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Corrosion behavior of MoS₂-incorporated PEO coatings prepared on Al alloy

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Aluminum (Al) alloys are used widely in the automotive and aerospace industries, but their corrosion resistance is insufficient in long-term service, particularly in a high-salinity environment. The incorporation of molybdenum disulfide (MoS₂) particles into plasma electrolytic oxidation (PEO) coatings formed on an aluminum alloy was investigated in this work. After oxidation, the coatings were investigated by a series of structural, morphological and electrochemical corrosion tests to understand the effect of molybdenum disulfide addition to the base electrolyte. The phase compositions and surface morphology of coatings were analyzed through X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM), respectively. The XRD results showed that all coatings were primarily composed of α -aluminum oxide (α -Al₂O₃), γ -aluminum oxide and molybdenum disulfide phases. The FESEM observations indicated that molybdenum disulfide particles were successfully incorporated in the ceramic coating and the apparent porosities decreased with increasing molybdenum disulfide concentration. The electrochemical corrosion tests indicated that the amount of coating porosity decreased and the corrosion current density decreased from 79.6 μ A/cm² in the bare aluminum alloy to 58.1 and 30.1 μ A/cm² in the PEO coatings without and with the molybdenum disulfide additive, respectively. This behavior could be attributed to the beneficial effect of the molybdenum disulfide particles, which might play an important role in blocking micropores and microcracks.

Notation

CPE _i	constant-phase element (CPE) of the inner layer
CPE _o	CPE of the outer layer
d	crystallite size (nm)
E_{corr}	corrosion potential
i_{corr}	corrosion current density
j	imaginary number
P	porosity percentage of the coating
R_i	inner layer resistance
R_o	outer layer resistance
R_p	polarization resistance
R_{ps}	corrosion resistance of the substrate
R_s	solution resistance
Y, n	frequency-independent parameters
Z	impedance of the CPE
β	full width of the peak at half maximum intensity (rad)
β_a	anodic Tafel slope
β_c	cathodic Tafel slope
ΔE_{corr}	potential corrosion difference between the substrate and the coating
θ	diffraction angle (°)

λ	wavelength of the incident X-ray beam (nm)
ω	angular frequency

1. Introduction

Aluminum (Al) and its alloys have been used widely in various fields of engineering, such as aircraft, electronic, automobile and architectural engineering, owing to the combination of light weight and high specific strength. However, despite having many advantages, aluminum alloys still have some limitations such as low hardness, bad wear resistance, high friction coefficient and susceptibility to corrosion.¹ Several reports have revealed that surface treatment methods such as conventional anodizing,² physical vapor deposition,³ chemical vapor deposition⁴ and sol-gel method⁵ can be used to improve the corrosion behavior and surface properties of aluminum alloys.

As one of the effective surface modification methods, plasma electrolytic oxidation (PEO) can improve the hardness, wear resistance and corrosion resistance of the surface of metals. The PEO process is based on the anodization of metals (aluminum,⁶ magnesium (Mg),⁷ titanium (Ti),⁸ zirconium (Zr),⁹ tantalum (Ta),¹⁰

niobium (Nb),¹¹ silicon (Si)¹², as well as of their alloys, in an aqueous solution at an applied potential that is greater than the breakdown voltage of the original oxide film. In PEO, the sample is placed inside an electrolyte (often alkaline), and due to the high voltage applied, local electrical discharge occurs on the sample surface, which increases the surface temperature of the substrate.¹³ During the anodizing process, a porous coating is produced at the sample surface, which has a low corrosion resistance.⁶ PEO coatings consist of two sublayers. The outer layer contains γ -aluminum oxide (γ -Al₂O₃) with hardness of about 500–1000 HV and has weak mechanical features (particularly in the case of wear),¹⁴ and the inner layer is between the base metal and the porous layer and contains both γ -aluminum oxide and α -aluminum oxide. Because of the presence of α -aluminum oxide, the hardness of this layer is about 900–2000 HV and it has good mechanical features.¹⁵ Therefore, the dense inner layer makes the coating produced by the PEO method exhibit a better corrosion behavior than that produced by anodizing.^{16–18} The coating properties depend on technical parameters such as processing time, substrate composition, electrolyte properties and electrical regime (direct current (DC), alternating current (AC) and bipolar). Meanwhile, electrolyte composition plays a very important role, as researchers have been trying to produce composites at the surface of the samples by changing electrolyte compositions.¹⁹

