Final Draft
of the original manuscript:

Kannan, M.B.; Dietzel, W.; Zettler, R.:

In vitro degradation behaviour of a friction stir processed magnesium alloy

In: Journal of Materials Science: Materials in Medicine (2011) Springer

DOI: 10.1007/s10856-011-4429-x

Biodegradation behaviour of a friction stir processed magnesium alloy

M. Bobby Kannan[a*], W. Dietzel[b], R. Zettler[c]

[a]*Discipline of Chemical Engineering, School of Engineering and Physical Sciences, James Cook University, Townsville, Queensland 4811, Australia*

[b]*Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Geesthacht D-21502, Germany*

[c]*Business Development and Technology Transfer Corporation of Schleswig-Holstein, Geesthacht Branch, Geesthacht D-21502, Germany*

ABSTRACT

In this study, the biodegradation behaviour of a friction stir processed AZ31 magnesium alloy was investigated. electrochemical experiments in simulated body fluid suggest that friction stir processing enhances the degradation resistance of the alloy. Scanning electron microscopy analysis on the investigated alloy reveals that the depth of localized attack decreases when the alloy is friction stir processed. However, quantitatively friction stir processing alone might not solve the issue of high in-vitro degradation of the alloy, but this treatment could be highly beneficial in combination with a biocompatible coating.

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

* Corresponding author.
Tel.: +61 7 4781 5080; fax: +61 7 4781 6788; e-mail: bobby.mathan@jcu.edu.au

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 dissolution of magnesium is known to generate pockets of hydrogen gas near the implant. These are further seen as a potential hazard 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].

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 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 studies 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. Materials and methods

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. Details of the process can be found elsewhere [11]. 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 ± 0.5ºC. The chemical

composition of SBF is listed in Table 1. The SBF was buffered with tris(hydroxylmethyl)aminomethan (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 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, was used for the electrochemical experiments. 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 Hz to 10^{-2} Hz. Prior to the beginning of the electrochemical experiments, the samples were kept immersed in the SBF for two hours 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 [13]. 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 significant dissolution of grain boundary precipitates occurs as a result of FSP, an observation which is consistent within the literature [10]. It was found that FSP of AZ series magnesium alloys dissolve the β ($Mg_{17}Al_{12}$) precipitates and produce a more homogeneous microstructure.

Fig. 2 shows the Nyquist plots of the untreated against the friction stir processed alloy. The equivalent circuit used for fitting the curves is given in Fig. 3, while the fitting data is presented in Table 2 (note: only the capacitive loops were modelled, and 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 [14]. The untreated as opposed to the friction stir processed alloy clearly exhibits a higher frequency capacitive loop as well as a second mid frequency capacitive loop. The R_t and R_f values are slightly higher for the alloy after FSP. It is reported that for magnesium alloys a high frequency capacitive loop corresponds to charge transfer resistance (R_t) and double layer capacitance (CPE_{dl}), while a mid frequency capacitive loop is indicative of the relaxation of mass transport through the corrosion product layer, represented in the equivalent circuit by R_f and CPE_f [15,16]. Hence, 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 [17], revealed that the R_p values for the friction stir processed alloy (200 $\Omega.cm^2$) was higher than that of the untreated alloy (170 $\Omega.cm^2$). 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 susceptibility to pitting corrosion [17]. 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. 4. The E_{corr} value after FSP (-1.600 V) was active by 20 mV as

compared to the untreated alloy (-1.575 V). The corrosion current (i_{corr}) calculated based on the cathodic curves (note: anodic curves were not considered for i_{corr} calculation due to the negative difference effect [18]) indicates that the friction stir processed alloy (190 $\mu A/cm^2$) was slightly more resistant to degradation than the untreated alloy (210 $\mu A/cm^2$). Both the samples revealed a passive-like behaviour in the anodic curves before showing a break-down. Interestingly, the passive current of the friction stir processed alloy was slightly higher than the untreated alloy, however the passivity region was larger by 20 mV after FSP.

Fig.5 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 enhances the in-vitro degradation resistance of AZ31 magnesium alloy. The improvement could be due to the dissolution of β precipitates during FSP, which increases the free aluminium in the alloy and consequently leads to increased passivity of the alloy. In addition, grain refinement might also have played a role in enhancing the stability of the passive film. Although an improvement in the degradation resistance was observed after FSP, quantitatively the improvement is not highly significant. This could be due to the low level of aluminium within the AZ31 alloy. It is envisaged that this effect would be more

pronounced for an AZ91 alloy, where the aluminium content is relatively high compared to the AZ31 alloy. 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 absorbable 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 hence enhancing the degradation resistance of this alloy. In addition, FSP could be used in combination with biocompatible coatings, such as calcium phosphate [7], for achieving higher degradation resistance in magnesium alloys.

