

Article

Effect of Ultrafine Grains on the Coating Reaction and Anticorrosion Performance of Anodized Pure Aluminum

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Abstract: This work analyzes the effects of ultrafine aluminum (Al) grains on the anodizing coating reaction and anticorrosion performance of anodized industrial pure Al. Equal-channel angular pressing (ECAP) was applied to cast pure Al continuously for 16 passes at room temperature, and its average grain size was dramatically refined to about 1.5 μm . The ultrafine-grain (UFG) pure Al was further anodized with a cast sample via a parallel anodizing circuit at a constant total input current. Benefited by the higher volume fraction of grain boundaries and higher internal energy of the UFG substrate, the anodizing process of the ECAP-processed pure Al was significantly accelerated, showing a more intense initial anodizing reaction, a faster initial coating thickening, and much earlier porous-layer formation compared to the cast sample. As the anodizing reaction continued, the newly formed thicker coating of the ECAP-coated sample significantly hindered the diffusion process, weakening the thermodynamic advantage and decreasing the anodizing current of the ECAP-processed sample. During the entire anodizing duration, the ECAP-processed pure Al experienced gradually decreased anodizing current, while the cast sample experienced increased anodizing current. Because of the more total reaction, the ECAP-coated sample always maintained a relatively thicker coating and better anticorrosion performance during the entire anodizing duration.

Keywords: industrial pure Al; ultrafine grains; anodizing coating; microstructure; corrosion resistance

1. Introduction

Industrial pure aluminum (Al) has the distinct advantages of low density, excellent plasticity, good thermal/electrical conductivity, and good corrosion resistance in the atmospheric environment [1–3]. However, wide application of industrial pure Al as a structural metallic material is limited significantly because of its extremely low absolute strength [4]. Alloying, such as adding silicon (Si), copper (Cu), magnesium (Mg), zinc (Zn), manganese (Mn), and other elements, is the most important and effective method for improving the strength of Al. Solid-solution strengthening, second-phase strengthening, and precipitation strengthening are the primary mechanisms to strengthen Al alloys [5–8]. However, with the exception of adding Mg and Mn, alloying always leads to a significant decrease in the corrosion resistance of Al because of the appearance of cathodic secondary phases, which create microcorrosion

cells with the Al matrix [9,10]. Generally, industrial pure Al can be strengthened by a conventional plastic deformation process, such as extrusion, cold rolling, and cryorolling [11–13]. The strength of industrial pure Al can be doubled after conventional plastic processing, but on many occasions still does not meet the strength required of structural metallic materials. Severe plastic deformation (SPD) technologies, such as high-pressure torsion (HPT) and equal-channel angular pressing (ECAP), are effective approaches for improving the strength of pure Al by several times because of the ultrafine grains (UFGs) in its microstructure [14–16]. Sufficient grain-boundary strengthening (fine-grain strengthening) and dislocation strengthening (work hardening) can be simultaneously achieved in the deformed Al matrix after the SPD process [17–20]. In addition, as reported by several researchers, the SPD process can improve the corrosion resistance of industrial pure Al to a certain extent. Stimulated by the mass of highly-energetic grain boundaries and intragranular dislocation, UFG Al can achieve faster formation of stable passivation film and enhanced corrosion resistance [21–25].

However, in some corrosive environments, especially a chloride ion (Cl^-)-containing environment, pure Al suffers from corrosion damage due to the insufficient stability and localized dissolution of its aluminum oxide (Al_2O_3) film [3,9,26]. Even the corrosion resistance of UFG pure Al is still insufficient. Anticorrosion coatings are effective for protecting the Al matrix against corrosion, such as electroplating [27], chemical conversion coating [28,29], and anodizing coating [30,31]. Among these, anodizing coating is the most widely used industrial technology in the corrosion protection of Al and Al alloys because of its low cost and high protection efficiency [32]. Thus, using an anodizing coating is also a promising method to further improve the corrosion resistance and service life of UFG Al in corrosive media. Many researchers have investigated and reported the scientific and engineering issues with anodizing Al and Al alloys based on the conventional coarse-grain Al matrix, such as optimization of anodizing parameters, evolution of anodizing reaction, and microstructure and anticorrosion performance of the anodizing coating [33–36]. Because the Al matrix is involved in the anodizing reaction, the special microstructure characteristics of the UFG Al matrix may have great impact on the anodizing reaction, as well as the coating's microstructure characteristics and anticorrosion performance. Therefore, it is of great scientific and practical significance to investigate the effect of Al's UFGs on the anodizing process and coating performance of anodized pure Al.

In this study, cast industrial pure Al was processed by a multi-pass ECAP process to achieve UFGs and the resultant UFG pure Al was further processed by anodizing. The microstructure and anticorrosion performance of the anodizing coating were investigated in detail for the entire duration of the anodizing process. Meanwhile, effects of UFGs in the substrate achieved by ECAP on the accelerated anodizing reaction were systematically revealed, including a faster coating thickening and thicker, more corrosion-resistant anodizing coating of the ECAP-processed pure Al.

2. Experiment

2.1. Processing Route

Industrial pure Al (purity of 99.7%, provided by the Aluminum Corporation of China Limited, Beijing, China) was used as the raw material. As illustrated in Figure 1, the cast pure Al was processed by ECAP and post-anodizing. The cast billets, with size of $20 \times 20 \times 45 \text{ mm}^3$, were cut from the cast ingot and processed by multi-pass ECAP to achieve dramatic grain refinement. Rotary-die (RD) ECAP technology was applied, the processing principles of which have been detailed in our previous works [37–40]. Graphite slurry was applied to the billets and mold channels to reduce friction during ECAP processing. Given the excellent ductility of the cast pure Al, the billets were continuously ECAP-processed at room temperature for 16 passes with a displacement rate of $0.5 \text{ mm} \cdot \text{s}^{-1}$. No macrocracks were detected in the ECAP-processed billet. We refer to the 16-pass ECAP-processed pure Al as the “ECAPed sample” and the cast pure Al as the “cast sample”.