The porosity of PEO coatings permits easy permeation of the aggressive solution into its interface. However, in order to obtain coatings with a more improved corrosion behavior, a few investigations have been carried out to form composite coatings during the PEO process by adding nano- or micro-sized particles into the PEO electrolytes for the treatment of metals.²⁰ Recent studies have tried to add particles, such as aluminum oxide,²¹ zirconium (IV) oxide (ZrO₂),²² titanium (IV) oxide (TiO₂),²³ zinc oxide (ZnO),²⁴ graphite²⁵ and diamond,²⁶ into PEO electrolytes to improve the corrosion resistance and mechanical properties of PEO coatings. These added particles can be incorporated into the PEO coatings during the processing, which will result in obtaining a compact coating.

To date, molybdenum disulfide (MoS₂) particles have been widely used in chemical conversion coatings with excellent corrosion resistance.²⁷ In recent years, very limited studies have been reported on the addition of molybdenum disulfide into electrolytes that finally resulted in the enhancement of PEO coating characteristics. Among these published studies, the work by Chang *et al.*²⁸ studied the effect of molybdenum disulfide particles with various concentrations on the tribological properties of a PEO-coated sample on a Ti–6Al–4V alloy, and they observed that the electrolyte with 4 g/l molybdenum disulfide additive resulted in a coating with the highest adhesion and wear performances. Lou *et al.*²⁹ prepared a PEO coating on an AZ31 magnesium alloy by adding molybdenum disulfide particles into the electrolyte, and the results indicated that molybdenum disulfide was successfully incorporated into the PEO coating and resulted in excellent corrosion and wear resistance. To the best of

the authors' knowledge, the addition of molybdenum disulfide particles into a PEO electrolyte for aluminum alloys has not yet been discussed in the literature. Therefore, in the present study, molybdenum disulfide-incorporated oxide layers were formed on an aluminum alloy through the PEO method in aluminate/phosphate (PO₄^{3−})-based alkaline electrolytes with different amounts of molybdenum disulfide powder as an additive in order to obtain possible anticorrosion coatings.

2. Materials and method

In the present study, the 1050 aluminum alloy was used as a substrate. The chemical compound contained 0.05% copper (Cu), 0.03% magnesium, 0.3% iron (Fe), 0.04% manganese (Mn), 0.05% zinc (Zn) and 0.03% titanium and the rest was aluminum. The aluminum samples were cut into specimens measuring 25 × 20 × 4 mm. The surface of the samples was polished with waterproof silicon carbide (SiC) to grade 1800. In the next step, the samples were cleaned in pure ethanol by using the ultrasonic method and then were washed with distilled water and dried in air before the PEO process was carried out. For the PEO process, the prepared electrolyte was placed into a stainless-steel container, which served as the counter electrode (cathode), and the working electrode (aluminum alloy substrate) was immersed in the electrolyte to serve as the anode. The surface treatment were conducted on a 20 kW (maximum voltage of 800 V and maximum current of 3 A) DC homemade power source. Four different electrolytes consisting of sodium aluminate (NaAlO₂; 99.9%, Merck Co., Germany), potassium hydroxide (KOH; 99.9%, Merck Co., Germany), sodium pyrophosphate (Na₄P₂O₇; 99.9%, Merck Co., Germany) and molybdenum disulfide (99.9%, 4–5 μ m, Alpha-Aldrich Co., Germany) were used in this study. The characteristic breakdown voltages of the used electrolytes are briefly listed in Table 1. Prior to the PEO process, the aqueous molybdenum disulfide suspension was stirred using a magnetic stirrer for 1 h and then sonicated using an ultrasonic bath cleaner for 2 h to prevent settling and agglomeration of the molybdenum disulfide particles. The conductivity of the electrolytes was measured using a Mettler Toledo InLab 730 probe (Switzerland), and the pH value was measured using a Metrohm pH meter (model 691, Switzerland).