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 dissolution of grain boundary precipitates in combination with grain refinement, leading to an increase of free aluminium and pacification of the alloy.

Acknowledgements

The authors would like to express their gratitude to J.F. dos Santos for providing the friction stir processed samples. Thanks are also due to R. Walter and E.Koc for their help in the electrochemical experiments.

References

[1] Witte F, Hort N, Vogt C, Cohen S, Kainer KU, Willumeit R, Et al. Current Opinion in Solid State and Materials Science 2008;12: 63-72.

[2] P.M. Staiger, A.M. Pietak, J. Huadmai, G. Dias, Biomaterials 2006; 27: 1728.

[3] M. Bobby Kannan, R.K. Singh Raman, Biomaterials 2008; 29: 2306.

[4] M. Bobby Kannan, R.K. Singh Raman, Scripta Mater. 2008; 59: 175.

[5] M. Bobby Kannan, Materials Letters 2010;64: 739-742.

[6] R. Walter, M. Bobby Kannan, Materials Letters (In Press)

[7] M. Bobby Kannan, Y. He, A. Sandham, Materials Science Forum 2010;654-656:2196-2199.

[8] M. Bobby Kannan, R.K. Singh Raman, Journal of Biomedical Materials Research Part A 2010;93A: 1050-1055.

[9] K.Y. Chiu, M.H. Wong, F.T. Cheng, H.C. Man, Surface and Coatings Technology 202 (2007) 590-598.

[10] Z.Y. Ma, A.L. Pilchak, M.C. Juhas, J.C. Willams, Scripta Materialia 58 (2008) 361-366.

[11] M. Bobby Kannan, W. Dietzel, R. Zeng, R. Zettler, J.F. dos Santos, Materials Science and Engineering A 460-461 (2007) 243-250.

[12] D.R. Ni, B.L. Xiao, Z.Y.Ma, Y.X. Qiao, Y.G. Zheng, Corrosion Science 52 (2010) 1610-1617.

[13] S.H.C. Park, Y.S. Sato, H. Kokawa, Scripta Mater. 49 (2003) 161.

[14] Fernández-Sánchez C, McNeil CJ, Rawson K, TrAC, Trends Anal Chem 2005;24:37.

[15] Guo LF, Yue TM, Man HC. J Mater Sci 2005; 40:3531.

[16] Zucchi F, Grassi V, Frignani A, Monticelli C, Trabanelli G. J Appl Electrochem 2006; 36:195.

[17] Jin S, Amira S, Ghali E. Adv Eng Mater 2007; 9:75.

[18] G. Song, A. Atrens, Adv. Eng. Materi.1, 1999, 11.

Table 1 Chemical composition of simulated body fluid

Reagents	Amount
NaCl (g)	8.036
$NaHCO_3$ (g)	0.352
KCl (g)	0.225
$K_2HPO_4 \cdot 3H_2O$ (g)	0.230
$MgCl_2 \cdot 6H_2O$ (g)	0.311
1 M HCl (mL)	40
TRIS[a] (g)	6.063
$CaCl_2$ (g)	0.293
Na_2SO_4 (g)	0.072
1 M HCl (mL)	0.2

[a] TRIS = tris(hydroxylmethyl)aminomethane

Table 2: EIS fitting results for untreated and friction stir processed alloy in simulated body fluid

Sample	R_s ($\Omega.cm^2$)	CPE_f ($\Omega^{-1}.cm^{-2}.s^{-n}x10^{-6}$)	n	R_f ($\Omega.cm^2$)	CPE_{dl} ($\Omega^{-1}.cm^{-2}.s^{-n}x10^{-6}$)	n	R_t ($\Omega.cm^2$)
Untreated	51	23.6	0.8921	100	2080	0.880	70
Friction stirred	48	22.7	0.895	115	1823	0.864	85

