Nanoparticles deposition effects on 1050A aluminum alloy anodic layers

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Abstract
The objective of this research is to investigate the electrochemical features of aluminum alloy owing to the deposition of SiO\(_2\) or TiO\(_2\) nanoparticles in an anodic aluminum oxide film (AAO) via electrophoretic deposition (EPD). The modified oxide layer shows potential in view of corrosion protection while retaining the adhesion promotion properties. The modified oxide layer with TiO\(_2\) nanoparticles was more effective in corrosion prevention.

1. Introduction
Anodizing aluminum and its alloys is a well-established technique for many ways of functionalizing the surface [1, 2]. An aluminum oxide produced in the anodizing process consists of two layers, i.e. a very thin nonporous barrier type layer located close to the surface and a porous layer with a much larger thickness [3]. In order to improve the corrosion resistance of aluminum alloys, the oxide produced on the surface is used for further treatment leading to sealing of existing pores [3–5]. Common sealing treatments of the open porosity which typically improve the corrosion resistance of the oxide layers have a counter effect on their adhesion promotion properties. The approach of this work is to deposition of SiO\(_2\) or TiO\(_2\) nanoparticles via electrophoretic deposition (EPD) inside a porous of anodic aluminum oxide film (AAO). In order to achieve partly pores fill, to improve the corrosion resistance as well as don’t affect the adhesion ability, a well-matched relation between the particle size and the pore diameter should be established. Controlled phosphoric acid bath is used in anodizing process to produce a suitable pore diameter [4]. Finally, corrosion resistance was compared between anodic aluminum oxide films after deposition of SiO\(_2\) or TiO\(_2\) nanoparticles, and evaluated when exposed to 3.5\%NaCl solution using different electrochemical techniques.

2. Experimental work
The material used was 1050A aluminum alloy having a composition Si–0.06, Fe–0.25, Cu–0.05, Mn–0.02, Mg–0.02, Cr–0.02, Zn–0.01, Ti–0.02 and balance Al (all in wt%).

The alloy sheet was degreased with ethanol then etched in NaOH (0.5 g l\(^{-1}\)) aqueous solution at 40 °C for 5 min and finally neutralized in HNO\(_3\) (25 vol\%) at room temperature for 2 min. To facilitate the insertion of particles inside pores, the porosity of the anodic films must exhibit pore diameter larger than the nanoparticles one (∼20 nm). Due to the need for big pores, the aluminum sheet was galvanostatically anodized (1.5 Adm\(^{-2}\)) in a temperature-controlled bath of phosphoric acid (0.4 mol l\(^{-1}\)) for 20 min where Pb sheet was used as a cathode [4]. The samples were rinsed completely in distilled water for later use after anodization.

Using electrophoretic deposition (EPD) technique, SiO\(_2\) or TiO\(_2\) nanoparticles were deposited. In which, anodized samples were set as the cathode and the lead foil as the anode. Particles deposition bath media was ready to be 2 wt\% percent by diluting SiO\(_2\) or TiO\(_2\) colloidal samples with ultra-pure water. The pH-value adjusted oneself on pH = 10. The sample was dried for subsequent use at ambient temperature.
JEOL JSM54 10 (Japan) computer-controlled Scanning Electron Microscope (SEM) examined the surface morphology of anodic oxide films before and after deposition step.

Using Voltalab 40 Potentiostat PGZ301 (Germany) and Volta Master 4 software, electrochemical measurements were conducted to measure and analyze corrosion.

