Influence of Al Content on the Corrosion Behavior of Biodegradable Magnesium Alloys in Simulated Physiological Solution

A. Raj Bharat[1], B. Sesha Sai Kumar[1], R. J. Phani Sarath[1], P. Akhil[1], G. Pradeep Kumar Reddy[2] and B. Ratna Sunil[1,*]

[1]Department of Mechanical Engineering, Rajiv Gandhi University of Knowledge Technologies (AP-IIIT), Nuzvid 520201, India

[2]Department of Mechanical Engineering, Vignana Bharathi Institute of Technology, Hyderabad 501301, India

Abstract: Magnesium (Mg) and its alloys have gained wide popularity in the biomedical field as promising candidates for degradable implant applications. Among Mg alloys, AZ (aluminum and zinc) series alloys are the most widely investigated for implant applications and reported in the literature. In all AZ series Mg alloys, aluminium content is the influencing factor that imparts different properties to the Mg alloys. In the present study, pure Mg, AZ31 and AZ91 Mg alloys were selected and the effect of aluminium content on the biocorrosion has been investigated in Ringer's solution. It was a clear observation that the increased aluminum content has a severe effect on the degradation behavior of magnesium. From the weight loss measurements, AZ31 has shown lower corrosion rate compared with pure Mg and AZ91. The surface morphologies also showed the formation of more pits on pure Mg and AZ91 Mg alloy compared with AZ31 Mg alloy. By correlating the degradation behavior with the microstructure, galvanic corrosion was found to be the main reason behind the accelerated corrosion rate in AZ91 Mg alloy compared with AZ31 alloy. The phases on the corroded sample surfaces were examined by X-ray diffraction (XRD) method and scanning electron microscopy (SEM) and found that the corrosion products which were deposited on the surfaces provided protection against the chloride ions which was indicated by the decreased corrosion rates as immersion time was increased.

Keywords: Magnesium, AZ series Mg alloys, Biocorrosion, Degradable, Temporary implants, Simulated physiological solution.

1. INTRODUCTION

Metals are the best suited candidates for load bearing implant applications compared with ceramics and polymers. Degradable implants avoid second surgical procedure to remove the implant after the damaged tissue is completely healed. Recently, magnesium (Mg) and its alloys have grabbed a great attention as excellent candidates for load bearing temporary implant applications [1]. Mg exhibits safe biodegradation in physiological environment and also the mechanical properties of Mg are close to that of natural bone that reduces the stress shielding effect, which is commonly associated with the other metallic implants [2]. On the other hand, uncontrolled degradation of Mg in biological environment is the major limitation that needs to be addressed in developing Mg based implants. AZ series (aluminium and zinc) is the common Mg alloy system widely used for structural applications. Among AZ series alloys, AZ31 and AZ91 alloys were widely investigated as biomaterials and reported in the literature [3-9].

Aluminum (Al) is the most influencing element in AZ series Mg alloys. The maximum solubility of Al in Mg at room temperature is limited to 1%. Mg-Al solid solution (α – phase) is formed up to 1% and the excess Al if exists more than 1%, results in the formation of Mg-Al compound (β – phase, $Mg_{17}Al_{12}$). This β – phase is hard, brittle and more stable in corroding environments compared with α –phase. The amount of β ($Mg_{17}Al_{12}$) phase in AZ31 Mg alloy is lower compared with AZ91 Mg alloy [12]. The corrosion behavior of these alloys having varying amounts of secondary phase is different and which is the prime interest behind carrying the present work. Therefore, pure Mg and AZ series Mg alloys one with lower Al (AZ31) and another with higher Al (AZ91) were considered for the present study and the corrosion behavior was assessed by immersing in simulated physiological solutions and the role of aluminium content on the corrosion behavior was studied.

