Improving the Corrosion Resistance of 6061 Aluminum Alloy Using Anodization and Nickel-Cobalt based Sealing Treatment

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In this study, 6061 aluminum alloy was used as the substrate to form the oxide layer using room temperature and low temperature anodization treatment. The adhesion, corrosion resistance, micro structure, and mechanical properties of the oxide layer are studied. After anodization treatment, the hardness of the oxide layers are greater than 450 Hv, the highest hardness occurred at the oxide layer after nickel-cobalt sealing which hardness can reach 536 Hv. The thickness of the oxide layer formed by low temperature anodizing is about 45-50 μm, and the thickness of the oxide layer formed by room temperature anodizing is only about 5-10 μm. All aluminum anodization layers have contact angles above 60°, and have high hardness, good hydrophobicity and high corrosion resistance. SEM, XPS, and TEM were used to analyze the chemical composition and microstructure of aluminum anodization layers prepared from different ratios of nickel and cobalt in the mixing solutions. The results show that when the ratio of nickel and cobalt is 8:2 in the mixing solutions, the aluminum anodization layer has the best sealing effect. When the substrates was carried out with anodization treatment and then sealed with the ratio of nickel-cobalt is 8:2, the lowest corrosion current density is 4.26×10^{-9} A/cm^2. The corrosion current density of the substrates that was carried out with anodization treatment and then only sealed by boiling water is 3.55×10^{-8} A/cm^2. When the substrates is only treated with anodization without sealing, its corrosion current density is only 5.8×10^{-7} A/cm^2.

1. INTRODUCTION

The physical property of aluminum is light and soft, so it is a light-weight metal commonly used in engineering. Its advantages include gloss, electrical conductivity, thermal conductivity, high ductility, processability, non-toxicity and low price. Therefore, aluminum alloys are often used in aerospace structures, optical parts, LED heat dissipation substrates, and semiconductor industry auxiliary process equipment cavity parts. Moreover, the chemical activity of aluminum is strong. In the atmospheric environment, a dense aluminum oxide film is easy to form on the surface. Generally, in order to increase the strength of aluminum, other alloy elements are added into pure aluminum to make aluminum alloy for use in engineering structures, the surface treatment will improve its wear resistance [1]、corrosion resistance[2] and insulation capabilities [3,4]. As early as 1970, many researchers had studied the anodization of aluminum and showed many models of porous oxide layer [5-9]. Keller et al. [10] proposed an ideal pattern of porous aluminum anodization layer, with a circular hole in the center and a hexagonal structure around the hole. Masuda [11] successfully used secondary anodic oxidation to prepare dense and regularly arranged porous aluminum anodization layer. Setoh and Miyata [12] indicated an important theory of aluminum anodization layer. They concluded that oxygen ions in the electrolyte would penetrate into the aluminum film from the buffer layer, and then react with the aluminum alloy to form aluminum oxide. Hunag et al. [13] reported that the use of hydroxyethylidene diphosphoric acid to replace traditional phosphoric acid. The anodization layer prepared form hydroxyethylidene diphosphoric acid is more environmentally friendly and has higher corrosion resistance than phosphoric acid. In recent years, aluminum alloy anodizing technology has also been applied to the field of biomedicine [14]. At present, the surface treatment technology widely used in the industry for aluminum alloys is anodizing treatment [15] and then sealing treatment [16], which is conducive to improving the resistance value and corrosion resistance of aluminum alloy. Due to the high porosity of the alumina layer, in order to improve its corrosion resistance and electrical resistance, it is necessary to fill the pores with a sealing method. Among them, boiling water sealing, nickel acetate sealing and nickel fluoride sealing are common sealing methods [17,18,19,20]. A sulfuric acid electrolyte is used for the anodization treatment. The operated parameters including: 15-20 wt% sulfuric acid in the bath, operated voltage at 14-22 V, temperature at 18-25°C and electrolysis time from 10 to 60 min, the thickness of the anodization layer can reach 3-35 μm. In sulfuric acid electrolyte bath, the obtained anodization layer then through the sealing treatment can improve the corrosion resistance of the substrates, and its advantages including low power loss, short anodization treatment time, colorless and transparent oxide film, strong adsorption capacity [21]. In the oxalic acid electrolyte, the thickness of anodization layer can reach 625 μm after long-term anodization treatment and the operated parameters including the oxalic acid concentration is 3-5 wt%, the operating voltage is 40-60 V, the temperature is 3-5°C [22]. In the phosphoric acid electrolyte, the obtained anodization layer has large pores, not dense, and it needs to be carried out under high voltage, and the production cost is high [23]. Anodization is to form a hexagonal stacked porous structure on the aluminum substrate through oxidation reaction,

forming straight and continuous pores on the wall of the tube. The diameter of the pores varies in different sizes depending on the anode reaction conditions. In the sealing process, the structure of anodization layer will change from amorphous to crystalline. After a period of time, the holes are completely sealed to form a high-density passivation layer. The density and thickness of the anodization layer will affect the corrosion resistance and insulation of the test piece, so the samples can effectively improve the corrosion resistance after sealing. The boiling water sealing process is a kind of hydration, which has two forms of reaction [24]. One of the reaction methods is to combine with water in an aqueous solution below 80°C and pH<4. This combination is only physically combined and this process is reversible, the reaction equation is as follows: $2AlO(OH) + 2H_2O \rightarrow Al_2O_3 \cdot 3H_2O \, (< 80°C)$. The second method of reaction is to combine alumina with hydration in a neutral aqueous solution above 80°C. This method is commonly referred to as the hydration sealing reaction. The reaction equation is as follows: $Al_2O_3 + H_2O \rightarrow Al_2O_3 \cdot H_2O \, (> 80°C)$. If the sealing liquid with nickel sulfate as the main salt is used for the sealing treatment, the nickel sulfate will be hydrolyzed in the pores to form nickel hydroxide precipitation and deposit in the pores. The reaction equation is as follows: $NiSO_4 + 2H_2O \rightarrow Ni(OH)_2 + H_2SO_4$. Other salts such as cobalt salts also have similar reactions. Different formulations and process conditions of the nickel salt and cobalt salt sealing solution will form a small amount of nickel hydroxide or cobalt hydroxide in the hole and show almost no color, so the color of the anodic oxide film will not be affected after sealing.

In this study, 6061 aluminum alloy was anodized and then sealed with nickel acetate solution with different proportions of cobalt. The effect of sealing with different nickel-cobalt ratios on the corrosion resistance of anodized 6061 aluminum alloy will be deeply studied. Anodization treatment is controlled by operating conditions such as electrolyte temperature, voltage and electrolyte type, and the thickness of the aluminum anodization layer on the workpiece will increase with the increase of the electrolysis time. However, its cost is higher than that of a sulfuric acid electrolyte bath, high power consumption, a cooling device, and a long processing time to obtain a thicker anodized aluminum anodization layer. The aluminum anodization layer is dense and has uniform pore distribution and high resistivity.

2. EXPERIMENTAL

The 6061 aluminum alloy has a dimension of $110 \times 90 \times 3$ mm, aluminum alloy is directly electropolished to make the surface roughness less than 1.0 μm. The polishing electrolyte contains sulfuric acid, phosphoric acid and deionized water, the weight percentages of which are respectively 40 wt%, 40 wt%, and 20 wt%, the operating voltage is 20 V, and the polishing time is 10 minutes. After electrolytic polishing, take out the aluminum alloy test piece and wash it with deionized water. After electrolytic polishing, the aluminum alloy test piece was subjected to anodizing treatment, and the treatment method was divided into low temperature anodized process and room temperature anodized process. Connect the anode to the aluminum alloy test piece and the cathode to the tin-lead plate. Use a 200 g/L sulfuric acid bath. The operating temperature is divided into low temperature (0-5 °C) and room temperature (20-25 °C). The operated voltage under low temperature condition is 40-50 V, the

anodization time is 1.5 hours, and the operated voltage under room temperature condition is 12-14 V, and the anodization time is 40 minutes. Finally, the anodized aluminum alloy test piece is sealed. The operated condition for only boiling water sealing treatment are that the test piece is immersed in 80 °C distilled aqueous solution, the pH value is 6.0, and the boiling water sealing time is 12-15 minutes. The nickel-cobalt sealing process involves immersing the test piece in a solution with 8 wt% nickel acetate and adding different proportions of cobalt. The temperature is 80 °C, the pH is 4.0, and the sealing time is 12-15 minutes. Due to the role of cobalt is to improve the corrosion resistance and lubricity of the oxide layer after sealing. Therefore, in this study, the ratios of nickel and cobalt in the nickel-cobalt sealing liquid are formulated as 9.5:0.5, 9:1, 8.5:1.5 and 8:2, respectively.

