

An Investigation of Pulse Anodization Duty Ratio and Sealing Treatment on the Corrosion Behavior of the Anodic Coating Layer in Magnesium AZ31B

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In this work, we describe the effect of pulse anodizing duty ratio on the corrosion resistance of anodic films in magnesium AZ31B. The process involves the application of square pulse potential for a constant period with a duty ratio varying from 40, 60 and 80%. In several samples, a sealing treatment for 30 minutes was conducted after anodization in order to seal the pores available in the anodic layer. After anodizing, the surface morphology of the anodic layer was examined using a scanning electron microscope (SEM Hitachi SU3500). The corrosion characteristics of the sample were evaluated through an open circuit potential (OCP) and potentiodynamic polarization test using potentiogalvanostat. SEM observation shows that the increase of anodization duty ratio (α) results in a more uniform anodic layer, with fewer pores and cracks. The increase of duty ratio (α) decreases the OCP value from approximately -1.475 to about -1.6 Volt, and significantly improves the corrosion resistance of the anodic coating by 68%. The combination of anodization and sealing treatment produces an anodic coating with a very low corrosion rate of 4.4 mpy.

Keywords: Anodization, Corrosion, Magnesium AZ31B, Sealing, Coating

1. Introduction

Recently, the development of magnesium and its alloys is being carried out all over the world. Magnesium and its alloy are a potential candidate material for the fabrication of biodegradable metal implant. Magnesium metal is suitable for biodegradable implant application in the human body because magnesium has higher biological (corroded) activity than conventional metals and non-toxic [1,2]. Because of this, when magnesium decays, it can be absorbed and does not produce toxic products for the human body [3]. Magnesium also has several interesting properties, such as light weight, high strength to weight ratio, and elastic modulus similar to human bones [3]. However, rapid rate of magnesium degradation in human body limits their clinical application [2]. One of the methods commonly use to regulate and control the rate of degradation of magnesium is surface protection by anodizing [4,5].

Anodizing is an electrochemical process which convert metal surfaces to anodic oxide layer which has a good corrosion

resistance and durable. In general, anodic oxide layers grow depend on the process time and applied voltages during anodization. Furthermore, the type of anodic layer formed on the metal surface due to anodization depends on the composition of electrolyte. Salman *et al.* [5] reported that during anodization of magnesium in NaOH electrolyte, the addition of $\text{Ca}(\text{OH})_2$ was improve the thickness and corrosion resistance of anodic layer. The addition of Ca in anodic layer was also expected to improve the anodic layer biological properties such as bioactivity and tissue regeneration. The anodic film formed during anodization of magnesium is generally porous [5-8]. Such a porous film will allow corrosive media to reach the substrate easily and will instead accelerate corrosion.

One way to regulate the pores formed in the anodized film layer is by using pulse anodizing [7,9-11]. In pulse anodizing, several additional parameters can be varied independently to control the pores formed in the anodic layer, such as pulse current or potential, pulse period and pulse duty cycle. To our knowledge, there are very limited reports discussing the effect of duty ratio during pulse anodizing of magnesium alloys [12]. In this work, the effect of the pulse duty ratio during anodization on the corrosion resistance

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Table 1. Chemical composition (wt%) of AZ31B Mg alloy

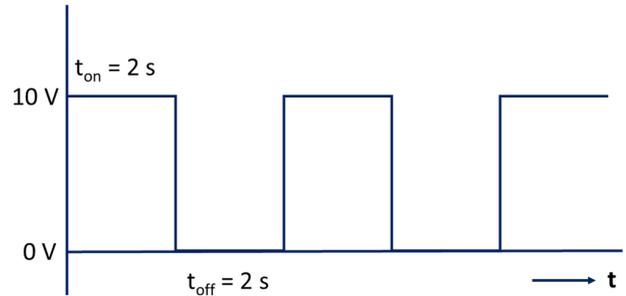
Mg	Al	Zn	Mn	Si	Cu	Ni	Fe
Bal.	3.0	1.0	0.43	0.01	< 0.01	< 0.001	0.003

of anodic layer will be investigated.