2. MATERIALS AND METHODS

Pure Mg (99.9 % purity) cast billet, AZ31 Mg alloy (2.75%Al, 0.91%Zn, 0.001%Fe, 0.01%Mn and remaining being Mg by wt.%) rolled sheets and die cast AZ91 Mg alloy (8.67%Al, 0.85%Zn, 0.002%Fe,

*[*]Address correspondence to this author at the Department of Mechanical Engineering, Rajiv Gandhi University of Knowledge Technologies (AP-IIIT), Nuzvid 521202, India; Tel: +91 9677119819; Fax: 08656 235150; E-mail: bratnasunil@gmail.com, bratnasunil@rgukt.in

0.03%Mn and remaining being Mg by wt.%) sheets were obtained from Exclusive Magnesium, Hyderabad, India. Samples of size $10 \times 10 \times 4$ mm^3 were cut from the Mg cast billet, AZ31 and AZ91 Mg alloy sheets. For metallographic observations, the samples were polished using different graded emery sheets up to 2000 grade followed by alumina and diamond paste (1-3 μm) polishing. The polished specimens were cleaned in ethanol and dried. Chemical etching was done by immersing the polished specimens for 20 sec in picric acid reagent (5 g of picric acid, 5 ml acetic acid, 5 ml distilled water and 100 ml ethanol) and gently washed, dried and then optical microscope (Leica, Germany) images were obtained.

Samples of identical size were immersed in 30 ml of Ringer's solution for 24, 48 and 72 h. The solution was maintained at 37 °C in a constant temperature water bath. Ringer's solution was prepared as per reported procedure [13] using 7.2 g NaCl, 0.37 g KCl, and 0.17 g CaCl$_2$ per one liter of de-ionized water. After different intervals of immersion time, the samples were removed and gently washed in de-ionized water and dried. The immersed samples were examined by using scanning electron microscope (SEM, FEI Quanta 200, Netherlands). The elemental composition of the immersed samples was obtained by energy dispersive X-ray (EDS) analysis. X-ray diffraction (XRD, D8 Bruker, USA) analysis was carried out before and after immersion test using CuKα radiation between 2θ ranging from 20° to 80° with a step size of 0.15. The corrosion products were removed by immersing the samples in a boiling solution of CrO$_3$ (180 g of CrO$_3$ per one liter of de-ionized water). After the corrosion products were dissolved in the chromate solution, the samples were dried and weights of the samples were measured. Weight loss of the samples was calculated with respect to the weight before immersion test and the corrosion rate was obtained as per the ASTM-G31-72 standard as given below [14].

$$CR = 8.76 * 10^4 \, W / ATD \qquad (1)$$

Where, W is the weight loss (g), A is the surface area of the sample before immersion (cm^2), T is the immersion time (h) and D is the density of the sample (g/cm^3).

3. RESULTS AND DISCUSSION

The microstructural observations as shown in Figure **1** clearly demonstrate the difference in the grain sizes and presence of α and β phases in the starting materials. Pure Mg has large grains compared with AZ31 and AZ91.
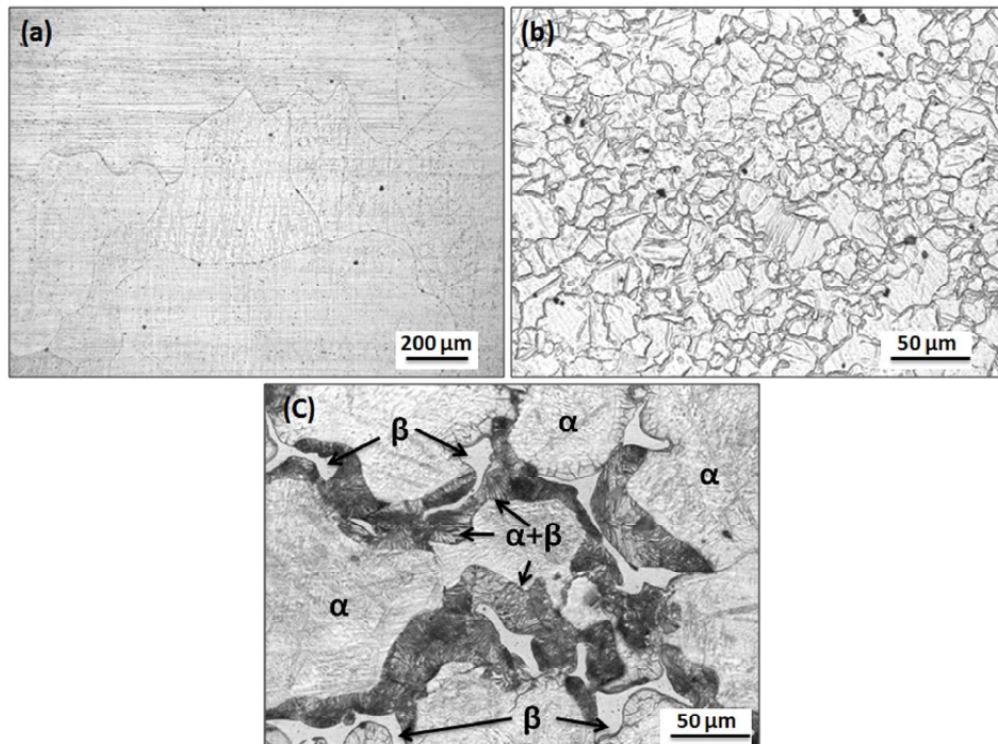