The surface microstructure and cross sections of the aluminum anodization layer were done by using a field scanning electron microscope (FSEM, Hitachi FESEM S-4800) and a transmission electron microscope (TEM, JEOL JEM-2100F). The chemical composition of the aluminum anodization layer were confirmed using an energy dispersive spectrometer (EDS). To understand the chemical reaction of the aluminum anodization layer under different sealing electrolyte, X-ray photoelectron spectroscopy (XPS) was utilized. XPS was carried out using a ULVAC-PHI, PHI 5000 Versa Probe. The X-ray photoelectron spectra of samples were calibrated using carbon 1s (284.6 eV). The surface of each coating was cleaned using Ar^+ ion sputtering for 300 s. After anodizing and nickel-cobalt sealing, the samples were cut into 15 mm*15 mm*3 mm, the two test pieces were bonded together by G1 glue Epoxy Bond 110 and finished the cross-section grinding and polishing. A Vickers microhardness tester (VHT-A1000ED) was used to measure the hardness, and the mean value for the hardness was calculated after 10 tests, loading with 0.1 g for 15 s. Contact angle of the samples was measured by a contact angle goniometer (Phoenix smart M) under room temperature with 3.5 wt.% NaCl solution. Took 5 different positions and calculate the average contact angle value. Using a dynamic and static friction coefficient tester to measure the friction coefficient of samples under the conditions of 200g, 500g, 1000g, and 1500g, respectively. The potentiodynamic polarization of the anodic aluminum oxide film were measured by a standard three-electrode cell system carried out with Zahner Zennium-E 41100. During the tests, the aluminum anodization layer was used as working electrode (WE), a saturated calomel electrode (SCE) was the reference electrode and a platinum plate was the counter electrode. The potentiodynamic polarization curves of the anodic aluminum oxide film were measured after 20 min immersion of specimens in 3.5 wt.% NaCl solution at room temperature in the potential range between -2.5 V and 1.0 V with a scanning rate of 0.5 mV s^{-1}, respectively. The corrosion behavior of the aluminum anodization layer was also evaluated by the salt spray test (SST).

3. RESULTS AND DISCUSSION

The FESEM images of aluminum anodization layers operated at room temperature and sealing with different condition are shown in Fig. 1. Fig. 1(a) shows the FESEM image of aluminum anodization layer without sealing, from the cross-sectional image can observe that the microstructure of anodic aluminum oxide film is dense, but it exist many holes in the surface of aluminum anodization layer. The EDS line-scan presents the chemical composition of aluminum anodization layer is alumina. The

thickness of film is approximately at 15 um. Fig. 1(b) shows the FESEM image of aluminum anodization layer carried out with a nickel-cobalt sealing process which nickel-cobalt ratio is 9:1, the surface of aluminum anodization layer become smooth and the quantity of holes decrease, the microstructure of alumina film is dense but it appear cracks in the surface of film. Fig. 1(c) shows the FESEM image of aluminum anodization layer carried out with a boiling water sealing process, the surface of aluminum anodization layer also become smooth and the quantity of holes decrease, the microstructure of alumina film is also dense and the cracks also appear in the surface of film.
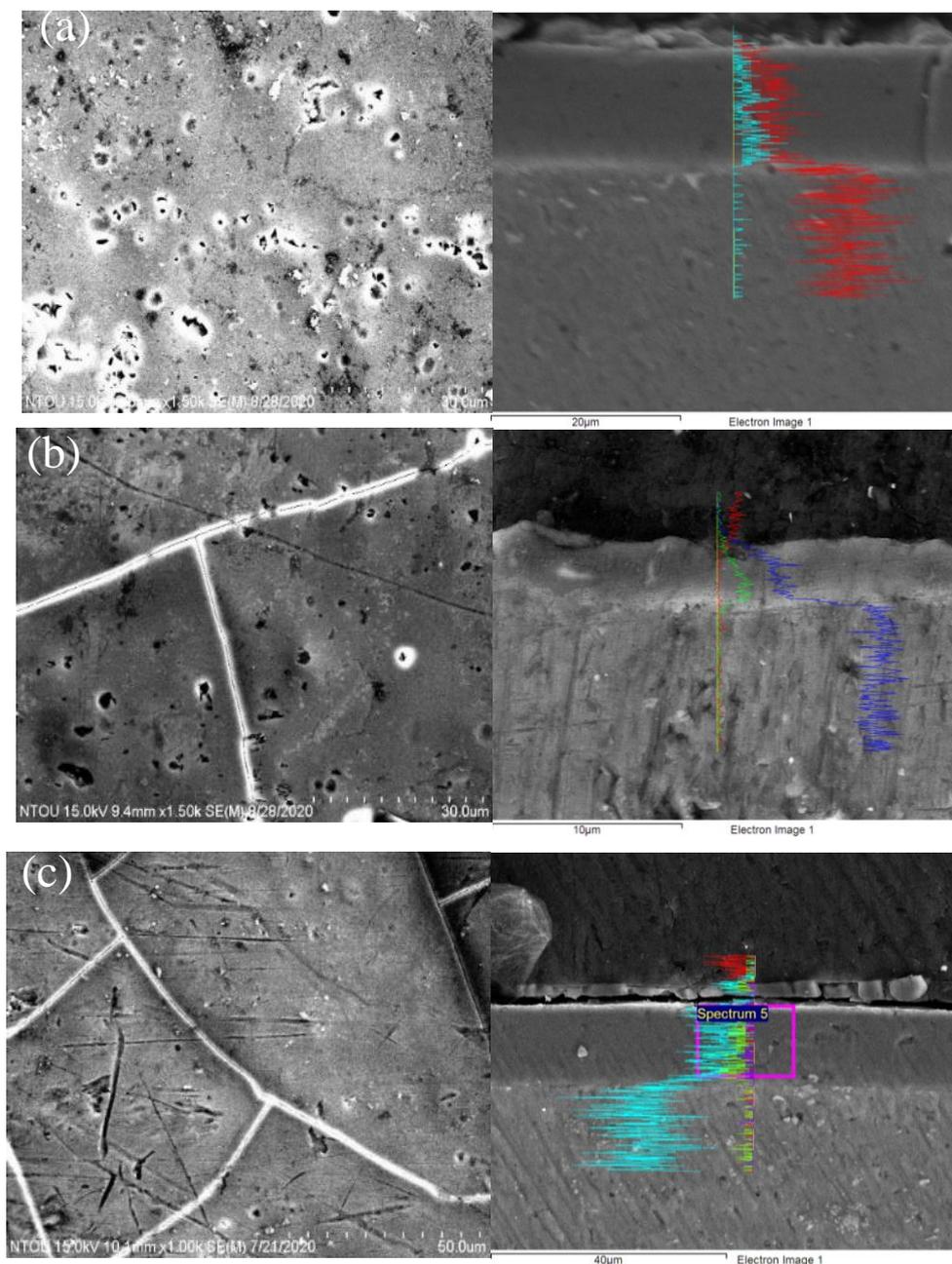

Figure 1. The FESEM morphology and cross-sectional images of anodic aluminum oxide films operated at room temperature and sealing with different condition (a) without sealing, (b) with a nickel-cobalt sealing process which nickel-cobalt ratio is 9:1, (c) with a boiling water sealing.