The phase composition of the coatings was studied by X-ray diffraction (XRD) measurement in parallel-beam geometry using an X-ray diffractometer (Ultima IV, Rigaku, Japan) operated at 40 kV and 30 mA, equipped with an X-ray source emitting copper K α radiation. The scans were acquired within the 2 θ range from 20 to 80° at a scan speed of 1°/min and at a step size of 0.05°. The average thickness of the coatings was measured five times for each specimen with a Phynix (FN 1.5, Germany) thickness meter to take the average value with the standard deviations. The average roughness of the coatings was measured by using a portable Kett roughometer (LH-900J, Japan). The surface microstructure of the PEO coatings and the microstructure of the polished cross-section mounted in epoxy resin (Akasol, Denmark) were studied using field-emission scanning electron microscopy

Table 1. Identification codes of the samples with their respective electrolyte compositions, pH, conductivities and breakdown voltages

Sample code	Electrolyte composition of PEO coating	pH	Conductivity: mS/cm	Breakdown voltage: V
S0	2.9 g/l potassium hydroxide + 0.64 g/l disodium dihydrogen diphosphate (Na ₂ H ₂ P ₂ O ₇) + 0.34 g/l sodium aluminate	12.13	25.41	580
S1	2.9 g/l potassium hydroxide + 0.64 g/l disodium dihydrogen diphosphate + 0.34 g/l sodium aluminate + 0.5 g/l molybdenum disulfide	11.46	23.55	637
S2	2.9 g/l potassium hydroxide + 0.64 g/l disodium dihydrogen diphosphate + 0.34 g/l sodium aluminate + 2.75 g/l molybdenum disulfide	11.42	21.74	675
S3	2.9 g/l potassium hydroxide + 0.64 g/l disodium dihydrogen diphosphate + 0.34 g/l sodium aluminate + 5 g/l molybdenum disulfide	11.43	19.28	720

(FESEM; Tescan Mira 3, Czech Republic). The mounted samples were sputter-coated with a layer of gold (Au) to reduce charging further. The average value of the porosity was estimated by analyzing the FESEM images using the ImageJ software. The elemental composition of the oxide coatings was analyzed using an energy-dispersive X-ray spectrometer (EDS; Oxford, UK) attached to the FESEM. Tensile tests were carried out using a WE-600 hydraulic universal material-testing machine (Jinhua Mingke Tool Equipment Co., Ltd, China) according to the standard HB 5476-1991.³⁰ The tensile rate was 2 mm/s, and the ultimate tensile strength was determined based on the average of at least three different tensile specimens. The electrochemical behavior of the samples was examined using a potentiostat (EG&G, model M263A, USA) in 3.5 wt% sodium chloride (NaCl) solution. A conventional three-electrode electrochemical cell, with platinum (Pt) foil as the auxiliary electrode, a saturated calomel electrode (SCE) with a Haber–Luggin capillary as the reference electrode and the sample as the working electrode was used. In order to stabilize the open-circuit potential, all electrochemical tests were performed after immersion in the 3.5 wt% sodium chloride solution (pH 6.5) at room temperature for 10 h. The AC frequency was extended from 1000 kHz to 100 MHz, with a 10 mV peak-to-peak sine wave being the excitation signal. The obtained electrochemical impedance spectroscopy (EIS) plots were analyzed using the ZView (version 3.1) software and were fitted according to appropriate equivalent circuit models with chi-squared values between 0.01 and 0.001. Polarization studies were carried out at a sweep rate of 1 mV/s and were analyzed with the CorrView software.

3. Results and discussion

In the XRD patterns of Figure 1, α -aluminum oxide (Joint Committee on Powder Diffraction Standards (JCPDS) card number 071-1125), γ -aluminum oxide (JCPDS card number 010-0425) and molybdenum disulfide phases (JCPDS card number 75-1539) were observed. It has been reported that rapid cooling of molten oxide when in contact with the cold electrolyte during the PEO process leads to the generation of the γ -aluminum oxide phase on the surface of the oxide coatings.³¹ In addition, X-rays can easily penetrate into the aluminum substrate, and aluminum-related peaks appeared in the XRD patterns because of the porosity and thinness of the PEO coatings. The molybdenum

