Production and Characterization of AAO/Ni-P Hybrid Coating on Aluminum Alloy and Evaluation of its Corrosion Behavior

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Abstract

In this research, firstly, an oxide coating was created on the aluminum 2024 substrate by anodizing method, and then, with the aim of improving the surface properties of the aluminum alloy as much as possible, an electroless nickel-phosphorus coating was applied on this oxide coating. This hybrid coating was further heat treated at 450 degrees Celsius. Coatings were characterized Field-Emission Scanning Electron Microscopy (FESEM), X-ray Diffraction (XRD) and Energy-dispersive spectroscopy (EDS). The results indicated the formation of amorphous alumina by anodizing method on an aluminum substrate that contained some sulfur according to the sulfuric acid solution used in the anodizing process. The nickel-phosphorus electroless coating had 9.4 wt.% of phosphorus. The effect of coatings on corrosion resistance was also evaluated using TOFFEL polarization test. Examining the results of these tests has shown that the corrosion performance of the aluminum substrate has improved because of the application of the hybrid coating. Conducting heat treatment of hybrid coating at 450 degrees caused a decrease in corrosion resistance because of the production of small galvanic cells on the surface of the coating.

Keywords: Electroless, Coat, Polarization, Phosphorus, Anodizing.

1. Introduction

Improving the surface properties of aluminum alloys to compensate the limitations of this metal such as low hardness, high friction coefficient, lubrication problems and the need for higher corrosion resistance has always been an attractive challenge. Several methods such as Chemical Vapor Deposition (CVD), sol-gel, Physical Vapor Deposition (PVD), electroless, etc. are used for these purposes. One of the methods is the use of ceramic coatings. Anodic Aluminum Oxide (AAO) ceramic coating can be created by anodizing or deposition using Zinc-Aluminum micro-arc. This process can be considered as a pre-designed process, i.e., a kind of controlled corrosion of the aluminum surface in acid to achieve a uniform and continuous protective oxide layer [1]. This action causes a ceramic coating of alumina, which is one of the hardest materials found in nature, to form on the surface of aluminum, and as a result, it enables the use of aluminum in parts subject to friction or corrosion. However, sometimes the need for greater corrosion and wear resistance is raised for aluminum alloys, and currently one of the significant solutions is to create a second phase in the porous coating and create secondary coatings applied on this oxide layer, which leads to creating hybrid or hybrid coatings. These coatings, in addition to filling the holes in the anodizing coating and improving the corrosion resistance of the substrate in the coating, can improve the wear properties of aluminum and increase the use of aluminum alloys, including Air Aluminum Alloy 2024, according to the type of material used. One of the best materials for filling the nanoholes in the anodizing layer is Nickel Phosphorus (Ni-P) Electroless Coating [2]. Electroless coating is a surface engineering process that involves depositing a metal-semimetal alloy coating on the substrate without applying an electric current.

In 2013, Whelan et al [3]. investigated the effect of two Silica-Based Sol-Gel Coatings, including tetraethyl-orthosilicate and phenyl-trimethoxy silane, on the surface of aluminum alloy 3003 anodized in sulfuric acid, oxalic acid, and phosphoric acid. The results indicated the penetration of silicon particles of the Sol-Gel coating in the holes of anodized aluminum and also the improvement of the corrosion behavior because of to the filling of the holes by the coating particles

Zhu et al. [4], investigated the effect of filling the holes of aluminum alloys 1070, 2024 and 7075 in boiling water solutions, dichromate solution, stearic acid solution and nickel fluoride solution on the corrosion and pitting behavior of these alloys. According to the results, the anodizing process leads to an increase in the corrosion resistance of aluminum alloys. However, the presence of alloying elements in these two alloys leads to the formation of intermetallic compounds and reduces the corrosion resistance to some extent. In both alloys, nickel fluoride and stearic acid provide better corrosion resistance and no pitting corrosion

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is formed on the surface. Archiazami et al. [5], also showed that the application of electroless coating on anodized aluminum and the production of AAO/Ni-P hybrid coating on 6061 alloy increases the hardness and corrosion resistance of the aluminized substrate, and the hybrid coating has lower corrosion resistance and more hardness than AAO coating, but they have not provided a complete analysis on how these effects are. According to the information mentioned, it is tried in this study to investigate the effect of this new type of coating on the surface properties of the substrate, including its corrosion resistance by creating and characterizing the AAO/Ni-P hybrid coating on the 2024 aluminum alloy.