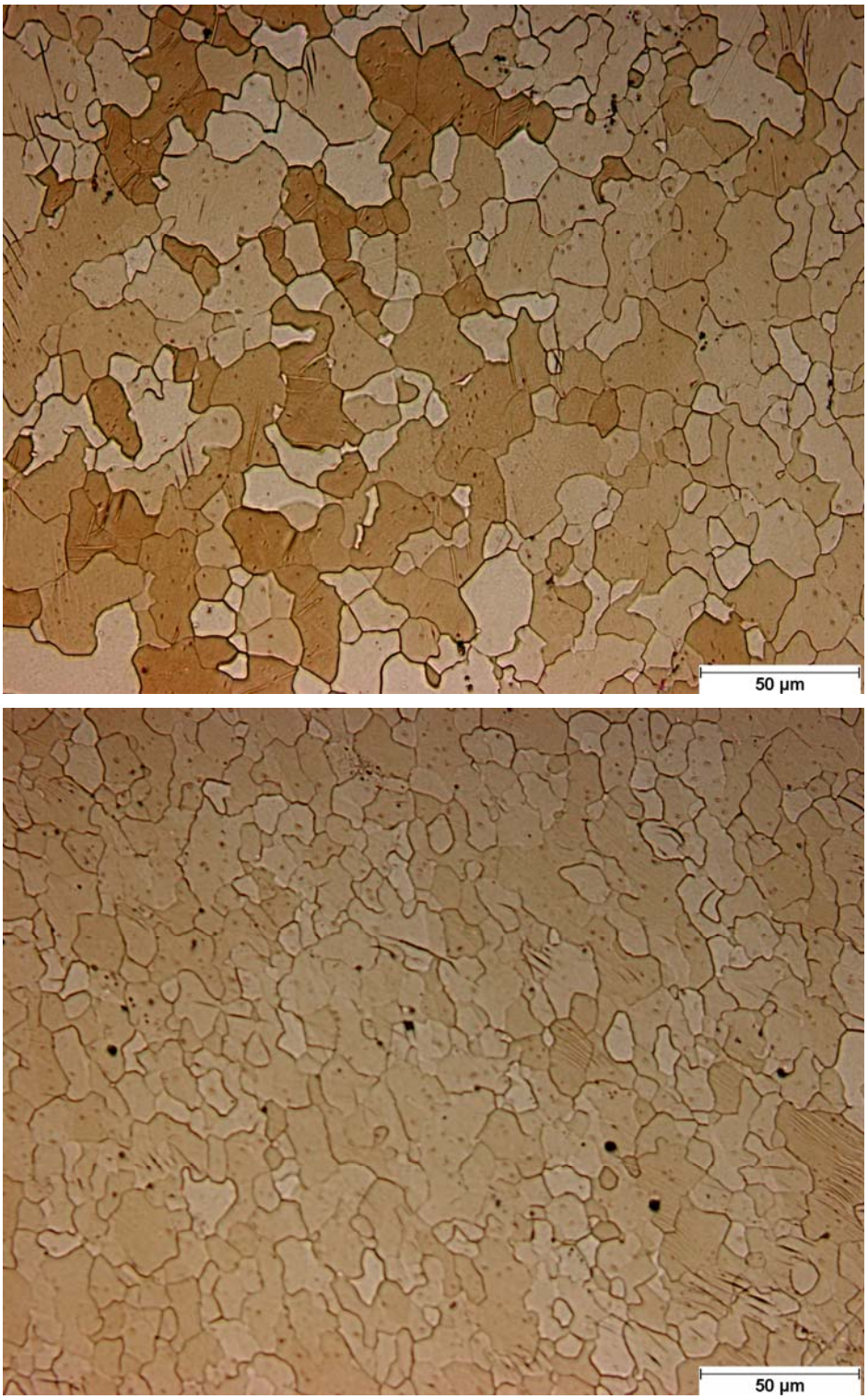

Fig. 1 Optical microstructures of untreated and friction stir processed AZ31 magnesium alloy.