As received aluminum alloy, sample (I), anodized aluminum oxide (AAO), sample (II), anodized aluminum oxide after SiO₂ nanoparticles deposition, sample (III), and anodized aluminum oxide after TiO₂ nanoparticles deposition, sample (IV) served as the working electrodes. As reference and counter electrode, respectively, a saturated calomel electrode (SCE) and a platinum disk were used. All electrochemical testing was conducted in 3.5% NaCl (Sigma Aldrich) solution. The sample’s open circuit (ocp) potential was evaluated for 60 min at first. Then Potentiodynamic polarization curves were performed to determine the corrosion potential and corrosion current density. At a scanning rate of 0.2 mVs⁻¹, the working electrode was polarized. In the frequency range from 50 kHz to 100 mHz, electrochemical impedance spectroscopy (EIS) was conducted. With regard to the open circuit potential, the amplitude of the applied signal was ± 10 mV. Finally, at a scanning rate of 10 mVs⁻¹, potentiodynamic cyclic anodic polarization was measured between −0.8 and + 0.2V. At room temperature, (25 °C), all measurements were performed. Consecutively, all spectra were measured four times. Under the chosen conditions the stability is extremely high so that differences of the spectra imperceptible.

3. Results and discussions

3.1. Surface morphology

Prior to anodizing, the morphology of the 1050A Al alloy surface developed throughout etching and de-smutting was examined by SEM figure 1(a). The smut layer shaped in NaOH solution was removed throughout immersion in nitric acid. The surface showed cavities wherever second phase had been lost either because of dissolution or detachment. Figures 1(b) and (c) show the surface pictures of the Al samples when anodizing. As will be seen, pores are embedded within the middle of hexagonal shape structures of the AAO layer. Those pore perpendicularly and parallel to each other and also perpendicularly and parallel to the barrier layer surface [5]. The diameter of the pores was around 100 nm. Figures 1(d) and (e) show the electrophoretic deposition (EPD) of SiO₂ and TiO₂ nanoparticles respectively in pores at pH 10. The common particle size (~20 nm) was smaller enough than the common pore diameter (~100 nm) so particles will be incorporated into pores structures of AAO.

3.2. Electrochemical impedance spectroscopy (EIS)

Figure 2 shows Nyquist and Bode phase plots of the tested samples in 3.5% NaCl. EIS spectra for nanoparticles deposited samples (III and IV) typically contain two time constants. The two time constants of nanoparticles deposited samples is the only prediction [4]. The two time constants are attributed to the barrier layer (low frequency range) and the porous layer (high frequency range) according to the Hoar and Wood models [4]. For SiO₂ deposited sample (III) the time constant of the porous and the barrier layer are coincide and indistinguishable. From Bode plots, figures 2(a) and (b), we observe one time constant for the as received aluminum sample (I) and AAO non–deposited sample (II) as shown by the single maximum in the phase angle plot. For AAO non-deposited sample (II) such behavior is observed because the outer layer is ‘transparent’ to EIS due to water intrusion [6].

The small difference of the impedance between the AAO non-deposited sample (II) and nanoparticles deposited samples (III and IV), figure 2(c), indicates that the deposition of the nanoparticles into the pores cannot be simply explained as an additional barrier. At the same time the values of charge transfer resistance Rct and double-layer capacitance Cdl, table 1, emphasize the corrosion resistivity of the nanoparticles deposited samples and the corrosion resistance of TiO₂ deposited sample (IV) was the highest.

3.3. Potentiodynamic polarization measurements

Figure 3 shows the polarization curves of the tested samples in 3.5% NaCl. All curves show a passive behavior over a wide potential range comparing with as received aluminum sample (I). Furthermore, the nanoparticles deposited samples (III and IV) show lower corrosion current densities and higher corrosion potential than AAO non-deposited sample (II), which means better corrosion resistance for nanoparticles deposited samples [7]. The open pores of the AAO non–deposited sample (II), allow diffusion of aggressive Cl⁻ ions into the structure of the oxide, in which the only hindrance is the barrier type layer [8, 9]. According to Tafel extrapolation method [10, 11], the corrosion potential (Ecorr), corrosion current density (Icorr) for the tested samples are calculated and listed in table 2. The TiO₂ deposited sample (IV) exhibited very low current densities, a 16 fold decrease from as received aluminum sample (I), 13 fold decrease from AAO non-deposited sample (II) and 9 fold decrease from SiO₂ deposited sample (III). Comparing between all
tested samples, the TiO$_2$ deposited sample (IV) with a higher corrosion potential and a lower corrosion current density showed excellent corrosion resistance.