2. Materials and Methods

In this research, first, round samples with a diameter of 50 mm and a thickness of 10 mm were prepared from aluminum alloy 2024 by wire cutting (chemical composition is shown in Table. 1). After sanding, polishing and degreasing the surfaces, the samples were anodized in 0.45 M sulfuric acid solution and 30 V voltage. Since the anodizing layer has an oxide nature and is not catalytically active, the activation processes were performed on it according to Table. 2. No. 2. After preparing the samples in order to produce hybrid coating, the electroless method, which is a kind of chemical method, was used for the electroless deposition of nickel-phosphorus on the anodized aluminum layer. The bath used was the well-known electroless solution made by Schlotter, Germany, namely SLOTONIP 70A. To improve the surface properties of electroless coatings, it is necessary to perform heat treatment at a temperature higher than 400 degrees Celsius [6]. For this purpose, heat treatment of hybrid coatings in this research was also done for 1 hour in a normal electric furnace at a temperature of 450 degrees Celsius. In order to investigate the corrosion behavior of the substrate and the coated samples and compare them with each other, the Potentiodynamic polarization test was used by a potentiostat device. The morphology and cross-sectional area of these coatings were investigated with the help of Field-Emission Scanning Electron Microscopy (FESEM) and the investigation of the phases in the single-layer and hybrid coatings was carried out with X-ray diffraction analyzer.

Table. 1. Chemical composition (wt.%) of 2024 alloy based on Emission spectroscopic test.

Al	Zn	Zn	Mg	Mn	Cu	Si	Fe
92.38	0.10	0.17	1.56	0.91	4.21	0.29	0.38

Table. 2. Details of the sensitization and activation of samples before entering the electroless bath.

Process	Bath composition ($g.l^{-1}$)	Time (s)	Temperature (℃)
Sensitization	$SnCl_2$: 10 HCl: 10	100	30
Activation	$PdCl_2$: 1 HCL: 10	45	55

3. Results and Discussion

The FESEM images obtained from the surface morphology of the anodizing oxide coating can be seen in Fig. 1. The main feature of this coating, i.e. being porous, can be seen in Fig. 1-a. This morphology includes holes of several nanometers to several microns with non-uniform distribution, the most important reason for this is the dissolution of the oxide caused by the electric field applied to the coating during anodizing. Another point about the morphology of the anodizing coating is the presence of many openings with a length of several microns. This phenomenon has been explained by Patramix et al. [7] that the local connection of the hole opening leads to the formation of many pores of different sizes and this will increase as the voltage of the anodizing process increases. This type of morphology can lead to mechanical locking for the subsequent applied coatings and ultimately improve the surface properties, especially the adhesion of the final hybrid coating. The thickness of the oxide coating is 21.8 micrometers as shown in Fig. 1-b. Fig. 2. shows the cross-section of the anodizing coating with higher magnification, which has nanocells that have grown from the aluminum substrate to the coating surface. Due to the catalytic inactivity of the oxide, sensitization and activation processes were carried out for the nickel-phosphorus electroless process. In the studies of other researchers, it has been mentioned that the electroless coating does not grow spontaneously in the solution on non-metallic materials such as oxides [8,9]. Therefore, it is necessary to deposit catalytically active nucleuses on their surface before entering into the electroless bath. For this purpose, after sensitizing the base in chlorine solution, the surface is exposed to chloropalladium solution so that metal palladium atoms germinate on the surface. At this stage, there is a possibility of electroplating the base material. Fig. 3-A shows the surface and morphology of the electroless coating produced on anodized aluminum. As it is known, this nickel-phosphorus layer has a spherical morphology, and by combining and placing these spheres together, a structure similar to a cauliflower is obtained. According to the reports of other researchers, this form of morphology has been able to cause the inherent lubrication properties of electroless coatings [6]. Also, with the help of the cross-section of this coating, the thickness of 13.3 micrometers of the produced electroless nickel-phosphorus coating can be seen in Fig. 3-b.

