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Scratch behavior of aluminum anodized in oxalic acid: Effect of anodizing potential

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ABSTRACT

Commercial purity aluminum sheets were anodized at 10–30 V in 10% oxalic acid solution at room temperature. The anodized specimens were tested for its resistance against scratch damage using a microscratch adhesion tester operated in the progressive mode. The specimens were studied also for crystal structure, chemical composition, surface morphology, surface topography, microhardness and electrical resistivity by X-ray diffractometry, energy dispersive X-ray spectroscopy, field emission scanning electron microscopy, stylus based surface profilometer, Vickers microhardness tester and four point probe method, respectively. Microscratch test results showed improved adhesion of the anodic aluminum oxide coating with the untransformed bulk, as the anodizing potential decreased. During scratch test, the specimens showed formation of cohesive cracks at a load of 1 N. Energy dispersive X-ray analysis showed that the concentration of oxygen increased marginally on increasing the anodizing potential. Field emission scanning electron microscopy showed comparatively less porous microstructure of the anodized specimens for anodizing conducted at potential 20 V or lower. The results of profilometry showed formation of smooth coating surface at potentials lower than 25 V. Microhardness test showed increased hardness of the anodized aluminum with increasing anodizing potential. The electrical resistivity of anodized aluminum was in the range of 10^6–10^9 Ω·cm. X-ray diffraction measurements indicated amorphous structure of the so obtained aluminum oxide coating.

1. Introduction

Anodizing is considered an important electrochemical surface modification technique for improving the corrosion resistance and mechanical properties of aluminum and other metals. It is already known that the surface of aluminum gets instantly covered by a very thin (2–9 nm) protective oxide film, when exposed to atmosphere [1]. However, this oxide film is so thin that it does not provide sufficient resistance to corrosion even in weakly corroding media like potable water [2]. In a much more aggressive medium like hydrochloric acid solution aluminum corrodes severely [3]. Therefore, a thick, adherent and mechanically strong oxide coating is made to form on aluminum and its alloys by anodizing technique. Different types of acidic baths have been used for forming the anodic oxide coating on aluminum [4–10]. Some of the baths commonly used are sulphuric acid [4], sulphamic acid [5], oxalic acid [6], citric acid [7], boric acid [7], phosphoric acid [8], tartaric acid [9] and also several combinations of these acids [10]. In addition to these commonly used baths, recently, Kikuchi et al. [11–15] reported several studies on anodizing of aluminum using unconventional baths such as squaric acid, selenic acid, acetylenedicarboxylic acid, cyclic oxocarbon acid and etidronic acid.

For the past few years, numerous works have been reported on anodizing of aluminum from different media [4–15]. There are many reports available covering the photoluminescence [5,7], optical [9], corrosion [3,16], mechanical [17] and tribological [17,18] properties of anodized aluminum. Among the studied mechanical and tribological properties, the most common are nanoindentation [17,19] and wear [18,20].

The scratch resistance of anodized aluminum is also an equally important property for applications in areas like corrosion protection, along with hardness and wear. The scratch test can provide valuable information regarding the critical load for adhesive failure of the anodic oxide coating with the untransformed underlying bulk as well as the critical load for cohesive damage in the coating itself. Vojkuvka et al. [21] made extensive use of nanoindentation and scratch tests augmented with FE-SEM image analysis to compare the mechanical behavior of nanoporous anodic alumina coatings obtained from three different acidic electrolytes. They came out with an interesting finding that the anodic alumina coatings obtained using phosphoric acid were able to deform under nanoindentation and scratch tests without breaking up, suggesting their potential applications in nanotechnology [21]. They reported that the anodic oxide coatings formed in oxalic acid and sulphuric acid

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solutions were brittle and showed comparable mechanical behavior [21]. We would like to point out that in the work of Vojkuvka et al. [21] the maximum applied load during scratch test was limited to 450 mN and they have not gone into the aspect of the adhesion of anodic oxide coating with the underlying substrate. Riddar et al. [22] reported the effect of aluminum microstructure and distribution of silicon particles therein on the scratch behavior of anodic aluminum oxide coating. They anodized the aluminum cylinders obtained by sand casting; permanent mold casting; extrusion and high pressure die casting methods, in sulphuric acid electrolyte [22]. They showed that depending upon the manufacturing method of aluminum substrate, the anodic oxide coating behaved differently during scratch test [22]. Similarly, Malayoglu et al. [23] compared the scratch behavior of oxide coatings produced by plasma electrolytic oxidation and hard-anodizing methods using sulphuric acid electrolyte on 6082 aluminum alloy. With the help of scratch adhesion test they found out that the coatings produced by plasma electrolytic oxidation gives better adhesion values [23]. Moreover, it also showed different failure mechanism in comparison to the hard anodic oxide coating [23]. However, so far, the effect of anodizing potential on the scratch behavior of anodic oxide coating formed on aluminum has not been reported. Anodizing potential is a very important parameter as it directly influences the structural properties of the coating by self-ordering of the pores and changes in the porosity and pore size [24,25].

