Effect of texture and twinning on mechanical properties and corrosion behavior of an extruded biodegradable Mg–4Zn alloy

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Abstract

Microstructure, texture, mechanical properties and corrosion behavior of the extruded Mg–4Zn alloy, as a biodegradable material, were investigated. A refined microstructure caused by dynamic recrystallization (DRX), and a general fiber texture were achieved after extrusion. Mechanical properties along different directions of the extruded samples were investigated using shear punch test (SPT). The shear yield stress (SYS) of 113.8 MPa obtained in the transverse direction (TD) was higher than the 106 MPa achieved for the extruded direction (ED) and 45° samples. This was attributed to the higher amounts of twins and also lower Schmid factor (SF) in the TD. On the other hand, encouraged activation of the basal slip system in the 45° samples resulted in improved room temperature formability, as indicated by the normalized displacement in the SPT diagram. Electron back scattered diffraction (EBSD) analysis of the surfaces corroded in the phosphate buffered saline (PBS) solution, showed that despite having similar grain sizes and second phase particles shape and volume fractions, surfaces containing grains near (0001) orientations and extension twins <1012> (TD and 45° samples) have lower corrosion rates, as compared to the ED specimens.

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1. Introduction

Permanent surgical bio-implants made from Fe, Ti or Co–Cr alloys, can be harmful to human body due to some adverse effects such as: producing toxic ions and wear debris, having a significant difference in their mechanical properties with the neighboring tissue and bone, and needing a second operation for their removal [1]. In contrast, use of biodegradable implants, especially Mg alloys, is a key effort to eliminate surgical and physiological problems [2]. The higher strength of Mg in comparison to polymers, similar elastic modulus of 41–45 GPa to the human bone [3,4], that is pivotal to reduce or avoid shielding effect, non-toxicity as well as necessity of Mg ions in metabolism make Mg alloys suitable choices for biodegradable implants [5].

Despite the above-mentioned beneficial properties, fast dissolution rate and low strength and formability of pure Mg are the main limitations for using it as orthopedic implants. Consequently, various practical methods have been employed to improve properties of Mg-based implants. Use of alloying elements [6], coatings [7], grain refinement, texture engineering thorough thermomechanical processing [8] such as extrusion [5], rolling [9], and severe plastic deformation methods [10] are the possible means for this purpose. Different alloying elements such as Zn [5], Mn [11] and rare earth elements (RE) [12] have been employed to improve mechanical and corrosion behavior of pure Mg. Among the developed alloys, those containing Zn are promising options for bio-engineering purposes because of their improved mechanical characteristics, caused by solid solution and/or precipitation.
strengthening mechanisms [13]. Zn is also capable of creating a thick and stable corrosion product on the surface of implants [14]. Besides, it is a necessary element in physiological processes in the human body that does not make any harmful effect to the cells and surrounding tissues [15].

It has been reported that when the Zn content of the Mg–Zn alloys is about 3–4\%wt, the precipitated Mg–Zn phases can become very fine after extrusion. These phases can pin the recrystallized grain boundaries and restrict the grain growth [16]. However, when the Zn content exceeds the mentioned range, various MgZn intermetallic phases which are more prone to corrosion can form, increasing the corrosion rate of the alloy due to acting as anodic sites [9]. There are several reports about corrosion resistance of the wrought Mg–Zn base alloys. The corrosion current density of 59.3 \( \mu \text{A/cm}^2 \) has been reported for the backward extruded Mg–2Zn alloy tested in simulated body fluid (SBF) [17], while in the case of Mg–6Zn, the corrosion current density was about 45.0 \( \mu \text{A/cm}^2 \) in the same corrosion environment [5]. These high corrosion current density values are in contrast to the lower current density of 39.8 \( \mu \text{A/cm}^2 \) obtained for the rolled Mg–4Zn alloy [18]. It has been also reported that Mg–4Zn–0.2Ca exhibits acceptable cyto-toxicity, which is important to develop biodegradable implants [19].