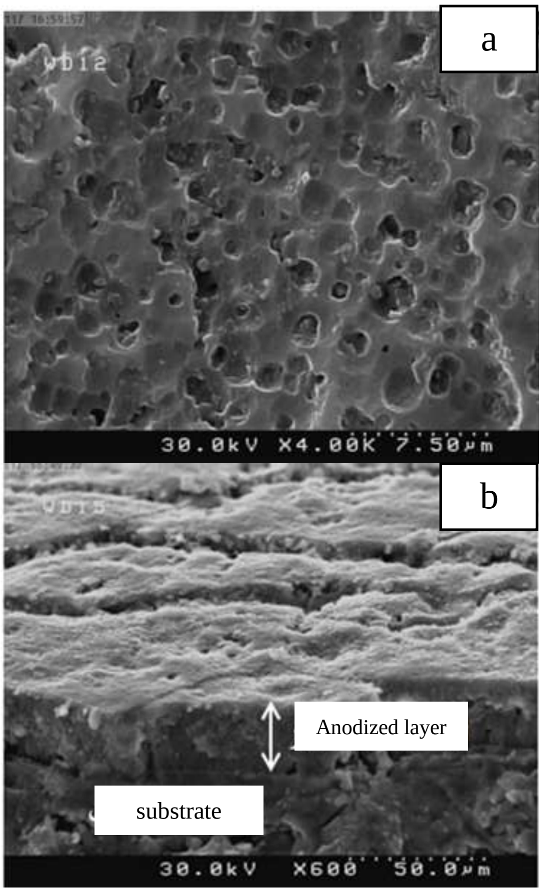

Fig. 1. FESEM images of a) surface morphology and b) cross-section of single-layer anodizing coating.

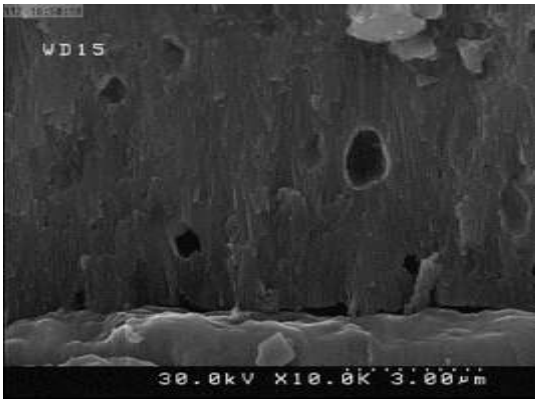

Fig. 2. FESEM image of the cross section of the anodized layer including the grown Nanocells.

The EDS results of the anodic coating resulting from anodizing are shown in Fig. 4. The main elements in the coating are oxygen and aluminum, which indicates the formation of the aluminum oxide layer on aluminum substrate. In addition to the two elements mentioned, the presence of sulfur ion is also due to the penetration and strength of this ion in the coating during the coating process by anodizing method in sulfuric acid solution. In fact, it can be said that the sulfur ion is trapped during the growth of the anodic layer, which has also been mentioned in other studies [9,10]. By examining the results of phasing and the diffraction pattern obtained from the anodizing coating in Fig. 5-a with the help of X'pert software, two issues are clearly evident.

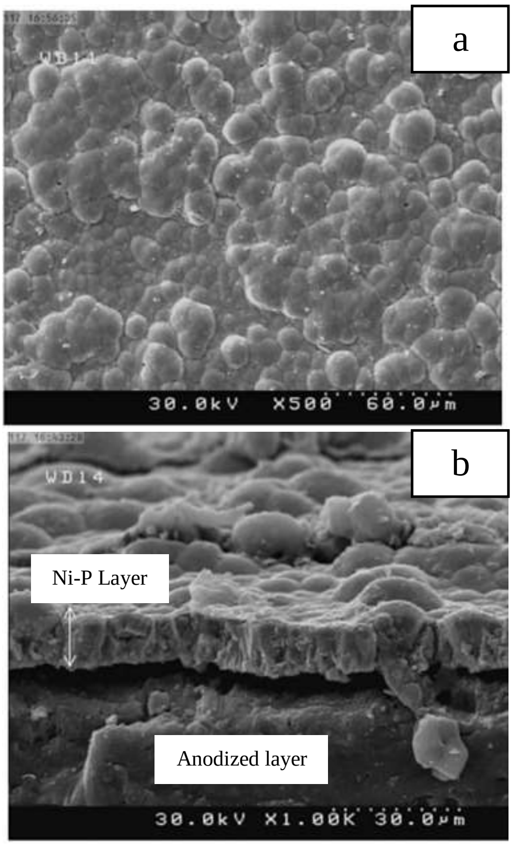

Fig. 3. FESEM images of a) surface morphology b) cross section of electroless nickel-phosphorus coating.

