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In vitro degradation behaviour of biodegradable magnesium alloys

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Biodegradable magnesium alloys are promising materials for orthopaedic implants. With their mechanical properties similar to native bone, magnesium alloys can overcome some significant disadvantages of conventional metallic implants. Nonetheless, the material degrades too fast for clinical approval. Therefore, the corrosion rate of the implant needs to be controlled and decelerated to guarantee sufficient mechanical support during the entire bone healing process. In this work, we analyse the corrosion behaviour of the magnesium alloy WE43 in a physiological environment and assess the influence of a plasma electrolytic coating to the corrosion process. The experimental results show that the coating significantly decreases the mass loss rate as well as the degradation of the material strength of the WE43 alloy.

1 Introduction

Biodegradable magnesium alloys have emerged as next-generation orthopaedic implants to overcome major disadvantages of conventional non-degradable metallic implants [1]. One substantial drawback of orthopaedic implants is related to mechanobiological processes. Bone implants will carry the external load on the fixed bone. If the elastic modulus of the implant does not match with the one of native bone, the surrounding bone tissue will be subjected to unphysiological low stress states which lead to undesired pathological changes during the remodelling process. The elastic moduli of magnesium alloys (40 - 45 GPa) are much closer to the human bone tissue (15 - 20 GPa) than conventional titanium alloys (114 GPa) [2, 3]. Therefore, pathological changes in bone tissue are minimized by the application of magnesium alloys. These negative remodelling effects will be amplified when non-degradable implants permanently remain inside the patient. More importantly, the degradation of magnesium alloys in the human body can avoid the subsequent implant removal surgery. However, the limiting factor for the application of biodegradable magnesium alloys in orthopaedic and load bearing implants is the fast degradation of the material in physiological conditions [4, 5]. Exceeding and uncontrolled material degradation cannot satisfy the requirement of the implant to mechanically support the bone tissue throughout the healing process, as shown in Figure 1. Hence, understanding the corrosion behaviour of biodegradable magnesium in a physiological environment is of significance to adequately design biodegradable next-generation implants.

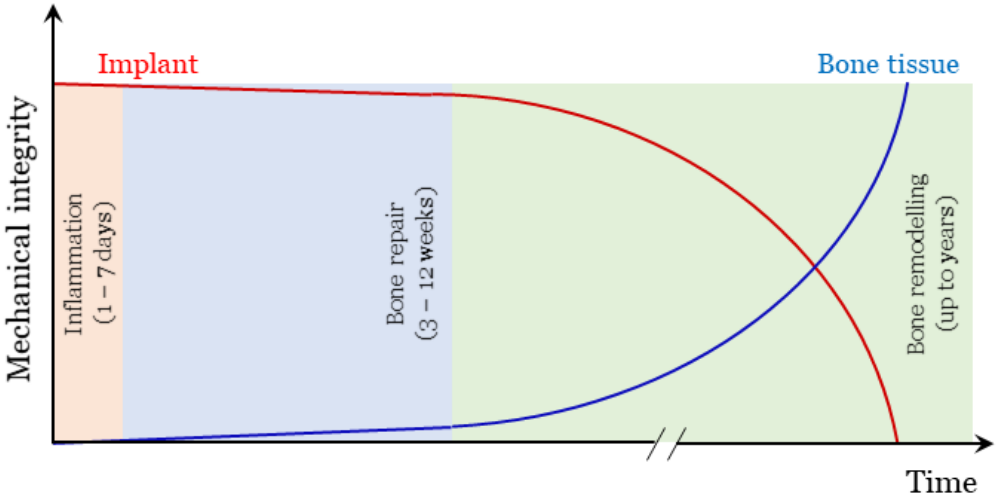

Fig. 1: Desired degradation of mechanical integrity of the magnesium implants and the bone strengthening during the fracture healing.

In the past years, a large number of studies has analysed the corrosion behaviour of various magnesium alloys in physiological environment [6, 7]. Experimental studies have revealed that the composition of the corrosion media is of significance

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to the experimental outcome of *in vitro* experiments [8, 9]. Thus, *in vitro* boundary conditions should be defined carefully. In a physiological environment, the ionic concentrations of the fluid should match the one of human blood plasma as high chloride concentrations have a detrimental effect resulting in high corrosion rates. To simulate the human blood plasma in its composition, additional components such as amino acids, vitamins and glucose can be added. However, the application of the complex medium lead to a higher contamination risk in the experiment and the difficulties of the implementation in aseptic conditions, especially for long corrosion periods. Micro-organic contamination will shift the pH to a non-physiological regime, and physiological experimental boundary conditions cannot be ensured. The integration of buffer systems into the media prevents pH changes that result from the chemical corrosion reaction of the alloy.

