



Plasma electrolytic oxidation in the presence of multiwall carbon nanotubes on aluminum substrate: Morphological and corrosion studies

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ABSTRACT

Plasma electrolytic oxidation processes were performed on aluminum substrates in a solution composed of KOH, $\text{Na}_4\text{P}_2\text{O}_7$ and NaAlO_2 compounds at constant applied potential, i.e. 520 V DC, with and without incorporating multiwall carbon nanotubes (MWCNTs). The morphology and chemical composition of PEO coatings was studied using SEM and XRD techniques. The SEM characterizations revealed that MWCNTs were incorporated into the PEO coating with the detrimental effect on the coating compactness, particularly in the inner barrier layer. In addition, the characteristic peaks corresponding to the $\gamma\text{-Al}_2\text{O}_3$ phase get more intensified by loading MWCNTs. The corrosion protection performance of the PEO coatings was also studied by the Electrochemical Impedance Spectroscopy (EIS) and Scanning Kelvin Probe (SKP) techniques. The results revealed that protective properties of the PEO coating are deteriorated with incorporating MWCNTs by reducing the compactness of the inner and outer layer of the PEO coating. The obtained results also demonstrated that both types of PEO coatings exhibit a similar mechanism of protection by barrier effects.

1. Introduction

Aluminum and its alloys have great applications in different industries due to their high strength to weight ratio, low density compared to steel and ease of fabrication and recycling potential [1].

Despite these outstanding properties, the application of aluminum alloys in some aqueous environments may be restricted due to corrosion problems. Thus, many efforts have been made to improve corrosion properties with the help of various surface treatment methods such as surface cladding [2], conversion and smart composite coatings [3–5], thermal spraying [6,7], chemical and physical vapor deposition [8,9], surface hydrophobization [10] and surface anodizing [10–12] and plasma electrolytic oxidation (PEO) [13–26].

Among the above-mentioned methods, PEO is a novel surface treatment technique which leads to the fabrication of the thick crystalline oxide layer on the metal substrate in an alkaline solution with applied voltage or current densities higher than those of conventional anodizing [13–35]. PEO coating grows by establishing plasma microdischarges due to the dielectric breakdown phenomenon under high electrical field. However, it should be noted that plasma microdischarges do not necessarily lead to coating growth and may propagate some microdefects in the coating, hence providing suitable paths for the corrosive species to reach and attack the underlying substrate [13–26].

Accordingly, many efforts have been devoted to increase the PEO

coating densification and hence to reduce the detrimental effects of porosities on the PEO coating properties [14–16,18,19,22,24,25,27–31]. One of these efforts is based on the PEO electrolyte loading with micro or nanosized particles and incorporating the particles into the coating by diffusion, electrophoresis or the mechanical entrapment phenomena [15,16,25,33].

A literature survey of the topic clearly indicates that carbon-based materials, i.e. graphite, Polytetrafluoroethylene (PTFE) and multiwall carbon nanotube, have been devoted more attention compared to other particles such as PEO coating additives, when optimizing the protective performance of alumina coatings are of interest [15,16,34].

For instance, Lv et al. [15] studied the effect of graphite additives on the microstructural and corrosion behavior of PEO coating on pure aluminum. They found that graphite additives reduced the porosity content, increased compactness of oxide coating and enhanced the corrosion protection properties of PEO coating.

Zhan et al. [34] studied the effect of PTFE incorporation on wear and the corrosion resistance of PEO coating on the 2024 aluminum alloy. The PEO process was performed using a pulsed DC source at a frequency of 150 Hz and a duty cycle of 40%. The obtained results have shown that both wear and corrosion resistances have been improved by PTFE particles. It was also demonstrated that PTFE particles were mainly incorporated within the coating micropores.

Lee et al. [16] also studied the influence of MWCNTs incorporation

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on microstructural and corrosion properties of PEO coating on the 7075 aluminum alloy. The process was conducted in a silicate-based electrolyte under galvanostatic conditions. They have reported that MWCNTs have increased the compactness of PEO coating by filling the micropores. In addition, an improvement in corrosion protection properties of PEO coating was reported by incorporating MWCNTs. In another study, Yürektürk et al. [31] have reported the influence of MWCNTs incorporation on increasing both hardness and the dry sliding wear resistance of PEO coating on the 6082 aluminum alloy. They have also recognized that the incorporation of MWCNTs increased surface roughness of PEO coating due to intensification of plasma discharges. However, they have not clearly defined the influence of MWCNTs on PEO coating densification.

A brief overview of the above literature clearly shows the lack of a profound study on the mechanism of corrosion protection by PEO coatings with a special emphasis on the influence of particle incorporation and coating morphology variations. MWCNTs, as it was also mentioned in the previous studies, improved corrosion protection properties of PEO coatings by filling the coating micropores as inert materials. In addition, due to the typical feature of MWCNTs, they have the potential to bridge cracks and thus prevent crack propagation in composite ceramic materials [36–38]. In other words, the MWCNTs seem to improve the protective properties of PEO coating by micropore filling and crack bridging.

The main objective of this work is to study the influence of MWCNTs incorporation on the morphology and protective properties of PEO coating. In addition, the influence of MWCNTs on the morphology of the inner barrier layer is of greater interest, which has received less attention than bulk morphologies in the previous publications. In addition, prolonged corrosion studies were carried out in sodium chloride solution using the electrochemical impedance spectroscopy technique to evaluate the influence of MWCNTs incorporation on protective performance of PEO coating and the mechanism of protection. Scanning Kelvin Probe was also employed to measure surface potentials of the samples after prolonged immersion. To the author's knowledge, apart from the fact that the SKP technique has already been used for different corrosion studies, it is not yet employed in studying the electrochemical and corrosion properties of PEO-coated aluminum alloys.