Figure 1: Optical microscope images of the samples: **a**) pure Mg, **b**) AZ31 Mg alloy and **c**) AZ91 Mg alloy.

The grains were found to be in the combination of columnar and equiaxed in the pure Mg sample. The grain size distribution was found to be 500-1500 μm and 5-25 μm in the pure Mg and AZ31 samples respectively. The average α grain size (as shown in Figure **1** (**c**)) in AZ91 was measured as 150 μm. The β ($Mg_{17}Al_{12}$) phase was observed as a network like structure distributed at α grain boundaries. The presence of eutectic α+β regions can be clearly seen at the interface of α grains and β phase. It is true that the AZ31 Mg alloy also contains β phase in very smaller amounts. However, the presence of this secondary phase is invisible in AZ31 Mg alloy as the amount is insignificant at the grain boundaries and therefore, optical microscope image of AZ31 has not shown any indication of β phase unlike AZ91 Mg alloy.
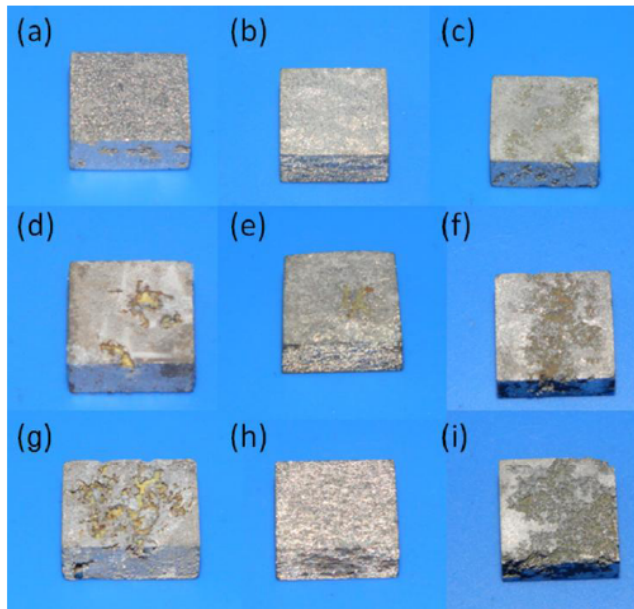

Figure 2: Typical photographs of the samples (of size 10×10×4 mm^3) after cleaning the corrosion products at different intervals of time during immersion test: **a**) pure Mg after 1 day, **b**) AZ31 after 1 day, **c**) AZ91 after 1 day, **d**) pure Mg after 3 days, **e**) AZ31 after 3 days, **f**) AZ91 after 3 days, **g**) pure Mg after 7days, **h**) AZ31 after 7 days and **i**) AZ91 after 7 days.

