Microstructural modification of pure Mg for improving mechanical and biocorrosion properties


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ABSTRACT

In this study, the effect of microstructural modification on mechanical properties and biocorrosion resistance of pure Mg was investigated for tailoring a load-bearing orthopedic biodegradable implant material. This was performed utilizing the friction stir processing (FSP) in 1–3 passes to refine the grain size. Microstructure was examined in an optical microscope and scanning electron microscope with an electron backscatter diffraction unit. X-ray diffraction method was used to identify the texture. Mechanical properties were measured by microhardness and tensile testing. Electrochemical impedance spectroscopy was applied to evaluate corrosion behavior. The results indicate that even applying a single pass of FSP refined the grain size significantly. Increasing the number of FSP passes further refined the structure, increased the mechanical strength and intensified the dominating basal texture. The best combination of mechanical properties and corrosion resistance were achieved after three FSP passes. In this case, the yield strength was about six times higher than that of the as-cast Mg and the corrosion resistance was also improved compared to that in the as-cast condition.

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1. Introduction

Magnesium based alloys and especially high-purity magnesium are known to possess excellent biocompatibility and biodegradability (Witte, 2010; Stager et al., 2006; Zhang et al., 2009). However, their biomedical applications are still limited due to some shortcomings including high corrosion rates in the physiological environment. The latter deteriorates the mechanical integrity of the material before tissues would be fully recovered. It has been reported that the purification of Mg could reduce the corresponding corrosion rate. However, the applications of pure Mg in orthopedics and for repairing...
the load-bearing bones are limited by its low yield strength (Cîte et al., 2007). Therefore, it is necessitated to develop Mg-based materials with good corrosion resistance and higher strength for further biomedical applications. Up to date, the development of Mg-based biomaterials has been mainly dealt with alloy modifications. Accordingly, less attention has been paid on applying any processing scheme, which might strongly influence on the mechanical and corrosion properties. Previous studies indicate that the grain refinement would improve mechanical strength and corrosion resistance (Gan et al., 2005; Wang et al., 2007; Ben Hamu et al., 2009; Gao et al., 2011; Alvarez-Lopez et al., 2010; Ralston et al., 2010) as well as bioactivity (Thirunagaram et al., 2010; Ratna Sunil et al., 2014). Different techniques have been employed at elevated temperatures such as extrusion at 350 °C by Han et al. (2013), backward extrusion at 420 °C by Peng et al. (2012), cyclic extrusion compression at 270 °C by Wu et al. (2012), high pressure torsion by Gao et al. (2011), surface mechanical attrition treatment and equal channel angular pressing by Hoog et al. (2008) to improve strength and corrosion resistance via refining the structure.

Following to the above mentioned findings, in the present study the friction stir processing (FSP), as an effective grain refinement method (Mishra and Ma, 2005; Chang et al., 2007; Asadi et al., 2012; Zhang et al., 2008; Mcnelley et al., 2008; Ma, 2008), has been aimed at improving both the mechanical properties and biocorrosion resistance of pure Mg. As well established, this method is capable of inducing a large degree of plastic deformation to a fairly thick surface layer of the material by mechanical stirring action of a rotating tool. Since FSP possesses the extremely high ability of grain refinement, it is a powerful candidate to enhance mechanical properties, corrosion resistance and bioactivity of pure Mg.

Most of the previous research has been conducted to study the effects of FSP on the mechanical properties of specific types of aluminum or magnesium alloys such as AZ31 and AZ91 (Chang et al., 2007; Asadi et al., 2012; Mcnelley et al., 2008). There are only a couple of works on FSP of pure Mg, where some promising results have been reported (Ma et al., 2013; Sunil et al., 2012). Hence, further detailed studies are crucial to clarify the effect of a predetermined FSP scheme on the desired properties. Consequently, this work has been defined to clarify the effects of FSP on the microstructure, mechanical and biocorrosion properties of pure Mg.