Owing to the limited slip systems, the properties of the deformed hexagonal closed packed (HCP) materials are very sensitive to the deformation mode and temperature, and thereby, orientation of unit cells that are recognized as texture characteristics [20,21]. Moreover, because of the slip difficulty, twinning is a possible deformation mechanism, particularly in the coarse-grained materials at low temperatures, due to the lower critical resolved shear stress (CRSS) in comparison to the basal slip system [22]. Significant differences have been reported in the strength [23], formability [24] and corrosion properties of Mg alloys [25,26], due to the textural and/or twinning effects. The impact of crystallographic texture on mechanical properties can be explained by some parameters such as Schmid-factor (SF) [27] and also the character of grain boundaries in terms of grain boundary angle [21].

Concerning the directionality of corrosion behavior, it has been suggested that corrosion rate of various crystallographic planes depends on atomic density and atomic bonding strength [25]. This dependency has been reported in different crystal structures. For instance, in FCC materials, it has been shown that (111) planes have higher resistance to corrosion environment [28]. In the case of pure Mg, the corrosion resistance of the basal and other planes can be arranged in the order of (0001) > (1120) > (0110) [29]. In addition to texture, the corrosion behavior of wrought Mg alloys can be affected by twinning. There are, however, some discrepancies in the effect of twinning on the corrosion rate anisotropy, due to the importance of the material dissolution and corrosion product initiation and growth. The influences of texture and twinning on the mechanical properties and corrosion behavior of the binary Mg–Zn alloy system have not been systematically investigated, and therefore, the present study aims at investigating such effects in an extruded biodegradable Mg–4Zn alloy.

2. Materials and methods

2.1. Material preparation

High purity magnesium (99.90\%) and Zinc (99.95\%) were melted at a temperature of 780 °C using a resistance furnace under the protection of a covering flux. After stirring with a stainless steel rod, the melt was held at 780 °C for five minutes before being poured in a cylindrical mold with diameter of 42 mm preheated to 200 °C. The details of melting and casting operations can be found elsewhere [30]. After homogenization of the cast billets at 380 °C for 10h, inductively coupled plasma spectroscopy (ICP-AES) was used to determine the chemical composition of the alloy. The homogenized billets were then extruded with a ratio of 11.5:1 at 350 °C.

2.2. Microstructural characterization

For microstructural, mechanical, and corrosion analyses, 10mm \( \times \) 10mm square shaped samples were cut along various directions, schematically shown in Fig. 1. As can be observed, ED is the surface perpendicular to extrusion direction, TD is parallel to extrusion direction, and 45° is the surface inclined 45° relative to the extrusion axis. Microstructural examination was carried out by Leitz optical and JSM-7600F (JEOL) scanning electron microscope equipped with energy dispersive x-ray spectroscopy (EDS) and electron backscattered diffraction (EBSD) detectors. After grinding with 4000 grit silicon carbide paper and polishing with alumina powder slurry, samples were etched in a nital solution (92ml ethanol, 8ml nitric acid) and then acid picral (6ml ethanol, 2.5ml acetic acid, 2ml distilled water and 0.4g picric acid). Phase identification was performed using a Rigaku Ultima IV X-ray diffractometer with a Cu-K\(\alpha\) radiation (\(\lambda = 1.5406\) Å). Detailed elemental analysis of the second phase particles and corroded surface of samples after electrochemical analysis was obtained using EDS. Grain orientation of different surfaces was determined using EBSD working at an accelerating voltage of 20kV, step size of 0.3\(\mu\)m and sample rotation of 70°. For EBSD analysis, the metallographic specimens were ion beam milled under the voltage of 5kV for 20 min. In addition to analyzing the surfaces of the ED, TD and 45° samples with EBSD after extrusion, this method was used for analyzing the surface of corroded samples for determining the differences between pitting on various planes. The measured data was analyzed using MTEX [31].
2.3. **Mechanical testing**

Due to the unique capability of shear punch test (SPT) in assessing the local mechanical properties of samples with complicated geometries and small dimensions, it would be of some interest to apply this method to the case of biodegradable materials. Accordingly, SPT was implemented on the 0.75–0.8 mm thick slices of the TD, ED and 45° samples, to compare their strength. The details of SPT including the specifications of the designed fixture are given elsewhere [32]. Tests were conducted at room temperature under an initial shear strain rate of \(1.77 \times 10^{-2}\) s\(^{-1}\), using a screw-driven SANTAM universal testing system. The load was measured automatically as a function of punch displacement, and the shear stress was calculated using the following equation

\[
\tau = \frac{F}{\pi Dt}
\]

where \(F\) is the applied load, \(t\) is the specimen thickness and \(D\) is the average of the punch and die diameters. Three different samples were studied in each condition to ensure the validity of results. The microhardness of the tested materials was examined by the Vickers hardness method, in which seven different indentations were made on each sample under a load of 1 N and the results were averaged.

