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## Control of biodegradation of a Mg alloy in simulated body fluid

### Abstract

Mg alloy AZ31 is an attractive candidate for coronary artery stents, as it possesses excellent biocompatibility in human body and good mechanical properties. However, AZ31 magnesium alloys generally have poor corrosion resistance in the body environment. This paper reports on the early stages of an investigation into the corrosion mechanism and the morphology of corrosion of AZ31 in simulated body fluid (SBF). The investigation will also consider ways of improving corrosion resistance of this alloy in SBF through the use of ionic liquids. The results to date have shown that AZ31 suffers severe localized pitting corrosion in SBF. The pits mainly develop adjacent to the Al-Mn intermetallic second phase in the  $\alpha$  matrix. Energy Dispersive X-Ray Spectroscopy results revealed the presence of Mg, O, Ca, and P in the layer of corrosion product. Treatment of the AZ31 alloy prior to corrosion testing in SBF with the ionic liquid trimethyl (butyl) phosphonium diphenyl phosphate (P 1444DPP) produced some increase in the corrosion resistance of the alloy.

### Keywords

control, body, biodegradation, fluid, mg, alloy, simulated

### Disciplines

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# CONTROL OF BIODEGRADATION OF A MG ALLOY IN SIMULATED BODY FLUID

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**SUMMARY:** Mg alloy AZ31 is an attractive candidate for coronary artery stents, as it possesses excellent biocompatibility in human body and good mechanical properties. However, AZ31 magnesium alloys generally have poor corrosion resistance in the body environment. This paper reports on the early stages of an investigation into the corrosion mechanism and the morphology of corrosion of AZ31 in simulated body fluid (SBF). The investigation will also consider ways of improving corrosion resistance of this alloy in SBF through the use of ionic liquids. The results to date have shown that AZ31 suffers severe localized pitting corrosion in SBF. The pits mainly develop adjacent to the Al-Mn intermetallic second phase in the  $\alpha$  matrix. Energy Dispersive X-Ray Spectroscopy results revealed the presence of Mg, O, Ca, and P in the layer of corrosion product. Treatment of the AZ31 alloy prior to corrosion testing in SBF with the ionic liquid trimethyl (butyl) phosphonium diphenyl phosphate (P<sub>1444</sub>DPP) produced some increase in the corrosion resistance of the alloy.

**Keywords:** Magnesium alloys, biodegradable coronary artery stents, Simulated Body fluid, pitting corrosion, ionic liquids

## 1. INTRODUCTION

The use of coronary stents is considered an effective treatment for coronary artery disease, as the stents have the mechanical strength to maintain the opening of an artery, and remodel the arterial wall to its original shape [1, 2]. For some time, permanent metallic stents have been widely used, but it is often claimed that the continued presence of the stent after vessel remodeling is unnecessary [2], and that the stent inside the coronary artery as a foreign object has long-term risks, such as including chronic inflammation, in-stent restenosis [3] and late thrombosis [4]. Considering those short-term clinical needs and potential long-term complications, biodegradable stents would be preferable to permanent stents, as they will provide the temporary opening of narrowed arteries, and be gradually dissolved after the arteries was remodeled [5]. Mg-based alloys are of interest as the candidates for biodegradable stents, because of (1) low toxicity of Mg<sup>2+</sup> ions: they are the fourth most abundant cation naturally present in the human body, they are involved in many metabolic reactions and physiological mechanisms, and excess Mg<sup>2+</sup> can be excreted by urine [6, 2], (2) the fast degradability of Mg alloys in the body; the stents in the body can be consumed and absorbed in a short period, and (3) the excellent mechanical properties of Mg alloys; the density and Young's Modulus of Mg ( $\rho=1.74\text{g/cm}^3$ ,  $E=45\text{GPa}$ ) are similar to that of the natural bone ( $\rho=1.75\text{g/cm}^3$ ,  $E=40\text{-}57\text{GPa}$ )[7], and the strength level of Mg alloys may be up to 330 MPa, which is high enough to maintain the opening of a coronary artery.

However, the main drawback of Mg alloys as potential materials for vascular stents is the low corrosion resistance in the body environment [8, 7]. Thus it is difficult for magnesium alloys stents to maintain their structural integrity before the arteries have been fully remolded [9]. Therefore, it is very important to find a method to control the biodegradation rate of Mg alloys in the body.

