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3D printed double flow cell for local through-thickness anodisation in aluminium

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ABSTRACT

Local through-thickness anodisation of aluminium sheets was performed in a specially designed double flow cell, which was realised by selective laser sintering. Hard anodisation (HA) conditions with voltages between 110 and 140 V including different pre-anodisations at mild conditions were tested employing oxalic acid as electrolyte. Partly transparent, porous alumina spots of 15 μm thickness and 3.5 mm diameter, predetermined by the cell geometry, were produced. The design of the presented cell allows tuning of electrolyte flow profile and electric field by adjusting the distance between counter electrode and aluminium specimen (working electrode) and therefore altering mass and heat transfer during the anodising process. As it enables localised oxide growth in HA regime from both sides of an aluminium sheet, process times for through-thickness anodisation can be reduced. Pore arrangement of the produced alumina spots was examined showing interpore distances in the range of 180 and 220 nm and pore diameters of 40 to 60 nm, both values increasing with applied HA voltage. Optical properties of the produced alumina spots were studied by means of UV-visible transmittance analysis.

1. Introduction

Even though anodic oxidation of aluminium and its products from barrier-type to porous-type alumina films and membranes has been constantly investigated for the last 100 years [1], it is recently gaining enormous attention, largely due to the discovery of self-ordering anodic aluminium oxide (AAO) pore arrays by Masuda and Fukuda [2]. Based on this, numerous studies were performed defining 'self-ordering regimes' for various electrolyte systems [2–5], suggesting formation mechanisms [5–7] and revealing ideal process parameters for the aspired porous structure. Applications, especially for nanoporous AAO, can be found in a broad range of research fields [1,7–10]. However, the growing number of possible applications for the very versatile self-ordered alumina implicates increasing demand for fast, simple, but tailored production methods. Concerning the process parameters, the introduction of the so-called "hard anodisation" (HA) [11,12] and/or critical potential anodisation [13], employing potentials or field strengths close to the breakdown potentials or field strengths in acidic electrolytes were one step towards acceleration of production, reducing the fabrication time for AAO membranes [14–17] significantly. However, to achieve an integral process optimization, it is of great importance to develop instrumental setups attuning to this diversity of electrochemical processes.

In this manner, 3D printing of electrochemical cells represents a simple, fast and highly flexible method in realising electrochemical cells and setups tailored to specific measurement requirements. Its flexibility is not limited to the cell's design, but also to its chemical and mechanical stability considering the variety of 3D printing methods and their material precursors.

In this work, an electrochemical double flow cell is presented, designed for local through-thickness anodisation of alumina sheets. In this way, partly transparent alumina sheets were produced and analyzed in terms of microstructural and optical characterisation.

2. Materials and methods

2.1. Chemicals and sample preparation

The starting material, a high purity aluminium foil (Merck, pro analysis, 0.3 mm thick), was cold-rolled to a final thickness of 15 μm. The aluminium sheets were ultrasonically cleaned in acetone for 10 min and electropolished in a Brytal solution containing 15 wt%

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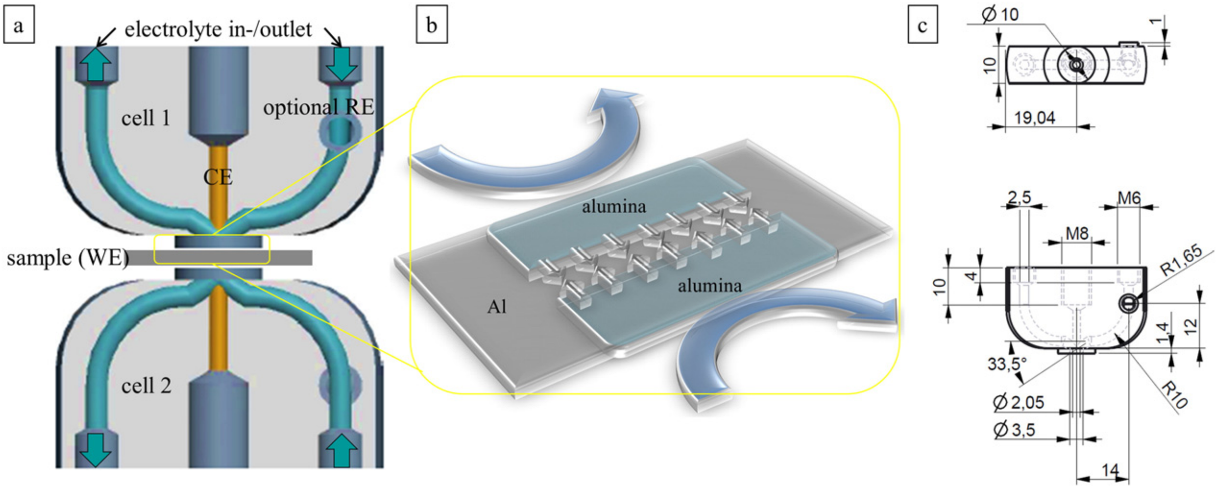

Fig. 1. Schematic presentation of the 3D printed double flow cell (a) and the alumina formation proceeding from both sides of the sample (b) as well as dimensions of the cell (c).