2. Experimental methods

2.1. Material and workpiece preparation

The FSP appropriate workpieces were prepared in dimensions of 100 × 50 × 8 mm³ from a commercially pure Mg ingot. The specimens were then friction stir processed (FSPed) using a conventional milling machine adapted for this purpose. A triangle FSP tool with the shoulder diameter of 20 mm was machined from the H13 tool steel. The workpieces were FSPed using single, double or triple passes under predetermined parameters (rotational (ω) and traverse (v) speeds of 1600 rpm and 63 mm/min, respectively). The tilt angle of 2° and the penetration depth (the shoulder intrusion down to the surface) of 0.1 mm were as previously applied in Ahmadkhaniha et al. (2015). The depth of the FSP-treated zone is approximately equal to the length of the tool tip, hence 5.4 mm.

2.2. Microstructural and mechanical properties characterization

FSPed workpieces were sectioned for preparation of metallographic specimens and the pieces were then treated by the standard metallographic procedure including grinding, polishing and etching. The corresponding microstructures were characterized by an optical microscope (OM, model GippanGDCE-30) and scanning electron microscopy with electron backscatter diffraction (SEM-EBSD). Specimens were prepared first by grinding them to 1200 grit, and then mechanically polished to 0.1 µm surface quality, polishing finally with a colloidal silica suspension. Samples were then stored in a vacuum chamber to prevent further contamination. For EBSD studies scanning electron microscope with electron backscatter device was used (Zeiss-Oxford instruments). The EBSD measurements were conducted using the accelerating voltage of 15 kV with an aperture of 120 µm and the working distance of 10 mm. The step size was kept large (between 1 and 4 µm), as the grain size was also relatively coarse.

Texture was analysed by an X-ray diffractometer (Inel-Equinox 3500, with a Mo source, λ = 0.709 Å).

A Vickers microhardness tester (HV-5, Laizhoubuayin testing instrument Co. LTD) was used to determine cross-sectional hardness profiles of the FSPed workpieces (along a line 3 mm below the surface) under an applied load of 200 gf for 10 s. Tensile test specimens were wire cut from the FSPed zone according to Fig. 1 and mechanically polished. An Instron 5585 tensile testing machine was used to determine the tensile properties at room temperature at the strain rate of 10⁻³ s⁻¹.

![Fig. 1 - Dimensions of tensile specimens.](image-url)
2.3. Electrochemical measurements

For electrochemical measurements, the samples were ground up to 1200 grade by emery papers and finally polished, removing about 0.5 mm material from the original surface. The roughness of the final polished surface was $R_a=0.1 \, \mu m$. The samples were washed in ethanol under sonication before starting the electrochemical measurements. They were then, immersed in a Avesta cell into the DPBS's solution containing (in g/l) of 0.20 KCl, 0.20 KH$_2$PO$_4$, 8.00 NaCl, 1.15 g Na$_2$HPO$_4$ (anhydrous), 0.10 MgCl$_2$6H$_2$O and 0.10 CaCl$_2$ at 37 °C. The exposed area of the samples in corrosion tests was a circle with a radius of 0.56 cm ($1 \, cm^2$ exposed area). The electrochemical impedance spectroscopy (EIS) values from 10 mHz to 100 kHz at open circuit potential (OCP) were measured after 96 hours of immersion (using PGSTAT302N, Metrohm Autolab B.V. instrument). A three-electrode electrochemical cell was used along with a saturated Ag/AgCl (3.5 M KCl, 0.205 vs. SHE/V) as the reference electrode and platinum as the counter electrode. The working electrodes were also untreated and FSP treated magnesium. ZSimpwin commercial software (USA) was used to fit the experimental data of the as-cast and FSPed Mg.

3. Results and discussion

3.1. Microstructure

The upper surface of an FSPed sample is shown in Fig. 2a revealing a typical appearance of an even and clean surface with faint oxidation. Fig. 2b shows an OM cross-sectional view of a specimen treated by a single FSP pass. Different zones which are typical features of FSPed samples are exhibited in Fig. 2b. The advancing side (AS) is related to the zone where the directions of the FSP tool rotation and travel are the same and retreating side (RS) assigned for the zone that the directions of FSP tool rotation and travel are opposite. Fig. 2c and d show the corresponding microstructures of different zones in the same workpiece, i.e., the nugget zone (NZ) and thermo-mechanically affected zone (TMAZ). The initial microstructure of the as-cast pure Mg (the base metal) is characterized by very coarse grains, larger than 1 mm (Fig. 2b). On the contrary, as shown in Fig. 2c, the microstructure of NZ is already highly refined by a single pass to the average grain size of about 25 μm. The homogeneous microstructure and grain refinement are due to the occurrence of dynamic recrystallization (DRX), as a result of high plastic strain at high temperature experienced during FSP (Mishra and Ma, 2005). As reported in the literature, severe