An approach currently being considered to control the biodegradation rate of Mg alloys is the use an ionic liquid (IL) barrier film applied to the surface of Mg alloys. An IL is a low temperature molten organic salt, with a melting point below 100°C [10]. ILs present many unique properties, such as having a high concentration of species reactive with a metal surface, high stability and good ion conductivity. Previous studies have found that some ILs could form a passive film on the surface of metals, such as lithium, Mg alloys and Al alloys [11-13].

This paper discusses the corrosion of magnesium alloys AZ31 in SBF, and the influence of an IL treatment on the corrosion behaviour.

## 2. EXPERIMENTAL METHODS

### 2.1 Materials

The material used in this investigation was a direct strip cast cylinder of AZ31 magnesium alloy with the following nominal chemical composition (in wt.%): Al: 2.4-3.6, Zn:0.5-1.50, Cu: <0.1, Mn>0.15. In order to have all specimens with a similar microstructure, they were taken from around the edge area of the cylindrical casting.

The IL used was trimethyl (butyl) phosphonium diphenyl phosphate ( $P_{1444}DPP$ ). It was prepared the laboratory and purified by passing through a column containing a filter agent, alumina and sand to remove any impurities. The schematic structures of the anion and cation that make up the molecule  $P_{1444}DPP$  are shown in Figure 1.

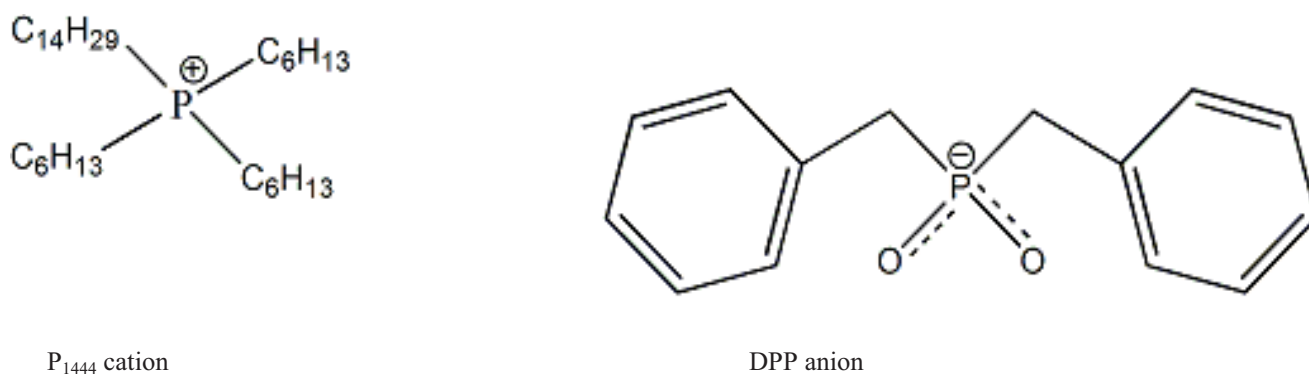


Figure 1 Schematic structures of  $P_{1444}$  cation and DPP anion [14]

A commercially available simulated body fluid (SBF) was chosen as the test solution due to its similar ion compositions to those of human blood plasma. Table 1 shows the inorganic ion composition of SBF used in this work, and a typical blood plasma. The pH of SBF solution was  $7.4 \pm 0.5$ .

Table 1: The inorganic ion composition of blood plasma and SBF

Solution	Inorganic Ions (mM)								
	$Ca^{2+}$	$Cl$	$Na^+$	$Cr$	$Mg^{2+}$	$K^+$	$HCO_3$	$SO_4^2$	$HPO_4^2$
Blood	2.5	103	142	103	1.5	5	27	0.5	1
SBF	2.6	103.6	147	-	1.5	5	6	0.5	1

### 2.2 Constant Immersion Corrosion Tests

The AZ31 specimens were mounted in epoxy resin and ground with SiC paper to a 4000 grit surface finish under running tap water, rinsed with distilled water, acetone, and then dried under a nitrogen stream. The exposed test surface area was 10x6 mm. Specimens were stored in a vacuum desiccator for 24 hours to stabilize the oxide film that forms immediately after abrasion upon exposure to the air environment. The interface between the specimen and epoxy resin was sealed using nail polish lacquer to avoid crevice corrosion. After removal from the desiccator, one specimen was pre-treated with IL. The pre-treatment consisted of covering the surface of the epoxy mounted specimen with a thin layer of IL, and leaving for 24 hours. After that time, the surface was rinsed with distilled water and ethanol to wash off any excess IL.

