Anticorrosive magnesium hydroxide coating on AZ31 magnesium alloy by hydrothermal method

Yanying Zhu¹², Guangming Wu¹ *, Qing Zhao², Yun-Hong Zhang², Guangjian Xing¹, Donglin Li¹
¹Beijing Institute of Petrochemical Technology, Beijing 102617, China, ²Beijing Institute of Technology, Beijing 100081, China

Email address: wuguangming@bipt.edu.cn

Abstract. Magnesium alloys are potential biodegradable biomaterials in orthopedic surgery. However, the rapid degradation rate has limited their application in biomedical field. A great deal of studies have been done to improve the resistance of magnesium alloys. In this article, An anticorrosive magnesium hydroxide coating with a thickness of approximately 100 μm was formed on an AZ31 magnesium alloy by hydrothermal method. The morphology of the coatings were observed by an optical microscope and SEM. And the samples were soaked in hank’s solution (37 °C) to investigate the corrosion resistance. Magnesium alloy AZ31 with magnesium hydroxide coatings present superior corrosion resistance than untreated samples.

1. Introduction
Metallic materials continue to play an essential role as biomaterials in orthopedic surgery. Previous studies have shown that magnesium alloys have potential as biodegradable materials. The fracture toughness of magnesium is greater than bioceramics, while the elastic modulus is closer to that of natural bone than other metallic implants [1]. Moreover, magnesium ion plays an important role in many physiological activities of human body and it has been proved that the magnesium and its alloy are biocompatible [2, 3, 4]. However, the poor corrosion resistance especially in the solution containing chloride ion, such as physiological environment of human body, inhibits their practical application as orthopedic implants. The mechanical integrity of the magnesium alloys are loosed before the tissue has healed. Fabricating protective coatings on the magnesium alloys are one of the most effective ways to overcome this drawback [5]. In this study, magnesium hydroxide coatings were deposited on magnesium alloy (AZ31) substrates by hydrothermal method. And so far, no report on increasing the
corrosion resistance of Mg alloy by magnesium hydroxide coating using hydrothermal method has been available. Furthermore, it is well documented that magnesium hydroxide coatings were non-toxic.

2、Experimental procedures

2.1 sample preparation
AZ31 magnesium alloy ingots were cut into discs of 2mm in thickness and 12 mm in diameter. Each sample was mechanically polished up to 2000 grit, cleaned in deionized water and ethanol, and then dried in open air.

2.2 magnesium hydroxide coatings formation
The Mg(OH)$_2$ coating was fabricated on the AZ31 alloy by hydrothermal method. The NaOH (6g) was added to 100ml deionized water, then the alkali solution was poured into a hydrothermal reaction vessel with a filling factor of 75%. The AZ31 samples were set in the vessel and the vessel was heated in an electric oven in order to prepare the anticorrosive coating. The temperature and the reaction time were 160°C and 3 h, respectively. The reactions in the hydrothermal reaction vessel may include the following reactions$^{[6]}$:

\[
\begin{align*}
\text{Mg(s)} & \rightarrow \text{Mg}^{2+}(\text{aq}) + 2e^- \quad (1) \\
2\text{H}_2\text{O}(\text{aq}) + 2e^- & \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \quad (2) \\
\text{Mg}^{2+}(\text{aq}) + 2\text{OH}^- & \rightarrow \text{Mg(OH)}_2(s) \quad (3)
\end{align*}
\]

2.3 morphology observation
The surface morphology was observed using an optical microscope and SEM. Then an across-sectional view of the obtained coatings was observed by SEM.

2.4 The soaked experiment$^{[7]}$
The degradation behavior of samples was investigated by immersion test in Hank’s solution. The composition of the Hank’s solution used was composed of 8 g/L NaCl + 0.4 g/L KCl + 0.14 g/L CaCl$_2$ + 0.1 g/L MgCl$_2$ • 6H$_2$O + 0.1 g/L MgSO$_4$ • 7H$_2$O + 0.06 g/L KH$_2$PO$_4$ + 0.06 g/L Na$_2$HPO$_4$ • 2H$_2$O + 0.35 g/L NaHCO$_3$ + 1.0g/L glucose. Before soaked in the solution, the dimensions and masses of samples were measured using a vernier caliper and an electric balance, respectively. The solution volume to specimen area ratio was 0.40 mL/mm$^2$. The containers were placed in the water bath and the temperature of the bath was kept at 37°C. The solution was renewed every two days. The samples were taken out after immersion 1, 3, 7, 15, and 31 days, respectively. Then the samples were cleaned with deionized water and ethanol, and removed the corrosion products using chromic acid. Finally, the samples were put in the dryer for 24h, and then the masses were measured.

