Remarkable improvement in corrosion resistance of anodized AZ31 alloy by sealing with beeswax-colophony resin

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Abstract. The nature of an anodic oxide film formed on Mg alloys is porous and cleaved. Sealing of the pores is necessary to enhance the corrosion resistance of the alloys. This work reports the effect of beeswax-colophony sealant on the corrosion resistance of anodic oxide layer formed on AZ31 magnesium (Mg) alloy. Anodization was conducted in 0.5 M Na3PO4 solution at 30°C at a constant voltage 5 V with variation time 10, 20, and 30 min. The resulting anodic film exhibited thicknesses of 6.3, 14.8, and 16.7 µm for 10, 20, and 30 min anodization time, respectively. The film was presumably composed of Mg(OH)2 and Mg3(PO4)2 as predicted by EDX analysis. Sealing was done by dipping the specimen in a mixture of beeswax-colophony with ratio 7:1. The corrosion test was performed by weight loss method in 0.9% NaCl solution at 37°C for 14 days. The unsealed and sealed specimens exhibited a similar increase in weight loss with increasing exposure time. However, the sealed specimens showed remarkably lower material loss below 3.8 mg/cm² relative to the unsealed specimens with weight loss up to 11.5 mg/cm². The corrosion rate of the sealed specimens was five times lower than the unsealed ones.

1. Introduction

The extensive application of Mg alloys for biodegradable implant material is still facing a challenge due to the high corrosion rate of the alloys when exposed to physiological solutions. The high corrosion rate led to robust hydrogen gas release and a threat of the mechanical integrity of the alloy [1]. There are two methods to reduce the corrosion rate of Mg alloys: intrinsic method (alloying and modifying the metal processing), and extrinsic method (surface treatment and coating) [2-4]. The simple and effective method for reducing the corrosion rate is by surface treatment or coating [5-8]. In general, there are two types of coatings: deposited coating and conversion coating. The deposited coating usually uses an organic-based solution. Meanwhile, the conversion coating can be done by chemical (immersion) or electrochemical (anodization) methods.

Anodization is one of a common method applied on light metals including Mg alloys to transform the metal surface into an anodic oxide film. Anodization proves to be an effective way to protect the alloy from the corrosive environment or as a pretreatment to improve adhesion for a final organic coating. The typical anodic film thickness formed as result of anodization was ranging from 5 to 200 µm [5]. The thickness was controlled by the process parameters especially the anodization time [5-8]. Increasing the thickness does not necessarily enhance the corrosion resistance of the alloys because of the formation of cracks in the layer. An optimum anodization time is required to obtain a proper thickness that provides the best corrosion protection.
Anodization on Mg alloys is typically performed in an inorganic base electrolyte such as chromate-based (Na₂CrO₄, K₂CrO₄), NaOH, Na₂SiO₃, Ca₃PO₄, and Na₃PO₄ [4-8]. Chromate-based electrolytes are toxic and certainly forbidden for biomedical application. The main consideration for the coating of a biomedical application besides the corrosion resistance is that the coating should be non-toxic. It was reported that the corrosion resistance of an anodic oxide film formed in Na₃PO₄ is higher than that of formed in NaOH and Na₂SiO₃ [5].

The anodic oxide film formed on Mg alloys as a result of anodization usually porous and has cracks [4-8]. The film often has more cracks as a result of hydration of the oxide film. The cracks are a disadvantage for corrosion resistance as they become path for the solution to penetrate the metal surface. Sealing is required to block the cracks and pores in the oxide film. Boiling the anodized alloys in water is one of the simplest and oldest sealing methods. However, since Mg is the most reactive metal, such a sealing method is not sufficient to provide good corrosion resistance in corrosive aqueous solution such as a physiological solution. In this work, for the first time, a mixture of beeswax and colophony resin is used as a sealant material for the anodic oxide film formed on AZ31 Mg alloy. The anodization was done in Na₃PO₄ solution with a variation of time 10, 20, and 30 min. The effect of sealing on the corrosion rate of anodized AZ31 specimens was studied by weight loss method.

2. Experimental Methods

The specimens used were rolled plate AZ31 with thickness 0.25 mm cut into 1.5 mm x 3 mm. The magnesium alloy AZ31 alloy was composed of 3 wt% Al and 1 wt% Zn. The observation area was 1.5 mm x 1.5 mm while the rest of the specimen was used as a contact. After cutting, the specimens were degreased in acetone and ethanol consecutively in an ultrasonic bath for 3 min.

2.1. Anodization

Before anodization process, the sample was pretreated in a mixed acid solution of 10% HNO₃ and 2% H₃PO₄ for 20 s and then neutralized in a hot 5% NaOH solution for 1 min. Anodization was carried out using a constant voltage of 5 volt in 0.5 M Na₃PO₄ solution at 30°C for 10, 20, and 30 min. After anodization, the specimens were cleaned in a running water for 3 min and then dried with an air stream.