2. Experimental Methods

Commercial magnesium AZ31B, with chemical composition shown in Table 1, was used as a substrate for pulse anodization process. Sample were cut from large sheets to form a rectangular shape with dimension of 50 mm × 10 mm × 2 mm. The samples were mechanically ground with abrasive SiC paper up to 2000 grit, then polished with alumina paste, up to a mirror finish. Finally, the sample was rinsed with water, followed by cleaning in ethanol solution and dried. The sample was set as an anode, and ready for anodization process.

The anodizing process was carried out in a 250 mL glass beaker. The sample were anodized in 1 M NaOH + 30 mM Ca(OH)₂ aqueous solution with a square pulse potential, as shown in Fig. 1. Magnesium AZ31B sample was set as an anode and titanium sheet was used as cathode. The electrolytic bath was maintained at a uniform temperature of ~25 °C. The anode-cathode distance was 20 mm in all tests. The schematic illustration of the electrochemical cell used for anodizing is presented in Fig. 2. For this experiment, square pulse potential was obtained from a function generator (Rigol) coupled to a Hokuto Denko HA-151B potentiogalvanostat [13]. Square pulse potential at constant pulse frequency of 0.5 Hz with an applied voltage of 10 volts were supplied to the anode during anodization. In all test, the anodizing was carried out for 30 minutes. Pulse potential duty ratio (α) are varied from 40%, 60% and 80% which are being controlled by a function generator. The detail experiment condition conducted in each

**Fig. 1. Waveform generated for applied square pulse potential**

test are shown in Table 2.

After anodizing, the surface morphology of anodic layer was examined using scanning electron microscope (SEM Hitachi SU3500) at high magnification. The corrosion characteristics of sample was evaluated by open circuit potential (OCP) and potentiodynamic polarization test using potentiogalvanostat equipped with Versastudio software. OCP measurement was carried out for 15 minutes to observe the free potential of sample in corrosive environment. In potentiodynamic polarization test, measurement was carried out in a potential range from -0.25 to +0.25 V_{SCE} Vs open circuit potential (E_{OCP}) with a scan rate set to 1 mV/second. All the electrochemical measurements were carried out using a conventional electrochemical cell equipped with three electrodes; graphite, saturated calomel electrode (SCE) and magnesium AZ31B sample which served as the counter, reference and working electrodes. Measurements were taken at 25 °C in ringer solution which are used as corrosive environment for the corrosion testing.

Table 2. Experiment condition in each test

Specimen code	Duty ratio (%)	Sealing	Applied voltage (V)	Pulse period (s)	Anodizing time (minute)
AZ31B	-	-	-	-	-
40	40	No	10	2	30
60	60	No	10	2	30
80	80	No	10	2	30
40S	40	Yes	10	2	30
60S	60	Yes	10	2	30
80S	80	Yes	10	2	30

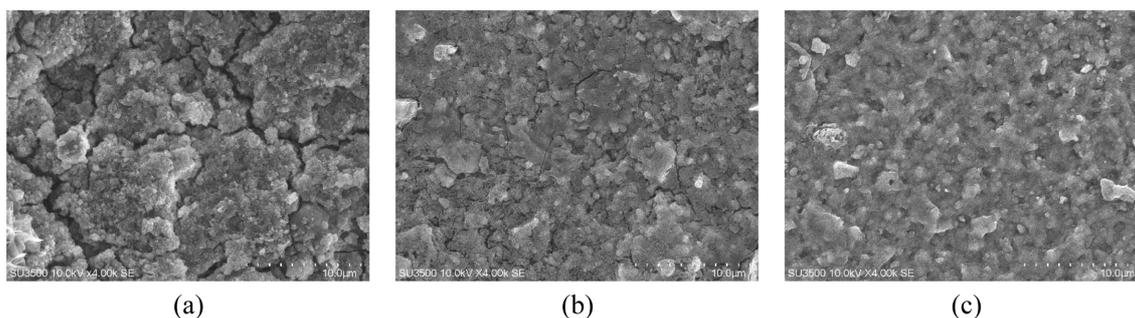


Fig. 2. SEM images for the surface of the anodic layer, as a function of the applied duty ratio, a) 40%, b) 60% and c) 80%

