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In vitro degradation behaviour of a friction stir processed magnesium alloy

M. Bobby Kannan · W. Dietzel · R. Zettler

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Abstract In this study, the in vitro degradation behaviour of a friction stir processed AZ31 magnesium alloy was investigated. Electrochemical experiments in simulated body fluid suggest that friction stir processing marginally enhances the degradation resistance of the alloy, which could be attributed to the dissolution of secondary phase particles. Homogenisation of the microstructure reduces galvanic corrosion. It is envisaged that the beneficial effect would be more pronounced for magnesium alloys which contain high volume fraction of galvanic corrosion inducing secondary phase particles.

1 Introduction

Magnesium is biocompatible, degradable in body fluid and its mechanical properties are similar to natural bone [1]. These attractive properties make magnesium a potential candidate for biodegradable implant applications. However, a major issue of concern is the extremely high degradation rate of magnesium given such physiological conditions [1, 2], since this has the potential for complete dissolution of a magnesium implant before healing of bone fractures occurs. Additionally, the high dissolution of magnesium is known to generate pockets of hydrogen gas near the implant. These are further seen as a potential risk affecting the healing process [1].

In recent years, a number of methods have been tested to enhance the degradation resistance of magnesium. A wide range of magnesium alloys have been evaluated [1–6]. Alloying elements such as aluminium, calcium and rare-earths have shown some improvement in the degradation resistance. Biocompatible coatings such as calcium phosphate on magnesium alloys have been evaluated recently, and demonstrate promising results [7]. A few researchers have also studied the effect of chemical surface treatments on magnesium alloys, and reported that alkali and fluoride treatments enhance the in vitro degradation resistance of magnesium alloys [8, 9]. The effect of mechanical surface treatment, especially friction stir processing (FSP) has not yet been explored. Such processing is acknowledged in engineering applications for its ability to alter the surface properties, particularly in reference to corrosion resistance of materials such as aluminium, magnesium and titanium alloys [10–12].

FSP is a hot metal working technology based on the principle of the friction stir welding (FSW) process. The main advantage of FSP is in mechanically homogenizing/tailoring the surface microstructure of the alloy rather than joining materials [10]. Like FSW the process typically employs a cylindrical and non-consumable tool consisting of a shoulder and smaller diameter pin. The tool is rotated and the tool shoulder makes intimate contact with the work piece surface. Friction between the tool and the work piece generates heat causing a plasticized zone to form under the tool. This locally plasticized material is then forced to flow

M. Bobby Kannan (✉)
Discipline of Chemical Engineering, School of Engineering and Physical Sciences, James Cook University, Townsville, QLD 4811, Australia
e-mail: bobby.mathan@jcu.edu.au

W. Dietzel
Institute of Materials Research, Helmholtz-Zentrum Geesthacht, 21502 Geesthacht, Germany

R. Zettler
Business Development and Technology Transfer Corporation of Schleswig–Holstein, Geesthacht Branch, 21502 Geesthacht, Germany

in the direction of tool rotation such that it is thermo-mechanically worked, resulting in grain refinement and homogenization of the pre-existing microstructure.

Our earlier study on the localized corrosion behaviour of friction stir welded AZ31 magnesium alloy in chloride-containing solution showed that the friction stirred zone (i.e., the zone in direct contact with tool pin/shoulder) had improved general corrosion resistance, including pitting corrosion resistance, when compared to the base alloy [11]. Recently, Ni et al. [12] reported that FSP of cast NiAl bronze improved the corrosion resistance of the material when placed in a chloride-containing environment. This was attributed to grain refinement and the elimination of porosity, as contained within the non processed casting. However, the application of this process in bioimplants in general, and magnesium-based implants in particular, has not been investigated. Hence, in this work the biodegradation behaviour of a friction stir processed AZ31 magnesium alloy was studied using electrochemical techniques in simulated body fluid.

