Effect of additive ethylene glycol on morphology and mechanical hardness of anodic oxide film formed on AA7075

M Farhan and A Anawati*
Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia

*Email: anawati@sci.ui.ac.id

Abstract. This paper reports the effect of additive ethylene glycol (EG) on the morphology and mechanical hardness of anodic oxide films formed on AA7075 by hard anodizing technique. Anodizing was conducted in 2 M H2SO4 solution with the addition of 0, 10, 20, and 30% EG at a constant current 300 A/m2 at 10°C. The cross-sectional morphology was studied by FE-SEM and the elemental composition was analyzed by EDX. The mechanical hardness was measured by a Vickers Hardness machine. The results indicated that the addition of EG improved the films adherent on the substrates by preventing the formation of cracks and the enrichment of the intermetallic phases at the film-substrate interface. The presence of EG accelerated oxidation reaction of the intermetallic phase. The competing oxidation reactions led to the significant decrease in film thickness from 38 µm down to below 20 µm with the addition of EG. The film formed in EG containing electrolyte composed not only aluminum oxide but also copper and zinc oxides. The film formed in EG containing electrolytes exhibited microvoids as a result of oxygen gas evolution which accompanied the oxidation reaction of the intermetallic phase. As a consequence, the mechanical hardness decreased with increasing EG concentration.

1. Introduction
High strength aluminum alloy AA7075 has been extensively used as the building materials in the aircraft and automotive industries. The main alloying element Cu, Zn, and Mg in the AA 7075 formed intermetallic precipitates that contributed in achieving high strength properties through precipitation hardening mechanism [1]. However, the presence of intermetallic precipitates increases the susceptibility of the alloy to local corrosion attack. Surface treatment or coating is necessary to improve the corrosion resistance of the alloy.

Anodizing is a common technique used for protecting the aluminum alloys surfaces from the corrosive environment. The process involved an electrochemical oxidation reaction of the metal surface in an acid electrolyte to convert the surface into a protective oxide layer. Anodizing at low voltage 5–10 V is usually employed on aluminum alloy to grow a porous oxide layer up to about 10 µm thick to improve adhesion of a final organic coating [2]. The porous film formed at low voltage did not provide significant protection from corrosion. Hard anodizing is a more advanced anodizing to grow a densely packed and hard oxide layer at a higher voltage [3-5]. The resulting oxide thickness ranges from 10 to 100 µm. Remarkable improvements in tribo-performance, mechanical properties, and corrosion resistance was reported on aluminum alloys protected by hard anodized layer [3-6].
The morphology and mechanical properties of the hard anodized film were affected by the process parameters [3-5] and microstructure of the metal substrate [6-8]. Addition of organics substances such as glycolic acid, oxalic acid, and glycerol in the anodizing electrolyte limits the chemical dissolution of the film at the film-substrate interface hence enhances the film hardness and the wear resistance [9].

The microstructure of the alloy is a challenge for the hard anodizing process. The presence of intermetallic phases especially the Cu-containing phase which is not oxidized during anodizing leads to detrimental effects such as the formation of cracks and pores. Ma et.al [10] found that the Cu-containing phase preferentially dissolved leaving voids while the iron-containing phase prevented oxidation creating highly porous volumes and voids in the coating.

The recent research investigates the effect of additives ethylene glycol on the morphology and mechanical hardness of a hard-anodized film formed on AA7075. Ethylene glycol (EG) is often used as a corrosion inhibitor for aluminum alloy [11]. The EG concentration was varied 10, 20 and 30%.

2. Experimental Methods

The material used is a rolled plate commercial aluminum alloy AA7075-T651 with a thickness of 2 mm. The plate was cut to give a dimension of 2 cm × 1 cm. The observation area was limited to 2.6 cm². The specimens were degreased in acetone followed by ethanol 3 min for each step in an ultrasonic bath.