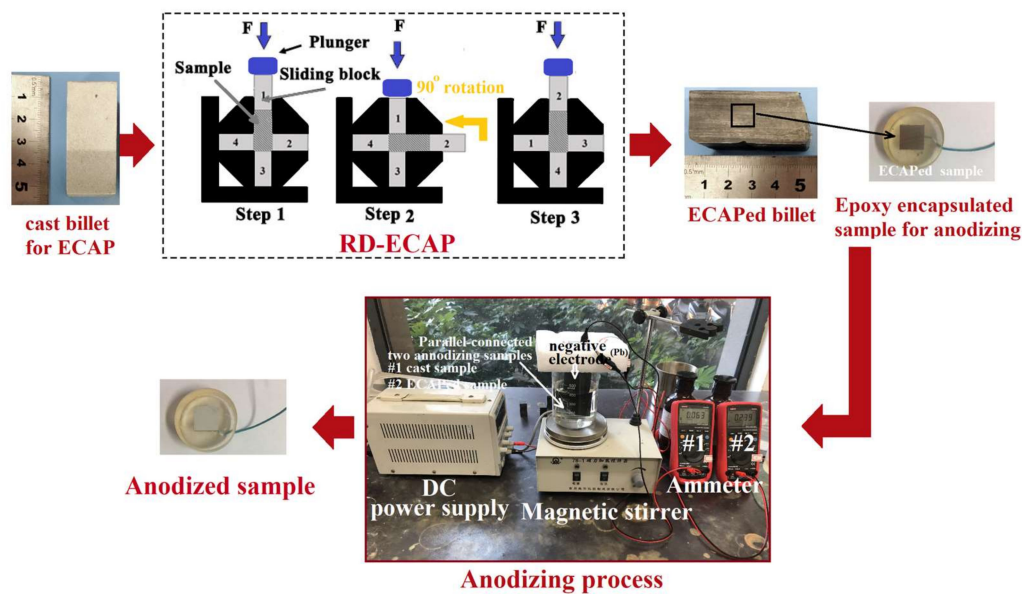


Figure 1. Combined Rotary-die (RD)-equal-channel angular pressing (ECAP) process and post-anodizing process of pure Al.

The square samples of the cast and ECAPed samples with a size of $10 \times 10 \times 2 \text{ mm}^3$ for anodizing were cut from the cast ingot and the ECAP-processed billet along the extrusion direction, respectively. As shown in Figure 1, samples were embedded in epoxy with an area of 1 cm^2 and connected by copper wire for conduction. Before anodizing processing, the samples were gradually polished by sandpaper and immersed in 3.5 wt.% sodium hydroxide (NaOH) aqueous solution for 5 min to remove the natural oxide film. Then, the samples were cleaned by deionized water and dried by air. As seen at the bottom of Figure 1, one ECAPed sample and one cast sample were anodized simultaneously via a parallel-connected anodizing circuit using 20 wt.% sulfuric acid as the anodizing electrolyte and the lead plate as the cathode. The anodizing current was supplied by a direct-current (DC) power supply, and two ammeters were connected to the cast and ECAPed samples in series circuits, respectively, to monitor the anodizing current of the samples. Meanwhile, electromagnetic stirring was applied to ensure electrolyte uniformity. The anodizing process was executed via a constant total input current of 0.12 A at room temperature. With such a specially designed anodizing circuit, the cast and ECAP-processed alloys could be anodized simultaneously under the same applied voltage, and the anodizing current of each sample could be continuously monitored by the two ammeters. After the anodizing coating, the samples were cleaned by deionized water and dried by hot air. We refer to the cast sample and ECAPed sample after anodizing coating as “cast-coated sample” and “ECAP-coated sample,” respectively. To investigate the evolution of the microstructure characteristics of the anodizing coatings, the samples were processed at different anodizing durations of 10, 25, 30, and 40 min.

2.2. Microstructure Characterization

The microstructure characteristics of the cast and ECAPed samples were observed and characterized by optical microscope (OM) (Olympus BX51M, Tokyo, Japan), transmission electron microscopy (TEM) (FEI Tecnai G2, Hillsboro, OR, USA), and electron backscattered diffraction (EBSD) (Nordlys EBSD detector, Oxford, UK). The samples for OM and EBSD observation were prepared by mechanical polishing and electrolytic polishing. Samples were mechanically polished to a state of mirror-like and then were electrochemically polished in a solution of 5% perchloric acid alcohol at -25°C and 15.5 V. The EBSD observation was conducted at an applied scanning voltage of 20 kV, and the step sizes for EBSD mapping were $10 \mu\text{m}$ and 150 nm to achieve sufficient resolution to reveal the coarse and UFG microstructures of the cast and ECAPed samples, respectively. The TEM

foil was mechanically polished to a thickness of 60 μm and then was electrochemically polished by a twin-jet electropolisher (MTP-1A, Shanghai Jiaoda Electromechanical Technology Development Co., Ltd., Shanghai, China) in a solution of 30% methanolic nitrate at $-30\text{ }^{\circ}\text{C}$ and 15 V. The microstructure characteristics of the anodizing coating of both anodized samples were observed by a scanning electronic microscope (SEM) (Coxem, EM-30 plus, Daejeon, Korea) from both the top view and the cross-sectional view.

2.3. Electrochemical Corrosion Test

The anticorrosion performance of the substrate and coated samples in 3.5 wt.% sodium chloride (NaCl) solution was investigated by electrochemical corrosion testing with a Parstat 2273 advanced potentiostat (Princeton, Oak Ridge, TN, USA). Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) were employed in the electrochemical corrosion test, and all the samples had an exposure of 1 cm^2 . EIS tests were conducted at frequencies ranging from 10 mHz to 10 kHz with 5 mV of applied sinusoidal potential. The PDP tests were conducted at a scan rate of $1\text{ mV}\cdot\text{s}^{-1}$. Before EIS and PDP testing, the samples were pre-immersed in the solution for 1 h to reach stable open circuit potential (OCP). To ensure data reproducibility, five parallel samples were tested with EIS and PDP testing.

3. Results and Discussion

3.1. Microstructure Characteristics

Figure 2 shows the optical microstructures of the cast and ECAPed samples. As seen in Figure 2a, the cast sample showed typical equiaxed coarse grains with a grain size of about 0.5 to 1 mm. After 16-pass ECAP processing, the microstructure of the pure Al was dramatically modified. At the same magnification, the ECAPed sample presented significantly dense plastic flow, which should be induced by SPD during the multi-pass ECAP processing. Based on the OM observation, one can deduce that dramatic grain refinement may be achieved in the ECAPed sample. Grain morphology, grain size, and detailed intragranular microstructure characteristics of the ECAPed sample were revealed by TEM and EBSD observation.

