Effects of zirconium and nitrogen plasma immersion ion implantation on the electrochemical corrosion behavior of Mg–Y–RE alloy in simulated body fluid and cell culture medium

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B. XPS
B. Ion implantation

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1. Introduction

Stainless steels, titanium-based, and cobalt–chromium-based alloys are common metallic biomaterials due to their combination of high mechanical strength and fracture toughness. However, most metallic biomaterials are not naturally degradable. In this respect, biodegradable implants are attractive in some applications because a follow-up surgery to remove the biomedical implants can be eliminated. Some commercial polymeric materials such as polydioxanone (PDS), polyglycolic acid (PGA), and polylactic acid (PLA) are biodegradable [1,2], but many common polymeric materials such as polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyglycerol (PG), and polyvinyl chloride (PVC) are not biodegradable [3]. Mg is a biodegradable metal and also an essential element in the human body. Furthermore, the density of Mg alloys ranges from 1.74 to 2.0 g/cm³ that is similar to that of human bones [1.74–2.0 g/cm³] and their Young’s modulus (GPa) of 41–45 is also closer to that of human bones (3–20 GPa) compared to Co–Cr alloys (230 GPa), hydroxyapatite (73–117 GPa), stainless steels (189–205 GPa), and Ti alloys (110–117 GPa). The better mechanical match reduces the stress at the implant/bone interface and can potentially induce rapid new bone growth and increase the implant stability [4]. Mg also plays an important role in bone growth, is an essential cofactor in different enzymes, and stabilizes the structures of protein and DNA [5]. However one of the major problems associated with Mg biomedical implants is the poor corrosion resistance as Mg is highly reactive and especially vulnerable in a physiological environment with large chloride concentrations [4,6–8].

In order to improve the surface corrosion resistance while preserving the biodegradability, alloying and surface modification are viable options. Various Mg alloys such as Mg–RE [7,9,10], Mg–Zn [11], Mg–Ca [12], Mg–Sr [13], Mg–Al–Zn [7], Mg–Nd–Zn–Zr [14], and Mg–Zn–Mn [15,16] have been developed and studied. In particular, Mg–Zn alloys have attracted much attention. Zn is an essential element in the human body and also plays an important role in the formation of bone [17]. The corrosion characteristics of Mg–Zn alloy have been compared to those of pure Mg [16]. Mg–Zn alloy shows small corrosion resistance enhancement in the early stage and the improvement is more noticeable in the later stage. However, galvanic corrosion can occur between the alloying element and Mg substrate as its standard electrode potential is −2.372 V which is comparatively more negative than other elements. The galvanic effect can be explained by the following relationship [18]:

\[ I = (E_c - E_{Sub})/(R_{Sub} + R_{P(C)} + R_s + R_{sub-c}) \]  

where \( E_c \) represents the corrosion potential of the cathode, \( E_{Sub} \) represents the corrosion potential of the anode, \( R_{Sub} \) and \( R_{P(C)} \)
represent the polarization resistance of the anode and cathode, respectively, \( R_s \) indicates the electrical resistance of the electrolyte, and \( R_{sub-c} \) represents the electrical resistance between the anode and cathode. To improve the corrosion resistance the galvanic current \( (i) \) should be smaller. There have been other studies on Mg–RE [7,9,10].

The other alloying element, Y, in Mg–RE is believed to play an important role in the corrosion resistance because Y has a standard electrode potential \((-2.372 \, V)\) similar to that of Mg. Mg–Y–RE (WE43) which is commercially available has been used in biodegradable stents. It has reduced restonosion rates compared to stainless steel stents and also possesses suitable antiproliferative and mechanical properties [19,20]. Witte et al. [7] have observed that WE43Mg alloy degrades entirely in 18 weeks in vivo. The corrosion behavior of pure Mg, Mg alloys, and surface modified Mg and Mg alloys has been evaluated by measuring the hydrogen evolution, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies [8,16,21–24]. Hydrogen evolution is a simple and quantitative method to determine the corrosion rate of Mg and Mg alloys and EIS is a useful and non-destructive technique to determine the corrosion resistance and mechanism.

