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Al_2O_3/Si_3N_4 nanocomposite coating on aluminum alloy by the anodizing route: Fabrication, characterization, mechanical properties and electrochemical behavior

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ABSTRACT

An Al_2O_3/Si_3N_4 nanocomposite coating was successfully fabricated on commercial aluminum alloy. Hardness measurements, polarization and electrochemical impedance spectroscopy (EIS) were employed to study the mechanical and corrosion behaviors of the coatings. Field-Emission Scanning Electron Microscopy (FE-SEM) equipped with Energy Dispersive Spectroscopy (EDS) and X-ray diffraction (XRD) were utilized to characterize the surface morphology and phase composition of the coatings. Also, coatings abrasive wear properties were evaluated with a modified ASTM G105 standard. FE-SEM image, EDS and XRD analysis revealed the presence of Si_3N_4 in the coating. Furthermore, the results showed hardness of the coatings to increase from 380 ± 50 HV for the anodized layer to 712 ± 36 HV for the composite coatings that were formed in an electrolyte containing 6 gr/lit Si_3N_4 nanoparticles. Electrochemical measurements indicated that corrosion resistance of the nanocomposite coating significantly increased compared to the anodized coating. In addition, the effect of Si_3N_4 nanoparticles into the nanocomposite coatings on abrasive wear mechanism and mass loss rate of the coatings was investigated.

1. Introduction

High strength-to-weight ratio in association with low density of aluminum and its alloys lead to use of these materials for a wide range of applications. However, some shortcomings of these alloys such as low hardness, high friction coefficient and low corrosion resistance, limit their applications [1,2]. In spite of these conditions, when these alloys are exposed to a medium atmosphere, a thin oxide layer begins to form on the surface of aluminum. Although this layer has low thickness, it significantly improves corrosion behavior, mechanical properties and wear resistance of the aluminum alloy. Anodized Aluminum Oxidation (AAO) process is a simple, controllable and inexpensive electrochemical method, which is used to increase the thickness of the oxide layer and thereby improving surface properties of these alloys [3–5].

It is generally believed that the properties of the formed anodic layer depend on parameters of the AAO process such as current density, time, additives and bath temperature. In order to improve the properties of this coating, numerous researches are dealing with the anodizing parameters, among which synthesis of composite coatings on the surface of these alloys has been an attractive field in the recent years [6–10].

Traditional works evaluated a two-step process to fabricate composite coatings on the surface of aluminum. In the first step, a porous film was created by performing hard anodic oxidation and at the second step, the pores of the anodic film were sealed with a solid lubricating material (such as polytetrafluoroethylene (PTFE)) [11–14]. The main drawbacks of this method was to be the high costs of the process and the long procedure. In addition, it is noteworthy to mention that the most self-lubricating materials are soft and the composite coatings produced with them cannot reach to a high hardness amount [11,12].

In recent years, various studies conducted to synthesis co-deposit composite films on the surface of aluminum alloys by adding hard particles in the electrolyte [6,7,14–17]. For this purpose, various additives such as TiO_2, Al_2O_3, SiC and PTFE have been evaluated to enhance the properties of anodized coatings such as hardness, lubricating, anti-wear properties, and the corrosion resistance [14–19]. Zeng et al. [18] used SiC, TiO_2, and Al_2O_3 powders in sulfuric acid electrolyte of anodizing and demonstrated that the thickness, hardness, and corrosion behavior of the obtained coatings were significantly improved [18].

Silicon Nitride (Si_3N_4) is being used in various applications because of its considerable properties such as high hardness, high wear resistance, and good inert chemical behavior [20].

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Nonetheless, there is no comprehensive study to evaluate the effect of adding Si_3N_4 particles as an additive into the electrolyte on the properties of anodic coatings formed on the anodized aluminum alloys.

According to mentioned above, synthesis of composite coatings on the surface of aluminum alloys could significantly influence the nature, microstructure, corrosion and mechanical properties of the ceramic coatings produced by Anodizing method. As mentioned, there was no comprehensive research dealing with this critical challenges and comparing the possible effects of adding Si_3N_4 nanoparticles on the properties of the Anodized coating. Therefore, the aim of this study is to examine the effect of synthesis nanocomposite coatings by adding Si_3N_4 nanoparticles in the anodizing electrolyte bath and survey the corrosion behavior, hardness measurements and wear resistance of the anodized coatings.

2. Experimental procedures

2.1. Starting materials

The material used in the present research as the substrate was AA 1050 by dimensions of $30 \times 30 \times 1$ mm^3 and in order to reach a smooth surface, specimens were polished by the mechanical ground to P1500 grade paper. The normality composition of this alloy is shown in Table 1. Prior to anodizing, the specimens were treated as follows: (a) degreasing by ultra-sonication in acetone for 10 min, (b) electro-polishing in a solution ethanol that contained of $HClO_4$ with the volume ratio of 4:1 at 20 V for 30 s, at the ambient temperature and finally (c) rinsing immediately with distilled water and then dried. It would be mention that the samples were rinsed in ethanol after both (a) and (b) stages.

