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Magnesium and its alloys have a wide range of attractive properties. These include high specific strength and stiffness, low density, good fluidity, hot formability, easy machinability and good damping. In particular, the light weight of magnesium alloys makes them very attractive for applications in the transportation industries.

AZ31 (3% Al 1% Zn, Mg alloy) belongs to the AZ (magnesium-aluminum-zinc) class of magnesium alloys, which are the most common magnesium alloy family. AZ alloys are very versatile, used in both casting and wrought applications. The microstructure is comprised of two main phases: the solid solution α-matrix phase and the Mg17Al12 β phase, which forms a network along the grain boundaries. The addition of aluminum allows solid-solution strengthening, precipitate hardening and improves the castability of magnesium. Zinc acts as a weak grain refiner in magnesium but also allows precipitation hardening and, like aluminum, it improves the castability of the alloy.

Unfortunately, the use of magnesium alloys, primarily the wrought alloys such as AZ31, is limited due to poor corrosion properties. Magnesium is very active thermodynamically, such that it will spontaneously and rapidly oxidize in environments containing oxygen or water. Due to the hexagonal unit cell of magnesium, mismatching exists between the metal and the structure of hydroxide and oxide films. The passive layer also possesses a greater molar volume than the metal which, alongside the mismatching, results in the passive layer being under compressive stress which leads to rupture and cracking. With cracks present in the passive layer, ingress of electrolytes can occur which leads to corrosion.

Up until recently the most common methods of cheaply improving the corrosion performance of magnesium alloys was through the use of chromate compounds. Chromates have been used for surface activation (through immersion in chromic acid) to form a base for other coatings (e.g. paint, sol-gels), to form chemical conversion layers (CCC), and as a component in electrolytes for anodising. However, these compounds have since been found to be highly toxic and carcinogenic. Environmental concern and regulations has led to the push for development of alternative environmentally friendly corrosion protection solutions.

Ionic liquids (ILs) are salts which contain often very large or unsymmetrical organic and/or inorganic anions and cations. The size and unsymmetrical nature of these ions restrict their capability to order into a solid phase and hence, by definition, exhibit a melting temperature below 100°C. Room temperature ionic liquids (RTILs – henceforth referred to simply as ‘ILs’) are ILs which are liquid at room temperature and thus they can behave as an electrolyte (due to the charged anion and cation species and therefore have relatively high ionic conductivity) without the need of an additional solvent. This lends these materials exclusive properties over other, ‘classical’, liquid electrolytes. Due to the unique combination of properties including the low vapor pressure, high thermal and chemical stability, high electrochemical stability and high ion conductivity ILs are an attractive material for use as electrolytes in a number of applications, including batteries, dye sensitized solar cells (DSSCs) and electroplating/electrodeposition of metals.

Howlett et al., in studies of lithium batteries using an IL electrolyte, found that a passive solid electrolyte interphase formed on the lithium electrode from the reduction products of the IL anion during cycling was key to successful cycling of the battery. This led to a broad hypothesis that certain ionic liquids could form protective layers on reactive metals that may be of use in both battery technology and corrosion protection. The use of ILs to form corrosion protective films on magnesium alloys in particular is still very new and has only had minor investigation in recent years. Some research has also gone into studying the corrosive effects of other ILs against different alloys rather than their ability to form films on alloy surfaces.

Early work into the protective quality of films formed from ILs was performed using tri(hexyl)tetradecyl phosphonium bis(trifluoromethanesulfonyl)amide ([P6,6,6,14][NTf2]) on Mg alloy AZ31. Significant reduction in the corrosion current in 0.1 M NaCl was experienced after 17 hours of IL treatment. The surface films formed from this IL were able to withstand 21–30 days in 100% humidity without significant evidence of corrosion. Studies investigating this IL have found that the [NTf2] anion plays a direct role in the film composition as EDS analysis of the films registered significant levels of F, C, P and S.

