CORROSION BEHAVIOUR OF AZ31 MAGNESIUM ALLOY IN SALINE CONTAINING GLUCOSE AT DIFFERENT CONCENTRATIONS

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Abstract

AZ31 magnesium alloy was subjected to corrosion tests in a 0.9% NaCl containing 0 to 5 g/L D-glucose at 37°C. Potentiodynamic measurements were performed in corrosive environments with natural pH and with the pH set to 7.4. The results show that glucose in the range of 0.1 to 5 g/L led to a deterioration of the corrosion resistance of AZ31 alloy in 0.9% NaCl at an initial pH of 7.4. If the corrosive environment did not have a set pH, then a slightly different behavior was observed. Addition of 0.1 g/L glucose to 0.9% NaCl resulted in inhibition of corrosion, while higher concentrations accelerated corrosion. The corrosion aggravation was related to the oxidation of glucose to gluconic acid, which together with chlorides degraded the $Mg(OH)_2$ layer on the AZ31 alloy surface. Surface analysis revealed that the corroded AZ31 alloy was covered with fine crystals in the absence of glucose.

Keywords: AZ31 magnesium alloy, corrosion, glucose, saline

1. INTRODUCTION

Magnesium is a metal characterized by light weight, high specific strength, good electromagnetic shielding performance, shock resistance, biocompatibility and biodegradability as well [1]. Mg alloys have a wide range of applications involving automotive, high-speed railways, aerospace and also biomedical fields. In medicine magnesium and its alloys can be used as biodegradable metallic materials; e.g. temporary fixation orthopaedic implants (screws, splints, pins, etc.) or coronary stents [1]. The disadvantage of magnesium and its alloys is the rapid and uncontrolled degradation in aqueous environments [2]. Therefore, the study of corrosion in the presence of various inorganic constituents has received considerable attention. It is well known that the presence of chloride ions in body fluids has a particularly significant impact on magnesium corrosion [2,3]. On the other hand, phosphates that are present in the blood can form insoluble compounds that can improve the corrosion properties of magnesium material [2]. In recent years, attention has also been paid on the role of organic substances on the corrosion behaviour of magnesium and its alloys. These molecules may participate in accelerating corrosion by limiting the formation of corrosion products, or retarding corrosion by promoting nucleation and growth of corrosion products [2].

The subject of this work will be glucose, which is a natural component of blood, and may interact with magnesium-based coronary stents [4]. Glucose is a monosaccharide that is found in nature only as D-glucose. In an aqueous environment, it cyclizes to a six-membered hemiacetal ring to form two anomers: α-D-glucopyranose and β-D-glucopyranose. In aqueous media at laboratory temperature, the β-D-glucopyranose anomer predominates and occupies about 64 %. Glucose is naturally found in the blood, where its concentration changes with food consumption. It is lower before consumption, whereas it is higher after consumption. In healthy individuals, the glucose concentration is between 4.4 and 6.1 mmol/l before eating and 7.8 mmol/l within 2 hours after eating. People with diabetes generally have elevated blood glucose levels. They usually have a glucose concentration of 7 mmol/l before a meal and can rise to more than 11.1 mmol/l

within 2 hours after a meal. Glucose as a 5% solution is also used as an artificial nutrition for intravenous administration [4].

Recently, several papers have been published dealing with the effect of glucose on the corrosion of magnesium and its alloys in different corrosive environments. Zeng et al. [5], for the first time, conducted an in-depth study in which they investigated the corrosion of pure magnesium in 0.9% NaCl solution containing glucose. According to their findings, the progress of corrosion in 0.9% NaCl solution with glucose occurred in several steps. The magnesium was covered with a layer of $Mg(OH)_2$ on which glucose and chlorides were adsorbed. The glucose was rapidly oxidized to gluconic acid, which dissolved the $Mg(OH)_2$ layer to magnesium gluconate. In addition to the gluconic acid, the surface of the material was also attacked by chloride anions, thereby disrupting the porous $Mg(OH)_2$ layer and allowing the solution to gradually permeate further through the pores. As a result, magnesium degradation took place faster than in the plain 0,9% NaCl [5].