Surface modification is a common method to improve the properties of Mg and Mg alloys [18]. Plasma immersion ion implantation (PIII) is especially promising because of the conformal nature and that selective surface properties can be optimized while the favorable bulk attributes can be preserved [18,25,26]. Liu et al. [27] and Zhao et al. [10,28] plasma implanted Ti and Al into Mg alloys and observed improved corrosion resistance as a result of the formation of TiO2 and Al2O3 layers on the surface. Wang et al. [29,30] plasma implanted Ta and Y into Mg alloy and also achieved better corrosion resistance because of the formation of a surface oxide layer. Xu et al. [31] plasma implanted Cr into Mg alloy and the enhanced corrosion resistance stemmed from the formation of chromium oxide on the surface. Zn and Si which is also important to bone formation [17,32,33] have also been plasma implanted into Mg and its alloys [9,34]. Zn ion implantation induces more rapid degradation because of the galvanic effects between Zn and Mg, but Si ion implantation improves the corrosion resistance because of the silicon oxide layer on the surface. Zr compounds are used in dental and orthopedic devices [35,36] as well as knee and hip replacements [37,38]. Our recent studies reveal enhanced corrosion resistance, cytocompatibility, and anti-microbial properties after Zr and O plasma treatment on Mg alloys [39,40]. The biological effects of nitrogen plasma treatment have also been studied. Nitrogen plasma treatment enhances osteoblast adhesion and early proliferation on poly[butylen succinate] [41], mesenchymal stem cell adhesion and their proliferation on poly-tetrafluoroethylene [42], and the corrosion resistance and in vitro and in vivo biocompatibility of Ti6Al4V alloy [43]. In addition, nitrogen plasma immersion ion implantation improves the corrosion resistance of Ni–Ti alloy in simulated body fluid (SBF) [44] and nitrogen plasma treatment of stainless steel stents introduces a high degree of covalent immobilization of human tropoelastin protein molecules consequently improving both endothelial cell proliferation and blood compatibility [45]. The high degree of covalent immobilization of bioactive proteins and extended retention of bioactivity on the surface of the nitrogen plasma treated samples have been observed [46] and Zr with N compounds possess good antibacterial activity as well [47]. Hence, the combined zirconium and nitrogen plasma treatment improves the corrosion resistance and enhances the biocompatibility of biomaterials, but the effects of dual Zr and N plasma treatment on the corrosion behavior of WE43Mg alloy have not been studied systematically. Therefore, in this work, the synergetic effects rendered by dual Zr and N PIII on the corrosion resistance of WE43Mg alloy are investigated in details in SBF and cell culture medium.

2. Experimental details

2.1. Plasma surface modification and characterization

As-cast WE43 plates (Mg with Y 4 wt.% and Nd 3 wt.%) having dimensions of 10 mm × 10 mm × 5 mm were used substrates. The samples were ground with SiC papers of different grit size, mechanically polished to a mirror finish using 1 μm alumina paste, cleaned ultrasonically in ethanol, and dried by compressed air. The samples were subjected to two plasma treatments, namely Zr plasma ion implantation followed by N PIII. The schematic diagram of the PIII process is shown in Fig. 1 and more details about the process can be found from our previous paper [25]. Zr plasma ion implantation was performed on the HEMII-80 ion implanter (Plasma Technology Ltd.) equipped with a zirconium cathodic arc source at 25 kV for 20 min and a base pressure of 8.0 × 10⁻⁶ Pa. N PIII was conducted on the GPI-100 ion implanter for 3 h at 8 kV (RF power = 1000 W, pulse width = 20 μs, pulse frequency = 80 Hz, nitrogen flow rate = 20 sccm, and base pressure = 10⁻⁶ torr). The elemental depth profiles and chemical states were determined by X-ray photoelectron spectroscopy (XPS) with Al Kx irradiation. The sputtering rate was estimated to be about 26 nm/min based on the analysis of a standard SiO2 film under the same conditions.

2.2. Electrochemical studies

The corrosion behavior of the untreated WE43Mg alloy (UT-WE43) and Zr & N plasma implanted WE43Mg alloy (ZrN-WE43) was assessed in simulated body fluid (SBF) and complete cell culture medium at 37 °C by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) conducted on the Zahner Zennium electrochemical work station. More details about the electrochemical experiments can be found from our previous papers [9,16,48,49]. The SBF used in this study had inorganic ion concentrations similar to those in human body fluids. The ionic concentrations (in mM) were: 142.0 Na+, 5.0 K+, 1.5 Mg2+, 2.5 Ca2+, 147.8 Cl⁻, 4.2 HCO3⁻, 1.0 HPO4²⁻, and 0.5 SO4²⁻. The SBF was prepared from the following reagent grade chemicals: 8.035 g/l NaCl, 0.355 g/l NaHCO3, 0.225 g/l KCl, 0.231 g/l K2HPO4, 3H2O, 0.311 g/l MgCl2·6H2O, 1.0 M HCl (39 ml), 0.292 g/l CaCl2, 1.0 M H2SO4 (39 ml), and 3.0 M HCl (39 ml).

![Fig. 1. Schematic diagram of the plasma immersion ion implantation process.](image-url)

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and 0.072 g/l Na₂SO₄ in distilled water and buffered at pH 7.4 using trishydroxymethyl aminomethane (TRIS, 6.118 g/l) and 1.0 M HCl [50]. The complete cell culture medium used in this study consisted of a mixture of Dulbecco’s modified eagle medium (DMEM) and 10% fetal calf serum. The DMEM powder was bought from Life Technologies Corporation and its composition [49] (in mg/L) was:

2.2.1. Amino acids
30 Glycine, 84 l-Arginine hydrochloride, 63 l-Cystine 2 HCl, 584 l-Glutamine, 42 l-Histidine hydrochloride·H₂O, 105 l-Isoleucine, 105 l-Leucine, 146 l-Lysine hydrochloride, 30 l-Methionine, 66 l-Phenylalanine, 42 l-Serine, 95 l-Threonine, 16 l-Tryptophan, 104 l-Tyrosine disodium salt dehydrate and 94 l-Valine.

