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Effect of Graphene Oxide Sealing on the Corrosion Resistance of Anodized Aluminum Oxide

Siska Prifiharni *,[1]
Yung Yung [2]
Gadang Priyotomo [1]
Arini Nikitasari [1]
Rahayu Kusumastuti [1]
Siti Musabikha [1]
Syamsul Bahtiar [2]
Emsal Yanuar [2]
Lalu Suhaimi [2]
Rita Desiasni [2]
Fauzi Widyawati [2]
Murni Handayani [3]
[1] *Research Center for Metallurgy, National Research and Innovation Agency, Management Building 720 KST. BJ. Habibie, Banten, Indonesia*
[2] *Departement Metallurgy Engineering, Sumbawa University of Technology, Jl. Raya Olat Maras, Sumbawa Regency, NTB, Indonesia*
[3] *Research Center for Advanced Materials, National Research and Innovation Agency (BRIN), Building 440, KST. BJ. Habibie, Banten, Indonesia*
*e-mail: siska.prifiharni@brin.go.id

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Abstract. Aluminum alloy materials are widely used in aerospace, construction industry, automotive, and other fields due to their low cost and typical properties, including high strength-to-weight ratio and good corrosion resistance. The role of the anodization process that forms anodic aluminum oxide (AAO) can improve corrosion resistance, but the aluminum surface is pivoted after the anodization process. This study was conducted to determine the effect of GO-sealed on the corrosion resistance of AAO. The results show that anodized aluminum with GO-sealed performs better corrosion resistance as indicated by higher R_{porous} and R_{solid} values when compared to unsealed anodized aluminum. Furthermore, anodized aluminum with GO-sealed has a smoother surface and harder than unsealed aluminum. It is indicated by surface characterization and hardness test.

Keywords: Anodic Aluminum Oxide (AAO), Corrosion Resistance, Graphene Oxide, Sealing Process

INTRODUCTION

Generally, aluminum alloy materials are used in various applications of human life, including aviation, construction industry, automotive, food and beverage equipment, and other fields due to its relative cost of production and outstanding properties, such

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as other fields due to their relatively low production costs and outstanding properties, such as high strength-to-weight ratio and relatively good corrosion resistance in various media (Li *et al*., 2014; Zhang *et al*., 2008). The corrosion resistance of aluminum alloy materials originates from an oxide layer of stable alumina oxide layer naturally forming on the surface due to oxygen (Caporali *et al*., 2010). However, the natural oxide layer cannot protect the aluminum surface in corrosive media, especially in solutions with high chloride content (Sherif, 2013). The modes of corrosion damage are localized corrosion, which includes uniform corrosion and pitting. In general, the process of corrosion enhancement is further after smelting and manufacturing of aluminum materials through anodizing. The anodization process electrochemically forms an alumina layer with a thick pore layer structure, which acts as a barrier to the external environment. On the other hand, an increase in mechanical properties also occurs, such as an increase in the hardness of the surface after the anodization process.

Porous filling on the surface of anodized aluminum with boiling water media, dichromate solution and nickel acetate solution sealing is common in manufacturing industries (Hu *et al*., 2015a). Furthermore, the sealing process of the anodized aluminum surface using potassium dichromate and nickel acetate solution through filling chromium and nickel elements in the pores of AAO pores increases corrosion in corrosive solutions (Zuo *et al*., 2003). In addition to filling the porosity on the surface of the AAO, the sealing function also provides more corrosion resistance and a good surface profile for anchor priming or topcoat. The adhesive strength of the primer applied to aluminum requires a good surface profile of the aluminum surface.

On the other hand, the sealing process using potassium dichromate and nickel acetate on anodized aluminum surfaces releases heavy metal ions into the environment, including chromium and nickel ions. So, a sealing process with an environmentally friendly filler solution is needed. One filler material that has the potential to be environmentally friendly is graphene oxide (GO) nanoparticles. Adding graphene oxide to the surface of the metal surface can improve corrosion resistance through sol-gel film (Kang *et al*., 2012). The charge transfer between metal surfaces and graphene induces a potential barrier at the graphene/metal interface, which impedes the electron transfer processes necessary for corrosion. Also, the electrochemical reduction of GO layers on aluminum substrates can significantly increase the thickness of the GO coating, leading to improved corrosion resistance (Badr *et al*., 2019).

