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RESEARCH ARTICLE

EFFECT OF MAGNESIUM FLUORIDE COATING ON CORROSION BEHAVIOR OF MAGNESIUM ALLOY

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ABSTRACT

Magnesium and its alloys are explored as potential biomedical materials for being lightweight, bio-absorbable, and having attractive biological properties. A major hindrance for their use is their high corrosion rate, in particular when exposed to body fluids. This study aims at suppressing the corrosion rate of a magnesium alloy (Mg1.0Ca) by coating it with magnesium fluoride (MgF2). The coating was done by immersion of the work-piece in hydrofluoric acid solution. For comparison, pure magnesium was also coated with MgF2. The MgF2 coated magnesium exhibits significantly lower corrosion rate than pure magnesium. The MgF2 coated magnesium alloy shows even lower corrosion rate. The MgF2 coating works in inhibiting corrosion on magnesium alloy Mg1.0Ca. The corrosion inhibition was also contributed by other compound formed during reaction between Mg1.0Ca and hydrofluoric acid and the alloy in Mg1.0Ca.

KEYWORDS

Biomedical, bio-absorbable, magnesium fluoride, alloy, hydrofluoric acid

1. INTRODUCTION

Metallic biomaterials are usually made of stainless steels, titanium alloys, or cobalt–chromium alloys. They serve well for medical devices that are directly in contact with human body, including implants (Gu et al., 2014; Shadanbaz and Dias, 2012; Chiu et al., 2007). However, these metallic implants are reported to lead to the problem of stress shielding effect which is caused by the mismatch in mechanical properties between these implant materials and human bone (Sara et al., 2014). This mismatch (metallic implant has much higher mechanical properties compared to bone) will cause stress concentration at bone–implant interfaces and consequently reducing stimulation of new bone growth and decreasing implant stability (Shadanbaz and Dias, 2012; Wang et al., 2012; Witte, 2010; Pietak et al., 2008; Song, 2007). In addition, the implants also remain as permanent fixtures, which is not ideal for bone trauma fixation. The implant needs to be removed with follow up surgery after the bone tissue has healed. This means additional cost and more inconvenience to the patient (Gu et al., 2014; Pietak et al., 2008).

For this temporary implants purpose and for tissue engineering scaffolds, biodegradable metals are being developed. Magnesium based alloys are potential candidates because of their physical and mechanical properties, including high specific strength and modulus elasticity close to cartilage and bone, and good effect on bone formation (Gu et al., 2014; Chiu et al., 2007; Wang et al., 2012; Yang et al., 2011). Magnesium (Mg) is an essential element for human metabolism (Shadanbaz and Dias, 2012; Sara et al., 2014; Staiger et al., 2006; Wan et al., 2008). When it degrades in body fluids or corrodes in aqueous environments that contain chloride ions, the magnesium can be resorbed by the body (Gu et al., 2014; Yang et al., 2011; Hassel et al., 2006).

Magnesium in itself does not have sufficient mechanical properties to be used as medical devices which require biodegradable metals. Common way to increase its mechanical properties is by alloying. Commercially available magnesium alloys intended for structural use can be used for this purpose, but they often contain non-biocompatible alloying elements (Dambatta et al., 2015). This study uses Mg-Ca alloy considering Ca is also an essential element for human bone, it degrades in body fluids with non-toxic degradation product, and it affects the corrosion rate of the alloy (Chiu et al., 2007; Harandi et al., 2013). Another main problem with magnesium and its alloys is their high corrosion rate. This high corrosion rate leads to loss of mass or structural integrity, which means their mechanical properties become even lower (Dambatta et al., 2015). For the intended application as temporary implants, the biomaterial is expected to degrade after the bone tissue heals, and not before. This expectation cannot be fulfilled by magnesium and its alloys for the time being because their corrosion rate is too high.

