In-vitro characterization of stress corrosion cracking of aluminium-free magnesium alloys for temporary bio-implant applications

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ABSTRACT

The complex interaction between physiological stresses and corrosive human body fluid may cause premature failure of metallic biomaterials due to the phenomenon of stress corrosion cracking. In this study, the susceptibility to stress corrosion cracking of biodegradable and aluminium-free magnesium alloys ZX50, WZ21 and WE43 was investigated by slow strain rate tensile testing in a simulated human body fluid. Slow strain rate tensile testing results indicated that each alloy was susceptible to stress corrosion cracking, and this was confirmed by fractographic features of transgranular and/or intergranular cracking. However, the variation in alloy susceptibility to stress corrosion cracking is explained on the basis of their electrochemical and microstructural characteristics.

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1. Introduction

Magnesium and its alloys are attractive biodegradable material because of their attributes of excellent biocompatibility, appropriate mechanical properties and suitable electrochemical characteristics [1–4]. In recent times, there has been an increasing interest in aluminium (Al)-free magnesium alloys as construction materials of implant devices for short-to-medium term applications [5–7]. Some of these Al-free magnesium alloys have been deployed successfully in animal trials and are currently being considered for use as cardiovascular stents and temporary implants in osteosynthesis [5,8,9]. However, it is yet to be established whether these alloys possess desired resistance to cracking under the influence of corrosive human body fluid.

1.1. Magnesium alloys as biodegradable implants

Traditional implants of stainless steels, cobalt-chromium alloys and titanium alloys have been widely used in medical applications because of their superior strength, ductility and resistance to corrosion [4]. When these traditional alloys are used as temporary implant devices, such as plates, screws and wires, a second surgery is required to remove the implant after tissues have healed. Besides the cost of this surgical procedure and inconvenience to patients, the traditional alloys also cause local inflammation due to potential release of cytotoxic ions. It would be very advantageous if such an implant material could be identified which degraded in the physiological environment after completion of the healing process. This approach will eliminate need for the second surgical procedure. In this regard, magnesium alloys are potential candidates for the use as biodegradable temporary implant devices because they can naturally degrade in the human body environment due to their high electrochemical activity (standard reduction potential of magnesium is -2.4 V vs. standard hydrogen electrode (SHE) [10]). Magnesium is also vital for human metabolism processes, including for the stabilization of DNA and RNA [11]. Any excess magnesium is harmlessly excreted with urine. Unlike traditional implant materials, the mechanical properties of magnesium are also very suitable for implant applications: they possess low density (ρ) $= 1.74$–2.0 g cm^{-3} and elastic modulus (E) $= 41$–45 GPa, both of which are similar to these properties of human bones [4]. Hence the problem of stress shielding, which is caused by a mismatch in the elastic modulus between natural bone and implant, can be mitigated if magnesium alloys are deployed as implant materials.

1.2. Stress corrosion cracking of magnesium alloy implants

Implants often experience considerable loadings during service. For example, a cardiovascular stent is continuously subjected to cyclic loading due to heartbeats [12,13]. The synergistic presence of mechanical loading combined with corrosive environment of human body fluid

may pose serious complications, such as sudden fracture of implants due to stress corrosion cracking (SCC) [14]. SCC is an embrittlement phenomenon that can occur even at stresses below yield strength, leading to a premature brittle failure. Brittle cracks generally initiate at locations with sharp contours such as root of a corrosion pit. Pre-existing macro/microscopic flaws (such as those developed during fabrication) can also markedly increase the susceptibility to premature SCC failure. SCC will be a serious concern when deploying implant devices comprising magnesium alloys because: (a) common temporary implant devices (such as screws, pins and plates) possess sharp contours and (b) magnesium alloys readily suffer pitting in chloride solutions [15,16]. Indeed, magnesium alloys have been reported to be susceptible to SCC in chloride solutions [17–19], including in simulated body fluid environments [14]. It is relevant to note that the traditional metallic implants (stainless steels and titanium alloys) are also reported to suffer premature, sudden and catastrophic SCC fracture during service [20,21].

Most studies on the deployment of magnesium alloys as implant material have aimed at improving their corrosion resistance in simulated human body fluid [22–24]. The literature on mechanical integrity/SCC behaviour of magnesium alloys in simulated body fluids is generally limited to a few preliminary studies, primarily on the Al-containing magnesium alloys [13,14,25,26]. All Al-containing magnesium alloys (such as AZxx (containing Al and Zn) and AMxx (containing Al and Mn)) have been reported to be susceptible to SCC in distilled water and chloride-containing solutions [27]. The susceptibility to SCC was generally found to increase with increasing Al concentration [28]. Accordingly, the avoidance of Al in the magnesium alloy biomaterials may be quite useful not only in addressing the commonly perceived toxicity issues due to Al, but also in attempts to develop alloys with improved resistance to SCC in human body fluid (that has considerable chloride content).