Recently, aluminium-free magnesium alloys alloyed with rare-earth elements have been studied more intensively. The magnesium alloy WE43 is a promising material for such next-generation implants as it is highly biocompatible and biosafe, while possessing better corrosion resistance which can be attributed to its rare earth and zirconium content. Castellani et al. [10] showed that a magnesium alloy containing rare earth, yttrium and neodymium is superior in bone-implant interface strength and osseointegration compared to a conventional medical titanium alloy. Nonetheless, for extensive biomedical applications the corrosion resistance needs to be further improved. Therefore, a wide variety of surface modification techniques are developed and their effect on the *in vitro* degradation of magnesium alloys is analysed [11–13]. One promising strategy to retard the corrosion is the surface modification by plasma electrolytic coating, where an oxidised surface layer is generated on the alloy.

In this work, we present experimental results on the *in vitro* corrosion behaviour of the WE43 alloy and the influence of a plasma electrolytic coating (PEO) in physiological environment using a complex corrosion media including organic compounds. To this end, we continuously monitor the corrosion process of the non-coated and coated alloy by measuring the hydrogen gas volume that evolves during the corrosion process and subsequently assess the degradation in the mechanical integrity of the alloy using tensile tests.

2 Materials and Methods

2.1 Corrosion experiments

The magnesium alloy WE43 was used in the corrosion experiments and its chemical composition is given in Table 1. Round tensile dog-bone specimens of the coated and non-coated alloy with a diameter 4 mm were provided by Medical Magnesium GmbH (Aachen, Germany). To limit the corrosion to a uniform surface area within the specimens' gauge length, both sample ends were covered. The specimens were vertically mounted into an inverted funnel, as shown in Figure 2, so that the sample surface exposed to the fluid was fully positioned underneath the funnel. The hydrogen gas evolving during corrosion is collected via the funnel in the burette and the gas volume is monitored using the fluid level in the riser.

Table 1: Chemical composition of the magnesium alloy WE43.

Y	Nd	Zr	Al	Mn	Fe	Mg
3.8 %	2.6 %	0.02 %	<0.01. %	0.0025 %	0.0065 %	Bal.

Prior to the experiments, the specimens and the experimental setup were sterilized. 500 ml of the organic cell culture medium Dulbecco's Modified Eagle's Medium (Biowest, Nuaillé, France) with ionic concentrations similar to human blood plasma was used as corrosion media. To reduce the risk of contamination the medium was supplemented with 5 ml Penicillin-Streptomycin (ThermoFisher Scientific Inc., Waltham, MA, USA) and 20 mg sodium azide (VWR International LLC, Radnor, PA, USA). The ionic concentations of DMEM and human blood plasma are compared in Table 2 .

Table 2: Ionic concentrations of human blood plasma and DMEM in mmol/l.

Ion	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Blood plasma	142	5	1.5	2.5	103	27	1	0.5
DMEM	154	5.4	0.8	1.8	119	44	1	0.8

The experimental setup was placed in the incubator throughout the entire experiment to assure a steady temperature level at 37° C +/- 1° C. After corrosion periods of 1, 2, 3, and 4 weeks, specimen were removed from the fluid and washed with distilled water and ethanol. The mass loss rate was subsequently calculated from the collected gas volume according to Kirkland et al. [14].

2.2 Tensile tests

Tensile tests were performed on a 858 Mini Bionix II (MTS Systems, Eden Prairie, USA) and the strain was monitored with a video extensometer (Carl Zeiss GOM Metrology GmbH, Braunschweig, Germany), see Figure 3. Data processing was performed according to EN ISO 6892-1 in MATLAB version R2018b.