1) The presence of a relatively wide peak (in the range of 20-40 degrees) indicates the presence of amorphous phase in the coating and 2) The sharp peaks in this pattern are only related to aluminum. Considering the oxide coating, how did aluminum appear as a separate phase in the corresponding pattern? In order to prove and diagnose how this happened, a low-angle X-ray diffraction test was performed to check the possibility of X-rays reaching the substrate. Comparing these two patterns, it is clear that the broad peak in the GIXRD pattern (Fig. 5-b) is exactly in the same range seen in the XRD diffraction pattern, which proves the amorphousness of the formed aluminum oxide layer. On the other hand, the peaks seen in the XRD pattern have been removed in this case, and it is clear that aluminum does not exist separately in the anodizing coating, or in better words, aluminum is not trapped in the coating.

Therefore, the aluminum peaks were related to the aluminum alloy substrate.

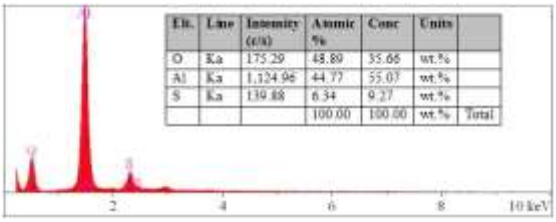

Fig. 4. The results of EDS analysis of the single-layer anodized coating surface.

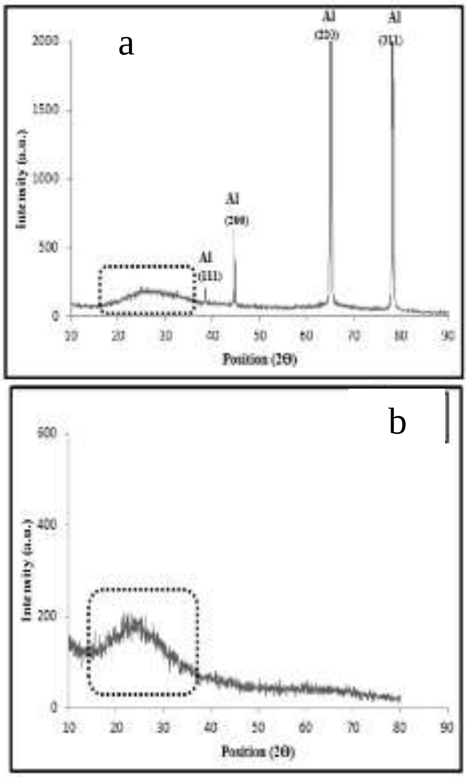

Fig. 5. Diffraction pattern results obtained from a) XRD test and b) GIXRD test of single-layer anodized coating.

The results of EDS analysis aimed at evaluating the chemical composition of the electroless coating applied on anodized aluminum alloy are shown in Fig. 6-a. This coating contains nickel and phosphorus, and according to the amount of phosphorus in the coating, it is placed in the category of high phosphorus electroless coatings. Therefore, we can expect the amorphous phase in the corresponding diffraction pattern. Fig. 6-b shows the results of XRD analysis of AAO/Ni-P hybrid coating. The sharp peaks are related to the aluminum substrate as in the previous two patterns. The broad peak observed in this pattern in the range of 40-50 degrees indicates the non-crystalline structure of the nickel-phosphorus coating. Such a peak for nickel-phosphorus electroless coatings due to having an amorphous structure has also been observed in other researches. In this hybrid coating, it is possible that the amorphous structure of the AAO coating is also effective on the observed broad peak. By performing heat treatment at 400°C for 1 hour, the chemical composition of the hybrid coating does not change, which is evident in the EDS analysis results (Fig. 7-a). However, phase changes are expected to occur due to the penetration of phosphorus and sulfur elements during heat treatment. In fact, at this temperature, the necessary activation energy for the formation of new phases is provided, and it is possible to form crystalline phases such as Ni, Ni_2P, and Ni_3P from the deposited non-crystalline phase, which can be seen in the pattern of Fig. 7-b. Another point about the formation of crystalline alumina phase from amorphous alumina is related to the anodizing coating, which is shown in Fig. 7-b.