2.2.2. Vitamins
4 Choline chloride, 4 l-Calcium pantothenate, 4 Folic acid, 4 Niacinamide, 4 Pyridoxine hydrochloride, 0.4 Riboflavin, 4 Thiamine hydrochloride and 7.2 l-Insotiol.

2.2.3. Inorganic salts
200 Anhydrous CaCl₂, 0.1 Fe(NO₃)₃·9H₂O, 97.67 anhydrous MgSO₄, 400 KCl, 6400 NaCl and 125 NaH₂PO₄·H₂O.

2.2.4. Other components
4500 d-Glucose (Dextrose) and 15 Phenol red.

The DMEM was prepared with the powder using distilled water and NaHCO₃ (3.7 g/l). The completed cell culture medium (DMEM + 10% fetal calf serum) was designated as cDMEM in this study. The electrochemical experiments were carried out using a conventional three electrode cell. The UT-WE43 and ZrN-WE43 formed the working electrode with the platinum sheet and saturated calomel electrode (SCE) serving as the counter and reference electrodes, respectively. Only 1 cm² of the UT-WE43 and ZrN-WE43 samples was exposed to the SBF and cDMEM. Potentiodynamic polarization was performed followed by EIS measurements at a scanning rate of 1 mV/s in the potential range between −250 mV in the cathodic direction and +500 mV in the anodic direction from their respective open circuit potentials (OCPs). By means of Tafel extrapolation, the corrosion potential (E_corr) and corrosion current density (i_corr) were calculated. The impedance spectra were recorded at their respective OCPs after stabilizing in SBF and cDMEM for 3 min by applying a sinusoidal perturbing signal of 10 mV (root mean square) in the frequency range between 10 kHz and 100 mHz. The EIS parameters were determined using ZsimpWin 3.21 software from the Nyquist plots. The Bode impedance and Bode phase angle plots were also recorded.

2.3. Corrosion product analysis
The surface morphology of the corrosion product after polarization studies in SBF and cDMEM was examined by scanning electron microscopy (SEM, JEOL JSM-820) and the elemental composition of the corrosion product was determined by energy-dispersive X-ray spectroscopy (EDS).

3. Results and discussion
The XPS depth profile of Zr-N WE43 is depicted in Fig. 2. The high-resolution Zr 3d, Mg 1s, Y 3d, O 1s, and N 1s XPS spectra of the ZrN-WE43 are depicted in Fig. 3. The ZrN-WE43 sample (Fig. 2) does not show a Gaussian Zr distribution but instead a Zr rich layer about 53 nm thick. Fig. 2 discloses a Gaussian shape N peak in the ZrN-WE43 with a thickness of about 66 nm. The high-resolution XPS spectra of Zr 3d in Fig. 3(d) shows that the binding energy of Zr 3d⁶5/₂ is 182.2 eV arising from Zr⁴⁺ and suggest that ZrO₂ is formed on the surface [51]. The high-resolution spectra show a broad peak at a depth of about 13 nm due to the presence of zirconium oxide and nitride [52]. The shift of the Zr 3d peak towards smaller binding energy is observed from the high-resolution XPS spectra in Fig. 3(d) revealing that Zr⁴⁺ corresponding to nitride changes gradually to Zr⁶⁺ with depth and only metallic Zr is observed at a depth of about 79 nm. The high-resolution XPS spectra of Mg 1s in Fig. 3(a) of the ZrN-WE43 show that Mg exists in the possible form of MgO and/or Mg₃N₂ [53,54] and the shift of the Mg 1s peak towards smaller binding energy suggests that Mg exists changes gradually to Mg⁰ with depth and at a depth of about 53 nm, only the metallic state is observed.

The open circuit potential of the UT-WE43 and ZrN-WE43 samples immersed for 180 s in SBF and cDMEM are depicted in Fig. 4. Compared to the UT-WE43 samples (−2028 mV vs SCE in SBF and −1997 mV vs SCE in cDMEM), the ZrN-WE43 samples (−2008 mV vs SCE in SBF and −1894 mV vs SCE in cDMEM) show shifts in the potential towards the noble direction. In SBF and cDMEM, both UT-WE43 and ZrN-WE43 show potential shifts towards the noble direction with respect to time and the extent of the potential shift is more pronounced for ZrN-WE43. After immersion for 180 s, UT-WE43 shows potential shifts of about 143 mV vs SCE and 63 mV vs SCE in SBF and 63 mV vs SCE in cDMEM, respectively, whereas ZrN-WE43 exhibits potential shifts of about 285 mV vs SCE and 312 mV vs SCE in SBF and cDMEM, respectively. The shifts towards the noble direction and more pronounced potentials shift over time observed from ZrN-WE43 suggest that it is better protected than UT-WE43 in SBF and cDMEM.