3. Results and Discussion

3.1 Surface morphology of anodic layer

Fig. 2 shows SEM images for the surface of the anodic layer, as a function of the applied duty ratio. As seen in Fig. 2a, the sample anodized with a duty ratio of 40% had cracks and pores that were quite large almost evenly across the surface. This is because the pulsed voltage acting during anodization has a shorter working time, which is unfavorable for the growth of the oxide layer. The presence of these cracks and pores makes the anodic layer formed on the surface more susceptible to corrosion. When we increase the pulse duty ratio during anodization to 60%, the formation of cracks and pores on the surface of the sample is significantly reduced (Fig. 2b). The rate of oxide formation on the sample surface becomes more dominant when compared to the dissolution rate of the oxide. Finally, at a duty ratio of 80%, almost no cracks or pores were visible on the sample surface (Fig. 2c). This is because the pulsed voltage during anodization has a longer working time so that the anodic layer formed is more compact and denser. From this fact, we can see that the pulse duty ratio during anodization has a very important influence in regulating the pore size and distribution in the anodic layer.

3.2 Open circuit potential measurement

Fig. 3 shows the variation of open circuit potential (OCP) as a function of time for anodic layer in magnesium AZ31B, immersed in Ringer solution. The OCP of magnesium AZ31B before anodization was approximately around -1.275 Volt vs SCE. With increasing time, the value of OCP fluctuates and tends to decrease. This shows that bare

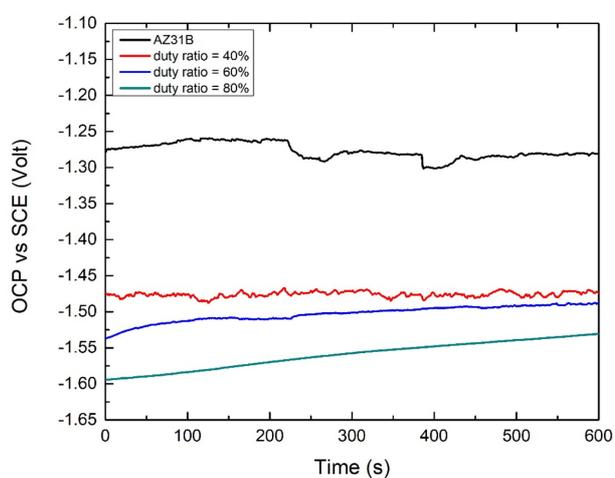


Fig. 3. The variation of open circuit potential as a function of time for anodic layer in magnesium AZ31B

magnesium AZ31B experiences corrosion in the solution.

The increase of pulse anodization duty ratio (α) from 40% to 80% decrease OCP value from approximately -1.475 to about -1.6 Volt. This shows that as the duty ratio increases, the anodic layer formed on the surface of the sample is easily oxidized in solution. With increasing time, the OCV curve tends to continue increasing towards a positive potential value. This indicates that the anodic layer formed on the sample surface exhibit a passive behavior in the test solution. In the case of anodic layer obtained from pulse anodization with duty ratio (α) 40%, the OCP curve fluctuates slightly, indicating that the anodic layer formed on the magnesium AZ31B surface is not dense. The presence of pores/cracks in the anodic layer can accelerate local corrosion rate in the solution, causing potential fluctuations during OCP measurements.