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The FESEM images of aluminum anodization layers operated at low temperature (0-5°C) and sealing with different condition are shown in Fig. 2. The EDS line-scan shows the anodization layers prepared at various condition, and all the chemical composition of them are alumina. The quantity of holes of aluminum anodization layers is significantly smaller than that of prepared in room temperature, and all the cracks within films are disappeared. All the aluminum anodization layers prepared from low temperature condition those thickness are approximately at 50 um. This can be attributed to the operated voltage in low temperature is higher than that in room temperature and cause the formation of greater thickness of aluminum anodization layer.
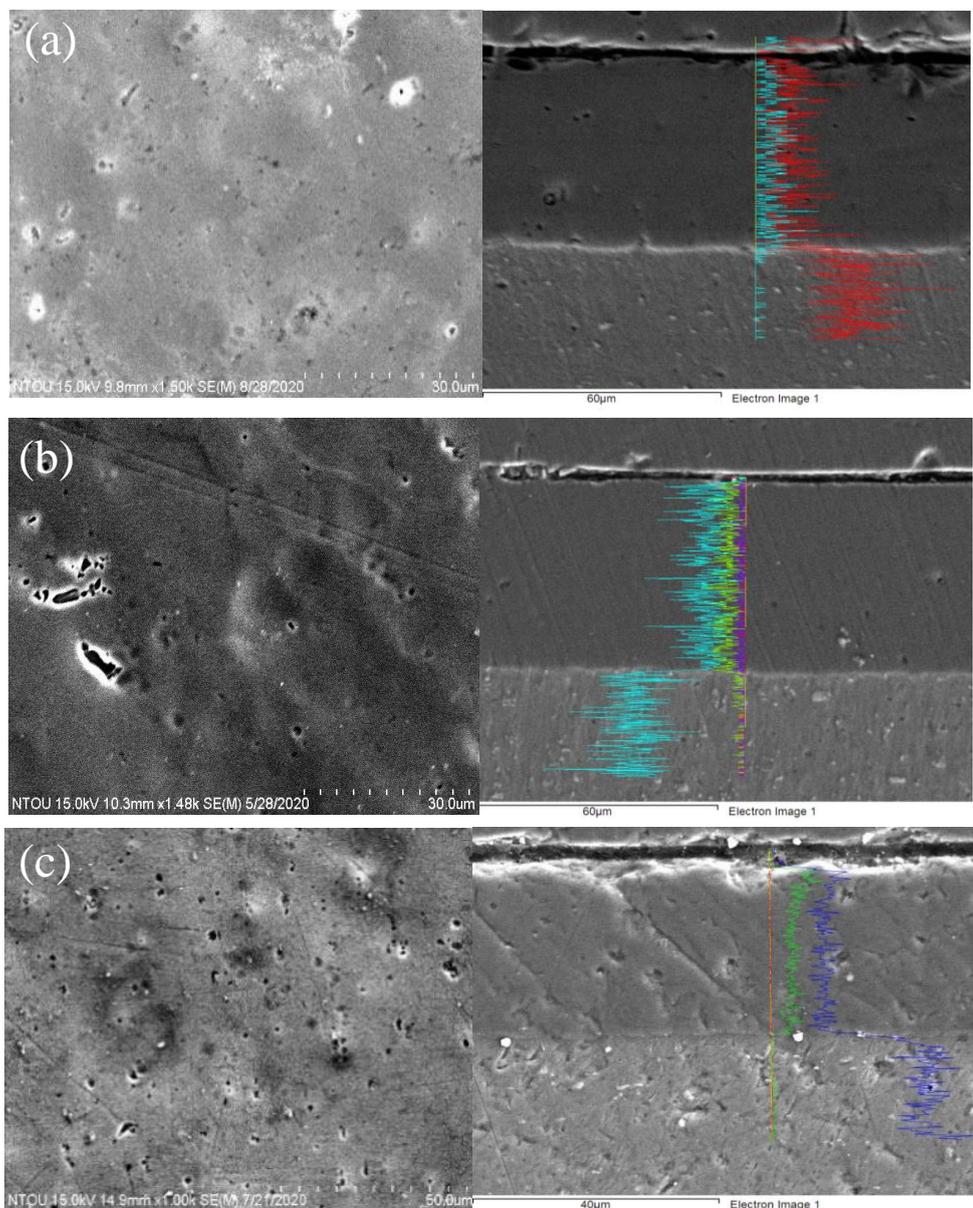

Figure 2. The FESEM morphology and cross-sectional images of aluminum anodization layer operated at low temperature (0-5°C) and sealing with different condition (a) without sealing, (b) with a nickel-cobalt sealing process which nickel-cobalt ratio is 9:1, (c) with a boiling water sealing.

Fig. 3 shows the potentiodynamic curves of aluminum anodization layers prepared in different condition which analyzed from 3.5 wt.% NaCl solution, the values of E_{corr} and i_{corr} are also shown in Table 1.
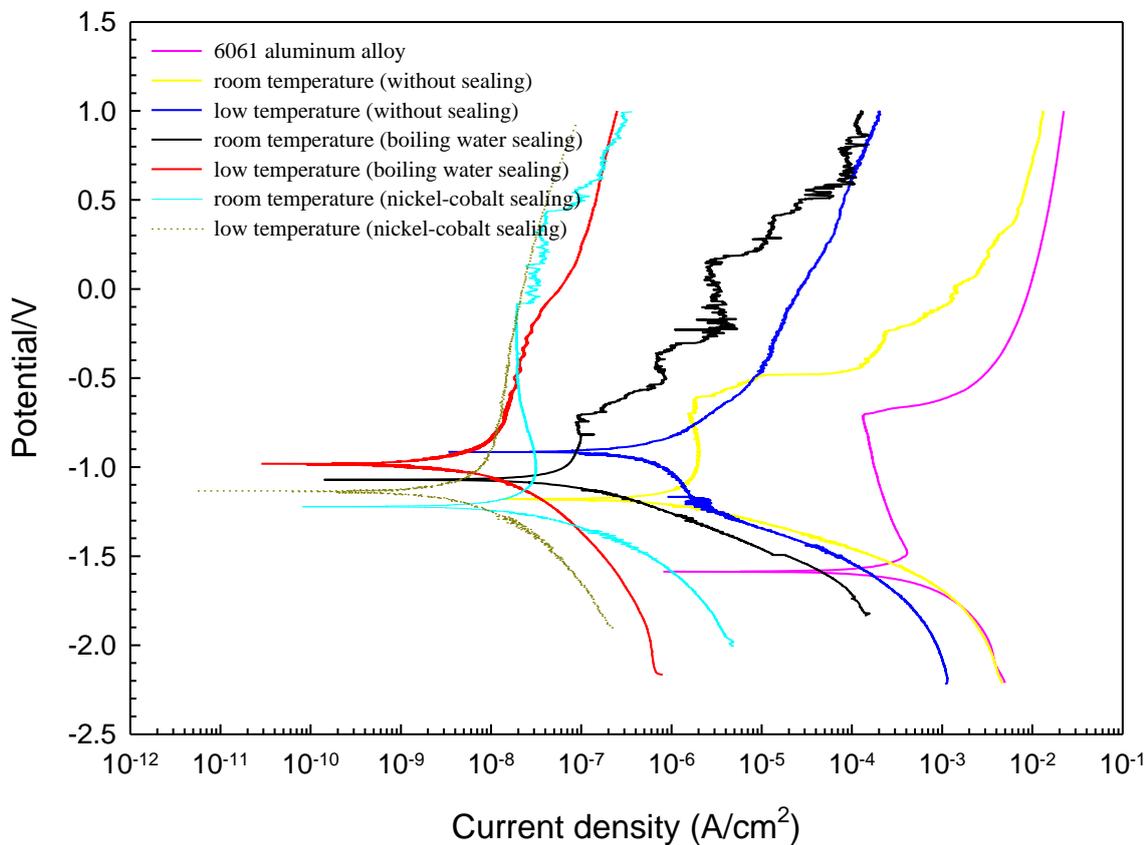

Figure 3. Potentiodynamic curves of aluminum anodization layers prepared in different condition which analyzed from 3.5 wt.% NaCl solution.