The Nyquist plots of UT-WE43 and ZrN-WE43 after immersion in SBF and cDMEM for 180 s are depicted in Fig. 5. The Nyquist plots acquired in SBF (Fig. 5a) show three well defined loops suggesting three time constants, but the diameters of the capacitive loops are different suggesting different corrosion rates. Xin et al. [55] observed three time constants from the untreated and coated AZ91Mg alloy in SBF and Jamesh et al. [16,56] observed three time constants from the untreated and coated AZ91Mg alloy immersed in Ringer’s solution as well as for pure Mg immersed in SBF. Song et al. [57] determined three time constants for AZ31Mg alloy immersed in SBF and Srinivasan et al. [58] observed three time constants from the untreated and polymer treated AZ31Mg alloy in SBF.

The capacitive loop in the higher frequency region is associated with the charge transfer resistance. This is because of the resistance during electron transfer in the Faradic process in parallel to the double layer capacitance at the interface between the surface of the metal and SBF. The medium frequency capacitive loop is attributed to mass transport in the solid phase arising from ion diffusion through the corrosion product layer. The inductive loop in
the lower frequency is attributed to the adsorption process. The equivalent electrical circuit obtained by fitting the EIS spectra of UT-WE43 and ZrN-WE43 in SBF are displayed in Fig. 6a. In the equivalent electrical circuit, \( R_S \) represents the solution resistance and \( R_1 \) indicates the charge transfer resistance. The constant phase element (CPE1) is used instead of the double layer capacitance (\( C_{dl} \)) because the Nyquist plots of UT-WE43 and ZrN-WE43 in SBF show depressed semicircles. \( R_2 \) indicates the resistance and CPE2 represents the capacitance of the corrosion product layer. \( L \) indicates the inductance and \( R_L \) is the inductive resistance. However, the Nyquist plots of UT-WE43 and ZrN-WE43 in cDMEM (Fig. 5b) show two well defined loops suggesting two time constants, but the diameters of the capacitive loops are different indicating different corrosion rates. Wu et al. [14,23] observed two time constants from the Mg–Nd–Zn–Zr alloy immersed in SBF and 0.9% NaCl solution and Wu et al. [49] also determined two time constants for the untreated as well as aged Mg–Al–Zn–Mn alloy immersed in the complete cell culture medium. Zhao et al. [59] found two time constants from the untreated and heat treated AZ91Mg alloy immersed in the complete cell culture medium and Badawy et al. [60] observed two time constant from the Mg, Mg–Al–Zn and Mg–Al–Zn–Mn alloy in aqueous acidic and neutral solutions. Similarly, Luo et al. [61] observed two time constant from the AZ91Mg alloys containing Y in 0.35% NaCl solution. The higher frequency capacitive loop is associated with the charge transfer resistance. The lower frequency capacitive loop is attributed to mass transport in the solid phase arising from ion diffusion through the corrosion product layer. The EIS spectra of UT-WE43 and ZrN-WE43 in

Fig. 3. High resolution XPS spectra of (a) Mg 1s, (b) O 1s, (c) Y 3d, (d) Zr 3d and (e) N 1s obtained at various sputtering time from ZrN-WE43.
cDMEM are fitted using the equivalent electrical circuit in Fig. 6b in which $R_S$ represents the solution resistance, $R_1$ and CPE$_1$ represent the charge transfer resistance and capacitance, respectively, $R_2$ is the resistance of the corrosion product, and CPE$_2$ indicates the corresponding capacitance. The equivalent electrical circuit is chosen based on the non-linear least square fit of the experimental data with less than 5% error. Table 1 shows the EIS parameters obtained from the Nyquist plots of UT-WE43 and ZrN-WE43 in SBF and cDMEM after fitting the data. The experimental and fitted data show good agreement with $\chi^2$ of about $10^{-4}$. Compared to UT-WE43, the diameter of the Nyquist plots of ZrN-WE43 is obviously large which also reflects the increased resistance decreased capacitance in both SBF and cDMEM. The rate of the electrochemical processes at the substrate/electrolyte interface is controlled by the charge transfer resistance which is the key factor to determine the corrosion resistance. ZrN-WE43 shows larger charge transfer resistance than UT-WE43 in both SBF and cDMEM (Table 1). This suggests that the plasma process hinders the charge transfer process at the substrate/electrolyte interface. Improved corrosion resistance is observed from ZrN-WE43 in both media. The EIS data showing that Zr & N plasma ion implantation leads to better corrosion resistance in SBF and cDMEM.