disulfide phase was detected in sample S2 and S3 coatings, and the amount of this phase in coating S3 was the highest. Thus, at 2.75 and 5.00 g/l concentrations of molybdenum disulfide in electrolyte composition, the particles diffused into the sample and the composite was developed on the aluminum alloy substrate. The coating crystallite size of the monoclinic phase of α -aluminum oxide was calculated using Scherrer's formula³² as given in the following equation

$$1. \quad d(\text{nm}) = \frac{0.9\lambda}{\beta \cos \theta}$$

d represents the crystallite size in nanometers; λ is the wavelength of the incident X-ray beam in nanometers; θ is the diffraction angle in degrees; and β represents the full width of the peak at half maximum intensity in radians. The crystallite sizes of the α -aluminum oxide phase of coatings S0, S1, S2 and S3 were 57.12, 55.71, 41.26 and 33.65 nm, respectively.

The average thickness and roughness of PEO coatings are shown in Figures 2(a) and 2(b). As the molybdenum disulfide concentration increased, the thickness of the coatings increased. Higher coating thickness was observed for the molybdenum disulfide particle-incorporated composite coatings than the base coating. The order regarding coatings thickness is as follows: S3 > S2 > S1 > S0. As mentioned in Table 1, the voltage was higher, which led to the more acute microarc discharges. Hence, the reactions were stronger in the PEO process, and the coating formation rate increased. As seen in Figure 2(b), the surface roughness decreased with increasing molybdenum disulfide concentration. This indicates that the incorporation of particles into the coating reduced the coating roughness by filling the pores formed by plasma discharges, suggesting that the addition of molybdenum disulfide decreases the irregularities of the surface. Bordbar-Khiabani *et al.*²⁴ incorporated zinc oxide nanoparticles into the oxide layer produced over an AZ91 magnesium alloy by PEO and observed a decrease in the roughness and porosity of the coatings as a result of the deposition of nanoparticles within their micropores.

The FESEM surface morphologies of coatings formed on aluminum alloy specimens at different concentrations of

Figure 1. XRD patterns of coated samples treated in electrolytes containing different concentrations of molybdenum disulfide particles

molybdenum disulfide particles are shown in Figure 3. The PEO coating without molybdenum disulfide showed a typical porous structure with some bulges and cracks on the surface.^{14,15} The micropores were formed by the molten oxide and gas bubbles thrown out of the micro-discharge channels. The microcracks were resulted from the thermal stress due to the rapid solidification of the molten oxide in the relatively cool electrolyte.^{12,14} As can be seen from Figures 3(b)–3(d), the surface of the coatings containing molybdenum disulfide particles was smoother in comparison with the convolute surface of the coating obtained in the base electrolyte without particles (Figure 3(a)). Moreover, the number and size of micropores in the coatings generated in the electrolytes containing the molybdenum disulfide additive apparently reduced. Analysis of

the obtained FESEM images performed using the ImageJ software allowed estimation of the coating porosity. The coatings fabricated in the base electrolyte had a maximal porosity of 23.4%. Samples S1, S2 and S3 had porosities equal to 18.5, 8.2 and 4.6%, respectively. It has been revealed that with the introduction of the particles into the growing PEO coating, the surface porosity decreased.^{21–25}