Li et al. [6] investigated the effect of glucose on AZ31 alloy in a 0.9% NaCl environment. They found that glucose concentration of 1 g/L decreased the corrosion rate, whereas at higher glucose concentrations (2 g/L and 3 g/L) the corrosion rate increased. This observation was explained by the authors as glucose formed complexes with magnesium ions that adsorbed on the surface of AZ31 alloy, forming a barrier to aggressive chlorides. At higher amounts of glucose, it was oxidized to gluconic acid, which effectively contributed to the disruption of the $Mg(OH)_2$ coating together with the chlorides. When Tris buffer (tris(hydroxymethyl)aminomethane) was also added to 0.9% NaCl, it was found that the rate of alloy corrosion increased with increasing glucose concentration (1-3 g/L). According to the authors, the presence of Tris led to an alkalinisation of the environment, which accelerated the conversion of glucose to gluconic acid and thus also to faster corrosion [6].

Opposite to the previous findings, another research group recently published a paper [4] in which corrosion of AZ31 alloy was again performed in 0.9% NaCl with 0, 1, 2 and 4 g/L glucose. The authors found that with increasing glucose content there was a more pronounced inhibition of AZ31 corrosion. This observation was explained by the fact that glucose slowed the rate of accumulation of Mg^{2+} and OH^- ions in solution, allowing more time for nucleation and growth of $Mg(OH)_2$ at the alloy surface. Unfortunately, they did not discuss their results with the earlier ones published by Li et al. [6].

The aim of our work is to investigate the effect of glucose at low and high concentrations on AZ31 alloy at temperature 37 °C in 0.9% NaCl under the condition of pH set to 7.4 and unadjusted pH. The corrosion behaviour was measured by potentiodynamic polarization and immersion test. The corrosion products were characterized by scanning electron microscopy with energy dispersive spectrometer (SEM-EDS).

2.   EXPERIMENTAL

AZ31 magnesium alloy samples (20 × 20 × 6 mm) were used for corrosion tests. The alloy chemical composition was determined using Glow-Discharge Optical Emission Spectroscopy (GDOES); 3.60 % Al, 1.34 % Zn, 0.28 Mn, 0.03 Si, 0.002 Fe and 0.01 Sn [7]. The samples of AZ31 alloy were ground using 320 and 1200 SiC grit abrasive papers, washed in distilled water and isopropyl alcohol and then dried by hot air.

The potentiodynamic measurements were performed at temperature 37 °C using the Bio-Logic VSP-300 potentiostat (BioLogic, Seyssinet-Pariset, France). The corrosion solutions were composed of 0.9% NaCl containing 0, 0.1, 0.2, 0.5, 1, 2, 5 g/L D-glucose. The samples with exposed area of 1 cm² served as a working electrode. Saturated calomel electrode (SCE) was used as a reference electrode and Pt wire as a counter-electrode. Open circuit potential (OCP) variations with time were recorded up to 30 min of exposure. Afterward, Tafel plot was obtained by carrying out potentiodynamic polarization in the potential range from −200 mV to 350 mV vs. OCP at the scan rate of 1 mV/s.

Surface analysis of the samples after corrosion was performed using scanning electron microscopy (SEM; Carl Zeiss Ltd., Cambridge, UK) with Energy-dispersive X-ray spectroscopy (EDS; model OXFORD

INSTRUMENTS X-MAX 80 mm^2) was used to examine the surface of the samples after electrochemical testing to specify the character of the corrosion products.