2.1. Anodizing

Prior to anodizing, the specimen was etched in a 10% NaOH solution for 20 s and further disrupted in 30% HNO₃ for 1 min. The specimen was then washed in (distilled) DI water and dried under an air stream. Anodizing was done in a galvanostatic mode at 300 A/m² in 2 M H₂SO₄ solution with additive 0, 10, 20 and 30% ethylene glycol (C₃H₆O₃) which further marked as 0 EG, 10 EG, 20 EG, and 30 EG, respectively. The electrolyte temperature was kept at 10°C and the electrolyte was constantly stirred at 300 rpm. The anodizing time was limited to 45 min for all specimens.

2.2. Characterization

The anodic film hardness was tested by Vickers microhardness machine (Stuers Durascan 1D model 622) with 5 kgf load. The specimen was indented at 5 points. The hardness is the average of the 5 points measurements.

The cross-sectional morphology of the anodic oxide film was investigated by field emission-scanning electron microscope (FE-SEM, INSPECT F5) and energy dispersive X-ray spectroscopy (EDX) for elemental composition.

3. Results and Discussion

Figure 1 shows the effect of ethylene glycol (EG) on the anodizing curves and the visual appearance of AA7075 specimens. The black curve which corresponded to the base electrolyte shows an increase in voltage output from 25 to 28 V followed by a small ripple in voltage at mid value 28 V. The ripple was commonly observed during anodization which attributed to the dynamic formation and dissolution of the anodic oxide film. The curve shifted towards higher voltage with increasing EG concentration. The voltage tended to increase with time for anodizing in the EG containing electrolyte. The terminal voltage increased consecutively from 28 to 30, 32 and 32 for anodizing in 10, 20 and 30 EG electrolytes, respectively. Anodizing in the base electrolyte (0 EG) turned the specimen appearance from metallic reflective to matte bronze. Addition of 10 EG in the anodizing bath changed the anodic film color into bright grey. The surface became dark grey with increasing EG concentration to 20 and 30%.

Figure 2 shows the effect of EG concentration on the morphology of the anodic oxide film formed on AA7075. All of the resulting films were densely packed and adhered well on the metal surface. The film formed on the base electrolyte exhibited a thickness of about 38 µm. The film thickness decreased significantly to 14 µm with the addition of 10 EG in the electrolyte but then increased again to 16.5
and 18.6 µm with increasing EG concentration to 20 and 30%, respectively. In general, the presence of EG in the electrolyte decreased the oxide film thickness. The presence of organic substance tended to decreased anodic film thickness formed on Al [3]. The oxide films formed on 0 EG and 10 EG (figures 2 (a) and (b)) exhibited few cracks while those grew in 20 EG and 30 EG electrolytes did not show any crack. The horizontal line path appeared in the film of 30 EG (figure 2(d)) was likely formed as a result of specimen preparation. Cracks in the anodic film which were induced by the voids or intermetallic typically propagate perpendicular to the substrate. The presence of EG reduced the formation of cracks in the film. The cracks observed in the 10 EG film penetrated through the metal-oxide interface while more superficial cracks were viewed in the 0 EG film. The cracks observed in the outer layer of film formed in the 0 EG electrolyte was probably formed as a result of hydration. While the cracks viewed in the film formed in 10 EG electrolyte looked like pore channels. The pore channel typically developed as a result of oxygen evolution [3, 4].

To understand the role of EG in the anodizing process, the film-substrate interface of each anodized specimens was investigated. Figure 3 shows the backscattered FE-SEM image of the film-substrate interface. The backscattered image was sensitive to atomic weight. The heavier element appears brighter than the light one. Figure 3(a) indicated that the dominant reaction occurred during anodizing in the base electrolyte was oxidation of the Al matrix to form Al₂O₃. The intermetallic phases in the substrate became enrich forming a nearly continuous layer at the film-substrate interface.

**Figure 1.** Voltage-time curves during anodizing of AA7075 specimens in the electrolyte with additive of 0, 10, 20, and 30 % ethylene glycol (EG).