Beakers containing 100 ml of the SBF were maintained at  $37^{\circ}C$  in a constant temperature water bath. Specimens with no-pretreatment were removed at 2 hours, 24 hours, and 168 hours. The specimen with the pre-treatment was removed at 24 hours.

## 2.3 Surface Characterization

After immersion, the corroded specimens were examined using scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) to identify the corrosion morphology and the composition of corrosion products. After examination, the nail polish was removed using ethanol, and the specimens were immersed for 60 seconds in a solution of 200g chromium trioxide, 10g silver nitrate, and 20g barium nitrate, in 1000mL of distilled water to remove the corrosion products. The specimens were again examined in the SEM, and optical profilometry using a Veeco Contour GT-K1 optical profilometer was carried out to determine the number of pits and pit depth. In order to collect the information from the entire specimen surface, the “stitching” function on the profilometer was used. The areas around the edges of the specimens covered with the nail polish were taken as the zero corrosion reference areas.

## 3. RESULTS

### 3.1 Corrosion Morphology of AZ31 in Simulated Body Fluid (SBF)

Figure 2 a, b and c is a series of SEM images of specimens after immersion in SBF for 2, 24 and 168 hours respectively. Layers of corrosion product were clearly visible covering the entire surface. “Mud cracking” was particularly evident on the specimens exposed for 24 and 168 hours. The cracks are thought to result from internal compressive stresses developed during drying in the SEM [15]. The greater extent of mud cracking on the surfaces of specimens exposed for 24 and 168 hours indicates thicker corrosion product layers. The EDS data obtained after 24 hours immersion in SBF (Figure 3) indicates the presence of oxygen, magnesium, calcium and phosphate on the surface of the corroded AZ31. The presence of oxygen and magnesium is consistent with a corrosion product of  $Mg(OH)_2$ , while the calcium and phosphate are thought to be associated with the SBF.

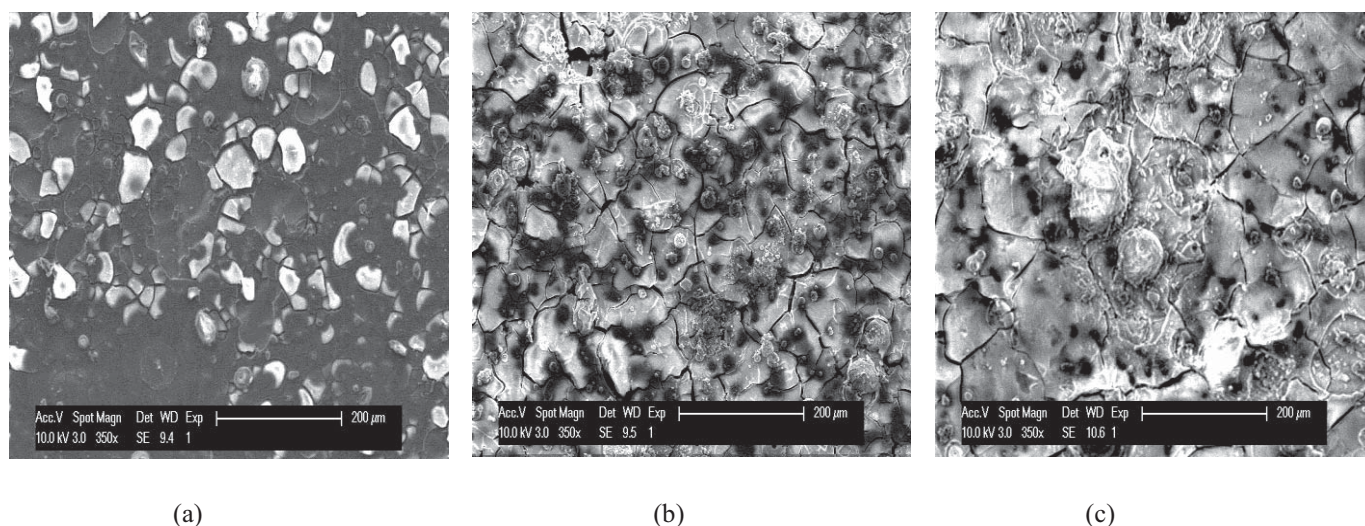


Figure 2 SEM micrographs of AZ31 specimens after immersion in SBF for (a) 2 hours, (b) 24 hours, (3) 168 hours