MATERIALS AND METHODS

Synthesis of Graphene Oxide (GO)

GO was synthesized using the hummers method presented in our previous report (Handayani *et al*., 2022, 2021). First, 0.5 gr graphite powder, 0.5 gr $NaNO_3$, and 2.55 gr $KMnO_4$ were added to the solution of 23.33 mL H_2SO_4, which was prepared under 20 ºC conditions using an ice bath. Then, the solution was stirred for 2 hours. After that, the solution was placed under 40 ºC conditions and stirred for another 16 hours. Then, 41.6 mL distilled water was added to the mixture and optimized for 30 minutes. After that, 3.33 mL H_2O_2 is slowly added. The mixture was then added with 133.33 mL of distilled water and then washed with HCl solution by centrifugation. The residual product was neutralized by pouring deionized water (DI) water and then dried at 60 ºC for 24 hours. The dried product was grounded with mortar to obtain graphite oxide. Add distilled water to graphite oxide with a 1 mg/mL ratio to produce GO powder. After that, the ultrasonication was done to exfoliate the graphite layer. The solution was filtered and dried at 60 ºC for 24 hours, then ground using mortar to obtain the GO powder.

Anodized Process

Aluminum with high purity content (99.99%) was used in this study. The aluminum was cut into dimensions 45 x 70 x 3 mm. Before the anodizing process, the aluminum was abraded with paper grit #1200 and degreased in acetone using an ultrasonic cleaner for 10 min. Afterward, the degreased sample was etched in 50 g/L NaOH and desmutted in 400 ppm HNO_3 for 1 minute at room temperature. After each process, the sample was rinsed with deionized water. The current was set at a constant 0.45 A in 50 g/L H_2SO_4 for 1 hour for the anodizing process.

GO Sealing Process

The GO was dispersed in DI water and ethylene glycol (EG) with a 0.5 mg/mL concentration for each solution. Right after the anodizing process, the sample was immersed in deionized water and ethylene glycol containing GO for 1 hour using ultrasonic and without ultrasonic. After sealing, the samples were sealed in boiling water for 1 minute.

Electrochemical Characterization

Anodized without GO sealing and with GO sealing were characterized using electrochemical impedance spectroscopy (EIS). The EIS measurement was conducted using Gamry software with a three-electrode system. The anodized sample with dimension ± 2.25 cm^2 was used as the working electrode. Saturated calomel electrode was used as the reference electrode, and carbon graphite was used as the counter electrode. The measurement was conducted in 3.5% NaCl at room temperature with a frequency range from 10^5 Hz to 10^{-1} Hz and 10 points per decade.

Surface Characterization

The surface analysis of anodized aluminum and anodized sealing GO was conducted using a scanning electron microscope (SEM) using JEOL.

RESULTS AND DISCUSSION

The synthesis of GO is confirmed by several characterizations such as UV-Vis spectroscopy, X-ray diffraction (XRD), Scanning Electron Microscope (SEM), and energy-dispersive X-ray (EDX) as shown in Fig. 1. The UV Vis measurement of GO reveals that the peak of GO appears at 230 nm, which is confirmed as the $\pi \rightarrow \pi*$ transition of the aromatic C=C bond (Affi *et al.*, 2023). The result of the GO XRD pattern depicts that there are two peaks at 10.9º and 42.6º, which confirms the (100) and (001) planes according to the previously reported study. The result of SEM analysis for GO morphology shows that the GO's surface is a wrinkled structure with a layered surface. The EDX spectra result of GO denotes that the element analysis of GO contents C and O, with a small element detected of S (sulfur) at ~ 2 eV in very small intensity, showing that the synthesis result of GO is high purity. We washed the GO before use to remove sulfur content

Electrochemical Impedance Spectroscopy

The EIS measurement resulted in a Bode plot, shown in Fig. 2. The diagram indicates