Fig. 2 – OM micrographs of FSPed samples (a) surface appearance, (b) overall cross-sectional image, (c) NZ, (d) TMAZ after 1 pass FSP; (e) NZ/TMAZ after 2 passes, and (f) NZ/TMAZ after 3 passes.
plastic deformation induced during FSP results in breaking the prior structure and creating a large number of low angle grain boundaries and misoriented subgrains (Feng and Ma, 2009; Suhuddin et al., 2009). In addition, preferred sites for nucleation of recrystallization are produced. Low angle boundaries transform to high angle ones and then, the fine nuclei grow to perfect grains thereby resulting in a fine equiaxed dynamically recrystallized (DRXed) grain structure.

The TMAZ adjacent of the NZ is shown in Fig. 2d, where the material experiences lesser strains and lower temperatures in comparison to the NZ. The heat affected zone (HAZ) beyond the TMAZ (as is seen in Fig. 2b) has experienced a thermal cycle, but does not undergo any plastic deformation and keeps the same grain structure as the base metal. Fig. 2e and f illustrate the NZ and TMAZ of the 2 and 3 passes FSPed samples, respectively.

Fig. 3 demonstrates the influence of the number of FSP passes on the mean grain size in various locations. According to Figs. 3 and 4, the grains are coarser in the surface layer and TMAZ than in the NZ. Higher frictional heat between the surface and shoulder and lesser strain in TMAZ result in this (Mishra and Ma, 2005). It is seen that the grain size becomes finer with successive passes. However, we can also realize that the difference between the grain sizes after two and three passes is not very pronounced anymore, so that for practical purposes three passes can be taken as the maximum number, the maximum investigated here. In addition, after repeated FSP passes, the grain size frequency distributed in a narrower range at lower values of grain sizes (not shown here), which indicates more intense grain refinement and more homogeneously dispersed equiaxed structure.

3.2. Mechanical properties

Hardness distributions across the FSPed zones are plotted in Fig. 5. The hardness of the as-cast Mg is shown for comparison. The profiles demonstrate that the maximum hardness is reached in the NZ. The hardness is increased by increasing number of FSP passes; obviously related to the grain size refinement (Fig. 3).

As seen in Fig. 5, after the first pass only a small difference can be noticed between the hardness values of the base metal and the treated zones. This differences become more significant with increasing the number of FSP passes. This may be related to higher strain accumulation induced in the treated zones and therefore sharper microstructural variation from the NZ toward the base metal (see Fig. 2d and e).

The tensile stress–strain curves of the FSPed materials are plotted in Fig. 6. For comparison, the flow curve of the unprocessed as-cast Mg is included. Table 1 lists the yield and maximum strength as well as the elongation both in engineering and true values. For the as-cast Mg, the yield strength is very low, followed by a stage with weak strain hardening. Following that, the hardening rate increases so that a “concave-up” stress–strain curve is seen. Such stress–strain behavior is different from those dominated by slip systems, whose hardening rate continuously decreases with increasing strain. It was suggested by Wang and Choo (Wang 2005).
that in an as-cast Mg plastic deformation is dominated by extension-twinning. Evidently, the FSPed materials possess considerably higher strength compared to those of the unprocessed one. This can be attributed to the significantly refined grain size of the FSPed materials. According to Fig. 6 and Table 1, increasing the number of FSP passes results in higher yield strength. A good ductility, higher elongation compared to that in the as-cast Mg after one pass and two passes, is also evident, though decreasing with successive passes.