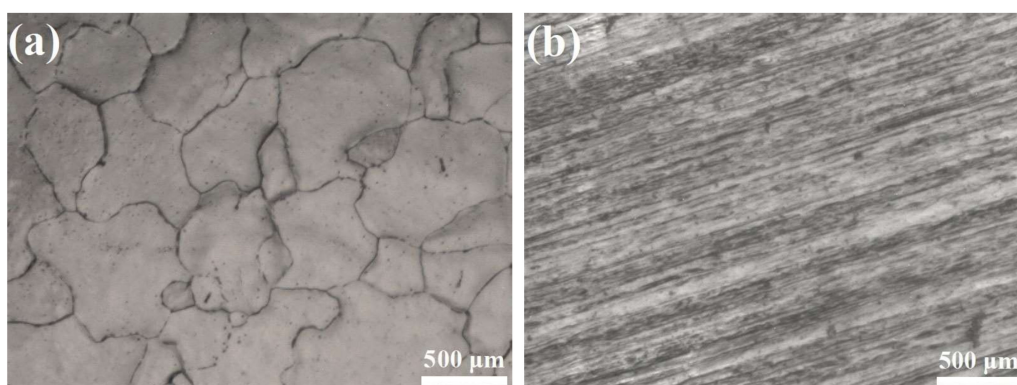


Figure 2. Optical microstructure of the (a) cast and (b) ECAPed samples.

Figure 3 shows the SEM top-view surface morphologies of the cast-coated and ECAP-coated samples fabricated by anodizing durations of 10–40 min. Microstructure characteristic evolution of the anodizing coating was clearly revealed from the SEM images for both coated samples. In general, the surface morphology of both coated samples underwent a process of transforming from a dense surface to a porous structure surface. However, the two coated samples showed significant differences in the time nodes at which the surface microstructure features evolved. As seen in Figure 3a,b, the cast-coated sample showed a typical dense coating surface after 10 min of anodizing, while some localized porous structures were created on the coating surface of the ECAP-coated sample. As the anodizing duration

increased to 25 min, different effects occurred on the top surfaces of the two coated samples. As seen in Figure 3c,d, the cast-coated sample still kept a dense coating surface, while the coating top surface of the ECAP-coated sample was already covered by the typical porous structure. When the anodizing duration further increased to 30 min, both sample coatings were covered by the porous structure, and the porous structure of the ECAP-coated sample was much coarser compared to that of the cast-coated sample. As the anodizing duration reached 40 min, further coarsening of the porous structure occurred for the coatings of both coated samples, and some coarse lamellar oxide was formed on top of the porous structure of the ECAP-coated sample (as seen in Figure 3h).

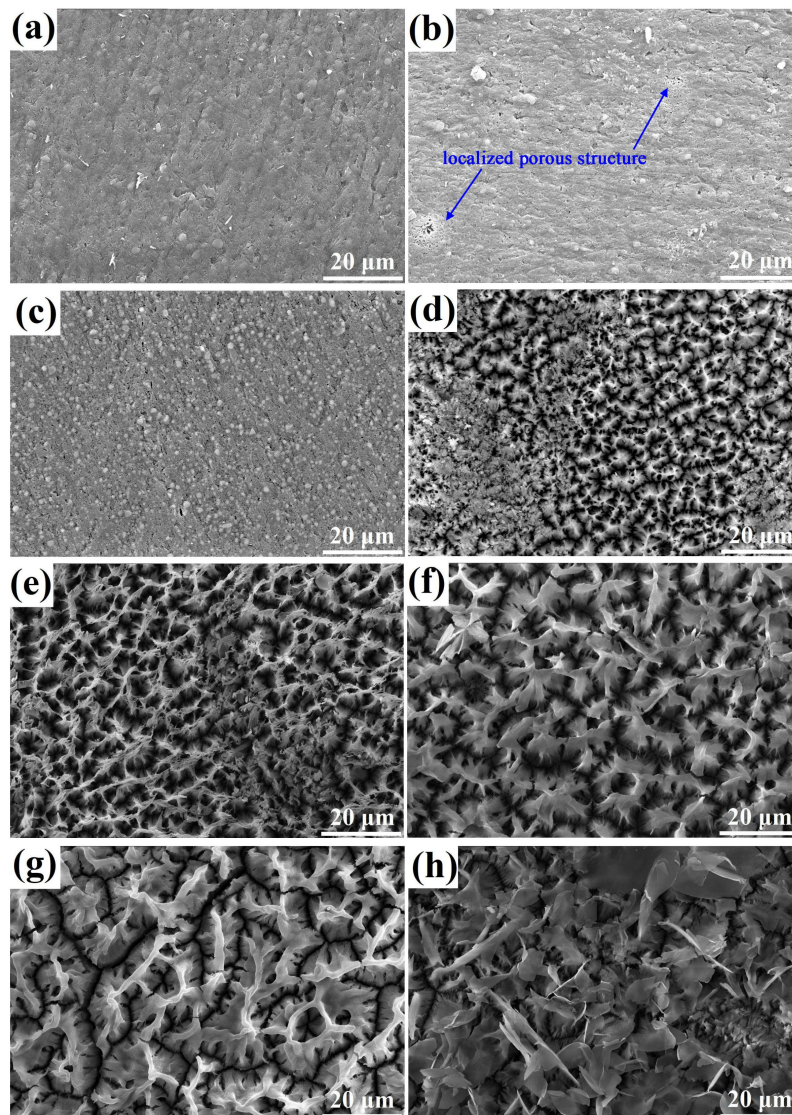


Figure 3. Scanning electronic microscope (SEM) surface morphologies of the coated samples with different anodizing durations: (a,c,e,g) are the cast-coated samples anodized for 10, 25, 30, and 40 min, respectively; (b,d,f,h) are the ECAP-coated samples anodized for 10, 25, 30 and 40 min, respectively.

Figure 4 shows the SEM cross-sectional morphologies of the cast-coated and ECAP-coated samples with anodizing durations of 10–40 min. Cross-sectional coating structure and coating thickness were clearly revealed from the SEM images. In general, the coatings of both coated samples underwent the evolution process from a single-dense-layer structure to a dual-layer structure with an inner dense layer and an outer porous layer. In addition, the coating thickness of both coated samples increased gradually during anodizing, especially in the initial anodizing period. However, their thickening rate

decreased gradually, and the trend of coating thickening of both coated samples was very weak at the end of anodizing. In addition to the above common laws, the two coated samples also showed a significant difference in the time nodes at which the porous layer formed. As seen in Figure 4a,b, both samples showed one single dense layer after anodizing for 10 min, and the ECAP-coated sample showed a thicker coating (about 35 μm) than that of the cast-coated sample (about 25 μm). When the anodizing duration increased to 25 min, significant coating thickening had been achieved for both samples. At this time, a porous layer was formed in the ECAP-coated sample, leading to a typical dual-layer structure, while the cast-coated sample still kept one single dense layer. Further anodizing created a typical dual-layer structure to both coated samples and further thickened both the inner dense layer and outer porous layer. At the end of the anodizing duration (40 min), the difference in coating structure and coating thickness was shown to be quite limited between the two coated samples. Throughout the entire anodizing duration, the ECAP-coated sample showed faster coating thickening in the early anodizing period but slower coating thickening in the late anodizing period compared to the cast-coated sample. Meanwhile, the anodizing coating of the ECAP-coated sample formed a typical porous layer much earlier than the cast-coated sample.