In this study, three Al-free biodegradable magnesium alloys, ZX50, WZ21 and WE43 (that are potential candidates for implant applications) were evaluated for their resistance to SCC in a simulated body fluid. The alloys WZ21 and WE43 are reported to meet the requirements of moderate and homogenous degradation for implant applications [5,9,29]. In addition, each of these alloys also exhibits high ductility (uniform elongation of 17–30%) and appropriate strength (ultimate tensile strength: 250–350 MPa), which are necessary for an alloy to serve as a suitable implant material. For example, stents require sufficient ductility for a uniform strain (optimally ≥ 15%) for the purpose of ballooning and for ease of fabrication and placement procedure, as well as they also require reasonable strength (ultimate tensile strengths ≥ 250 MPa) to support the blood vessels adequately [30,31]. Temporary implants for osteosynthesis require good ductility for geometrical adaption by the surgeon [32]. In-vitro and animal studies also show each alloy to possess good cytocompatibility [5,8]. The WE43 alloy was chosen as a reference material in this study because it has already been employed in stent applications and found to meet other requirements for implant applications [33,34]. However, the resistance to environmentally-assisted cracking is one critical property that has not yet been characterized for these alloys.

2. Materials and methods

2.1. Materials and environment

The ZX50, WZ21 and WE43 magnesium alloys were produced by direct chill casting, using magnesium and alloying elements (purity ≥ 99.9%). The melting was carried out in an electric furnace at ~690 °C, and subsequently casting at a velocity of 1.3 mm/s, with continuous water cooling. The extrusion ratio was 30:1 for WZ21 and ZX50, while it was 25:1 for WE43 [5,31,35]. The alloys were evaluated in their as-extruded conditions. The nominal chemical compositions of the alloys are shown in Table 1.

The test medium was a modified-simulated body fluid (m-SBF) that was maintained throughout the test at the nominal body temperature of

Table 1
Nominal chemical composition (in wt. %) of ZX50, WZ21 and WE43 alloys.

Alloy	Mg	Zn	Zr	Ca	Mn	Y	Nd	Other rare earths (REs)
ZX50	Bal.	5	–	0.25	0.15	–	–	–
WZ21	Bal.	1	–	0.25	0.15	2	–	–
WE43	Bal.	–	0.6	–	0.15	4	2.25	1

37 °C using a water bath. A comparison of m-SBF solution used in this study with the Hank's solution and actual human blood plasma is provided in Table 2 [36,37]. The m-SBF solution was buffered with 2-(4-(2-hydroxyethyl)-1-piperazinyl) ethansulfonic acid (HEPES) for the purpose of maintaining a physiological pH of 7.4. As Table 2 shows, the chemical nature of m-SBF solution is largely identical to that of blood plasma, except for the concentration of HCO_3^-, which was set to the saturation level with respect to calcite [36]. To simulate the flowing body fluid, a submersible pump was used for continuously circulating the m-SBF (volume = 1 L, flow rate = 15 mL/s) through a container in which the test specimen was immersed, as shown in the experimental set-up in Fig. 1.

2.2. Slow strain rate tensile (SSRT) testing

The SCC susceptibility of the magnesium alloys was investigated using slow strain rate tensile (SSRT) testing. This study used cylindrical round tensile specimens with gauge dimensions of 20 mm (length) and 3 mm (diameter). The specimen axis direction was aligned with the extrusion direction. These specimens were ground with SiC paper up to 2500 grit, and were cleaned with acetone and deionised water prior to the testing. Fig. 1. shows details of the experimental set-up. In SSRT testing, strain rate is a critical parameter. The literature reports that strain rates in the range of $10^{-7}\,s^{-1}$ render magnesium alloys susceptible to SCC in chloride solutions [17,18,38]. In the present study, specimens were pulled at a strain rate of $3.1 \times 10^{-7}\,s^{-1}$ until fracture, while the elongation was measured using a linear variable displacement transducer (LVDT).

The SCC susceptibility of each alloy was established on the basis of the SCC susceptibility index (I_{SCC}). The I_{SCC} is defined as [39]:

$$I_{SCC} = \frac{(\text{UTS or Elongation})_{air} - (\text{UTS or Elongation})_{m-SBF}}{(\text{UTS or Elongation})_{air}} \times 100\%.$$

The higher the value of I_{SCC} the greater is the SCC susceptibility, whereas I_{SCC} tending to zero suggests immunity to SCC.

To investigate the mechanism of SCC in a separate set of experiments, specimens were continuously charged cathodically at a constant potential of 200 mV (vs. SCE) negative to the corrosion potential using a potentiostat, while straining the specimens simultaneously in m-SBF. A

Table 2
Chemical composition of m-SBF solution compared with Hank's solution and the inorganic portion of human blood plasma.

Ion	m-SBF (mM) [36]	Hank's solution (mM) [37]	Blood plasma (mM) [36]
Na^+	142	142	142
K^+	5.0	5.8	5.0
Mg^{2+}	1.5	0.8	1.5
Ca^{2+}	2.5	2.5	2.5
Cl^-	103	145	103
HCO_3^-	10	4.2	27
HPO_4^{2-}	1.0	0.3	1.0
SO_4^{2-}	0.5	0.8	0.5