Therefore, the present work focuses on the scratch behavior of aluminum anodized at different potentials. In this work, anodizing has been done in oxalic acid solution since it forms hard and thick oxide coating, which is preferred for applications requiring wear and corrosion resistance. Besides scratch test, X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), field emission scanning electron microscopy (FE-SEM), surface profilometry, microhardness and electrical resistivity measurements have also been conducted.

2. Experimental

2.1. Anodizing procedure

Specimens of dimension 30 mm × 25 mm were cut from the commercial purity aluminum sheet of thickness 1 mm and used for conducting the experiments. Table 1 shows the chemical composition of the aluminum used in this study. The specimens were polished using successive grades of SiC papers. Just prior to anodizing, the specimens were first cleaned in 10% NaOH solution at 45 °C to remove the oxides present on its surface. The specimens were subsequently desmutted in 50% HNO_3 to remove the black stains. The black stains are caused by the formation of hydroxides of Fe, Cu and Si, present in the aluminum as impurities, during cleaning in NaOH solution [26]. The anodizing bath was prepared by dissolving the known amount of analytical grade oxalic acid crystals into 250 ml of de-ionized water, with the help of a magnetic stirrer. Experiments were conducted in a glass beaker at room temperature with slow stirring of the solution for 1 h in potentiostatic mode at an applied potential of 10–30 V, varied in steps of 5 V for separate specimens. Studies available on anodizing of aluminum in oxalic acid solutions show that at temperatures lower than room temperature the growth rate of aluminum oxide is considerably low, whereas, at room temperature, the rate of growth of the oxide is substantially high [27,28]. On the other hand, at temperatures higher than room temperature the growth rate increases further but the size of the pores of aluminum oxide also increases significantly [29]. Therefore in the present work anodizing was conducted at room temperature.

Table 1
Chemical composition of aluminum sheet used in the study.

Element	Al	Si	Fe	Cu	Zn
Wt.-%	96.17	1.71	1.08	0.609	0.431

During anodizing, the temperature of the bath was monitored continuously with the help of a digital thermometer. No significant change in the temperature of the bath could be noticed when different potentials were applied (in the range of 10–30 V) and the temperature remained close to room temperature (30 °C). Therefore the solution was not cooled. The anodizing potential range was chosen based on the studies reported in the literature [30]. It may be noted that the anodization of aluminum in oxalic acid solution is possible within a large potential window (potentials lower than 5 V and higher than 60 V have been reported) [30,31]. However, the pore size of anodic alumina increases significantly with the increase in applied potential [25]. The presence of large pores is detrimental for applications such as corrosion protection due to easy penetration of the corrosion causing ions through these pores up to the very thin barrier layer present on the aluminum base. Therefore the chances of corrosion of the underneath base metal are increased. In order to circumvent this problem an expensive sealing treatment is required [32]. Furthermore, at higher anodizing potentials (exceeding 30 V), the volume expansion of the anodic oxide is very high [30]. This can result in generation of large amount of internal stresses in the coating leading to the formation of cracks in the coating. On the other hand, use of very low potential (less than 10 V) makes the coating soft and also results in high pore density. Consequently, such coatings have inferior mechanical properties. Therefore, in the present work, anodizing was carried out in the potential range of 10–30 V. Table 2 lists the details of the electrochemical cell used for carrying out the anodizing experiments.

2.2. Characterization of anodized aluminum

In the characterization part, for every test two samples prepared under identical conditions were used. The chemical composition of the aluminum used for anodizing was measured by X-ray fluorescence (XRF; Innov-X, Delta). The crystal structure of the anodized aluminum was determined by both Bragg–Brentano (θ-2θ) XRD (ITAL STRUCTURES Italy, HRD 3000) measurements and grazing incidence X-ray diffraction (GIXRD; X'Pert PRO MRD, PANalytical B.V.) measurements, using monochromatized $Cu_{K\alpha}$ radiation at a wavelength of 0.154 nm. During GIXRD measurements the incidence angle was fixed at 1°. The chemical composition of the anodized specimens was measured by EDS (Bruker; AXS Microanalysis GmbH) whereas the surface morphology was analyzed by FE-SEM (ZEISS, AURIGA) at an accelerating voltage of 5 kV. The EDS measurements were carried out on the surface of the anodized aluminum. During FE-SEM analysis, the secondary and the backscattered electrons were detected by the SE and the EsB detectors, respectively. Also, a thin layer of gold was sputtered on the anodized specimens to make the specimen surface electrically conductive for FE-SEM examination. The thin layer of gold was deposited at a pressure of 10 Pa, for the time duration of 30 s, using an ion sputter coater (SEC Korea; MCM-100; 220VAC, 50 Hz) that consisted of a gold target of 50 mm diameter. A diamond stylus based surface profilometer (NANOMAP-500LS), operated in the stage scan mode was employed to measure the surface topography and average roughness (R_a) of the specimens. In order to obtain more representative information about the surface topography profilometry was done on a relatively larger area (1 mm × 1 mm). Parameters of the profilometry analysis are given in Table 3. The thickness of the anodic oxide coating was

Table 2
Anodizing cell details.

Oxalic acid concentration	10%
Anode	Commercial purity Al sheet
Cathode	AISI SS316 L sheet
Anodizing potential	10–30 V
Stirring speed	50 rpm
Bath temperature	30 °C
Anodizing time	1 h and1 h 20 min