Effect of magnesium fluoride coating on corrosion behaviour 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 workpiece 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.

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 [1-3]. 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 [4]. 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 [2, 5-8]. 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 [1,7].

For this temporary implants purpose and also 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 [1,3,5,9]. Magnesium (Mg) is an essential element for human metabolism [2,4,10,11]. When it degrades in body fluids or corrodes in aqueous environments that contain chloride ions, the magnesium can be resorbed by the body [1,9,12].
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 [13]. 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 [3,14].

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 [15]. 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 [8]. In order to enhance the corrosion resistance of magnesium, several techniques have been suggested, including fluoride conversion coatings [5,9,16-18]. This fluoride conversion coating is done by immersion of magnesium workpiece 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 workpiece surface after this immersion treatment [3,14]. The presence of this thin layer coating increases polarisation 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 [3,14]. Similar fluoride conversion coating was also applied on some magnesium alloys, including AZ31 [19]. 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 (Mg$_{1.0}$Ca) by fluoride conversion through immersion in hydrofluoric acid solution. Similar treatment was also conducted on pure magnesium for comparison.

2. Materials and methods
The workpiece materials in this study are pure Mg and Mg$_{1.0}$Ca. 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 [14]. 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 Mg$_{1.0}$Ca 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 polarisation test. The polarisation test was carried out to study the corrosion behaviour 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 VersaSTAT Instrument Potentionstat and VersaSTAT 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 Mg2Ca phase [14]. The eutectic Mg2Ca 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 [11]. 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 [20]. In addition to the presence of MgF2 and Mg(OH)2, there is possibility that CaF2 and Ca(OH)2 phases were grown on the workpiece 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.

![Figure 1](image1.png)

**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 MgF2 coating on the workpiece’s surface. The thickness of the MgF2 coating is about 5±1 μm for both magnesium and magnesium alloy workpieces. The MgF2 coating appears to be well adhered to the substrate. From the appearance and possible chemical reaction, the MgF2 coating grew by replacing some of the Mg(OH)2 layer and on top of the residual Mg(OH)2 layer [3,10].
The corrosion rate of the magnesium and magnesium alloy workpieces was determined by using potentiodynamic polarisation method. The effect of current charging was obtained to determine the Tafel slopes and corrosion rate as presented in Fig. 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 [5,9,16-18]. The indicators for higher corrosion resistance of the treated workpiece were the increased voltage and lower current compared to those of the pure Mg (Figs. 3a and 3b). The main contributor is the presence of MgF$_2$ layer on the treated workpiece’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 workpiece’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 [14]. 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 workpiece. The indicator was that fluoride-coated Mg1.0Ca alloy showed higher voltage and lower current compared to its pure Mg counterpart (Figs. 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 workpieces. 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 [14].

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 $\alpha$-Mg matrix with Mg$_2$Ca 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 workpiece 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 workpiece 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 workpiece. 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.
Figure 3. Tafel extrapolation at polarisation curves for (a) pure Mg, (b) fluoride-coated Mg, and (c) fluoride-coated Ma1.0Ca.
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