Fig. 4 shows the variation of open circuit potential as

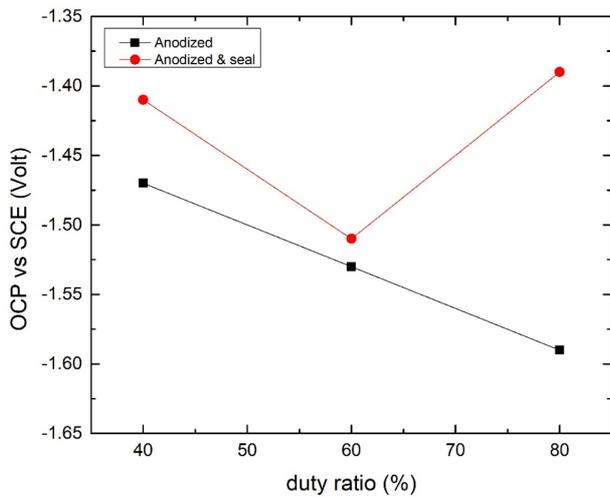


Fig. 4. The variation of open circuit potential as a function of pulse anodizing duty ratio (α)

function of duty ratio (α) for anodic layer in magnesium AZ31B during immersion in Ringer solution, before and after sealing treatment. After sealing, the OCP value of anodic layer is increased when compared to the OCP value of the anodic layer before sealing. In addition, the pores or cavities that exist in the anodic layer was closed. The interaction between anodic layer and solution is inhibited, as the aggressive ion in the solution are difficult to penetrate the compact/dense anodic layer. As a result, the OCP value shifted towards a positive potential value. The effect of sealing treatment was very significant on the anodic layer obtained from pulse anodization with a duty ratio (α) of 80%.

3.3 Potentiodynamic polarization measurement

The corrosion behavior of the anodic layer in magnesium AZ31B was evaluated using potentiodynamic polarization tests in Ringer solution at 25 °C with 0.1 mV/S scan rate. The variation in current density of sample with potential are shown in Fig. 5. The potentiodynamic polarization curve for bare magnesium AZ31B was also included. The polarization curve of anodic layer in magnesium AZ31B was shifted towards the negative potential value when compared to the polarization curve of bare magnesium AZ31B. This shows that the anodic layer on the sample surface tends to oxidize in solution when compared to bare magnesium AZ31B. Salman *et al.* [5] reported that the presence of calcium in the anodic layer decreases anodic layer corrosion potential, because calcium had lower standard reduction potential ($E^{\circ} = -2.76$ V) when compared to magnesium ($E^{\circ} = -2.38$ V). As

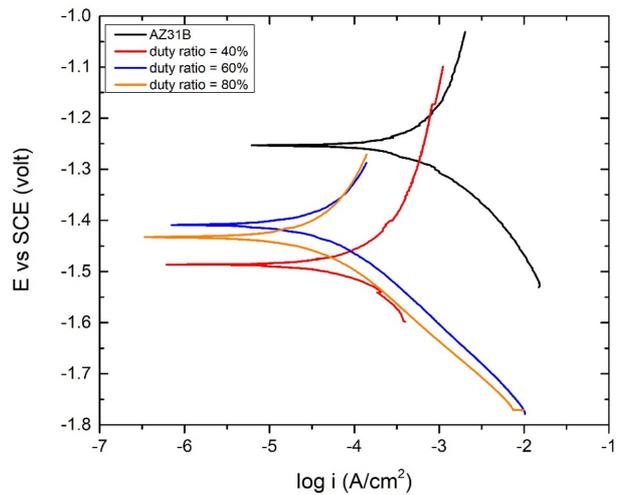


Fig. 5. Potentiodynamic Polarization Curve for anodized layer in Mg AZ31B

a result, the corrosion potential of the anodic layer is more negative when compared to the corrosion potential value of bare magnesium AZ31B.