Corrosion resistance of magnesium alloys is influenced by multiple factors, including the alloying elements, purity of the alloys, and the presence of protective coatings (Song, 2007). In order to enhance the corrosion resistance of magnesium, several techniques have been suggested, including fluoride conversion coatings (Wang et al., 2012; Yang et al., 2011; Li et al., 2014; Thomann et al., 2010; Razavi et al., 2014). This fluoride conversion coating is done by immersion of magnesium work-piece in hydrofluoric acid (HF) at room temperature. On pure magnesium, it was reported that a thin layer of MgF_2 and small amount of $Mg(OH)_2$ was formed on the work-piece surface after this immersion treatment (Chiu et al, 2007; Harandi et al, 2013). The presence of this thin layer coating increases polarization resistance and reduces the corrosion current density, resulting an overall lower corrosion rate of treated magnesium compared to pure magnesium when exposed to simulated body fluid (Chiu et al., 2007;

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Harandi et al., 2013). Similar fluoride conversion coating was also applied on some magnesium alloys, including AZ31 (Yan et al., 2010). The treated magnesium alloy was reported to show higher corrosion resistance compared to untreated magnesium alloy. There is limited information yet on the effect of fluoride conversion coating on magnesium alloys with calcium as the alloying element. This study aims at suppressing the corrosion rate of a magnesium- calcium alloy (Mg1.0Ca) by fluoride conversion through immersion in hydrofluoric acid solution. Similar treatment was also conducted on pure magnesium for comparison.

2. MATERIALS AND METHODS

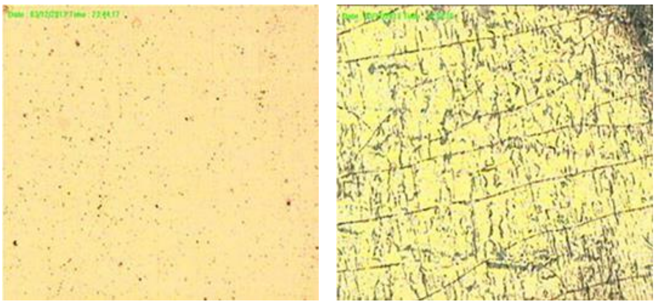
The work-piece materials in this study are pure Mg and Mg1.0Ca. The magnesium alloy was obtained through alloying done in house, using pure magnesium ingot (99.99% Mg) and calcium-magnesium master alloy (Mg–32Ca) as starting materials; the process as reported in (Harandi et al., 2013). The samples were cut into dimension of 10 mm × 10 mm × 10 mm by using saw and then were mounted, ground and polished until the surface are homogeneous, smooth, and free from scratches. Surface roughness test was conducted on the samples' surface using portable surface roughness tester Mitutoyo SJ-400. It was recorded that the samples have a surface roughness (Ra) of 0.04 µm.

Chemicals used were of reagent grade, purchased from Sigma Aldrich. Initial treatment was immersion of the samples in sodium hydroxide solution for two hours. Afterwards, the solution of hydrofluoric acid with concentration of 48wt% was used to perform fluoride conversion coating on the pure Mg and Mg1.0Ca surfaces through immersion technique. The immersion was done at room temperature for 24 hours.

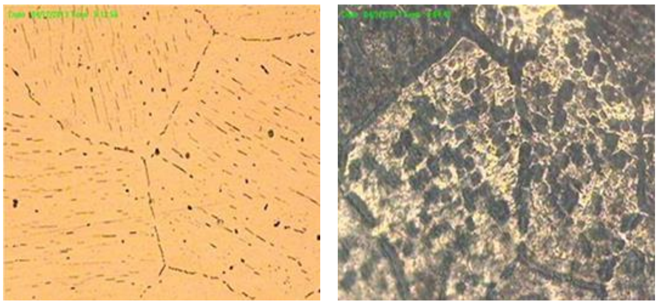
Surface characterization was conducted by using optical microscope and scanning electron microscopy (SEM), and then followed by corrosion testing using potentiodynamic polarization test. The polarization test was carried out to study the corrosion behavior of the Mg and its alloy in simulated body fluid (SBF). The SBF used in this study was physiological saline (0.9% NaCl) solution that was prepared by mixing sodium chloride in distilled water. The electrochemical cell with three electrodes was connected to Versa STAT Instrument Potentionstat and Versa STAT software was controlled by computer to measure the polarization curves of samples.

