Nanoporous Anodized Aluminium Coatings for Biomedical Applications

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Introduction. Nanoporous anodized aluminium oxide (AAO) has become increasingly important in biomedical applications over the past years [1] due to its biocompatibility, increased surface area, and the possibility to tailor this nanomaterial with a wide range of surface modifications. AAO nanopores are formed in an inexpensive anodisation process of pure aluminium or its alloys, which results in highly ordered, vertical nanotubes with well-controllable pore diameters, depths, and interpore distances. Because of these outstanding properties AAO nanopores have become excellent candidates as nanostructured substrates for cell-interface studies [1]. Applications of nanoporous alumina membranes in biotechnology and medicine are unlimited, for instance, the use of nanoporous AAO as implant modifications, coculture substrates, or immunoisolation devices [1, 2]. Also, AAO can be used for DESI (desorption electrospray ionization) technique [3], where performance of nanoporous alumina surface is compared with that of PMMA, which is a widely used surface in the previous DESI experiments.

Currently used coated bone implants frequently suffer from aseptic loosening as a result of failure of the interface between implant and coating [2]. AAO coating system aims to address this problem by having interface bond strength greater than that of bone. The nano-porous structure might be loaded by materials having specific biological response, leading to a composite implant coating tailored for specific applications. The shear strength of the interface between AAO coating and substrate has been measured and the biological performance of AAO coatings on titanium substrates has been assessed using human osteoblast-like cells and compared with other implant materials [2].

Experiment. (1) Sulphuric acid bath: Two step anodizing was performed in a 20 wt % sulphuric acid solution at ~ 1 °C using a 2 electrode electrochemical cell at 500 rpm. Electropolished Al samples were anodized at potential of either 15 or 21 V for 10 min. After a first anodizing step, samples were immersed into solution of CrO$_3$ (1.8 wt %) and H$_3$PO$_4$ (6 wt %) for 10 and 15 min respectively, at ~60 °C to remove oxide layer after first anodizing. In this way, we achieved a pre-patterned aluminium surface for pores to grow inwards during the second anodizing step at a constant potential of either 15 or 21 V for 97 and 20 min respectively at ~ 1 °C. The pore size 16 and 27 nm was obtained (Fig.1).
(2) **Oxalic acid bath**: AAO samples were produced in oxalic acid electrolyte to obtain various pores having diameter 25 to 80 nm. They were also produced by two step anodizing. Electrolyte was 0.3 M oxalic acid with an agitation speed of 800 rpm. Parameters such as temperature, potential and time were selected according to the results Pasaoglu obtained in his research. First step anodizing was performed at 25 °C for 1h at potential 40 V. Oxide removal procedure have been performed in the same solution as for sulphuric acid only the its duration was longer (1h). After oxide removal samples were anodized at 5 °C at 70 V for 1h. Time was adjusted to produce the same thickness of AAO as it was obtained in sulphuric acid bath ~17µm. The initial pore diameter after 2 step anodizing was ~25 nm (Fig. 2a). Finally, pores were widened at room temperature (~25 °C) by immersion of as-received AAO in H₃PO₄ (5 wt %) for different durations. Time was chosen according to the pore diameters needed (Fig. 2).

**Results and discussions.** Nanoindentation tests were performed over a wide range of normal loads (2-200 mN) to study the mechanical behaviour of anodized aluminium oxides. The investigation of nanoindentation imprints and surrounding areas was done by SEM (Fig. 3). The corners of the imprints are shown in Fig. 3 (a - c), its are surrounded by regular pore structure, while the pores appear to be deformed within the imprint due to an overall collapse of the porous structure. Rather than through pure material plasticity, the overall structure of the AAO is

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**Fig 1.** SEM images of AAO obtained at 15 V (a) and 21 V (b) from sulfuric acid bath

**Fig 2.** SEM images of AAO produced in oxalic acid bath with ~ 25 (a), 45 (b) and 75 nm (c) pore diameters
progressively deformed on indenter loading. Although no major cracks are observed either within or around the imprints, a difference is easily noticed between oxalic and sulphuric acid produced samples. It can be observed (Fig 3a) that AAO particles are smeared in the pores during indentation making the pores invisible or less visible, while in Fig. 3c which belongs to oxalic acid sample with a pore diameter of 45nm, pores can be seen clearly without being smeared by AAO. Hexagonal structure is still present even in the imprint. This can be linked to the composition of AAO. As for samples produced in sulphuric acid, anion contaminated outer layer consists of AAO and sulphur.

![Fig 3. SEM images of nanoindentation imprints on AAO coatings at pore diameter: 16 (a, d), 27 (b,e) and 45 nm (c,f)](image)

![Fig 4. Evolution of nanohardness (a) and elastic modulus (b) with penetration depth](image)

Data on hardness and elastic modulus are plotted in Fig.4 versus indentation depth. At low indentation depth, a large scatter in hardness (e.g. ~9.5 GPa, ~5.4 GPa and
~8.5 GPa for 5 mN, Fig. 4 a) and elastic modulus (~11 GPa, ~10 GPa for 5 mN Fig. 4 b) are observed. It is noticed that the scatter is large in the case of AAO with 16 nm pore diameter. This scatter may be due to the high surface roughness and the presence of different structures (such as remains of electrolytes or anion contamination) inside the pores. Similar scatter is noticed at AAO produced in oxalic acid bath with 25 nm pore diameter. At large indentation depth, hardness and elastic modulus exhibit a lower scatter for all samples tested. These properties vary not only depending on the pore diameter but also on electrolyte used for anodization.

Conclusions. Well-ordered nanoporous AAO film was obtained with relative small pore diameters of 16 and 45 nm from sulphuric and oxalic electrolytes. Hardness and Young’s modulus of highly ordered alumina were measured by nanoindentation. The hardness and elastic modulus values depend on the load applied. Hardness can reach up to 10 GPa at 2 mN on AAO films. At increasing loads the nanopores collapse in ‘shear bands’, rather than being cracked as observed around the indent, suggesting that the pores in the alumina lead to a higher toughness in the transverse direction. The Young’s modulus of AAO also depends on the porosity level and the anodizing bath. For a given porosity, oxalic acid anodizing produces an oxide layer with higher elastic modulus as compared to samples prepared from the sulphur-based electrolyte.

Acknowledgement. This research was funded by a grant (No. MIP-031/2014) from the Research Council of Lithuania, and by Moldavian project for young researches nr. 72/ind.

References

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In order to produce different types of AAO the anodization of electropolished samples has been carried out in 2 electrolytic baths. Nanoporous oxides where obtained with pore diameters from 16 till 45 nm. The nanohardness measurements revealed that AAO can resist under normal loading without essential cracking, which is strongly important for further biomedical engineering with participation of nanoporous AAO.