A number of studies have focused on the influence of applying a potential bias to the system. The IL trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphate ([P6,6,6,14][C60]PO2) was used to treat both AZ31 and ZE41 at potentials of ±0.1 V vs. OCP and up to 0.5 V vs. Ag/AgCl respectively. In both cases the use of an anodic potential led to increased surface resistance (measured by EIS). XPS analysis of ZE41 treated with [P6,6,6,14][C60]PO2 at 0.25 V vs. Ag/AgCl for an hour found evidence of phosphate species (PO2 and PO3), magnesium hydroxide and magnesium oxide. The authors concluded that the film formed on the surface was a composite between the oxide and hydroxides and the IL anion. Most recently, the electrochemical behavior of AZ31 in [P6,6,6,14][C60]PO2 was investigated in our laboratories up to potentials of 4.5 V vs. OCP. We found that cycling AZ31 in the IL electrochemically passivated the surface. In a separate study we were able to form an 80 nm film by galvanostatically anodising AZ31 in the IL to 18 V. These studies suggest that the IL is generating an anodised film on the magnesium alloy surface. Due to the absence of bulk water in solution we expect the process of anodic film growth in...
IL is likely to be different to traditional growth mechanisms. Hence this study investigates the composition of the films formed under anodising conditions and correlates this with their corrosion performance in 0.01 M NaCl.

**Method**

**Materials.**— Commercial AZ31 magnesium alloy was obtained from a 125 mm diameter direct strip cast (DSC) cylinder. Specimens were taken from the edge of the cylinder for use in experiments. No heat treatments were performed on the ingot after being received. The microstructure of the alloy consists of the α-phase (Mg₁₇Al₁₂) as well as Mn rich intermetallics (most likely Al₃Mn). Mounted specimens were prepared by attaching an electrical wire to the metal using adhesive Cu conducting tape. Struers Epo-Fix cold-mounting epoxy resin was used to encapsulate the 0.5 × 0.5 cm specimens.

Ionic liquid triethyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate ([P₆,₆,₆,₁₄][(C₈)₂PO₂]) was purchased from Sigma-Aldrich with a purity of ≥95%. Purification of the IL was achieved by first dissolving in high purity liquid chromatography (HPLC) grade acetone and passing through a column containing coarse sand (SiO₂), activated charcoal, basic activated alumina and filter agent (fine SiO₂). The solution was then passed through μm filter paper and a μm hydrophobic syringe filter. Excess acetone and water was evaporated off on a vacuum line until the water levels were between 700–1500 ppm (as measured by a Metrohm KF830 Coulometer). ICP analysis returned values for the impurities of Fe, Ar, Zn, Pb, Cd, Cu, Mn, F, Si and excess P as below 2 μg/L. The structure of [P₆,₆,₆,₁₄][(C₈)₂PO₂] is shown in Fig. 1.

**Surface Preparation.**— ‘As-polished’ AZ31 specimens were ground to a P4000 grit surface finish on SiC papers under running water. Surfaces were rinsed with acetone between papers and finally rinsed with acetone and dried under a nitrogen gas stream. No deionised water as per.30 Surfaces were rinsed with deionised water before pickling or anodising conditions and correlates this with their corrosion performance.

**Pickled surfaces** were prepared by immersion for 60s in a mixture of 605 mL/L phosphoric acid (H₃PO₄) and 30 mL/L nitric acid (HNO₃) at room temperature for one hour prior to use. The samples thus prepared were denoted ‘as-polished control’ specimens and were used for comparative measurements. All other surface preparations (e.g., pickling or anodising) were performed at La Trobe University on a Munster ION-TOF ToF-SIMS Instruments Aztec (version 1.0) software were used.

Anodising.— A potential transient for AZ31 anodised in [P₆,₆,₆,₁₄][(C₈)₂PO₂] IL at 0.1 mAcm⁻² to a cutoff potential of 18 V is presented in Fig. 2. The potential increases with treatment time and this is associated with the increasing resistance of a growing/thickening surface film, following Ohm’s Law. Anodising AZ31 at 0.05 mAcm⁻² in this IL has been previously shown to result in a film approximately 80 nm thick, 29 which is close to the thicknesses of other electrolyte IL films previously formed on magnesium alloys.10,25 The efficiency of anodising is represented by the linearity of the potential transient. Fig. 2 shows a reduction in the anodising efficiency by the decrease in the steepness of the curve with increasing time. The tangent overlays on the curve show the segmented decrease in the slope of the curve, which begins at 5 V.

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**Results**

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**Surface characterization.**— Scanning Electron Microscope (SEM) was performed on Phillips XL20 SEM at an accelerating voltage of 5 keV with an Oxford Instruments X-Max Energy Dispersive X-ray Spectroscopy (EDS) attachment at 8 mm W.D. with a collection time of 2 minutes. Philips Microscope Control XL and Oxford Instruments Aztec (version 1.0) software were used.

