



Mechanical properties and interface toughness of metal filled nanoporous anodic aluminum oxide coatings on aluminum



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ABSTRACT

The mechanical properties and coating/substrate interface toughness of nanoporous anodic aluminum oxide thin films, both unfilled and metal-filled, are investigated in the current study. A two-step anodization process is used to grow the porous oxide, which is subsequently filled with Ni. The mechanical properties of the coating are probed using nanoindentation and the micro-cantilever deflection technique is used to study the interface toughness. The results are discussed and suggestions for improving the interface toughness are made.

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1. Introduction

In the present study, the suitability of nanoporous anodic aluminum oxide (AAO) as the base layer for metallic coatings on aluminum is investigated. Due to its unique honeycomb like structure consisting of regular nanopores that can be filled with different metallic, ceramic or polymeric materials, AAO has been intensively investigated as an attractive material for various applications in optics, electronics and magnetism in recent years [1]. The nanoporous structure can also be used as an attractive base layer for coatings on aluminum and its alloys, especially in cases where the layer adhesion on the substrate is critical for a successful application. Thus, it could also be used as an alternative to the zincate-plating process [2], in which a zinc layer is produced by galvanic displacement of aluminum with zincate. This zinc layer prevents further oxidation of aluminum and serves as substrate for subsequent metallizations. Although it has been in use for many decades, obtaining well adhering coatings using the zincate process is still challenging and leads to high rejection rates in production. Therefore, there is a strong industrial demand for an alternative process with improved process control.

The basic idea of this work is to grow an anodic alumina layer with a regular nanoporous structure, which is afterwards filled with Ni. This should serve as an industrially relevant example for metallization on aluminum. The filled porous structure should then act as a mechanical anchor for the film on the substrate. This strategy is known to have an advantageous influence on coating adhesion [3]. Therefore, in the current study, an AAO layer is grown on a high purity aluminum substrate,

which is subsequently filled with Ni to form a nanocomposite thin film consisting of an alumina matrix filled with Ni nanowires. The mechanical properties of the coating are probed by nanoindentation and the toughness of the substrate/coating interface is quantitatively measured using the micro-cantilever deflection technique [4,5].

2. Experimental

2.1. Coating deposition

For film deposition, 0.5 mm thick Al disks (99.999%) are degreased in 1.25 N NaOH at 60 °C for 5 min, neutralized in 5.55 N HNO₃, and then electropolished in HClO₄:C₂H₅OH = 1:3 at 10 °C for 2 min at 20 V. Afterwards, a two-step anodization process is applied in order to obtain well organized nanopore arrays. The first anodization is achieved in 0.3 M H₂SO₄ at 3 °C for 8 h at 25 V. The obtained oxide layer is subsequently dissolved by immersion in 0.4 M H₃PO₄ + 0.2 M H₂CrO₄ at 60 °C for at least 1 h. The second anodization is carried out under the same conditions as the first one for 1800 s. Directly after that, the anodization potential is exponentially decreased down to 7.5 V through 60 steps of 20 s each, and finally maintained at 7.5 V for 600 s. This last step allows thinning and homogenizing the barrier oxide layer in order to facilitate subsequent electrodeposition.

Then, the porous anodic aluminum oxide is filled with Ni by potentiostatic reverse pulse deposition in 0.73 M H₃BO₃ containing 0.154 M Ni(NH₂SO₃)₂, 0.7 mM SDS and 10.9 mM saccharine at 45 °C. The potential waveform consists of a cathodic pulse of 8 ms at −11 V followed by a short anodic pulse of 2 ms at 7.5 V. This period is repeated 360,000 times. Al disks and chemicals are purchased from Goodfellow and Sigma-Aldrich respectively. A Julabo refrigerated/heating circulator

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F12-ED is used for accurate control of electrolyte temperature and all electrochemical experiments are conducted using a potentiostat/galvanostat Autolab PGSTAT302N equipped with a voltage multiplier.

2.2. Nanoindentation

Nanoindentation tests are performed on unfilled AAO and Ni-filled AAO using a Hysitron Ubi 1 system (Hysitron Inc., Minneapolis). A maximum load of 3 mN is applied to yield penetration depths of ~150 nm. The indentation depth is less than 10% of film thickness (of 2.6 µm) and well within the range to avoid substrate effect [6]. High sample roughness due to filling up and overflow of the AAO pores with Ni poses a challenge in terms of indenting flat surfaces and measuring the mechanical properties of the composite. Performing grid indents blindly would have resulted in undesirable artifacts in measurements due to the indenter tip landing on slant surfaces, indenting only Ni and large scatter in experimental data. This problem is tackled by performing surface topography scans using the indenter tip (SPM feature in this instrument) and placing the indents in relatively flat areas. This provides consistent results over a large region tested on the sample.

The recorded load–displacement data of all tests are evaluated using the Oliver–Pharr method [7]. The hardness and modulus values determined for AAO are for the overall porous structure. This is in contrast to the proposal by Ng et al. [8] to measure the true solid area of the residual indents, i.e. the gross indent area minus the area of the pores, in order to obtain the hardness of the solid AAO.

