Electrochimica Acta 220 (2016) 1–10

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Anti-corrosive properties of silane coatings deposited on anodised aluminium

Jarosław Wojciechowski[a], Karol Szubert[b], Ralf Peipmann[c], Mathias Fritz[c], Udo Schmidt[c], Andreas Bund[c,1], Grzegorz Lota[a,*,1]

[a] Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, Berdychowo 4, 60-965 Poznan, Poland
[b] Adam Mickiewicz University, Faculty of Chemistry, Umultowska 89b, 61-614 Poznan, Poland
[c] Technische Universität Ilmenau, Electrochemistry and Electroplating Group, Gustav-Kirchhoff-Straße 6, 98693 Ilmenau, Germany

ARTICLE INFO

Article history:
Received 28 June 2016
Received in revised form 6 October 2016
Accepted 12 October 2016
Available online 13 October 2016

Keywords:
Aluminium
Corrosion protection
Anodised aluminium oxide
Organosilicon coatings

ABSTRACT

Aluminium anodisation processes were carried out in two different solutions i.e. in oxalic and sulphuric acid. Part of the samples was subjected to hydrothermal sealing in order to seal the pores on the oxide surface. Silane coatings were deposited from two solutions containing triethoxyoctylsilane and tetraethoxysilane. Surface analysis and spectroscopic methods were applied to characterize the pristine and coated samples. Anti-corrosive properties of all samples were assessed using electrochemical methods. It can be concluded that due to the condensation reaction between the anodised aluminium and silane compounds Al-O-Si covalent bonds are created. Fitted equivalent circuit parameters are distinctively different for the investigated systems. Additionally, the size of the particles in colloidal silane solutions was determined. Due to their size the colloidal particles cannot enter into the pores of the oxide layer but form a silane film on top. Thus they create a composite coating containing trapped air in the pores.

1. Introduction

Corrosion protection of metals and alloys is mainly based on using a wide range of methods for example electrochemical protection, inhibitors and also various types of protective coatings e.g. metallic, inorganic and organic. In recent years, a great deal of attention has been paid to conversion coatings (e.g. chromate and phosphate), which are widely utilized due to their ability to regenerate. Nevertheless, there is intensive research for an alternative approach to this type of corrosion protection. It is associated with the toxic properties of the coatings formed on the basis of hexavalent chromium [1–3]. Promising candidates to replace chromium based conversion coatings seem to be organosilicon compounds, which are organic-inorganic hybrids. A significant number of papers has been published, describing the use and methods of silane deposition on the surface of alloys, steels and metals such as iron, aluminium or copper [4–24]. Alkoxy groups, which can undergo hydrolysis reactions in aqueous solutions, make it possible for the self-assembled monolayers of silane compounds to form spontaneously covalent bonds on the surface of a metal or alloy. Such metal-oxygen-silicon bonds are created via condensation reactions. Furthermore, the aliphatic chains attached to silicon can form a tight, hydrophobic barrier. Additionally, functional groups in silane compounds can be the basis for successive coating layers of other kinds. Zhu et al. [18] demonstrated that a bis-silane compound on the surface of an aluminium alloy provides better corrosion protection than monosilanes. A greater number of silicon atoms in the molecule increases the number of alkoxy groups, capable of forming covalent bonds between the surface element and a deposited film [18].

Due to their properties, aluminium alloys are often utilized in aerospace and automotive industries [25–27]. Thanks to their low density, high electrical and thermal conductivity they are widely used in many areas of science. In addition, aluminium passivates in air and water [2,3]. The thin film of aluminium oxide protects the base material against further corrosion. Therefore, depending on the use, aluminium is often subjected to electrochemical anodising to form a porous coating with a thickness of several tens of micrometres. This process is carried out typically in sulphuric, oxalic or phosphoric acid solutions at different values of applied potentials or current densities [26–31]. The resulting oxide layer

---

[*] Corresponding author.
E-mail address: grzegorz.lota@put.poznan.pl (G. Lota).
[1] ISE member.

http://dx.doi.org/10.1016/j.electacta.2016.10.080
0013-4686/

dissolves during the process. There is a steady state between the formation and dissolution. Aluminium surfaces have some defects. An externally applied electric field is concentrated on these defects. By this, the structure of the oxide layer contains pores. The size and the distribution of these pores depends on many factors, including the nature of the electrolyte, applied voltage and the temperature [26–31]. An aluminium oxide produced in the anodising process consists of two layers, i.e. a very thin non-porous barrier type layer located close to the surface and a porous layer with a much larger thickness. In order to improve the corrosion resistance of aluminium alloys, the oxide produced on the surface is used for further treatment leading to sealing of existing pores, which takes place, among other things, when the aluminium is immersed in a cold NiF_2 solution or in a boiling distilled water [31,32]. During this process the walls of the pores dissolve. Any space is filled with dissolution reaction products. In 1986, on the basis of electrochemical impedance spectroscopy measurements Hitzig et al. [32] discussed the presence of two layers, i.e. a barrier layer and a porous layer. Each layer has its own time constant in the Bode plots.