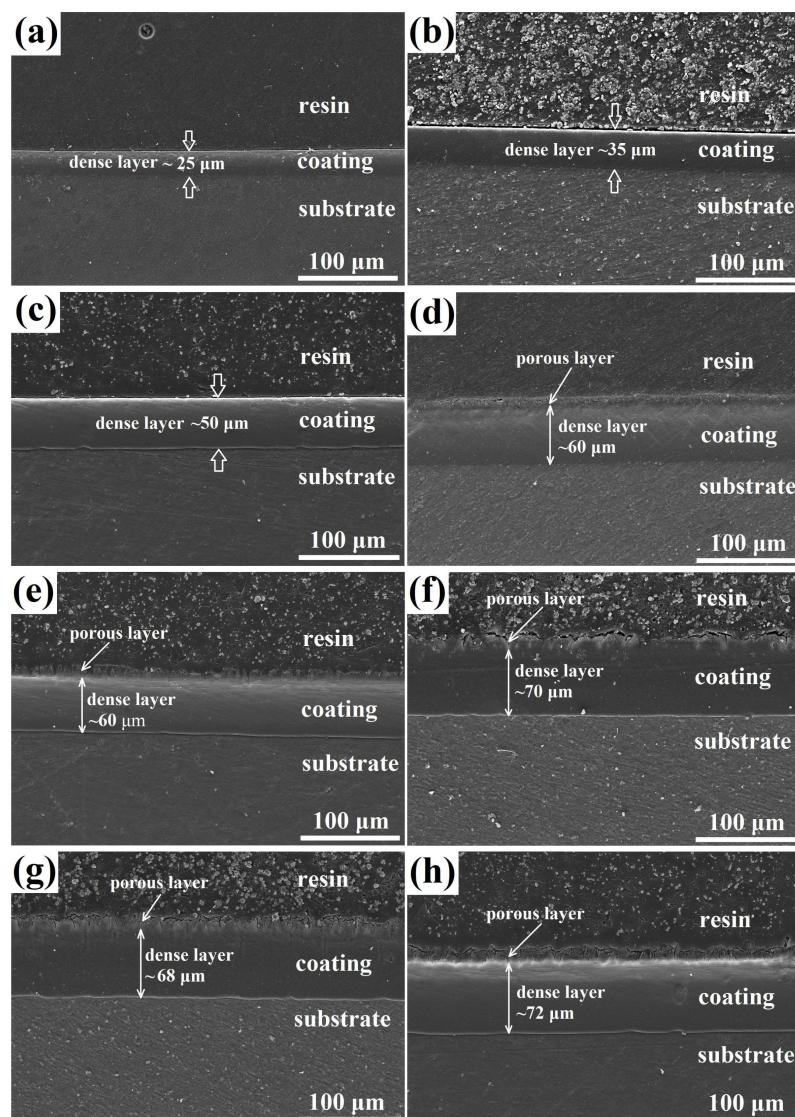


Figure 4. SEM cross-sectional morphologies of the coated samples with different anodizing durations: (a,c,e,g) are the cast-coated samples anodized for 10, 25, 30, and 40 min, respectively; (b,d,f,h) are the ECAP-coated samples anodized for 10, 25, 30 and 40 min, respectively.

As reported by many researchers, the anodizing process of Al in acidic solution comprises the interrelated reactions of dissolution of Al matrix, migration of ions in solution, electrode discharge, and anodizing coating formation by oxidation [32–34,41]. In the first stage of the anodizing process of Al, the formation of a barrier layer occurs in the electrolyte/matrix interface because of the electrochemical reaction when the anode current is applied to the Al sample. As the anode (Al matrix) loses electrons and the cathode gains electrons, a dense, thin anodizing coating forms on the sample surface, the composition of which is Al_2O_3 . This thin coating isolates the sample substrate from the electrolyte, and therefore the thin coating is called as the barrier layer. As generally believed, the barrier layer is continuous and nonporous. With increasing anodizing duration, the barrier layer gradually thickens, but it also undergoes the dissolution process because of the dissolution reaction of Al_2O_3 in the strong acid electrolyte. During the anodizing process, undulation of the sample surface occurs because of the volume expansion induced by the formation of Al_2O_3 from Al. Such undulation significantly affects the current distribution on the barrier layer, resulting in relatively strong polarization between the concave and convex surfaces. At the same time, the dissolution of anodizing coating in strong acid electrolyte makes the coating surface more uneven. The above two factors lead to the partial dissolution of the barrier layer and the gradual formation of a porous structure above the barrier layer. As the anodizing process progresses further, the dissolution of the barrier layer is constantly strengthened, and the intensified surface unevenness creates obviously different distributions of electrolyte concentration and potential. With increasing anodizing duration, the difference in concentration and potential becomes more significant. Driven by the two differences, the Al^{3+} moves to the electrolyte/coating interface and contacts the electrolyte. Meanwhile, the hydroxide (OH^-) and oxygen (O^{2-}) migrate to the anodizing coating pores. The anodic ions (Al^{3+}) react with both cathodic ions (OH^- and O^{2-}), creating hydrated oxide ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) at the outermost layer of the anodizing coating pore structure. Those reactions lead to pore-structure thickening and coarsening, creating a porous layer above the barrier layer. As the anodizing duration continues, the growth rate and dissolution rate of the anodizing coating reaches a dynamic equilibrium, and the thickness of the anodizing coating does not increase significantly.

Based on the microstructure characterization of the anodizing coating and the mechanism analysis of anodizing coating formation, one can deduce that the ECAPed sample underwent the accelerated anodizing process compared to the cast one.

