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Influence of strain on the corrosion of magnesium alloys and zinc in physiological environments

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ABSTRACT

During implantation load-bearing devices experience stress that may influence its mechanical and corrosion profile and potentially lead to premature rupture. The susceptibility to stress corrosion cracking (SCC) of the Mg-Al alloy AZ61 and Zn was studied in simulated body fluid (m-SBF) and whole blood by slow strain rate (SSR) testing in combination with electrochemical impedance spectroscopy (EIS) and further ex situ analysis including scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy. AZ61 was found to be highly susceptible to SCC. EIS analysis show that although the majority of cracking occurred during the apparent plastic straining, cracking initiation occurs already in the elastic region at ~50% of the ultimate tensile strength (UTS). Shifts in EIS phase angle and open circuit potential can be used to detect the onset of SCC. Zinc demonstrated a highly ductile behavior with limited susceptibility to SCC. No significant decrease in UTS was observed in m-SBF but a decrease in time to failure by ~25% compared to reference samples indicates some effect on the mechanical properties during the ductile straining. The formation of micro cracks, ~10 μm deep, was indicated by the EIS analysis and later confirmed by ex situ SEM. The results of SSR analysis of zinc in whole blood showed a reduced effect compared to m-SBF and no cracks were detected. It appears that formation of an organic surface layer protects the corroding surface from cracking. These results highlight the importance of considering the effect of biological species on the degradation of implants in the clinical situation.

Statement of Significance

Strain may deteriorate the corrosion properties of metallic implants drastically. We study the influence of load on the corrosion properties of a magnesium alloy and zinc by a combination of electrochemical impedance spectroscopy (EIS) and slow strain rate analysis. This combination of techniques has previously not been used for studying degradation in physiological relevant electrolytes. EIS provide valuable information on the initial formation of cracks, detecting crack nucleation before feasible in slow strain rate analysis. This sensitivity of EIS shows the potential for electrochemical methods to be used for in situ monitoring crack formation of implants in more applied studies.

1. Introduction

Biodegradable metallic implants present an attractive alternative to permanent implants in applications where the implant is only required during the healing and remodeling phases, e.g. bone fixation screws or cardiovascular stents. Permanent implants may cause long term adverse effects or necessitate explant surgery resulting in increased healthcare costs and patient risks [1]. The most studied metallic material system for biodegradable applications is magnesium based alloys, attractive due to their low toxicity and beneficial mechanical properties [2]. However, the corrosion rate of Mg based implant materials tends to be too high for most clinical applications [2]. As an alternative to magnesium based biomaterials, zinc based alloys have received growing interest during the last few years [3–6]. Both *in vitro* and *in vivo* studies demonstrate a suitable corrosion rate and mechanism [3–7]. A potential concern of using zinc as a biodegradable implant material is its cytotoxicity as demonstrated by *in vitro* analysis [7,8]. However, current standards for *in vitro cytotoxicity* for evaluation of biodegradable metallic materials are under discussion [9]. More

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importantly, *in vivo* studies of zinc alloys demonstrate excellent biocompatibility [5,10]. A review on zinc in cardiovascular applications can be found in reference [6].

Despite recent progress in biodegradable metallic materials [2,6,11], there is still a gap between the desired material properties for clinical applications and available materials. Development and analysis of novel materials by alloying, processing or other techniques will continue to be important.

A concern for any new degradable metallic implant material is the influence of load on the degradation profile. Forces are applied to implants through every day movement and the ability of implants to withstand such forces is critical for patient wellbeing. In the most common suggested applications for biodegradable metallic alloys, i.e. bone fixation screws, vascular closure devices and cardiovascular stents, the implanted material must withstand application of forces. In the case of bone fixation screws the load is induced when the patient moves. For vascular closure devices and stents extensive loading is exerted during the initial deployment and subsequently from contractions with heartbeats [12]. For some materials, loading may increase the corrosion rate which under worst case situations can induce stress corrosion cracking (SCC), leading to failure.

Premature failure of implants may have dire consequences for the patient. It is therefore of outmost importance to evaluate the sensitivity of SCC of any newly developed material for biodegradable applications.