2.4. **Electrochemical measurements**

As two rapid and common methods, polarization and electrochemical impedance spectroscopy (EIS) were accomplished to assess the corrosion properties of different samples in a VersaStat 3 Potentiostat/Galvanostat device. For the simulation of human body environment, a beaker solution containing 100 ml of a phosphate buffered saline (PBS) (pH = 7.4) with chemical composition of 8.0 g/l NaCl, 0.2 g/l KCl, 1.15 g/l Na\(_2\)HPO\(_4\) and 0.2 g/l KH\(_2\)PO\(_4\) in distilled water was used for each specimen. EIS was carried out by applying a sinusoidal perturbation with an amplitude of 10 mV in the frequency range from 100 kHz to 10 mHz. The polarization test was performed using a standard three-electrode configuration including a sample as the working electrode, an Ag/AgCl electrode as the reference, and a platinum electrode as the counter by polarizing the electrode ±250 mV from its open circuit potential (OCP) at a scan rate of 1 mV/s. The cathodic-anodic curve was achieved at a scanning rate of 1 mV/s and the \(I_{\text{corr}}\) and the \(E_{\text{corr}}\) were directly estimated from the extrapolation of Tafel region in the \(E-I\) diagram. The distance between the reference, the counter and the working electrodes (i.e., sample) was about 20 mm for all tests. For these tests, the samples were finely polished to decrease the effect of surface roughness on corrosion behavior, and then ultrasonically washed with ethanol. To analyze a specific surface of a sample, all other faces, were coated with a liquid resist resin and then specimen was exposed to corrosive media.

3. **Results and discussion**

3.1. **Microstructural characteristics and textural evolution**

Optical micrographs of the three surfaces of the extruded material are shown in Fig. 2. It is obvious that all microstructures consist of a uniform equiaxed grain structure of \(\alpha\)-Mg, which has been caused by dynamic recrystallization (DRX) of the homogenized cast structure after hot deformation. The absence of elongated grains parallel to the extrusion direction in the TD surface confirms the occurrence of complete DRX. Another feature of the obtained microstructures is that, while the ED sample structure is almost free from twins, the other two surfaces of TD and 45° contain a high amount of twins. The volume fractions of the twins were measured by using the EBSD orientation map to quantify the fraction of corresponding color by the Clemex vision professional image analysis program. These were found to be 1.1, 5.7 and 14.6% in the ED, 45° and TD surfaces, respectively. In addition, since twins are able to shear the grains, they can result in some heterogeneity in the microstructure, as shown in Fig. 3(a). Analyzing the SEM image and X-ray diffraction (XRD) pattern allowed the exploration of the second phase compounds in the tested samples. SEM micrograph of the ED surface, shown in Fig. 3(a), contains a few MgZn\(_2\) particles with 0.5–2 \(\mu\)m in size both on the grain boundaries and inside the grains. These particles were also detectable in the microstructures of the other two surfaces of the material.

XRD pattern, presented in Fig. 3(b), includes peaks corresponding to \(\alpha\)-Mg and MgZn\(_2\). Low intensity of the detected MgZn\(_2\) phase is indicative of low volume fraction of this phase in the extruded sample. Second phase particles can strongly affect the mechanical properties [33] and corrosion behavior [34] of Mg alloys. In the present study, Mg–Zn particles are able to act as cathode in the corrosion process.
Accordingly, shape, volume fraction, and distribution of the MgZn₂ particles are considered as effective parameters that could influence the overall behavior of the alloy in the corrosive medium. Nevertheless, because of the similarity of these parameters in all surfaces in this study, the role of the particles is scant.

Fig. 4 exhibits the (0001) pole figures obtained for different surfaces of the extruded sample, reconstructed from the EBSD data. Coordinate axes are indicated underneath each pole figure. The results demonstrate that there is a strong rotation of basal plane of Mg lattice around extrusion axis in the ED specimen, creating a component with a maximum intensity of 4.5 that is usually known as fiber texture and has been reported in other Mg alloys [33]. As expected, in the other two samples, the positions of maximum intensity of basal normal direction are rotated relative to the ED. Compared to the ED sample having c-axis slightly parallel to the normal direction (ND), the transverse direction (TD) material showed a strong and simple basal texture with the c-axis deviated about 30° from the center of pole towards the ED. In the case of the 45° specimen, poles are located about 35° to 60° with respect to the ED. The texture intensity in the TD is higher than that in the ED and 45°.