Figure **2** shows the photographs of the samples at different intervals of time after the immersion test carried out in Ringer's solution. From the images, it can be clearly seen that the pure Mg and AZ91 exhibited more degradation compared with AZ31. As the immersion time was increased to 3 and 7 days, the level of degradation was observed as more for pure Mg and AZ91 compared with AZ31. Figure **3** shows typical SEM images of the samples after 3 days of immersion test. The surfaces were found to be completely covered

with corrosion products. Needle like clusters which resembles tiny spheres have appeared on all the three samples. These morphologies of the deposited phases are similar to what reported in the literature [3]. The formation of magnesium hydroxide and magnesium chloride are the reasons behind appearance of these clusters. Corresponding EDS analysis also indicated the presence of Mg, O, Ca, P, Cl and Al. The presence of Al is from the base materials. Presence of Mg and O are due to the formation of magnesium hydroxide $Mg(OH)_2$ and magnesium oxide (MgO) which is confirmed by the XRD analysis as shown in Figure **4**. Further, the presence of smaller amount of Cl suggests the formation of magnesium chloride but the indication of this phase was not clearly observed from the XRD analysis. Interestingly, Ca and P appeared in the EDS analysis of all the samples.

Presence of CaO on the samples was observed from the XRD analysis. It may also be possible to form any Ca/P mineral phase such as apatite on the samples as observed in other studies when immersed in simulated biological solutions [3, 4]. However, in the present study, no indication of any Ca/P phase on the samples was observed from the XRD analysis. But, there is a possibility that the deposited Ca/P mineral phases were lower in amount than the detecting range of XRD analysis and therefore, not appeared in the present analysis.