3.2. Electrochemical Corrosion Behavior in NaCl Medium

Figure 5 illustrates the EIS Bode plots (Figure 5a) and Nyquist plots (Figure 5b) after immersion in 3.5 wt.% NaCl solution for 1 h. Coated samples showed three time constants in the Bode plots, including two capacitive peaks in the high/middle frequencies and one capacitive peak in the low frequency. Double peaks (as marked by the two blue arrows in Figure 5a) are the typical EIS characteristics for coated samples, of which one peak relates to the single response from the coating/substrate interface and one peak relates to the response from the coating [42,43]. In this study, a third capacitive peak was also found, which may relate to the single response from the outer porous layer of the anodizing coating. Different from the coated samples, the two substrate samples presented two time constants in Bode plots, including one capacitive peak in the high/middle frequencies (as marked by the black arrow in Figure 5a) and one capacitive peak in the low frequency. As generally believed, the capacitive arc diameter of the EIS Nyquist plots is a reasonable indicator of corrosion resistance, and the larger capacitive arc diameter represents better corrosion resistance [44,45]. Figure 5b clearly shows the coated samples having an obviously larger capacitive arc than the substrate samples. For all the coated samples, their capacitive arc increased with increasing anodizing duration, and the ECAP-coated sample always had a larger capacitive arc diameter compared with the cast-coated sample. However, the difference in capacitive arc diameter between the ECAP-coated sample and the cast-coated sample decreased with increasing anodizing duration.

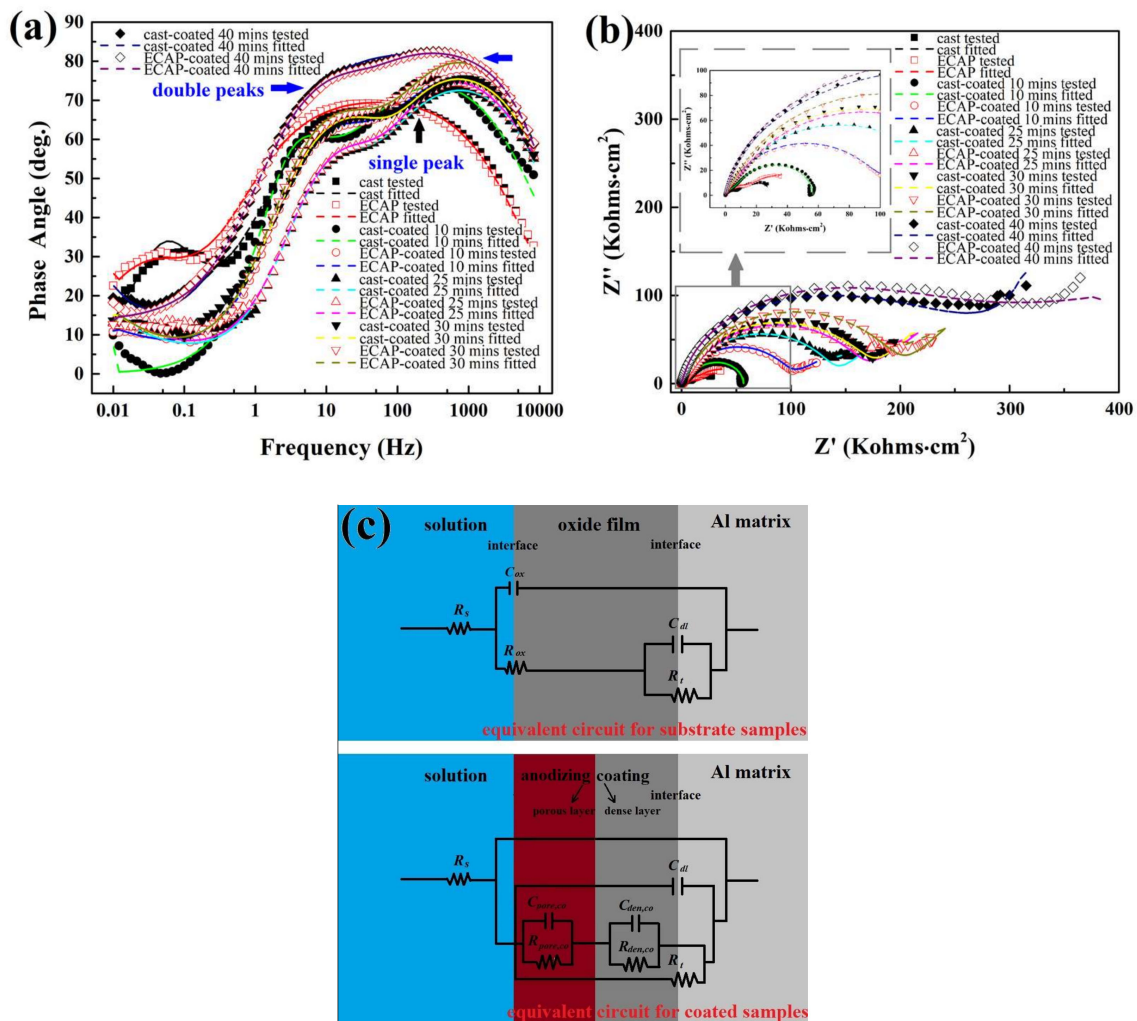


Figure 5. Electrochemical impedance spectroscopy (EIS) Bode plots (a), Nyquist plots (b) of the coated and substrate samples in NaCl solution, and the illustration of equivalent circuits (c).

The $R_s(C_{dl}(R_t(C_{ox}R_{ox})))$ - and $R_s(C_{dl}(R_t((C_{den,co}R_{den,co})(C_{pore,co}R_{pore,co}))))$ -equivalent circuits were used to fit and further interpret the EIS data of the substrate and coated samples, respectively. Meanwhile, the illustration of the equivalent circuits and their physical meanings were shown in Figure 5c, and the fitted EIS parameters are listed in Table 1. In both equivalent circuits, R_s is the electrolyte solution resistance, and C_{dl} and R_t , respectively, represent the double-layer capacitance and charge transfer resistance of the substrate-oxide film interface of the substrate sample and the substrate-coating interface of the coated samples. C_{dl} reflects the surface integrity of the substrate, and R_t can be used to evaluate the corrosion resistance of the substrate. To the equivalent circuit of substrate samples, C_{ox} and R_{ox} represent the capacitance and resistance of the hydrated oxide film of the sample, respectively [21,46]. Note that, the C_{dl} and C_{ox} refers to the high-frequency and low-frequency time constants of the substrate samples of Figure 5, respectively. To the equivalent circuit of coated samples, $C_{den,co}$ and $R_{den,co}$, respectively, represent the capacitance and resistance of the inner dense (barrier) layer, while $C_{pore,co}$ and $R_{pore,co}$, respectively, represent the capacitance and resistance of the outer porous layer [47]. Note that, the C_{dl} , $C_{den,co}$, and $C_{pore,co}$ refer to the high-frequency, middle-frequency, and low-frequency time constants of the coated samples of Figure 5, respectively. As seen in Table 1, all the coated samples showed obviously larger total resistance than that of the substrate samples, indicating high-efficiency anticorrosion performance of the anodizing coating. Meanwhile, greater $R_{den,co}$ and $R_{pore,co}$ values indicate better anticorrosion performance of

the ECAP-coated sample as compared with the cast-coated sample. This phenomenon is particularly obvious in short-term anodizing and gradually weakens as anodizing time increases.

