

# <sup>1</sup>MAGNESIUM AND MAGNESIUM ALLOYS AS DEGRADABLE METALLIC BIOMATERIALS

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## ABSTRACT

Drawbacks associated with permanent metallic implants lead to the search for degradable metallic biomaterials. Magnesium has been considered as it is essential to bodies and has a high biodegradation potential. For magnesium and its alloys to be used as biodegradable implant materials, their degradation rates should be consistent with the rate of healing of the affected tissue, and the release of the degradation products should be within the body's acceptable absorption levels. Conventional magnesium degrades rapidly, which is undesirable. In this study, biodegradation behaviours of high purity magnesium and commercial purity magnesium alloy AZ31 in both static and dynamic Hank's solution have been systematically investigated. The results show that magnesium purification and selective alloying are effective approaches to reduce the degradation rate of magnesium. In the static condition, the corrosion products accumulate on the materials surface as a protective layer, which results in a lower degradation rate than the dynamic condition. Anodised coating can significantly further reduce the degradation rate of magnesium. This study indicates that magnesium can be used as degradable implant materials as long as the degradation is controlled at a low rate. Magnesium purification, selective alloying and anodised coating are three effective approaches to reduce the rate of degradation.

## 1 INTRODUCTION

Magnesium and its alloys are broadly used for structural applications in the aerospace and automotive industries as well as in consumer electronics, benefiting from their light-weight property. Poor corrosion resistance of magnesium is a big concern in those structural applications, however, in biomedical applications, the high reactivity of magnesium in corrosive media can be used as an advantage. Magnesium alloys have been considered as candidate materials for biodegradable orthopaedic implants [1] and vascular stents [2]. Notable work in this direction has been done over the last years [3-6]. While fast corrosion kinetics is generally beneficial in biodegradable implants, the problem for magnesium alloys is that their corrosion rate is too high.

For magnesium and its alloys to be usable as biodegradable implant materials, the key issue here is that their degradation rate needs to be reduced and controllable to match with the rate of healing of the affected tissue, and the release of the degradation products should be within the body's acceptable absorption levels [4,7]. In this study, the biodegradation behaviour of high purity magnesium and commercial purity magnesium alloy AZ31 in the physiologically simulated solution is investigated. In order to slow down the degradation process, an anodizing technique has been developed and an acceptable degradation rate for the practical implant applications is achieved.

## 2 MATERIALS AND METHODS

The two materials used in this study are high purity magnesium (HPMg, the purity is higher than 99.99 %) and commercial purity magnesium alloy (AZ31, made from magnesium ingot with purity of 99.9%). HPMg and AZ31 castings were cut into 20×20×4 mm coupons and 4×4×20 mm rods. The edges of the specimens were ground. The specimens were then polished with 4000 grid SiC paper and degreased with ethanol.

Degradation test was conducted by immersing the specimens in a Hank's balanced salt solution with a composition: CaCl<sub>2</sub> 0.14 g/l, KCl, 0.4 g/l, NaCl 8.0 g/l, MgSO<sub>4</sub> 0.1 g/l, KH<sub>2</sub>PO<sub>4</sub> 0.06 g/l, NaHPO<sub>4</sub> 0.05 g/l and D-Glucose 1.0 g/l. The immersion test was used to simulate the biochemical reaction of the magnesium material in human physiological conditions. The temperature of the solution was controlled at 37.5±0.5°C. Two types of immersion test were conducted, (i) a static test is designed to simulate the situation of hard tissue replacement, (ii) a dynamic test is designed to simulate the implantation applications in vessels, such as stent. In the static test the coupon specimens were suspended in Hank's solution for 1, 2, 5, 10, 15 and 20 days. The pH of the solution was monitored by a portable pH meter and adjusted at a value of 7 by using 1N HCl and 1N NaOH. In the dynamic test the solution is keeping flowing. The rod specimens were placed into a plastic tube and the Hank's solution was flowing through the tube at a

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constant speed. After the specified immersion time, the specimens were observed in an optical microscope to record the surface appearance. The specimens were then washed with a solution containing  $\text{CrO}_3$  and  $\text{AgNO}_3$  to remove the corrosion products and weighed. Two samples were used for each immersion time and the average of the weight loss results was taken. The electrochemical measurements were also conducted to evaluate the corrosion resistance of the specimens.