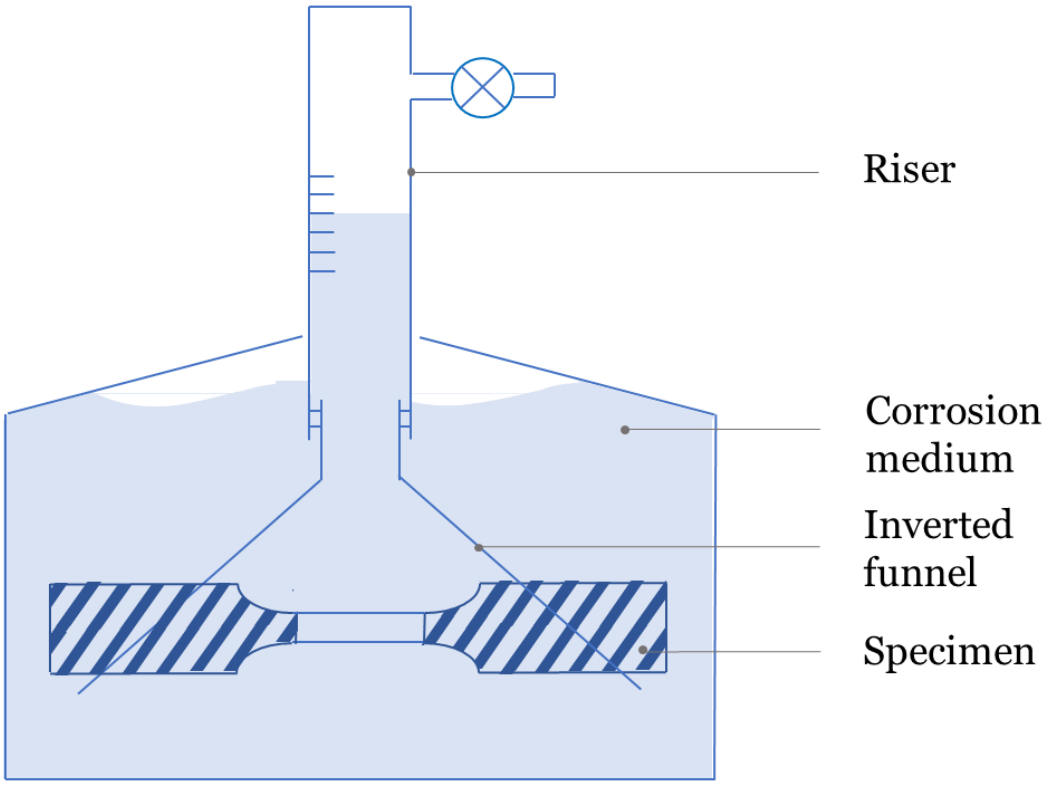

Fig. 2: Experimental setup of corrosion experiments.

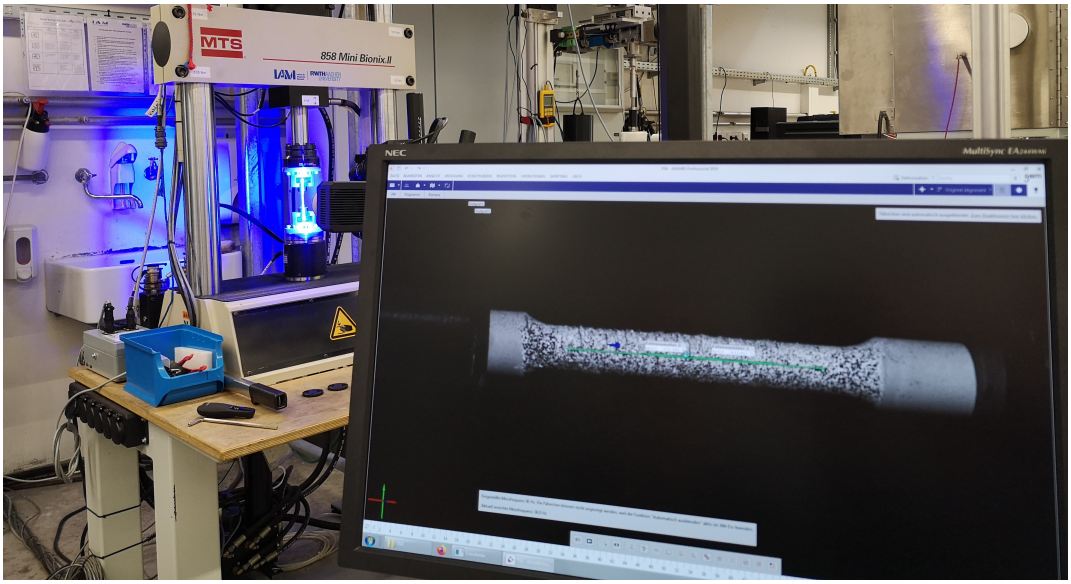

Fig. 3: Experimental setup of tensile tests. The testing system in the background and the video extensometer in the front.

