Enhanced Growth Rate of Anodized Film on Al with Addition of Ethylene Glycol

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Abstract. The additive organic substance has been used in the anodizing electrolyte to improve the growth rate and characteristics of the oxide film formed by hard anodizing technique. The effect of additive ethylene glycol (EG) on the growth rate of the hard anodic film is investigated in this work by recording the voltage-time curves, observing the surface appearance, and measuring the film thickness. Anodizing was carried out at a constant current of 300 A m⁻² in 2 M H₂SO₄ solution at 10°C. The anodizing process was terminated at 30, 45, and 60 min. The additive EG was introduced in the electrolyte with concentrations 0, 10, 20, and 30%. The results indicates that addition of EG enhances the electrochemical reaction rates occurred on the Al metal surface as demonstrated by the increase of slopes from 0.1 V/min to 0.6 V/min with increasing EG concentration in the voltage-time curves. The acceleration of the reaction rates contributes to the increase of the film thickness ranging from 30-56 µm. Meanwhile, in the absence of EG, the voltage output is relatively constant at 20 V and the film thickness (26 – 43 µm) is controlled by the anodizing time.

1. Introduction
Aluminum (Al) metal has been widely used in many engineering application owing to its low density (2.7 g/cm³), easy to form, high conductivity, and good corrosion resistance [1]. The corrosion resistance of Al is attributed to the protective oxide film of a few nm formed naturally on its surface. The oxide film serves as a barrier layer between the metal surface and the corrosive environment. The high resistivity of the oxide film does not allow the layer to grow more than a few nm. The oxide film, however, destabilizes in the presence of impurity or trace elements especially the low melting elements such as Pb, In, Sn, and Bi which segregate under the oxide film as a result of thermo-mechanical treatment of the metal as reported earlier [2, 3].

For engineering application which is exposed to harsh environment and temperature, it is necessary to improve the corrosion resistance of the Al metal. In general, there are two ways for improving the corrosion resistance of the metal: an intrinsic way by alloying and modifying the manufacturing method, and an extrinsic way by surface treatment and anodizing [4]. The simple and effective way of protecting Al surface is by anodizing. Anodizing is an electrochemical process involving the application of external voltage to transform the metal surface into an oxide layer. Anodizing of the Al surface is popular for decades and has been commercialized in many industrial sectors. The type I and type II anodizing Al produce a porous layer with a thickness in the range of 5-10 µm which is usually used as transition layer for a final organic coating that gives an aesthetically colourful appearance [4, 5]. For an advanced protection, type III anodizing, which is also called hard anodizing, is typically
applied to Al metal [6-8]. The resulting oxide provides superior corrosion resistance, tribop-erformance, and improvement in mechanical properties [8-10].

The characteristics of hard anodic film are influenced by the anodizing process parameters [6-8] and the metal composition [9, 10]. The presence of impurities or alloying element contributes to the discontinuities of the porous oxide [11]. The composition of electrolyte determines the film resistivity due to the incorporation of the electrolyte species in the oxide film [6, 8]. An organic substance such as glycolic acid, oxalic acid, and glycerol is used as the additive to the anodizing electrolytes to improve the film growth rate and hence the hardness and wear resistance [12]. In this work, we investigate the effect of additive ethylene glycol (EG) in the electrolyte on the growth rate of the hard Al-anodized film. EG is beneficial for serving as a corrosion inhibitor for Al metal [13].

2. Experimental Methods

The material used in this work is a commercial pure (CP) aluminum plate with a thickness of 1 mm. The plate was cut to give a working area of 5 cm². The specimens were then degreased in acetone followed by ethanol in an ultrasonic bath each for 3 min.

Pretreatment was performed on the specimens prior to anodizing by dipping the specimens in a 10% NaOH solution for 20 s. The specimen was then desmutted in 30% HNO₃ solution for 1 min and then cleaned in DI water. Hard anodizing was conducted in a galvanostatic mode at 300 A.m⁻² at a constant temperature of 10°C for 30, 45, and 60 mins. The electrolytes were 2 M H₂SO₄ with additive ethylene glycol (EG) of 0, 10, 20, and 30% further marked as 0 EG, 10 10 EG, 20 EG, and 30 EG. The electrolyte was stirred at 300 rpm. The film thickness was measured by coating thickness gauge (DEKKO CM-8826FN).