Anodised coating was applied on the surface of the specimens to provide corrosion resistant coating. The coating was prepared in two electrolytes: 10 min in an electrolyte containing 12%  $\text{NaOH}$ , 10%  $\text{Na}_4\text{B}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  and 6.6%  $\text{Na}_2\text{SiO}_4$ , and then 10 min in another electrolyte consisting of 1.0%  $\text{KOH}$  and 1.6%  $\text{K}_2\text{SiO}_4$ . The composition of the coating was analysed by XPS. The microstructure of the coatings was observed by SEM. The degradation behaviour was also evaluated using immersion test.

### 3 RESULTS AND DISCUSSION

#### 3.1 Biodegradation behaviours

The degradation behaviour of HPMg and AZ31 samples was investigated in static and dynamic immersion tests under simulated physiological conditions. The weight loss after a preset number of days of immersion was measured for all the samples. The degradation rate was calculated as grams per exposure-area per time, and was converted to thickness loss rate of a constant area sample, in millimetre per year as follows:

$$DR = \frac{WL}{A \cdot t \cdot \rho} \quad (1)$$

where  $DR$  is the degradation rate in mm/year,  $WL$  is the weight loss,  $A$  is the original surface area exposure to the simulated physiological solution,  $t$  is the immersion time,  $\rho$  is the material density. The results are plotted in Fig. 1. The degradation process, starting off with a very high degradation rate, is seen to slow down with the immersion time. In the static test condition, it is found that both materials degrade fast at beginning, then stabilise at a rate of 0.25 mm/year. In the dynamic test condition, it is also found that the degradation rate of both materials decrease quickly at beginning and then stabilise at about 0.8 mm/year for pure magnesium and at about 1.3 mm/year for AZ31 magnesium alloy.

In the static condition, the degradation rate is much lower than that in dynamic condition. During the degradation process, the main corrosion product is

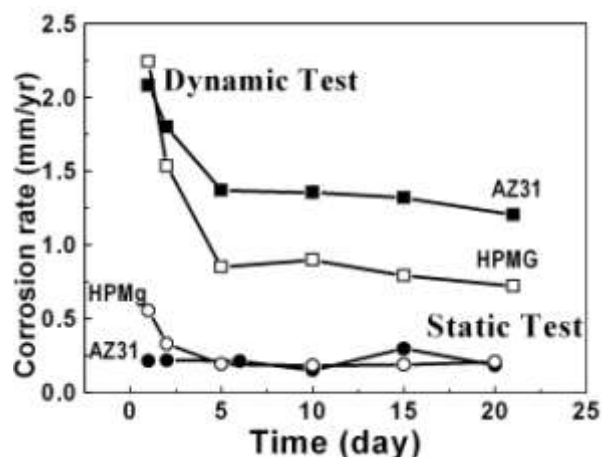


Fig. 1. Degradation rate of HPMg and AZ31 samples in Hank's solution under static and dynamic conditions.

magnesium hydroxide, as well as other magnesium phosphates and carbonates, which tend to accumulate on the specimen surface. This has been verified by XPS analysis of the exposed samples. The accumulated corrosion products form a protective layer on the surface, retarding the corrosion process. In the dynamic test, the constant flowing of the solution prevents the corrosion products from accumulating on the surface. Fig. 2 shows the appearance of the corroded AZ31 specimens. The static samples have less corrosion while the dynamic samples have more severe corrosion, but have a clean surface. The corrosion damage in static test is mainly localised pitting, as shown by the arrows, due to the formation of the protective layer. In the dynamic sample the corrosion is nearly uniform corrosion. The similar appearance difference has been observed for the HPMg samples in static and dynamic tests.