Table 1. The values of E_{corr} and i_{corr} of aluminum anodization layers prepared in different condition which analyzed from 3.5 wt.% NaCl solution

	----	Anodizing temperature					
	6061 aluminum alloy	**room temperature (without sealing)**	**low temperature (without sealing)**	**room temperature (boiling water sealing)**	**low temperature (boiling water sealing)**	**room temperature (nickel-cobalt sealing)**	**low temperature (nickel-cobalt sealing)**
E_{corr} (V)	-1.578	-1.118	-0.901	-1.215	-1.313	-1.062	-0.993
i_{corr} (A/cm^2)	4.1×10^{-4}	1.92×10^{-6}	5.8×10^{-7}	3.55×10^{-8}	3.55×10^{-8}	5.76×10^{-8}	7.67×10^{-9}

The i_{corr} of 6061 aluminum alloy is only 4.1 X 10^{-4} A/cm^2. The i_{corr} of aluminum anodization layer prepared from room temperature and low temperature (0-5°C) without sealing is 1.92 X 10^{-6} and 5.8 X 10^{-7} A/cm^2, respectively. It can see that the corrosion resistance of the aluminum anodization layer prepared from low temperature is significantly better than that of room temperature, this can be attributed to a crack-free structure exist in the aluminum anodization layer prepared from low temperature and cause a better corrosion resistance (see Fig. 1 and Fig. 2). This result is agreement with previous study that the corrosion resistance of aluminum anodization layer prepared from different anodization current density [2]. Both the i_{corr} value of aluminum anodization layer prepared from room temperature and low temperature and then carried out with boiling water sealing equal to 3.55 X 10^{-8} A/cm^2, indicating that the boiling water sealing process can significantly enhance the corrosion resistance of aluminum anodization layer. The i_{corr} value of aluminum anodization layer prepared from room temperature and low temperature and then carried out with nickel-cobalt sealing equal to 5.76 X 10^{-8} and 7.67 X 10^{-9} A/cm^2, respectively. The results shows that the lower I_{corr} value occurred at the aluminum anodization layer prepared from low temperature and then carried out with nickel-cobalt sealing process. Moreover, the best corrosion resistance of aluminum anodization layer occurred at the film prepared at low temperature condition and then carried out a nickel-cobalt sealing process which the value of i_{corr} is 7.67 X 10^{-9} A/cm^2. The significantly improvement in the corrosion resistance of aluminum anodization layer after sealing can be attributed to the corrosion current density of anodized aluminum alloy can be further significantly decreased by a sealing treatment, which fills nanopores of oxide layer, so that a penetration of corrosive media toward base aluminum is inhibited [25]. In this study, the corrosion resistance of aluminum anodization layer after sealing is agreement with the previous study [26].

samples \ time	0h	168h	336h
6061 aluminum alloy			

Figure 4. Optical images of 6061 aluminum alloy after salt spray test for various durations.

time samples	0h	168h	336h	700h	1000h
(a) without sealing					
(b) nickel-cobalt sealing					
(c) boiling water sealing					

Figure 5. Optical images of aluminum anodization layers prepared from room temperature with different condition after salt spray test for various durations: (a) without sealing, (b) nickel-cobalt sealing, (c) boiling water sealing

Fig. 4 shows the optical images of 6061 aluminum alloy after salt spray test for various durations. When the salt spray test is 0h, the surface of the 6061 aluminum alloy test piece presents a gray metallic luster and no rust spots are formed. At the 36th hour of the salt spray test, the surface of the test piece has golden luster and rust spots.

samples \ time	0h	168h	336h	700h	1000h
(a) without sealing					
(b) nickel-cobalt sealing					
(c) boiling water sealing					

Figure 6. Optical images of aluminum anodization layers prepared from low temperature (0-5°C) with different condition after salt spray test for various durations: (a) without sealing, (b) nickel-cobalt sealing, (c) boiling water sealing.

After the 336th hour of the salt spray test, the golden luster of the sample surface weakened, and it was covered with corrosion products and corrosion points. Fig. 5 presents the optical images of aluminum anodization layers prepared from room temperature with different condition after salt spray test for various durations. Fig. 5(a), (b), (c) shows the salt spray test results of aluminum anodization layers prepared from room temperature carried out with without sealing, nickel-cobalt sealing and boiling water sealing procedure, respectively. After 1000 hours of salt spray test, there is no rust or corrosion on the surface of the test piece. The same result presents in the sample that prepared on low temperature condition (Fig. 6). This result proves that the prepared aluminum anodization layer has a good protective effect in a corrosive environment, regardless of whether it is prepared at room temperature or low temperature.

Table 2. The aluminum anodization layer prepared under various conditions is measured for friction coefficient under different load

Sample code		Anodizing temperature					
		room temperature (without sealing)	low temperature (without sealing)	room temperature (boiling water sealing)	low temperature (boiling water sealing)	room temperature (nickel-cobalt sealing)	low temperature (nickel-cobalt sealing)
		Friction coefficient					
load	200 g	0.416	0.230	0.155	0.135	0.150	0.113
	500 g	0.428	0.239	0.156	0.135	0.156	0.116
	1000 g	0.423	0.270	0.154	0.176	0.154	0.135
	1500 g	0.476	0.279	0.156	0.181	0.156	0.144

The micro-hardness of 6061 aluminum alloy is only 101 Hv. The micro-hardness of aluminum anodization layer is approximately at 450 Hv, the micro-hardness of aluminum anodization layer after nickel-cobalt sealing procedure can be increased to 536 Hv. Table 2 shows the aluminum anodization layers prepared under various conditions are measured for friction coefficient under the load of 200 g, 500 g, 1000 g, and 1500 g, respectively. The aluminum anodization layer prepared at room temperature without sealing process has the friction coefficient from 0.416 to 0.476 under different load, the friction coefficient of aluminum anodization layer prepared at low temperature without sealing process decrease to 0.230-0.279. The aluminum anodization layer prepared at room temperature then after boiling water sealing process has the friction coefficient from 0.154 to 0.156 under different load, the friction coefficient of aluminum anodization layer prepared at low temperature then after boiling water sealing process is 0.135-0.181. The aluminum anodization layer prepared at room temperature then after nickel-cobalt sealing process has the friction coefficient from 0.150 to 0.156 under different load, the friction coefficient of anodized oxide film prepared at low temperature then after nickel-cobalt sealing process is 0.113-0.144. The above results show that the aluminum anodization layer prepared at low temperature then after nickel-cobalt sealing process has the smallest friction coefficient. Moreover, low temperature aluminum anodization layer has lower friction coefficient than that of room temperature. Materials with a low coefficient of friction will also have a lower surface roughness, which can reduce surface abrasion, and can effectively increase life cycle in corrosive environments such as air and seawater. The contact angle of anodized oxide film prepared at room temperature and low temperature are 45.052° and 50.674°, respectively. The contact angle of aluminum anodization layer prepared at room temperature and low temperature then after water sealing process are 49.513° and 58.582°, respectively. The contact angle of aluminum anodization layer prepared at room temperature and low temperature then after nickel-cobalt sealing process are 68.081° and 71.703°, respectively. The result of contact angle indicates the nickel-

cobalt sealing process can significantly increase the contact angle of aluminum anodization layer (Table 3). The hydrophobic material can effectively prevent foreign matter and water droplets from adhering to the surface, thereby improving the corrosion resistance of the surface of the test piece. Zhao et al. [27] and Wang et al. [28] indicated that hydrophobicity is closely related to corrosion resistance, i.e. the higher the contact angle, the better the corrosion resistance.