3. Results and Discussion

The effect of EG on the voltage-time curves measured during 60 min hard anodizing is presented on Figure 1. The curve for anodizing in the base electrolyte shows a relatively constant voltage at 25 V for 60 min anodizing. The film grows simultaneously through electrochemical reactions at the metal-electrolyte interface. The reaction rate is constant as indicated by a flat voltage output of the black curve on Figure 1. In the presence of 10 EG, the voltage-time curve shows a slight increase in the voltage at 30 min anodizing resulting in a terminal voltage of 30 V. Increasing EG to 20% leads to a linear increase in the voltage started at about 20 min anodizing. The slope ends at a voltage value of 43.9 V. Anodizing in the 30 EG electrolyte results in a linear increase of voltage output from the start of anodizing at 30 V up to the potential of 60 V. The Addition of EG induces gradient in the voltage-time curves during hard anodizing of pure Al. The slope increases from 0.1 V/min in 10 EG to 0.3 V/min in 20 EG and finally to 0.6 V/min in 30 EG electrolytes. The results indicate that the reaction rate occurred on the specimen surfaces increases with the addition of EG.

![Figure 1. Effect of addition EG on voltage-time curves during 60 min hard anodizing of pure Al.](image-url)
Discoloration on the specimen appearance occurred as a result of variation in anodizing time and EG concentration in the electrolyte is shown in Figure 2. The specimen surfaces exhibit a bright grey color as a result of 30 min anodizing in all type of the electrolytes. The specimen becomes darker with increasing anodizing time. The effect of EG on the specimen appearance is visible at the anodizing time of 45 and 60 min. Variation of color from grey to black is observed on the specimen surface resulting from 45 min anodizing. Increasing anodizing time to 60 min produces a dark grey surface which becomes darker with increasing EG content in the electrolyte.

Figure 2 shows the anodic film thickness as functions of EG concentration and anodizing time measured by coating thickness gauge. The film grew in the base electrolyte exhibit a thickness of 27, 39, and 43 for anodizing time 30, 45, and 60 min, respectively. The film thickness displays a similar linear increase in thickness with anodizing time for all type of the electrolytes. A significant increase in thickness is obtained by additive 10 EG. Higher concentration of EG does not increase the thickness any further. In fact, the thickness tends to decrease although still higher than that of anodizing in the base electrolyte, with increasing EG concentration to 20 and 30%. The thickness of the film formed for 60 min varies from 43 to 56 µm although the surface appearance similarly black (Figure 2) indicating that the surface discoloration attribute to the change in film composition rather than changing in thickness. Incorporation of carbon in the film leads to the darkening of the film [6].

During anodizing, the application of anodic current induces the release of Al ion from the metal surface which is further transported outwards to the metal-solution interface to react with the oxygen ion forming aluminum oxide [11]. The resulting oxide may deposit or dissolve back into the electrolyte. If the formation rate of oxide is higher than the dissolution rate, the film is deposited on the surface. At a high formation rate, a layer of oxide is obtained on the surface. The oxide layer formed on the Al surface grows thicker with anodizing time. The film thickening develops faster during anodizing from 30 to 45 min but slow down at extended time of 60 min. The ions transport is more difficult as the oxide film grows thicker. In other words, the film resistivity increases with film thickness.

Ethylene glycol is an organic compound with chemical formula C₂H₄O₂. EG has a dual function as an antifreezing when used at low temperature and coolant at elevated temperature [13]. The presence of EG in the electrolyte accelerates the growth of the anodic layer formed on Al as indicated by the increase in film thickness with the addition of EG (Figure 3). The low temperature used during hard anodizing tends to lower the ion mobility, hence, decreases the reaction rate for the film formation. The presence of antifreezing chemical EG helps to enhance the ion mobility and therefore increases
the reaction rate as validated by the anodizing curves on Figure 1. The resulting oxide film formed in the EG containing electrolyte is also thicker than that of formed in the base electrolyte (Figure 3). The thickness ranges from 26 to 43 µm for the films formed in the base electrolyte, while thicker films in the range of 30-56 µm are developed in the EG containing electrolytes. However, since EG is involved in the electrochemical conversion process of the metal surface into the anodic oxide film, the carbon molecules from EG is presumably incorporated in the film formed on the Al substrate. The incorporation of carbon in the film darkens the resulting film [13].

**Figure 3.** The effect of anodizing time and EG concentration on the film thickness.

### 4. Conclusions

The effect of additive organic substance ethylene glycol (EG) on the growth of anodic oxide film on the Al surface has been studied. The results show that the presence of EG enhances the film thickening formed on the Al surface. The acceleration growth mechanism is assumed to involve enhancement of ion mobility which contributes to the reaction rate during anodizing. The acceleration in reaction rate is displayed by the increase of voltage-time slope with EG concentration during 60 min anodizing. The film growth rate is limited by the film resistivity which becomes higher with increasing film thickness. The optimum anodizing time is 45 min which resulted in oxide thickness in the range 39-46 µm.

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