The Bode impedance and Bode phase angle plots are displayed in Fig. 7. ZrN-WE43 shows larger impedance at higher and lower frequencies than UT-WE43 in both SBF and cDMEM (Fig. 7). UT-WE43 shows phase angle maxima of $-28^\circ$ and $-61^\circ$ in SBF and cDMEM, respectively and ZrN-WE43 shows larger phase angle maxima of $-64^\circ$ and $-81^\circ$ in SBF and cDMEM, respectively (Fig. 8). The larger impedance and phase angle maxima observed from ZrN-WE43 indicate improved corrosion resistance in both SBF and cDMEM after dual Zr & N plasma ion implantation compared to UT-WE43. Zr-N-WE43 exhibits a larger phase angle maximum of $-81^\circ$ and larger phase angles over a wide range of frequency. Moreover, UT-WE43 and Zr-N-WE43 have two time constants in the Bode impedance plot in which a steady increase in the impedance is observed from UT-WE43 up to 70 Hz and ZrN-WE43 shows a similar increase up to 0.9 Hz. In addition, the Nyquist plot of ZrN-WE43 discloses a near capacitive behavior, suggesting improved corrosion resistance of ZrN-WE43 in both media although the effect is more pronounced in cDMEM.

The potentiodynamic polarization curves obtained from the UT-WE43 and ZrN-WE43 in SBF and cDMEM are displayed in Fig. 9 and Table 2 lists the corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) derived from the polarization curves.

![Fig. 4. Open circuit potential of the UT-WE43 and ZrN-WE43 samples immersed in SBF and cDMEM at 37 °C for 180 s.](image)

![Fig. 5. Nyquist plots of UT-WE43 and ZrN-WE43 samples recorded after immersion for 180 s in (a) SBF and (b) cDMEM at 37 °C.](image)

![Fig. 6. Equivalent electrical circuit of UT-WE43 and ZrN-WE43 samples immersion in (a) SBF and (b) cDMEM.](image)
Generally, the cathodic region of the polarization curve describes the cathodic hydrogen evolution reaction associated with water reduction and the anodic part of the polarization curve represents dissolution of the sample at an elevated potential. In comparison, the cathodic branch of ZrN-WE43 shifts towards a lower current density than UT-WE43 in both SBF and cDMEM, indicating that the cathodic hydrogen evolution reaction is suppressed on ZrN WE43 in both media. In contrast to UT-WE43, ZrN-WE43 exhibits the characteristic of two-regime anodic polarization behavior in SBF (Fig. 9(a)). In the anodic region, the dissolution rate of ZrN-WE43 suddenly turns from slow to rapid when the potential is raised to a certain value. This shows that ZrN-WE43 may be vulnerable to pitting corrosion at an elevated potential in SBF. The surface morphology of UT-WE43 and ZrN-WE43 after the potentiodynamic polarization test in SBF is depicted in Fig. 10. UT-WE43 shows uniform corrosion whereas ZrN-WE43 shows pitting corrosion. This is in agreement with the anodic branch of the polarization curve (Fig. 9(a)) where UT-WE43 shows a slow increase in the current density whereas ZrN-WE43 shows a slow to sudden increase. However, ZrN-WE43 (Fig. 10(d)) reveals less surface damage than UT-WE43 (Fig. 10(c)), suggesting that ZrN-WE43 offers better corrosion resistance than UT-WE43 in SBF. In cDMEM, UT-WE43 exhibits the two-regime anodic polarization behavior whereas ZrN-WE43 shows a simple activation controlled anodic behavior (Fig. 9(b)). The exposed sample is susceptible to pitting corrosion as the applied potential exceeds the corrosion potential because the sample is in the active anodic region with respect to its polarization curve. The surface morphology of UT-WE43 and ZrN-WE43 after potentiodynamic polarization tests in cDMEM are depicted in Fig. 11 and both UT-WE43 and ZrN-WE43 experiences pitting corrosion. This is in agreement with the anodic branch of the polarization curve (Fig. 9(b)) where UT-WE43 and ZrN-WE43 are in the active region at higher applied potential. However, ZrN-WE43 (Fig. 11(b)) shows less surface damage than UT-WE43 (Fig. 11(c)), suggesting that ZrN-WE43 offers better corrosion resistance than UT-WE43 in cDMEM.