Na_2CO_3 and 5 wt% Na_3PO_4 at 80 °C. As anodising electrolyte, 2.7 wt% oxalic acid was used. All solutions were prepared from analytical reagents without further purification and deionised water.

2.2. Double flow cell

Anodising was performed with a double-flow cell, schematically depicted in Fig. 1, which was specifically designed for applications where mass and heat transport as well as removal of emerging gas bubbles is of great importance. The cell was designed in CAD software and realised by selective laser sintering of polyamide (PA12) with a spatial resolution of ± 0.3 mm (EOSINT P800, EOS GmbH, Germany). The material shows chemical resistance against the oxalic acid electrolyte used in this work without revealing any changes to mechanical or optical properties even after long-term immersion in the electrolyte. Moreover, no swelling of the material or a change in mass could be observed. For usage of other electrolytes, which are dissolving polyamide, the cell can be also fabricated out of other polymers like acrylonitrile butadiene styrene (ABS) by fused deposition modeling. It contains a height-adjustable counter electrode, which is a gold-plated stainless-steel thread rod. By controlling the distance between the sample as working electrode and the counter electrode, which simultaneously acts as breaker forcing the electrolyte solution to pass by close to the sample surface, the electrolyte flow profile as well as the electric field can be adjusted. Alternatively, when a 3-electrode setup is needed, a micro-reference electrode can be inserted. Electrolyte is pumped from a temperature controlled tank through the U-shaped flow channels of the cells, featuring a roundish cross section with 2.6 mm diameter, with a flow rate of 75 ml min^{-1}. The complex flow channel geometry including the height-adjustable counter electrode, creating the advantages mentioned above, can be easily fabricated in 3D printing process, but can hardly be realised by standard mechanical manufacturing from a polymer block. For this reason and its cost-effectiveness and reproducibility, 3D printing is chosen as production method.

To ensure a constant electrolyte flow rate in both cell compartments, each is equipped with a separate electrolyte pump. Electrolyte hoses are kept as short as possible (>40 cm). The high flow rate ensures effective temperature control of the sample surface. The lower of the two cell compartments is mounted on a lifting plate, fixating the sample by upwards motion and pressing against the upper static cell, which is equipped with a force sensor ensuring a constant contact pressure.

2.3. Anodisation

Anodisation is performed similar as proposed by Lee et al. [11] in a two-step process: After pre-anodisation for 1 or 5 min at 40 V in oxalic acid (1 °C), the voltage was linearly increased with a rate of 0.5 V s^{-1} towards the final HA voltage of 110, 120, 130 or 140 V. All electrochemical experiments were carried out using a Keithley Sourcemeter 2400.

2.4. Characterisation

Surface and cross-sections of anodised alumina samples were examined by scanning electron microscopy (SEM) and performed with a ZEISS 1540XB CrossBeam. Optical transmittance spectra were recorded with a PerkinElmer UV/VIS/NIR spectrometer Lambda 1050.

3. Results and discussion

Anodisation in the double-flow cell was conducted in a two-step process in order to form a protective oxide layer on the aluminium sample at MA conditions before main anodisation is conducted at hard anodisation parameters. Fig. 2 shows the current-time transients recorded during a HA step at applied voltages from 110 to 140 V after the sample was pre-anodised at 40 V for 1 min. The exponential decay of the current as function of time has already been observed in earlier studies [11,12] and was attributed to diffusion-limitation of anodisation

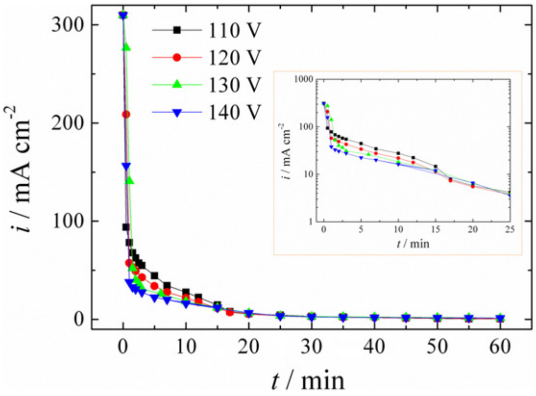

Fig. 2. Current density transients recorded during hard anodisation step at different applied voltages. Detail featuring logarithmic scale showing first 25 min of anodisation.