The corrosion rate was calculated as follows:

\[
\nu = \frac{m_0 - m_1}{St} \quad (4)
\]

where $\nu$ is the corrosion rate, $m_0$ is the sample mass before soaked experiment, $m_1$ is the mass after soaked experiment, $S$ is the surface area of an sample, $t$ is the corrosion time.

3、Result and Discussion

3.1 Morphology of magnesium hydroxide costing
Figure 1(a) is the optical micrograph of the magnesium hydroxide coating. It can be seen that there are many cracks on the surface. Figure 1 (b) is the SEM micrograph of the coating. The grains of the magnesium hydroxide on the surface are about 20~80nm. Figure 1 (c) is SEM morphology of the cross-section of the coated AZ31 sample. It can be see that the coating is formed on the substrate of the AZ31 alloy and the thickness of the coating is about 100μm. The cross section graph of the sample also shows that coating is uniform and dense.

![Figure 1](image1.png)

**Figure 1**  
(a) Optical micrograph of Mg(OH)$_2$ coating on AZ31 magnesium alloy  
(b) SEM micrograph of surface of micrograph  
(c) Cross-sectional SEM micrograph of Mg(OH)$_2$ coating on AZ31 magnesium alloy

Figure 2 shows the image of samples after immersion time 1,3,7,15 and 31 days in Hank’s solution. It can be seen that after 1 and 3 days, bare AZ31 magnesium alloy samples was slightly corroded, and the corrosion products covered the surface. The corrosion of bare samples became serious after 7, 15 and 31 days. The pitting holes appeared, developed and became enlarged. By comparison, the coated AZ31 has a better corrosion resistance than bare AZ31. The coatings were still basically intact after 31 days immersion in Hank’s solution.

![Figure 2](image2.png)

**Figure 2** Appearance of the samples after 0,1,3,7,15, and 31 days immersion in Hank’s solution

The mass loss of the samples was measured after immersion 1,3,7,15,31 days in Hank’s solution. The corrosion rates of the samples were calculated according to the equation (4), and the corrosion rate curves
are showed by figure 3. It can be seen that the corrosion rates are decreased with the prolonging of immersion time. It is probably because the corrosion products covered the surfaces of samples, and decelerated the reaction. It was also showed that the coated samples showed better corrosion properties than that of bare AZ31 alloy samples. Therefore, the AZ31 magnesium alloy samples with magnesium hydroxide coating can decrease the corrosion rate effectively after implantation in the body.

**Figure 3** Variation of the corrosion rate of samples with coating and without coating with immersion time in Hank’s solution.

4. **Summary**

The present study demonstrated that the magnesium hydroxide coating was successfully formed by hydrothermal method on the AZ31 magnesium alloy substrate and improved the corrosion resistance of the magnesium alloy effectively to compare with the bare alloy. Formation of magnesium hydroxide coating on the Mg alloy substrate can provide a potential material for the appropriate orthopedic surgery, and further studies will focus on the biocompatibility of the magnesium hydroxide coatings.

**References**

[1] M. P. Staiger et al. 2006 *Biomaterials* **27** 1728

[2] Saris NEL. 2000 *Clin Chim Acta* **294** 1

[3] Okuma T. 2001 *Nutrition* **17** 679

[4] Hartwig A. 2001 *Mutat Res/Fund Mol Mech Mutagen* **475** 113

[5] J. E Gray and B. Luan 2002 *Journal of Alloys and Compounds* **36** 88

[6] Frank Witte, Norbert Hort et al. 2009 *Current Opinion in Solid State and Materials Science* **12** 63

[7] American Society for Testing and Materials. 2004 ASTM G31-72 Standard Practice for Laboratory Immersion Corrosion Testing of Metals *American Society for Testing and Materials 2004 Annual Book of ASTM Standards* (Philadelphia Pennsylvania USA:ASTM vol 03.02) p5