From Fig. 5, we can also see that the increase of duty ratio (α) during pulse anodization modify the corrosion behavior of anodic layer in magnesium AZ31B. With the increase of pulse anodization duty ratio from 40 to 80%, the polarization curve was shifted toward a positive/noble corrosion potential value, with a lower corrosion current density. This shows increased corrosion resistance in the anodic layer. Several researchers [13,14] reported that the increase of duty ratio during pulsed anodization decreased the pore size and surface porosity of the anodic film. The maximum pore diameter was less than 1 μm and the surface porosity was about 11 times lower than that for samples anodized at a constant voltage. Higher anodization duty ratio will result in more uniform anodic layer, as more current is available for magnesium oxidation reaction. On the contrary, lower anodization duty cycle will result in more irregular anodic layer, with more micropores/microcrack, as less current is available to support magnesium oxidation reaction.

Fig. 6 shows the potentiodynamic polarization curve of anodized magnesium AZ31B before and after sealing treatment with duty ratio from (a) 40%, (b) 60%, and (c) 80%. The potentiodynamic polarization curve for bare magnesium AZ31B was also included. The polarization curve of anodic layer in magnesium AZ31B after sealing treatment was shifted toward negative potential value compared to the polarization curve of bare magnesium

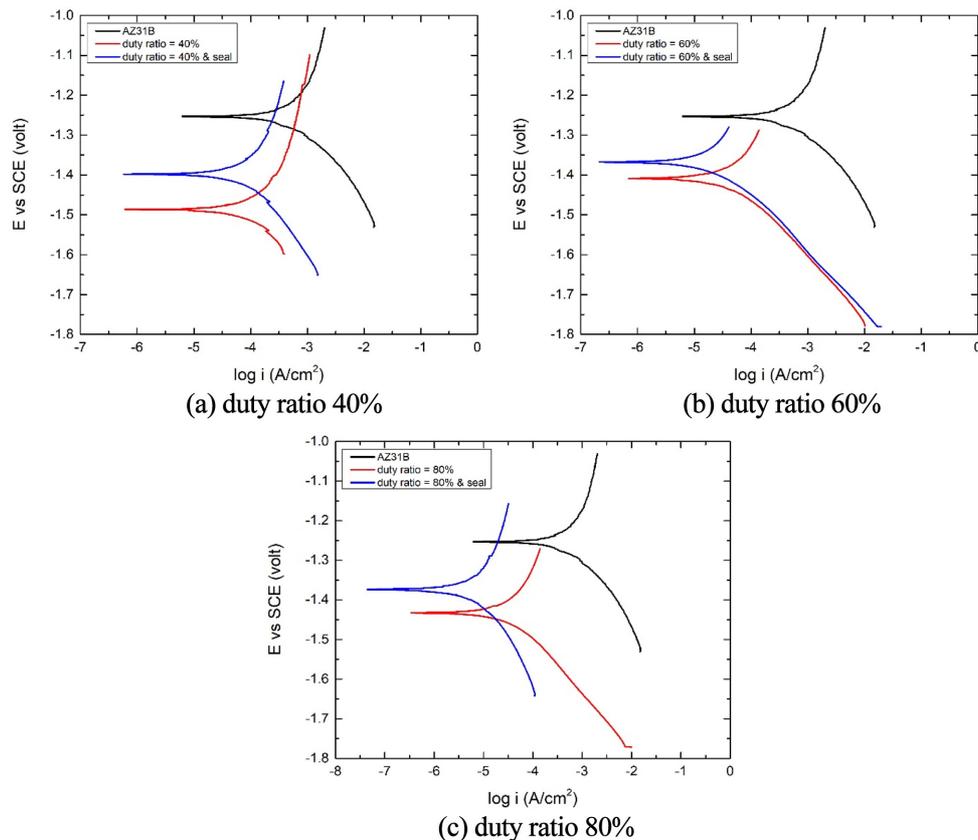


Fig. 6. Potentiodynamic polarization curve for anodized layer in magnesium AZ31B before and after sealing with (a) duty ratio 40%, (b) duty ratio 60% and (c) duty ratio 80%

AZ31B. This indicated that the anodic layer which form in the surface of sample after anodization and sealing treatment had more negative corrosion potential value compared to bare magnesium AZ31B.

