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CORROSION BEHAVIOR OF 2024 ALUMINUM ALLOY ANODIZED IN SULFURIC ACID CONTAINING INORGANIC INHIBITOR

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Abstract

The effects of potassium permanganate, as a corrosion inhibitor, in different concentration on morphology, composition and thickness as well as corrosion resistance of anodic film formed on 2024-T3 aluminum alloy in sulfuric acid were investigated in this paper. Surface morphology and chemical composition of oxide film were studied using field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX). Potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) were conducted to assess the corrosion performance of the coatings. The results showed that presence of potassium permanganate during anodizing process results in more compact and thicker anodic film with smaller pore size. Effects of potassium permanganate increased with concentration. Using permanganate ions improved corrosion resistance of the formed anodic layer, which is about 45% and 94% inhibition for 0.01 and 0.1M permanganate, respectively.

Introduction

The 2024-T3 and 7075-T6 aluminum alloys are the most important alloys utilized in aerospace industries because of their excellent mechanical and weight-saving properties [1, 2]. Copper rich second-phases in aluminum matrix are responsible for their suitable mechanical properties, which are unpleasant from corrosion perspective [3, 4]. Implying some surface coatings are effective way to enhance the corrosion performance of these alloys. Chromate coatings have been known as a proper corrosion resistant coating for aluminum alloys; however, its toxicity and carcinogenic properties limits further application of this coating. This means that a alternative should be found for chromate coating as a protective coating for 2024 and 7075 Al-alloys [3, 5, 6]. Many investigations have been done in order to find appropriate coating for this aim, like cerium, phosphate and anodizing conversion coating [2, 7, 8], organic-inorganic hybrid [9, 10] and composite coatings [11].

Modified anodizing coatings using corrosion inhibitors can be considered as a suitable replacement for the chromate coating [12-17]. Chromates, molybdate, permanganate and phosphate compounds are such as these inhibitors [13-16]. Moutarlier et al. [14, 17] reported that presence of molybdate and permanganate increase corrosion resistance of anodizing coatings, while permanganate performs better than molybdate in this application.

In this study, the effects of various concentrations of potassium permanganate on various properties of the anodized coating on 2024-T3 aluminium alloy were investigated.

Materials and Methods

Before the anodizing process, 2024-T3 aluminum alloy specimens (chemical composition in wt.%: Cu 4.5, Mg 1.44, Mn 0.6, Si 0.06, Fe 0.13, Zn 0.02, Cr 0.10, Ti 0.03), were degreased with acetone, air dried, and immersed in an aqueous solution of 5 wt% NaOH for 5 minutes. Subsequently, the specimens were immersed in a 30 wt% nitric acid solution at room temperature for 2 minutes. After each step, the specimens were rinsed in distilled water.

Anodizing processes were done using a three electrode cell in an aqueous solution of 17wt.% sulfuric acid and certain concentration of potassium permanganate (0, 0.01, 0.05, 0.1 and 0.25M), at contact voltage of 20 V and room temperature for 30 min. During coating process, the anodizing electrolyte were magnetically stirred in order to prevent localize raising temperature close to the electrodes.

The anodic layer film thicknesses were determined using eddy currents (Dual Scope MP40, Fischer, Switzerland). Field emission scanning electron microscopy (FESEM) was used to study the morphology of anodized layer.

Electrochemical behavior of the anodized samples was investigated using polarization and electrochemical impedance spectroscopy (EIS) methods. Polarization tests were conducted at the room temperature in 3.5 wt% NaCl solution a potentiostat/galvanostat (μAutolab Type III Eco Chemie BV, The Netherlands). A standard three-electrode cell was used composed of platinum as a counter electrode, and Ag/AgCl (+199 mV vs SHE) as reference electrodes. Polarization tests were performed in the range of -0.25 to 0.75 V vs open circuit potential (OCP) at constant scan rate of 1 mV/s. The corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) of each sample were deduced from the Tafel plots.