### Table 1

<table>
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<tr>
<th></th>
<th>SBF</th>
<th>cDMEM</th>
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<tr>
<td></td>
<td>UT-WE43</td>
<td>ZrN-WE43</td>
</tr>
<tr>
<td>$R_t$ ($\Omega \text{ cm}^2$)</td>
<td>13.48 ± 1</td>
<td>13.81 ± 1.2</td>
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<td>CPE$_1$ ($\Omega^{-2} \text{ cm}^{-2} \text{ S}^{-1}$)</td>
<td>(1.168 ± 0.136) $\times 10^{-4}$</td>
<td>(6.167 ± 0.152) $\times 10^{-4}$</td>
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<td>$n_1$</td>
<td>0.74</td>
<td>0.47</td>
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<tr>
<td>$R_t$ ($\Omega \text{ cm}^2$)</td>
<td>42.97 ± 4</td>
<td>82.87 ± 20</td>
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<tr>
<td>CPE$_2$ ($\Omega^{-2} \text{ cm}^{-2} \text{ S}^{-1}$)</td>
<td>(4.077 ± 0.126) $\times 10^{-5}$</td>
<td>(3.53 ± 3.91) $\times 10^{-6}$</td>
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<td>$n_2$</td>
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<td>0.94</td>
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<tr>
<td>$R_t$ ($\Omega \text{ cm}^2$)</td>
<td>8.64 ± 1</td>
<td>7.37 ± 19</td>
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<tr>
<td>$\chi^2$</td>
<td>6.178 $\times 10^{-5}$</td>
<td>2.675 $\times 10^{-4}$</td>
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Fig. 7. (a and c) Bode impedance and (b and d) Bode phase angle plots of UT-WE43 and ZrN-WE43 recorded after immersion for 180 s in (a, b) SBF and (c, d) cDMEM at 37 °C.
damage than UT-WE43 (Fig. 11(a)), indicating that ZrN-WE43 offers better corrosion resistance than UT-WE43 in cDMEM. Compared to UT-WE43, \( E_{\text{corr}} \) of ZrN-WE43 shifts towards the noble direction and \( i_{\text{corr}} \) decreases in both SBF and cDMEM. In SBF, UT-WE43 has \( i_{\text{corr}} \) of 368 \( \mu \)A/cm\(^2\) and ZrN-WE43 shows 29.8 \( \mu \)A/cm\(^2\) which is 12 times smaller. In cDMEM, UT-WE43 shows 36.6 \( \mu \)A/cm\(^2\) and ZrN-WE43 shows 0.51 \( \mu \)A/cm\(^2\) which is 71 times lesser. Wu et al. [14] observed decrease in the corrosion current density on the Mg–Zn–Zr alloy from 4.341 \( \times \) 10\(^{-4}\) A/cm\(^2\) to 1.834 \( \times \) 10\(^{-4}\) A/cm\(^2\) for the 3 h O implanted sample, 1.671 \( \times \) 10\(^{-4}\) A/cm\(^2\) for the 5 h O implanted sample, 1.527 \( \times \) 10\(^{-4}\) A/cm\(^2\) for the Al & O implanted sample, and 3.832 \( \times \) 10\(^{-5}\) A/cm\(^2\) for the Cr & O implanted sample in SBF. Xu et al. [62] observed decrease in \( i_{\text{corr}} \) from pure Mg from 2.58 \( \times \) 10\(^{-4}\) A/cm\(^2\) and 6.52 \( \times \) 10\(^{-5}\) A/cm\(^2\) to 2.63 \( \times \) 10\(^{-5}\) A/cm\(^2\) and 1.88 \( \times \) 10\(^{-6}\) A/cm\(^2\) for C implanted sample in SBF and DMEM, respectively. Jamesh et al. [39] observed decrease in \( i_{\text{corr}} \) from the Mg–Zn–Zr alloy from 4.09 \( \times \) 10\(^{-4}\) A/cm\(^2\) to 7.0 \( \times \) 10\(^{-5}\) A/cm\(^2\) for the ZrN coated AZ91Mg alloy in SBF [64]. The corrosion protection of Mg–Ca and Mg–Sr alloys [39, 40]. Zr & O plasma ion implantation followed by oxygen PIII produced a robust ZrO\(_2\) layer which enhanced the corrosion resistance of Mg–Zn–Zr, Mg–Ca and Mg–Sr alloys [39, 40], Zr & O plasma ion implantation and larger phase angle maxima are observed from the Mg–Zn–Zr alloy in SBF. Xin et al. observed improved corrosion resistance from the Mg–Nd–Zn–Zr alloy [63].

\begin{table}  
\begin{tabular}{|c|c|c|c|}  
\hline  
\textbf{SBF} & \textbf{UT-WE43} & \textbf{ZrN-WE43} & \textbf{cDMEM} \\
\hline  
\textbf{\( E_{\text{corr}} \) (mV vs SCE)} & \(-1997 \pm 9\) & \(-1820 \pm 57\) & \(-1780 \pm 108\) & \(-1517 \pm 112\) \\
\hline  
\textbf{\( i_{\text{corr}} \) (\( \mu \)A/cm\(^2\))} & \(368 \pm 124\) & \(29.8 \pm 31\) & \(36.6 \pm 34\) & \(0.51 \pm 12\) \\
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\end{tabular}  
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Fig. 9. Potentiodynamic polarization curves acquired after the EIS measurement of UT-WE43 and ZrN-WE43 samples immersed in (a) SBF and (b) cDMEM at 37 °C. 