The result indicates that alloying with Al and Zn significantly slows down the degradation of magnesium. Indeed, commercial purity magnesium without these alloying elements experiences a much faster biodegradation under similar testing conditions [8]. Song et al. attribute the reduced degradation rate in AZ series alloys to the barrier effect of  $\beta$  phase formed in the alloy. The other benefit from the alloying is increasing the strength of the magnesium material. In practice, it should be noted that alloy elements will dissolve together with magnesium. Some of the elements are unfavourable or detrimental to the health of the human body. This should be considered when alloying is used to slow down the degradation process, thus the alloying needs to be selective.

Another approach to slow down the degradation is using high purity magnesium. Fig. 1 indicates that high purity magnesium can achieve a similar low degradation rate as the magnesium alloy. In the dynamic test it is even lower than the AZ31. However, it should be noted that usually pure magnesium only has half of the yield strength of natural bone (strength of femur is  $\sim 110$  MPa). Mechanical processing or selective alloying needs to be incorporated to improve its yield strength for bio-applications.

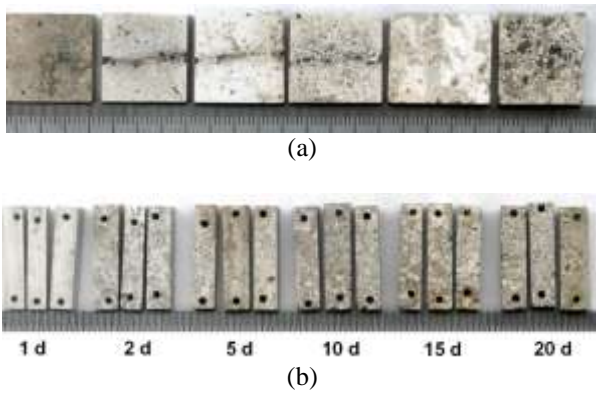


Fig. 2. Surface appearance of AZ31 samples that have been immersed in Hank's solution for up to 20. (a) from static test and (b) from dynamic test.

### 3.2 Electrochemical test

The polarisation curves of HPMg and AZ31 were measured in order to verify the corrosion behaviours observed in the immersion test. The polarisation curves of both materials in Hank's solution are shown in Fig. 3. After Tafel simulation, the corrosion current density of HPMg is found to be  $2.2 \times 10^{-6}$  A/cm<sup>2</sup> and the corrosion potential is about -1.54V. While the corrosion current density of AZ31 alloy is  $4.34 \times 10^{-6}$  A/cm<sup>2</sup> and the corrosion potential is -1.46V. The values reveal that the corrosion density of AZ31 is higher than that of HPMg, indicating that HPMg has a lower degradation rate than AZ31 in the Hank's solution. The results are consistent with that from the immersion test, confirming that high purity and alloying are two effective approaches to reduce the biodegradation rate of magnesium in the simulated body fluid. It should be noted that the corrosion current density for both materials are much lower than the commercial purity magnesium [9].

Electrochemical impedance spectra of both materials were measured to monitor the variation of corrosion rate, which may provide some information on the formation of the corrosion products during the degradation process. The measurement data are represented in a diagram in which the imaginary part of the impedance  $Z$  is plotted against its real part. Such diagrams usually exhibit several semi-circles corresponding to distinct individual processes in the electrode system. A typical EIS of AZ31 and HPMg in the static test is shown in Fig. 4. There is clearly a semi-circle (albeit somewhat deformed and not fully symmetric) found in each EIS measurement. This indicates that there is at least a simple electrochemical process dominated by the mechanism of charge transfer across the interface between the magnesium and the solution involved in the degradation of magnesium in Hank's solution.

The polarization resistance of the samples immersed in the solution can be obtained from the diameters of the near semicircular spectra. The results are plotted in Fig.

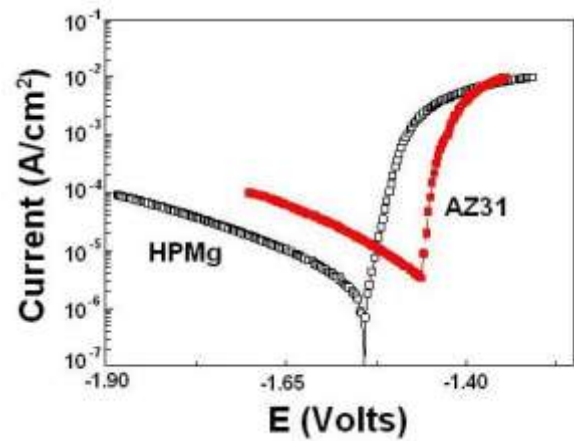


Fig. 3. Polarisation curves of HPMg and AZ31 in Hank's balanced solution.