Electrochemical impedance spectroscopy measurements were performed in the frequency range of 100 kHz–100 mHz and the perturbation amplitude of 5 mV in the mentioned solution. The spectra of EIS were analyzed in terms of an equivalent circuit using "ZSimpView" software.

Result and discussion

Surface morphology of the samples anodized in presence of 0, 0.05, 0.01 and 0.25M of potassium permanganate are shown in Figure 1. Morphology of the anodic film formed in sulfuric acid without inhibitor (Figure 1(a)) shows that it has classical model of "honeycomb" morphology [17]. Figure 1 indicates that addition of permanganate concentration in the anodizing solution did not change the whole morphology of the anodic film. Indeed, permanganate ions just affect the holes size of the coating, and make them smaller. Therefore, increase in permanganate concentration led to more compact coating.

Figure 2 shows variation of coating thickness as a function of permanganate concentration in the electrolyte. As can be seen, thickness of the oxide layer increased continuously by potassium permanganate concentration. This can be due to the oxidizing power of permanganate that encourage aluminum surface to have more reaction with solution and form oxide layer [14].

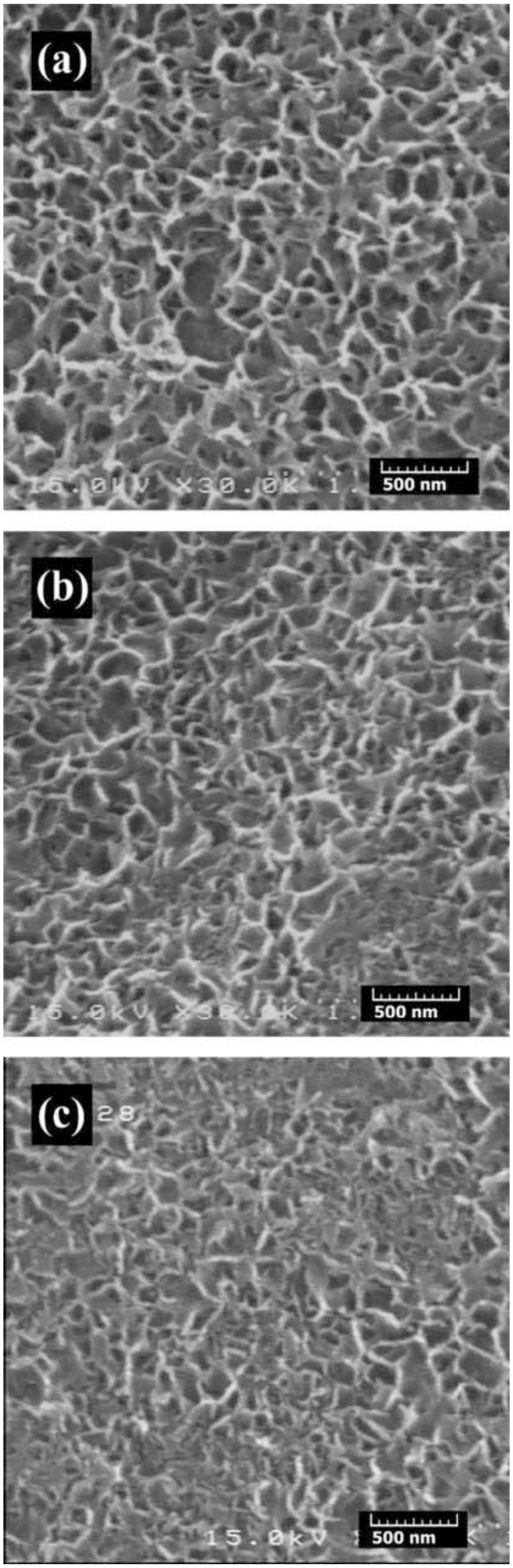

Figure 1. Surface morphology of the anodized films formed in potassium permanganate concentration of (a): 0 M, (b): 0.05M, (d): 0.1 M

EDX results also showed that manganese content of the anodized coating increased as the concentration of permanganate ions increased in the electrolyte. This can be attributed to higher MnO_4^- ions in the solution that have the chance to incorporate in oxide film, despite decreasing in pore size of the oxide layer by increase in permanganate concentration [17].

