Electrochemical Corrosion Behaviour Analysis of Mg-Alloys Used for Orthopaedics and Vascular Implants

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Abstract

Mg-alloys having bone liked mechanical properties are biodegradable, biocompatible and osteoconductive metallic materials are potential candidates used for orthopaedics and vascular implants. Therefore, present experimentation is an effort to analyse the corrosion behaviour of Mg based alloys such as AZ81 and ZM21 for their usage as bio-degradable implant materials. The corrosion behaviour is analysed using the electrochemical workstation. SEM and EDS are used for high-resolution images and composition of magnesium-based alloys. Using Potentiodynamic polarization curves and Nyquist plots, corrosion rates were observed for 3.0 hours studies on ZM21 (193.53 mm/year) and AZ81 (24.22 mm/year) for Mg-alloys. AZ81 shows higher corrosion resistance than ZM21. The results of these experimental findings may be helpful for the designers and researchers in selecting and improving the clinical performance of Mg-based implants for biomedical applications.

Keywords: Mg-alloys, Biomaterials, Corrosion rate, SEM, EDS

1. Introduction

Magnesium-alloys; being non-toxic, completely degrades in human body environment, having similar mechanical properties to that of bone have good potential for being used in orthopaedics and vascular implants. These implants should have good biocompatibility, high wear and corrosion resistance and should have degradation rate matched with the bone healing rate [1]. Magnesium, being enzymes cofactor stabilizes the structures of RNA and DNA, is very essential for human metabolism [3-4]. Magnesium and its alloys being lightest as compared with all other metals, having higher specific strength and low elastic modulus (45GPa) nearly same as the natural bone (10-30 GPa) makes them easy to be machined [5] and eliminates the impact of stress shielding effect to a greater extent [6].

For the applications of orthopaedic, the mechanical integrity as well as corrosion rate or degradation rate of biomedical implant plays an important role. An eligible biodegradable implant is one whose rate of corrosion matched with the rate of healing of bone, properties is self enough to supply the expected endorsement during the period of bone healing, completely degrades inside the corpus when the objective bone healed totally [7]. For the implantation of magnesium in the human and animal body, many types of biodegradable Mg based alloys are being developed, but approximately all suffering from fast degradation rate and mechanical support is also relatively insufficient [3,8].

Despite several challenges, Mg-alloy implant clinical performance can be improved by optimising implant design, mechanical functioning, surface treatments, and compositions. Surface changes and their appropriate alloying combinations can be used to achieve regulated deterioration rates. As a result, many alloying options for Mg-based alloys have been considered.

Due to continuous efforts of clinical researchers on Mg based alloys for biomedical applications, significant success has been achieved in vitro and in vivo work, such as Mg–Nd–Zn–Zr [9], Mg–Ca [10,11], Mg–Zn–Ca [12,13] and Mg–Mn–Zn [14–16].

In command to improve the mechanical integrity and controlled degradation rate, various alloying options for magnesium-based alloys have been investigated [17-21]. The selection of alloying...
elements, should greatly improve the corrosion resistance property, refine the grain structure, forms phase transitions between metals, thus magnify their power and aiding them in their manufacturing [9].

Alloying elements like Zinc (Zn), Manganese (Mn), Calcium (Ca), Strontium (Sr) and Zirconium (Zr), already part of human body showed minimum adverse effects. Therefore, alloying possibilities, which can improve the Mg-alloys performance, are discussed herein.

Zn is a crucial nutrition tenor, which is present in body of all human beings. Zn with Mg is the best alloy combination for biomedical applications. With the adding of Zinc in Mg, the mechanical and corrosion resistance property also improves [20, 21]. One of the most important effects of Zn is in deficiency of H₂ growth [18, 22]. In a binary Mg - alloy, the addition of Zn (maximum 3%) helps in reducing grain size and improving their mechanical strength [17]. It is reported by Zhang et al. [23] that the adding of Zinc content in ternary Mg–Zn–Ca alloy enhances the tensile strength. The elongation, tensile strength and bio corrosion resistance were reported improved by adding of Zn to Mg [24]. The ultimate tensile strength in Mg-alloy is amplified with 22% with the adding of Zn [25].