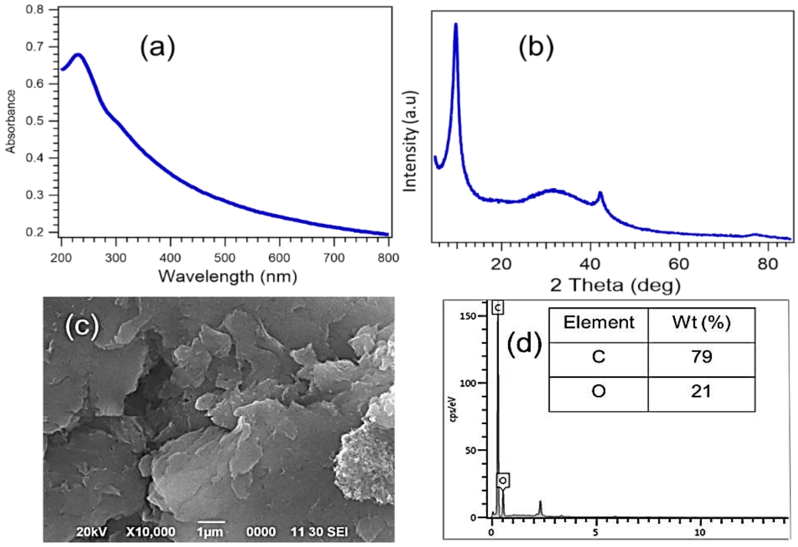

Fig. 1: The characterization of GO : (a). UV-Vis analysis of GO, (b) XRD pattern of GO, (c) Morphology surface of GO by SEM and (d) The element analysis of GO by EDX analysis

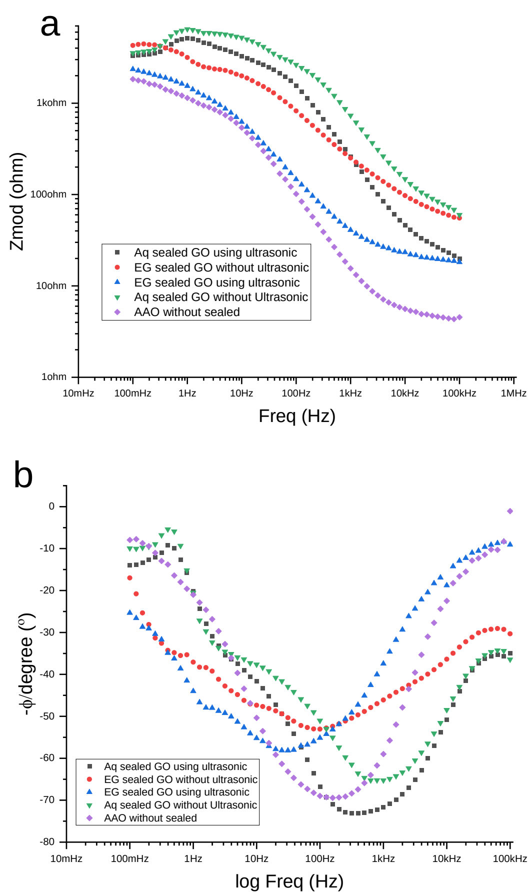

Fig. 2: Bode plot of anodized aluminum with different methods of GO-sealed

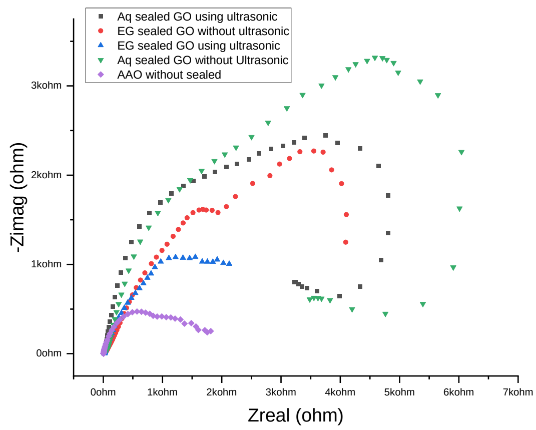

Fig. 3: Nyquist plot of anodized aluminum with a different method of GO sealed

that the sample anodized aluminum without GO-sealed has the lowest impedance value than the anodized samples with GO-sealed. The highest impedance was found in the GO-sealed water using DI water sealed without ultrasonic. This suggests that aluminum with GO sealed improves the corrosion resistance of anodized samples. From these results, the GO-sealed using DI water proved the best sealing solution for the anodized process.

The Nyquist plots of anodized aluminum without and with GO sealed are shown in

Fig. 3. The Nyquist plots show semi-circular impedance diagrams. The greater the semi-circular, the better the corrosion resistance of the samples. Fig. 3 shows anodized aluminum with GO sealing has improved the corrosion resistance of anodized samples. The equivalent circuit, which represents the electrochemical behavior of anodized samples with and without GO sealed, is shown in Fig. 4. R_{seal} is the resistance of sealed samples, R_{sol} is the resistance of the solution, R_{porous} is the resistance of the porous formed on the surface, and R_{solid} is the resistance of solid phase on the surface. The result of fitting parameters on Nyquist mode is shown in Table 1.