Table 1. Fitted results of the EIS spectra.

Sample	R_s ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	R_t ($\text{k}\Omega \cdot \text{cm}^2$)	C_{ox} ($\mu\text{F} \cdot \text{cm}^{-2}$)	R_{ox} ($\text{k}\Omega \cdot \text{cm}^2$)	$C_{den, co}$ ($\mu\text{F} \cdot \text{cm}^{-2}$)	$R_{den, co}$ ($\text{k}\Omega \cdot \text{cm}^2$)	$C_{por, co}$ ($\mu\text{F} \cdot \text{cm}^{-2}$)	$R_{por, co}$ ($\text{k}\Omega \cdot \text{cm}^2$)
Cast	9.03	22.93	11.12	24.85	18.91	-	-	-	-
ECAPed	10.31	21.65	19.34	16.73	41.14	-	-	-	-
Cast-coated 10 min	12.03	1.6	16.91	-	-	1.06	41.63	1.58	10.93
ECAP-coated 10 min	8.53	0.84	23.50	-	-	0.79	72.74	1.16	34.91
Cast-coated 25 min	11.42	0.82	26.92	-	-	0.63	92.35	0.92	42.24
ECAP-coated 25 min	14.14	0.73	30.22	-	-	0.58	124.33	0.84	53.56
Cast-coated 30 min	9.07	0.67	31.25	-	-	0.52	130.44	0.81	65.89
ECAP-coated 30 min	7.92	0.63	35.41	-	-	0.51	140.12	0.77	69.42
Cast-coated 40 min	12.2	0.62	33.62	-	-	0.50	158.51	0.68	88.41
ECAP-coated 40 min	9.60	0.60	37.37	-	-	0.48	165.63	0.62	94.51

Figure 6 shows the PDP curves of the substrate and coated samples after immersion in 3.5 wt.% NaCl solution for 1 h, demonstrating the electrochemical corrosion behavior of the samples under strong polarization. Electrochemical parameters obtained from the PDP curves are summarized in Table 2, such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and pitting corrosion potential (E_{pit}). Generally, both the substrate and coated samples presented sufficient anodic polarization, indicating the passive ability of the samples in NaCl solution. Compared to the substrate samples, the coated samples had significantly and gradually enhanced anodic polarization, presenting a larger potential range for passive maintaining, higher E_{pit} , less current density for passive maintaining, and less I_{corr} . All the electrochemical parameter data obtained from the PDP curves proved the excellent and gradually enhanced anticorrosion performance of the anodizing coating with increased anodizing duration. Meanwhile, at all anodizing times, the ECAP-coated sample presented better corrosion resistance than that of the cast-coated sample.

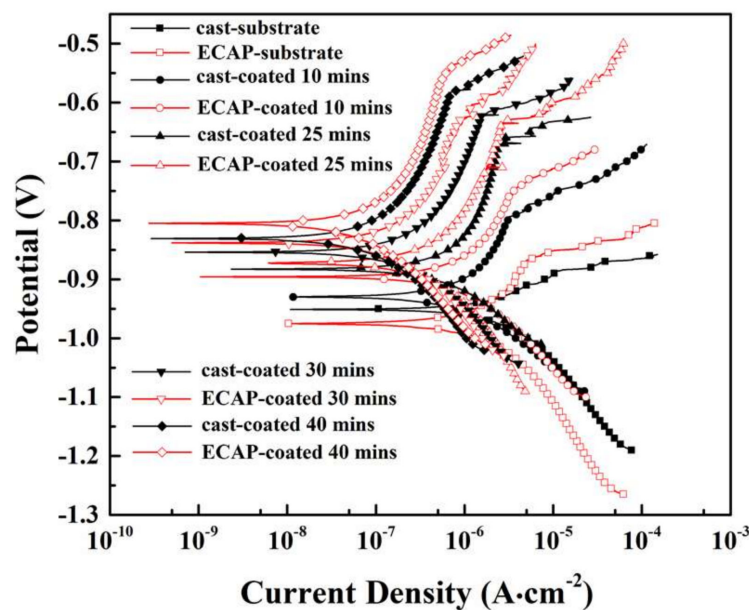


Figure 6. Potential dynamic polarization curves of the coated and substrate samples in NaCl solution.

Table 2. Electrochemical parameters of the coated and substrate samples obtained from the potentiodynamic polarization (PDP) curves.

Sample	E_{corr} (V)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{pit} (V)
Cast Substrate	−0.950	2.682	−0.885
ECAP Substrate	−0.975	2.261	−0.870
Cast-Coated 10 min	−0.930	1.473	−0.795
ECAP-Coated 10 min	−0.897	1.075	−0.750
Cast-Coated 25 min	−0.883	0.744	−0.660
ECAP-Coated 25 min	−0.872	0.556	−0.631
Cast-Coated 30 min	−0.855	0.273	−0.622
ECAP-Coated 30 min	−0.837	0.167	−0.587
Cast-Coated 40 min	−0.830	0.105	−0.580
ECAP-Coated 40 min	−0.804	0.08	−0.534

3.3. Effect of UFG Al Matrix on Accelerated Anodizing Reaction

Generally, the electrochemical process of the anodizing reaction is heavily dependent on the electrolyte solution and the applied electrical parameters, such as anodizing voltage, current density, and applied waveform [31–33]. In addition, the internal factor (e.g., the substrate microstructure) also plays a critical role in the formation and performance of coatings [48]. The coverage of the newly generated anodizing coating also plays a barrier role in the direct contact of electrolyte and substrate metal because of its dense layer and high resistance and greatly influences the subsequent anodizing reaction [49,50]. In view of the parallel circuit anodizing system and the total constant input current of this study, a real-time competition relationship was shown between the cast and ECAPed samples when obtaining the anodizing current density, and the sum of the anodizing currents of the two samples was always kept constant. Thus, the anodizing reactions of the cast and ECAPed samples were dominated by the synergistic effect of substrate microstructure and the newly generated anodizing coating.