3.   RESULTS AND DISCUSSION

Potentiodynamic measurements were performed in 0.9% NaCl solution without pH adjustment containing 0.1 - 5 g/L glucose. The characteristic potentiodynamic curves obtained are shown in **Figure 1** and the parameters obtained as i_{cor} and E_{cor} are summarized in **Table 1**. The results show that the corrosion current density (i_{cor}) or corrosion rate was lower only

for 0.1 g/L glucose compared to 0.9% NaCl. Increasing the amount of glucose in 0.9% NaCl caused an acceleration of corrosion of AZ31 alloy, with 5 g/L concentration having the most significant impact on corrosion. The corrosion potential (E_{cor}) for concentrations below 1 g/L glucose was slightly more positive than for 0.9% NaCl, but for higher concentrations (including 1 g/L) of glucose the corrosion potential was around the value as in the case of the plain 0.9% NaCl. The potentiodynamic curves also clearly show that glucose had an effect on the anodic reaction.
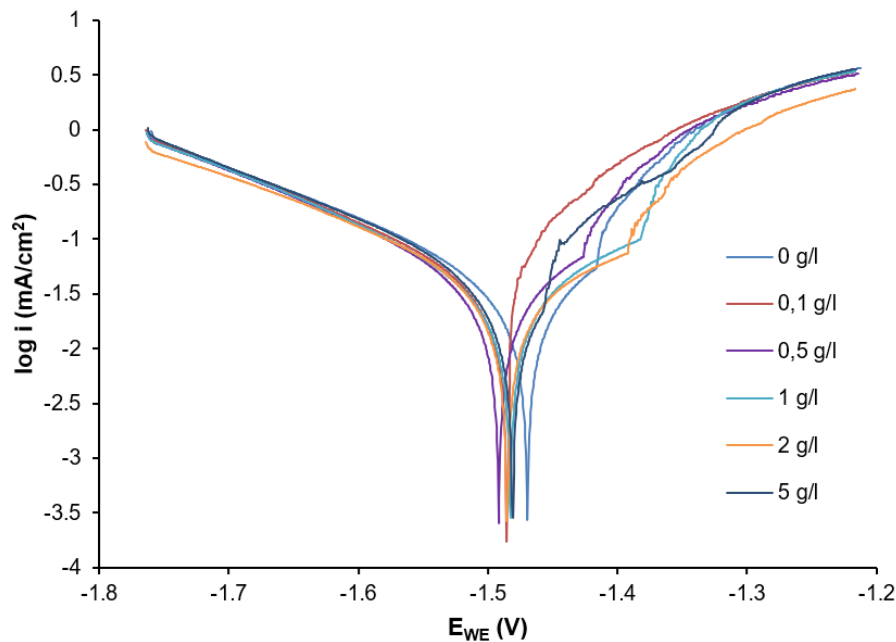

Figure 1 Potentiodynamic curves for different concentrations of glucose (Glc) in 0.9% NaCl without pH adjustment. Dependence of logarithm of current density (i) on potential (E)

Figure 2 shows the potentiodynamic curves that were obtained for AZ31 alloy in 0.9% NaCl for various concentrations at a pH adjusted to an initial value of 7.4. The curves and evaluated parameters (see **Table 1**) show that corrosion is accelerated in the presence of glucose. A more detailed analysis reveals that the corrosion aggravation increases with increasing glucose concentration from 0.1 to 0.5 g/L. However, the corrosion behaviour for glucose concentrations from 1 to 5 g/L was very similar and was characterized by a lower corrosion current density compared to 0.9% NaCl containing 0.1 to 0.5 g/L glucose. Despite this, the i_{cor} values were still higher than in the plain 0.9% NaCl. In this respect, the corrosion behaviour differed from that described above for corrosive environments without pH adjustment. Thus, it appears that the course of corrosion is sensitive to the initial pH. From the point of view of biomedical applications, the results that are more significant are of course those realized in environments with a pH of 7.4 corresponding to the natural pH of blood. The potentiodynamic curves in **Figure 2** also clearly show that glucose had an effect on the course of the anodic reaction. The increase in the anodic current density with increasing polarization potential can be