2.2. Sealing

The anodized specimens were further sealed in a mixed beeswax-colophony resin. Beeswax is an organic compound with formula C₁₅₅H₂₁₂COOC₃₈H₆₁ while the colophony composed of abietic acid [9]. The ratio of beeswax: colophony was 7:1. The resin was prepared similarly as reported earlier [10] by melting each component at 80°C and then mixed the two components together in a beaker and stirred for 5 min. The anodized specimens were sealed by dipping the specimens into the resin for 30 min. Afterward, the sealed specimens were left dried in air for 24 h.

2.3 Corrosion test

The corrosion behaviour of the specimens was examined by weight loss method by soaking the specimens in physiological solution of 0.9% NaCl solution at 37°C. The specimen was immersed individually in a hanging configuration in 100 ml solution. The weight loss was measured and the solution was refreshed every other day until 14 days. The corrosion test was repeated on three replicate specimens to ensure the reproducibility. The corrosion rate (CR) was then calculated by using equation as follow:

\[
CR = \frac{w}{DA_t} \times 87500
\]

where \(w\) is weight loss (g), \(D\) is metal density (g/cm³), \(A\) is specimen area (cm²) and \(t\) is time (s).

2.4 Characterization
The surface morphology and elemental composition were studied by FE-SEM and EDX (FEI INSPECT F-50 & EDAX EDS Analyzer). The thickness of the oxide layer was measured using coating thickness gauge (DEKKO CM-8826FN) where an average value and standard deviations were determined for 5 point measurements on each surface.

3. Results and Discussion
The surface of the AZ31 specimen which priory exhibited a metallic reflective appearance turned into matte white to greyish appearance after anodized for 10, 20, and 30 min. The thickness of the resulting anodic oxide layer was tabulated in table 1. The anodic layer became thicker with increasing anodization time. A significant increase in thickness from 6.3 to 14.8 µm was attained as the anodization time extended from 10 to 20 min while only about 2 µm thickening with prolonging anodization time of 30 min. The oxide layer presumably developed a significant resistivity after anodization for 20 min and therefore limited the ions exchange required for the oxide growth.

Figure 1 shows the surface appearance of the anodic oxide film formed on the AZ31 specimen after 20 min anodization. FESEM observation indicated that the resulting oxide film formed for 10 and 30 min also had similar morphology to that of formed on 20 min. The oxide layer shows a porous structure decorated with microcracks. Such an oxide structure is commonly formed on Mg alloys as a result of anodization or high-temperature oxidation [2, 5]. EDX analysis in figure 1(b) shows that the oxide composed of Mg, O, P, Na, and Al. The species Na and P from the electrolyte were incorporated in the oxide compound while the element Al which probably existed in a metallic state was enriched in the oxide during selective oxidation of the surrounding Mg matrix. Al is not oxidized at such low potential [5]. The EDX results indicated that the oxide might consist of Mg₅(PO₄)₂ and MgO. The

| Sample          | Film thickness (µm) |
|-----------------|---------------------|
| Anodized 10 min | 6.3                 |
| Anodized 20 min | 14.8                |
| Anodized 30 min | 16.7                |

Figure 1. (a) Surface morphology of the anodic oxide film formed on AZ31 specimen anodized for 20 min and (b) the corresponding EDX elemental composition.
Mg(OH)$_2$ phase was likely also formed in the outer layer [11]. The cracks formed in the oxide film is unavoidable due to the high ratio in the volume expansion of the corresponding oxides to the metal [2, 3]. The ratio is called the Pilling-Bedworth ratio (PBR). The Mg$_3$(PO$_4$)$_2$ phase has PBR of 2.85 while the MgO phase is 0.80. Ideally, a protective oxide layer has PBR value of 1. The typical oxide film formed with PBR above 2 is cracked while PBR less than 1 is porous and unprotective. Therefore, it is necessary to seal the pore and cracks to enhance the corrosion resistance of the specimen.

Figure 2 shows the comparison of material weight loss as a function of immersion time between the anodized and anodized-sealed specimens. Both specimens showed an increase in the material loss with exposure time. However, the weight loss of anodized-sealed specimens was significantly lower than that of the anodized one. The material loss measured for anodized-sealed specimens was attributed to the dissolution of both metal and sealing resin. The actual metal loss itself was remarkably low. The specimens anodized for 20 min showed a tendency to have the lowest weight loss relative to the others specimens in both anodized and anodized-sealed conditions. The results indicated that the optimum anodization time to obtain less defective sites in the anodic layer was 20 min. The anodization treatment improved the adhesion of sealing material on the surface. Direct application of the beeswax-colophony resin on the AZ31 surface did not give significant enhancement in corrosion resistance of the alloy as the resin layer easily detached from the surface during weight loss test [10].

