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# Surface characterization and cytotoxicity response of biodegradable magnesium alloys



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#### A R T I C L E I N F O

#### ABSTRACT

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#### 1. Introduction

Biological implants have been used in many different applications today, such as orthopedic and cardiovascular. Typical biomaterials encompass stainless steel alloys, cobalt-chrome alloys, titanium alloys, alumina, zirconia, poly-methyl-methacrylate (PMMA), poly-lactic acid (PLA), etc. Most of the biomedical devices made from these materials are designed to stay permanently in the body. However, it has been reported that long-term implantations lead to complications, including sensitizations and allergies. There is also a need for secondary surgery to remove implants which may increase health care cost and mortality rates [1]. To overcome these limitations associated with permanent implant materials, biodegradable materials are proposed. Biodegradable magnesium alloys are considered potential materials for the fabrication of medical implants. Magnesium possesses an important property such as biodegradability; characteristic of the material to degrade in a biological environment such as the human body [2]. Magnesium alloys are considered an alternative material useful for the fabrication of cardiovascular, orthopedic and trauma stomach devices [3–7]. Magnesium alloys have similar density and Young's modulus as bones (E =40–45 GPa for Mg and E = 3-20 GPa for bone) [8]. Even the strength/ density ratio is greater than stainless and titanium alloys [9]. Moreover, magnesium is the fourth most abundant cation in the human body, with an estimation of 1 mol of magnesium in a normal 70 kg adult [2].

\* Corresponding author. *E-mail address:* haiderw@utpa.edu (W. Haider). Magnesium alloys have raised an immense amount of interest to many researchers because of their evolution as a new kind of third generation materials. Due to their biocompatibility, density, and mechanical properties, magnesium alloys are frequently reported as prospective biodegradable implant materials. Moreover, magnesium alloys experience a natural phenomenon to biodegrade in aqueous solutions due to its corrosion activity, which is excellent for orthopedic and cardiovascular applications. However, a major concern with such alloys is fast and non-uniform corrosion degradable implants. In this investigation, three different grades of magnesium alloys: AZ31B, AZ91E and ZK60A were studied for their corrosion resistance and biocompatibility. Scanning electron microscopy, energy dispersive spectroscopy, atomic force microscopy and contact angle meter are used to study surface morphology, chemistry, roughness and wettability, respectively. Additionally, the cytotoxicity of the leached metal ions was evaluated by using a tetrazolium based bio-assay, MTS.

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Magnesium serves as co-factor for many enzymes and delivers functions as a stabilizer for DNA and RNA structures [2,10]. Magnesium can even accelerate bone tissue growth [11]. However, it is important to take into consideration that high rate of magnesium alloy ions and particles released from an implant in the human body can be toxic. The high concentration of metal ions such as zirconium, aluminum, and rare earth metals produced through the corrosion activity may lead to harmful diseases inflammatory cascades and tissue damage [2, 12–15]. High aluminum concentration is also harmful to neurons and osteoblasts and may cause dementia and Alzheimer's disease [16,17].

A major drawback with magnesium is its corrosion resistance. Most of the time such inadequate characteristic has deferred its wide scale use in many applications. Magnesium alloys corrode in aqueous solutions, and the different oxidation–reduction reactions are affected by the different alloying elements. Typically, the corrosion of magnesium will produce hydrogen gas and magnesium hydroxide. The following are the common anodic, cathodic and net reactions [18]:

Anodic 
$$Mg \rightarrow Mg^{2+} + 2e^{-}$$
 (1)

Cathodic  $2H_2O + 2e^- \rightarrow H_2 + 2(OH^-)$  (2)

Net reaction  $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2.$  (3)

Previous works [11,19–22] reported that organic and inorganic components could influence the corrosion rate of magnesium alloys. Due to this corrosion activity, the mechanical integrity can be affected before

## Table 1 Chemical composition of PBS solution (g/l).

NaCl	Na <sub>2</sub> HPO <sub>4</sub>	NaHCO <sub>3</sub>	KCl	KH <sub>2</sub> PO <sub>4</sub>	MgSiO <sub>4</sub>	$CaCl_2$
8.0	0.06	0.35	0.4	0.06	0.2	0.14

certain tissues heal without any negative effects e.g., hard-tissue implantation repairs may require at least 12 weeks [2].

The process of alloying elements with magnesium leads to an improvement in both corrosion resistance and corrosion rate of magnesium [20,23]. It is reported that addition of aluminum into magnesium increases the ductility, yield strength and ultimate tensile strength via the formation of  $\beta$ -Mg<sub>17</sub>-Al<sub>12</sub> phase [17,24]. Similarly, the addition of zinc into magnesium improves corrosion resistance, creep behavior, yield strength and tensile strength of the alloy when the Zn content is less than 6 wt.% [24,25]. Decrease in elongation and tensile strength

takes place when Zn content is over 6 wt.% [10]. Zn can also encumber the movement of the recrystallized grain boundary to refine the microstructure [17]. The addition of zirconium to magnesium enhances grain refinement. However, zirconium cannot be used with Mg containing aluminum because it can be removed from solid solution due to the formation of stable compounds [26].

Surface modifications are known to significantly improve surface properties of magnesium alloys. Since magnesium alloys are considered biodegradable alloys, they can only receive certain types of surface modifications. These types of surface treatments are chosen according to the environment the implant will be placed in [27]. Anodization is an electrochemical treatment that changes the surface chemistry of the metal by oxidation, producing a stable oxide layer. A thin layer at the metal-oxide interface, followed by a less dense porous oxide layer, characterizes the structure of the oxide film [28]. The anodizing behavior is strongly influenced by the voltage, current, temperature, and

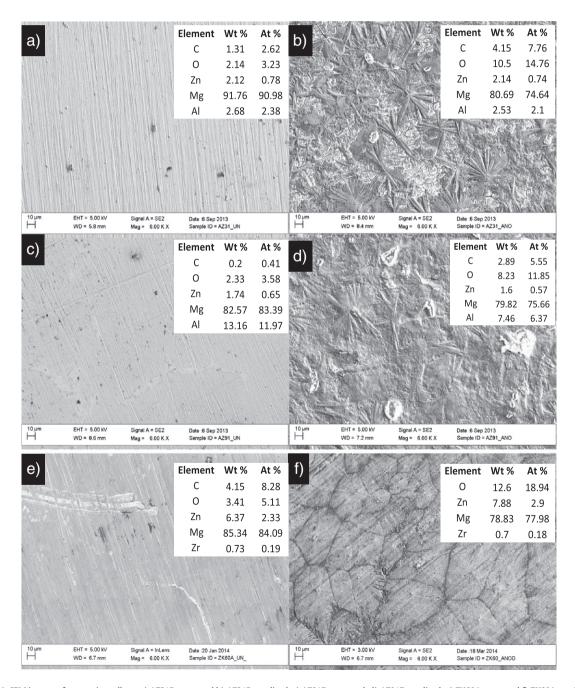


Fig. 1. SEM images of magnesium alloys: a) AZ31B untreated b) AZ31B anodized, c) AZ91E untreated, d) AZ91E anodized, e) ZK60A untreated f) ZK60A anodized.

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