explained by the oxidation of glucose to gluconic acid, which disrupts the Mg(OH)$_2$ layer on the surface of AZ31 alloy together with chlorides. This explanation is consistent with the literature [5,6,8-10]. The decrease in the corrosion rate for higher glucose concentrations (1-5 g/L) can be related to the increase in the viscosity of the solution and consequently the limitation of the mobility of ions and molecules at the surface of the magnesium material. This mobility limitation may have facilitated the formation of Mg(OH)$_2$. The corrosion potentials of E$_{cor}$ for solutions containing glucose were more negative than those in 0.9% NaCl, indicating the susceptibility of AZ31 to corrosion in glucose-containing environments.
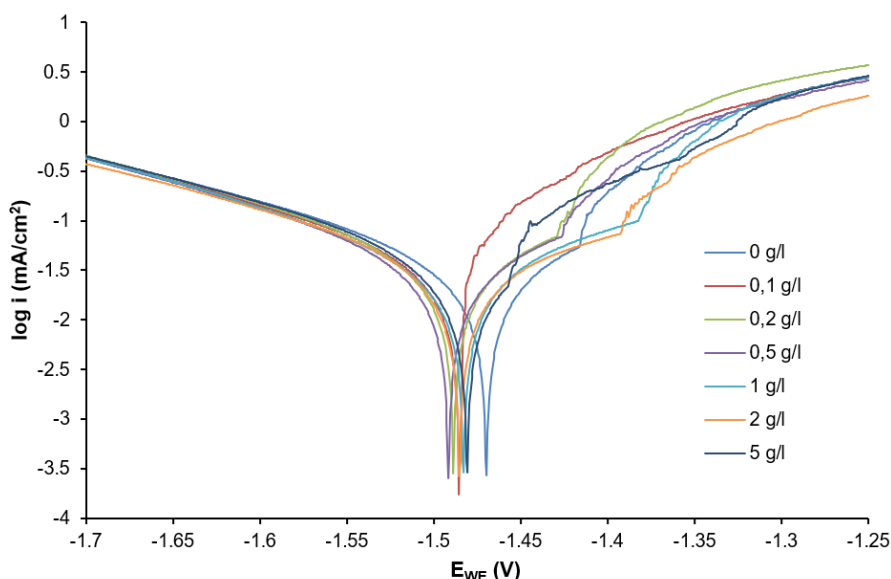

Figure 2 Potentiodynamic curves for different concentrations of glucose (Glc) in 0.9% NaCl at initial pH 7.4. Dependence of logarithm of current density (i) on potential (E)

Figure 3A and **Figure 3B** show the surface of AZ31 alloy after immersion tests in 0.9% NaCl and in 0.9% NaCl with 5 g/L glucose, respectively. The surface of AZ31 alloy corroded in plain 0.9% NaCl appears to be more uneven and containing coarser particles compared to the surface of the same alloy corroded in 0.9% NaCl with 0.5 g/L glucose. Moreover, a more detailed analysis revealed that the surface in the absence of glucose in solution was covered with very fine Mg(OH)$_2$ crystals. The presence of similar and low amounts of carbon in both environments (see **Table 2**) indicates that glucose or its oxidized form was not likely to adsorb to the surface of the corrosion products.

Table 1 Electrochemical parameters obtained from potentiodynamic curves for corrosive environments with and without pH adjustment

