Impact of the preliminary surface treatment of aluminum on its electrochemical behavior

Christian Girginov, Stephan Kozhukharov

Abstract: *The influence of the preliminary treatment of pure aluminum (99.5%) specimens on their surface characteristics is studied. This study was performed by means of atomic force microscopy (AFM). Samples with electrochemically polished or chemically matted surface were evaluated by two electrochemical methods: electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). A noticeable influence of the preliminary treatment on the obtained voltammetric curves, as well as on the recorded impedance spectra can be observed. This paper introduces a concept for the determination of the surface roughness by analysis of the kinetic curves, acquired during aluminum anodization in isothermal-galvanostatic regime.*

Keywords: *aluminum, pretreatment, etching, surface analysis, atomic force microscopy*

INTRODUCTION

The preliminary surface treatment of aluminum and its alloys is an ordinary procedure, prior to conducting any technological and/or electrochemical treatment. On one hand this aims to clear the metallic surface and the other to achieve certain characteristics. In some cases the appearance and surface quality of aluminum is satisfactory for many applications even before surface treatment. However, there are many other reasons for treating the samples' surfaces. Examples of attributes that can be changed by surface treatment include: surface structure, color, corrosion resistance, hardness, wear resistance, reflectivity, electrical insulation etc. The most common surface pretreatments of aluminum and its alloys are polishing (chemical, electrochemical) and etching (development of the surface). In order to investigate the surface topography, before and after pretreatment, various methods can be employed [1]. X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been used [2] to characterize aluminum surfaces, which have been pretreated by mechanical polishing and acid or alkaline etching.

It has been found that a number of phenomena, such as pitting corrosion of aluminum alloys are sensitive to the type of surface treatment [3]. The surface pretreatment influences significantly the processes of oxide film formation on aluminum [4] and its alloys [5]. In recent years, there has been great interest in the formation of porous oxide films on aluminum in electrolytes, containing fluoride ions [6-8]. The present work presents results for the observation of the aluminum surface morphology, using AFM, as well as the influence of the preliminary treatment on some electrochemical relations.

EXPERIMENTAL

The samples were cut from technical purity (99.5%) aluminum sheets, with an exposed working area of 8 cm^2. They were then put through a standard pretreatment procedure, which consists of: annealing at 400°C for 3 h, thus removing mechanical stress, electropolishing (electrolyte 210 ml H_2O, 40 g CrO_3, 450 g H_3PO_4 (85%) and 150 g H_2SO_4 (96%)), at 0.2 A cm^{-2}, 80˚C for 3 min) and matting (2% NaOH and 3% $NaNO_3$ aqueous solution, at 80°C for 10 min). Prior to each experiment, the respective sample was cleaned with double distilled water.

The surface of the aluminum specimens was observed by atomic force microscope "EasyScan"-2, Nanosurf (Switzerland).

The electrochemical measurements were performed by Autolab PGSTAT 30, driven by GPES and FRA software (Eco Chemie, The Netherlands). A standard three-electrode flat cell was used. The counter electrode was a Pt mesh, situated symmetrically around the working electrode and (Ag/AgCl/3 M KCl) as a reference electrode. All experiments were conducted in (0.5 M $(NH_4)_2SO_4$ + 0.075 M NH_4F), at constant temperature (20±1°C)

[6]. The EIS spectra were recorded at a constant potential of 0 V, in the frequency range (10 kHz - 10 mHz), the amplitude of the perturbation signal was 40 mV. Each impedance spectrum recording was followed by a LSV-potentiodynamic measurement. The LSV curves were obtained with a potential sweep rate of 10 mV/s, from -600 mV to 600 mV, in respect to the open circuit potential (OCP). These values were determined prior to each LSV measurement. This sequence of measurements (LSV after EIS) was preferred, because the former method (e.g. LSV) causes irreversible damage to the samples due to the partial dissolution of the metal during anodic polarization.

RESULTS AND DISCUSSION

Effect of preliminary treatment on the surface morphology

The topological features of the specimens, after two different surface modifications, were observed by atomic force microscopy (AFM). The obtained results are presented in Figure 1: (a) electrochemically polished and (b) matted specimen.

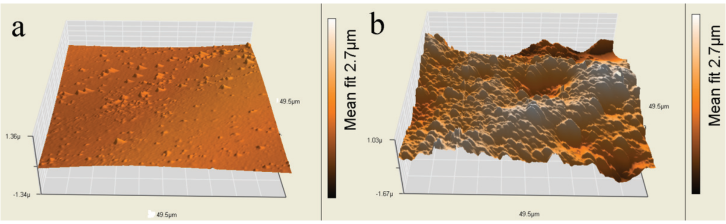

Fig.1 AFM images of (a) electropolished and (b) matted aluminum samples

From the obtained AFM-images values of certain parameters, which characterize the roughness of the surface, were estimated: S_a (average roughness value) is the average sum of the module of distances of all points from the measured surface, in direction, perpendicular to the conditional plane; S_q is root mean square value; S_m (mean roughness value) is also defined by the same average sum, but here the positive or negative values of the vectors are taken into account; S_v (valley depth) notes the distance between the conditional plane and the lowest point of the measured surface; S_p (peak height) is the distance between the highest point of the measured surface and the conditional plane; S_y (peak valley height) is the distance between the highest (S_p), and the lowest (S_v) points of the measured surface. These parameters are presented in Table 1.