The cross-sectional morphology and the corresponding EDS spectra of sample S1 are shown in Figure 4. As can be seen, the thickness of the simple PEO coating was estimated to be 9 μm. This might be attributed to the cross-sectional morphologies and the corresponding typical elemental distribution across the S2 and S3 coatings, as presented in Figures 5 and 6, respectively. It can be seen that the thickness of the S2 and S3 coatings was about 13 and 27 μm, respectively. EDS map analysis of the cross-sections showed that aluminum, oxygen (O), molybdenum (Mo) and sulfur (S) were dispersed across the coatings.²⁴ Both of the PEO coatings without and with incorporated molybdenum disulfide occupied a bilayered structure that consisted of an outer porous layer and a compact inner barrier layer.³³ The figures clearly show that micrometer-sized particles as white spots and aggregates of these particles existed inside the oxide layer, when molybdenum disulfide particles were added to the electrolyte. The EDS map analysis confirmed the particles inside the oxide layer to be molybdenum disulfide. Such molybdenum disulfide particles kept absorbing during the growth of the oxidation layer in the PEO process, which allowed the incorporation of molybdenum disulfide particles inside the oxide layer. As shown by the EDS elemental maps, the distribution of the elements molybdenum and sulfur in the outer layer was higher than that in other regions. It should be noted that the molybdenum disulfide particles within the substrate and the inner layer, shown by the red arrows in Figures 5(a) and 6(a), could be caused by the spread of molybdenum disulfide particles in the process of sample surface preparation.³⁴ The chemical distribution of the PEO coatings as detected by EDS analysis is shown in Table 2. With the increase in molybdenum disulfide addition, the content of molybdenum and sulfur elements in the PEO coatings increased. The cross-sectional morphology of the PEO coatings in Figures 5 and 6 shows that the PEO coating was integrated firmly into the aluminum alloy substrate by sintered interlocking, and the average tensile strengths were 37.13 ± 6.61 and 64.85 ± 8.34 MPa for samples S0 and S3, respectively, suggesting the enhanced bonding strength of the coating with the incorporation of molybdenum disulfide particles. The outstanding bonding strength of the PEO coating has also been reported by other researchers.³⁵

Potentiodynamic polarization curves of the examined samples are shown in Figure 7(a). The related parameters including the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) and anodic and cathodic Tafel slopes (β_a and β_c) were determined from the polarization curves using the Tafel extrapolation method. The polarization resistance (R_p) was calculated from the Stern–Geary equation⁴¹

Figure 2. Average (a) thickness and (b) surface roughness of the coated samples treated in electrolytes containing different concentrations of molybdenum disulfide particles

Figure 3. FESEM surface morphology of the PEO-coated samples: (a) S0; (b) S1; (c) S2; (d) S3

$$2. \quad R_p = \frac{\beta_a \times \beta_c}{2.3 \times i_{corr} \times (\beta_a + \beta_c)}$$

The results of the polarization test are tabulated in Table 3. Based on these electrochemical parameters, it was found that with the increase in molybdenum disulfide addition into the electrolytes, the corrosion potential of the PEO-coated samples shifted positively first and then shifted negatively, while the corrosion current of the coated samples decreased. A lower i_{corr} and a

positive E_{corr} indicate that the coating provided better corrosion resistance. Surface porosity and cracks are important influencing factors on the corrosion properties of PEO coatings.⁴² Equation 3 clarifies the relation between the porosity percentage of the PEO coatings and the electrochemical parameters acquired from the potentiodynamic polarization curves^{24,43}

$$3. \quad \%P = \left(\frac{R_{ps}}{R_p} \right) \times 10^{-|\Delta E_{corr}/\beta_a|} \times 100\%$$

Figure 4. (a) FESEM cross-sectional morphology of sample S1; (b) EDS spectrum obtained by EDS analysis of the specified area in (a)

Figure 5. (a) FESEM cross-sectional morphology and (b) EDS mapping of sample S2

Figure 6. (a) FESEM cross-sectional morphology and (b) EDS mapping of sample S3

Table 2. Chemical composition of the specimens as measured by the EDS point analysis

Sample	Aluminum: wt%	Oxygen: wt%	Molybdenum: wt%	Sulfur: wt%	Gold: wt%
S0	55.32	29.96	0.00	0.00	14.72
S1	50.84	33.91	0.00	0.00	15.24
S2	43.49	38.85	3.09	1.85	12.72
S3	41.66	36.40	6.57	4.18	11.19

Figure 7. (a) Potentiodynamic polarization curves of (A) S0, (B) S1, (C) S2, (D) S3 and (E) bare aluminum alloy in 3.5 wt% sodium chloride solution; (b) polarization resistance as a function of the various surface treatments methods in 3.5 wt% sodium chloride solution