3.4. Potentiodynamic cyclic anodic polarization measurements

Figure 4 shows the results of the potentiodynamic cyclic anodic polarization measurements for the tested samples in 3.5% NaCl solution. It is clearly shown that the nanoparticles deposited samples (III and IV) samples have stable passive behavior over a wide potential range accompanied with shifting in corrosion potential to more positive values comparing with AAO non-deposited sample (II).

Nanoparticles deposition clearly protects the anodic layer from pitting corrosion and maintains passive behavior of the layer over a wide potential range. Sample after deposition of SiO$_2$ and TiO$_2$ showed better efficiency where the hysteresis loop observed during the inverse anodic scan, indicating the likelihood of pitting corrosion, was diminished entirely. In addition, compared to the remainder of the sample, a small change towards more passive exchange current was observed for the TiO$_2$ deposited sample (IV). Polarization and the EIS data, tables 1 and 2, provided evidence that the TiO$_2$ deposited sample (IV) offered the best corrosion resistance.

Figure 1. SEM micrographs of the surface of 1050 Al alloy after etching (a) after anodizing low magnification (b) and high magnification (c) after SiO$_2$ deposition (d) and after TiO$_2$ deposition (e).
Figure 2. Bode (a), (b) and Nyquist (c) plots of as received aluminum (I), AAO (II), after SiO₂ deposition (III) and after TiO₂ deposition (IV) in 3.5 wt% NaCl solution.

Table 1. Electrochemical parameters fitted from EIS measurement for as received aluminum (I), AAO (II), after SiO₂ deposition (III) and after TiO₂ deposition (IV) in 3.5 wt% NaCl solution.

| Samples | $R_s$ kohm.cm² | $C_{dl} \mu F \text{ cm}^{-2}$ |
|---------|----------------|-------------------------------|
| I       | 0.6993         | 127.4                         |
| II      | 1.792          | 14.03                         |
| III     | 2.953          | 13.47                         |
| IV      | 4.749          | 7.687                         |

Table 2. Corrosion potentials and corrosion current densities for as received aluminum (I), AAO (II), after SiO₂ deposition (III) and after TiO₂ deposition (IV) in 3.5 wt% NaCl solution.

| Samples | $E_{corr}$ mV | $I_{corr} \mu A \text{ cm}^{-2}$ |
|---------|---------------|---------------------------------|
| I       | −725.7        | 14.34                           |
| II      | −719.7        | 11.92                           |
| III     | −684.6        | 7.40                            |
| IV      | −658.7        | 0.87                            |
The open porous structure, which is maintained after the deposition process, realizes the necessary big surface in perspective of pre-treatment before adhesive bonding [12].

The main experimental results of the present study indicate that, the TiO2 deposited sample (IV) possess higher corrosion resistance than the SiO2 deposited sample (III) which might be due to the standard corrosion potential of TiO2 and SiO2 [13].

4. Conclusion

From the point of view of corrosion safety while maintaining the adhesion characteristics of 1050A aluminum alloy anodized oxide layer. In the present work, the electrochemical characteristics due to the deposition of SiO2 and TiO2 nanoparticles by electrophoretic deposition in a porous anodic aluminum oxide film were studied. The surface morphology showed deposition of SiO2 and TiO2 nanoparticles in AAO pores and on its surface. The results of electrochemical impedance spectroscopy, potentiodynamic polarization and potentiodynamic cyclic anodic polarization measurements which employed to evaluate the corrosion resistance of resulting anodized coating in 3.5 wt% NaCl solution showed significantly corrosion resistance character of nanoparticles deposited samples but the TiO2 deposited sample was more effective.
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