



Pulse electrodeposition of adherent nickel coatings onto anodized aluminium surfaces



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ABSTRACT

Aluminium is one of the mostly used elements in the industry because of its abundance and low weight. However, the deposition of a metallic coating requires performing the so-called zincate pre-treatment in order to allow the formation of inter-metallic bonds and thereby achieving sufficient adherence. In this work, porous anodic aluminium oxide (AAO) is used as an anchoring intermediate layer for nickel coatings. AAO is grown anodically in sulfuric acid and nickel coatings are deposited by potentiostatic reverse pulse electrodeposition onto as-anodized aluminium surfaces. The electrodeposition of nickel is initiated onto the electrochemically thinned barrier layer of AAO and pursued until the complete covering of the oxide. The electrochemical behavior of Watts and sulfamate baths is investigated by cyclic voltammetry for different barrier layer thickness, allowing to validate the thinning conditions and to determine the appropriate deposition potential of nickel. GD-OES measurements show that low duty cycles are necessary to achieve high filling ratio of the AAO. SEM micrographs show that a smooth uniform coating is obtained when nickel is deposited in presence of additives.

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1. Introduction

It is well known that the surface of aluminium requires a specific pretreatment in order to electrodeposit adherent coatings [1]. The zincate process consists of the deposition of a thin Zn layer by galvanic displacement. This layer offers a protection against oxidation and thus prevents the formation of a native oxide dielectric layer which would otherwise exclude the establishment of inter-metallic bonds between the electrodeposit and the substrate [2]. This process is widely used in industry for further electrodeposition of corrosion and wear resistant coatings. However, alternative processes can be required either when the presence of a zinc intermediate layer is prohibited or when the aluminium alloy composition induces a low reliability of the zincating step.

For the last decades, anodization of aluminium has attracted many scientific interests because, in appropriate conditions, it leads to the growth of a porous oxide layer with arranged nanopores. More particularly, Masuda and Fukuda [3] have developed a

two-step anodization method which allows obtaining a high ordering of nanopores whose axis is perpendicular to the substrate. The pores are organized in a hexagonal close-packed cell which leads to very high pore density. Furthermore, the pore and cell dimensions can be tuned via the anodization conditions [4–7] and it has been shown that nanopores with a diameter smaller than 10 nm can be obtained in sulfuric acid [8]. The oxide film consists of two distinct parts: the porous oxide and the barrier layer. The thickness of the porous layer is dictated by the anodization duration whereas the barrier layer thickness is proportional to the anodization potential (1–1.2 nm/V) [9,10].

The electrochemical deposition of metals, semiconductors and polymers within nanopore arrays has been intensively studied for the fabrication of nanowires [11–13]. However, direct electrodeposition within anodic aluminium oxide (AAO) remains a challenge because of the presence of an oxide barrier layer at the nanopore bottom. High potentials are thus required in order to tunnel electrons through this dielectric layer. To facilitate the electron tunneling, Nielsch et al. [14] developed a method which allows thinning down the barrier layer by gradually decreasing the applied potential after the second anodization step. Further related studies have demonstrated the possibility to form branched

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nanopores during the thinning process and the hierarchy of multiple branched pores can be controlled via the shape and duration of the potential decrease [15,16]. Additionally, Winkler et al. [17] proposed a method to completely remove the barrier layer localized at the nanopore bottom by successively decreasing the potential, carrying out a chemical pore widening and, applying a cathodic polarization in potassium chloride. Alternatively, Jagminas et al. [18] reported an original process to decrease the barrier layer resistivity. It consists of doping the barrier layer by fluoride through a re-anodization in the presence of fluoride salts.

The electrodeposition within as-anodized AAO has been investigated for many different materials by continuous deposition [19], AC deposition [20], and by pulse techniques [14]. It has been shown that continuous depositions may eventually damage the oxide layer either because of cathodic side reactions or by Ohmic heating [21]. Therefore, the elaboration of Ag, Ni, Fe, Bi, Co, Cu and Au nanowires has been investigated by AC electrodepositions since it offers the opportunity to rectify the barrier layer impedance [21–28]. Unfortunately, it has been proven difficult to control the nanowire morphology through AC electrodeposition. More efforts were then dedicated to the optimization of the method proposed by Nielsch et al. [14] which consists of performing a reverse pulse deposition onto the thinned barrier layer. Typically, the metal is deposited during a short cathodic pulse which is followed by a short positive polarization in order to discharge the barrier layer capacitance. Then, a pause can be applied in order to relax the diffusion layer. Sousa et al. [29] have shown that a uniform barrier layer thickness of 10 nm is the most appropriate for uniform nickel deposition. This method was also applied to the electrochemical deposition (ECD) of other materials such as silver [30]. However, the cathodic pulses were always applied in galvanostatic mode. Thus, it is very sensitive to active surface area modifications which may occur during the different stages of the nanopore filling.

