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A potential anti-corrosive ionic liquid coating for Mg alloy AZ31 in simulated body fluids

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SUMMARY: Magnesium alloys are attractive materials for biomedical applications, due to their excellent biocompatibility. However, these alloys show fast corrosion rates in the body that limits their clinical applications. Low-toxic ionic liquid (IL) trimethyl(butyl)phosphonium diphenyl phosphate P₄44dpp has been investigated to provide corrosion protection for magnesium alloy AZ31 in simulated body fluids (SBFs). This work reports a preliminary exploration of the influence of different treatment temperatures on the corrosion protection properties of IL films for the magnesium alloy AZ31 in SBFs. Results show that the IL treatment at room temperature did not bring significant improvement in the corrosion performance of the AZ31 in SBF. However, when the treatment temperature was increased to 75°C, the IL treatment resulted in a substantial reduction of the corrosion, in particular the reduction of localized pitting corrosion. The influence of ionic liquid treatment on the corrosion performance of the magnesium alloys AZ31 in SBFs has been investigated by electrochemical impedance spectroscopy (EIS) tests and immersion tests.

Keywords: Magnesium alloys AZ31, Simulated Body Fluids, Ionic liquid, Treatment Temperature

1. INTRODUCTION

Coronary artery disease has become one of the leading causes of death worldwide recently. Implanting stents into narrowed arteries is an effective therapeutic option for this disease [1]. Most of the existing stents used in clinic recently would stay in the body permanently, which could incite an immune response [2]. In this context, a biodegradable stent is a better choice, which can provide a temporary support to the diseased vessel, and then be gradually dissolved by the body. Mg alloys have gained the interest as the candidate materials for biodegradable stents, due to (1) the biocompatibility and biodegradability of Mg element in the body [3], (2) the excellent mechanical properties of Mg alloys [3]. To date, several pioneering works on implantation of Mg-based stents in animals and a preterm baby have been reported [4, 5]. However, fast corrosion rate of Mg alloys in the body [6, 7] limits the wide application of these alloys in clinic.

One of the most effective ways to improve the corrosion resistance of Mg alloys and obtain the required longer degradation time in the vessel is to form a coating on the surface to isolate the base material from the environment [8]. Considering this specific application, the surface coating needs to be biocompatible without any adverse effects to the body. To date, most of subsistent coatings (e.g. phosphate permanganate conversion coating and chromate conversion coating) are unlikely to be
biocompatible. Over recent years, various biocompatible coatings have been widely investigated. However, these coatings have yet to advance to a point that would enable their widespread clinic use, and there are still no commercial coating products available in the biomedical implants sector. Thus, the development of a surface coating for Mg alloy based biomedical implants remains a great challenge.

Recently, ionic liquids (ILs) films as environmental-friendly organic-based coatings are increasingly attracting interest for the corrosion protection of Mg alloys. In general, Ionic liquids (ILs) are liquid salts at room temperature, possessing lots of unique properties, such as high thermal and electrochemical stability, and low vapor pressure [9]. The use of ionic liquids to form corrosion protective films on magnesium alloys is still a very new topic, and only a few investigations have been carried out. Early works [10-14] have shown that phosphonium phosphate ion liquids could form a film on the surface of magnesium alloys, which provides a certain corrosion protection for Mg alloys in chloride-containing aqueous solutions. However, corrosion of Mg alloys still occurs even with the presence of IL film on the surface. For a passive surface film for Mg-based coronary artery stent application, this film should make sure that the coronary artery stent can keep its mechanical integrity before the diseased vessel returns to its original shape, and at least does not significant corrosion occurring at the first half-year implantation of stents in the vessels [3]. In order to achieve this requirement, there are many aspects referring to IL conversion coating that can be improved, and increasing temperature is a fairly straightforward way. Under a higher temperature, the ionic species in the ILs move fast and collide more frequently with the magnesium substrate. For most cases, the rates of chemical reactions rate are expected to increase.

Electrochemical impedance spectroscopy (EIS) is a useful electrochemical technique, which has been used successfully for the evaluation of the corrosion behavior occurred at the interface. Various parameters that can be obtained from impedance data, such as the magnitude of minimum phase angle at medium and/or high frequencies [15], and the surface film resistance extracted from the fitting of equivalent circuit to the EIS loop [16], are useful to estimate the degree of deterioration of coating and chemical reaction on the metal surface.

This paper investigates if increasing treatment temperature can form an IL film on Mg alloy AZ31 with improved corrosion performance in SBFs. Ionic liquid tributyl(methyl)phosphonium diphenyl phosphate (P1444dpp) was chosen in this study. In previous study, the cyto-toxicity of this IL to primary human coronary artery endothelial cell has been tested, and its toxicity was considered acceptable to coronary artery cells [17]. The corrosion behaviors of AZ31 samples in SBFs were investigated by monitoring the variation in the surface film resistance and phase angle, which were extracted from the EIS loops. The corroded surfaces of these samples after immersion in SBFs were then examined by second electron microscopy (SEM).