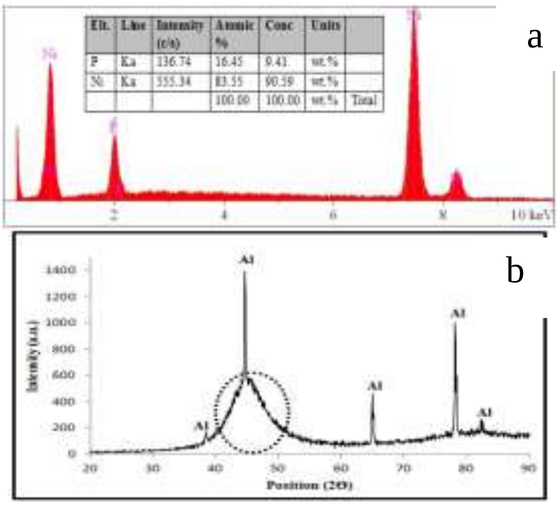

Fig. 6. The results of a) EDS analysis and b) X-ray diffraction pattern of anodized/nickel-phosphorus hybrid coating without heat treatment.

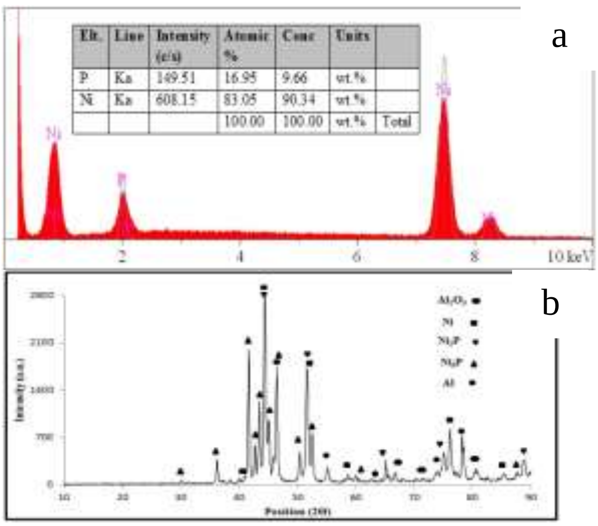

Fig. 7. The results of a) EDS analysis and b) XRD tests of anodized/nickel-phosphorus hybrid coating after heat treatment.

In order to check and compare the corrosion performance of the samples, the potentiodynamic polarization test was performed. In this regard, the samples were subjected to 3.5 wt.% NaCl solution under open circuit conditions for 2 hours. Fig. 8-A shows the potentiodynamic polarization diagram related to the 2024 aluminum substrate. In the polarization curve, the diagram has 2 anodic and cathodic branches. Cathodic branch is related to hydrogen release and anodic branch changes is depended on surface conditions. The results of TOFFEL extrapolation of the aluminum substrate are presented in Table. 3. As it is known, a relatively high corrosion current has been obtained from the graph for this sample, which shows the inability of this aluminum alloy in the test conditions. In the following, the polarization behavior of single-layer and hybrid coatings is investigated. In figure 8-b, the polarization curve of these two samples can be seen. AAO/NiP coating in the anodic branch shows a more passive behavior than AAO. The corrosion potential (Ecorr.) and the corrosion current density (icorr.) extracted from the potentiodynamic polarization diagrams by TOFFEL extrapolation method are reported in Table. 3. According to the results of this table, the amount of corrosion current has been reduced by 50 times by applying electroless coating, which indicates the improvement of corrosion performance. Various parameters can affect the corrosion behavior of coatings. The three parameters of thickness, phase structure and porosity were considered the most important factors affecting the corrosion behavior of coatings [11]. Therefore, a significant improvement in the corrosion behavior of the hybrid coating is because the AAO/NiP coating has been able to be more resistant to corrosion attacks during the polarization test due to blocking the pores of the AAO coating and also creating a dense protective layer [12]. The greater thickness of the hybrid coating can also have an effect on this improvement in corrosion performance, but it seems that reducing the porosity and filling the anodized holes by electroless method with the help of special sensitization and activation processes have been able to have very favorable effects on this issue. The polarization diagram of the sample with heat-treated hybrid coating can be seen in Fig. 8-c. As it is known, in this case, the corrosion behavior has decreased compared to the case of hybrid without heat treatment. It seems that the phase structure parameter has an effect on the corrosion behavior here.

The reasons for this are the transformation of the amorphous and corrosion-resistant phase of the nickel-phosphorus coating and the formation of crystalline particles of nickel phosphide and crystalline nickel on the surface of the coating, which lead to the reduction of phosphorus in some areas of the surface. Also, the resulting nickel phosphide particles create active-passive corrosion cells, which intensifies corrosion [11].