2.3. Fracture mechanics testing

For the cantilever fabrication, a Ni-filled AAO specimen is cut in half using a water cooled wire saw and low cutting speeds to minimize heating of the specimen. One of the halves is subsequently ground to achieve a flat cutting surface and afterwards mechanically polished using alumina suspension with a particle size of 0.25 µm. The surface layer, plastically deformed by polishing, is removed by focused ion beam (FIB) machining with a Tescan Lyra dual beam FIB/SEM workstation at 30 keV with 7 nA ion current. The free-standing microcantilevers are subsequently FIB milled with currents decreasing from 5 nA for coarse milling to 90 pA for fine polishing to reduce FIB damage. The nominal target size of the cantilevers is a length of $L = 3 \mu\text{m}$, a thickness of $B = 1 \mu\text{m}$ and a width of $W = 1 \mu\text{m}$, with the interface lying 0.4 µm from the cantilever base. The dimensions of each cantilever are measured after the last polishing step. Subsequently, a notch is introduced into the cantilevers directly at the interface using FIB machining at low ion current conditions (30 keV, 10 pA). Fig. 1 shows a sketch of the orientation of the cantilevers with respect to the coating structure.

The cantilevers are tested in-situ in a ZEISS DSM962 tungsten filament scanning electron microscope (SEM). An ALEMNIS microindenter with a 500 mN load cell and a spheroconical indenter (tip radius = 710 nm) are used for testing in displacement control with a

displacement rate of 3 nm/s. Cantilever bending inside the SEM allows easy positioning of the indenter on the cantilever, as well as the monitoring of deformation and the onset of crack growth on the specimen. The bending length l , i.e. the distance between the notch and the indenter contact point, is measured for each cantilever prior to testing. The load–displacement data are thermal-drift corrected by measuring the load change during a 300 s holding step applied both before and after testing. The load measured during the tests is offset by the loading rate determined in these holding steps. A total of 10 specimens are tested. Four samples show pronounced plastic deformation in the Al substrate at the cantilever base before crack growth initiation and are therefore not taken into account for the interface toughness measurement.

Post-mortem analysis of the fracture surfaces is conducted in a Hitachi S4800 high resolution SEM (HRSEM). The initial notch depth a of each cantilever is measured on the fracture surfaces and is $0.43 W < a < 0.55 W$.

The measured load F and notch length are used to calculate the fracture initiation toughness K_C according to [9]:

$$K_C = \frac{6Fl}{BW^2} \sqrt{\pi a} f\left(\frac{a}{W}\right), \quad (1)$$

with the dimensionless geometry factor

$$f\left(\frac{a}{W}\right) = \sqrt{\frac{2W}{\pi a} \tan \frac{\pi a}{2W} \frac{0.923 + 0.199(1 - \sin \frac{\pi a}{2W})^4}{\cos \frac{\pi a}{2W}}}. \quad (2)$$

The resulting K_C is converted into an energy release rate G_C using the relationship

$$G_C = \frac{K_C^2}{E^*}, \quad (3)$$

with [10]

$$\frac{1}{E^*} = \frac{1}{2} \left(\frac{1}{E_F} + \frac{1}{E_s} \right). \quad (4)$$

Here E_F is the film's Young's modulus determined using nanoindentation and $E_s = 70 \text{ GPa}$ is the Young's modulus of the Al substrate.

3. Results

A top-view HRSEM image of the unfilled AAO structure is given in Fig. 2a. The islands visible on the top of the AAO stem from coating the film with gold to prevent charging. A FIB-machined cross-section of the Ni-filled coating is shown in Fig. 2b, with a magnified view of the interface area shown in Fig. 2c. The thickness of the coating is 2.6 µm. The bright lines ranging from the substrate to the top of the coating (Fig. 2b, c) are the metallic Ni nanowires filling the porous AAO structure. The metallic nature of the nanowires is also confirmed by XRD measurements, from which an average grain size of 30 nm is calculated using the Scherrer equation (not reported in this manuscript). Using HRSEM, the pore diameter is determined to be around 28 nm and the interpore distance to be about 65 nm, which results in a porosity $V_p = 14.8\%$ and a pore density of $2.4 \times 10^{10} \text{ cm}^{-2}$ in the film plane. The cross-section reveals that not all pores are completely filled with Ni. Furthermore, a thin continuous alumina barrier layer is found at the interface between the aluminum substrate and the porous AAO.

The results of the nanoindentation measurements are given in Table 1. For the unfilled AAO, the indentation hardness H_{AAO} and Young's modulus E_{AAO} are $4.4 \pm 0.3 \text{ GPa}$ and $113.4 \pm 3.3 \text{ GPa}$, respectively. The hardness H_F and Young's modulus E_F of the film consisting of Ni-filled AAO are $4.4 \pm 0.7 \text{ GPa}$ and $101.4 \pm 8.9 \text{ GPa}$.

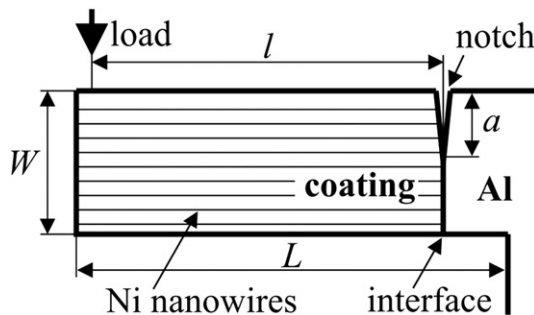


Fig. 1. Sketch of the cantilever orientation with respect to coating orientation and denominations.

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