2. Experimental

2.1. Sample pretreatment

All experiments were conducted on commercially pure aluminum plates (Al 98.73 wt%, Si 0.23 wt%, Fe 0.60 wt%, Mg 0.22 wt%, Zn 0.01 wt%, Pb 0.05 wt%, Ti 0.01 wt%, Sr 0.11 wt%, V 0.01 wt% and Sn 0.03 wt%) with a dimension of 15 mm × 15 mm × 3 mm. A 1.6 mm threaded hole was made in the cross section of each sample and screwed with a threaded rod to ensure a proper electrical connection. Silicon washers and heat shrinks were used to prevent current leakage from the connection rod. The substrate samples were mechanically polished using 320, 500, 800, 1000 and 1200 grit emery paper before being fastened by the threaded rod. Prior to PEO treatment, the samples were cleaned in 5 wt% KOH solution by applying 5 V cathodic potential for about 10 s, rinsed in distilled water and immersed in PEO electrolyte.

2.2. PEO treatment

Plasma electrolytic oxidation processes were performed using a 30 kW PEO equipment (manufactured manually in the lab) at a constant applied potential of 520 V DC for 300 s. The PEO electrolyte was a mixture of 0.05 M KOH, 0.04 M Na₄P₂O₇ and 0.04 M NaAlO₂. The pH and conductivity of PEO solution were measured ~10.5 and ~6.4 mS cm⁻¹, respectively. These parameters were measured using a Consort C933 multi-parameter analyzer.

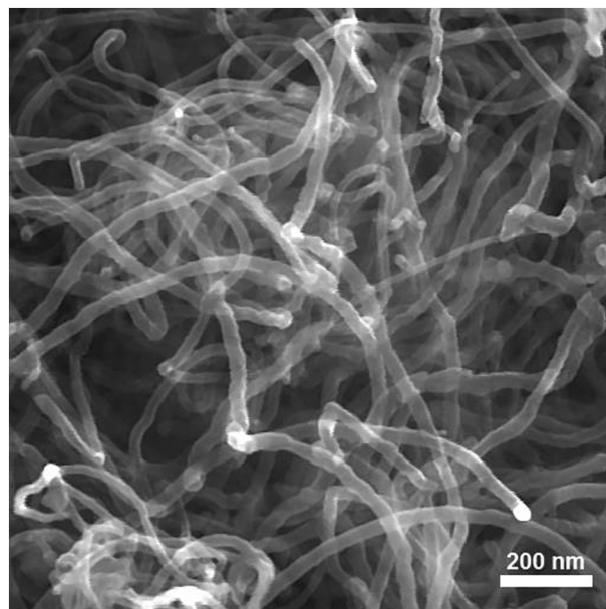


Fig. 1. FESEM images of pristine MWNTs used in this study.

A set of samples were treated in the base electrolyte and the others were processed in the base electrolyte containing 2 g/l MWCNT. The pH and conductivity of the MWCNTs-containing solution were also measured ~10.3 and ~6.5 mS cm⁻¹, respectively. The CNTs used in this study were multiwall carbon nanotubes (MWCNTs), synthesized by catalytic decomposition of 20% methane in hydrogen over diverse proportions of Co–Mo/MgO catalysts at 900–1000 °C (Research Institute of Petroleum Industry, Iran). The average diameter and length of MWCNTs were around 25 nm and 1.5 μm, respectively and their surface area was between 250 and 300 m² g⁻¹ (Fig. 1). In this work, MWCNTs were used in the functionalized form. However, our laboratory experiences indicated that the application of surfactants to disperse MWCNTs is virtually impossible as they increase the foaming tendency of the solution during the PEO process. The functionalization process was performed in an acid solution containing H₂SO₄ and HNO₃ with the volume ratio of 3:1. The load of MWCNTs was 4 g for 1000 ml of the acid solution. The acid solution was added into a flask containing MWCNTs. The mixture was then refluxed at 80 °C for around 4 h. After that, the mixture was diluted with distilled water and stirred for around 8 h. The MWCNTs were washed thoroughly and vacuum-filtered over a 0.22 μm PTFE filter. After the filtration process, the MWCNTs were dried in an oven for around 24 h at 60 °C. According to the literature, this type of chemical modification grafts the carboxyl (–COOH) and hydroxyl (–OH) functional groups onto the MWCNTs [39–41]. The functionalization process is expected to improve the dispersion of MWCNTs in the PEO electrolyte. Next, the functionalized MWCNTs were added to the PEO electrolyte and dispersed with an ultrasonic homogenizer at a power of 125 W for around 120 min. The dispersion of MWCNTs was examined using particle size distribution and Zeta potential measurements. Samples were taken after around 120 min sonication of MWCNTs in the PEO electrolyte, and then diluted as they were suitable for the mentioned measurements. Particle size distribution of the dispersed MWCNTs was measured using the light scattering method by the LLS instrument (LLS, MAL1008078, Malvern Instruments Ltd., UK). In addition, the zeta potential value was measured by laser Doppler velocimetry using a Zetasizer NanoZS (Malvern, UK) apparatus.

Plasma electrolytic oxidation processes were conducted in a 1600 cm³ glass cell. A pump/heat exchanger system was employed for cooling and circulating the PEO electrolyte. Using this system, the solution temperature was maintained at 25 ± 2 °C during the PEO

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