Corrosion protection of zinc alloy ZA12 using anodizing process in acidic media

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Abstract Zinc alloys are used in very wide industrial applications due to their excellent physical and mechanical properties. To improve the corrosion resistance, anodizing process is used. Anodizing of Zinc Alloy ZA12 is investigated in 1 M H₂SO₄ solution for 10, 20, 30, 40 and 50 mins at a constant voltage of 5V. Atomic force microscope (AFM) used to study the surface roughness of the anodic film. The results show that the surface roughness of anodic film is primarily depending on the anodizing time and coating average thickness. Furthermore, the microhardness also increases with the anodizing time. The corrosion performances in sea water of both anodized and non-anodized zinc specimens are acquired by potentiostatic polarization. Corrosion current density (i_Corr) and corrosion potential (E_Corr) are obtained from potentiostatic polarization studies. The studies show that the corrosion current density and corrosion rate were reduced with increasing the anodizing time which enlarges anodic film average thickness. The results of corrosion rates indicate an enhancement in corrosion resistance of anodized Zinc Alloy ZA12 in the sea water. Contact angle test measurements for ZnO layer formation on zinc alloy AZ12 were detected which indicate that the contact angle of un-anodized film seems to be elevated than that of anodized film after sealing the anodic film.

Keywords: Corrosion, Zinc alloy, Anodizing, Potentiostate, Contact Angle

1. Introduction
In recent times, a wide range of researchers’ attention is seen to be attracted on the zinc alloys as a future material owing to its certain properties that make them used in many purposes for instance solar cells [1], gas detector [2], water purification [3], Light discharging diodes [4,5] and photo-catalysts.

Due to the low corrosion resistance of zinc, anodizing is important to make the application of protective coating layers. Anodizing is a technique utilized for a long time as corrosion protection of Zinc alloys. Anodic films on zinc, zinc alloys and electrodeposited zinc are extensively applied by industry due to their high corrosion resistance and diminish their cost. Anodizing of zinc makes certain such elevated corrosion resistance that it may be employed to protect any zinc-coated or zinc die-cast article from corrosion either in the majority aggressive marine or environments of industries [5,6].
Zinc anodizing was recognized for several times [6-8]. As a commercial process, it was finally launched in the late 60s utilizing International Lead Zinc Research Organization Inc. Anodic films can be able to utilize for a wide range of applications, either with thin transparent coatings that add disruption (interference) effects to light reflected or with thick porous coatings layer that may absorb dyes. Now, the researcher’s interest is to investigate a new method of anodizing as it improved the preparation of nanostructured metal oxides with unique chemical and physical properties [8, 9, 11].

Anodization is an electrochemical method of passivating a metal surface by creating a new layer on it. This layer represents metal oxide. In some situations, for example, explanation of the form of electrolyte, a range of nanostructures may also be synthesized. It has been found that anodization of valve metals (i.e. titanium [6,11,13] and/or zirconium [12]) can be led to the configuration of 1D-nanotube arrays and this nanostructure may then be applied for detector production [6,12].

In this paper, anodization of zinc in acidic solutions will be discussed. The effect of process time on the roughness, coating thickness, micro-hardness and corrosion behavior of the coating layer at the same current density was demonstrated. Zinc anodic surface also provides some esthetic value increases abrasion resistance and provides a excellent bonding surface for painting.

2. Mechanism of Anodic Film Formation

The mechanism of anodization method might be explained dissolution of zinc metal and Oxygen gas evolution. Anions in the electrolyte initially have to move toward the anode and subsequently inter into the anodic layer film coatings [3]. The universal reactions, taking place in the anodizing progression for Zn, are given as follow:

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \quad (1) \\
4\text{OH}^- & \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \quad (2) \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn} (\text{OH})_2 \quad (3) \\
\text{Zn} (\text{OH})_2 & \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

Figure 1. illustrates the anodizing process in aqueous solutions.

![Figure 1. Electrode Processes in aqueous solutions](image-url)
3. Experimental work

The specimens for this study were commercial zinc alloy ZA12, the composition of the commercial ZA12 is listed in table 1 (in wt %) [Analysis of these specimens was done in the state company for engineering rehabilitation and testing:

Table 1 Chemical Composition of Zinc alloy AZ 12.

| Metal | Al | Cu | Fe | Mn | Pb | Cd | Sn | Zn |
|-------|----|----|----|----|----|----|----|----|
| Wt %  | 11.5 | 1.2 | 0.075 | 0.03 | 0.006 | 0.006 | 0.003 | Balance |

Specimens of AZ 12 are cut into the dimension of 3×2×0.5 cm. After the alloy surface can be grinded through the use of emery paper up to the No.1000 followed by 0.05 μm diamond paste as polishing step, the specimens were cautiously cleaned by water, washed with acetone and finally dehydrated under dry air.