Table 3. The aluminum anodization layer prepared under various conditions is measured for contact angle using 3.5 wt% NaCl droplets

Sample code	Anodizing temperature					
	room temperature (without sealing)	low temperature (without sealing)	room temperature (boiling water sealing)	low temperature (boiling water sealing)	room temperature (nickel-cobalt sealing)	low temperature (nickel-cobalt sealing)
	Average contact angle (degree)					
	45.052	50.674	49.513	58.582	68.081	71.703

In order to study the effect of nickel to cobalt ratio on the corrosion resistance of the aluminum anodization layer during nickel-cobalt sealing process, the ratios of nickel and cobalt in the sealing liquid are formulated as 9.5:0.5, 9:1, 8.5:1.5 and 8:2, respectively. All the aluminum anodization layers are prepared from low temperature condition. Fig. 7 shows the potentiodynamic curves of aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid. The values of E_{corr} and i_{corr} are also shown in Table 4.
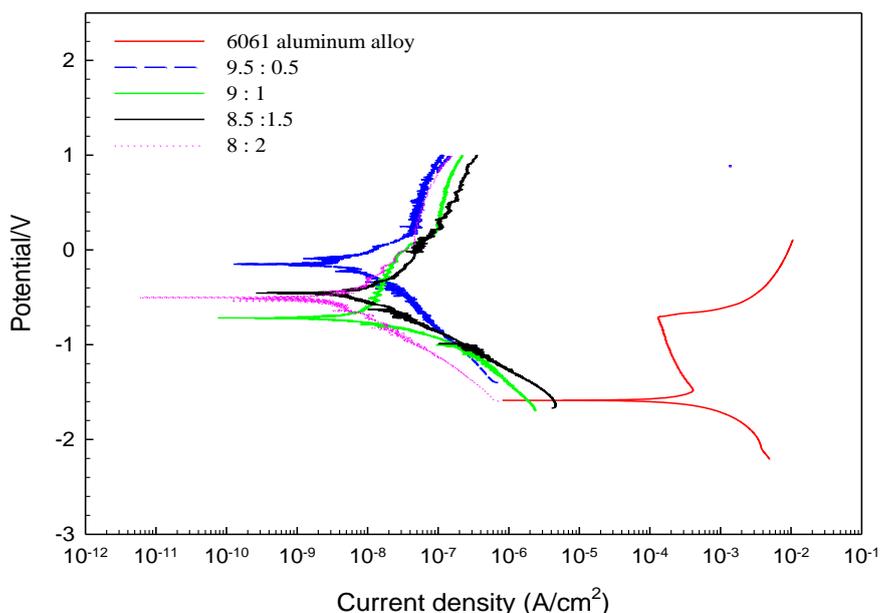

Figure 7. Potentiodynamic curves of aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid which analyzed from 3.5 wt.% NaCl solution.

The result indicates that the ratio of nickel and cobalt in the sealing liquid is 8:2 will make the best corrosion resistance of aluminum anodization layer which the value of i_{corr} is 4.26 X 10^{-9} A/cm^2. The condition for the second best corrosion resistance is the ratio of nickel and cobalt in the sealing liquid is 9:1 which the value of i_{corr} is 7.67 X 10^{-9} A/cm^2. The corrosion resistance of both of them is at the same level. Fig. 8 shows the salt spray test results of aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid, respectively. After 1000 hours of salt spray test, all the samples there are no rust or corrosion on the surface of the test piece.

Table 4. The values of E_{corr} and i_{corr} of aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid which analyzed from 3.5 wt.% NaCl solution

	6061 aluminum alloy	Nickel to cobalt ratio			
		9.5:0.5	9:1	8.5:1.5	8:2
Sealing temperature (°C)	----	85-90			
E_{corr} (V)	-1.578	-0.090	-0.705	-0.468	-0.511
I_{corr} (A/cm^2)	4.1 X 10^{-4}	9.52 X 10^{-9}	7.67 X 10^{-9}	1.24 X 10^{-8}	4.26 X 10^{-9}

Table 5. The aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid is measured for friction coefficient under different load

Nickel to cobalt ratio		9.5:0.5	9:1	8.5:1.5	8:2
Sealing temperature (°C)		85-90 °C			
load	200 g	0.143	0.135	0.135	0.118
	500 g	0.148	0.148	0.137	0.119
	1000 g	0.153	0.141	0.137	0.121
	1500 g	0.153	0.150	0.138	0.124

Table 5 shows the aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid is measured for friction coefficient under the load of 200 g, 500 g, 1000 g, and 1500 g, respectively. The ratio of nickel and cobalt in the sealing liquid is 9.5:0.5 will make aluminum anodization layer has friction coefficient from 0.143 to 0.153. The ratio of nickel and cobalt in the sealing liquid is 9:1 will make aluminum anodization layer has friction coefficient from 0.135 to 0.150. The ratio of nickel and cobalt in the sealing liquid is 8.5:1.5 will make anodic aluminum oxide film has friction coefficient from 0.135 to 0.138. The ratio of nickel and cobalt in the sealing liquid is 8:2 will make anodic aluminum oxide film has friction coefficient from 0.118 to 0.124. The results indicates that the friction coefficient of aluminum anodiz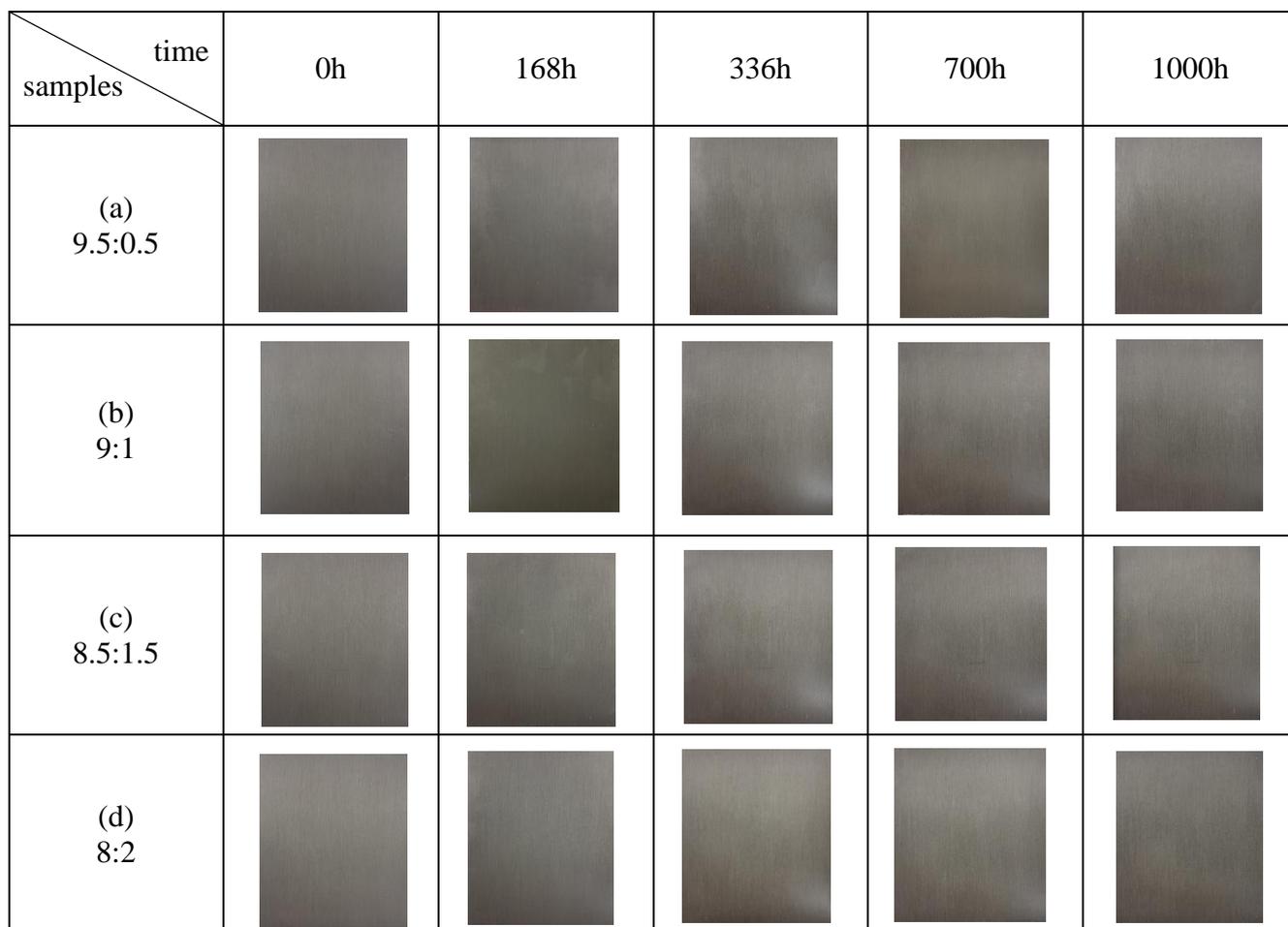ation layer decrease with the increase of addition content of cobalt. Table 6 shows the aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid is measured for contact angle

using 3.5 wt% NaCl droplets. The value of contact angle of aluminum anodization layer increase with the increase of addition content of cobalt.