Figs. 5 and 6 illustrate the EBSD inverse pole figure maps and grain boundary misorientation angle distribution histograms of the analyzed surfaces, respectively. The Clemex vision professional image analysis program was used to measure the grain size according to the ASTM E112 standard. Detailed statistical analyses of the EBSD maps and grain size distribution imply that all different surfaces show almost normal grain size distributions with the average grain sizes of 14.6, 13.7 and 15.1 for the ED, 45° and TD samples, respectively. The grain structure data including grain size, volume fraction of HAGBs, DRXed grain percentage, twin fraction, together with mechanical properties are summarized in Table 1. It is evident that all three surfaces show similar behavior in terms of grain size, HAGBs, and DRXed grain percentage. According to the misorientation angle distribution histogram (Fig. 6), a sharp peak is evident at 85–86° which is indicative of the <1012> extension twins in the wrought Mg alloys [35]. The peak at 86° for the TD sample being much sharper than that of the ED and 45° specimens, confirms that the fraction of twins is much higher in this sample. The twin fractions are 1.1, 5.7 and 14.6% in the ED, 45° and TD surfaces, respectively.

3.2. Mechanical properties

SPT is an attractive method for evaluating mechanical properties of materials when they are available in small volumes. This method has found a widespread use in the assessment of mechanical properties of different Mg alloys [27,36,37]. Recently, this method was used to evaluate the mechanical properties of a biodegradable Mg–2Zn–1Gd–1Ca alloy [38]. The SPT curves corresponding to different surfaces of the extruded bar are depicted in Fig. 7. The nature of these curves is similar to the conventional tensile test diagrams, and thus, they can be correlated with such results according to von–Mises yield criterion in the pure shear state [21]. They consist of an initial linear elastic part, the shear yield stress (SYS) corresponding to 1% normalized displacement, and a region of plastic deformation terminated by a maximum point, which is considered as the ultimate shear strength (USS). After this instability point, necking happens and the curves drop to lower levels continuously until fracture occurs. It can be seen that all three samples have similar shear stress-normalized displacement curves, although the highest SYS and USS values are obtained in the TD sample.

As tabulated in Table 1, the SYS of ED, 45° and TD specimens are 106.3, 105.9, 113.8 MPa, respectively. These values are the average of at least three separate samples tested in each direction to confirm reproducibility of the data. One
important feature of this figure is the larger normalized displacement of 0.41 for the 45° sample in comparison to other directions (Table 1). The achieved SYS values are equivalent to the tensile yield stress values of 183.4–197.1 MPa, based on von-Mises criterion. Considering the strength of human long bones of 106–133 MPa [16], it can be deduced that the present extruded Mg–4Zn alloy can be a suitable choice to be used as a bio-implant. Microhardness was performed on the three surfaces of the samples and the obtained results are also shown in Table 1. Similar to SYS and USS values, TD sample possesses the highest hardness of 46.4 Hv, and the hardness of other surfaces show the same trend as those already obtained for the strength of the ED and 45° specimens.

It is well accepted that grain boundaries, solute atoms, second phase particles, dislocation density, SF and twins can all affect the strength of pure Mg [33,39]. The difference between the strength of the ED, TD and 45° samples can be ascribed to the amount of twins, and SF. It is believed that the lower critical resolved shear stress of the basal planes in Mg alloys at room temperature makes it as the predominant slip system compared to those of prismatic and pyramidal planes [40]. Considering the pole figures (Fig. 4), it is obvious that in the ED specimen, the HCP unit cells tend to be located perpendicular to the extrusion axis in such a way that {0001} planes are parallel to ED. The SF for this condition was found to be 0.21, as calculated from the EBSD analysis. In the case of 45° surface, a considerable deviation occurred with respect to the ED and average SF increased to 0.32. Consequently, the activation of basal slip systems will be relatively easier and the SYS of the 45° sample is expected to be lower than that of the ED (Fig. 7). Similar texture softening has been reported for the ZK60 [41] and AM60 [39] Mg alloys after severe plastic deformation, due to the development of a certain type of shear texture component with a higher SF value. Despite the presence of texture softening in the 45° samples, the strength results obtained from SPT, shown in Table 1, indicate a minute difference between the ED and 45° samples, the effect that might be attributed to the formation of twins. Twinning is known to affect the directional properties of Mg alloys.