With the adding of Zn in Mg alloys, cleavage fracture changed to quasi-cleavage fracture. Moreover, as percentage of Zn content increased up to 3 wt%, Zn particles affect the crack initiation sites [26].

For Mg based alloys, Zn concentration of less than 3% is preferred as beyond 3% Mg-alloys elongation decreases significantly.

Manganese, along with magnesium used as a ternary alloy, is another essential element [27, 28], which improves their corrosion resistive property without disturbing their mechanical properties [14, 29, 30]. Mg–Mn alloy shows good anti-corrosion property with the addition of 1% zinc [20]. Furthermore, its addition in the Mg - alloy controls the impurities harmful effects [18]. For Mg–Zn–Mn based alloys, Rosalbino et al. [31] observed a fourfold growth in resistance of corrosion in the Ringer physiological solution while Zhang et al. [24] concluded about their high mechanical strengths. In addition, Zhang et. al [32] in their in vivo perusal observed that later eighteen weeks, magnesium degradation in Mg–1.2Mn–1.0Zn alloy implant didn’t origin any harmful effects on the kidney.

Zr is one of the powerful grain refiners for the alloys of magnesium [33]. In vitro and in vivo study, Zr shows good biocompatibility and is mostly suitable in ternary Mg-alloys [20, 34]. Its addition in Mg based alloys helps in improving their mechanical strength, reduced degradation rate (by 50%) and resulted in damping stresses and vibrations at the implant/bone interface. For biodegradable Mg-alloys applications, its alloying content should be less than 0.8 wt %.

Thus, we can conclude that Mg-based alloys performance can be enhanced through controlled alloying composition. Therefore, for the corrosion analysis, magnesium based alloys such as AZ81 and ZM21 have been selected in the present research work for their use as biodegradable implant materials.

2. Experimental Setup

2.1. Material preparation

In the present investigation, Mg-alloys rolled plates are used for the experimental work. The micro structure and chemical composition of work materials are shown in figure 1 & 2. The specimens were prepared on wire-cut EDM (SprinCut-Electronica Ltd., India) and sample size of 20 mm * 20 mm * 4.0 mm of Mg alloys was used in this experimental work. For polishing of WEDM machined surface, grit paper of various grades such as P500, P600, P1000, P1200, P1500, P2000 etc. have been used. These prepared samples are clean-ups ultrasonically with acetone and purified water, and then desiccated in the open air. SEM and EDS analysis are also being used for high-resolution image of the inspected area and to find out the exact chemical composition of the material sample.
2.2. **Electrochemical workstation (Electrochemical corrosion study)**

In the present experimental work, electrochemical work station (Autolab PGSTAT-302N, Metrohm, Switzerland) is used for measurements of electrochemical corrosion. Three electrode configuration: graphite electrode served as a counter and Ag/AgCl (1 M KCL) served as reference electrode and prepared sample with a surface area of 1cm² served as a working electrode. Simulated body fluid (SBF) at 37°C is used as an electrolyte in the present investigation. The SBF was prepared according to Kokubo et al.[36]. It was buffered at 7.4 potential of Hydrogen with 0.1 M HCl and tris-hydroxymethyl aminomethane. For stabilizing the OCP, prepared samples were dipped in SBF at 37°C for 30 minutes. After stable OCP, potentiodynamic polarization measurements were taken out within the range of −100 mV to +100 mV for the 3-hour standard testing period.

3. **Results and Discussions**

3.1. **Elemental analysis**

The high resolution images of the surfaces of Mg-alloys were taken by the SEM technic and the configuration of the Mg-alloys was measured through EDS technic. The SEM micrographics of the polished AZ81 Mg-alloy and EDS spectrum images along with composition table are shown through figures 1(A) & 1 (B) respectively. Simmilarly, figures 2 (A) & 2 (B) corresponds to ZM21 Mg-alloy.