Table 6. The aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid is measured for contact angle using 3.5 wt% NaCl droplets

| Nickel to cobalt ratio	Sealing temperature	1	2	3	Average contact angle
9.5:0.5	85-90 ℃	76.272	79.962	77.622	77.953
9:1	85-90 ℃	75.681	73.161	72.803	73.884
8.5:1.5	85-90 ℃	81.283	80.853	78.323	80.152
8:2	85-90 ℃	81.204	81.454	80.481	81.043

The de-convolution curve fitting results on the binding energy peaks of Al, Ni and Co elements in the measured XPS spectra of the aluminum anodization layers after nickel-cobalt sealing process using ratio of nickel and cobalt is 9.5:0.5 in the sealing liquid are shown in Fig. 9.

Figure 8. Optical images of aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid after salt spray test for various durations: (a) 9.5:0.5 (b) 9:1 (c) 8.5:1.5 (d) 8:2.

The peak position of Al 2p composed of Al^0=75.85 eV and Al^{3+}=75 eV, the formation of trivalent aluminum ions indicates the formation of an Al_2O_3 anodic aluminum oxide film. The peak position of Ni $2p_{3/2}$ composed of Ni^0=852.4 eV and 870 eV, the formation of metallic nickel ions indicates the reduction of nickel ions from nickel acetate in the sulfuric acid bath. The peak position of Co $2p_{3/2}$ composed of Co^0=778.2 eV and 792.2 eV, the metallic cobalt ions indicates the