Fig. 7 shows EBSD images of the NZ in FSPed samples after the first pass and two passes (Fig. 7a and b, respectively) and also the grain boundary misorientation distributions for them (Fig. 7c). High angle grain boundaries (HAGBs) and low angle grain boundaries (LAGBs) were depicted by black and gray lines, respectively. It can be noticed that the grain size, defined to include the LAGBs, is refined from about 15 to 12 μm from the single pass to double pass sample, and to 8 μm after the third pass. Simultaneously the basal texture is intensified, seen in increasing number of red colored grains, by the applied second pass. It can also be realized that the structures are characterized by DRXed grains containing twins with two orientation ranges (Fig. 7c). The twins in the 25–30° range have approximately the same color as the grains where they were formed in, while the other twins with the misorientation close to 90° have a different color respect to the surrounding grain. The latter angle corresponds to the position of reported twins in magnesium: 86°<111\overline{2}> rotation orientation relationship between the {101\overline{2}} tensile twins and the untwinned matrix (Biswas et al., 2010). Double twinning {10\overline{1}1} – {10\overline{1}2} is indicated by with 38° rotation between the twin variants and the untwined matrix (Biswas et al., 2010).

According to Changizian et al. (2012), twinning can have a great influence on DRX in an AZ81 magnesium alloy in hot compression. The twin band related DRX nucleation was mainly attributed to the {10\overline{1}1} – {10\overline{1}2} double twinning. However, where the {10\overline{1}2} extension twinning was the dominant activated type, the nucleation of DRX was mainly assigned to the original grain boundaries. The high density of dislocation tangles in twin-wallied grains within twins make them favorable sites for developing sub-grains. New DRX grains can be formed by in situ evolution of the subgrains with the growth of low angle grain boundaries to high angle grain boundaries (Changizian et al., 2012).

The relatively low stacking fault energy (SFE) of the magnesium alloys (60–78 m2/m2) decreases the chance of cross-slip, and therefore it favors deformation twinning under high-strain rate deformation loading conditions (Saxby et al., 1969). In the hcp structure, deformation twins are formed in the grains resisting basal slip. Twin boundaries are transformed to random HAGBs at high strain due to their interaction with mobile dislocations (Feng and Ma, 2009). Compared with the single-pass sample, two main changes are manifested in the double-pass sample (Fig. 7b): the frequency of mechanical twins (Fig. 7c) and grain size were reduced. A greater propensity for mechanical twinning of larger grains compared to the fine-grained materials has been confirmed previously by many researchers (Wang et al., 2006; Yuan et al., 2011; Guang et al., 2014).

Barnett et al. (2004) argued that there is a critical grain size for the twinning-slip transition. Twinning occurs at the early stages of plastic flow. Despite the limited contribution of twinning itself to the total plasticity, there is a possibility of the reactivation of other slip systems due to the abrupt change in orientation by twinning (Wang and Huang, 2007). When considerable volume fraction of twins formed, second slip and twinning within the primary twins can have a sizeable contribution to the strain and they improved tensile ductility of the FSPed samples, as seen in Fig. 6.

Texture is another microstructural factor, which can strongly affect the plastic deformation in Mg and its alloys (Galiyev et al., 2001; Park et al., 2003). Magnesium alloys generally possess low ductility due to the limited number of independent slip systems (ASM Speciality Handbook, 1999). X-ray diffraction patterns of the surface layers of the as-cast pure Mg and the 2 pass FSPed sample were displayed in our previous paper (Ahmadkhania et al., 2016). From them as well as from Fig. 8, it is observed that the as-cast structure does not exhibit any strong texture. However, FSP has

![Fig. 6 – Tensile flow behaviors of the as-cast and FSPed Mg samples.](image)

<table>
<thead>
<tr>
<th>Table 1 – Engineering and true values of yield strength, maximum strength and elongation of different samples.</th>
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<tr>
<td><strong>Yield strength (MPa)</strong></td>
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<tr>
<td>--------------------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>As-cast Mg</td>
</tr>
<tr>
<td>1 pass FSPed Mg</td>
</tr>
<tr>
<td>2 pass FSPed Mg</td>
</tr>
<tr>
<td>3 pass FSPed Mg</td>
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developed a texture with the basal plane parallel to the upper surface due to the influence of the tool shoulder. With increasing number of FSP passes the intensity of this texture became strengthened, as shown in the figure. In previous studies it has been reported that under the influence of the tool shoulder, the basal planes tend more and more align with the shoulder surface in the upper NZ, i.e., surface layer (Park et al., 2003; Woo and Choo, 2006; Woo et al., 2008). The basal texture results in an additional reinforcement effect when the stress axis is parallel to the basal plane because of the inhibition of the basal slip system as well as the decrease of likelihood of activation of the (1012) (1011) twining system in the tensile direction; thus, the yield strength increases (Suhuddin et al., 2009).