The comparison data from Table 1 shows the resistance of anodized aluminum was changed with different solutions and methods of sealing. The R_{porous} and R_{solid} of unsealed aluminum has the lowest value compared to the sealed anodized aluminum. The difference between unsealed and GO-sealed is very visible. When GO sealed the anodized alumunium, the R_{porous} and R_{solid} value was higher. It indicates that anodized aluminum with GO-sealed has better corrosion resistance than unsealed aluminum. As shown in Table 1, anodized aluminum with GO-sealed in DI water media has the highest value of R_{porous} among all, and the highest R_{solid} was obtained by EG and sealed with an ultrasonic process.

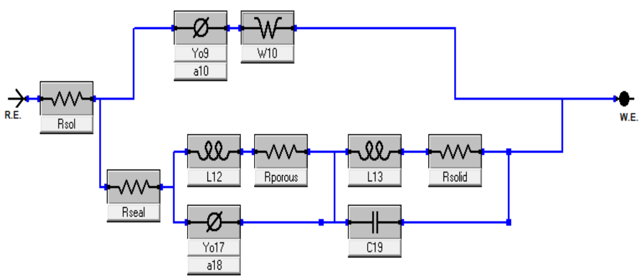

Fig. 4: Equivalent circuit model

This may occur because the surface of anodized aluminum sealed with GO becomes smoother and more homogeneous (Yu *et al.*, 2019). This is also found in aluminum anode oxide using nickel acetate sealing (Hu *et al.*, 2015b). The porous layer's resistance and barrier layer's resistance are higher when compared to unsealed aluminum. An interesting difference in using graphene oxide is that the barrier's resistance with the ultrasonicated EG solution has a greater value. So, the anodized aluminum with GO-sealed has a better corrosion resistance compared to the unsealed.

Table 1. EIS fitting parameters on the anodized sample without and with GO sealed

	R_{sol}	R_{seal}	R_{porous}	R_{solid}
Unsealed	4.40	1.01×10^{-3}	1251	533.2
EG Sealed Ultrasonic	1.82×10^{-3}	51.68×10^{-3}	7251	1.67×10^{5}
EG sealed	13.81	1.38×10^{-3}	1501	1.67×10^{3}
Aq Sealed Ultrasonic	14.67	1.91×10^{-1}	14500	3.04×10^{3}
Aq Sealed	10.59	2.87×10^{-1}	7628	1.03×10^{3}

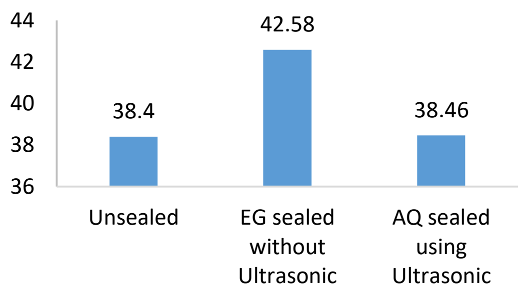

Fig. 5: The hardness of anodized aluminum with different Go sealed methods.

Hardness

The hardness of the anodized aluminum samples unsealed and with GO-sealed was conducted using hardness Rockwell B, which is shown in Fig. 5. The results show that the hardness of anodized aluminum with GO-sealed was slightly higher compared to the unsealed sample. The hardness of anodized aluminum also depends on the voltage. Higher voltage can increase the hardness of anodized aluminum (Adyono and Lestari, 2020; Wisnujati *et al*., 2023).

The highest hardness value was found in the anodized sample using ultrasonic with 42.58 HRB. It suggests that anodized aluminum with a GO-sealing process improves the surface hardness of aluminum oxide by increasing the denseness of the surface (Yu *et al*., 2023).

Surface Characterization

The samples of anodized aluminum with and without GO sealed were examined using SEM, as shown in Fig. 6. Sample anodized aluminum unsealed shows a porous and unhomogenized surface (Fig. 6a). It reveals that an oxide layer was formed on the surface of aluminum which EDS proves with high oxygen content. Fig. 6b shows the anodized sample with GO-sealed in DI water without ultrasonic. It shows a smoother surface compared to the unsealed sample. The porous was still visible but covered with sealing GO, which EDS shows with a high content of carbon and oxygen on the surface. This is because GO covalently interacted with the silanol group from the vhydrolyzed GPTMS monomer to create silane functionalized GO (silane-GO), which filled defects and strengthened the adherence of GO to adjacent GO and the film to the substrate (Hu *et al*., 2015c; Xue *et al*., 2016). Fig. 7 shows the cross-section of the anodized sample from Fig. 6a. It shows the thickness of the anodized sample, which is approximately 258 μm. The films seem homogenous, dense, and strongly bound to the surface.