Magnesium alloys in general and Mg-Al alloys in particular are known to be susceptible to stress corrosion [13]. The generally accepted main mechanism of SCC in Mg alloys is deterioration of the mechanical properties through hydrogen embrittlement [13]. Load induced imperfections in the protective layer allows for diffusion of hydrogen produced in the cathodic reaction into the metal matrix. The absorbed hydrogen causes local embrittlement and induces cracking. The crack then propagates through the brittle material until it reaches the elastic bulk were it halts. However, the corrosion at the crack tip will continually produce hydrogen and when enough hydrogen has diffused into the metal matrix in front of the crack tip the brittle fracture resumes [13]. In addition to hydrogen embrittlement SCC in Mg-Al alloys is also believed to be influenced by preferential anodic dissolution. The mechanical stress causes localized rupture of the protective film and exposes a bare metal surface at the crack tip. The cathodic potential of the bare metal surface compared to the surrounding area increase the corrosion rate and crack propagation at the crack tip. Typically hydrogen embrittlement is associated with transgranular cracking and preferential anodic dissolution with intergranular cracking of Mg alloys [13]. Although extensive research has been performed on magnesium alloys and SCC for e.g. applications in the automobile industry there is a lack of research on SCC of magnesium alloys for medical applications [12]. Choudhary et al. have found the AZ91 and the Mg3Zn1Ca alloys to be susceptible to SCC in modified simulated body fluid (m-SBF) [14–16]. The observed transgranular cracking suggests that the prime mechanism is hydrogen embrittlement [13,15,16]. However a better understanding of the cracking mechanism is required in order to design materials less susceptible to SCC.

Unlike magnesium based alloys, pure zinc is rarely used as load-bearing construction material due to its low tensile strength. Therefore not much is known of the effect of a corrosive environment on its mechanical properties. Although zinc is generally not believed to suffer from SCC, evaluation [17] of the effect of strain in a physiological environment is important in order to confirm the suitability of zinc as a biodegradable implant material.

Initial screening of new materials by *in vitro* methods present an attractive option to *in vivo* animal studies as these are often costly and time consuming. In addition, *in vitro* methods offer the possibility to employ several in situ techniques to gain further insight into the details of the degradation mechanisms. Electrochemical impedance spectroscopy (EIS) is a powerful technique used to characterize surfaces in situ. It is widely used to study the evolution of corroding surfaces with time since the interface is unaffected by the analysis. By monitoring the electrochemical impedance during slow strain rate testing (SSR) complementary information of the changes in surface properties during the straining is obtained. SSR provides information on the effect of a corrosive environment on the mechanical properties while EIS determine the effect of strain on the corrosion. The combination allows for determining the relation and interdependence of surface corrosion and mechanical properties in corrosive environments.

Additionally, by studying the effect of strain on the surface impedance for materials suffering from SCC it may be possible to use impedance as a detection method for SCC when studying biodegradable metals in more applied *in vitro* environments. EIS may also contribute with further insights into cracking initiation and propagation mechanisms. There are some previous studies of impedance analysis of stainless steels during SSR. Petit et al. related crack initiation to a maximum in impedance phase angle at a fixed frequency [18]. Bosch et al. developed a model to simulate the impedance of a cracked surface [19]. The model was used to predict the shift in phase angle between strained and unstrained samples at different frequencies and for various crack sizes. The model was verified by observing the phase shift of samples subjected to SSR test or constant load test. The predicted phase shift occurred and thus identified the time of crack initation [20]. Bastos et al. used EIS to characterize the influence of straining on the electrochemical behavior of stainless steel during SSR test. The characteristic phase angle shifted towards lower frequencies and lower maximum phase angle with increasing levels of stress [21].

In this study the SCC of the magnesium alloy AZ61 as well as the influence of strain on the corrosion of zinc was characterized by in situ EIS. Ex situ examination by scanning electron microscopy (SEM) of both surface and cross sections and Fourier transform infrared spectroscopy (FTIR) was performed to confirm the analysis of the impedance results. The corrosive environment, m-SBF, was chosen to simulate the ionic concentration of body fluids. Zinc was further evaluated in citrated human whole blood to examine the influence of proteins, cells and other biological species.

2. Materials and methods

Magnesium alloy rods AZ61 (6 wt% Al, 1 wt% Zn) and Zn rods (purity 99.9%) were obtained from Goodfellow Cambridge Ltd. The rods were machined into test specimens according to ASTM standard G0049 [22] with gauge length 20 mm and gauge diameter 3 mm. The samples were polished with SiC paper down to 4000 grit prior to testing. The samples were coated with silicon adhesive in order to only expose the gauge length to the electrolyte. The surface area exposed to electrolyte was 1.6 cm^2. m-SBF was prepared as described by Oyane et al. [23]. Donated citrated human whole blood was obtained from the Karolinska University Hospital, Stockholm, Sweden. Whole blood have previously been reported as a suitable *in vitro* environment to simulate *in vivo* corrosion of zinc but unsuitable for studies of magnesium corrosion [24,25]. Therefore only zinc was evaluated in whole blood.

All tests were performed in ambient conditions at room temperature and replicated at least two times. The slow strain rate (SSR) tests were performed using a Zwick/Roel 2.5 materials testing machine according to ASTM standard G0129 [26]. Reference samples were exposed to laboratory air during analysis. The AZ61 and Zinc samples were tested with a crosshead travel speed of 5.5×10^{-6} mm s^{-1} and 3.2×10^{-5} mm s^{-1} respectively.