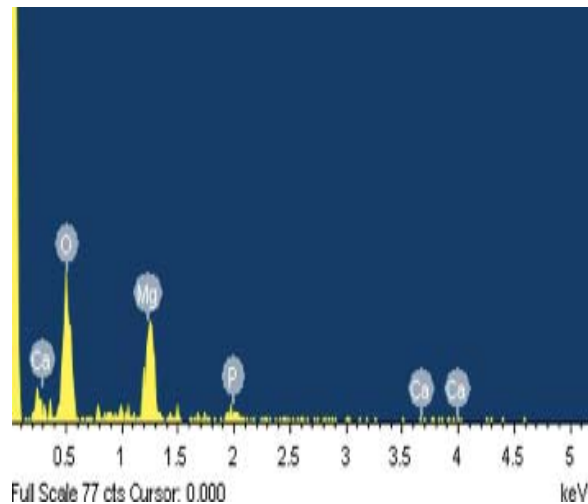


Figure 3 EDS data obtained from corrosion product on the surface of a specimen after immersion in SBF for 24 hours

Figure 4 shows the SEM images of specimens after the corrosion products had been removed. Some corrosion product was still present on the specimen exposed for 168 hours. The corrosion product was probably too thick to be removed by immersion in the chromic acid solution for 60 seconds. These micrographs show that the surface of the alloy was pitted, and that pitting became more extensive and deeper with longer immersion time.

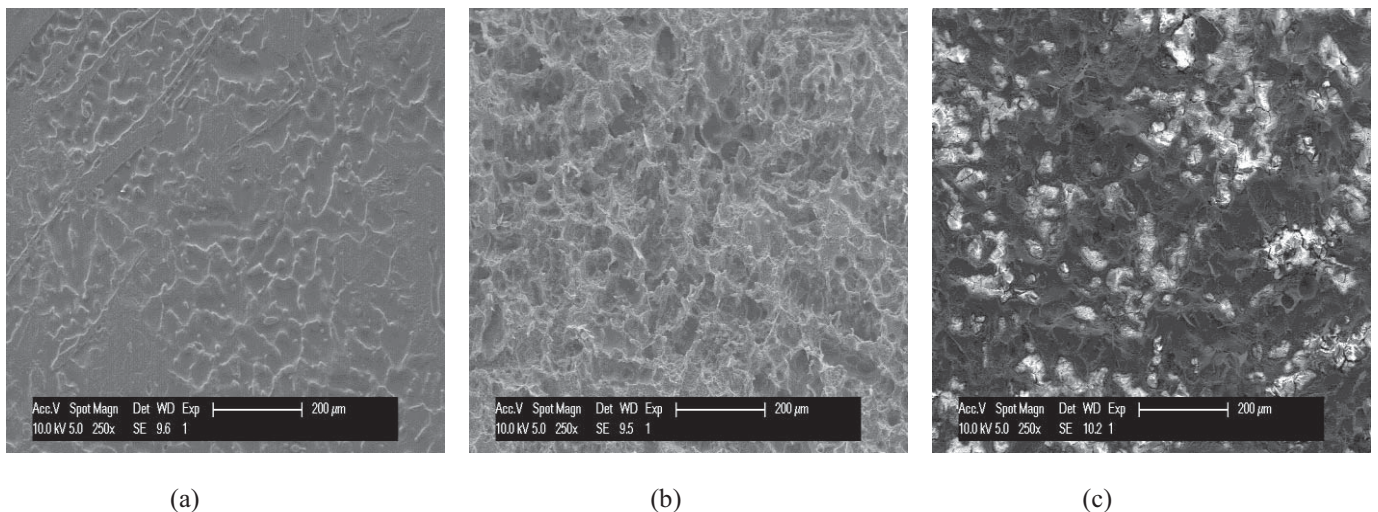


Figure 4. SEM micrographs of AZ31 specimens after immersion in SBF for (a) 2 hours, (b) 24 hours, (3) 168 hours with the corrosion product removed.

