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Corrosion performance of MAO coatings on AZ31 Mg alloy in simulated body fluid vs. Earle's Balance Salt Solution

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ABSTRACT

Earle's Balance Salt Solution (EBSS) provides an alternative to the conventional simulated body fluids (c-SBF) and has been shown to better simulate the corrosion conditions in vivo. In this work, a series of tests were conducted to explore the corrosion performance of MAO-coated AZ31 samples in EBSS vs. c-SBF. Samples were produced by varying MAO process parameters and then immersed up to 21 days in both EBSS and c-SBF. The corrosion rates were evaluated by the electrochemical impedance spectroscopy and potentiodynamic scanning. Scanning electron microscope (SEM) was used to compare the progression of microcracks across the surface of the coatings. The evaluation of cross-sectional thickness showed an increase in MAO coating thickness with the process voltage. MAO samples with a thicker coating generally have higher impedance and lower current density at the initial immersion time point of 0.5 h. Samples in EBSS showed higher initial impedance and lower current density values as compared to c-SBF counterparts for all process groups. Samples in EBSS demonstrated a much slower corrosion rate than c-SBF samples because of the decreased chloride content and CO_2 buffering mechanism of the EBSS.
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1. Introduction

Materials currently considered for use in orthopedic repair of bone damage may include metallic alloys, ceramics, and polymers [1]. Within these major classifications of materials exists a smaller population of options which have acceptable biocompatibility, corrosion resistance, and strength properties. Recent research in metallic biomaterials is focused on improving the properties listed above to expand the possible choices available to physicians, and develop materials better suited for implant as temporary bone support. The most common metallic based implants for orthopedics are stainless steels, cobalt, and titanium based alloys [2–4]. Success of these materials is owing to their excellent strength, biocompatibility, and corrosion resistance [3]. However, there is concern of reduction in biocompatibility in these materials brought on by wear of the implant and release of metallic ions into the blood [5,6]. Furthermore, a stress shielding effect, leading to bone resorption, can occur with materials which are much stronger than the bone tissue they support [7]. As a result, research interest has steered toward use of alloys and materials which more closely match the mechanical properties of human bone, such as magnesium [2].

In addition to mechanical strength and modulus closer to that of bone, magnesium degradation in the body provides a basis for a biodegradable implant material [8,9]. Use of magnesium as the basis for an implant material, however, is limited by rapid corrosion within the body which produces excessive hydrogen gas which could delay healing and affect local pH [10]. In a chloride-rich physiologic environment, Mg and $Mg(OH)_2$ react to form $MgCl_2$ exacerbating the breakdown of Mg [2,11]. Mg–Al–Zn based alloys have shown that an increase in Al content increases the corrosion resistance of these materials [12]. However, increased Al content is also linked to toxic effects in body including Alzheimer's and dementia [10]. Thus, the enhanced corrosion resistance brought on by Al alloying is limited by the concern of Al exposure. Among the Mg–Al–Zn based alloys, AZ31 Mg alloy is commercially available and popular in biomedical research due to low Al content, favorable mechanical properties, and corrosion resistance [13].

In addition to alloying, there are a variety of coating techniques being developed to further tune the corrosion performance of Mg alloys. A large number of conversion and deposition coatings for magnesium–aluminum alloys have been explored involving chemical conversion [14,15], anodization [16], sol–gel [17,18],

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Table 1
Common simulated body fluids reported in the literature.

	Ion concentration in solutions (mmol/L)							
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Blood Plasma [28]	142	5	1.5	2.5	103	27	1	0.5
Original SBF [29]	142	5	1.5	2.5	148.8	4.2	1	0
c-SBF [29]	142	5	1.5	2.5	147.8	4.2	1	0.5
m-SBF [30]	142	5	1.5	2.5	103	10	1	0.5
Hank's Solution [31]	142	5.8	0.8	2.5	145	4.2	0.3	0.8
EBSS [32]	144	5.4	0.4	1.8	125	26	1	0.4
Minimum Essential Media (MEM) [32]	143	5.4	0.4	1.8	125	26	0.9	0.4

electrodeposition [19], and polymer dip [20]. One type of conversion coating which is of particular interest for Mg, Al, and Ti materials is the method of Microarc Oxidation (MAO), also known as Plasma Electrolytic Oxidation (PEO) [21]. Discharges on the material surface produce oxides of substrate and electrolyte material grown in both directions from the substrate surface [22]. This conversion method can provide a hard, well-adhered coating which aids in wear and corrosion resistance [22,23]. Previous research related to corrosion of MAO coating on AZ31 in c-SBF has shown the dependence of corrosion performance on process parameters such as pulse frequency, oxidation time, electrolyte concentration, and voltage [24–27]. This potentially provides a basis for a "tunable" coating.

