Effect of Zinc Oxide Concentrations on Anodic Coated AZ91D Mg Alloy for Surface Modification Applications

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Abstract: The AZ91D Magnesium (Mg) Alloy is broadly known as an attractive material with many applications ranging from military goods and aerospace to automobile applications due to its excellent properties in lightweight, machinability, and castability. Unfortunately, Mg Alloys are also prone to corrosion resulting in degradation of the components, which can lead to severe component failure and injuries. Thus, corrosion prevention is required for the AZ91D Mg alloy to increase its performance in the environment. This paper uses the anodising method to study the influence of Zinc Nitrate's electrolyte concentrations on anodic coated AZ91D Mg Alloys. This method formed a thin film layer on the AZ91D Mg Alloy's samples known as an anodic film, which can potentially reduce the corrosion activity on the surface of the substrate. To investigate the corrosion activity of the anodised samples, the corrosion rate value was calculated by immersion of coated samples in a salt solution. The coated and corroded surfaces' morphology, structure, and thickness are observed using a Scanning Electron Microscope (SEM). At the same time, the element content of the material will be determined using X-ray diffraction (XRD). Thus, the resulting influence of Zinc Nitrate electrolyte concentration by anodising method shows which concentration value successfully formed the best Zinc Oxide (ZnO) coating layer on AZ91D Mg Alloy samples. Furthermore, an anodisation method using suitable concentrations of Zinc Nitrate electrolyte can be further developed to form an appropriate surface treatment for automotive applications in resisting corrosion in its environment.

INTRODUCTION

AZ91D Mg Alloy is widely used in automotive industries due to their low density, high specific strength, and excellent machinability. However, this alloy has poor corrosion resistance, which can lead to severe failure of the components [1]. Therefore, several surface treatment methods have been investigated,

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including conversion treatment, electroplating, and anodising, to increase its corrosion resistance. Anodizing method has been selected due to its high corrosion resistance, low cost, ease to control, non-toxic, and environmentally friendly [2]. Previous studies report the development of Zinc Oxide coatings depending on various types of electrolyte solutions and coating methods. The previous experiment used Potassium hydroxide (KOH), Sodium hydroxide (NaOH), Sodium Sulphate (Na2SO4), Carbonate based (CO2), Ammonium based (NH4), Sulfuric acid (H2SO4), Hydrochloric acid, and Phosphoric acid as an electrolyte solution for anodising [3]. Thin film Zinc oxide (ZnO) can be produced by various methods such as chemical vapour deposition, the sol-gel method, electron beam evaporation, spin coating, conversion coating, electrochemical deposition, and many more [4].

However, the use of Zinc Nitrate as an electrolyte solution in anodising to form a Zinc Oxide (ZnO) coating on the AZ91D Mg Alloy has not been studied.

Thus, this study aims to investigate the influence of Zinc Nitrate electrolyte concentrations on the anodic coated AZ91D Mg Alloy by anodising method and its corrosion activity by immersion in a salt solution. The outcome of the coating at different Zinc Nitrate electrolyte concentrations and corrosion tests will be analysed using Optical Microscope (OM), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX), and X-Ray Diffraction (XRD).

METHODOLOGY

Figure 1 shows the overall flow of the study. After the samples were prepared, anodising was performed on the samples. The coating of the samples was then observed and analysed. Coated samples were also immersed in a salt solution for corrosion testing, and the corroded surface was also observed and analysed.

Sample preparation
AZ91D Mg Alloys (Al 9.1 wt%, Zn 0.85 wt%, Mn 0.27 wt%, and Mg balance) with a 10 x 10 x 10 mm size were used as a sample. The samples were connected with Pure Nickel wire and then cold-mounted. After curing, the sample was polished with emery paper #1200, exposing only one side of the sample.

Anodizing
The Zinc Nitrate electrolyte was prepared at different concentrations of 0.01M, 0.1M, and 0.3M by dissolving Zinc Nitrate Hexahydrate with 1 litre of distilled water [5]. The anodising process was conducted at a constant voltage of 20V for 3 minutes at room temperature. After

anodising, the samples were dried for 24 hours at 70 ±2°C.