**Figure 2.** The cross-sectional FE-SEM images of the anodic oxide films formed on AA7075 specimens in the electrolyte with additive of 0, 10, 20, and 30 % ethylene glycol (EG).
as shown in figure 3(a), marked by arrows, as well as the intermetallic rich region near the interface with numerous fine particles. Oxidation of the intermetallic phases was considered minim in the pure sulfuric acid solution as also reported earlier [3-5]. However, with the addition of 10 EG in the electrolyte, the enrichment of intermetallic phases at the film-substrate interface reduced significantly leaving only a few particles at the interface as indicated by arrows in figure 3(b). The intermetallic phases were apparently oxidized during anodizing in EG containing electrolytes. The oxidation reaction of the intermetallic phases consumed the electrical charge. Therefore, the voltage-time curves for anodizing in EG containing electrolyte increased with time (Figure 1) although the resulting oxide was thinner. The existence of micro-sized voids in the oxide formed in EG electrolyte is also proved that the intermetallic phase was oxidized. The oxidation of the intermetallic phase, in particular, the Cu-containing phase was reported to cause the formation of micron-scale pores or voids in the film due to oxygen evolution that accompanied the oxidation reaction [10]. The interface became clear from intermetallic with increasing EG concentration to 20 and 30%. The results indicated that the oxidation rate of the intermetallic phase increased with EG concentration. As a consequence, film adhesion to the metal substrate was improved with the presence of additive EG. The cracks shown at the interface of the film formed in 0 EG (figure 3 (a)) which lowered the film adhesion was no longer observed in the film formed in 10, 20 and 30 EG.

The EDX elemental composition of the film formed in the 0 EG and 10 EG are listed in table 1. The point analysis was marked in figure 3. The main composition of both oxide films was aluminum oxide (Al2O3). The Al concentration detected in the oxide formed in 10 EG was slightly lower than that of in 0 EG but the O concentration was higher indicating the presence of others oxidized phases besides aluminum oxide. The possible oxidized phases were copper and zinc oxides because the Zn and Cu content in the oxide formed in the 10 EG were higher than that of in the 0 EG. In agreement

Figure 3. The morphology of film-substrate interface for the film formed in (a) 0 EG, (b) 10 EG, (c) 20 EG, and (d) 30 EG, showing enrichment of Cu-containing precipitates indicated by arrows.
with the FE-SEM observation, additive EG in the electrolyte accelerated the oxidation reaction of the intermetallic phases existed in the alloy.

Figure 4 shows the effect of additive EG on the mechanical hardness of the resulting anodic oxide film formed on AA7075 specimens. Anodizing in the base H$_2$SO$_4$ electrolyte produced a hard anodic oxide layer with an average hardness of 196.2 HV which was much higher than that of the metal substrate (136 HV). Addition of 10 EG in the anodizing electrolyte yielded in a slightly lower film hardness of 177.8 but still higher than that of the metal substrate. The film hardness decreased consecutively down to 115.2 and 107.6 HV with increasing concentration of EG to 20 and 30 % in the electrolyte which were lower than that of the substrate. Reduction in mechanical hardness was attributed to the existence of voids in the film formed in EG containing electrolyte as a result of the oxidation reaction of the intermetallic phases. Voids and pores in the hard anodic layer resulted in less compact layer and therefore tended to reduce mechanical hardness of the layer [3, 5, 7].