Fig. 7 – Surface EBSD images (orientation map) of (a) single pass, (b) double pass FSPed samples, and (c) grain boundary misorientation distributions. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Fig. 8 – Pole figures of as-cast and FSPed Mg samples in different conditions.
The grain size refinement is always reported to result in increased strength and ductility, but the role of texture seems to be more complex. The activation of non-basal slip systems is crucial for the ductility in Mg and its alloys. Mishra et al. (2008) showed that texture can change the tensile behavior significantly. Mukai et al. (2001) reported that the random texture in a Mg-alloy results in better elongation than that of preferred texturized samples. Ha et al. (2010) also concluded from their data that the random texture results in higher elongation than the basal texture does. Hence, the intense basal texture seems to have a detrimental contribution to ductility. According to the results of Bhargava et al. (2010), if the combination of fine grain size and texture can activate non-basal slip systems, then the strength and ductility are enhanced. del Valle et al. (2015) concluded that the FSP is a flexible processing technique that can improve the ductility and yield strength in the instance of careful selection of the processing parameters.

In the present study, the as-cast pure Mg with the grain size coarser than 1 mm was used as the base material, and its grain size was refined to about 25 μm by FSP. In agreement with common observations in the literature, this grain refinement increased the strength and elongation in the first pass, as shown in Fig. 6. However, in the 2 and 3 passes FSPed samples, the strength increased further but the elongation decreased. The grain size was still reduced slightly, but the basal texture became intensified on the surface of the processed samples, as seen in Fig. 8. Hence, it can be concluded that the alignment of the basal planes parallel to the FSPed surface and tensile direction reduces the activation of possible slip systems and thereby decreases elongation, in agreement with the results in Mukai et al. (2001) and Ha et al. (2010).

Furthermore, the basal planes are characterized by a low SFE (36 mJ m⁻²) (Smith, 2007). Therefore, as the texture approaches closer to basal ones, the type of DRX phenomenon changes from continuous DRX to discontinuous DRX. Due to the low SFE in the basal plane, extended dislocations cannot cross-slip to prismatic/pyramidal planes, whereas the reverse is possible (Biswas et al., 2010). As a result, during the FSP, the dislocation density on the basal planes increases and leads to strain hardening. Therefore, during plastic deformation strain hardening of the basal planes can result in higher strength and lower elongation in 2 and 3 pass FSPed samples.

This effect increases with the number of passes. Considering the aforementioned discussion, it can be concluded that the variation of tensile properties caused by FSP may be attributed to both the changes in the grain size and texture modification.

### 3.3. Electrochemical measurements

Fig. 9a shows the Nyquist curves of the materials after immersion into the DPBS solution for 96 h. The curves exhibit different shapes and diameters suggesting different corrosion mechanisms and rates, as discussed in Ascencio et al. (2014), Ibrahim et al. (2015), King et al. (2014) and Nam et al. (2012). The plot of the as-cast Mg consists of three time constants: the capacitance loop at high frequency, which is related to the charge transfer and oxide film resistance, the middle frequency capacitance loop, attributed to the diffusion of Mg²⁺ ions thorough the corrosion products, and the inductive loop, related to the adsorption of different species (Ascencio et al., 2014; Ibrahim et al., 2015). On the contrary, the Nyquist curves of the FSPed Mg samples show two time constants without the inductive loop. According to Fig. 9a, applying FSP has improved the corrosion resistance of pure Mg revealed by the larger diameter of the loops and two pass FSPed sample has the highest corrosion resistance.