where P is the porosity percentage of the coating; R_{ps} and R_p are the corrosion resistances of the substrate and the coating, respectively; β_a is the substrate anodic branch slope; and ΔE_{corr} shows the potential corrosion difference between the substrate and the coating. Usually the corrosive ions in the sodium chloride solution need to pass through the opening defects such as the micropores and cracks of PEO coatings, in particular the micropores or cracks in the barrier layer, in order to corrode the substrate.⁴⁴ With the placement of the related parameters from Table 3 into Equation 3, decreasing coating porosity with the incorporation of molybdenum disulfide particles is proved. Sample S3 had the lowest porosity percentage (8.74%) and the lowest corrosion current density (30.1 $\mu\text{A}/\text{cm}^2$) and therefore the highest polarization resistance (114.9 $\text{k}\Omega\text{cm}^2$). The shift of E_{corr} to negative values for sample S3 is mainly attributed to the high conductivity of molybdenum disulfide particles (electrical resistivity is equal to $\sim 10^{-3}\Omega\text{m}^{27}$). Meanwhile, the coating containing particles of the conducting material continued to perform protective functions with decreasing porosity and

increasing thickness. For comparison, the several R_p values of the various surface treatments methods of aluminum alloys in 3.5 wt% sodium chloride solution were plotted together with respect to the types of the surface treatments that were incorporated into the oxide film as shown in Figure 7(b). As seen, the aluminum oxide/molybdenum disulfide coating prepared in the present study exhibited proper corrosion resistance compared with the other cases.^{36–40}

Figure 8 shows the Nyquist, Bode module and Bode phase plots for the oxide layer in 3.5 wt% sodium chloride solution. The Nyquist plots in Figure 8(a) show that the diameter of the semicircle in the high-frequency range for the sample formed under S3 conditions was larger than those under other conditions, suggesting that a less porous oxide layer was formed on the surface of the aluminum alloy. As can be seen in the Bode module plots (Figure 8(b)), the highest impedance module ($|Z|$) is related to sample S3 at low frequencies. Thus, it is concluded that the best obtained corrosion behavior was that of the coating

Table 3. Electrochemical parameters related to the potentiodynamic polarization of the bare and PEO-coated aluminum alloys

Sample	E_{corr} : mV	i_{corr} : $\mu\text{A}/\text{cm}^2$	β_a : mV/decade	β_c : mV/decade	R_p : $\text{k}\Omega\text{cm}^2$	P : %
Bare aluminum alloy	-776.6	79.6	113.4	118.3	30.5	—
S0	-767.0	58.1	314.8	318.6	114.9	4.14×10^{-2}
S1	-782.3	57.7	152.1	165.9	136.3	1.12×10^{-2}
S2	-802.6	47.9	298.5	271.5	479.5	1.89×10^{-4}
S3	-781.8	30.1	377.2	368.4	1360.0	4.95×10^{-4}

Figure 8. (a) Nyquist, (b) Bode module and (c) Bode phase plots of PEO-coated aluminum alloy in 3.5 wt% sodium chloride solution

produced at a molybdenum disulfide concentration of 5 g/l (sample S3). The Bode phase plots (Figure 8(c)) for the PEO-treated sample showed a gradual increase in the phase angle from near -10° at the highest frequency, approached -80° at intermediate frequencies and remained constant between 10^2 and 10^{-1} Hz. This behavior confirmed that the composite oxide film over the surface was insulative and protective in nature.²⁴

The equivalent circuit model was applied to simulate the EIS experimental data. Taking into account the microstructure of the oxide layers, an equivalent circuit model is proposed to explain the corrosion behavior, as shown in Figure 9, and the corresponding fitting results are represented as a solid line in Figure 8. In order to include a surface inhomogeneity factor and a possible diffusional factor, a more general constant-phase element (CPE) was used instead of a rigid capacitive element.⁴⁵ The CPE is defined by the following equation

$$4. \quad Z_{\text{CPE}} = 1/[Y(j\omega)^n]$$

where Z is the impedance of the CPE; j is an imaginary number; ω is the angular frequency; and Y and n are frequency-independent parameters. The value of n ranges between 0 and 1. If $n = 0$, the CPE is a pure resistor; if $n = 1$, the CPE is a pure