2 Experimental procedure

AZ31 alloy sheet (Mg–3Al–1Zn–0.2Mn, by wt%) having 1.9 mm thickness was used for this investigation. FSP was performed at the Helmholtz-Zentrum Geesthacht, Germany, using a Tricept TR805 FSW machine. The FSW tool consisted of a 13 mm diameter shoulder coupled to a 5 mm diameter threaded pin. Pin stick out length was 1.7 mm with the tool tilted 1.5° away from the direction of the travel. The tool rotation speed was 1400 rpm and the travel speed was 300 mm/min, with an axial load of 5.5 kN. The microstructure analysis of the untreated and friction stir processed alloy was carried out using a standard metallographic procedure. The samples were etched in a solution containing 3.5 g picric acid, 6.5 ml acetic acid, 20 ml water and 100 ml ethanol, and were examined through optical microscopy.

In vitro degradation studies were carried out in simulated body fluid (SBF) maintained at an equivalent body temperature of 36.5 ± 0.5°C. The chemical composition of SBF can be found elsewhere [13]. The SBF was buffered with tris(hydroxylmethyl)aminomethane (TRIS) at a physiological pH of 7.4. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were used to study the degradation behaviour of the alloy. A potentiostat and a frequency response analyser (Model VersaSTAT3) driven by VersaStudio, and a typical three electrode system, consisting of graphite as a counter electrode, Ag/AgCl (satd. KCl) electrode as a reference electrode and specimen as a working electrode, were used for the electrochemical experiments. The EIS data was analysed using ZSimpWin V. 3.21 software. The samples were ground with SiC paper up to 2500 grit, then polished to 1 μm (alumina powder) followed by washing with distilled water and ultrasonic cleaning in acetone prior to the electrochemical experiments. Potentiodynamic polarisation experiments were carried out at a scan rate of 0.5 mV/sec. The EIS experiments were performed at the open circuit potential with an AC amplitude of 5 mV over the frequency range 10^5–10^{-2} Hz. Prior to the beginning of the electrochemical experiments, the samples were kept immersed in the SBF for 2 h to establish a relatively stable potential.

3 Results and discussion

The micrographs of untreated and friction stir processed AZ31 Mg alloy are shown in Fig. 1. Here the processed alloy demonstrates a finer grain structure as compared to the untreated alloy. This is attributed to dynamic recrystallisation having occurred during processing [14]. A closer look at the micrographs demonstrates that the grain boundaries are more prominent in the untreated alloy as compared to the friction stir processed alloy. This suggests that dissolution of grain boundary precipitates, which homogenises the microstructure, occurs as a result of FSP. This observation is consistent within the literature which suggests that β ($Mg_{17}Al_{12}$) precipitates dissolves during FSW due to the sufficient temperature rise of the alloy during the process [15, 16].

The Nyquist plots of the untreated against the friction stir processed alloy and the equivalent circuit used for fitting the curves is given in Fig. 2a, where R_s corresponds to solution resistance, CPE_{dl} the double layer capacitance, R_t the charge transfer resistance, and R_f and CPE_f represent the film effect. The constant phase elements (CPE) were used in place of pure capacitors to offset the non-homogeneity of the system [17]. The fitting data is presented in Table 1. The untreated and friction stir processed alloy clearly exhibit a high frequency capacitive loop as well as a second mid frequency capacitive loop, which is an indication of the formation of corrosion product layer or passive film [18]. The higher R_f value for the friction stir processed alloy compared to that of the untreated alloy suggests that passivation tendency increases as a result of FSP. Also, the polarisation resistance (R_p) of the samples calculated by adding R_t and R_f [19], revealed that the R_p values for the friction stir processed alloy (200 Ω cm^2) was slightly higher than that of the untreated alloy (170 Ω cm^2). At low frequencies, there was also evidence of an inductance loop for both untreated and friction stir processed alloy. It is widely accepted for magnesium alloys that a low frequency inductance loop is indicative of alloy