The EIS data were fitted by the equivalent circuit shown in Fig. 9b and the results are listed in Table 2. For better comparison, the inductive loop in as cast Mg was omitted and a constant phase element (CPE) was added in Fig. 9b to model the electrode capacitave behavior. CPE is often used to describe a non-ideal capacitive behavior owing to different factors such as surface roughness and heterogeneities, electrode porosity, slow adsorption reactions or a non-uniform potential and current distribution (Ibrahim et al., 2015; Thomas et al., 2014). In the equivalent circuit, $R_s$ is indicated as the electrolyte resistance between the working and reference electrode. $R_t$ is related to the charge transfer resistance and oxide layer. $CPE_1$ assigned for electrochemical double layer capacitance at the substrate/electrolyte interface. $R_2$ and $CPE_2$ are associated to the diffusion of ions through the corrosion layer. Better protection of the surface by corrosion products results in reduction of adsorption of species and pitting as evidenced by disappearing the low frequency inductive loop in FSPed Mg (Fig. 9a). Therefore, we can realize that higher corrosion resistance is achieved in FSPed Mg than that of the as-cast Mg in agreement with the observation in the previous study for the two passes FSP Mg (Ahmadkhaniha et al., 2016).

Magnesium and its alloys degrade in aqueous environments via the following electrochemical reactions (1) and (2) (Thomas et al., 2014):

![Fig. 9](image-url)
Table 2 – Fitting data for different samples immersed in DPBS after 96 h of immersion.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$R_o$, cm²</th>
<th>$Q_v$, cm² *s⁻¹</th>
<th>$n_1$</th>
<th>$R_o$, cm²</th>
<th>$Q_v$, cm² *s⁻¹</th>
<th>$n_2$</th>
<th>$R_o$, cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>as cast</td>
<td>8.63E+01</td>
<td>3.07E-05</td>
<td>7.74E-01</td>
<td>7.71E-02</td>
<td>7.74E-06</td>
<td>9.20E-01</td>
<td>3.51E+01</td>
</tr>
<tr>
<td>1 pass</td>
<td>7.78E+01</td>
<td>4.98E-05</td>
<td>7.78E-01</td>
<td>2.48E-03</td>
<td>1.73E-03</td>
<td>7.72E-01</td>
<td>8.46E-02</td>
</tr>
<tr>
<td>2 pass</td>
<td>1.02E+02</td>
<td>3.87E-05</td>
<td>7.91E-01</td>
<td>1.09E-04</td>
<td>3.65E-03</td>
<td>9.28E-01</td>
<td>1.79E-03</td>
</tr>
<tr>
<td>3 pass</td>
<td>8.92E+00</td>
<td>2.62E-05</td>
<td>8.20E-01</td>
<td>8.13E-03</td>
<td>2.15E-03</td>
<td>8.42E-01</td>
<td>1.91E-03</td>
</tr>
</tbody>
</table>

Mg → Mg²⁺ + 2e⁻ (1)

H₂O + e⁻ → OH⁻ + 1/2 H₂ (2)

Therefore, magnesium hydroxide is corrosion product of the total corrosion reaction (reaction (3)):

Mg + 2H₂O → Mg(OH)₂ + H₂ (3)

Magnesium hydroxide accumulates on the surface as a corrosion protective layer in water, but when the chloride concentration in the corrosive environment exceeds above 30 mmol/l, magnesium hydroxide starts to convert into highly soluble magnesium chloride according to reaction (4) (Song et al., 2009). Therefore, severe pitting corrosion can be expected in Mg alloys in the body fluid with chloride content of about 150 mmol/l (Song et al., 2009; Atrenslohi et al., 2011; Guan et al., 2000).

Mg(OH)₂ + 2Cl⁻ → MgCl₂ + 2(OH)⁻ (4)

In the DPBS solution, OH⁻ ions reduce H₂PO₄⁻ and HPO₄²⁻ to PO₄³⁻ according to the reactions (5) and (6) (Song et al., 2009):

H₂PO₄⁻ → 2OH⁻ → PO₄³⁻ + 2H₂O (5)

2HPO₄²⁻ → 2OH⁻ → 2PO₄³⁻ + 2H₂O (6)

Then PO₄³⁻ ions can react with Ca²⁺ and Mg²⁺ in the electrolyte and result in formation of calcium phosphate base precipitations according to reaction (7) (Rettig and Virtanen, 2009). The formation of calcium phosphate base precipitations was confirmed by fourier transform infrared spectroscopy in our previous research (Ahmadkhanija et al., 2016).