cobalt element added in the sulfuric acid bath. The deep profile curve indicates the formation of Al_2O_3 layer and both nickel and cobalt elements exist near the surface of anodic aluminum oxide film.
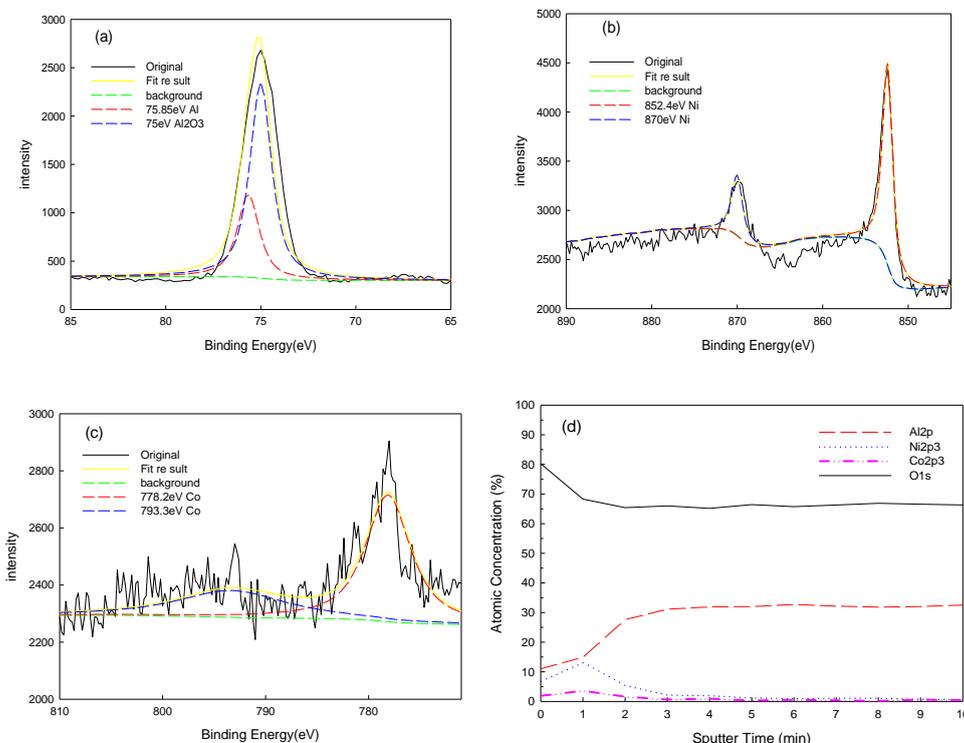
Figure 9. The de-convolution curve fitting analyses on the binding energy peaks of elements in the measured XPS spectra of the aluminum anodization layers after nickel-cobalt sealing process using ratio of nickel and cobalt is 9.5:0.5: (a) Al element, (b) Ni element, (c) Co element, (d) depth profiles.
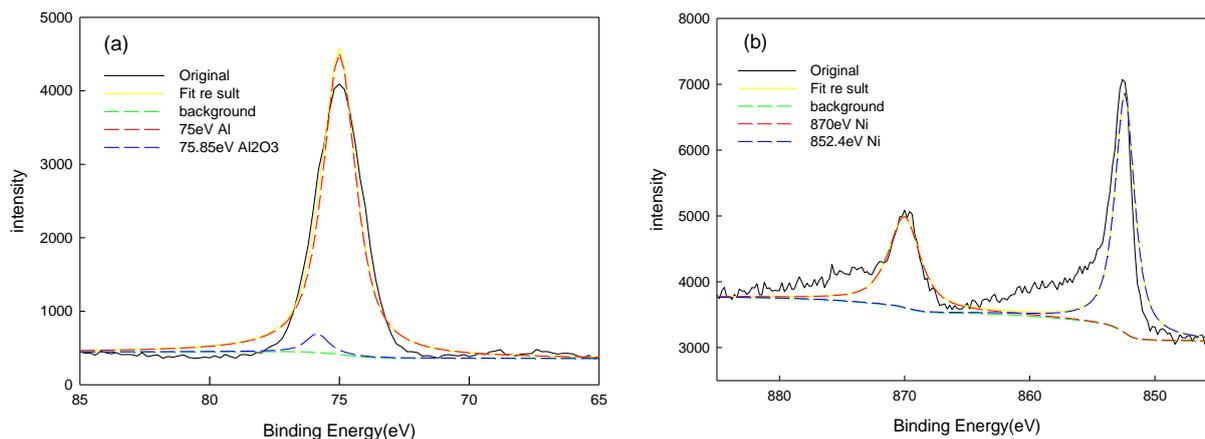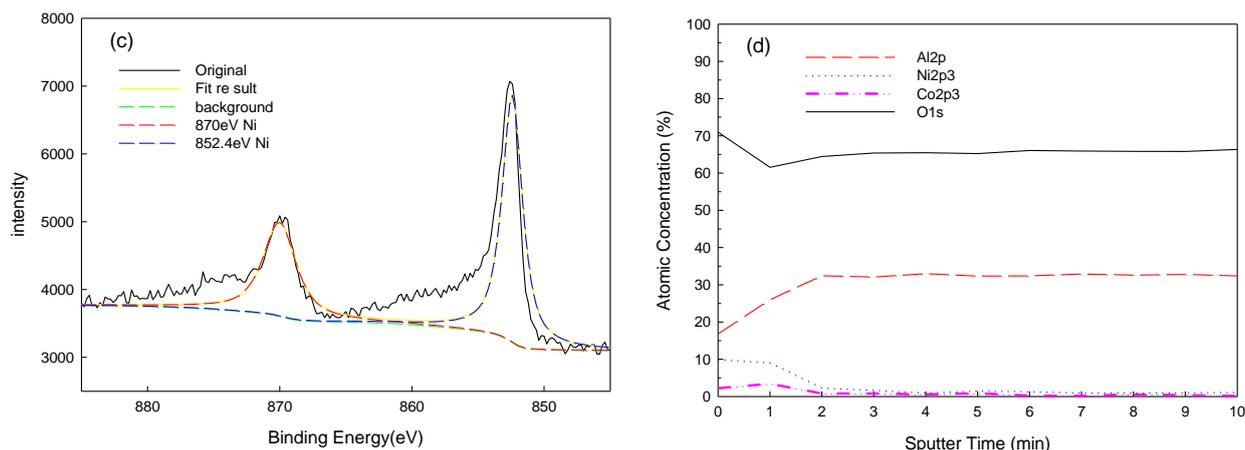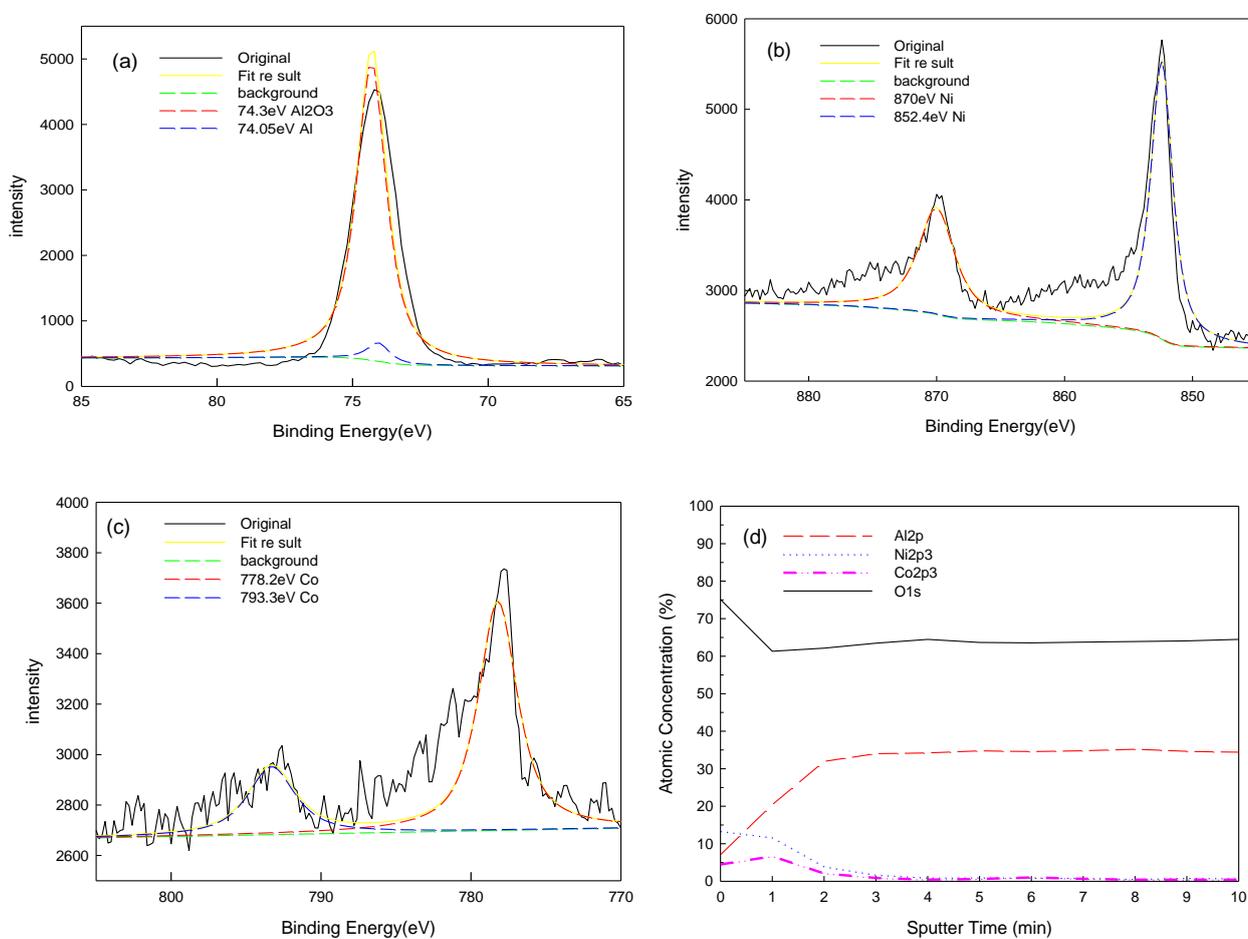
Figure 10. The de-convolution curve fitting analyses on the binding energy peaks of elements in the measured XPS spectra of the aluminum anodization layers after nickel-cobalt sealing process using ratio of nickel and cobalt is 9:1: (a) Al element, (b) Ni element, (c) Co element, (d) depth profiles.
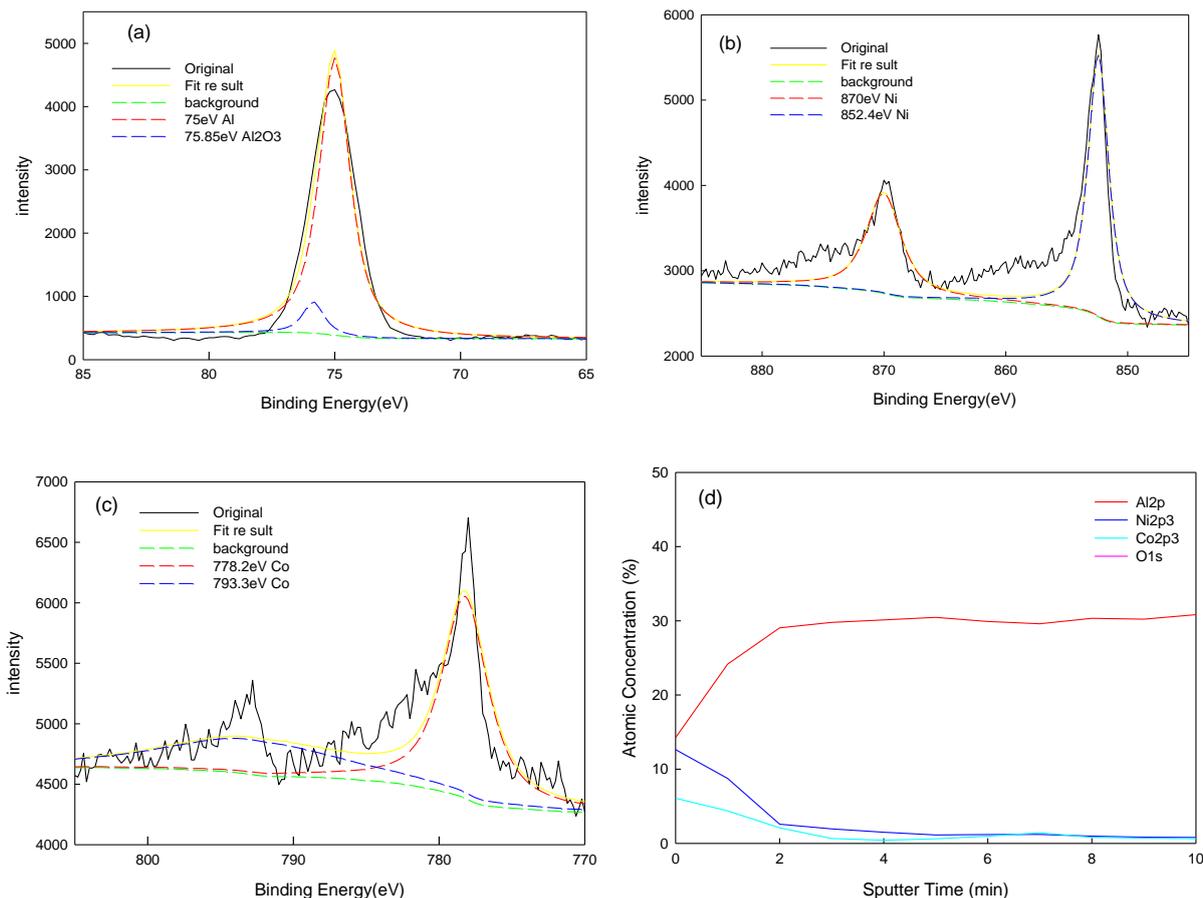

Figure 11. The de-convolution curve fitting analyses on the binding energy peaks of elements in the measured XPS spectra of the aluminum anodization layers after nickel-cobalt sealing process using ratio of nickel and cobalt is 8.5:1.5: (a) Al element, (b) Ni element, (c) Co element, (d) depth profiles.