2.2. Anodizing process

The chemical composition of anodizing solution is given in Table 2. Anodizing process was conducted for 60 min by using a potentiostat/galvanostat rectifier (SL 2/25 PCS, I.R. Iran), with a direct current density of 4 A/cm^2 and at the electrolyte temperature of 10 °C. A two–electrode configuration was employed for the process in which the Al sheets were selected as anode and a steel sheet (SS316) as cathode which was larger than the sample size. To fabricate Al_2O_3/Si_3N_4 nanocomposite coating, 2–8 gr/lit Si_3N_4 nanoparticles was added to the electrolyte. The average particle size of α-Si_3N_4 nanopowder was 32 nm (Fig. 1). It should be noted that before adding the nanoparticles into the electrolyte, the particles were pickled in hydrochloric acid (1:1) and then they were cleaned by deionized water. Also, due to make the desperation of particles in aqueous solution, the nanoparticles treated by anionic surfactants ($C_{12}H_{25}C_6H_4NaO_3S$) and small amount of distilled water. In the next step, the suspension was subjected to ultrasonic dispersion for 20 min and then added to the electrolyte solution. Followed, the suspension stirred by magnetic stirrer for 20 min to make sure that Si_3N_4 nanoparticles were well drenched and dispersed in electrolyte solution.

Table 1
Chemical composition of substrate.

Composition	Si	Cu	Fe	Mn	Mg	Zn	Al
Weight percentage	0.17	0.001	0.26	0.001	0.047	0.01	Balance

Table 2
The chemical composition of anodizing electrolyte.

Composition	Content
H_2SO_4	200 g/L
$H_2C_2O_4$	20 g/L
$C_7H_6O_6S \cdot 2H_2O$	10 g/L
C_3H_8O	10 ml/L
$Al_2(SO_4)_3$	3 g/L
$C_{12}H_{25}C_6H_4NaO_3S$	0.5 g/L
Si_3N_4	0–8 g/L

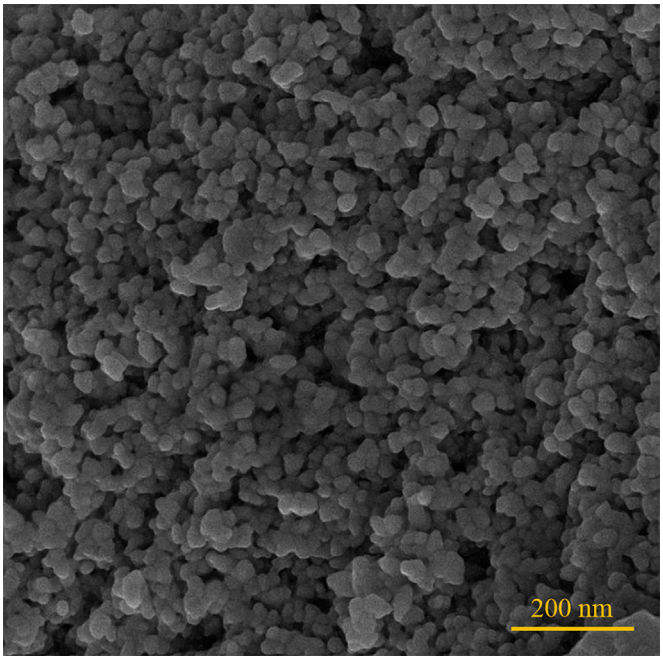

Fig. 1. SEM of α-Si_3N_4 fine nanoparticles with average particle size of 32 nm used in this investigation.

2.3. Characterization of coatings

2.3.1. Micro-hardness measurements

Vickers micro-hardness machine (Buehler model 1600-6100, USA) based on ASTM B578 standard and 25 gr load for 15 s was used to examine the hardness of the coatings. All measurements were carried out in five distinct points flatly distributed on the surface of specimen and finally an average value is reported.

2.3.2. Surface morphology and phase analysis of the coatings

The surface morphology and cross-section of the anodized and composite coatings were characterized by a field emission scanning electron microscopy (Mira 3-XMU) in both secondary electron (SE) and back-scattered electron (BSE) modes. In addition, to study homogeneity and quantitate analysis of the coatings, element distribution was studied by the FE-SEM equipped with energy dispersive X-ray (EDS) analyzer.

The phase analysis of the composite coating carried out by X-ray diffraction (STOE, STADI P, Germany). Also, it could be mentioned that the XRD test was applied with Cu K_α radiation ($\lambda = 1.54178$ Å) on a Philips X'pert rig.

2.3.3. Electrochemical measurements

In order to evaluate electrochemical properties of the samples, a potentiostat/galvanostat (Autolab, PGSTAT302N) was used based on extrapolation method and ASTM-G102-98 standard. For this