Figure 7 shows the anodizing current density of the cast and ECAPed samples in the anodizing reaction system. The two samples experienced exactly the opposite anodizing current evolution: the cast sample experienced gradually increased anodizing current, while the ECAPed sample experienced decreased anodizing current. At the beginning of the anodizing, the ECAPed sample had nearly five-times higher anodizing current than the cast sample. At this stage, the newly formed anodizing coating was thin, and its blocking effect to the anodizing reaction was limited. Thus, in this situation, the substrate microstructure played a dominant role in the anodizing reaction. The obvious larger anodizing current and more intense anodizing reaction of the ECAPed sample should be closely related to its special ECAP-processed microstructure. With increasing anodizing duration, the blocking effect of the generated anodizing coating increased dramatically, while the effect of the substrate microstructure on the anodizing reaction decreased, leading to rapid decrease in the anodizing current of the ECAPed sample. In view of the competitive relationship and constant total input current, the increased anodizing current of the cast sample was stimulated by the decreased anodizing current of the ECAPed sample, leading to the opposite anodizing current evolution of the cast and ECAPed samples. After anodizing for 10 min, the anodizing current of the cast sample was slightly higher than the ECAPed sample. After that, the anodizing current of the cast sample experienced slow growth and stabilization, while the ECAPed sample experienced slow decline and stabilization.

Shown in Figure 7, the area formed by the anodizing current evolution curve and the time axis was used to roughly judge the mass of the anodized reactants, also reflecting the evolution of the coating thickness obtained by the reaction. Judging from the estimation of the area before 10 min of anodizing, the ECAP-coated sample was obviously larger than the cast-coated sample, which is fully consistent with the coating thickness shown in Figure 4e. With increasing anodizing duration, the gap in area between the cast-coated and ECAP-coated samples gradually narrowed. These area changes are consistent with the evolution of coating thickness shown in Figure 4.

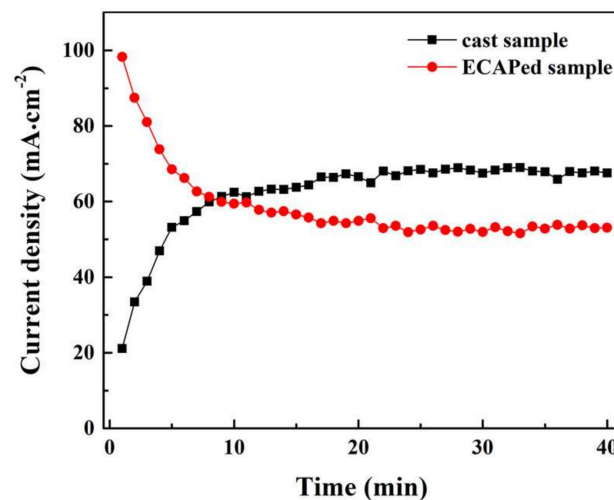


Figure 7. Evolution curves of the individual anodizing current density of cast and ECAPed samples.

Because the Al matrix is involved in the anodizing reaction and plays a dominant role early in the anodizing process, the accelerated anodizing process of the ECAPed sample should have a close relationship with the special microstructure characteristics of the UFG substrate. EBSD and TEM characterization of the ECAPed sample were conducted to further understand the key microstructural characteristics leading to the different coating formation processes. As shown in Figure 8 (EBSD inverse pole figure (IPF) mappings) and Figure 9 (grain-size distributions), the cast sample had typical coarse grains with an average grain size of 1.47 mm. The multi-pass ECAP process greatly refined the microstructure of the pure Al, achieving typical UFGs with an average grain size of about 1.52 μm . As generally believed, the formation of UFGs in many ECAP-processed metals results from the continuous evolution of dislocations. Sufficient input strain stimulates the discrete dislocations to form tangles, cells, walls, subgrain boundaries, and grain boundaries to finally achieve dramatic grain refinement [51–54]. Because of the high stacking-fault energy of the Al crystals, dynamic recrystallization readily occurs in the deformed Al matrix, leading to low intragranular dislocation density and restricted grain refinement [55,56]. In our study, the pure Al was ECAP-processed at room temperature 16 passes to reach the equilibrium grain size via dynamic recrystallization due to the severely accumulated strain. As shown in the TEM micrograph (Figure 10a), clean UFGs formed in the ECAPed sample matrix, and only limited dislocation walls and subgrain boundaries were seen in the deformed UFG Al grains (Figure 10b). Based on the EBSD and TEM characterization, one can infer that the ECAPed sample had the typical UFG microstructure with profound dynamic recrystallization.

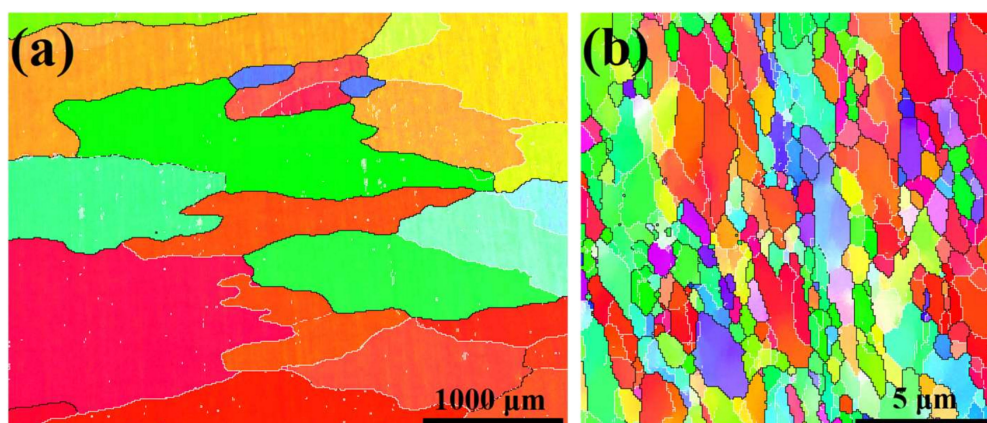


Figure 8. Electron backscattered diffraction (EBSD) inverse pole figure (IPF) mapping of the substrate sample: (a) cast sample and (b) ECAPed sample.