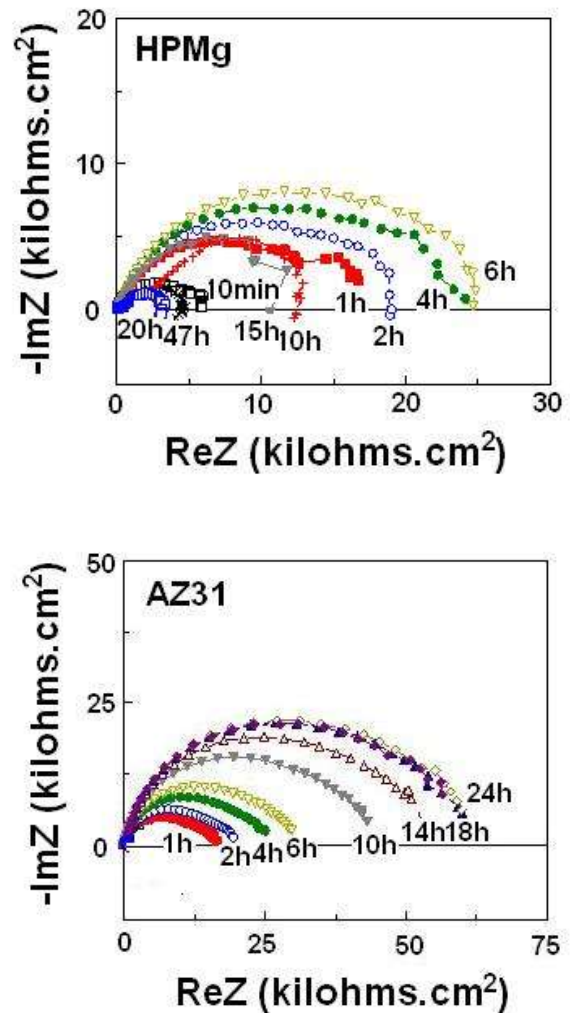


Fig. 4. Electrochemical Impedance Spectroscopy of HPMg and AZ31 samples immersed in Hank's solution.

5 as a function of the immersion time. Since the resistance can be related to the corrosion rate through the Geary-Stern equation [10], the changes of the measured spectra with the immersion time to some extent represent the corrosion behaviour of HPMg and

AZ31 in the Hank solution. For both materials, the corrosion resistance increases with time initially and then decreases with time. The increase of polarisation resistance with time suggests that a protective film may have formed on the surface of the specimens while they are immersed in the solution. It means that a protective film (magnesium hydroxide or magnesium oxide) is deposited on the surface in the beginning, then is broken down under the attack of chloride ion. The increase of the corrosion resistance is much significant in AZ31 than in HPMg. For AZ31 the corrosion resistance increases with time up to 24 hours, then decreases with time until it reaches a stable value in about 100 hours of immersion. It can be conjectured that the film is more readily formed on the AZ31 alloy in Hank's solution and has a protective effect. This is the reason why in the static immersion test, AZ31 from the lower purity magnesium has a similar low corrosion rate as the high

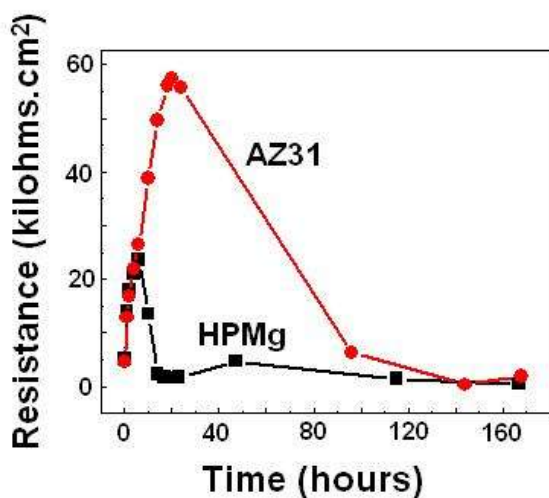


Fig. 5. Time dependence of the polarisation resistance of HPMg and AZ31 immersed in Hank's solution.