Although twinning has limited contribution to the total plasticity, the abrupt change in orientation due to twinning may give rise to the reactivation of other slip systems [42]. Twinning acts as an additional barrier to dislocation movement and the stress for slip in the twinned materials is higher than un-twinned regions [43]. The higher volume fraction of twins in the 45° surface can justify the higher strength obtained in this condition. The higher ductility, as indicated by the normalized displacement, of the 45° direction is likely caused by the preferred basal slip in the twinned regions due to the alignment of the basal pole along about 35 to 55° to the loading axis (Figs. 4 and 5). In contrast to the ED and 45° samples, a higher level of strength is obtained in the TD specimen. The enhanced strength can be caused by the placement of the {0001} planes relatively parallel to the surface of the TD specimen (Fig. 4), in which the loading direction is perpendicular to the basal planes. This situation induces hardening due to the limited slip capacity on the basal planes, being confirmed by low SF value of 0.18 for this sample. Another reason for the improved strength is the higher amount of twins (~14.6%) in the TD sample that makes some microstructural inhomogeneity and hinders the

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**Table 1**

<table>
<thead>
<tr>
<th>Analyzed surface</th>
<th>Grain size (μm)</th>
<th>HAGB fraction (%)</th>
<th>DRX (%)</th>
<th>Twin fraction (%)</th>
<th>SYS (MPa)</th>
<th>USS (MPa)</th>
<th>Hardness (Hv)</th>
<th>Normalized displacement (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED</td>
<td>14.6</td>
<td>95.4</td>
<td>92.1</td>
<td>1.1</td>
<td>106.3 ± 1.9</td>
<td>124.8 ± 1.5</td>
<td>44.5 ± 1.2</td>
<td>0.29</td>
</tr>
<tr>
<td>45°</td>
<td>13.8</td>
<td>94.8</td>
<td>91.4</td>
<td>5.7</td>
<td>105.9 ± 0.9</td>
<td>124.1 ± 1.4</td>
<td>44.2 ± 0.8</td>
<td>0.41</td>
</tr>
<tr>
<td>TD</td>
<td>15.1</td>
<td>94.1</td>
<td>85.3</td>
<td>14.6</td>
<td>113.8 ± 2.4</td>
<td>130.5 ± 3.1</td>
<td>46.4 ± 2.2</td>
<td>0.35</td>
</tr>
</tbody>
</table>

![Fig. 5. EBSD orientation maps of the ED, 45° and TD surfaces.](image-url)
dislocation movement. Furthermore, it should be noticed that the volume fraction of DRXed grains in the TD sample is lower than the two other specimens (Fig. 5 and Table 1). This implies that the TD sample contains more deformed regions with low angle grain boundaries in the form of sub-grains that act as obstacles against dislocation movements.

3.3. Corrosion behavior

Fig. 8(a) exhibits the polarization curves, indicating the electrochemical reactions at the electrode–solution interface inside the PBS at ambient temperature. The electrochemical results of all specimens are listed in Table 2. All samples have similar behaviors in terms of cathodic and anodic branches, except that a significantly higher corrosion current density ($I_{\text{corr}}$) of 39.7 μA/cm² is obtained for the ED sample. In the PBS media, corrosion rate of the ED, TD and 45° specimens are 39.7, 28.5 and 21.2 μA/cm², respectively. A higher corrosion rate of 59.3 μA/cm² and more negative corrosion potential of −1.5 V have been reported for the backward extruded Mg–2Zn alloy tested in simulated body fluid (SBF) [16], while in the case of Mg–6Zn, the corrosion rate has been found to be about 45.0 μA/cm² [5]. The observed higher corrosion rates, in comparison with those obtained for Mg–4Zn presented here, can be ascribed to the less stable corrosion products and the higher volume fractions of the second phase particles. A common feature of the polarization curves is a distinct breakdown potential ($E_{\text{b}}$) illustrating the tendency for localized corrosion in the anodic branch of all specimens. This type of behavior has been reported for some other Mg alloys such as AZ31, WE43, ZK60 and ZX60 [44] and Mg–6Zn [5].