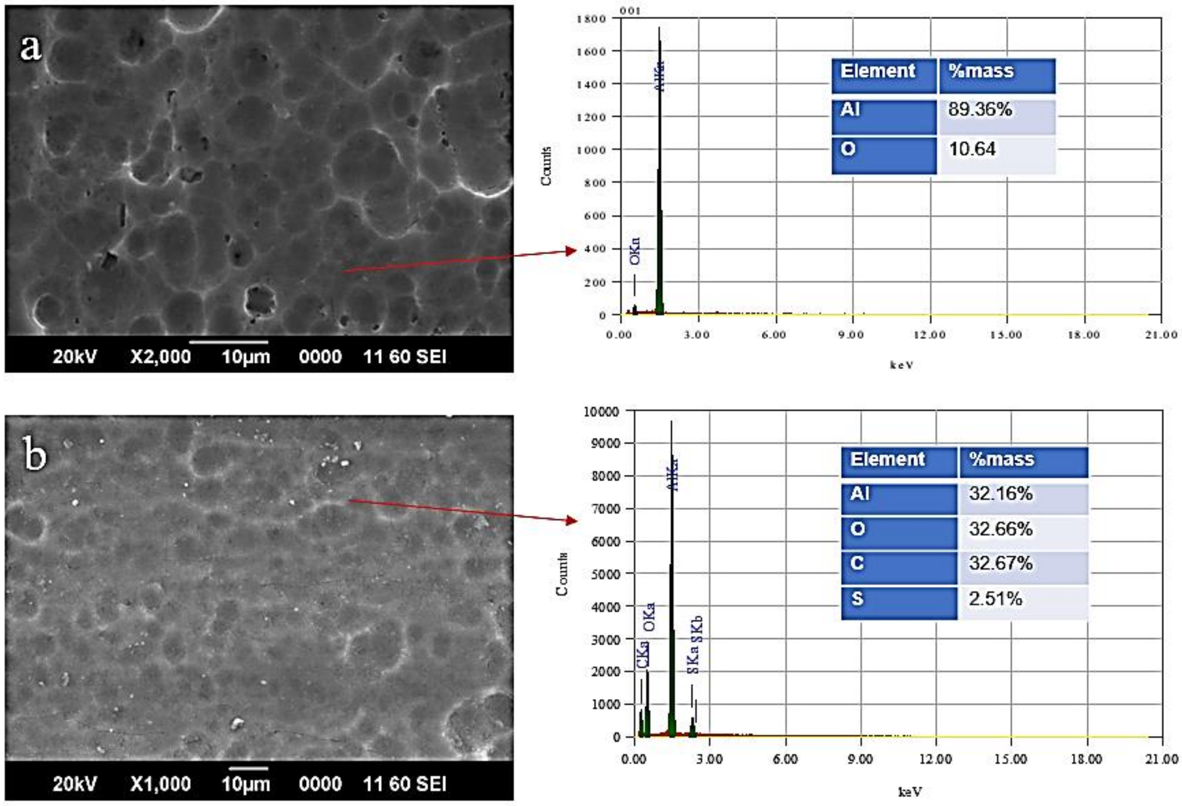

Fig. 6: SEM micrograph of anodized aluminum (a) unsealed, (b) GO-sealed DI water

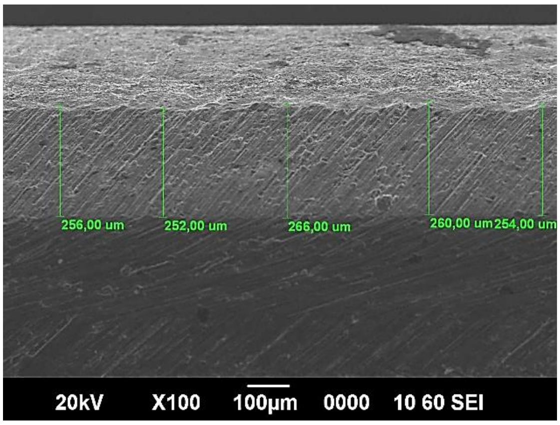

Fig. 7: Cross-sectional SEM micrograph of anodized aluminum

CONCLUSIONS

This paper experimentally determines the effect of GO sealing of anodized aluminum oxide on corrosion resistance. The sealing process was performed using different solutions and methods. The results show anodized aluminum with GO-sealed has better corrosion resistance, which is indicated by higher R_{porous} and R_{solid} values when compared to unsealed anodized aluminum. GO sealing on anodized aluminum also enhances the hardness properties of anodized aluminum by increasing the denseness of the surface, which is seen in the SEM micrographs that the surface of anodized aluminum with GO-sealed has smoother and homogenized surface than the unsealed.

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