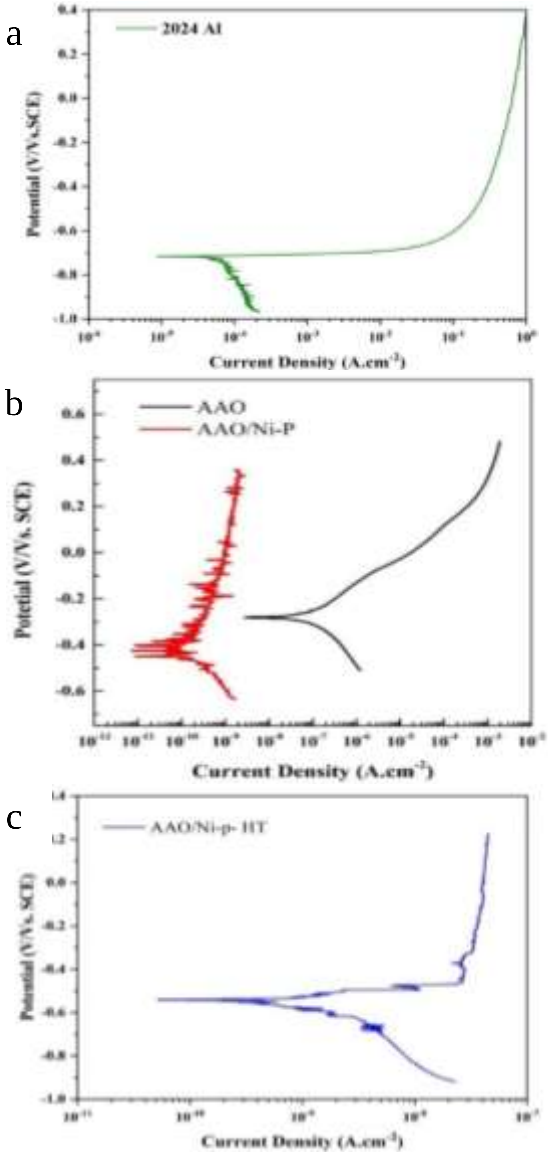

Fig. 8. The obtained potentiodynamic polarization diagram related to a) aluminum 2024 b) single-layer and hybrid coatings c) heat-treated hybrid coatings after 2 hours of immersion in 3.5 wt.% NaCl solution.

On the other hand, it has been stated in some articles that the heat treatment causes the electroless nickel-phosphorus coating to contract, and this problem causes the coating to crack (cracks in Nano size) and the base metal to come into contact with the environment [13,14]. It should be noted that the formation of crystalline phases of alumina with the heat treatment of the hybrid coating can also increase the corrosion current of the hybrid coating due to the heat treatment. Of course, even in this case, the hybrid coating has better corrosion behavior than the single-layer anodizing coating, which is due to the same two thickness parameters and especially the filling of the pores with the application of the second layer. The last point is the general comparison of the coatings with the substrate, which shows that all three types of coatings investigated in this research have significantly improved the corrosion performance of the aluminum substrate.

Table. 3. Electrochemical parameters extracted from the potentiodynamic polarization diagram in Fig. 8

Sample	$E_{corr.}$ (mV/vs. SCE)	$i_{Corr.}$ (nA.cm^{-2})
Aluminum alloy substrate	-712.647	45216
AAO	-278.966	50.92
AAO\Ni-P	-399.056	0.09
AAO\Ni-P-HT	-510.842	8.13

4. Conclusion

1. The oxide coating resulting from anodizing has an amorphous structure and an oxide nature that has a porous morphology.
2. The oxide coating has sulfur amounts due to the anodizing process in sulfuric acid environment.
3. By applying electroless coating on anodized aluminum and producing a hybrid coating, the thickness of the final hybrid coating was obtained with the help of Scanning Electron Microscopy images of about 35 micrometers. The thickness of anodized and electroless layers were calculated as 21.8 micrometers and 16.3 micrometers, respectively.
4. Investigating the corrosion behavior of the coatings showed that due to the filling of the anodized coating holes and the greater thickness of the hybrid coating compared to the single layer, the corrosion current decreased by 50 times, which shows the high effectiveness of this hybrid coating.

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