### 3.2 Effect of IL pre-treatment on the corrosion behaviour of AZ31 in SBF

The SEM images in Figure 5 show the differences in the alloy surface (with corrosion products removed) for the untreated condition and the IL treated condition after exposure to SBF solution for 24 hour. The SEM images show that pits of a greater range of depths covered the whole surface of untreated specimen (Fig 5 a). While there was similar pitting on the IL specimen (Fig5 b), there were still some areas that had not been attacked by the SBF.

Figure 6 a and b show the surface morphology determined using optical profilometry analysis of untreated AZ31 and IL treated specimens after immersion in SBF for 24 hours. The 3-D images reveal that the variation in depth and density of the pits on the specimen surface. The pits appeared to be evenly distributed all over the surface of the untreated specimen (Figure 6 a). However, some areas on the IL treated specimen were protected from pitting (Figure 6 b). The optical profilometry 3-D images are similar to those obtained with the SEM results. A histogram (Figure 7) prepared from the optical profilometry

analysis shows the distribution of the pit depths with corresponding pit numbers. These data demonstrate the effects of the pre-treatment. Pit depths on the IL treated specimen were up to 50  $\mu\text{m}$  deep, while the pits depths on the untreated specimen were up to 75  $\mu\text{m}$  deep. Furthermore, there were a greater number of pits on the untreated specimen compared to the IL treated specimen. Also, the IL treated specimen had a significantly larger non-corroded area. Zero pit depth corresponds to areas of no corrosion. Values on the x axis little greater than zero correspond to peaks associated with the grinding damage from specimen preparation.

The volume of alloy removed from the surface due to pitting was calculated from the optical profilometer data obtained over an area of 21  $\text{mm}^2$  for specimen treated with IL and with no treatment. The results in Table 2 clearly show that with the IL treatment a smaller volume of alloy was removed by corrosion during the immersion for 24 hours.