Figure **5** shows the corrosion rate of the samples with respect to the immersion time. From the results, it can be clearly observed that the AZ31 has lower corrosion rate compared with pure Mg and AZ91. For the first day, pure Mg has shown lower corrosion rate compared with AZ31 and AZ91. This may be due to the quick formation of $Mg(OH)_2$ and MgO layer on pure Mg compared with AZ31 and AZ91. Interestingly, as the immersion time is increased to 3 and 7 days, the rate of corrosion for Mg was more compared with first day unlike AZ31 and AZ91. Usually when Mg is immersed in any aqueous solution, the corrosion products such as $Mg(OH)_2$ and MgO are formed on the surface during the early hours of the immersion. Among the corrosion products, $Mg(OH)_2$ layer is unstable particularly in the presence of chloride ions [1, 6, 7]. Therefore in the present study, all the samples were observed as degraded further after 3 and 7 days. Presence of MgO was found to be predominant on Mg after 7 days of immersion as shown in XRD patterns (Figure **4**). The corrosion rates of AZ31 and AZ91 were found to be lower after 3 and 7 days of immersion compared with
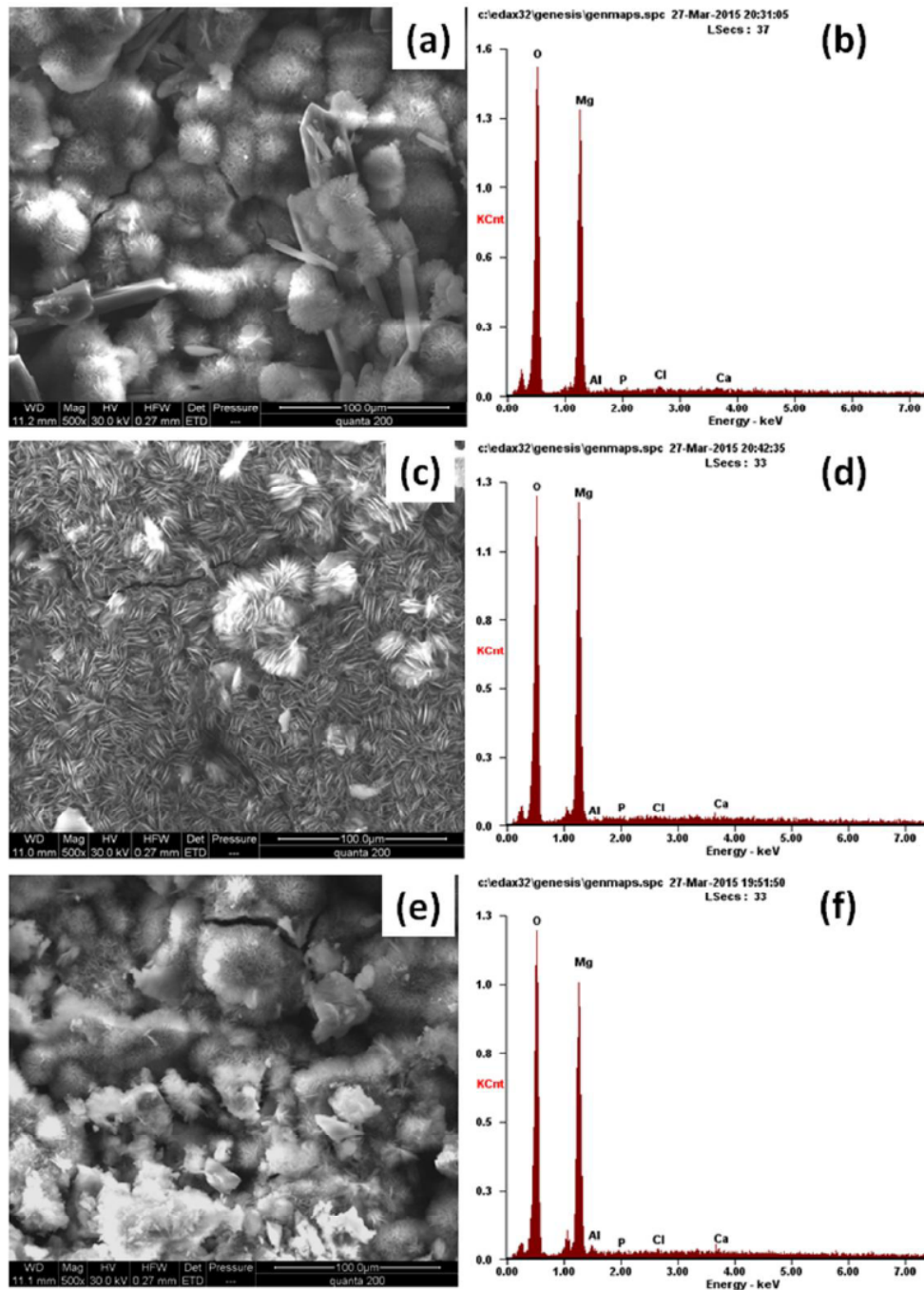
Figure 3: SEM images of the samples and corresponding EDS analysis after 3days of immersion: **a**) Pure Mg, **b**) corresponding EDS analysis, **c**) AZ31, **d**) corresponding EDS analysis, **e**) AZ91 and **f**) corresponding EDS analysis.

the corrosion rates after day one. The intensities of XRD peaks corresponding to MgO were also observed as lower for AZ31 and AZ91 compared with Mg. Therefore, from the results, it can be understood that the corrosion products which still remained on the surface of the samples have reduced the actual surface area that was directly exposed to the corroding environment. Hence, the corrosion rates were reduced after 3 and 7 days for AZ31 and AZ91.