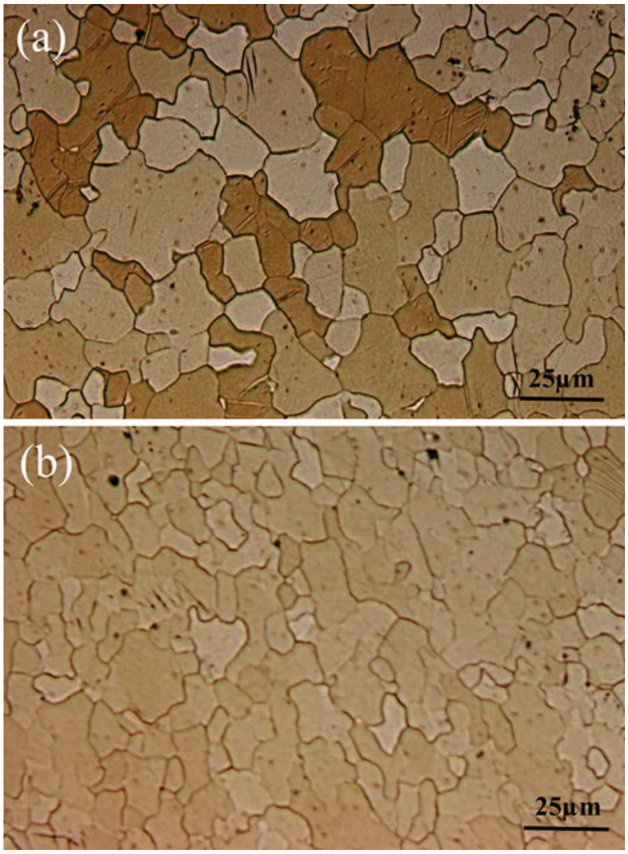

Fig. 1 Optical microstructures of AZ31 magnesium alloy: **a** Untreated and **b** Friction stir processed

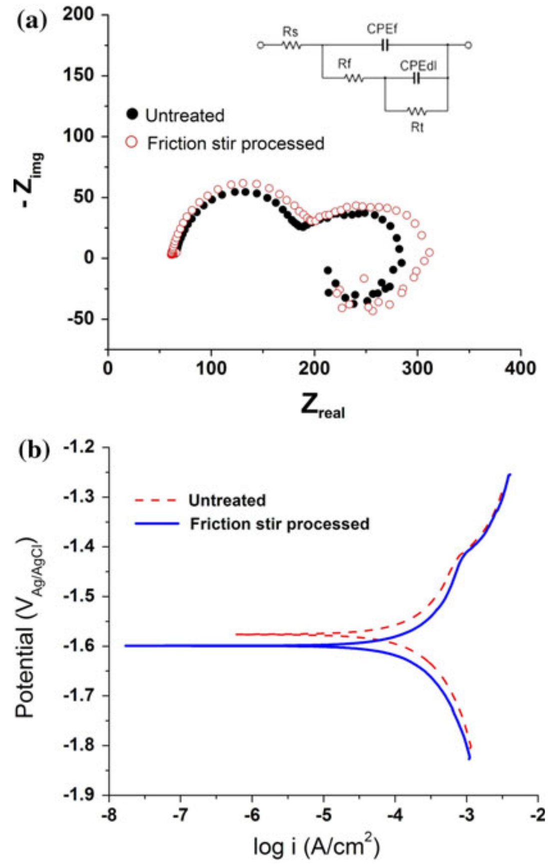

Fig. 2 Electrochemical results of untreated and friction stir processed magnesium alloy in simulated body fluid: **a** Nyquist plots and equivalent circuit; **b** Polarisation curves

susceptibility to pitting corrosion [6, 19]. This suggests that both the untreated and friction stir processed alloy are prone to pitting corrosion.

The polarisation curves for the untreated and friction stir processed alloy are shown in Fig. 2b. The corrosion current (i_{corr}) calculated based on the cathodic curves indicates that the friction stir processed alloy (190 μA/cm^2) was slightly more resistant to degradation than the untreated alloy (210 μA/cm^2). Both the samples revealed a passive-like behaviour in the anodic curves before showing a breakdown. Interestingly, the anodic current of the friction stir processed alloy was slightly higher than the untreated alloy. This could be due to the presence of relatively stable secondary phase particles (β phase) in the untreated alloy. However, the passive-like region was larger by 25 mV after FSP.

Figure 3 shows the SEM micrograph of untreated as opposed to the friction stir processed alloy after potentiodynamic polarisation. Both the samples demonstrate pitting corrosion, which supports the EIS interpretation (i.e., low frequency inductive loop) of the pitting corrosion susceptibility of untreated and processed alloys. However, the nature of pitting attack in the friction stir processed sample was different from the untreated alloy. Here deep pitting was observed in the untreated alloy, whereas in the friction stir processed alloy pitting was relatively shallow. Also, a mud-like cracking texture was distinctive in the untreated alloy, whereas this feature was not observed in the friction stir processed alloy.