Table 1. EDX elemental composition of the anodic oxide films formed on AA7075 specimens in the electrolytes with additive 0 and 10 % ethylene glycol (EG).

| Element | 0 EG wt% | 0 EG at% | 10 EG wt% | 10 EG at% |
|---------|----------|----------|-----------|----------|
| C       | 6.27     | 10.32    | 3.00      | 4.89     |
| O       | 43.32    | 53.49    | 51.59     | 63.09    |
| Na      | 2.40     | 2.06     | 0.14      | 0.12     |
| Mg      | 0.47     | 0.38     | 0.50      | 0.40     |
| Al      | 44.29    | 32.42    | 42.14     | 30.56    |
| Si      | 0.33     | 0.24     | 0.15      | 0.10     |
| K       | 0.66     | 0.33     | 0.33      | 0.17     |
| Ti      | 0.12     | 0.05     | 0.16      | 0.06     |
| Cr      | 0.26     | 0.10     | 0.00      | 0.00     |
| Mn      | 0.31     | 0.11     | 0.00      | 0.00     |
| Fe      | 0.46     | 0.16     | 0.11      | 0.04     |
| Cu      | 0.69     | 0.22     | 1.04      | 0.32     |
| Zn      | 0.41     | 0.12     | 0.85      | 0.25     |

Figure 4. Hardness of the anodic oxide films formed on AA7075 in the electrolytes with additive of 0, 10, 20, and 30 % ethylene glycol (EG).
4. Conclusions
The effect of additive ethylene glycol (EG) in the anodizing process of high strength aluminum alloy AA7075 has been investigated. The results showed that the additive EG improved the adherent of the resulting anodic oxide film by preventing the formation of cracks at the film-substrate interface. As a consequence, the interface became smooth and the film adhered well to the substrate. The cracks formed in the base electrolyte were induced by the enrichment of the intermetallic phase while the surrounding Al matrix was being oxidized to form Al2O3 during anodizing. In the presence of EG in the electrolyte, the intermetallic phase was oxidized thus preventing enrichment of the phase. The increase of voltage output in the anodizing curves of EG containing electrolyte was attributed to the competing oxidation reaction of the intermetallic phase. The resulting oxide film composed not only aluminum oxide but also zinc oxide and copper oxide as confirmed by the EDX analysis. The oxidation of the intermetallic phase, however, released oxygen gas that led to the formation of voids in the film. The presence of voids tended to decrease the mechanical hardness of the film. The film hardness decreased with increasing EG concentration in the electrolyte.

Acknowledgements
This work was fully supported by Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa (PITTA) Universitas Indonesia with contract no. 2227/UN2.R3.1/HKP.05.00/2018.

References
[1] Ringer S P, Sakurai T, Polmear I J 1997 Acta Mater. 45 (9) 3731
[2] Wang S, Peng H, Shao Z, Zhao Q, Du N 2016 Surf. Coat. Technol. 286 155
[3] Sieber M, Morgenstern R, Scharf I, Lampke T 2018 Metals 8 139. Doi: 10.3390/met8020139.
[4] Bononi M, Giovanardi R, Bozza A 2016 Surf. Coat. Technol. 307 861
[5] Kikuchi T, Takenaga A, Natsui S, Suzuki R 2017 Surf. Coat. Technol. 326 72
[6] Arunnelaiappan T, Arun S, Hariprasad S, Gowtham S, Ravisankar B, Rama Khrisna L, Rameshbabu N 2018 Ceram. Int. 44 874
[7] Klakurkova L, Julis M, Celko L, Horynova M, Hegr E, Svejcar J 2015 Eng. Fail. Anal. 56 300
[8] Lammel C, Heubner C, Beckert W, Michaelis A 2017 Electrochim. Acta 249 271
[9] Giovanardi R, Fontanesi C, Dallabarba W 2011 Electrochim. Acta 56 3128
[10] Ma Y, Zhou X, Thompson G E, Curioni M, Zhong X, Koroleva E, Skeldon P, Thompson P, Fowles M 2011 Corros. Sci. 53 4141
[11] Gerengi H, Solomon M M, Kaya E, Bagci F E, Abai E J 2018 Measurement 116 264
[12] Gordovskaya I V, Hashimoto T, Walton J, Curioni M, Thompson G E, Skeldon P, 2014 Electrochim. Soc. 161 (14), C601