3. RESULTS AND DISCUSSION

Figure 1 shows the surfaces of pure magnesium (Mg) and magnesium-calcium alloy Mg1.0Ca, untreated and fluoride-coated. The grain size of the magnesium-calcium alloy seems to be larger than pure magnesium's. Based on previous analysis done in house on Mg-Ca alloys, the untreated Mg1.0Ca alloy microstructure has predominantly α-Mg content and some Mg_2Ca phase (Harandi et al., 2013). The eutectic Mg_2Ca phase are distributed on the grain boundaries and within grains of α-Mg matrix, seen as small precipitates are observed within the microstructure. The width of the grain boundary of the magnesium alloy also was wider compared to pure magnesium, in agreement with previous study (Wan et al., 2008). For treated magnesium and magnesium alloy samples, dark regions of magnesium fluoride were formed, with the latter showing more obvious dark regions. The dark regions are likely to be a form of magnesium hydroxide, which might be developed by the magnesium in reaction with sodium hydroxide (Bakhsheshi-Rad et al., 2013). In addition to the presence of MgF_2 and $Mg(OH)_2$, there is possibility that CaF_2 and $Ca(OH)_2$ phases were grown on the work-piece surface during the immersion processes. The magnesium alloy showed even more oxidized regions on its surface, indicating more residual magnesium hydroxide, which might be due to the presence of more magnesium or the calcium on its surface.



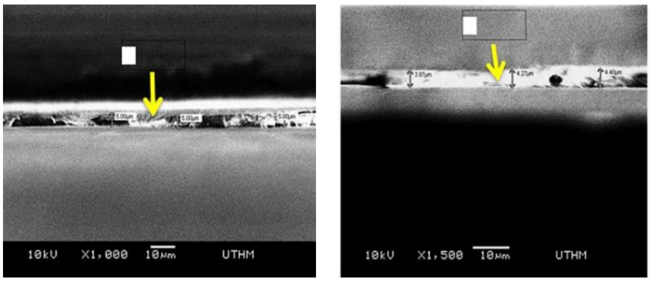
(a) (b)



(c) (d)

Figure 1: Surface characteristic of (a) uncoated Mg, (b) fluoride-coated Mg, (c) uncoated Mg1.0Ca, and (d) fluoride -coated Mg1.0Ca.

The SEM micrograph of the cross-section of fluoride-coated for both pure Mg and Mg1.0Ca is as depicted in figure 2. Also, in figure 2, there is uniform thin layer of MgF_2 coating on the work-piece's surface. The thickness of the MgF_2 coating is about 5±1 µm for both magnesium and magnesium alloy work-pieces. The MgF_2 coating appears to be well adhered to the substrate. From the appearance and possible chemical reaction, the MgF_2 coating grew by replacing some of the Mg $(OH)_2$ layer and on top of the residual $Mg(OH)_2$ layer (Chiu et al., 2007; Staiger et al., 2006).



(a) (b)

Figure 2: SEM micrograph of the cross section of fluoride coated on (a) pure Mg (b) Mg1.0Ca.

The corrosion rate of the magnesium and magnesium alloy work-pieces was determined by using potentiondynamic polarization method. The effect of current charging was obtained to determine the Tafel slopes and corrosion rate as presented in Figure 3. For pure magnesium, the corrosion rate was estimated to be about 8.80 mm/year. Meanwhile, fluoride-coated pure magnesium shows a much lower corrosion rate of 0.35 mm/year. This significantly lower corrosion rate of fluoride coated Mg compared is consistent with previous studies (Wang et al., 2012; Yang et al., 2011; Li et al., 2014; Thomann et al., 2010; Razavi et al., 2014). The indicators for higher corrosion resistance of the treated work-piece were the increased voltage and lower current compared to those of the pure Mg (Figures 3a and 3b).

The main contributor is the presence of MgF_2 layer on the treated work-piece's surface. The MgF_2 layer functions as barrier coating, preventing the corrosive action on the Mg substrate. In addition to the presence of MgF_2 layer, small amount of $Mg(OH)_2$ might also present on the work-piece's surface. It is expected that the corrosion rate of Mg1.0Ca alloy to be slightly lower than pure magnesium. This is related to the slight change in corrosion potential. Addition of 1.0 wt% Ca to pure Mg changed the corrosion potential towards more cathodic values, because Ca has higher electronegativity compared to Mg (Harandi et al., 2013).

Fluoride-coated Mg1.0Ca alloy estimated the corrosion rate to be about 0.25 mm/year. This corrosion rate is higher than that of fluoride coated Mg work-piece. The indicator was that fluoride- coated Mg1.0Ca alloy showed higher voltage and lower current compared to its pure Mg counterpart (Figures 3b and 3c). These translated to about 40% improvement in corrosion rate. The improvement might be due to the presence of CaF_2 and $Ca(OH)_2$ phases in addition to MgF_2 and $Mg(OH)_2$ which present in both work-pieces. Another possible reason for the improvement is the fact that Mg1.0Ca substrate is more cathodic for having Ca which is more electronegative compared to Mg (Harandi et al, 2013).