Figure 12. The de-convolution curve fitting analyses on the binding energy peaks of elements in the measured XPS spectra of the aluminum anodization layers after nickel-cobalt sealing process using ratio of nickel and cobalt is 8:2: (a) Al element, (b) Ni element, (c) Co element, (d) depth profiles.
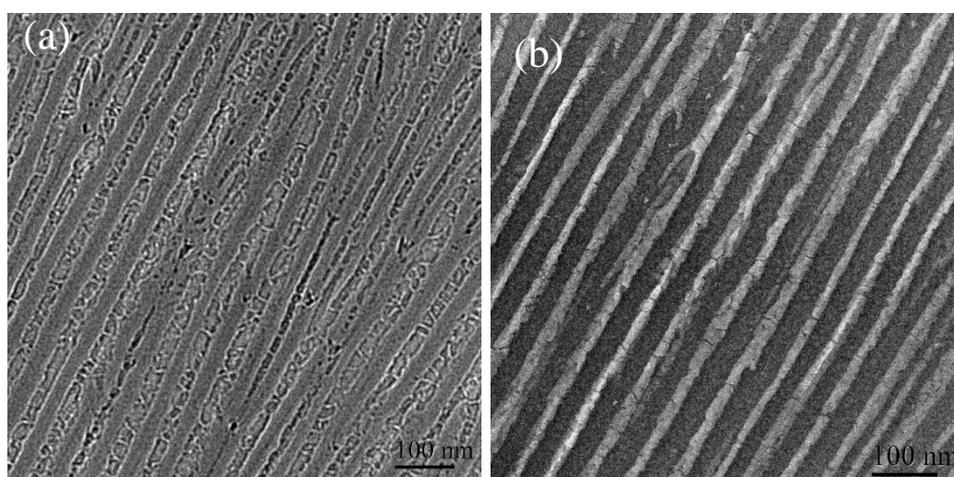

Figure 13. The TEM images of aluminum anodization layers: (a) after nickel-cobalt sealing process using ratio of nickel and cobalt is 8:2, (b) without sealing process.

The same XPS analyzed result presents in the anodic aluminum oxide films after nickel-cobalt sealing process using ratio of nickel and cobalt is 9:1, 8.5:1.5 and 8:2 in the sealing liquid (see Fig. 10-12). Fig. 13 presents the TEM images of anodic aluminum oxide films that after nickel-cobalt sealing process using ratio of nickel and cobalt is 8:2, and without sealing process [11]. The picture shows that the hole is indeed filled, which means that the sealing process has been completed.

4. CONCLUSIONS

1.   In terms of microstructure analysis, 6061 aluminum alloy is anodized and then sealed. The surface density and color uniformity of the sealed aluminum alloy are better than the unsealed aluminum alloy.

2.   The hardness of 6061 aluminum alloy after anodizing has been significantly improved, the highest microhardness is 536 Hv. After measuring the contact angle of samples, it can be found that cobalt can be added during the sealing process to improve the hydrophobicity of the test piece and achieve the effect of corrosion resistance. The highest contact angle is 81.043° occurred at the ratio of nickel and cobalt in the sealing liquid is 8:2.

3.   The ratio of nickel and cobalt in the sealing liquid is 8:2 will make the best corrosion resistance of aluminum anodization layer which corrosion current density (i_{corr}) is 4.26 X 10^{-9} A/cm^2.

4.   The results of salt spray test present aluminum anodization layers after nickel-cobalt sealing process using different ratios of nickel and cobalt in the sealing liquid, all the samples there are no rust or corrosion on the surface of the test piece after 1000 hours of salt spray test.

References

1.   R. K. Choudhary, P. Mishra, V. Kain, K. Singh, S. Kumar, J. K., *Surface and Coatings Technology*, 283 (2015) 135.
2.   S. J. Lee, S. J. Kim, *Applied Surface Science*, 481 (2019) 637.
3.   S. Lee, D. Kim, Y.Kim, U. Jung and W. Chung, *Met. Mater. Int.*, 22 (2016) 20.
4.   S. Wernick, R. Pinner, Ralph B. Mason, *Journal of Electrochemical Society*, 104 (1967) 180C.
5.   J. P. O'Sullivan, G. C. Wood, *Proceedings of the Royal Society of London Series A*, 317 (1970) 511.
6.   A.Lasia, *International Journal of Hydrogen Energy*, 18 (1993) 557.
7.   A.Lasia, A.Rami, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 294 (1990) 123.
8.   T. P. Hoar, J. Yahalom, *Journal of The Electrochemical Society*, 110 (1963) 612.
9.   C. J. Dell'Oca, P. J. Fleming, *Journal of The Electrochemical Society*, 123 (1976) 1487.
10. C. S. Hsu, H. B. Lee, C. S. Lin, C. Y. Lee, *Metallurgical and Materials Transactions A*, 41 (2010) 768.
11. H. Masuda, K. Fukuda, *Science*, 268 (1995) 1466.

12. S. Setoh, A.Miyata, *Scientific papers of the Institute of Physical and Chemical Research*, Tokyo, (1932) 2772.
13. H. Huang, J. Qiu, X. Wei, E. Sakai, G. Jiang, H. Wu, T. Komiyama, *Surface and Coatings Technology*, 393 (2020) 125767.
14. X. Huang, H. Mutlu and P. Theato, *Colloid. Polym. Sci.*, 299 (2021) 325.
15. F. Keller, M. S. Hunter, D. L. Robinson, *Journal of The Electrochemical Society*, 100 (1953) 411.
16. V. López, E. Otero, E. Escudero, J.A. González, *Surface and Coatings Technology*, 154 (2002) 34.
17. Y. Suzuki, K. Kawahara, T. Kikuchi, R. O. Suzuki and S. Natsui, *Journal of The Electrochemical Society*, 166 (2019) C261.
18. J. Y. Kim, Y. S. Won, C. H. Kim, J. C. Yoo, H. T. Yum, *Surface and Coatings Technology*, 169-170 (2003) 592.
19. A.P. Li, F. Muller, A. Birner, K. Nielsch, and U. Gosele, *Journal of Applied Physics*, 84 (1998) 6023.
20. F. Snogan, C. Blanc, G. Mankowski, N. Pebere, *Surface and Coatings Technology*, 154 (2002) 94.
21. J. J. Suay, E. Gimenez, T. Rodriguez, K. Habbib, J. J. Saura, *Corrosion Science*, 45 (2003) 611.
22. C. L. Liao, C. W. Chu, K. Z. Fung, I. C. Leu, *Journal of Alloys and Compounds*, 441 (2007) 1.
23. H. Masuda, K. Yada, A. Osaka, *Japanese Journal of Applied Physics*, 37(1998)1340.
24. B. R. Cheng, L. Hao, *Metal Finishing*, 98 (2000) 48.
25. F. Wang, J. Liu, Y. Li, Y. Wang, *J. Appl. Polym. Sci.*, 123 (2011) 2906.
26. H. Jo, S. Lee, D. Kim, J. Lee, *Materials*, 13 (2020) 4904.
27. K. Zhao, K.S. Liu, J.F. Li, W.H. Wang, L. Jiang, *Scripta Materialia*, 60 (2009) 225.
28. Y. B. Wang, H. F. Li, Y. F. Zheng, S. C. Wei, M. Li, *Applied Physics Letters*, 96 (2010) 251909.