Body solutions which simulate the ion composition of human blood are a standard tool for the evaluation of corrosion performance of prospective orthopedic implants (Table 1) [28–32]. Several different solutions exist that are commonly used to evaluate material corrosion which hinders the ability to easily compare results between research labs. Furthermore, in vitro results have generally shown more severe corrosion than in vivo results, showing a gap in the ability to simulate corrosion accurately. Witte found lower overall corrosion of Mg alloy implants in vivo compared to immersion in a simulated body solution [33]. Increased chloride content in the simulated environment compared to actual body fluid was cited as the reason for this discrepancy [33]. Use of a CO_2–bicarbonate buffer has been employed in order to match the biological buffering mechanism in the body [31,32]. Abidin found good agreement between in vivo and in vitro corrosion rate results for CO_2 buffered Hank's Solution for Mg and WZ21 alloy [31]. Walker explored in vivo vs. in vitro results through use of Lewis rats and benchtop immersion weight loss testing in minimum essential medium (MEM), MEM containing 40 g/L bovine serum albumin (MEMp), and EBSS [32]. The results of the solution comparison testing showed no significant difference in corrosion rate between EBSS and the in vivo testing. Walker concluded that EBSS is an appropriate predictor of in vivo corrosion performance, and could be used to reduce animal testing when comparing a range of early stage implant concepts [32]. These results were also found in an additional study of coated Mg by Shadanbaz [34]. With this information in mind, this experiment aims to compare c-SBF vs. EBSS head to head to better understand the gap in corrosion rate for an MAO-coated AZ31 material. In addition, process varied MAO coatings were analyzed to determine trends between process settings and corrosion rate in EBSS, which has not been observed to date. Information from this experiment may aid in planning future MAO in vitro and in vivo testing through an understanding of immersion time required to observe corrosion damage in different solutions.

2. Experimental setup

2.1. Sample preparation

Substrate material AZ31 (2.5–3.5 wt% Al, 0.7–1.3 wt% Zn, 0.2–1.0 wt% Mn, 0.05 wt% Si, 0.01 wt% Cu, and Mg balance, purchased from Dongguan Fu Tai Metal Materials Co., Ltd.) was cut to 20 mm × 20 mm × 1 mm and polished with SiC paper to a roughness of approximately 1.6 μm. The samples were then cleaned ultrasonically in preparation for MAO treatment in an electrolyte bath of 10 g/L Na_3PO_4 (purchased from Sinopharm Chemical Reagent Co., Ltd.) in distilled water. MAO was performed using MAD-20 (Chengdu PULSETECH Electrical Co., LTD China). The apparatus included stainless steel bath (cathode), AZ31 substrate (anode), stirring and cooling system. Process parameters were varied to produce run groups corresponding to constant voltages of 250 V, 300 V, 325 V, and 350 V at a pulse frequency of 100 Hz and deposition time of 5 min. Samples for immersion were then cut to 10 mm × 10 mm × 1 mm, including an uncoated variation, resulting in 5 test groups in total, as shown in Table 2.

Table 2
MAO process parameters used for the MAO coating production.

Group	Voltage (V)	Frequency (Hz)	Duty cycle	Deposition period (min)
1	250	100	0.3	5
2	300	100	0.3	5
3	325	100	0.3	5
4	350	100	0.3	5
5	Uncoated	–	–	–

2.2. Immersion solutions and time points

Two SBF variants (c-SBF and EBSS) were prepared per the ion compositions in Table 3 for immersion and electrochemical testing [28,29]. As for the chemicals used for the preparation of c-SBF and EBSS solutions, NaCl, $MgSO_4$, and tris (hydroxymethyle) minomethane ($(CH_2OH)_3CNH_2$) were purchased from Fisher Scientific, and all the other chemicals were purchased from Sigma–Aldrich. All the solution preparation, sample immersion, and electrochemical testing were conducted within a pH range of 7.2–7.4 at 37 °C. The c-SBF solution was buffered with $(CH_2OH)_3CNH_2$ and pH was adjusted using 1 mol/L HCl. The solution was prepared by mixing the reagents shown in Table 4 in order in deionized (DI) water under constant stirring [29,35]. The EBSS solution was produced by mixing NaCl, $NaHCO_3$, KCl, $MgSO_4$,

Table 3
Ion concentrations of blood plasma, c-SBF, and EBSS solutions.

	Ion concentration (mmol/L)		
	Blood plasma [28]	c-SBF [29]	EBSS [Calculated]
Na^+	142.0	142.0	143.6
K^+	5.0	5.0	5.4
Mg^{2+}	1.5	1.5	0.8
Ca^{2+}	2.5	2.5	1.8
Cl^-	103.0	147.8	125.3
HCO_3^-	27.0	4.2	26.2
HPO_4^{2-}	1	1	1
SO_4^{2-}	0.5	0.5	0.8
pH	7.2–7.4	7.2–7.4	7.2–7.4

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