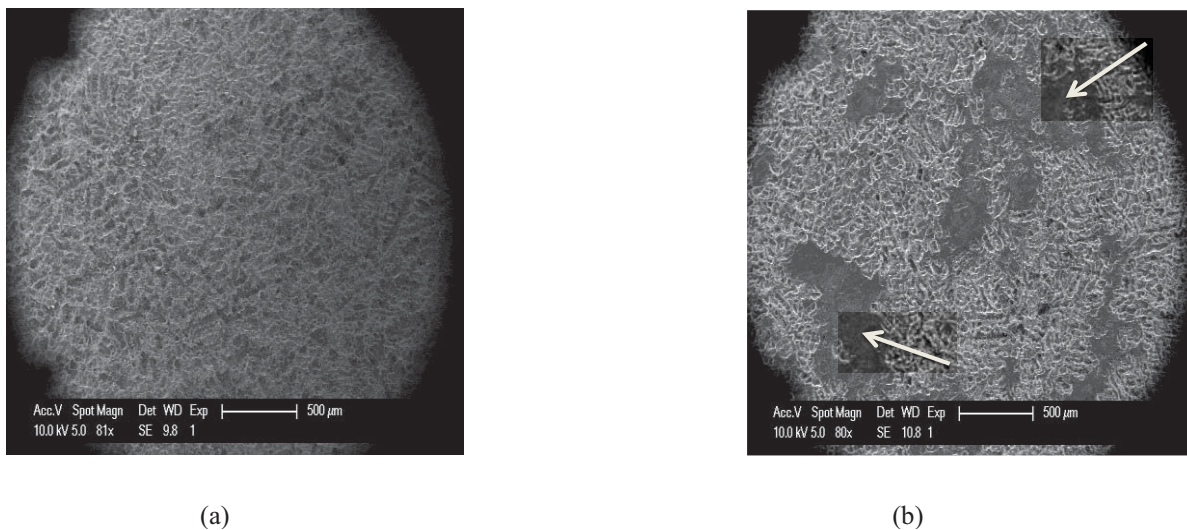
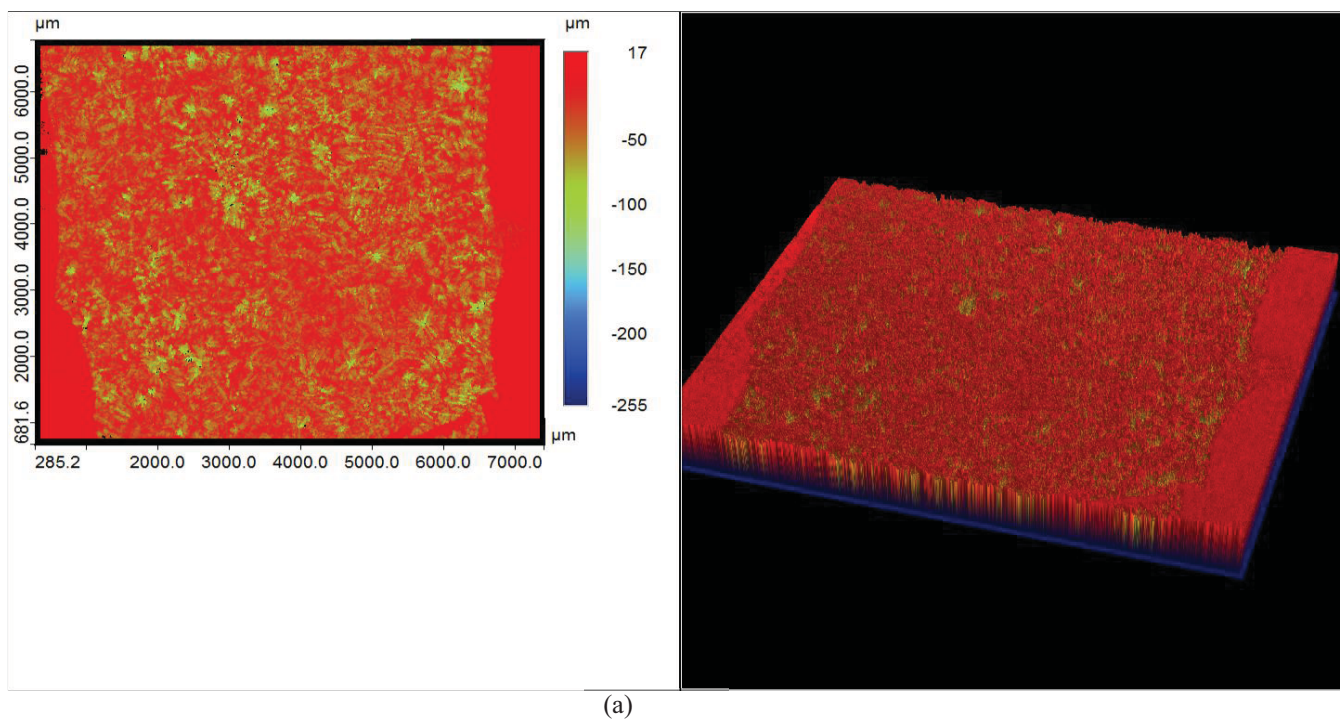
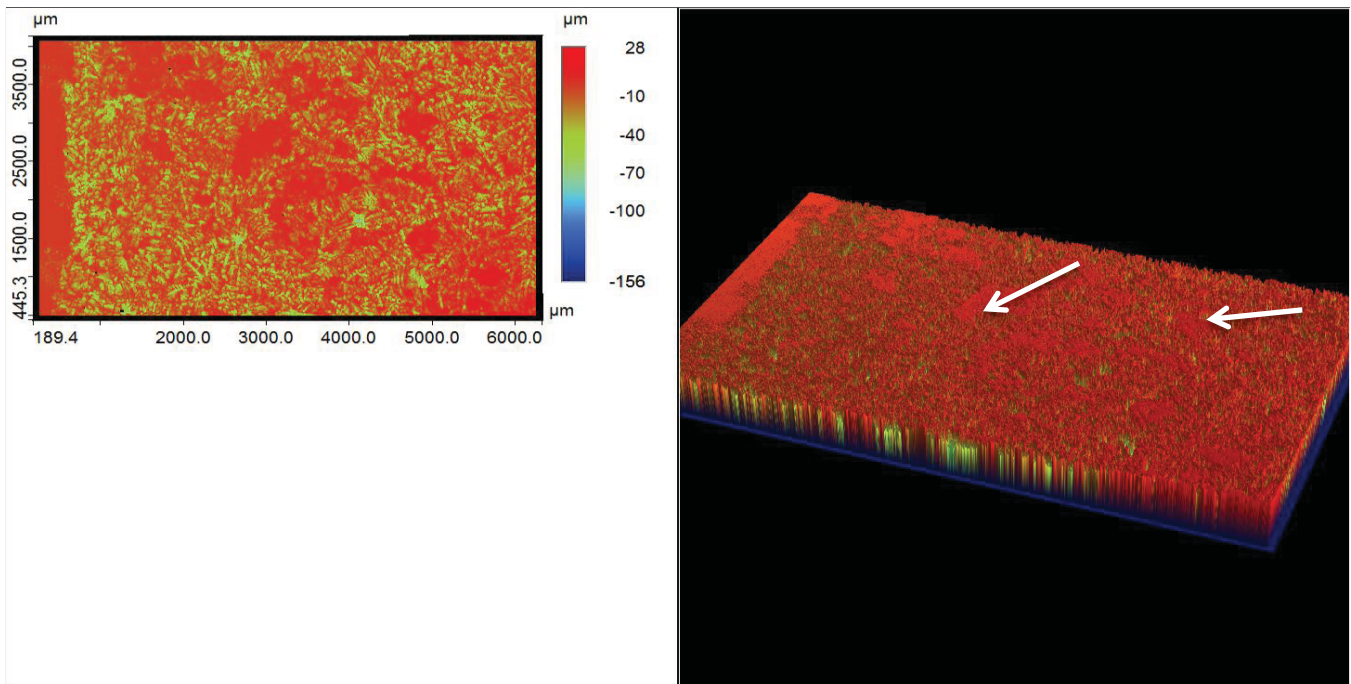