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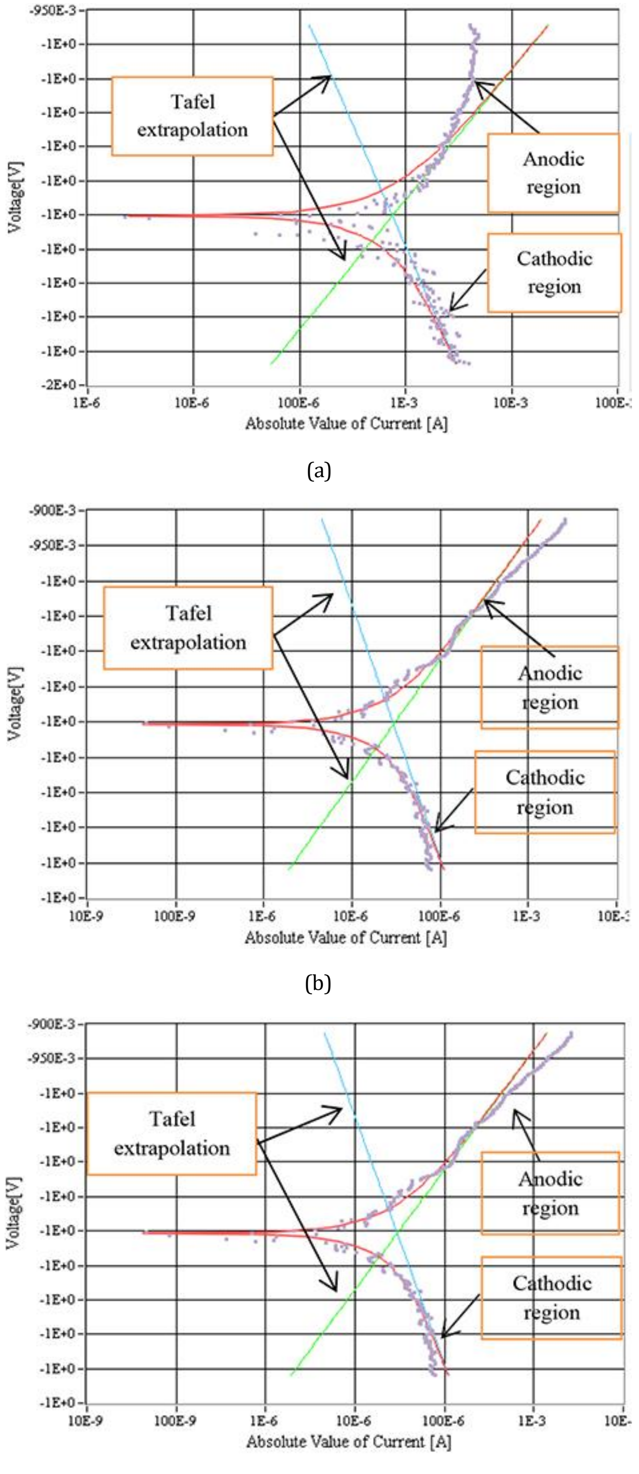

(a)

(b)

(c)

Figure 3: Tafel extrapolation at polarisation curves for (a) pure Mg, (b) fluoride-coated Mg, and (c) fluoride-coated Ma1.0Ca.

4. CONCLUSION

The effect of magnesium fluoride coating on corrosion behavior of magnesium alloy has been investigated. The fluoride coating was done by immersion process. The Mg1.0Ca alloy consisted of α- Mg matrix with Mg_2Ca distributed on the grain boundaries and as small precipitates within the grains. The treated Mg1.0Ca alloy has MgF_2 coating and some amount of $Mg(OH)_2$. After corrosion test in saline solution, it was found that fluoride-coated Mg1.0Ca work-piece showed higher voltage and lower current compared to fluoride coated pure magnesium. In terms of corrosion rate where the lower value is the better, fluoride coated Mg1.0Ca work-piece showed lower corrosion rate (of 0.25 mm/year) compared to fluoride coated pure magnesium (of 0.35 mm/year). This indicates the presence of CaF_2 and $Ca(OH)_2$ phases within the fluoride treated Mg1.0Ca work-piece. When compared to pure Mg, the fluoride coated magnesium and magnesium alloy showed much lower corrosion resistance. This means fluoride coating has the potential to inhibit corrosion to occur in magnesium-calcium alloys.

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