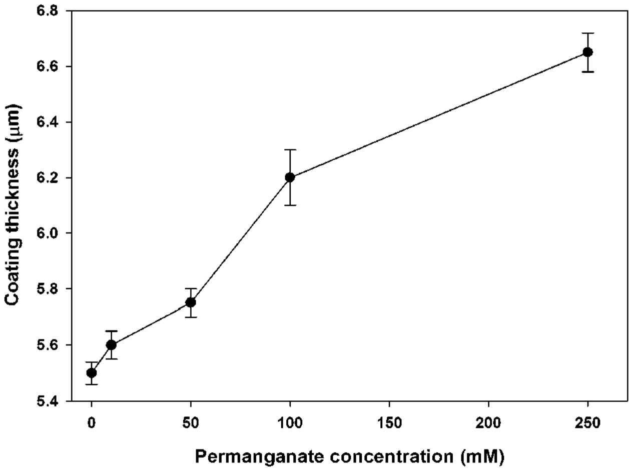

Figure 2. Thickness of anodic film as a function of inhibitor concentration

Figure 3 compares the polarization curves of the anodic films formed in presence of various concentration of permanganate with that of simple anodic coating. Inhibition efficiency (IE) of the inhibitors in the final corrosion resistance of the anodic coating could be calculated as:

$$IE = 100(1- i/i_0) \qquad (1)$$

Where i and i_0 are corrosion current densities of the anodized coatings that were produced in the electrolyte with and without corrosion inhibitors, respectively. The corrosion parameters determined from the polarization curves and inhibition efficiency of various concentration of permanganate are reported in Table I. Figure 3 shows considerable change in the anodic current density of the anodized samples with the inhibitor concentration. The corrosion current densities of the coating decreased as the concentration of the permanganate anions increased. The efficiency of the corrosion inhibitors is evident from both the reduction in the corrosion current density and the increase in corrosion potential [8].

Table I. Corrosion parameters the investigated anodic coatings determined from the polarization curves

Permanganate Concentration (mM)	0	10	50	100	250
$E_{Corr.}$ (mV)	-633	-578	-555	-543	-531
i_{Corr}. (mA/dm^2)	0.223	0.123	0.0411	0.0134	0.0026
Inhibition Efficiency (%)	-	45	81	94	98.8

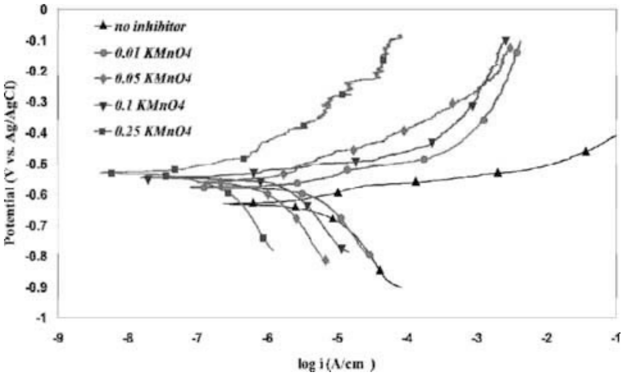

Figure 3. polarization curves of anodic films formed in various concentration of permanganate

For example, addition of 0.01M and 0.1M permanganate to the anodizing electrolyte respectively lowered the corrosion current density of the oxide film from 0.223mA/dm^2 to 0.123 and 0.0134mA/dm^2. Inhibition efficiency of permanganate increased with its concentration and shows that this additive significantly improved corrosion resistance of the anodic coating in saline solutions.