![Figure 1](image1.png)  
**Figure 1.** (A) SEM magnificence and (B) EDS spectrums along with composition table of AZ81 Mg-alloy

![Figure 2](image2.png)  
**Figure 2.** (A) SEM magnificence and (B) EDS spectrums along with composition table of ZM21 Mg-alloy
3.2 Corrosion Analysis

The rate of corrosion of the Mg based alloys was measured by electrochemical workstation. The corrosion potential ($E_{corr}$) for ZM21 and AZ81 Mg-alloys are -1.6735 V and -1.4988 V respectively tabulated in Table 1. Corrosion potential of ZM21 Mg-alloy is greater than the corrosion potential of AZ81 Mg alloy. In continuation, the current density ($I_{corr}$) for ZM21 and AZ81 Mg-alloys are 0.00847 A/cm$^2$ and 0.00106 A/cm$^2$ respectively. Corrosion current of ZM21 magnesium is higher than the corrosion current of AZ81 Mg-alloy.

Table 1. Electrochemical parameters observed during corrosion studies (test) on electrochemical workstation

| Mg alloys     | ZM21 Mg-alloy | AZ81 Mg-alloy |
|---------------|---------------|---------------|
| $E_{corr}$ (V) | -1.6735       | -1.4988       |
| $I_{corr}$ (A/cm$^2$) | 0.00847       | 0.00106       |
| Corrosion Rate (mm/year) | 193.53       | 24.22         |
| Polarisation resistance (Ω) | 108.64        | 378.21        |

Figures 3(A) and 3(B) shows the polished samples before and after the corrosion test. The circular signs observed on the materials surface in figure 3(B) are the cross sectional areas on which solution strikes during a corrosion study on the electrochemical workstation.

The corrosion rates were observed for 3.0 hours studies on ZM21(193.53 mm/year) and AZ81 (24.22 mm/year) for Mg-alloys. Clearly, AZ81 shows higher corrosion resistance than ZM21. The potentiodynamic polarisation (PDP) curves and Nyquist plots for 3 hours studies on ZM21 and AZ81 are shown through figures 4 and 5 respectively. After 3 hours of immersion, the $E_{corr}$ for ZM21 rise to -1.61 V, whereas this rise is less in AZ81 Mg alloy with value of -1.49 V w.r.t to open circuit potential value. The simultaneous drop in $I_{corr}$ suggest that formation of oxide layers by the presence of aluminium successfully resist the interaction of aggressive ions with Mg matrix. EIS study have been performed to get detailed insight of corrosion phenomena. The Nyquist plot of ZM21 figure 4(b) comprised only two time constants, firstly a capacitive loop of elevated frequency and second one an inductive loop of low frequency. The occurrence of inductive loop signify excessive pitting corrosion due to poor corrosion resistance. In contrast, AZ81 figure 5(b) comprised three time constants, two capacitive loops of elevated frequency and average frequency and a small inductive loop of low frequency which signify the formation of protective oxide layer between corrosive media and substrate due to the presence of aluminium in alloy. Therefore, AZ81 shows higher corrosion resistance than ZM21.
Figure 3: (A) polished samples of Mg-alloys and (B) polished samples of Mg-alloys after corrosion study

Figure 4. PDP curve and Nyquist plot for ZM21 Mg-alloy
Figure 5. PDP curve and Nyquist plot for AZ81Mg-alloy
4. Conclusions

In the present analysis, the corrosion behaviour of Mg-alloys is analysed using electrochemical workstation. PDP curves and Nyquist plots are used to analyse corrosion rates. SEM and EDS are used for high-resolution images and composition of magnesium-based alloys. The following conclusions drawn from the present research work are:

- In the present study, corrosion rates were observed using 3.0 hours studies on ZM21 (193.53 mm/year) and AZ81 (24.22 mm/year) for Mg-alloys.
- In AZ81 Mg-alloy, the simultaneous drop in $I_{corr}$ suggests that formation of oxide layers by the presence of aluminium successfully resist the interaction of aggressive ions with Mg matrix. EIS study have been performed to get detailed insight of corrosion phenomena. Nyquist plots signify the formation of protective oxide layer between corrosive media and substrate due to the presence of aluminium in AZ81 Mg-alloy. Thus, AZ81 shows higher corrosion resistance than ZM21.
- These results may be helpful for the researchers in improving the performance and selection of Mg-alloys implants for biomedical applications.

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