2. EXPERIMENTAL METHODS

2.1 Materials used

The magnesium alloy used in this study was from a direct strip cast cylinder of AZ31 magnesium alloy with a nominal composition (in wt.%): Al: 2.40-3.6, Zn:0.5-1.50, Cu: <0.1, Mn>0.15. All samples were taken from the circumferential edge of the cylinder to keep the consistency of the microstructures. The samples with the surface area of 5mm × 5mm were mounted in the epoxy resins and abraded with SiC paper to 4000 grit surface finish under running distilled water, and dried under a nitrogen stream.

The low toxic ionic liquid Trimethyl(butyl)phosphonium diphenyl phosphate (P1444dpp) was used and prepared in the laboratory. The IL was purified through a column containing a filter agent, alumina and sand to remove impurities. The structure of P1444dpp is shown in Fig 1.
Figure 1. The structure of (a) trihexyl(tetradecyl)phosphonium cation ($P_{1444}^+$) and (b) diphenyl phosphate anion (dpp$^-$)[17].

All electrochemical measurements were performed at 37°C in simulated body fluids (SBFs) at pH of 7.4 ± 0.5. The SBF solutions were chosen as the test solutions due to their similar ionic compositions to the human blood plasma [18]: 103 mM Cl$^-$, 147 mM Na$^+$, 2.6 mM Ca$^{2+}$, 1.5 mM Mg$^{2+}$, 5 mM K$^+$, 6 mM HCO$_3^-$, 0.5 mM SO$_4^{2-}$, 1 mM HPO$_4^{2-}$. HEPES (2-[4-(2-hydroxyethyl)-1-piperazin-1-yl] ethanesulfonic acid) was used as a buffer agent in SBFs.

2.2 Ionic Liquid (IL) Treatment

IL coating treatments on magnesium alloys AZ31 were performed by pipetting 0.25 mL of the IL on the alloy surface for 1 hour. The treatment temperatures were room temperature (RT) and 75°C, respectively.

2.3 Electrochemical Tests

Electrochemical Impedance Spectroscopy (EIS) tests were done using a three-electrode cell connected with an EG&G PAR VMP2/Z multi-channel potentiostat. These tests were performed in 150 ml SBF solution using epoxy-mounted samples with 0.25cm$^2$ surface area exposed. The counter electrode was a Titanium mesh and the reference was a saturated calomel electrode (SCE). The EIS measurements were carried out over a frequency range of 200 kHz to 50 mHz with eight points per decade using a 10 mV amplitude perturbation. EIS spectra were acquired at 10-min intervals, and last for 2.5 hours. The Z-fit program in the EC-Lab Software was used to fit the equivalent circuit to the EIS experimental data.

2.4 Surface characterization

Immersion tests were performed by immersing samples into 100 mL of SBF solution at 37°C for 2 hours. After immersion, the corroded surfaces were examined using scanning electron microscopy (SEM).

3. RESULTS

The EIS spectra for bare AZ31 sample in SBFs and the choice of the equivalent circuit have been studied in previous study [17]. The EIS spectra for IL-treated AZ31s are similar to the spectra for bare AZ31. Both of them contain two semicircles, and these two semicircles increased in size with immersion time. The equivalent circuit used to fit the spectra consists of a resistor representing the solution resistance, Rs, and two RC units in series- a capacitance associated with the surface film and
the double layer capacitance. This equivalent circuit was chosen due to its simplicity. The surface film resistances of AZ31 samples were extracted from fitting of the equivalent circuit to the 1st loop of EIS spectra. Figure 2 is a bar chart of the surface film resistances versus different samples (bare AZ31 and AZ31s IL-treated at RT and 75°C). The higher surface film resistances for these IL treated samples indicate the formation of corrosion protective films during the IL treatments. Evidently, the treatment temperature played an important role in the formation of the IL film on the surface of Mg alloys. The room temperature treatment only led to a slight increase in surface film resistance, as compared to the bare AZ31, whereas when the treatment temperature was increased to 75°C, there was an obvious increase in the surface film resistance.

Figure 3 is the bar chart of the minimum phase angle at high frequency region as a function of various AZ31 samples. The minimum phase angle at high frequency region is related to the surface coating capacitor. What can be seen in this figure is that with increasing the treatment temperature, the minimum phase angle is reduced. In particular when the treatment temperature was increased to 75°C, this minimum was reduced obviously, as compared to bare AZ31 However, it is noticed that the minimum phase angles for these IL treated samples vary between -20°C to -30°C, which is much higher than -90°C.