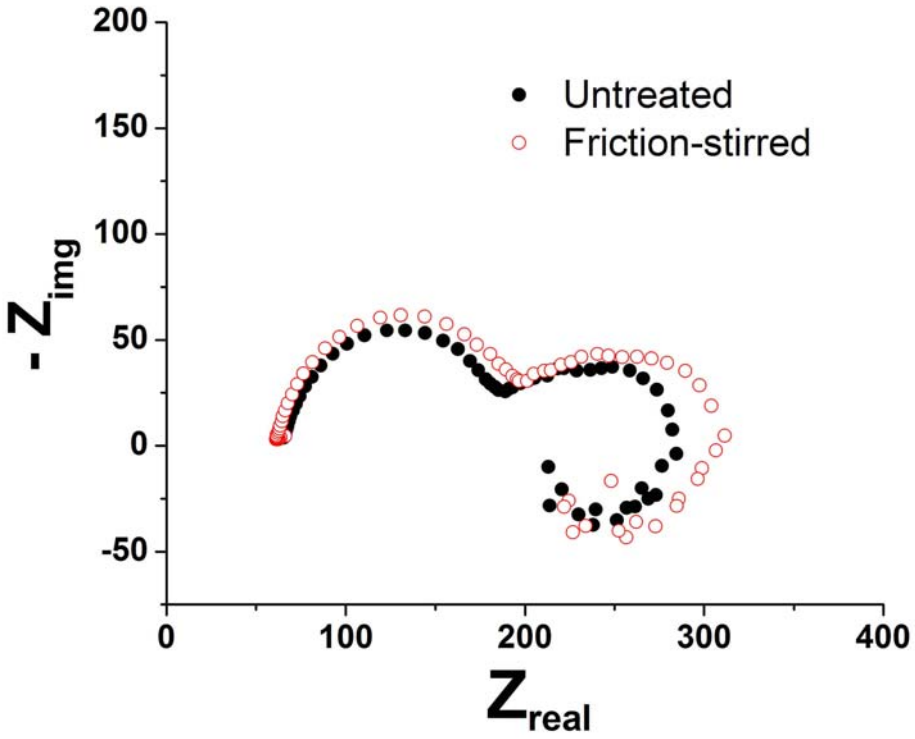

Fig. 2. Nyquist plot of untreated and friction stir processed AZ31 magnesium alloy in simulated body fluid.

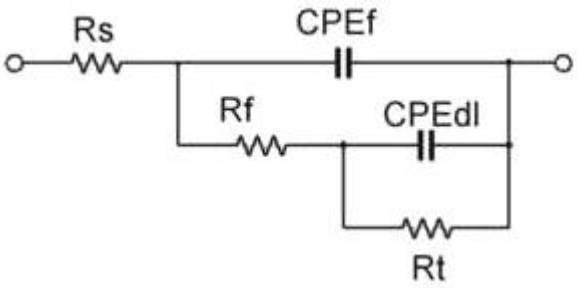

Fig. 3. Equivalent circuit used to fit the Nyquist plot of untreated and friction stir processed AZ31 magnesium alloy.

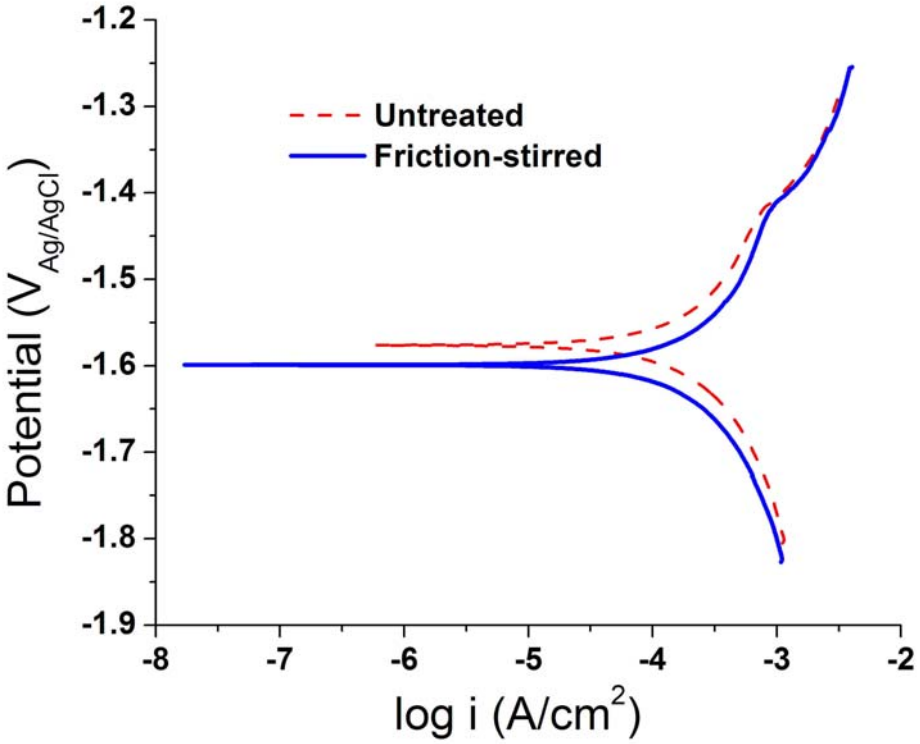

Fig. 4. Polarisation curves of untreated and friction stir processed AZ31 magnesium alloy in simulated body fluid.