3 Results

3.1 Corrosion experiments

The mass loss rate of the non-coated WE43 alloy is presented in Figure 4a revealing that the mass loss is the fastest during the first 24 hours after immersion, followed by a continuously decreased mass loss rate with the corrosion time. After 4 days the mass loss rate seems to be steady. This agrees well with the findings by Ascencio et al. [15] who studied the corrosion of the alloy WE43 in a modified-simulated body fluid observing a quasi-constant corrosion rate after three days after an initial

fast corrosion. A corrosion product has formed on the substrate surface that slows down the corrosion of the underlying alloy. The decelerating corrosion process of the alloy WE43 is quite contrary to the accelerating corrosion of pure magnesium in non-physiological corrosion environment [16].

The experimental results of the PEO coated WE43 alloy are presented in Figure 4b. The mass loss rate is the fastest within the first 24 hours, followed by a significant decrease in the corrosion rate. The initial high mass loss rate derived from a large gas volume that was collected within the first 24 hours. This large gas volume might not be solely referred to hydrogen gas evolution due to corrosion, but also to the spontaneous release of the gas filling in the pores of the coating. Nonetheless, the results show that after an initial high mass loss during the first 24 hours, the coating decelerates the corrosion process, especially for longer corrosion periods. Arrabal et al. [11] reported that the improved corrosion resistance of their particular PEO coating on WE43 alloy in NaCl solution at room temperature was limited to the initial stages and corrosion layers were found underneath the coating.

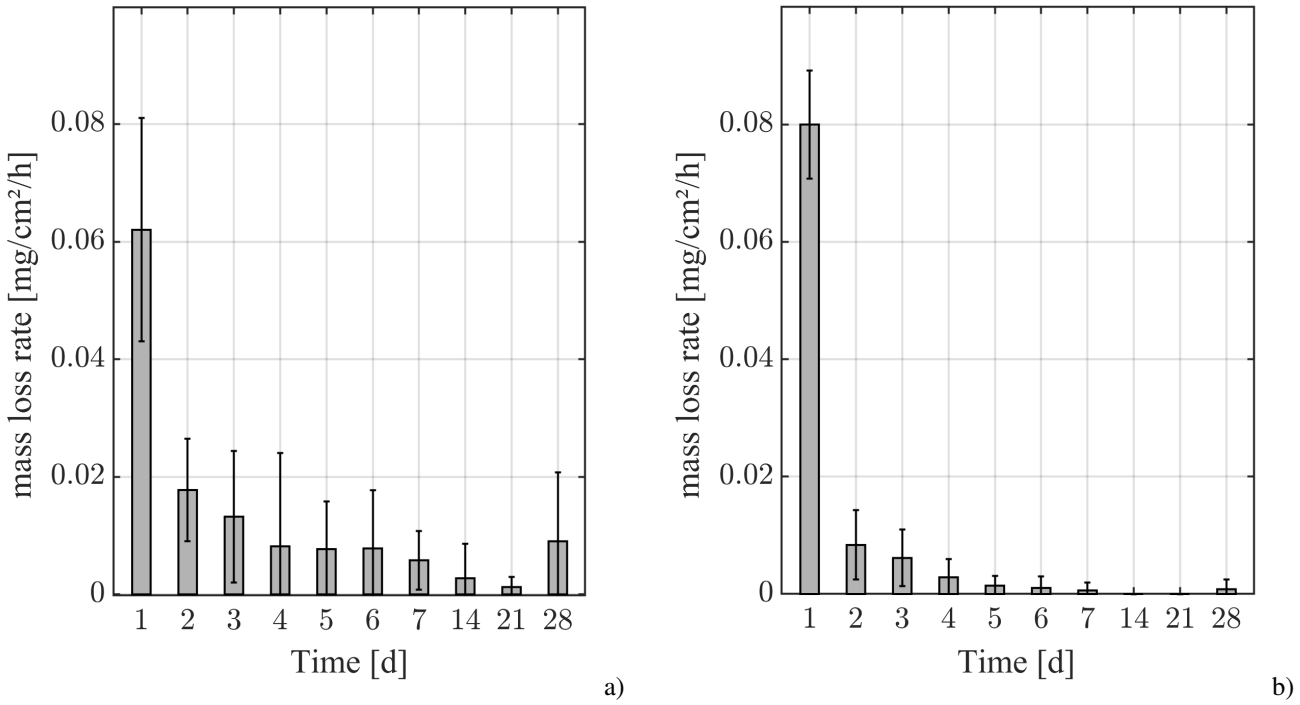

Fig. 4: Mass loss rate during *in vitro* corrosion experiments of the uncoated alloy **a** and the coated alloy **b**.