**Contact angle measurements** were performed using a Biologic VMP3 multi-channel potentiostat with biologic EC-Lab version 10.11.

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Corrosion protecting properties of deposited surface films on as-polished AZ31.—Fig. 3 shows PP curves for AZ31 anodised at a number of current densities to a cutoff potential of 18 V. After treatments, the anodic reaction current is greater than the as-polished AZ31 control specimen in all cases. This effect is increased for lower current densities (and hence slower anodising). This means that, despite the fact that a surface film of approximately 80 nm has been shown to form on AZ31 following this anodising treatment, the films are not protective. It is not entirely clear why this effect is observed, nor why the lower current densities appear to make the film even less protective.

It is possible that a high level of porosity and poor adhesion, enabled in part by a highly heterogeneous substrate, leads to such poor corrosion performance. It is well known in the coatings field that, before metals are coated or anodised they often undergo a series of surface cleaning and etching/pickling steps. This not only removes impurities from the surface (including the oxide/hydroxide film) but it can also form a precursor film that allows for greater adhesion of the coating/anodised layer to come. In the work discussed thus far, the only step in surface preparation was through grinding of the AZ31 specimens to a P4000 grit finish followed by rinsing in acetone and drying under a nitrogen gas stream. Recently, we have reported the role of chemical surface pretreatment and the resulting surface homogenisation in improving the corrosion resistance and coating performance of the [P6,6,6,14][NTf2] IL on an AZ91D alloy. The remainder of this paper focuses on the deposition of an IL based film onto an AZ31 substrate that has first undergone a pickling step to allow for greater homogenisation of the surface as well as roughening that should aid adhesion.

The effect of acid pickling on the surface composition, IL deposition and corrosion activity of AZ31.—Many of the solutions used to pickle magnesium alloys are not considered safe. That is, they often contain chromates (which are toxic) or hydrofluoric acid (HF - which is extremely dangerous). Based on results which showed attack of both the α-phase and β-phase, the acid mixture selected was taken from a study by Zhu et al. AZ31 was pickled for 60 seconds in a mixture of 30 mL/L nitric acid (HNO3) and 605 mL/L phosphoric acid (H3PO4). Pickling in this solution was performed to homogenize the surface (due to removal and redistribution of cathodic elements) and pickling in H3PO4 has been shown to also form a thin and protective magnesium phosphate (Mg3PO4) film.

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Figure 5. SEM and EDS maps of AZ31 after 60 seconds immersion in HNO3 and H3PO4: (a) SEM of AZ31, (b) Mg EDS map, (c) Al EDS map, and (d) Zn EDS map.

Fig. 6 compares the corrosion performance of the acid pickled surfaces with as-polished AZ31. The pickling of the surface has dramatically shifted the potential of $E_{corr}$ to more anodic and noble values, taking it from approximately $-1560 \pm 10$ mV to $-1280 \pm 82$ mV. This accounts for an anodic shift of almost 300 mV. In addition, the anodic current is significantly reduced by over an order of magnitude, and the cathodic current is significantly increased by an order of magnitude. Therefore, the changes to the surface from the pickling process accelerate the cathodic reaction, but decrease the anodic reaction. Similar corrosion behavior was reported by Orlov et al. on magnesium alloy ZK60. They attributed this behavior (increased cathodic reaction, decreased anodic reaction) with redistribution or re-solutionising of significant cathodic Zn. The Zn maps in Fig. 4 and 5 show a considerable redistribution of the Zn after pickling, however, the redistribution is most likely due to material re-depositing onto the surface after being dissolved by the acid.

Fig. 6 also compares the PP curves for AZ31 after pickling with and without IL treatment. With the application of a galvanostatic anodised IL film, instead of the corrosion performance worsening, it improves. The anodic reaction current density decreases another half order of magnitude, $i_{corr}$ is reduced to 1.1 ± 0.3 $\mu$Acm$^{-2}$ and $E_{corr}$ is shifted positive approximately by another 80 mV. In addition, the cathodic reaction is also reduced (in comparison to the pickled control). This results in approximately 1.5 orders of magnitude decrease in the anodic reaction current density in comparison to the as-polished AZ31 and a 3x reduction in $i_{corr}$.

