yttrium had a net degradation promoting effect on MgY in DI water because the degradation layers were not very stable. This instability was demonstrated by surface fragments flaking off of the samples. MgY_O degradation was slower than MgY_P degradation in DI water because the thermal oxide layer provided superior protection compared to the degradation layer formed in water.

B. Effects of Degradation in PBS

Mg had a different degradation mode in PBS than DI water. The degradation layer was more irregular and accumulated white precipitates (figure 1E,F). There was little significant inward migration of the samples edges. Instead, Mg broke apart near the center into several large fragments. The fragments then continued degrading until completely dissolved. Mg_O and Mg_P degraded in a similar manner in PBS. Both Mg samples initially gained mass in PBS, and then rapidly lost mass (figure 2B).

MgY_O shed much larger fragments in PBS than in DI water (figure 1G). Undermining of the alloy by Cl^- was responsible for the increased size of the fragments falling out. Visible degradation appeared at the sample's edges first and then spread inward. MgY_O in PBS had the most rapid mass gain and loss observed in this series of experiments (figure 2B). MgY_O degradation caused an initial alkaline peak in PBS due to its rapid degradation (figure 3B).

MgY_P shed smaller fragments from its edges at a slower rate than MgY_O. Degradation products initially occurred sparsely on the surface of MgY_P, until further deposition covered the entire surface (figure 1H). MgY_P also initially gained mass in PBS, but the following loss of mass was slower (figure 2B). MgY_P degradation in PBS created a similar pH curve to Mg, but less alkaline (figure 3B).

The results of this study were similar to our previous work in which we demonstrated that yttrium only inhibited degradation when the sample surface was protected by a stable degradation layer [6]. Yttrium accelerated the MgY_O degradation rate in PBS, but reduced the MgY_P degradation rate. This was because the absence of a stable degradation layer on MgY_O caused yttrium to display net degradation promoting activities. The presence of a stable and protective degradation layer on MgY_P caused the degradation inhibiting behavior of yttrium to be dominant over the degradation promoting behavior. The smaller oxygen content of MgY_P also created a surface layer with less susceptibility to Cl^- attack. Undermining of MgY_P was less severe, and so the fragments falling out of the surface were smaller and less frequent. Incorporation of carbonates and phosphates into the MgY_P degradation layer made it much more stable and protective than the degradation layer formed in DI water. Yttrium in the MgY_P degradation layer minimized the cathodic current, further inhibiting degradation.

C. Surface Microstructure and Composition

MgY_O was the only sample with significant surface cracks before degradation (figure 4 IIIA). Incubation in DI water or PBS created cracks in the surfaces of all samples. Incubation in PBS also created a

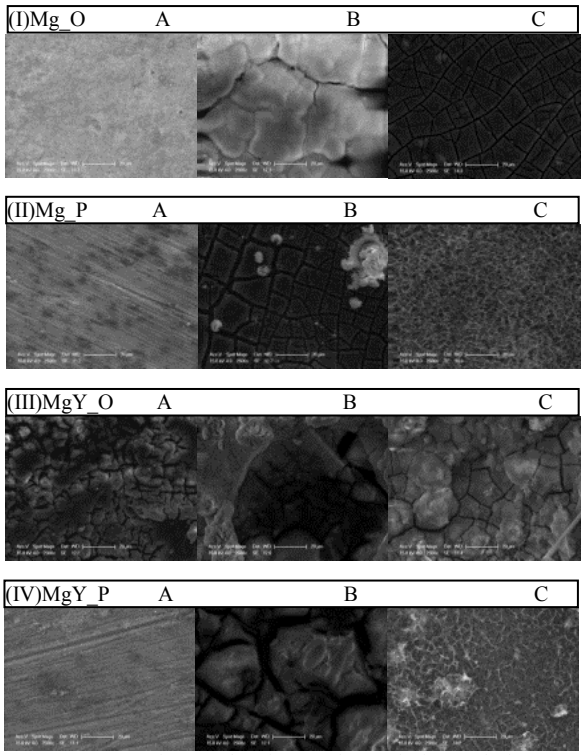

Figure 4: SEM micrographs of Mg and MgY before and after 24 hr degradation. The accelerating voltage was 15 kV and the magnification was 2500X.
(A) Before degradation.
(B) After degradation in DI water.
(C) After degradation in PBS.

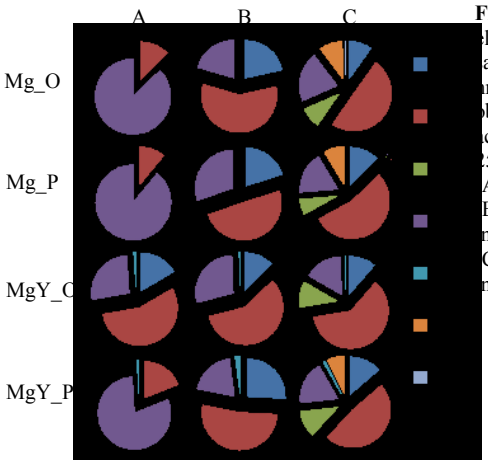

Figure 5: Surface elemental composition of samples before and after 24 hr degradation. Data was obtained by EDS at 15 kV accelerating voltage and 2500X magnification.
(A) Before degradation.
(B) After 24 hr degradation in DI water.
(C) After 24 hr degradation in PBS.

network-like deposition of degradation products upon the surfaces of the polished samples.

Degradation had a profound effect upon the surface elemental composition of Mg and MgY (figure 5). MgY_O that had been incubated in PBS had the lowest surface magnesium concentration, explaining its rapid degradation. MgY_P that had been incubated in PBS incorporated more carbonates and phosphates into its surface. These protective constituents allowed MgY_P to form a stable degradation layer in PBS.

IV. Conclusions

This study showed that sample degradation was controlled by interactions between immersion media composition, alloy composition, and alloy surface type. Yttrium had a net degradation inhibiting effect for polished surfaces in PBS. Conversely, yttrium had a net degradation promoting effect for both sample surfaces in DI water, and for oxidized surfaces in PBS. This implies that alloying magnesium with yttrium may provide protection from environments rich in aggressive ions, but actually reduce degradation resistance in environments without aggressive ions. Physiological environments contain numerous aggressive ions, and so polished magnesium-yttrium alloys have great potential for use as biomaterials.

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VI. References

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