purity magnesium. Especially at the beginning the protective film is stable, which makes AZ31 material exhibiting a low corrosion rate compared with HPMg (see Fig. 1). In the dynamic flow situation, the protective film can not be stably formed. AZ31 exhibits a higher corrosion rate and the low rate at the beginning is also disappeared. XPS analysis of samples immersed in Hank's solution has identified the main constituents of the layer deposited as a result of a reaction between AZ31 and the solution as  $Mg_3(PO_4)_2$ ,  $Ca_3(PO_4)_2$ ,  $Mg(OH)_2$  and some  $CaCO_3$  [11].

### 3.3 Anodised coatings

Anodised coatings have been prepared on AZ31 surface. The typical microstructure of the anodised coating is shown in Fig. 6. It is an irregular porous ceramic-like coating. The size of the pores is in the range of several micrometers, varied with the type of coating. The anodised coating consists of 69.6% O, 23.4% Si, 6.3% Mg and 0.7% Na. Further high resolution XPS

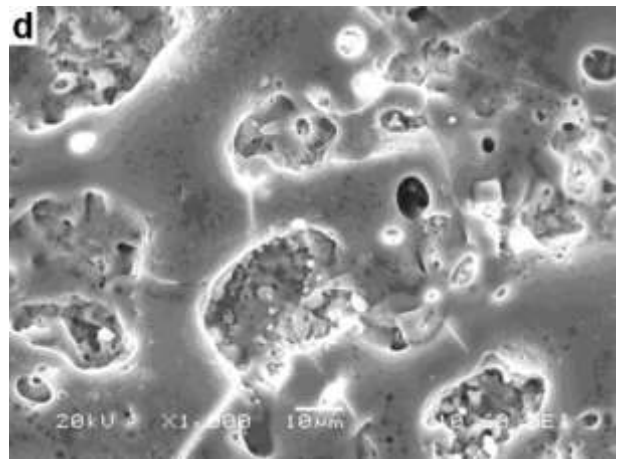


Fig.6. Typical microstructures of the anodised coatings on AZ31.



Fig. 7. Surface appearance of the anodised AZ31 samples after 15 days immersion in Hank's solution.

analysis shows the binding energy of Mg 1s is 1303.7 eV, Mg 2p is 50.1 eV, Mg KLL is 306.6 eV, and Si 2p is 102.1 eV. Analysis of O 1s peak reveals that it is a combination of three peaks with binding energy: 532.5 eV from  $OH^-$ , 531.6 eV from  $SiO_3^{2-}$  and 530.4 eV  $CO_3^{2-}$  respectively. Therefore the anodised coating mainly consists of  $Mg(OH)_2$ ,  $MgSiO_3$  and a small amount of  $MgCO_3$  (from the absorption of carbon dioxide from atmospheric environment).

An immersion test was carried out on the anodised coatings, the test being conducted in static condition in the Hank's solution for 15 days. Fig. 7 shows the appearance of the exposed anodised samples, this anodised coating significantly improves the degradation performance of magnesium materials, slowing down the biocorrosion. The materials are almost unattacked after 15-days exposure.

## 4 CONCLUSIONS

The biodegradation of high purity magnesium and commercial purity magnesium alloy in Hank's solution was evaluated. The results show that both magnesium purification and selective alloying can be the effective approach to reduce the degradation rate of magnesium.

In the static condition, the corrosion products accumulate on the materials surface served as an protective layer, which results in a lower degradation rate than in dynamic condition. Anodised coating significantly further reduced the degradation rate of magnesium. The coating has an irregular porous ceramic-like structure with the pore size of several micrometers. The degradation can be controlled by using the thickness of anodised coatings and a two-layer coating. This study indicates that magnesium can be used as degradable implant materials as long as the degradation is controlled at a low rate. Magnesium purification, selective alloying and anodised coating are three effective approaches to reduce the degradation rate.

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