Figure 5 SEM images for (a) untreated AZ31 and (b) IL treated AZ31 after immersion in SBF for 24 hours with corrosion product removed





(b)

Figure 6 Optical profilometry images showing the distribution of pitting on the surface of (a) untreated AZ31 and (b) IL treated AZ31 in SBF for 24hours

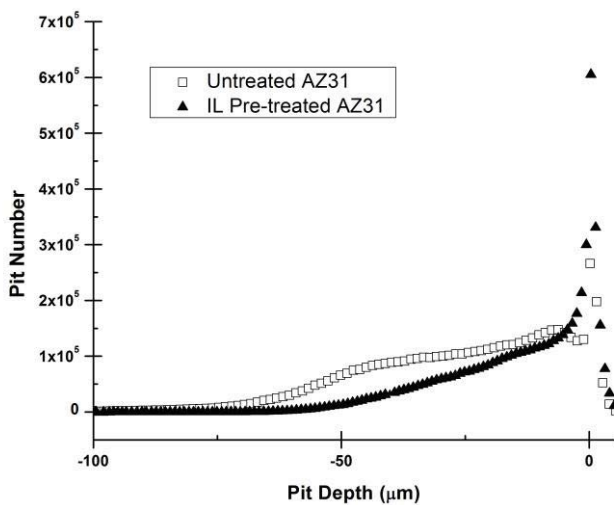


Figure 7 Histogram results from optical profilometry analysis of the untreated AZ31 and pre-treated AZ31 after immersion in SBF for 24 hours.

#### 4. DISCUSSION

The SBF is an aggressive solution, which contains about 0.1M Cl<sup>-</sup> as shown in Table 1. Therefore when AZ31 was immersed in SBF solution, it suffered severe pitting corrosion (See SEM micrographs in Figure 5). The surface of the alloy was covered with a layer of corrosion product, the thickness of which increased with increased immersion time. Mg, O, Ca and P elements were found in the corrosion product layer. Mg and O suggest that the corrosion product was most likely Mg(OH)<sub>2</sub>. Mg dissolves in aqueous environments by an electrochemical reaction with the formation of magnesium hydroxide and hydrogen