Corrosion Test
After drying, the samples were then immersed in NaCl solution for 72 hours at 35 ±2°C and then dried again for 24 hours at 70 ±2°C. The NaCl solution and corrosion rate were prepared and calculated according to the standard JIS 0541:2003 [6]. The sample's weight was recorded after each drying process to calculate the corrosion rate, R by weight loss, using the formula below:

$$R = \frac{8.76 \times 10^4 W}{ADt} \tag{1}$$

Where W, A, D, and t are weight change (g), active area (cm2), density (g/cm3) and immersion time (h), respectively.
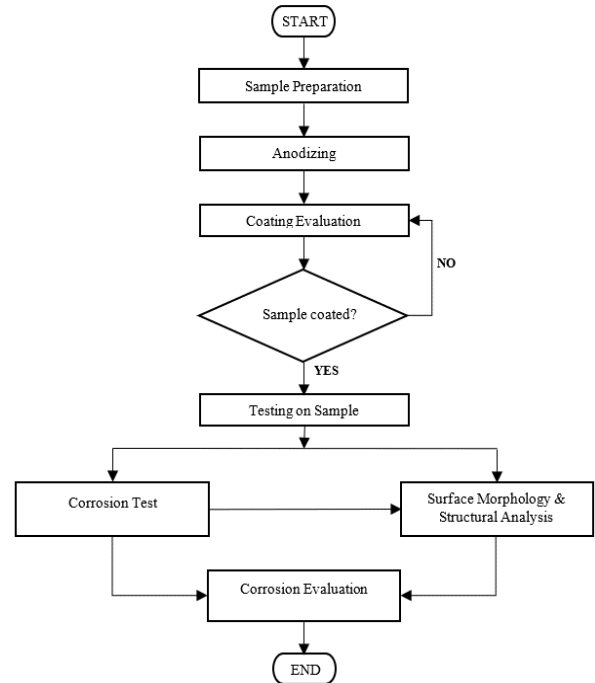

Fig 1. Flow chart of the study

RESULT AND DISCUSSION

The corrosion rate, surface morphology, and structure of the AZ91D Mg alloy samples were evaluated by weight loss calculation, Optical Microscope (OM), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX), and X-Ray Diffraction (XRD).

Coating Morphology Analysis
Figure 2 and 3 shows the OM and SEM images of the uncoated sample (a) and samples that were anodised at electrolyte concentrations of 0.01M (b), 0.1M (c), and

0.3M (d). Figure 2 (a) shows the substrate surface with parallel scratches due to polishing. In Figure 2(b), a few scratched areas of the substrate can be seen due to incomplete and non-uniform coating distribution. Meanwhile, for the anodised sample at 0.1M and 0.3M, a denser surface fully coated by Zinc Oxide (ZnO) can be seen.

Figures 3(a) shows the SEM images of the uncoated sample surface, which has smooth and parallel scratches due to the polishing process. Based on Figure 3(b) for 0.01M, it can be seen that the coating was not uniformly distributed. The image of the coating surface appeared flaky and rough like crusted sheets, and the flake size was relatively small with many microcracks compared to the surface appearance of the sample 0.1M (3c) and 0.3M (3d).

As the concentration increases from 0.1M to 0.3M, it can be seen that the size of the flakes becomes more expansive, and the microcracks reduce. This shows that the concentration of Zinc Nitrate influences the anodised surface. The anodised surface becomes rougher as the Zinc Nitrate concentrations increases. The previous study found that an anodised surface with minimal microcracks and an uneven surface exhibited the most significant corrosion resistance [2].
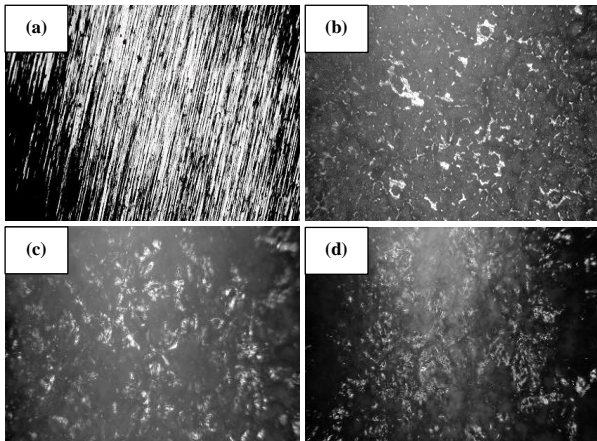

Fig 3. SEM images of anodized morphology: (a) Uncoated; (b) 0.01M, (c) 0.1M, (d) 0.3M of electrolyte concentration.