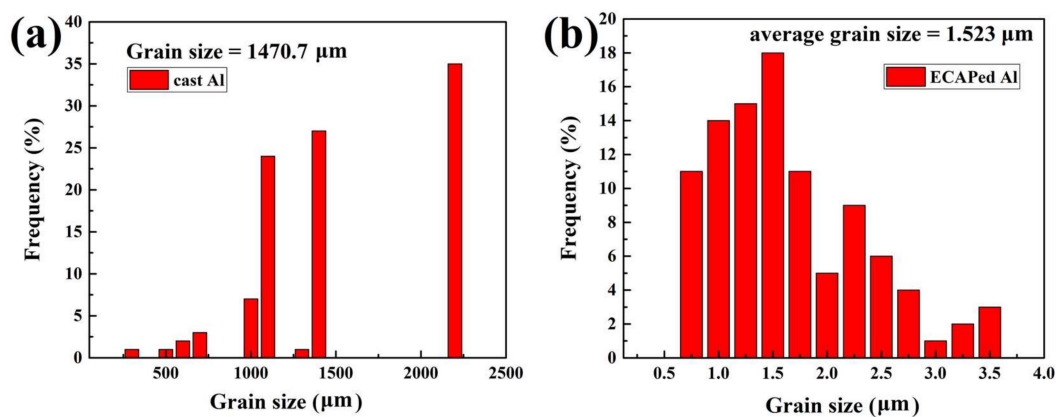


Figure 9. Grain-size distribution of the substrate sample: (a) cast sample and (b) ECAPed sample.

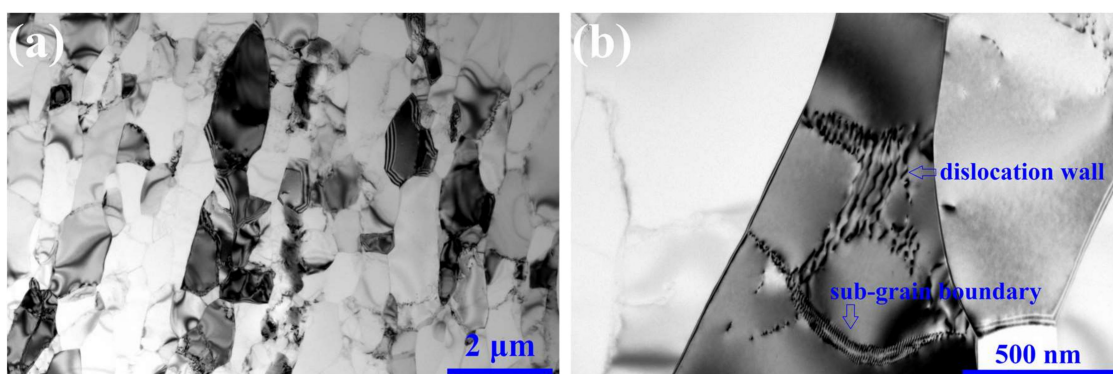


Figure 10. TEM micrographs of ECAPed sample: (a) grain size and morphology with lower magnification and (b) intragranular microstructure with higher magnification.

The UFGs with extremely higher volume fraction of grain boundaries in the ECAPed sample significantly changed the anodizing coating process from both thermodynamics and kinetics perspectives. First, the stored higher grain boundary energy offered a much higher driving force to the initial coating nucleation on the ECAPed sample. From a kinetics perspective, grain boundaries acted as shortcuts for atom diffusions for the coating formation. This is the dominant reason explaining the significantly higher anodizing current of the ECAPed sample in the beginning of anodizing, as shown in Figure 7. Judging from the more intense initial anodizing reaction, faster initial coating thickening, and much earlier porous-layer formation in the ECAP-coated sample, one can deduce that the anodizing process of the ECAPed sample was accelerated by the UFG substrate.

As the anodizing reaction continued, the faster formation of the anodizing coating (dense layer) built up a barrier for diffusion of electrolyte and metallic ions, and the anodizing reaction gradually transitioned from nucleation control to diffusion control. In other words, the thermodynamic advantage in the ECAPed sample was offset by its newly formed thicker coating. Therefore, an immediate rapid drop and an increase in anodizing current were seen in the ECAPed and the cast samples, respectively. When the anodizing reaction continued to proceed, the thermodynamic advantage no longer played a decisive role in the reaction rate, and the diffusion started to govern the reaction rate as the coating became thicker. In this situation, the ECAPed sample presented less anodizing current than the cast sample due to the lower diffusion caused by its newly formed thicker coating. However, because of the more total reaction, the ECAP-coated sample always obtained a relatively thicker coating for the entire anodizing duration compared to the cast-coated sample.

4. Conclusions

In summary, UFG pure Al was achieved via a 16-pass ECAP process at room temperature. The cast and ECAPed samples were simultaneously anodized in 20 wt.% sulfuric acid electrolyte via a parallel circuit under a constant total input current. The evolution of the coating microstructure and corrosion resistance during different anodizing durations were systematically investigated. The influence mechanism of UFG substrate on the anodizing reaction of pure Al was revealed. The main conclusions are as follows:

Competition existed between the cast and ECAPed samples in obtaining the quota of the anodizing current. The cast sample experienced gradually increased anodizing current, while the ECAPed sample experienced decreased anodizing current. Early in the anodizing duration, the ECAPed sample had a more intense initial anodizing reaction, faster initial coating thickening, and much earlier porous-layer formation compared to the cast sample. However, the ECAPed sample presented less anodizing current than the cast sample later in the anodizing duration. Because of the more total reaction, the ECAP-coated sample always kept a relatively thicker coating during the entire anodizing duration.

At the beginning of the anodizing, the reaction was controlled by the coating nucleation. In this stage, benefited by the higher volume fraction of grain boundaries of the UFG substrate, the ECAPed sample had the obvious thermodynamic advantage of a more intense anodizing reaction and faster coating thickening. As the anodizing reaction continued, the newly formed thicker coating of the ECAP-coated sample greatly hindered the diffusion process, which weakened the thermodynamic advantage and decreased the current density of the ECAPed sample. However, throughout the entire anodizing duration, the anodizing process of the ECAPed sample was accelerated by its UFG substrate.

Because of the sufficient anticorrosion efficiency of the anodizing coating, all the coated samples presented obviously better corrosion resistance in the NaCl solution compared to the substrate samples, and their corrosion resistance improved with increasing anodizing duration. Due to the thicker anodizing coating and better corrosion resistance of the UFG substrate, the ECAP-coated sample had better corrosion resistance compared to the cast-coated sample in each tested anodizing duration.

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