Nyquist and Bode plots of all the mentioned samples are shown in Figures 4 and 5, respectively. To model the EIS results, an equivalent circuit should be selected based on the structure of the aluminum anodic layer. It is well known that the anodized coating structure includes a thin, compact barrier layer at the coating/metal interface and a thick porous layer on top. Figure 6 shows the schematic of this structure, which describes the electrochemical behavior of the system. The equivalent circuit that is reported in Figure 6 is proposed here to model EIS results of the anodized layers on aluminum [18]. In this equivalent circuit, R_s represents the electrical resistance of bulk of the solution. Current flows through the coating in two parallel paths: the pores and the pore walls.

It can be assumed that no electron passes through the second path, pore wall, as Al_2O_3 is considered a non-conductive ceramic. Therefore, the role of pore walls in the electrochemical behavior of the coatings can be modeled using only one capacitance.

The first path, however, is more complicated. Regarding to the proposed equivalent circuit, R_{el} show the electrical resistance of the electrolyte in the pores. Dissimilarity between the ions concentration of the solution in the pores and those in the bulk of solution makes R_{el} and R_S different. R_C is charge transfer resistance at the barrier layer/solution interface, and C_P is the constant phase element in parallel with R_C. R_b and C_b are the resistance and constant phase element of the barrier layer, respectively. Constant phase element (CPE) is an equivalent electrical circuit component that has been introduced to model the electrochemical behavior of an imperfect capacitor and can be used to explain the system heterogeneity and distribution in the values of some physical properties of the system. Impedance of the CPE is defined through:

$$Z=1/Q(i\omega)^{\alpha} \qquad (2)$$

in which Q is defined as a fitting constant with the units of $Fcm^{-2}S^{(\alpha-1)}$ and a represents the deviation of the element from ideal capacitive behavior. α in a constant phase element is defined as:

$$\alpha=A/A_0 \qquad (3)$$

where A and A_0 are the apparent and real surface area, respectively. Thus, the value of α is either less than one, for an imperfect capacitance, or one, for a perfect capacitance.

The important parameters calculated by fitting the proposed model to EIS experimental results of the coating are listed in Table II. Since the resistance of the electrolyte in corrosion tests, R_S, was approx. 15 Ωcm^2 in all samples, it was omitted from this table.

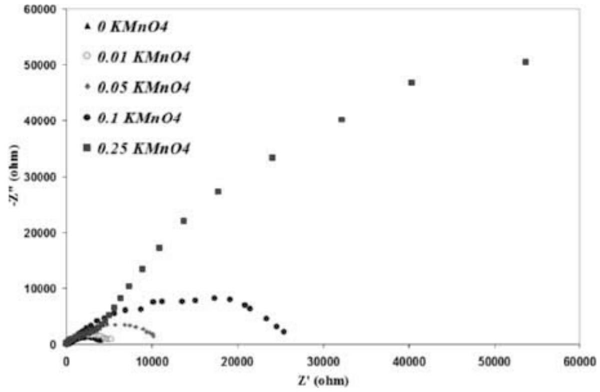

Figure 4. Nyquist plots of anodic films formed in various concentration of permanganate

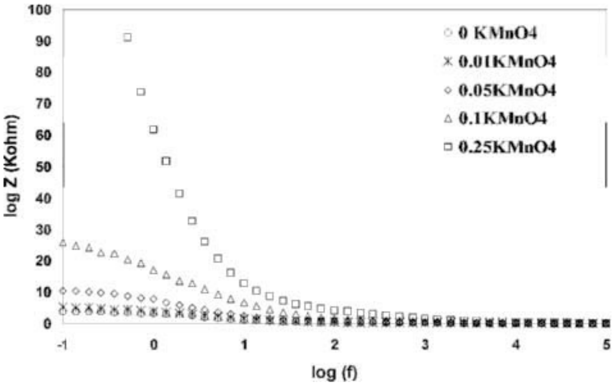

Figure 5. Bode plots of anodic films formed in various concentration of permanganate