To assess the protective effect of these IL films against corrosion, the increase in the surface film resistance during the immersion of these AZ31 samples in SBFs was calculated in Figure 4. From this figure, the surface film resistance for both the bare and IL treated samples increased during immersion in SBFs. However, the surface film resistances for these IL treated samples did not increase as much as the bare AZ31 with immersion time. The IL treated sample with treatment temperature of 75°C had a lowest increase of surface film resistance in SBF.

Figure 5 shows the corroded surface morphologies of the samples after being exposed in SBFs for 2 hours. The improved corrosion performance for these IL treated samples is apparent in this figure. The localized pitting corrosion (pointed by white arrows in Figure 5) can be observed on the bare AZ31 surface. The EDS analysis shows these pits appeared mainly adjacent to the intermetallic particles, due to the galvanic difference between these intermetallic particles and Mg matrix. IL film on the AZ31 surface seems to reduce the pitting corrosion on the surface, with a less number of “pits” observed on the surface of IL treated sample, in particular on the surface IL treated at 75°C.
Figure 2 Surface film resistances extracted from the 1st EIS spectra for different AZ31 samples.
Figure 3 The minimum of phase angle at high frequency region of 1st Bode impedance plot versus different AZ31 samples.
Figure 4 The increase in the surface film resistance for AZ31 samples during 2.5 hours immersion in SBF.
4. DISCUSSION

Electrochemical impedance spectroscopy was used to evaluate the corrosion performance of IL treated AZ31s in SBFs in this work. To investigate the properties of these IL films formed on the samples, and avoid the influence of corrosion on the films, the EIS measurements were carried out immediately, once the samples were exposed into SBFs. Thus, the 1st loop of EIS spectra obtained at the beginning of immersion can represent the native surface films of these samples, that is to say the native passive MgO/Mg(OH)$_2$ film for bare sample, and IL modified surface films for these IL-treated samples. Thus the observation in Figure 2 that the surface film resistances for these IL-treated samples are larger than the bare sample indicates the existence of IL films on the surface. And with increasing treatment temperature to 75°C, a more resistive IL film has been formed, compared to the film formed at RT.

Phase angle is another important parameter used in this work for the evaluation of the IL films. Compared with the surface film resistance, which is usually extracted from the fitting of equivalent circuit to the EIS loops, phase angle is a more straightforward and fast method to perform the evaluation of the coating systems, without complex equivalent circuit fitting procedure. The IL coating system formed at 75°C shows the more characteristic of capacitance, compared to the coating formed at RT. However, an intact coating should have a phase angle measured in middle or high frequency domain in bode plots close to -90° [19], the minimum phase angle varies between -20° to -30° possibly indicate these formed IL films are imperfect, with possible porous and/or defective in the films.
With immersion in SBF, corrosion products started to accumulate on the surface of sample, which led to an increase of surface film resistance. Compared with the bare AZ31, IL treated samples show a smaller increase of the surface film resistance, which indicates less corrosion products precipitated on the surface, and thus a better corrosion performance in SBFs. Among these samples, AZ31 IL-treated at 75°C has the best corrosion performance in the solution.

Hence, increasing temperature during the IL treatment process is beneficial in the development of more intact surface film. The SEM observations (Figure 5) show that these formed IL films on the surface could reduce the number of localized pits. This is possibly due to the preferential deposition of IL films adjacent to the intermetallic particles during the IL treatment. The formed IL film would lead a reduction of potential difference between the intermetallic particles and Mg matrix, which thus resulted in less pitting corrosion.

However, it is noticed that corrosion still occurred on the surface after IL treatment, and this possibly suggests that the formed IL film was heterogeneous and/or defective. For a film to provide sufficient corrosion protection for Mg-based coronary artery stents, an intact / less defective film with uniform coverage across the entire surface will be required. Such a film is expect to protect the surface of stents against corrosion, or bring an ‘ideal’ slow rate of corrosion in the vessel in the first half year of implantation; after the initial half year, stents would corrode with a rate of corrosion that the body can tolerate, and be gradually degraded and absorbed in the body. Increasing the treatment temperature seems to be an aspect, which can help access to this situation. In addition, there are still many other aspects that can be improved as the future work, including and not limited to: choosing appropriate pretreatment process prior to conversion IL coating, controlling water content in the IL, and trying anodizing to deposit IL on the surface.

5. CONCLUSIONS

(1). Increasing treatment temperature during the IL treatment helps the formation of an IL film with better corrosion performance on Mg alloy AZ31.

(2). The IL film formed at higher temperature can effectively reduce the deposition of the corrosion products on the surface, and effectively reduce localized pitting corrosion for Mg alloy in SBF.

6. REFERENCES


7. AUTHOR DETAILS

Yafei Zhang is a PHD student in IFM, Deakin University, and under the supervision of Prof. Maria Forsyth and Prof. Bruce Hinton.