Bode plots in Fig. 7 compare the impedance and phase angle of as-polished AZ31, 60 s acid pickled AZ31, and as-polished AZ31 anodised at 0.1 mAcm$^{-2}$, in 0.01 M NaCl solution. The magnitude of the impedance at low frequency corresponds to the resistance of
the film on the AZ31 surface and the change in this impedance indicates the performance of the surface film in the corrosive media. Immediately after immersion in solution the impedance is greatest for the 60 s acid pickled surface, followed by as-polished AZ31 and anodised as-polished AZ31. After 60 minutes immersion in 0.01 M NaCl the impedance increases. Whilst a higher impedance is usually associated with a more resistive surface, in this case the increase is associated with the accumulation of corrosion product; the surface which corrodes most rapidly having the greatest increase in impedance as the accumulation of corrosion product increases the resistance of the surface film. Therefore, both the as-polished untreated specimen and the as-polished anodised specimen exhibit greater corrosion rates than the 60 s acid pickled AZ31 specimen, when immersed in 0.01 M NaCl. This is also supported by the phase angle data in Fig. 7b which indicates the coverage and quality of a film, where −90° is a perfect capacitive film. There are two capacitive elements in this data; the one at high frequency corresponds to the double layer between the solution and the surface and the lower frequency capacitive element corresponds to the surface film. Initially the peaks are at approximately −23° (as-polished anodised) and −30° (as-polished and 60 s acid controls). After 60 minutes immersion in NaCl solutions the phase angles increase to −54°, −56° and −46° for the as-polished anodised, as-polished control and pickled control AZ31 surfaces respectively. The increase in the phase angle with immersion time can also be related to the deposition of a corrosion product film on the surface; the greatest change in phase angle corresponds to an increase in corrosion product and the least change, (as for the pickled control) suggests less corrosion is occurring, in agreement with the polarization data (Fig. 6).

**Figure 8.** EIS response of 60s acid pickled AZ31 (blank-control) and 60s acid pickled AZ31 after anodising in [P6,6,6,14][C5H2PO2] IL at 0.1 mA cm⁻² in 0.01 M NaCl after 0 and 60 minutes immersion: a) Bode plot of impedance with frequency; b) Bode plot of phase angle with frequency.

**Figure 9.** Positive ion ToF-SIMS 2D elemental mapping of AZ31 anodised at 0.1 mA cm⁻² to 18 V of (a) as-polished AZ31; (b) acid pickled (60s HNO₃ and H₃PO₄) AZ31. C₃₂H₆₈P⁺ is the cation. The total count represents the detected amount of each particular species. This value can be compared against the total ion count for the relative detection of each species.

Fig. 8 shows Bode impedance plots of pickled AZ31 surfaces with and without an IL film formed at 0.1 mA cm⁻². Fig. 8a shows that the impedance of the treated surface is initially greater than the untreated specimens and does not change as significantly following the 60 minute immersion in contrast to the control. The increase in impedance in case of the control can be related to the accumulation of corrosion product on the surface as discussed above. Similar behavior can be seen in Fig. 8b with the phase angles. With the application of an IL film the phase angle is increased from approximately −33° (the control) to −51° (IL film), corresponding to a more capacitive film on the surface. After 60 minutes immersion the phase angle of the IL treated surface remains unchanged. This shows that the IL film is not only more capacitive and covers a greater portion of the surface, but is also more stable in the 0.01 M NaCl solution. This shows a significant improvement over the as-polished AZ31 surface with a combination of a pickling pre-treatment and deposition of an IL film.

**Film composition.**—Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) was used to obtain elemental spectra and 2D maps of AZ31 anodised to a cutoff potential of 18 V at 0.1 mA cm⁻² on as-polished and 60 s pickled AZ31. The positive ion spectra maps are shown in Fig. 9a and 9b for as-polished and pickled treated surfaces respectively. In Fig. 9 we can see that intact cation (i.e., C₃₂H₆₈P) is present in the surface film. The distribution of the cation is mostly uniform on the as-polished surface but more localized on the pickled
Figure 10. Negative ion ToF-SIMS 2D elemental mapping of AZ31 anodised at 0.1 mAcm$^{-2}$ to 18 V of (a) as-polished AZ31; (b) acid pickled (60s HNO$_3$ and H$_3$PO$_4$) AZ31. C$_{16}$H$_{34}$PO$_2^-$ is the anion. The total count represents the detected amount of each particular species. This value can be compared against the total ion count for the relative detection of each species.