Mg²⁺ + Ca²⁺ + PO₄³⁻ → Ca₃Mg₆(PO₄)₄ (7)

The corrosion behavior is attributed to the accumulation of calcium phosphate based precipitation, forming a layer that reduces chloride attack. This behavior is evidenced by the second time constant at middle frequency (Fig. 9a). It should be noticed that the product layer on the as-cast Mg surface is not as protective as one on the surfaces of the FSPed Mg samples since the $R_o$ value in the as-cast Mg is significantly lower than in the two and three passes FSPed Mg (see Table 2). The higher $R_o$ values notably result in higher $R_1$ values and consequently enhance corrosion resistance.

Grain refinement results in a larger number of grain boundaries which can relieve corrosion localization. Op’t Hoog et al. (2008) argued that introducing numerous grain boundaries in the bulk material can be an effective way to release the mismatch between the surface layer and the inner bulk and lead to better adherence of passive or oxide layer. Further, they claimed that the oxide layer on Mg is not stable in aqueous solutions owing to high compressive stresses inside the layer. Due to geometrical mismatch between the oxide layer and hexagonal Mg lattice, numerous cracks tend to be formed in the oxide layer.

As well established, the grain boundaries have higher energies than that of grain interiors and they are more chemically active; hence, a high density of grain boundaries enhances the reactivity of the surface by increasing the electron activity and diffusion. The increased reactivity coupled with more numerous sites for the nucleation of oxide layer on the surface of grain refined materials enhance more rapid formation of the protective layer. These results are in good agreements with those reported by Zhang et al. (2012). However, corrosion resistance improvement cannot be attributed just to grain size refinement during FSP, since 3 pass FSPed sample with the finest structure does not hold the highest corrosion resistance (Fig. 9a). Therefore, other microstructural factors in addition to the grain size such as twinning frequency and texture must also be considered. It has to be realized that microstructure in the single pass FSPed material is less homogeneous than that after two and three passes. In addition, a higher fraction of twins were observed after the first pass than after the second pass (Figs. 2c and 7c). Since the twinning stress increases with decreasing grain size, the finer grain size can be the most important factor for the suppression of twinning in Mg FSPed in two or three passes. It was observed by Esfandi Harandi et al. (2011) that irrespective to grain refinement induced by forging, corrosion resistance of Mg-1Ca alloy was reduced due to the intensified twinning. Furthermore, the cathodic process is remarkably accelerated by twinning according to the results of Zhang et al. (2011).

It has been reported that surfaces with the closed-packed basal orientation have the lower surface energy than the surfaces with less compact prismatic planes (Pu et al., 2012; Song and Xu, 2012; Xin et al., 2009; Song and Xu, 2012). Fig. 8 demonstrated that the as-cast Mg consists of coarse grains oriented relatively randomly, but FSP induced the basal texture that became more intense with increasing number of deformation passes. This can be the third reason for higher corrosion resistance of Mg, FSPed in two or three passes. Hence, the 3 passes FSPed Mg has finer structure with more intensified basal texture on the surface, but it demonstrated lower corrosion resistance than 2 passes FSPed Mg. Other microstructural factors such as residual stresses should be examined for further clarifying the corrosion behavior which is the aim of the future study.
4. Summary

Friction stir processing (FSP) was applied to an as-cast commercially pure Mg to investigate the influence of structural refinement on mechanical and biocorrosion properties. The following main results were obtained and conclusions drawn:

1. FSP results in intense refinement of grain size. The finest grain size is formed in the nugget zone. The grain size becomes finer with successive passes applied.

2. The maximum hardness achieved by three FSP passes is more than two times higher than that of the as-cast Mg.

3. Tensile properties are significantly enhanced by FSP. The highest yield and tensile strengths are achieved after three FSP passes (the maximum number studied), the yield strength being about six times higher than that of the as-cast Mg. Refined grain size and basal texture are the enhancing factors. The elongation is also improved significantly by a single pass of FSP, though decreases with further passes.

4. Nyquist curves indicate that after FSP, Mg possesses better corrosion resistance after 96 h of immersion in the DPBS than in the as-cast condition.

5. Homogeneous fine grain size, decrease in twinning frequency and intensified basal texture are the microstructural factors which improve the corrosion resistance in the FSP treated Mg.

The results of the work demonstrate that tailoring the microstructure by applying an adequate degree of deformation by friction stir processing can be an effective method to improve both the strength and biocorrosion properties of pure Mg.

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