Among all the samples, as immersion time is increased to 3 and 7 days, AZ31 has shown better corrosion resistance. This interesting behavior can be explained by considering the alloying effect. By adding Al and Zn to pure Mg, AZ series Mg alloys are produced. Keeping Zn amount constant ($\approx$ 1%), mechanical and corrosion properties can be altered in AZ series Mg alloys by varying Al content. Basically, AZ31 is a wrought alloy whereas AZ91 is a cast alloy.
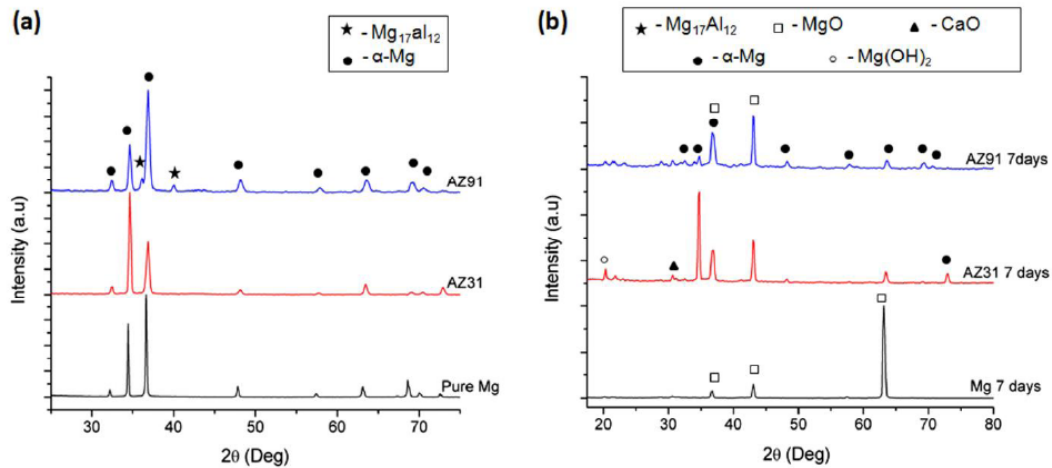
Figure 4: XRD patterns of the samples: **a**) before immersion test and **b**) after 7 days of immersion in Ringer's solution.

AZ31 contains major fraction of solid solution of Mg and Al (called as α phase) and very lower amount of secondary phase (β, $Mg_{17}Al_{12}$). Compared with pure Mg, solid solution alloy of Mg, Al and Zn promotes corrosion resistance. But in AZ91, along with α grains, considerable amount of β phase (as shown in Figure **1**(**c**)) also can be seen. The hard and brittle compound of Mg and Al ($Mg_{17}Al_{12}$) usually appears at the grain boundaries act as cathode and the α grains act as anode which lead to formation of a localized electrochemical cell. Therefore, galvanic corrosion was predominantly promoted in AZ91 compared with pure Mg and AZ31 and shown higher corrosion as the immersion time is increased to 7 days. Overall, the corrosion rate of all the samples was observed as decreased after 7 days of immersion. Interestingly, the deference between the corrosion rates for the same material after different intervals (day 1, 3 and 7) of immersion time was also observed as decreased. Therefore, similar trend of decrease in corrosion rate is expected for longer periods and the samples may degrade marginally with a constant corrosion rate.

The real physiological environment contains many other ions, proteins, growth factors. The tissue interactions with the degrading implant also influences the degradation behavior of Mg. However, the corrosion behavior in simulated physiological solution (Ringers solution in the present study) helps to understand the materials corrosion behavior in the real complex biological environment. In the literature, other studies were carried out in evaluating the degradation behavior of Mg alloys in different simulated biological solutions such as Hank's solution [9], simulated body fluid (SBF) [10], super saturated SBF [3, 4] and phosphate buffered solution (PBS) [11] and similar kind

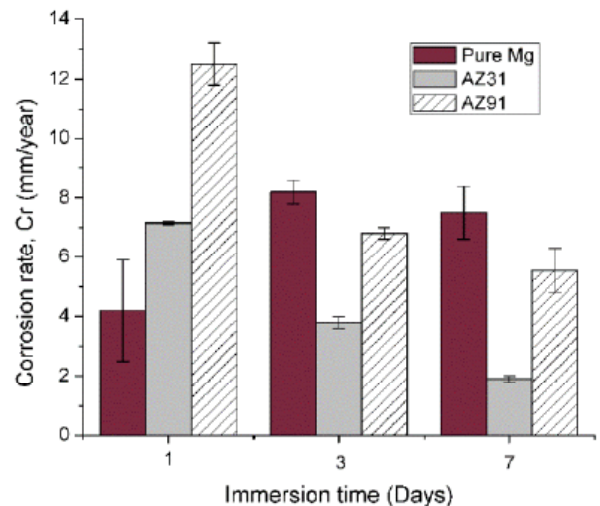of degradation behavior was reported compared with the present study.