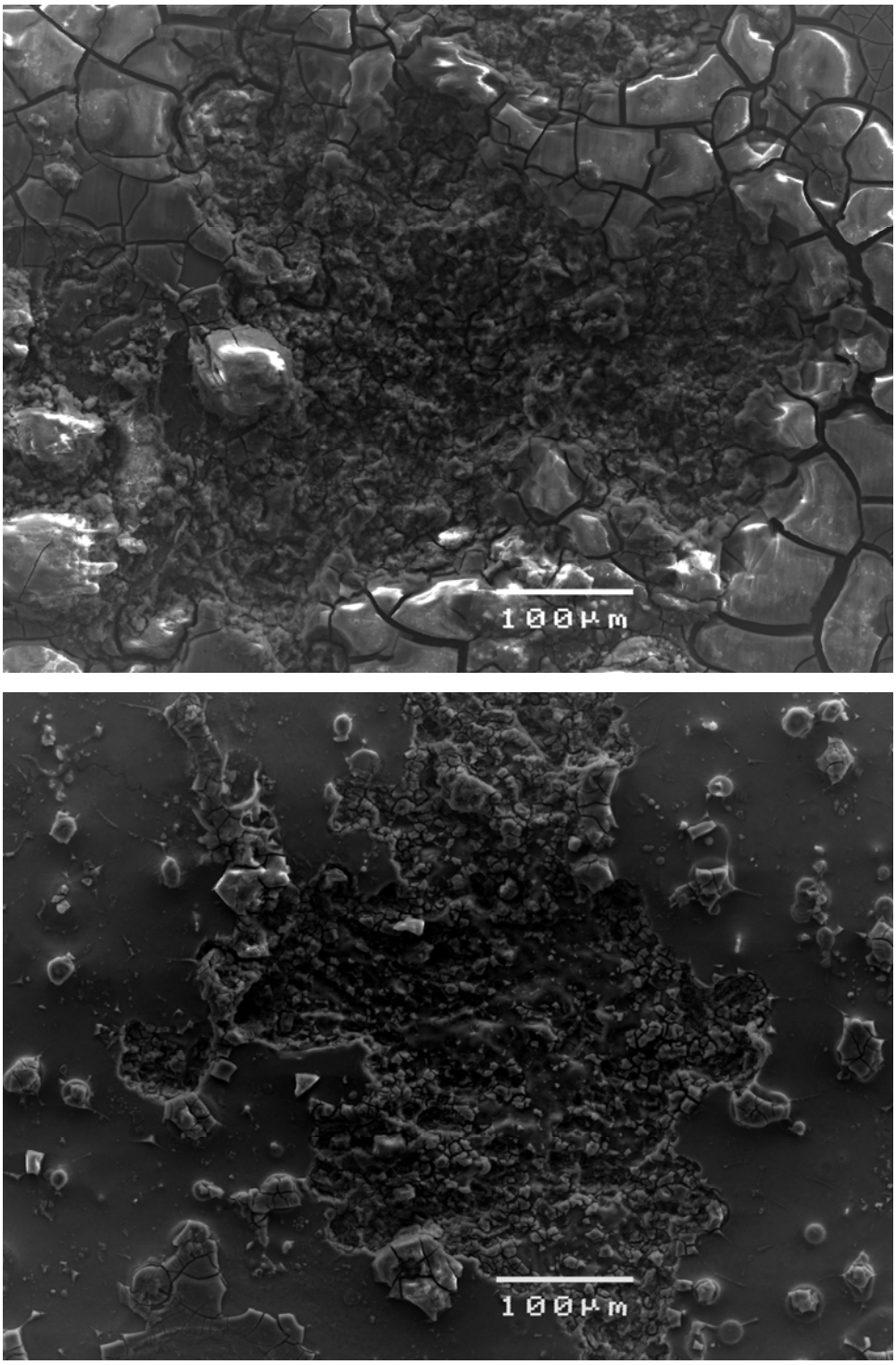

Fig. 5. SEM micrographs of untreated and friction stir processed alloy after polarisation experiments in simulated body fluid.