Anodization was carried out in (1 M H$_2$SO$_4$) at 5 volts for 10, 20, 30, 40 and 50 min. at room temperature. In order to anodize the Zinc alloy, it was attached to the positive anode of the power supply. Whereas a stainless steel counter electrode was joined to the negative electrode of the power supply (i.e. cathode). The distance between two these electrodes (anode and cathode) fixe at 10 cm for all experiments at room temperature. After anodization, each specimen was washed using deionized water and after that rinsed by methanol. Lastly, it was dehydrated via dry air by applying compressed air. Sealing of anodic film is very important, this process is done by immersion the specimens in a sealing solution such as a hot 10 % (by volume) solution of sodium silicate for 10-15 minutes followed by drying by hot air. Average coating thickness can be determined by using eddy current testing technique (coating thickness gauge TT260 ITALY made).

Atomic-Force Microscopy (AFM) analysis was done by utilizing (220V, AA3000, Angstrom Advanced Inc. USA), which may be employed for morphological and structural characterization. The computerized optical microscopy (Type MeF) in cooperation with the digital camera can be applied to study the microstructure of each specimen. Contact angle tests have been investigated with a computerized contact angle meter (CAM 110-04 W, Taiwan) at room temperature. Water droplets were jumped down quietly onto the surface of a sample. Five points of each sample have been investigated as well as the average value of the five right and left contact angles has been estimated as the measured fixed contact angle [4].

A contact angle test device applied as an optical instrument (CAM 110, T-1 Taiwan) to measure the contact angle degree for the base, anodizing, and sealing specimens. The main contact angle was determined in a series of three measurements using distilled water, the mean value for these results are recorded.

4. Results and Discussion

4.1 Effect of Anodization time on the Average Coating Thickness

Table 2 and Figure 2 show the effect of anodizing time on the average coating layer thickness on the Zn 12 zinc alloy, the Average coating thickness seems to be increased with increasing the time, which can be attributable to the thick layer that typically precipitates on the metal surface.

This result is agreed with Shuanghu Heet.al [14], that investigated the increase in coating thickness with time when anodize zinc alloy by using KHCO$_3$, NaHCO$_3$ as electrolyte
Table 2 Effect of coating thickness at a different anodizing time.

| No. | Anodizing time (min.) | Average Coating Thickness (μm) |
|-----|-----------------------|--------------------------------|
| 1   | as                    | 0                              |
| 2   | 10                    | 11                             |
| 3   | 20                    | 16                             |
| 4   | 30                    | 21                             |
| 5   | 40                    | 24                             |
| 6   | 50                    | 32                             |

Figure 2. The effect of anodizing time of AZ 12 Zinc alloy on average coating thickness in 1 M H₂SO₄ at room temperature.

4.2 Effect of anodizing time on the microhardness

Table 3 and Figure 3 show that the average microhardness value of AZ12 zinc alloy increase with increasing in the anodizing time due to the formed a new layer of zinc oxide on the metal surface.

Table 3 Effect of anodizing time on average microhardness.

| No. | Anodizing time (min.) | Microhardness (HV) |
|-----|-----------------------|--------------------|
| 1   | 10                    | 25                 |
| 2   | 20                    | 27                 |
| 3   | 30                    | 37                 |
| 4   | 40                    | 44                 |
| 5   | 50                    | 51                 |
The effect of anodizing time of AZ 12 Zinc alloy on micro-hardness in 1 M H$_2$SO$_4$ at room temperature.