Cross-Sectional Analysis

Figure 4 shows the SEM images of a cross-sectional analysis of an anodised sample at different Zinc Nitrate concentrations. In Figure 4 (a-b), the coating thickness of the anodised sample at 0.01M and 0.1M concentrations shows a very thin layer of coating which is the grey area between the dark area and the sample. Figure 4(c) shows the anodised sample at 0.3M concentration form a thicker Zinc Oxide (ZnO) layer. Due to the denser coating layer produced, the anodised sample at 0.3M concentration will provide better protection than 0.01M and 0.1M.

Fig 2. Optical Microscope of anodizing coating with Zinc Nitrate Hexahydrate Zn (NO3)2 electrolyte at different concentration (a) Uncoated; (b) 0.01M; (c) 0.1M; (d) 0.3M.
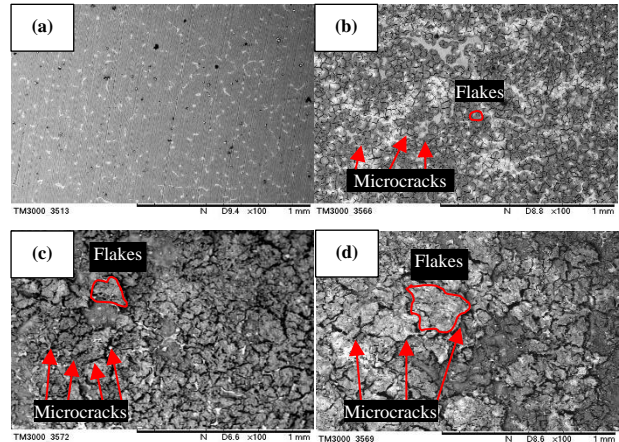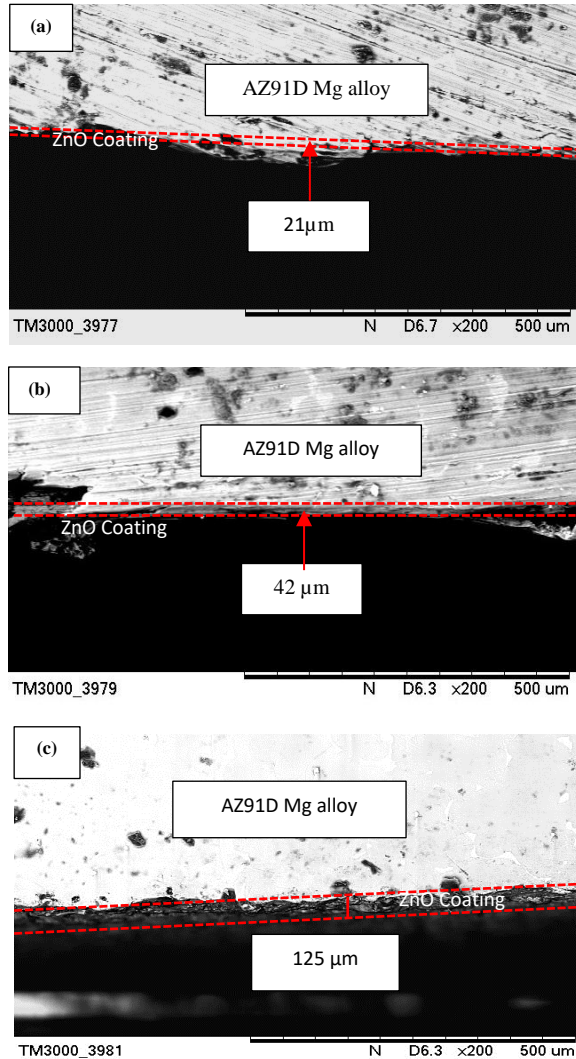
Fig 4. SEM images of the coating thickness: (a) 0.01M, (b) 0.1M and 0.3M Zinc Nitrate concentrations.