The study suggests that FSP marginally enhances the in vitro degradation resistance of AZ31 magnesium alloy. The improvement could be due to the dissolution of β precipitates during FSP which reduces the galvanic corrosion, since β precipitates are cathodic in nature [20] which could enhance the dissolution of anodic matrix. In addition, grain refinement and possible increase in the free aluminium due to β precipitates dissolution might also have contributed to the improvement in the degradation resistance of the alloy. It should be noted that even in AZ31 alloy, which contains small volume fraction of secondary precipitates, there was a noticeable increase in the degradation resistance due to FSP. Hence, it is envisaged that this effect would be more pronounced for magnesium alloys, e.g., AZ91 and

Table 1 EIS fitting results for untreated and friction stir processed alloy in simulated body fluid

Sample	R_s (Ω cm^2)	CPE$_f$ (Ω^{-1} cm^{-2} s^{-n} $\times$ 10^{-6})	n	R_f (Ω cm^2)	CPE$_{dl}$ (Ω^{-1} cm^{-2} s^{-n} $\times$ 10^{-6})	n	R_t (Ω cm^2)
Untreated	51	23.6	0.8921	100	2080	0.880	70
Friction stirred	48	22.7	0.895	115	1823	0.864	85

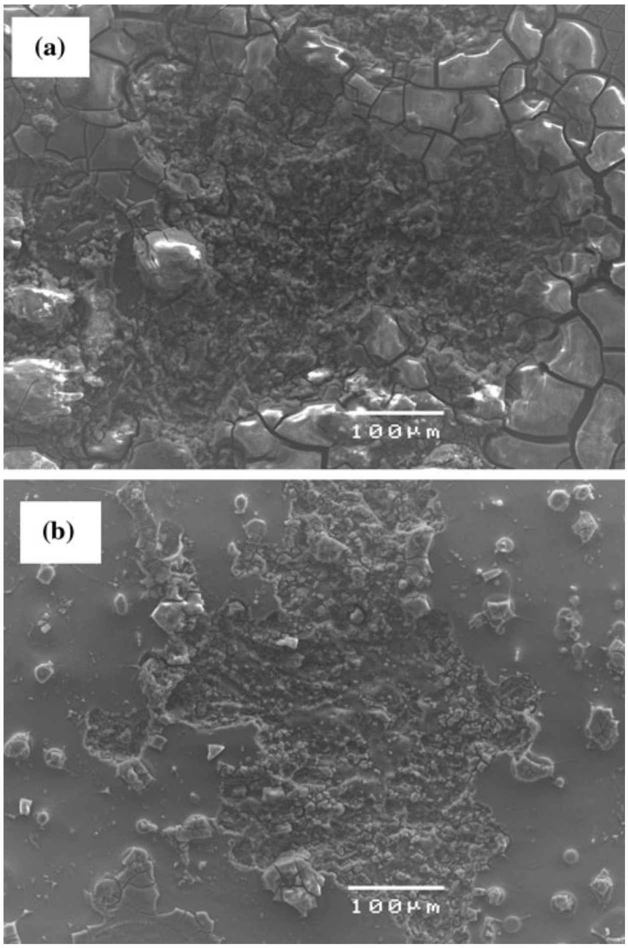

Fig. 3 SEM micrographs of AZ31 magnesium alloy: **a** Untreated and **b** Friction stir processed alloy, after polarisation experiments in simulated body fluid

rare-earth containing magnesium alloys, which contain high volume fraction of secondary phase particles. It is worth mentioning here that a recent study by one of the authors [5], suggests that the die-cast microstructure of AZ91 magnesium alloy may not be suitable for resorbable implant applications due to the high volume fraction of secondary phase particles, which are chemically-stable in body fluid. The results coming from this study, however, would suggest that FSP of AZ91 alloy could be highly beneficial in homogenizing the surface microstructure and further enhancing the degradation resistance of the alloy.

4 Conclusion

Electrochemical impedance spectroscopy and potentiodynamic polarisation studies on a friction stir processed AZ31 magnesium alloy suggest that the processing marginally enhances the in vitro degradation resistance of the alloy. The improvement could be attributed to the homogenisation of the alloy, i.e., dissolution of grain boundary precipitates, and hence reducing the galvanic corrosion effect.

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