4.3 AFM Investigation

The roughness of surface film before and after anodization process was determined by AFM as shown in Fig. 4. The AFM image reveals that a rough film formed on the zinc alloy surface after anodizing. The RMS roughness is increased as the time increase due to the anodic layer created on the surface. Precipitation procedure counts on surface cleaning; the existence of a small amount of impurities (particularly Fe and Cu) leads to reduce the anodizing process in these sites. Table 4 and Figure 5 shows the effect of anodizing time on film thickness

Basheer [12] indicates that the roughness of the anodic film is principally based on both the anodizing time and the average coating thickness, the ZnO layer creates on the surface by anodizing process for magnesium alloy by the alkaline solution at a constant voltage.
Roughness Average = 6.02 nm

Roughness Average = 7.3 nm

Roughness Average = 8.04 nm
Figure 4. 2D and 3D AFM images for AZ12 zinc alloy (a) polished Surface   (b) 10min.Anodizing
(c) 20min.Anodizing   (d) 30min.Anodizing  (e) 40 min. Anodizing   (f) 50 min. Anodizing

Table 3 the effect of anodizing time on average roughness

| No. | Anodizing time min. | Average Roughness nm |
|-----|---------------------|----------------------|
| 1   | as                  | 1.37                 |
| 2   | 10                  | 6.02                 |
| 3   | 20                  | 7.3                  |
| 4   | 30                  | 8.04                 |
| 5   | 40                  | 8.58                 |
| 6   | 50                  | 24.5                 |
Figure 5. The effect of anodizing time on surface roughness of AZ 12 zinc alloy.

4.4 Microstructure test
Fig. (6-a) shows the polished surface of AZ 12 zinc alloy while fig (6-b) illustrates the microstructure of the specimen. Figure (6-c) indicates microstructure for specimens after 50 minutes anodizing. These figures show the change in the surface morphology and a new structure was observed. It contains dark spots which indicate that anodizing process is deposited the oxide of ZnO on the metal surface. No cracks were observed on the anodized layer but also precipitation of the oxide layer was found on the surface [8].

Figure 6. Computerize Optical Microscope view (a) polish specimen, (b) microstructure specimen, (c) anodized specimen, 500X.
4.5 Polarization Measurement

Tafel extrapolation method was applied to investigate the corrosion behavior of the anodic layer created on AZ12 zinc alloy before and after anodizing process. The potentiostate used for this test is (MLAB 200-Germany made). The polarization was accomplished in a one-litre beaker comprised of working, counter and reference electrodes immersed inside 3.5% NaCl as shown in figure 7.

Figure 7. Potentiostat equipment for the electrochemical test.

The working electrode (WE) was (1×1) cm of AZ12 zinc alloy held by aluminium jigs designed to fix the specimen, it can be covered with shrinkage tube to prevent the electrical bad contact and make it stable in the electrolytic cell. The counter electrode (or Auxiliary electrode (AE)) was graphite that directly seated in opposite direction to the working electrode. Moreover, the reference electrode (RE) was a standard calomel electrode (SCE) type (Tacussel model- C4) bridged by a Laggin-Haber probe. A thermometer was employed to keep up the electrolyte temperature within the range of ± 1°C.

The polarization curve is a plot the relation between the logarithms of current density versus the electrode potential. Figure (8) reveals such curves for AZ 12 zinc alloy before and after anodizing inside 3.5 wt% NaCl solution (sea water). The results of both corrosion potential (E\text{corr}) and the corrosion current density (i\text{corr}) values have been illustrated in table 4. The corrosion current density can be obtained from the polarization curve with the aim of using it in the calculations of corrosion rates. Corrosion rates may generally be calculated by applying the subsequent relationship (4.1):

\[ CR (mpy) = \frac{0.13 \times i_{corr} \times E.W}{\rho} \]  

where:

- \( i_{corr} \): corrosion current density, \( \mu A/cm^2 \)
- E.W.: specimen equivalent weight (65 g. / equivalent).
- \( \rho \): Specimen density (6 g./ cm\(^3\)).

The calculations of corrosion rate of AZ12 zinc alloy in sea water (3.5% NaCl) as received and anodized specimens can be shown in table (4). The superior corrosion rate is obtained for un-anodized specimens; while the rate of corrosion is decreased very clearly in anodized specimens after anodizing due to higher film thickness created on the surface of the metal.

These results have an agreement with Ramanauskas, et.al [13] who studied the characterizations of oxide films on Zn and Zn alloy coatings, their study was shown that the formation of the oxide layer on...
the metal surfaces of Zn, Zn–Co (0.6 wt-%), Zn–Fe (0.5 wt-%) and Zn–Ni (12%) coatings throughout the anodic polarization inside bicarbonate electrolyte had given a good corrosion resistance as a result of the oxide layer creation on the surface.