Phase composition analysis

EDX analysis of the AZ91D Mg alloy was discussed in Table 1. The oxide particles were incorporated into the anodised coating, and as proved by EDX analysis, elements such as magnesium (Mg), oxygen (O), aluminium (Al), and zinc (Zn) were detected. The results show that the anodised sample at 0.01M has the highest oxygen element (O) of 61.06%. The 0.3M sample has the lowest magnesium (Mg) at 24.97% compared to other samples but has the highest Zinc (Zn) content at 16.94%.

A higher percentage of zinc (Zn), aluminium (Al), and low magnesium (Mg) elements by increasing Zinc Nitrate concentration are suggested for a better corrosion resistance performance because it will form the best Zinc Oxide (ZnO) coating to protect the AZ91D Mg alloy's surface [7].

Table 1. EDX analysis of uncoated and anodised samples at different Zinc Nitrate concentrations.

Zinc Nitrate Concentration (M)	Element content (wt%)			
	Mg	O	Al	Zn
Uncoated	88.7	3.3	7.6	0.3
0.01	25.7	61.06	8.63	4.6
0.1	30.11	56.16	3.64	4.08
0.3	24.97	48.18	9.92	16.94

X-Ray Diffraction (XRD)

The XRD patterns shown in Figure 5 show that the coating mainly comprises ZnO according to JCPDS PDF card number 01-079-2205. The peaks of Zinc Oxide (ZnO) at about (002) and (101) (diffraction line at $2\theta= 34.4º$ and $36.2º$) appear at all the anodised samples of 0.1M and 0.3M Zinc Nitrate concentration. The anodising method using Zinc Nitrate electrolyte simultaneously forms the Zinc Oxide (ZnO) [8].
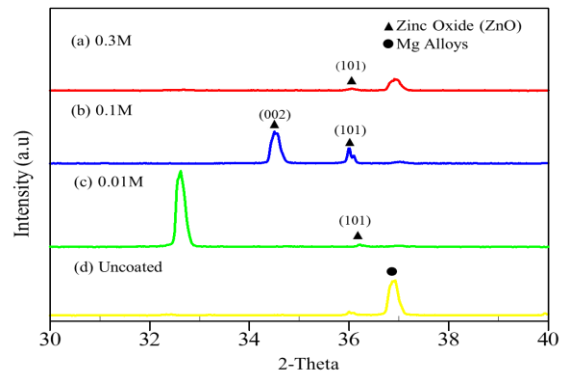

Fig 5. XRD patterns of Zinc Oxide (ZnO) coating at (a) 0.3M, (b) 0.1M, (c) 0.01M and (d) Uncoated.

Corrosion Evaluation

The graph in Figure 6 shows the corrosion rate in millimetres per year (mm/year) for all samples immersed in NaCl solution for 72 hours. The anodised sample with the Zinc Nitrate concentration of 0.01M has shown the second highest corrosion rate of 21.00 mm/year, and the sample with 0.1M concentration shows the highest corrosion rate of 31.43 mm/year. Meanwhile, the anodised sample with 0.3M concentration has shown the lowest corrosion rate of 10.92 mm/year. The uncoated sample resulted in a corrosion rate of 22.54 mm/year, higher than samples 0.01M and 0.3M but lower than sample 0.1M.

This observation shows that the Zinc Nitrate concentration has influenced the coating structure and corrosion rate of the AZ91D Mg alloy.
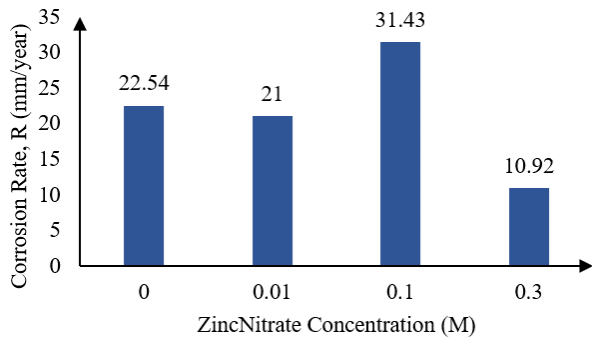
Fig 6. The corrosion rate of samples with Zinc Oxide (ZnO) coatings in various electrolyte concentrations.