The enhancement in the corrosion resistance is more pronounced in cDMEM. Smaller corrosion current density, larger resistance, bigger impedance, and larger phase angle maxima are observed from WE43Mg after Zr & N plasma ion implantation. Mg3N2, ZrN, ZrO2, Y2O3, and MgO are formed in the ZrN-WE43 sample. Huang et al. [63] observed decrease in the corrosion current density on the ZrN coated steel in 5% NaCl and 1 M H\(_2\)SO\(_4\) with 0.05 M KSCN solutions. Xin et al. observed improved corrosion resistance from the ZrN coated AZ91Mg alloy in SBF [64]. The corrosion protection behavior of Mg(OH)\(_2\) will be discussed later in this paper and ZrO\(_2\) provides better corrosion resistance. We observed that Zr ion implantation followed by oxygen PIII produced a robust ZrO\(_2\) layer which enhanced the corrosion resistance of Mg–Zn–Zr, Mg–Ca and Mg–Sr alloys [39, 40].
increases the corrosion resistance of ZK60Mg alloy in SBF as evidenced by 37-folds decrease in $i_{\text{corr}}$ and 62-folds increase in $R_p$ [39]. Zr & O plasma ion implantation enhances the corrosion resistance of Mg–Ca and Mg–Sr alloys in SBF, tryptic soy broth (TSB; Bacto), and cell culture medium [40]. Xin et al. [55] observed two orders of magnitude decrease in the corrosion current density from ZrO$_2$ coated AZ91Mg alloy in SBF. Ardelean et al. [65] observed significant improvement in the corrosion resistance from AM50 and AZ91Mg alloys coated with ZrO$_2$ in Na$_2$SO$_4$ solution and after cathodic and anodic polarization, the ZrO$_2$ remained unaffected in the Na$_2$SO$_4$ solution. Liang et al. [66] observed stable and noble potentials from ZrO$_2$ coated AM50Mg alloy after exposure to a 0.1 M NaCl solution for 50 h. The presence of Y$_2$O$_3$ on the Mg alloy also enhances the corrosion resistance [9,67]. Hence the presence of ZrN, ZrO$_2$ and Y$_2$O$_3$ in the ZrN layer of the Zr & N plasma ion implanted WE43Mg alloy samples may be responsible for the improved corrosion resistance. These also suggest that the improvement in corrosion resistance results from the few nm thick implanted layers forming a passive protective layer by reducing galvanic effects. Wu et al. [23] observed second phases from the surface of C$_2$H$_2$ plasma treated Mg–Nd alloy whereas the plasma modified surface gave rise to significant improvement in the corrosion resistance on Mg–Nd alloy in 0.9% NaCl solution. The second phase in the plasma treated samples is also observed here (Figs. 10 and 11). The galvanic effect can be explained by the following relationship [18]:

$$I = (E_c - E_{\text{Sub}})/\left(R_{p(\text{Sub})} + R_{p(\text{C})} + R_s + R_{\text{Sub-C}}\right).$$  \(1\)

where $E_c$ represents the corrosion potential of the cathode, $E_{\text{Sub}}$ represents the corrosion potential of the anode, $R_{p(\text{Sub})}$ and $R_{p(\text{C})}$ represent the polarization resistance of the anode and cathode, respectively, $R_s$ indicates the electrical resistance of the electrolyte, $R_{\text{Sub-C}}$ represents the electrical resistance between the anode and cathode, $R_s$ depends on the geometry of the system and conductivity of the electrolyte, and $R_{\text{Sub-C}}$ is related to the conductivity between the implanted layer cathode and Mg alloy substrate anode.

![Fig. 10. Surface morphology of (a, c, e) UT-WE43 and (b, d, f) ZrN-WE43 samples (at different magnification) after the potentiodynamic polarization test in SBF at 37 °C.](image-url)

 UT-WE43 in SBF (lower magnification) ZrN-WE43 in SBF (lower magnification)

 UT-WE43 in SBF (medium magnification) ZrN-WE43 in SBF (medium magnification)

 UT-WE43 in SBF (higher magnification) ZrN-WE43 in SBF (higher magnification)
(Table 1) and can increase the polarization resistance of the anode which may decrease the galvanic current ($I$).

Generally, Mg alloys offer better corrosion resistance in the presence of a protein containing medium than without due to adsorption of protein molecules onto the surface [68]. However, the corrosion resistance of plasma modified ZrN-WE43 is more pronounced in cDMEM than SBF. Plasma modification can generate a covalent binding surface for protein molecules [69]. Bilek et al. [70] have proposed that the covalent binding on the plasma treated surface may be due to the generation of a free radical density $n_0$ of about $6 \times 10^{25}$ m$^{-3}$ on the surface. The plasma treated surface produces layers with unpaired electrons yielding a platform to bind protein and provide enough electron mobility inside the layer. The amino acids in the protein molecules can be covalently linked by the unpaired electrons present in the free radicals. Ho et al. [71] and Nosworthy et al. [72] observed good covalent binding of

Fig. 11. Surface morphology of (a, c, e, g) UT-WE43 and (b, d, f, h) ZrN-WE43 samples (at different magnification) after the potentiodynamic polarization test in cDMEM at 37°C.
protein molecules on plasma treated surfaces. Moreover, Yin et al. [46] observed better covalent binding of protein molecules on the nitrogen plasma treated surface than that without nitrogen plasma treatment. Hence, the pronounced corrosion resistance observed from the plasma modified ZrN-WE43 in cDMEM may be due to the covalent binding of proteins on the plasma modified surface.