Figure 5: Corrosion rates of the samples calculated from the weight loss measurements.

Hence from the results, it can be understood that the presence of Al in AZ series Mg alloys has a great influence on the corrosion behavior and which is suggested to be lower if the application is intended for corroding environment such as degradable biomedical implants. The material-tissue interactions affect the healing rate of the tissue which is influenced by the rapid corrosion of Mg. The evolution of hydrogen gas due to the corrosion of Mg and its alloys influence the cell activities at the implant and tissue interface. It was also reported that the lower degradation rates of Mg and its alloys favor better cell growth and proliferation [3, 4, 15, 16]. Presence of more Al in Mg alloys is also not advised in the biomedical applications as Al may cause other health issues such as abnormal neural

disorders [17, 18]. However, if the amount is within the tolerable limits, Al can be used as alloying element. A few reports have clearly shown that the lower amounts of Al (< 3 wt. %) do not induce any toxicity effect [3, 4, 5]. Therefore, the present study demonstrates the significant effect of Al on corrosion behavior of AZ series Mg alloys and suggests that the AZ31 can be an appropriate alloy with promising corrosion properties compared with pure Mg and AZ91 Mg alloy for temporary implant applications such as degradable plates, fixtures, screws and nails used in orthopedic implants.

4. CONCLUSION

In the present work, the influence of aluminum content on the corrosion behavior of pure Mg and its alloys intended to use as material for degradable implants was investigated. Pure Mg, AZ series Mg alloys; one alloy with lower aluminium (AZ31) content and one with higher aluminium (AZ91) content were immersed in simulated physiological solution for 1, 3 and 7 days respectively and their degradation behavior was investigated. Pure Mg and AZ91 Mg alloys have shown higher corrosion rates compared with AZ31 Mg alloy. Galvanic corrosion was found to be prominent in AZ91 Mg alloy, which contains two phases (α and β). The corrosion rates were found to be decreased for all the samples as the immersion time is increased to 7 days. Hence from the present study, it has been clearly demonstrated that the higher amounts of Al promotes corrosion rate of Mg alloys and AZ31 Mg alloy is promising for biomedical applications with less corrosion rate.

ACKNOWLEDGEMENTS

REFERENCES

[1]   Kirkland NT, Birbilis N. Magnesium Biomaterials Design, Testing, and Best Practice. New York: Springer Science and Business Media 2014. http://www.springer.com/us/book/9783319021225

[2]   Hermawan H, Dubé D, Mantovani D. Developments in metallic biodegradable stents. Acta Biomater 2010; 6: 1693-1697.
http://dx.doi.org/10.1016/j.actbio.2009.10.006

[3]   Ratna Sunil B, Arun Anil Kumar, Sampath Kumar TS, Uday Chakkingal. Role of biomineralization on the degradation of fine grained AZ31 magnesium alloy processed by groove pressing. Mater Sci Eng C 2013; 33: 1607-1615.
http://dx.doi.org/10.1016/j.msec.2012.12.095

[4]   Ratna Sunil B, Sampath Kumar TS, Uday Chakkingal, Nandakumar V, MukeshDoble. Nano-hydroxyapatite reinforced AZ31 magnesium alloy by friction stir processing: A solid state processing for biodegradable metal matrix composites. J Mater Sci: Mater Med 2014; 25: 975-988.
http://dx.doi.org/10.1007/s10856-013-5127-7

[5]   Wang H, Estrin Y, Fu H, Song GL, Zúberová Z. The effect of pre-processing and grain structure on the bio-corrosion and fatigue resistance of magnesium alloy AZ31. Adv Eng Mater 2007; 9: 967-972.
http://dx.doi.org/10.1002/adem.200700200