EIS as a rapid, nondestructive and sensitive testing procedure can well characterize the corrosion behavior and degradability in term of Nyquist plots. These plots are presented for the tested conditions in Fig. 8(b). Comparison of the plots of the three specimens indicates various number of time constants. Only one capacitive loop is observed for the ED sample, which corresponds to complex processes on the metal surface, including the dissolution and charge transfer processes [45]. Conversely, two larger capacitive loops at both high and low frequencies are recognized for the TD and 45° specimens that are generally attributed to charge transfer, effects of the corrosion products layer, and mass transfer [46]. The impedance at low frequencies displays the polarization resistance ($R_p$) value calculated by adding charge transfer resistance ($R_{\text{ct}}$) and film resistance ($R_f$) [47]. Larger radius of the Nyquist diagram in the 45° sample means lower corrosion rate that is consistent with corrosion current density results. It can be inferred that grain size and second phase particles have limited effects on the corrosion behavior, due to the similar values of these parameters for the three tested samples.

Equivalent circuits (EC) are usually used to propose a model or mechanism for the interpretation of corrosion process. Fig. 9 demonstrates the EC for the ED, TD and 45° samples. These models include some components such as
homogeneity, phase (CPE2) products and with reaction solution (TD).

Fig. 2

<table>
<thead>
<tr>
<th>State</th>
<th>( R_\text{ct} ) (Ω cm²)</th>
<th>( R_1 ) (Ω cm²)</th>
<th>( n )</th>
<th>( R_\text{f} ) (Ω cm²)</th>
<th>( CPE_1 ) (Ω⁻¹ cm⁻² s⁻¹)</th>
<th>( CPE_2 ) (Ω⁻¹ cm⁻² s⁻¹)</th>
<th>( \chi^2 )</th>
<th>( I_\text{corr} ) (μA/cm²)</th>
<th>( E_\text{corr} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED</td>
<td>1207.4</td>
<td>4.683 × 10⁻⁵</td>
<td>0.83</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0047</td>
<td>1207.4</td>
<td>39.7 ± 0.9</td>
</tr>
<tr>
<td>TD</td>
<td>1390.3</td>
<td>3.605 × 10⁻⁵</td>
<td>0.87</td>
<td>374.1</td>
<td>1.590 × 10⁻³</td>
<td>0.0033</td>
<td>1764.4</td>
<td>28.5 ± 1.1</td>
<td>−1.445</td>
</tr>
<tr>
<td>45°</td>
<td>1698.5</td>
<td>3.159 × 10⁻⁵</td>
<td>0.86</td>
<td>682.2</td>
<td>1.205 × 10⁻⁵</td>
<td>0.0025</td>
<td>2380.7</td>
<td>21.2 ± 1.9</td>
<td>−1.476</td>
</tr>
</tbody>
</table>

Table 2
Electrochemical parameters of the tested samples.

Fig. 8. (a) Potentiodynamic polarization curves and (b) Nyquist plots of the tested conditions.

Fig. 9. Equivalent circuit models for the ED, TD and 45° specimens.

solution resistance (\( R_\text{ct} \)). In addition, the \( R_\text{ct} \) related to the reaction at the interface of the PBS and substrate together with CPE1 (electric double layer capacity at the same region) and in the case of TD and 45° samples, \( R_\text{f} \) of the corrosion products layer and the corresponding constant phase element (CPE2) are presented in this figure [48]. Often, a constant phase element acts as a capacitor to compensate for the non-homogeneity in the system. The fitting results are expressed in Table 2. Larger \( R_\text{ct} \) and \( R_\text{f} \) and smaller CPE1 values are obtained for the 45° sample, indicating more resistivity of this sample to corrosive media. For all of the samples, the value of \( n \), which represents deviation from ideal capacitance [48], is greater than 0.8. The chi-square (\( \chi^2 \)) of less than 0.01 indicates a suitable accuracy of the data.