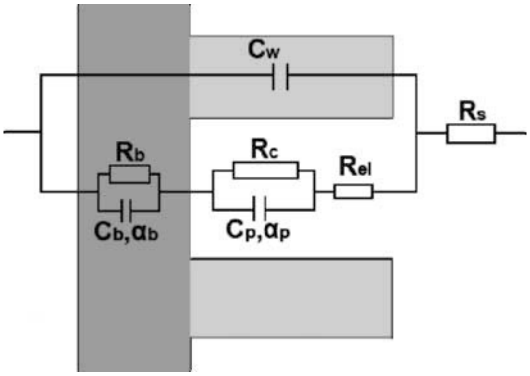

Figure 6. Schematic of equivalent circuit for modeling the impedance spectra of the anodic films

The results of the EIS analyses confirm the polarization results and indicate that higher concentration of permanganate ions resulted in better corrosion resistance of coatings.

R_b, which is the impedance of the barrier layer and shows the resistance of this layer in the anodized coatings, increased continuously with permanganate concentration. For instance, it increased from 4295 Ωcm2 to 5526 and 27200 with addition of 0.01M and 0.1M permanganate, respectively.

Higher content of manganese in the anodic layer as a strong oxidant, more compactness of the coating and its higher thickness are responsible for better corrosion performance of anodic film with increase in permanganate concentration in the anodizing electrolyte. Therefore, the coating formed in higher concentration of permanganate seem to be more corrosion resistant since they restrict the chloride ions movement into the anodic layer and limit accessibility of the aluminum surface [17].

Furthermore, variation of the barrier layer thickness, which can be determined by capacitance of the barrier layer, may be another reason for corrosion performance improvement of anodic film with permanganate concentration [16]. Capacitance of the barrier layer, C_b, can be associated with the dielectric constant in vacuum (ε_0), the relative constant for aluminium oxide (ε), the electrode surface (S) and the barrier layer thickness (e_b), by following relation [16]:

$$e_b = \varepsilon_0 . \varepsilon.S/C_b \qquad (4)$$

It can be assumed that ε is same for all of the anodized coatings. Therefore, the decrease in C_b can be corresponded to the increase of the thickness of the barrier layer (e_b). According to Tables II, increasing the permanganate concentration leads to lower C_b, and consequently thicker barrier layer. Since a thicker barrier layer is more resistant to penetration of the corrosive solution and ions [14], a coating that is fabricated in a higher concentration of corrosion inhibitors is expected to have better corrosion resistance.

Table II. Calculated parameters obtained by fitting proposed model for the anodic coatings

Permanganate Concentration (mM)	0	10	50	100	250
R_{el} (Ω)	8	10.54	19.76	83.49	121
Cp (μF)	1.79	1.98	3.16	5.99	2.13
α_P	1	0.8945	0.2713	0.6343	0.6079
R_C (Ω)	140	197	458	763	4175
C_b (μF)	37.9	34	20	8.88	2.94
α_b	0.6609	0.6572	0.7778	0.6674	0.825
R_b (Ω)	4295	5526	9027	27200	148000

Conclusion

In this study, the influences of various concentration of potassium permanganate as a corrosion inhibitor on morphology, thickness and corrosion behavior of anodized coating were investigated. The main conclusions can be drawn as follows:

- Presence of permanganate ions in the anodizing electrolyte decrease pore size of the anodic film and increase its compactness, which is more significant in higher concentration of permanganate ions.
- The thickness of anodized coating, in both parts of barrier and porous layers, grew up as the concentration of permanganate ions increased.
- Potassium permanganate has positive effect of corrosion performance of the oxide film. The anodized layer formed in higher concentration of permanganate anions shows more corrosion resistance in the salty solution.

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