Table 2 Net volume of alloys removed during corrosion

	Untreated AZ31	IL Pre-treated AZ31
Volume lost	526.7 μm <sup>3</sup>	291.3 μm <sup>3</sup>



gas generation [16]. The evolution of hydrogen and associated pH changes are not desirable for in-vivo biological situations. Ca and P elements that were observed using EDS, arise from other components in the SBF solution. Ca and P deposition were always found with the presence of Mg and O. This suggests that Mg corrosion may have an influence on the precipitation process of Ca and P from the SBF. The relation between Mg corrosion and the deposition of calcium phosphate has previously been discussed [17]. Because hydroxyl ions are generated by Mg corrosion, the local pH around cathodic sites increases compared to the bulk solution. At higher pH,  $\text{HPO}_4^{2-}$  is unstable and likely to convert to  $\text{PO}_4^{3-}$ . As a result, calcium phosphate precipitates rapidly from solution. The accumulation of calcium phosphate has also been found during in-vivo tests [18]. The presence of calcium phosphate deposits are undesirable and could under some circumstances threaten the life of a patient with an Mg implant, as large precipitates that develop may block an artery near the stent or travel to the other parts of body. A reduction in corrosion rate would mean a smaller increase in local pH, which in turn would influence the deposition process.

Figure 4 show that AZ31 in SBF suffered severe localized pitting corrosion. The corrosion mechanism for AZ31 in SBF has previously been discussed [19]. The microstructure of AZ31 magnesium alloy consists of  $\alpha$  phase (solid solution) with a small fraction of  $\beta$  phase ( $\text{Mg}_{17}\text{Al}_{12}$ ), and Al-Mn intermetallic particles, which are mainly distributed in the  $\alpha$  phase [16]. Because the content of the  $\beta$  phase in AZ31 is small, and the corrosion potential of Al-Mn is higher than other phases in this alloys [20], the influence of  $\beta$  phase on the corrosion behavior of AZ31 is thought to be less compared with the influence of the Al-Mn particles. The localized corrosion mainly initiates adjacent to Al-Mn particles in  $\alpha$  phase. Pits with a range of depth occurred adjacent to the Al-Mn particles over the whole surface. Pit depths increased with immersion time, and with time precipitated corrosion product eventually covered the entire specimen surface. As shown by the SEM images and 3-D profilometry results, some small areas on IL treated surface were not attacked in SBF. It seems that IL may have reacted with AZ31 surface and protected some parts of surface from corrosion but not others. At this time, it is not known exactly how the IL interacts with the magnesium alloy, and how the IL provides protection for the alloy surface. However, it is hypothesized that the IL reacts to form a barrier film on the magnesium-rich  $\alpha$  phase, which provides the protection from corrosion of AZ31 in SBF. However, this barrier film was non-uniform in its coverage of the surface. In some regions where the film may have been too thin or absent, corrosion pitting was able to occur. For a film to provide protection on an Mg alloy, a homogeneous film with uniform coverage across the entire surface is required, and achieving this is the aim of future work.

Based on the optical profilometry analysis, the range of the pits depths and the total number of pits on the IL treated specimen were lower in comparison with the untreated specimen. Therefore, even in the corroded areas, corrosion of the IL treated specimen was reduced in comparison with the untreated specimen. The effectiveness of the pre-treatment with IL was also shown by the reduced volume of total pits when the IL was present.

## 5. CONCLUSIONS

- (1). Magnesium alloy AZ31 suffered localized pitting corrosion in SBF.
- (2). The corrosion product layer included Mg, O, Ca, and P. The Mg and O indicate the presence of  $\text{Mg}(\text{OH})_2$ . The Ca and P are the result of the reaction between the Mg and the SBF solution.
- (3). It is proposed that trimethyl (butyl) phosphonium diphenyl phosphate ionic liquid interacts with AZ31 to form a protective film to provide some localized corrosion protection. However, the film produced by the current simple pre-treatment processes was not uniform and therefore some corrosion of the Mg alloy did occur.

## 6. ACKNOWLEDGMENTS

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## 8. AUTHOR DETAILS



Yafei Zhang is a PHD student in ITRI, Deakin University, and under the supervision of Prof. Maria Forsyth and Prof. Bruce Hinton. She finished her undergraduate study in 2010 from the Department of Materials Engineering at Monash University. In her final year project, she did her research about using Ce(dpp)<sub>3</sub> to control of corrosion of Aluminum alloy. Her recent investigation work tries to improve the corrosion resistance of AZ31 in SBF through the use of biocompatible ionic liquid.