3.4. Surface characterization after corrosion test

The corrosion product morphology of various samples after polarization tests are shown in Fig. 10. This figure discloses a more cracked corrosion-affected surface for the ED and TD in comparison to the 45° sample, which has more integrity that provides better protectiveness. Elemental analysis of the surface corroded layer revealed Mg (32.4 at%) and O (54.5 at%) as the predominant components together with Zn (1.1 at%), P (6.7 at%), Na (3.1 at%) and Cl (2.2 at%). Elemental distribution maps show the distribution of Mg, O, Zn, P, Na and Cl in different regions of the

Fig. 10. SEM micrographs of samples after polarization test.
reaction product (Fig. 11). It is evident that in the cracked region Mg, O and Cl are more available than other elements. This localized cracked structure shows the probability of more severe corrosion under the layer. Among the above mentioned elements, Zn can significantly increase the charge transfer resistance of magnesium and thus reduce the corrosion rate [17]. In addition, it has been suggested that exposing Mg alloy to some biological solutions such as PBS [34] and SBF [4] result in the formation of Mg(OH)₂ on the surface. Furthermore, the presence of high contents of Zn in the alloy and testing in a solution including P element, zinc-containing phosphate may be formed on the surface of magnesium alloy, acting as a protective layer on the surface [49]. Accordingly, Mg(OH)₂ and zinc containing phosphate compounds can protect the Mg–4Zn substrate against PBS penetration.

The influence of crystallographic orientation on the corrosion behavior of the 45° sample, which is the most corrosion resistant condition, was examined by EBSD. EBSD orientation map of this sample after immersion in the PBS for 2 min is presented in Fig. 12. As inferred from this figure, basal planes are more corrosion-resistant than the pyramidal and prismatic planes. The severity of pitting on the surface of different grains with different orientations can be recognized as black points. According to the color key, the grains with red or orange color, indicating the near {0001} orientations, are more stable than the blue or green grains which correspond to {1210} and {0110} orientation, respectively. The respective surface energies for the (0001), {1010} and {1120} planes of Mg have been found to be $1.54 \times 10^4$, $3.04 \times 10^4$ and $2.99 \times 10^4$ J/mol, indicating that the (0001) surface in Mg possesses the lowest surface energy, and thus, this plane should be dissolved more slowly [50]. The measured corrosion rates of the various crystallographic planes of Mg has shown that the corrosion resistance of the surface mainly consisting of (0002) basal planes was about 18–20 times higher than that of (0110) and (1120) prismatic planes [51].

Fig. 11. Elemental analysis of the corroded ED sample.

Fig. 12. EBSD image of the 45° specimen after immersion in PBS. Twins are marked by arrows.
Increased number of activated atoms in the twinning planes, and stress concentration at grain-twin interface have adverse effects on the corrosion resistance [52]. However a compact oxide layer on the twinning plane can be formed that improves corrosion resistance [53]. Considering the role of twinning, it seems that an optimum volume fraction of twins is preferred to improve corrosion behavior of the Mg–4Zn alloy. The effect of twinning on retardation of corrosion rate is dependent on the majority of crystallographic planes (prismatic, pyramidal or basal), inside of which twinning happened [54]. In the case of Mg–4Zn, it is evident that higher volume fraction of twins and more resistant basal planes in the TD and 45° samples are effective to reduce corrosion rate compared to ED, but an optimum amount of twins is necessary to achieve the best resistance. It can be inferred from Fig. 12 that the grains containing twins, marked by arrows, have been slightly corroded, in comparison to other similarly oriented grains without twins.

4. Conclusions

The effects of texture on the mechanical properties and corrosion behavior of an extruded Mg–4Zn alloy was investigated. The most important conclusions are summarized as bellow:

1. The three surfaces of the extruded sample showed uniform microstructures with similar recrystallized grain sizes but different twinning volume fractions.
2. Shear strength in different directions was influenced by the texture component and volume fraction of twins. Higher shear formability of the 45° specimen was attributed to a higher Schmid factor of 0.32.
3. EBSD analysis of the corroded surfaces revealed the superior corrosion resistance of the (0001) planes. Due to the similarity of grain sizes and second phase particle sizes and volume fractions, the observed corrosion behavior can be ascribed to the twinning and crystal orientation effects.
4. An optimum volume fraction of twins (5.7%) was found to be necessary to improve the corrosion resistance of the Mg–4Zn alloy, achieved in the 45° sample.

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Declaration of Competing Interest

None.

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