The improvement in protection by the anodised IL film when the surface has been pickled may be due to a number of reasons. Firstly, the pickling causes significant surface roughening that will aid adsorption of the IL to the surface. Secondly, the thin magnesium phosphate film that is believed to form following pickling in the phosphoric acid solution may allow for better coordination of the IL anion and cation to the surface, improving adsorption. Finally, the magnesium phosphate film formed on the surface after reaction with the phosphoric acid may slow Mg dissolution when polarized to 18 V, which will also aid the film deposition and adsorption by controlling deposition kinetics. Furthermore, electrochemical homogenisation of the surface should allow for greater coverage of the IL film as opposed to as-polished AZ31. The redistribution of the more cathodic alloying elements after pickling leads to a large coverage of Zn on the surface (Fig. 5d) resulting in an increase in the cathodic reaction kinetics (Fig. 6) and as well as a decrease in anodic reaction kinetics. Application of the anodised IL film leads to a further reduction in the anodic kinetics, which suggests that the film preferentially deposits over magnesium rich regions where dissolution of the magnesium upon anodising will lead to film deposition.

During anodising the AZ31 surface becomes positively charged, so we expect that migration of the anion toward AZ31 will be promoted, whilst the cation will migrate away from the AZ31 surface. Previous studies, which have analyzed the elemental composition of IL films on magnesium alloys, and indeed other reactive metals, found that the anion of the IL greatly dominated the surface chemistry. In the current systems reported here, the ToF-SIMS revealed that both the cation and anion are present in the film. Interestingly, the expected cation fragments were not identified in the spectra, and the cation could only be identified as a whole molecule.

There are three main ways the IL can interact with the surface. The interactions will depend on whether the cation or anion coordinate with Mg(OH)$_2$, MgO or Mg$^{2+}$. Accordingly, the strength of the bonds will be different. The weakest bonds will be between the MgO and the cation. MgO can physically adsorb the cation due to weak electrostatic interactions of the negative charge of the O atom and the positive charge of the cation. Slightly stronger hydrogen bonding can occur between the H atom in Mg(OH)$_2$ and an O atom in the phosphinate of the anion. The strongest bond will be chemical adsorption between the Mg$^{2+}$ ions and the O atoms of the phosphate anion. It is also possible, if the film is porous, that capillary adsorption of the IL will take place. If we consider Fig. 9b and Fig. 10b, both the intact anion and cation occupy the same localized area. This suggests that some of the IL may have absorbed into, or become entrapped within, the anodic film without dissociation of the molecules.

The position of localized anion deposition (Fig. 9) at the same area where high counts of PO$_2$ were detected suggests the distribution of PO$_2$ is from fragmentation of the anion, which suggests good coverage over the surface. A possible reaction of the IL anion with Mg may be through the following:

$$\text{Mg}^{2+} + \text{O}^2P_{\text{R2}} \rightarrow (\text{MgO}_{2}P_{\text{R2}})^+$$

Where R is C$_8$H$_{17}$.

In addition, the presence of a large amount of OH in the ToFSIMS maps suggests the 1500 ppm present in the IL contributes to the growth of Mg(OH)$_2$, possibly in a similar manner to what is expected in traditional anodising. As a result the film likely has a composite structure incorporating Mg(OH)$_2$ and both the anion and the cation of the IL.

Conclusions

This study has shown that [P$_{6,6,6,14}$][C$_8$H$_{17}$PO$_2$] IL can be used as an electrolyte to electrochemically form a stable film on AZ31.
for corrosion protection. The corrosion performance of these films was greatly improved after acid pickling in a mixture of nitric and phosphoric acid. The process of acid pickling followed by anodising in IL resulted in films which were not only stable in 0.01 M NaCl, but led to a 300 mV anodic shift in $E_{corr}$ and a reduction in the anodic reaction kinetics by an order of magnitude. The corrosion current density, $i_{corr}$, was also reduced from $3.6 \pm 1.1$ to $1.1 \pm 0.3 \, \mu\text{Acm}^{-2}$. This improvement is likely due to a combination of surface homogenisation, and improved film deposition and adhesion.

Both the phosphonium cation and phosphinate anion played a role in the composition of the film. The phosphinate anion was likely chemisorbed onto the surface whilst some cation and anion molecules become entrapped as whole IL ion pairs in the film. The significant presence of Mg(OH)$_2$ suggests that the film was likely a composite between the IL and hydroxide. The consistently higher counts of IL species over the surface after pickling show that the type of surface preparation is crucial in the deposition of this IL film on AZ31.

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References