In this work, nickel was potentiostatically deposited within AAO templates by reverse pulse methods. The purpose was to reach more stable growth conditions over the filling of the different levels of the branched nanopores and the growth of the covering layer. The appropriate potential for nickel deposition was determined by voltammetry techniques for a diluted Watts bath and diluted sulfamate baths with or without additives. The resulting multilayered coatings were characterized by scanning electron microscopy (SEM) and Glow Discharge Optical Emission Spectroscopy (GD-OES).

2. Experimental

2.1. Electrochemistry

All electrochemical experiments were conducted in a two-electrode electrochemical cell using a platinum counter electrode and a potentiostat/galvanostat Autolab 302N equipped with a voltage multiplier. The electrolyte temperatures were accurately controlled by a Julabo refrigerated/heating circulator F12-ED and validated with a glass thermometer before each experiment. 0.5-mm thick aluminium (99.999%) disks were purchased from Goodfellow. The substrates were first degreased in 1.25 M NaOH at 60 °C for 5 min then neutralized in 5.55 M HNO₃ before being electropolished in HClO₄:C₂H₆O = 1:3 at 10 °C for 120 s at 20 V. Nickel electrolytes were prepared using boric acid and nickel sulfate and nickel chloride for the Watts or nickel sulfamate for the sulfamate bath. Sodium dodecyl sulfate (SDS) and saccharine were added as additives to the nickel sulfamate electrolyte when mentioned. NaOH (98%), HNO₃ (70%), H₃PO₄ (85%), H₃BO₃ (99.5%), NiSO₄ (99%), NiCl₂ (98%), and Ni(NH₂SO₃)₂ (98%) were purchased from Sigma

Aldrich whereas HClO₄ (85%), C₂H₅OH (99.8%), H₂CrO₄ (99%), SDS (97%), and saccharine (99%) were provided by Fluka.

2.2. Electron microscopy

High resolution SEM images were acquired with a Hitachi S-4800 FE-SEM with an acceleration voltage of 2 kV. Cross sections and tomography images were obtained by using a focused ion beam (FIB)/SEM Tescan workstation equipped with a Shottky Field emission gun electron beam. The FIB Lyra was operated with a gallium source at 30 kV and 15 pA. The 3D reconstruction was done by combining 36 slices with Fiji ImageJ Freeware software and the 3D image resolution is $x = 6.7$ nm, $y = 6.7$ nm, $z = 19.8$ nm.

2.3. X-ray diffraction

X-ray diffraction patterns were recorded using a Bruker D8 Discovery diffractometer in Bragg-Brentano configuration, using the Cu K α radiation ($\lambda = 1.5418$ Å). The structural coherence length was evaluated through individual peak profile analysis using the Fullprof suite of programs and the Scherrer formula, after correction from the instrumental resolution function.

2.4. Filling ratio

GD-OES measurements were performed with a Jobin Yvon JY 5000 RF with a pressure of 600 Pa and an output power of 12 W. When required, the nickel covering layer was minutely mechanically polished with SiC abrasive paper. Nickel has been calibrated using a pure nickel (99.999%) reference material. It thereby allowed determining the nickel quantity present in the AAO template by integrating the Ni signal over a specific time range. The uncertainty of the results was calculated by the uncertainty propagation formula.

3. Results and discussion

3.1. Anodization: structure of AAO grown from Al

Porous AAO layers were prepared by a two-step potentiostatic anodization process at 25 V in 0.3 M sulfuric acid at 3 °C. The first step consists of applying a long anodization of 8 h. It gives rise to an unordered porous oxide which is subsequently dissolved in a mixture of 0.4 M H₃PO₄ and 0.2 M H₂CrO₄ at 60 °C for 1 h. This first step allows the formation of a honeycomb-like pattern on the aluminium surface. Afterwards, the pre-structured substrate was anodized for 30 min under the same conditions as the 1st anodization. This 2nd anodization leads to the formation of ordered nanopore arrays. Then the barrier layer was thinned down by exponentially decreasing the applied voltage through 60 steps of 20 s. Finally, the barrier layer thickness was homogenized by maintaining the last potential value for 600 s. It is well known that the barrier layer thickness is proportional to the anodization potential and it can then be monitored by adjusting the last potential value, later called “the thinning potential”.

Fig. 1 shows the potential form applied for the 2nd anodization step and the resulting current density. The part (a) corresponds to the steady state anodization performed at 25 V. During the first instants, the barrier oxide layer is built up and the current density drops to its minimum value. Afterwards, the current density increases due to the formation of cracks in the oxide which serve as nucleation sites for the pore growth. During the part (b), the anodization potential was exponentially decreased through 60 steps of 20 s until it reached the selected potential value which corresponds to the targeted barrier layer thickness. During this stage, the average current density decreases exponentially. For

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