3.2 Tensile tests

The yield strength of the non-coated alloy is 306 MPa, which is much higher than the one of cortical bone (105-114 MPa) [3]. Figure 5a shows the time-dependent degradation of the material strength. After 7 days corrosion, the material strength decreased and the material strength further decreases in a linear manner with corrosion time. The loss of material strength corresponds well to the steady mass loss rate (see Figure 4a) that was observed in the corrosion experiments.

Figure 5b shows the degradation in the material strength of the coated alloy. The experimental results indicate, that the yield strength of the coated alloy does not change during the first 14 days of corrosion, which confirms the assumption that the initially measured large gas volumes can be referred to gas release from the porous coating structure and not to the hydrogen gas evolution due to corrosion. Only after longer corrosion periods of more than two weeks, the yield strength is reduced. It is revealed that the coating retards the material corrosion.

4 Conclusion and Outlook

The biodegradable magnesium alloy WE43 has promising potential in the application of non-permanent orthopaedic implants. Biodegradable bone implants need to be carefully designed to meet the medical requirements for the bone healing process. Therefore, a deep understanding of the corrosion mechanism in physiological environment plays an important role to retard the corrosion process. The present experimental results show that the used plasma electrolytic oxidation coating in our work decelerates the corrosion process of the alloy WE43. The PEO coating retards the degradation of the mechanical strength for a period of 14 days. The measurement of mass loss can only quantify the average corrosion rate or relatively homogeneous

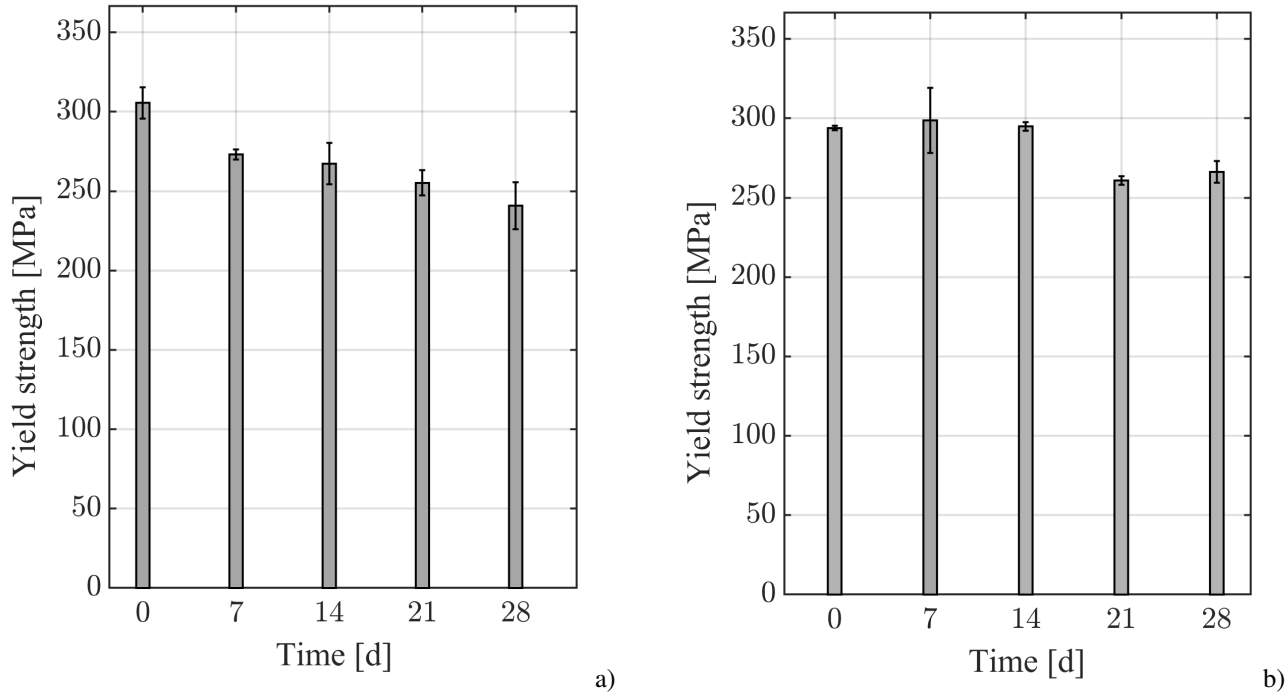

Fig. 5: Degradation of the mechanical properties: Yield strength of the alloy WE43 **a** and the coated WE43 alloy **b** before and after corrosion.

corrosion attack along the material's surface. Therefore, an experimental method to quantify deep corrosion pits that appear very locally and lead to more critical scenario of the material degradation should be included in future studies.

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