The EDS results acquired from the corroded and intact regions of UT-WE43 and ZrN-WE43 after polarization in SBF and cDMEM are depicted in Figs. 12 and 13 respectively. The corroded regions on UT-WE43 and ZrN-WE43 contain Mg, Ca, P, and O and the intact areas contain Mg after immersion in SBF and cDMEM. The intensity of Ca and P is larger in UT-WE43 than ZrN-WE43 sample after immersion in SBF (Fig. 12) but it is larger on ZrN-WE43 than UT-WE43 sample after immersion in cDMEM (Fig. 13). However, the atomic concentration excludes oxygen which cannot be detected by EDS. Moreover, ZrN-WE43 (spectrum 3) shows stronger Mg peaks than UT-WE43 (spectrum 1) in both SBF (Fig. 12) and cDMEM (Fig. 13). This suggests that the thickness of the corrosion product layer is larger on UT-WE43 than ZrN-WE43. Jamesh et al. [39] has also observed thicker corrosion products on

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**Fig. 12.** Surface morphology of (a) UT-WE43 and corresponding EDS spot analysis of the corroded region, (b) UT-WE43 and corresponding EDS spot analysis of the intact region, (c) ZrN-WE43 and corresponding EDS spot analysis of the corroded region, (d) ZrN-WE43 and corresponding EDS spot analysis of the intact area after the potentiodynamic polarization test in SBF at 37 °C.
untreated ZK60 than Zr & O implanted ZK60 samples after immersion in SBF for 30 h. This may be due to the protective effects rendered by the implanted layer which reduces surface damage compared to the untreated Mg alloy.

The corrosion products are possibly Mg(OH)$_2$ and calcium phosphate as reported previously [16,39,49,57]. Song et al. [57] observed the formation of protective calcium phosphate as a corrosion product on the AZ31Mg alloy after immersion in SBF for 1 h. Wu et al. [49] observed the formation of protective calcium phosphate as a corrosion product on the Mg–Al–Zn–Mn alloy immersed in the cell culture medium for 24 h. Hence, the calcium phosphate here can be protective in nature. When WE43Mg alloys are immersed in SBF and cDMEM, the intermetallic compound serve as the cathode and Mg matrix serve as the anode. As a result of this galvanic couple, the following electrochemical reaction occurs on the anode and cathode. Dissolution of Mg into Mg$^{2+}$ occurs at the anode:

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-.$$
Hydrogen evolution occurs at the cathode.

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  

(Mg(OH)\(_2\)) precipitate is formed by the following overall reaction:

\[ \text{Mg}^2+ + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \]  

The SBF solution contains Cl\(^-\) ions at a concentration 147.8 mM and phosphate ions (from inorganic salt) at a concentration 147.8 mM and 147.8 mM, respectively.

OH\(^-\) reduces the phosphate ions in the SBF [6, 49, 57]:

\[ 2\text{H}_2\text{PO}_4^- + 2\text{OH}^- \rightarrow \text{PO}_4^{3-} + 2\text{H}_2\text{O}. \]  

The phosphate ions quickly react with Ca\(^2+\) in the SBF depositing calcium phosphate as the corrosion product. Among the different kinds of calcium phosphate thermodynamically stable with the smallest solubility constant of \(K_{sp}\) of \(1.6 \times 10^{-58}\) calcium phosphate hydroxyapatite (\(\text{Ca}_10(\text{PO}_4)_6(\text{OH})_2\)), HA is the most stable phase among those investigated in bone formation. The present study reveals that dual Zr & N plasma ion implantation increases the corrosion resistance of WE43Mg alloy in both SBF and cDMEM. The initial corrosion rate can be reduced by Zr & N plasma ion implantation and the corrosion rate can be tailored by varying the Zr and N ion implantation fluence and energy. The flexibility, simplicity, and controllability of this method is attractive to clinical applications.

4. Conclusion

The corrosion behavior of UT-WE43 and ZrN-WE43 is evaluated in both SBF and cDMEM by potentiodynamic polarization and EIS. The following conclusions can be drawn.

1. Dual Zr & N plasma ion implantation forms a 53 nm thick Zr rich layer and 66 nm thick N rich layer on the WE43Mg alloy.
2. In SBF and cDMEM, ZrN-WE43 shows smaller \(i_{corr}\) bigger \(R_t\) & \(R_p\), smaller \(CPE_2\), and larger phase angle maxima than UT-WE43, suggesting enhanced corrosion resistance possibly due to the formation of ZrN, ZrO\(_2\) and Y\(_2\)O\(_3\) in the ZrN implanted layer.
3. ZrN-WE43 in SBF shows a 12-folds decrease in \(i_{corr}\) whereas ZnN-WE43 in cDMEM shows a 71-folds decrease in \(i_{corr}\) together with a near capacitive EIS behavior suggesting that the corrosion resistance is more pronounced in cDMEM.
4. Calcium phosphate is detected from the corrosion product on UT-WE43 and ZrN-WE43 after immersion in SBF and cDMEM.

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