Corrosion Morphology Analysis

Figure 7 shows the OM images of the anodised sample in various Zinc Nitrate concentrations after 72 hours of immersion in NaCl solution. Figure 7 (a) shows the corroded uncoated sample's surface. Figure 7 (b) shows that the anodised sample at 0.01M has a large cloudy dark area representing the corroded area compared to samples at 0.1M and 0.3M.
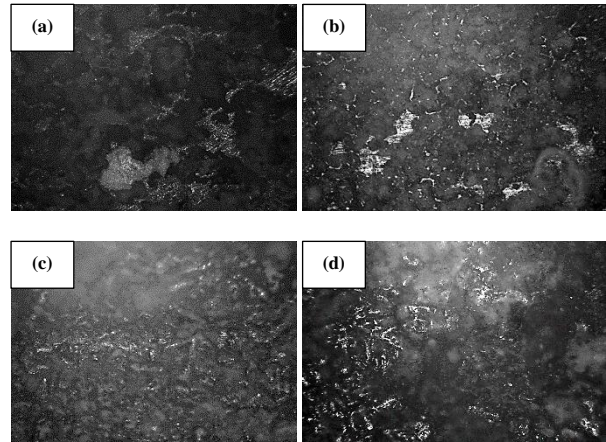

Fig 7. Optical Microscope images of sample after immersed in NaCl solution (a) Uncoated, (b) 0.01M, (c) 0.1M, (d) 0.3M of electrolyte concentration.

Figure 8 presents the SEM images of the sample after immersion in NaCl solution for 72 hours. Figure 8 (a) shows the uncoated surface with a pitted area due to a corrosion attack. SEM images of the anodised coating at 0.01M, figure 8 (b), and 0.1M, figure 8 (c) revealed a porous surface and larger-sized corroded area. The anodised surface, which has many tiny pinholes, appears before a pitting corrosion attack. The deep hole pitting corrosion occurs with the small corrosion cracks on the surface. Figure 8(d) shows that the surface of 0.3M concentration has less deep hole area and pores due to the thick Zinc Oxide coating influenced by Zinc Nitrate concentration.
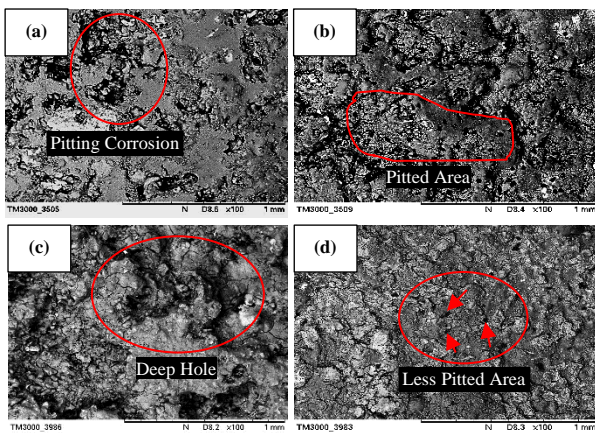
0.01M and 0.1M concentrations. Moreover, the effect of anodised coating gives effective corrosion resistance by comparing the corrosion rate with the uncoated sample. Consequently, the impact of different Zinc Nitrate electrolyte concentrations on anodic coated AZ91D Mg alloy can provide surface treatment for corrosion resistance.

Fig 8 SEM images of sample after immersed in NaCl solution (a) Uncoated, (b) 0.01M, (c) 0.1M, (d) 0.3M of electrolyte concentration.

CONCLUSION

The anodising method successfully produced a Zinc Oxide (ZnO) coating on the surface of AZ91D Mg alloy using Zinc Nitrate as an electrolyte. The Zinc Oxide (ZnO) layer formed a thicker thin film coating at 0.3M concentration, and the corrosion rate was lower than the

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