It can also be seen from Fig. 6 that the polarization curve of anodic layer after sealing treatment shifted toward a positive/noble potential value, with a lower corrosion current density, compared to the polarization curve of anodic layer before sealing treatment. This trend was similar for all polarization curve with different anodization duty ratio, as observed in Fig. 6a, b and c. The potentiodynamic polarization results clearly indicated that corrosion behavior of anodic layer after sealing treatment was improved if compared to that before sealing. Kim *et al.* [15] reported that micropores and microcrack available in the anodic oxide layer was suppressed and closed during sealing due to expansion of $Mg(OH)_2$ film. As a result, the anodic layer becomes more thermodynamically stable in the Ringer's solution after the sealing treatment.

Table 3 show the electrochemical parameters calculated from potentiodynamic polarization curves in Fig. 5. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) was estimated by Tafel extrapolation of the anodic and cathodic branches of polarization curves. Corrosion current density (i_{corr}) was related to the corrosion rate, CR (mpy) of sample according to equation (1).

$$CR = 0.128x (i_{corr} \times a)/(n \times d) \quad (1)$$

Where CR is corrosion rates (mpy), i_{corr} is corrosion current density (A/cm^2), a is atomic weight of Mg, n is number of electron involved in corrosion reaction, and d is density ($gram/cm^3$).

As expected, bare magnesium AZ31B sample shows a very high corrosion rates in ringer solution approximately of 270 mils-per-year (mpy), with a corrosion potential (E_{corr}) of -1.24 volts and corrosion current density (i_{corr}) of $3.1 \times 10^{-4} A/cm^2$. This is mainly due to magnesium high reactivity in

Table 3. Electrochemical parameter calculated from potentiodynamic polarization curve

Sample	E_{corr} vs SCE (Volts)	I_{corr} (A/cm ²)	CR (mpy)
AZ31B	-1.24	3.1E-04	270.71
40	-1.49	8.9E-05	77.82
60	-1.39	3.9E-05	34.51
80	-1.40	2.8E-05	24.60
40S	-1.40	4.8E-05	41.99
60S	-1.33	1.5E-05	12.85
80S	-1.37	5.0E-06	4.43

aqueous and chloride media. On the other hand, all the anodized magnesium AZ31B sample with different duty ratio and sealing treatment exhibited lower corrosion rates.

The increase of duty ratio from 40% to 80% for anodized sample, significantly improves corrosion resistance of anodic layer from 77.8 mpy to 24.6 mpy. This indicate that the anodic layer obtained from anodization with duty ratio of 80% is more uniform and denser than that of the specimens anodized at duty ratio of 40%. As a result, Cl⁻ ions in solution find it more difficult to penetrate the anodic layer.

We can also see that sealing treatment conducted after pulse anodizing, significantly improve the corrosion resistance of anodic layer. The increase of duty ratio from 40% to 80% for anodized and seal sample, significantly improves corrosion resistance of anodic layer from 41.9 mpy to 4.4 mpy.

Sample which has the best corrosion resistance was obtained from pulse anodizing experiment with duty ratio of 80% followed by sealing treatment. The corrosion rate is very low, approximately about 4.4 mpy. After sealing treatment for 30 minutes in boiling water, the open pore structures which is commonly found on the anodized magnesium alloy were mostly covered and leveled by magnesium hydrate layer. The surface of anodized magnesium alloy is impermeable to diffusion of aggressive ion in the solution.

5. Conclusions

In this work, the effect of pulse anodization duty ratio on the corrosion characteristics of magnesium AZ31B alloy were examined. A square pulse potential with constant pulse period was applied on the electrode surface in 1 M NaOH + 30 mM Ca(OH)₂ solution. The corrosion resistance of magnesium AZ31B increased as duty ratio (α) increased, both in anodized and post seal-treated sample. Sample which

has the best corrosion resistance was obtained from pulse anodizing experiment with duty ratio of 80% followed by sealing treatment, with the corrosion rate approximately about 4.4 mpy.

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