Figure 9. Equivalent circuits for fitting the impedance data for the PEO-coated aluminum alloy

capacitor. The equivalent circuit consists of the solution resistance (R_s) and two CPEs of the coating – namely, the outer layer resistance (R_o) of the PEO coating in parallel with the constant-phase element CPE_o and the inner layer resistance (R_i) of the PEO coating in parallel with CPE_i .^{25,29,43} The corresponding values of the equivalent elements are listed in Table 4. It can be seen that R_i

is higher than R_o for all coatings, indicating that the inner layer plays a main role in providing corrosion resistance. This finding is in a good agreement with the literature.^{43,44} In Table 4, the R_o value decreases from 7.71 kΩ cm² for sample S3 to 1.17 kΩ cm² for sample S0, which indicates that the outer layer of sample S3 acts as a much better barrier to penetration of the solution to the aluminum alloy substrate; hence, it has much higher corrosion resistance compared with sample S0, in accordance with the results of potentiodynamic polarization tests (Figure 7(a)). The n_o value of the composite coating is higher than that of the simple PEO coating. Generally, increasing this value means developing a smoother surface with lower roughness with deposition of molybdenum disulfide particles, which confirms the roughness measurements in Figure 2(b).⁴⁴

Schematic illustrations of the corrosion mechanism of the PEO and molybdenum disulfide-incorporated PEO coatings are shown in Figure 10. During the PEO processing, molybdenum disulfide particles could be trapped into the coating; they are particularly more easily embedded in the inner layer, making the coating more compact and thicker.²² It has been reported that oxide defects – for example, surface porosity and deep cracks – and the oxide thickness can affect the corrosion resistance of PEO-grown oxide layers.⁴³ The diffusion of corrosive agents such as chloride (Cl⁻) ions through the micropores and microcracks of the coatings is a prerequisite for beginning the corrosion of the aluminum alloy substrate. As seen in Table 3, the coatings with molybdenum disulfide particles had the lowest pore density. A PEO coating with few defects can restrain the penetration of chloride ions. This

behavior indicates that molybdenum disulfide particles can act as a physical barrier to inhibit the penetration of deleterious species to the coating/substrate interface. Moreover, as seen in Figure 2(a), the thickness of the oxide layer increased due to the incorporation of molybdenum disulfide particles into the electrolyte composition. Diffusion of corrosive ions in the coating with molybdenum disulfide reduced toward the substrate, which could be a reason for the increased corrosion resistance of the molybdenum disulfide-incorporated coatings compared with that of the PEO coating.^{24,46}

4. Conclusion

Aluminum oxide/molybdenum disulfide composite coatings on an aluminum alloy were prepared by using the PEO method in aluminate-based electrolytes with molybdenum disulfide particles. When the concentration of molybdenum disulfide was 5 g/l, the coating had superior corrosion resistance. XRD analysis showed that molybdenum disulfide particles were distributed uniformly in the PEO coating and did not react with other elements during the PEO process. The thickness and roughness characteristics indicated an inverse behavior; in this case, a remarkable increase in the thickness and a reduction related to the surface roughness of the coatings were observed. Potentiodynamic polarization and EIS tests showed that molybdenum disulfide particles improved the corrosion performance of the coatings, in comparison with the coatings treated for the same time but without molybdenum disulfide. Importantly, incorporation of molybdenum disulfide particles into the PEO coating affords a higher degree of coating compactness, giving rise to superior corrosion resistance in

Table 4. EIS simulated data of the bare and PEO-coated aluminum alloys in the equivalent circuits

Sample	R_s : Ω cm ²	(CPE-T) _i : (S/cm ²)/s ⁿ	n_i	R_i : kΩ cm ²	(CPE-T) _o : (S/cm ²)/s ⁿ	n_o	R_o : kΩ cm ²
S0	25.30	1.53×10^{-5}	0.81	10.66	6.68×10^{-5}	0.88	0.81
S1	25.15	1.38×10^{-5}	0.95	14.93	3.07×10^{-4}	0.89	1.17
S2	28.22	4.28×10^{-6}	0.73	17.54	2.58×10^{-6}	0.91	3.66
S3	29.12	1.52×10^{-6}	0.73	21.18	9.08×10^{-7}	0.94	7.71

CPE-T, pseudo capacitance

Figure 10. Schematic representation of the corrosion resistance of the (a) PEO coating without the molybdenum disulfide additive and (b) PEO coatings with the molybdenum disulfide additive

aggressive environments. Using this coating could be useful in the development of aluminum alloys in various fields such as the automotive and aerospace industries, which suffer from some restrictions due to corrosion.

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