Table 1. Surface parameters, acquired by AFM

samples	S_a [nm]	S_q [nm]	S_y [nm]	S_p [nm]	S_v [nm]	S_m [pm]
polished	87	102	619	413	-206	213
mat	377	486	3186	1286	-1900	160

The presented values are averaged from nine independent measurements (three points on three specimens). The images show that alkaline etching results in the formation of well developed, uniform surfaces.

Effect of preliminary treatment on aluminum electrochemical performance

It was of interest to trace the influence of surface pretreatment on some electrochemical measurements. Two types of specimens, undergone different surface modifications, were characterized, using two classical electrochemical techniques: electrochemical impedance spectroscopy and linear sweep voltammetry.

Impedance spectra were obtained after 10 min exposition of the respective specimen to the electrolyte. During these measurements, the potential was held constant at 0 V. Figure 2 represents the impedance response of investigated specimens.

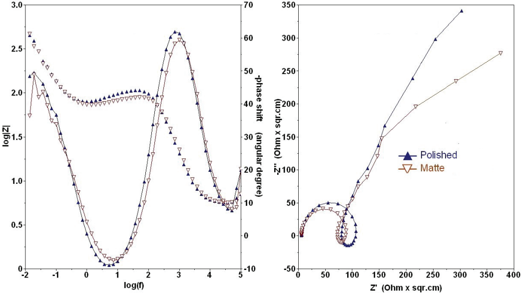

Fig. 2 Impedance spectra of aluminum specimens after respective surface modifications

The impedance spectra of the respective samples are relatively distinguishable, whereas, the results, obtained by linear sweep voltammetry (LSV), reveal rather large differences. The larger inductance loop for the polished samples is a consequence of the more efficient coverage of its lower contact surface by hydrogen gas bubbles, originated during its cathodic polarization (in acidic conditions) during the EIS measurement.

The conducted LSV-measurements indicate even more remarkable differences, which can be seen in Figure 3. Polarization of the samples during EIS measurements may account for these differences.

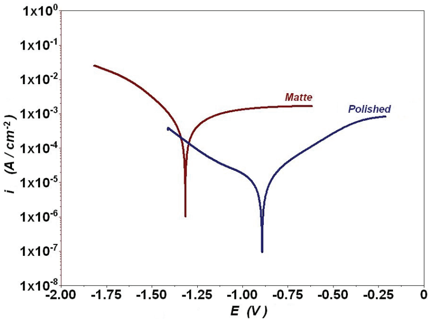

Fig. 3 Current density vs. potential curves, obtained for mat and polished samples

The results reveal remarkable differences in the electrochemical behavior of the respective specimens, according to their preliminary treatment. The corrosion potential E_{corr} of the polished samples is shifted in anodic direction, compared to the matted ones. Moreover, the polished specimens exhibited E_{corr} = -811 mV, while the matted sample showed E_{corr} = -1258 mV. Also, the corrosion current density of the polished is by entire orders of magnitude lower than the matted (e.g. i_{corr} = 296.1 μA cm^{-2}, compared to only 3.1 μA cm^{-2}, respectively). This difference could be due to their polarization resistances: R_{p} = 0.13 kΩ cm^2 and 4.82 kΩ cm^2, respectively.

The preliminary investigations confirm the expected influence of the surface treatment of aluminum samples on their electrochemical behavior.

It should be noted, that there is a method for the quantitative evaluation of the surface area development rate (σ), based on the kinetic curves acquired during their anodization in isothermal galvanostatic regime. It is known [9] that at these conditions, during the anodization of aluminum in non-dissolving electrolytes (formation of barrier type oxides) the intensity of the electric field (E) remains constant:

$$E = \frac{zF\sigma\rho}{M}\left(\frac{\Delta U_f}{\Delta Q}\right)_{J,T},$$

where: z is the charge of the transferred ion; F is the *Faraday's* constant, σ is the roughness factor (ratio between real and geometrical surface), ρ is the oxide density, M is the molar mass of the anodic film, and $(\Delta U_f/\Delta Q_f)_{J,T} = m$ is the slope of the kinetic curve. The variation of the current density in relatively narrow ranges, does not cause a distinguishable change in the field intensity [10]. If for polished samples $\sigma \approx 1$ is assumed, then the roughness of Al samples could be estimated by the slopes of the kinetic curves for polished (m_{pol}) and etched (m_{treat}) specimens: $\sigma = \left(m_{pol}/m_{treat}\right)$. This approach is still being developed and will be used to interpret the present results in near future.

CONCLUSION

The alkaline etching of the aluminum samples results in well developed and uniform surface. This result could be observed both by naked eye and using AFM. It has been found that the preliminary treatment influences the electrochemical behavior of the respective specimens. The current density vs. potential curves and the respective EIS-spectra reveal significant differences for samples of 99.5% Al, undergone two pretreatments. For a more detailed clarification of the correlation between surface parameters and electrochemical behavior of Al samples, systematic sets of experiments are underway (influence of electrolyte concentration, temperature, anodization duration, etc).

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This paper has been reviewed