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Assessment of localized corrosion under simulated physiological conditions of magnesium samples with heterogeneous microstructure: Value of X-ray computed micro-tomography platform

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ABSTRACT

Accurate assessment of magnesium degradation is crucial for the development of safe medical devices. X-ray computed microtomography is one of the methods that are recently used to evaluate the corrosion of magnesium. This work validates the potential of this method to discern the different corrosion rates of different surfaces of a magnesium coupon, representing a real advantage of this technique over other methodologies that only evaluate the overall corrosion behaviour. The results also show that magnesium corrodes faster in zones with high twin density and that its corrosion product formation varies in different simulated physiological fluids.

1. Introduction

Biodegradable metallic materials for medical applications have received considerable attention in recent years. One of the reasons is that they provide high potential for fabrication of temporary load-bearing orthopaedic implants such as bone fixation implants. The main advantage of temporary or biodegradable devises is that they avoid the second surgery, which might be needed to remove the permanent implant after bone healing. This can increase the patient's safety and lower the cost of the medical treatment. Magnesium (Mg) is an excellent candidate for the fabrication of biodegradable implants due to its biocompatibility and relevance for biological body functions. Furthermore, its mechanical properties are more similar to bone than those of biostable metals currently used in medicine [1–3]. Unfortunately, application of Mg is limited by its high corrosion rate. Several studies have been focused on the control of Mg degradation rate in simulated physiological conditions *in vitro* through various approaches such as development of new Mg alloys [4–6] and formation of anticorrosive coatings on Mg substrates [7–9]. Further studies evaluated the *in vivo* response of some new alloys and/or coatings using animal models [10–12]. The methodologies commonly used to assess the degradation rate of Mg include mass loss, hydrogen evolution, pH monitoring, ion release and electrochemical test (either potentiodynamic polarization or electrochemical impedance spectroscopy) [1,3,13]. More recently, the use of X-ray computed microtomography (μCT) has been introduced [11,14–17], but it is still barely exploited method in the biomaterials field.

μCT is a non-destructive method that is used to visualise and analyse the inner structure of an object. The method is based on the acquisition of several X-ray images obtained at various angular views around the object commonly between 0 and 180° or 360°. The set of images collected is mathematically reconstructed using the filtered back projection algorithm to get tomographic slices representing the virtual cross-sections of the object [18]. These virtual sections can be used further on to observe a three-dimensional (3D) reconstruction of the object. This method was already used to study the *in situ* corrosion of aluminium and iron based alloys obtaining object resolutions up to 3 μm [19,20]. However, the maximum size of the studied samples was only 500 μm. New developments in X-ray μCT technology had allowed studying the corrosion of aluminium alloys for aircraft applications using bigger samples [21]. In biomaterials field, and more specifically in the studies of biodegrad-

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able Mg implants, μCT has been used to study Mg degradation in living animals using clinical μCT systems [14,15] and to study explanted samples [11,16,17]. These studies proved the effectiveness of μCT for determination of the Mg degradation rate in living animal models or after *in vivo* studies. Apart from these numerous studies of overall corrosion of the samples/implants, further work is needed to demonstrate the efficiency of μCT in determination of the localized corrosion rate of Mg implants *in vitro*, *i.e.* under physiological simulated conditions. Only based on this, the μCT methodology for *in vivo* studies can be established to assess the detailed biodegradation behaviour of Mg implant. In future, this method can be useful tool for design and characterisation of implantable devices with tailored degradation zones, matching particular *in vivo* requirements.

The aim of this work is to prove that standard μCT analysis is a quantitative, robust, reproducible and accurate technique to assess the localized corrosion of commercially pure Mg under physiological simulated conditions. In the study, discs from wrought Mg bar with heterogeneous microstructure were used to promote non-uniform degradation, which occurred preferentially on the edge of the sample. The efficiency of μCT method was compared with that of conventional analytical methods which are commonly used for evaluation of the degradation of Mg and its alloys.

2. Material and methods

2.1. Magnesium samples

A commercially pure Mg bar (99.9%, 12.7 mm in diameter, MG007924, Goodfellow, UK) was cut into 5 mm thick discs. While the top and bottom circular surfaces of the discs were mechanically ground up #1000 SiC paper, the edge surface was tested as supplied to promote differences in corrosion rate. Before the corrosion test, samples were ultrasonically cleaned in ethanol and dried in hot air. For metallographic observation, the top circular surface, as well as disc cut in transverse direction along the axis, were prepared using techniques which are usually used for Mg and its alloys. Every preparation step was carefully planned to avoid any affection of the microstructure. Microstructures were revealed by 2% HNO_3 solution and observed using an optical microscope (Olympus DSX 510) and scanning electron microscope (SEM; TESCAN Lyra3). Grain size was measured in accordance with Planimetric Method ISO 643. Yield strength, tensile strength and elastic modulus were determined by tensile test according to ISO 6892-1. Normalized samples for tensile test were machined from the same Mg bar as the disc samples. The tensile test was performed at a strain rate of 2 mm/min using a Zwick Z250 universal test machine. Values were calculated as an average of three measurements.