This paper presents new insights into the anti-corrosive properties of silane coatings deposited on the surface of an anodised aluminium oxide (AAO). The anodising process was performed in two different solutions, i.e. in oxalic and sulphuric acid. Then silane films were deposited on the surface of thus obtained oxide layers with sealed and open pores. This allowed creating Al-O-Si bonds between the silicon and aluminium atoms. Anti-corrosive properties of the samples were evaluated by the application of electrochemical methods. Additionally, analysis of the surface morphology was performed. There are correlations, and differences in inhibition of the corrosion process between the porous and non-porous anodic coatings with the deposited silane compounds.

2. Experimental

2.1. Anodisation in oxalic and sulphuric acid

Initially, the aluminium disc (ALMG4, VEB Robotron) with the following composition: 3.7-4.7 wt-% Mg, 0.46 wt-% Zn, 0.2 wt-% Cu, 0.1 wt-% Mn, 0.1 wt-% Cr, max 0.08 wt-% Si, max 0.08 wt-% Fe and a diameter of 2.79 cm was immersed in 5% NaOH solution (p.A., VWR) for 5 minutes to degrease the surface and remove any residual oxid layer. Then the aluminium disc was immersed in 5% HNO_3 solution (VWR) for 5 minutes to remove remaining contaminations and to neutralise the surface.

After rinsing with distilled water, the samples were placed in 0.4 mol.dm^{-3} oxalic acid solution. Two aluminium plates were placed in a distance of 5 cm at both sides as cathodes. The anodising process lasted 60 minutes at 20 °C at a voltage of 40 V. For this purpose, a BM 2183 DC power supply and a Haake B3 thermostat (with Haake C1 temperature control unit) were used. The current density was approximately 1 A.dm^{-2}. Half of the AAO samples were immersed in boiling distilled water for 5 minutes in order to seal the pores on the surface. Then, a thickness gauge (Miniset 4000, Elektro-Physik Köln) was used to check the thickness of the resulting coatings, which reached 16–17 μm.

For comparison, aluminium samples were anodised in 20% sulphuric acid solution (VWR) at 18 °C. The surfaces of the aluminium discs were cleaned as described above. Anodising was carried out at a voltage of 15 V for 30 minutes. For this purpose a Statron type 3206 DC power supply was used. The current density was 1.5 A.dm^{-2}. Part of the samples was dipped in boiling distilled water for 5 minutes in order to seal the pores on the surface. The thickness of the resulting coatings was 15–16 μm.

2.2. Silane surface treatment

At first, 5% triethoxyoctylsilane (OTES, Sigma Aldrich) solution in methanol (Sigma Aldrich) was prepared at a 5:95 volume ratio and stirred at 25 °C for 30 minutes. Then 20 ml of triethoxyoctylsilane (OTES) and 11 ml of tetraethoxysilane (TEOS, Sigma Aldrich) were added to 33 ml of methanol to prepare the second solution with a pH equal to 4, adjusted by acetic acid. The solution was stirred at 25 °C for 72 hours. Anodised aluminium oxide (AAO) samples (open and sealed pores) were put into the thus obtained mixtures. The beakers, containing the samples in the two solutions were placed in an ultrasonic bath for 15 minutes. Finally, the samples were cured in an oven in a vertical position at 80 °C for 1 hour. Table 1 shows the nomenclature of all AAO samples.

2.3. Analysis of the surface morphology

A scanning electron microscope (SEM/EDS, Hitachi, SU3500) was used to characterise the surface morphology of the samples. Additionally, FT-IR spectra were recorded with a Bruker Tensor 27 Fourier transform spectrometer equipped with a Golden Gate diamond ATR unit. In all cases 16 scans at the resolution of 2 cm^{-1} were collected for a spectrum.

2.4. Water contact angle measurements

A Krüss GmbH instrument (model DSA 100 Expert), equipped with a fully automatic dosing system was used to determine the static water contact angle (WCA) values of all specimens. The measuring method was based on the shape analysis of the drops which were embedded on three different, randomly selected sample surface regions. The average values of the results were considered.

2.5. Particles size analysis

Distribution of particle size in the silane sol-gel solutions was determined using a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK), operating-based-on-the-non-invasive back-scattering (NIBS) technique.

2.6. Electrochemical measurements

Electrochemical measurements were performed in a Plexiglas® cell using a three-electrode configuration. Bare aluminium, anodised aluminium oxide (AAO) and anodised aluminium oxide with deposited silane coatings served as the working electrodes. A saturated calomel electrode (SCE) and a platinum disc were used as the reference and counter electrode, respectively. All the

Table 1
Nomenclature of bare aluminium and all combinations of AAO samples with or without deposited silane coatings.

Sample	Acid	Pores	Silane coating
Aluminium	–	–	–
OA-o-0	oxalic	open	–
OA-s-0	oxalic	sealed	–
OA-o-1	oxalic	open	OTES
OA-s-1	oxalic	sealed	OTES
OA-o-2	oxalic	open	OTES + TEOS
OA-s-2	oxalic	sealed	OTES + TEOS
SA-o-0	sulfuric	open	–
SA-s-0	sulfuric	sealed	–
SA-o-1	sulfuric	open	OTES
SA-s-1	sulfuric	sealed	OTES
SA-o-2	sulfuric	open	OTES + TEOS
SA-s-2	sulfuric	sealed	OTES + TEOS