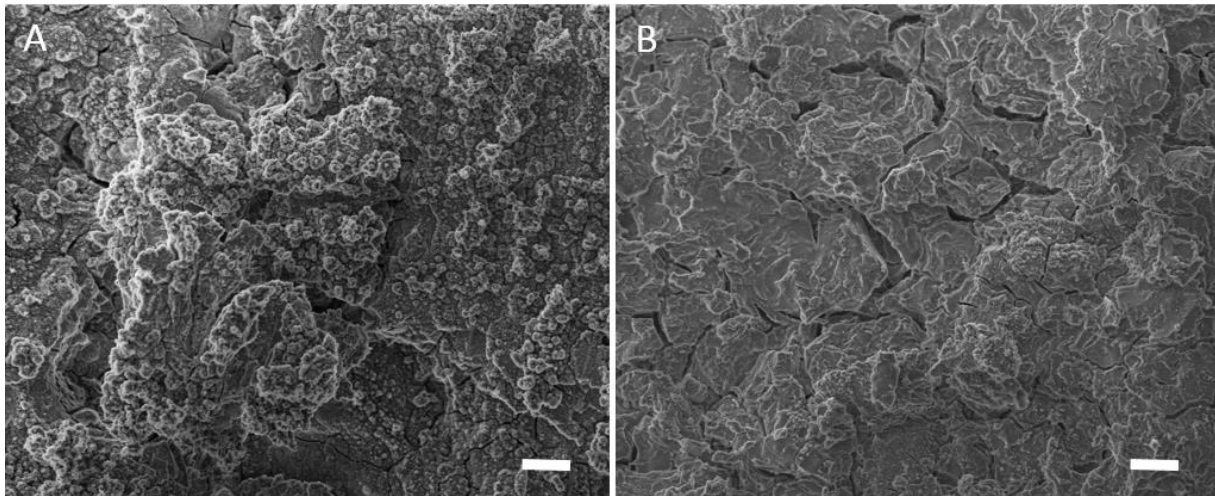| Glucose concentration (g/L)	Without pH adjustment		With pH adjustment 7.4	
	E$_{cor}$ (V)	i$_{cor}$ (µA/cm^2)	E$_{cor}$ (V)	i$_{cor}$ (µA/cm^2)
0	-1.47	25.57	-1.42	16.18
0.1	-1.45	21.82	-1.47	31.23
0.2	-	-	-1.47	33.78
0.5	-1.45	171.0	-1.47	44.31
1	-1.48	109.6	-1.46	28.25
2	-1.48	116.3	-1.47	30.97
5	-1.48	235.7	-1.46	25.39

Figure 3 SEM images of corrosion products on the AZ31 alloy after one week corrosion in 0.9% NaCl without glucose at pH 7.4 (A) and in 0.9% NaCl with 0.5 g/L glucose at pH 7.4 (B). Bar represents 100 µm

Table 2 Elemental analysis of corrosion products after one week of corrosion in 0.9% NaCl without glucose at pH 7.4 and in 0.9% NaCl with 0.5 g/L glucose at pH 7.4

Element	0.9% NaCl		0.9% NaCl with 0.5 g/L glucose	
	Average (wt%)	Average (at%)	Average (wt%)	Average (at%)
C	1.86	2.96	4.39	6.85
O	49.89	59.58	50.71	59.41
Mg	46.74	36.72	39.28	30.29
Al	0.73	0.51	2.92	2.03
Cl	-	-	2.71	1.43
Zn	0.78	0.23	-	-

4. CONCLUSION

Glucose causes the deterioration of corrosion resistance of AZ31 magnesium alloy in a 0.9% NaCl environment at 37 °C and at an initial pH of 7.4. It was observed that increasing glucose concentration from 0.1 to 0.5 g/L increased the corrosion rate, which subsequently decreased from a glucose concentration of 1 g/L. However, the corrosion rate was still higher than that in 0.9% NaCl. If corrosion tests were performed in an environment without pH adjustment, a slightly different behavior was observed. The 0.9% NaCl solution with 0.1 g/L glucose increased the corrosion resistance compared to 0.9% NaCl. Further addition of glucose resulted in accelerated corrosion as observed in the pH adjusted environment of 7.4. This highlights the importance of the initial pH of the corrosion environment. The aggravation of corrosion is related to the oxidation of glucose to gluconic acid, which together with chlorides upset the $Mg(OH)_2$ layer at the surface of the AZ31 alloy, in accordance with the literature. It seems that the presence of glucose had a slight effect on the surface morphology, since the surface of AZ31 alloy after corrosion in plain 0.9% NaCl was additionally covered with fine $Mg(OH)_2$ crystals.

ACKNOWLEDGEMENTS

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