2.2. Degradation immersion test

Immersion test was performed in simulated physiological conditions using Hank's solution according to ISO 11845. The solution was prepared without glucose using analytical grade reagents (Lach Ner) according to the following molar composition: 1.26 mM $CaCl_2$, 0.49 mM $MgCl_2{\cdot}6H_2O$, 0.41 mM $MgSO_4{\cdot}7H_2O$, 5.33 mM KCl, 0.44 mM KH_2PO_4, 4.17 mM $NaHCO_3$, 137.93 mM NaCl and 0.34 mM Na_2HPO_4 [22]. In addition, 0.9% NaCl (30093; Lach Ner) solution was used for the comparison of the results. Mg samples (each with a total initial surface area of 452.8 mm^2) were immersed individually in 50 ml of solution and the temperature was kept at $37 \pm 1\,^{\circ}C$ in a climatic chamber (Binder KMF 115). Once a week, distilled water was added to keep the total volume of test solution constant. Two samples were removed from the solution every week, up to a maximum of 8 weeks, rinsed with distilled water and dried.

2.3. Variations of pH and Mg^{2+} concentration in the immersion media

Variations of the pH of the immersion media were determined every week with a pH meter (ALMEMO 2590 Ahlborn). The release of Mg^{2+} from the metallic sample to the immersion media was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Thermo Scientific iCAP 6500 Duo) in radial mode on ionic emission line at 279.553 nm.

2.4. Characterization of the solid corrosion products

The macroscopic aspect of the samples (with the corrosion products) after the immersion test was documented, afterwards, the detailed microstructure of the corrosion products formed on Mg surface was observed by SEM. Samples for SEM observation were coated with a thin carbon layer prior the analysis to prevent the sample charging. The crystalline phase composition of the corrosion products was determined using X-ray diffraction (Rigaku SmartLab 3 kW CF2) by scanning in Bragg–Brentano geometry, using Cu Kα radiation with scan range in between 10 and 90° and scan speed of 3°/min. Rietveld refinement of the obtained patterns was performed with High Score software to determine the percentage of crystalline phases using the Inorganic Crystal Structure Database (ICSD). The presence of amorphous phases was neglected.

2.5. Overall corrosion rate of magnesium samples

Two different methodologies were used to determine the mass of the Mg samples after complete removal of the corrosion products by sample immersion in CrO_3 and Ag_2CrO_4 solution according to ISO 8407. The first method corresponded to the typical gravimetric quantification using an analytical weighing scale (Discovery Ohaus). The second method used was the determination of sample volume by μCT in accordance with the next section. Afterwards, the changes in sample volume were converted in mass variations, assuming the density of the Mg samples as the theoretical density of pure Mg (1.74 g/cm^3 at 20 °C). Finally, corrosion rate (v_{corr}) was determined using the Eq. (1). Corrosion rates determined by gravimetric method and μCT are indicated as $v_{corr-Grav}$ and $v_{corr-\mu CT}$, respectively.

$$v_{corr} = \frac{(M_0 - M_t)}{At\rho} \quad (1)$$

where M_0 is the initial mass of the sample and M_t is the mass of the sample at experimental time point, A is the initial area of the sample exposed to the corrosive environment, t is the immersion time and ρ is the density of pure Mg.

2.6. X-ray computed microtomography

The μCT analysis was conducted using the GE phoenix *v*|tome|*x* L 240 system equipped with a 180 kV/20 W maximum power nanofocus X-ray tube and high contrast flat panel detector DXR250. The tomographic measurement was performed at the temperature of 21 °C, 80 kV acceleration voltage and 150 μA X-ray tube current. The X-ray spectrum of tungsten target was modified by 0.5 mm thick aluminium filter. The exposure time per step was 500 ms in every of 2000 positions around 360°. The isotropic linear voxel size (voxel resolution) of obtained volume was 25 μm. The sample tomographic reconstruction was performed with GE phoenix datos|*x* 2.0 software, using the object shifting correction and the beam hardening correction in the different material modes. The two-dimensional (2D) and 3D visualization of the samples, as well as the structural parameter quantifications, were performed using VG Studio MAX 2.2 software.

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