Many types of research [14,15,16,17] indicated that the anodic layer shaped over the metal surface can improve the corrosion resistance against different corrosive media.

| Sample No. | Anodizing time, min. | $I_{corr.}$ (µA/cm²) | $E_{corr.}$ (mV) | Corrosion rate (mpy) |
|------------|----------------------|----------------------|------------------|---------------------|
| As.        | 0                    | 18.26                | -125.8           | 25.35               |
| 1.         | 10                   | 7.36                 | -124.3           | 10.37               |
| 2.         | 20                   | 6.86                 | -120.8           | 9.661               |
| 3.         | 30                   | 6.07                 | -112.3           | 8.549               |
| 4.         | 40                   | 4.03                 | -110.5           | 5.676               |
| 5.         | 50                   | 0.594                | -104.6           | 0.837               |

Figure (8) show the corrosion behavior of AZ12 zinc alloy before and after anodizing in different anodizing time (10, 20, 30, 40 and 50 min.). it indicates that the current density decreases from(18.26 µA/cm²) before anodizing to (0.594 µA/cm²) after anodizing for 50 min. and also the potential moves to more noble direction from (-125.8 V to -104.6V), this is due to the oxide layer formed on the zinc surface. This formed layer is a barrier layer between the metal surface and sea water solutions. Figure 9 shows the effect of anodizing time on corrosion rate according to the potentiostate testing. Niyamat Beedri, et.al [7], confirmed in their research that the rate of corrosion decreases when an increase in average coating thickness of anodize pure zinc metal in the glycerol-based electrolyte.

Sami, and Basheer [18], study the anodic layer formed on aluminium alloy (3003) using (15% H₂SO₄) as an electrolyte, the study showed that the microhardness and surface roughness for the anodized samples is higher than that of un-anodized samples due to very much thicker oxide film created on the surface for anodized specimens, while atmospheric oxide layer created on the surface of un-anodized specimens. The anodic film was improved different properties like physical and chemical specifications. Furthermore, the obtained rates of corrosion for anodized samples were seen to be decreased in comparison with un-anodized ones.
Figure 8. Potentiostatic polarization behavior of AZ12 zinc alloy in 3.5% NaCl at room temperature (a) Without anodizing, (b) anodizing time 10 min. (c) anodizing time 20 min. (d) anodizing time 30 min (e) anodizing time 40 min. (f) anodizing time 50 min.
Figure 9. The effect of anodizing time on corrosion rate.

4.6 Contact Angle Test
Figures (10 and 11) and table 5 illustrate the variation in the contact angle values of zinc alloy AZ12 and the anodized coating (before and after sealing the anodic film). It is obvious that the anodizing process prompts a salient alter in the surface properties of the films. On the other hand, the test results of the water contact angle prove that the surface of zinc alloy was hydrophobic with an angle of $87.3 \pm 2.3^\circ$. It can be observed that the contact angle of the anodized film less than that of zinc alloy. This finding can proof that the anodized films are more hydrophilic due to the porous anodic film. The contact angle of sealing anodic film is more than for the anodic film because of the porous was filled with dyes and other materials.

This phenomenon was due to the porous anodic film, where the contact angle of sealing anodic film was increased as shown in Table (5) because the porous structure was filled with dyes and other materials. It is obvious that as the pore size of the porous surface decreases, the contact angle increases (e.g., more hydrophobic) as reported by Alsalhy et. al. [19].

Shalaleh Gilani et al [4] had studied the contact angle of the anodic film formed on pure zinc foil by using NaOH and oxalic acid electrolyte. The obtained results were shown that the contact angle of the anodized film less than that of pure zinc foil.

Figure 10. Schematic diagram for the contact angle test.
Figure 11. Contact angle test, (a) base metal (b) anodized layer (c) sealing anodic film

Table 5. Effect of anodizing on contact angle.

| No. | ZA12 anodic film | Average Contact Angle |
|-----|------------------|-----------------------|
| 1   | Before anodizing | 96.63°                |
| 2   | After Anodizing  | 50.37°                |
| 3   | After sealing    | 76.78                 |

5. Conclusion

The results obtained from this study show that:

1. The average coating thickness after anodizing process appears to be increased with increasing the time, which can be attributable to the thick layer that typically precipitates on the metal surface.
2. The surface roughness (Ra) after anodizing process increases with increases in anodizing time due to the anodic layer created on the surface.
3. The average microhardness of AZ12 zinc alloy increases with increasing in the anodizing time due to the formed a new layer of zinc oxide on the metal surface.
4. The rate of corrosion is decreased very clearly in anodized specimens after anodizing due to higher film thickness created on the surface of the metal.

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