[6]   Song Y, Shan D, Chen R, Zhang F, Han EH. Biodegradable behaviors of AZ31 magnesium alloy in simulated body fluid. Mater Sci Eng C 2009; 29: 1039-1045.
http://dx.doi.org/10.1016/j.msec.2008.08.026

[7]   Witte F, Fischer J, Nellesen J, Crostack HA, Kaese V, Pisch A, *et al*., *In vitro* and *in vivo* corrosion measurements of magnesium alloys. Biomaterials 2006; 27(7): 1013-8.
http://dx.doi.org/10.1016/j.biomaterials.2005.07.037

[8]   Witte F, Feyerabend F, Maier P, Fischer J, Störmer M, Blawert C, *et al*., Biodegradable magnesium-hydroxyapatite metal matrix composites. Biomaterials 2007; 28(13): 2163-74.
http://dx.doi.org/10.1016/j.biomaterials.2006.12.027

[9]   Bobby Kannan M, Singh RKR. A mechanistic study of *in vitro* degradation of magnesium alloy using electrochemical techniques. J Biomed Mater Research: Part A 2010; 93(3): 1050-5.
http://dx.doi.org/10.1002/jbm.a.32576

[10] Yong Wang, Mei Wei, Jiacheng Gao, Jinzhu Hu, Yan Zhang. Corrosion process of pure magnesium in simulated body fluid. Materials Letters 62 (2008) 2181-2184.
http://dx.doi.org/10.1016/j.matlet.2007.11.045

[11] Alvarez-Lopez M, Pereda MD, Valle JA, Fernandez-Lorenzo M, Garcia-Alonso MC, Ruano OA, Escudero ML. Corrosion behaviour of AZ31 magnesium alloy with different grain sizes in simulated biological fluids. Acta Biomater 2010; 6: 1763-1771.
http://dx.doi.org/10.1016/j.actbio.2009.04.041

[12] Avedesian MM, Baker H. ASM specialty handbook. Magnesium and magnesium alloys. USA; ASM International 1999.   http://www.asminternational.org/search/-/journal_content/56/10192/06770G/PUBLICATION

[13] Richard C, Teresa A, Peter C, Howard P, Anthony S, Frank V, John S. Eds. Oxford Dictionary of Biochemistry and Molecular Biology. 2nd ed. UK, Oxford University Press 2006.
http://dx.doi.org/10.1093/acref/9780198529170.001.0001

[14] ASTM Standard G31-72. Standard practice for laboratory immersion corrosion testing of metals. West Conshohocken. PA: ASTM International 2004.
doi:10.15s20/G0031-72R04.

[15] Ratna Sunil B, Sampath Kumar TS, Uday Chakkingal, Nandakumar V, Mukesh Doble, Devi Prasad V, Raghunath M. *In vitro* and *in vivo* studies of biodegradable fine grained AZ31 magnesium alloy produced by equal channel angular pressing. Mater Sci Eng C 2016; 59: 356-367.
http://dx.doi.org/10.1016/j.msec.2015.10.028

[16] Ratna Sunil B, Sampath Kumar TS, Uday Chakkingal, Nandakumar V, Mukesh Doble. Friction stir processing of magnesium – nanohydroxyapatite composites with controlled *in vitro* degradation behaviour. Mater Sci Eng C 2014; 39: 315-324.
http://dx.doi.org/10.1016/j.msec.2014.03.004

[17] Helsen JA, Breme HJ, Eds. Metals as biomaterials. England; John Wiley & Sons 1998. http://as.wiley.com/

WileyCDA/WileyTitle/productCd-0471969354.html

[18] El-Rahman SSA. Neuropathology of aluminum toxicity in rats (glutamate and GABA impairment). Pharm Res 2003; 47: 189-94.
http://dx.doi.org/10.1016/S1043-6618(02)00336-5