The corrosion rates calculated from the weight loss data by using equation (1) are presented in table
specimens corroded with the rate in the range of 3-6 mmpy. The rate for anodized-sealed specimens might have been significantly lower if the resin weight loss was excluded. The corrosion rate of anodized-sealed specimens was about five times lower than that of the anodized specimens. Beeswax-colophony resin effectively sealed the pores and cracks in the anodic layer thus retarded corrosion of the underlying metal.

Figure 3 shows the surface morphology of the anodic oxide layer resulting from 20 min anodization without and with sealing after corrosion test in 0.9% NaCl solution at 37°C for 14 days. The surface of the anodized specimen (figure 3(a)) became rough and covered by the corrosion product (inset image in figure 3(a)). The anodic oxide layer was mostly dissolved into the solution during immersion exposing the metal substrate. Mg metal corrodes by releasing Mg ions that spontaneously hydrolyzed to form Mg(OH)$_2$ [11]. The Mg(OH)$_2$ is sparingly soluble and further reacts with chloride ions to form MgCl$_2$ and other chloride complexes. Meanwhile, observation on the anodized-sealed specimens revealed that the specimens remained intact with few hydrated spots. The hydrated spots appeared as white areas while the rest of the specimens remained yellowish (beeswax-colophony resin). The beeswax-colophony sealant prevented the corrosive solution to penetrate the anodic oxide layer by blocking the pores and cracks in the anodic layer. In fact, the beeswax-colophony resin was strongly attached in the anodic film due to the presence of pores and cracks. Confirming the weight loss tests,

| Specimen                  | Corrosion rate (mmpy) |
|---------------------------|------------------------|
| Anodized 10 min           | 16.2                   |
| Anodized 20 min           | 16.5                   |
| Anodized 30 min           | 14.9                   |
| Anodized 10 min + sealed  | 5.6                    |
| Anodized 20 min + sealed  | 3.8                    |
| Anodized 30 min + sealed  | 3.9                    |

The surface of the anodized-sealed specimen was free from corrosion and still covered by the sealant resin (figure 3(b)), in contrast to the anodized specimen which was severely corroded (figure 3(a))
after 14 days immersion in NaCl solution. Thinning of the resin probably occurred during immersion giving a rough appearance as shown in the inset image in figure 3(b) that contributed to the weight loss presented in figure 2.

4. Conclusions
The effect of beeswax-colophony sealant on the corrosion behavior of anodized AZ31 specimen has been investigated by weight loss method. The results showed that the sealant remarkably improved the corrosion resistance of the specimens about five times. After immersion in 0.9% NaCl solution for 14 days the anodized-sealed specimens remained unaffected by corrosion in contrast to the anodized specimens which was severely corroded as the surface was fully covered by corrosion product. The cracks and pores existed in the anodic oxide layer were filled by the sealant material and thus prevented penetration of the layer by the corrosive solution. The beeswax-colophony resin shows promise as an effective biodegradable sealant material for anodized Mg alloys.

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References
[1] Witte F, Hort N, Vogt C, Cohen S, Kainer K U, Willumeit R, Feyerabend F 2008 Curr. Opin. Solid State Mater. Sci. 12 63
[2] Hornberger H, Virtanen S, Boccaccini A R 2012 Acta Biomater. 8 2442
[3] Pekguleryüz M O, Kainer K U, Kaya A A 2013 Fundamentals of Magnesium Alloy Metallurgy (Cambridge, UK: Woodhead Publishing Ltd.)
[4] Chen X B, Birbilis N, Abbott T B 2011 Corrosion 67 (3) 035005
[5] Blawert C, Dietzel W, Ghali E, Song G 2006 Adv. Eng. Mater. 8 511
[6] Anawati A, Asoh H, Ono S 2017 Materials 10 11
[7] Gu X N, Li N, Zhou W R, Zheng Y F, Zhao X, Cai Q Z, Ruan L 2011 Acta Biomater. 7 1880
[8] Anawati A, Asoh H, Ono S 2015 Surf. Coat. Technol. 272 182
[9] Abdikheibari S, Parvizi R, Moayed M, Zebarjad S, and Sajjadi S 2015 Metals 5 1645
[10] Gumelar M D, Putri N A, Anggaravidya M, Anawati A. 2018 Proc. Int. Symposium on Metallurgy and Materials (American Institute of Physics) 1964 020035
[11] Nordlien J H, Nisancioglu K, Ono S, Masuko N 1996 J. Electrochem. Soc. 143 2564