Through-Hole, Self-Ordered Nanoporous Oxide Layers on Titanium, Niobium and Titanium–Niobium Alloys in Aqueous and Organic Nitrate Electrolytes

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In the past decades, a variety of self-aligned functional oxides have successfully been grown on a wide range of metals using electrochemical, self-organizing anodization. The earliest reports on highly ordered oxide structures included porous aluminum oxide layers grown by optimized anodization of Al in oxalic acid.[1] These nanoporous oxides found a considerable number of direct applications, such as size-exclusion filters[2] and waveguide structures,[3] or sacrificial uses, such as templates for secondary material deposition for the production of nanowires and tubes.[4, 5]

A very versatile self-organizing anodization approach was introduced in 1999 by Zwillin et al., which used fluoride-containing electrolytes for the fabrication of ordered TiO2 nanotube arrays on Ti.[6] These fluoride-based electrolytes were optimized over the last ten years to enable the growth of self-organized oxide layers on many metals and alloys, including Ti,[7] Zr,[8, 9] Hf,[10] Nb,[11, 12] Ta,[13] W,[14] Ti–W,[15] and Ti–Nb.[16] A detailed overview can be found in Ref. [7].

In 2005, Masuda et al., followed by others,[16–19] showed that by using perchlorate or chloride electrolytes, another type of nanotubes, the so-called rapid-breakdown anodization (RBA) nanotubes could be grown on Ti and W surfaces. This process was later extended to Ti–Nb, Ti–Zr and Ti–Ta alloys to form mixed-oxide nanostructures.[20, 21] In this anodization approach, the formation of tubes occurs with a high current flow, and tubes grow as bundles from a specific surface site on the metal into the electrolyte.[17–21] Due to the localized nature of the process and high current densities, mechanistically, the formation process was attributed to repeated anodic breakdown events of the surface oxide layer.[18]

Over the past ten years, considerable efforts have been directed toward the finding of other electrolyte types that would lead to the formation of self-organized nanostructured metal oxides. While nitrate-based electrolytes were used to etch Ti through a porous alumina template and, thus, can form etch channels,[22] we recently showed that nitrate-based electrolytes also may be a promising new route to achieve truly self-organized oxide structures in the context of Ti and Ta anodization.[23]

In the present work, we explore the use of nitrate-containing electrolytes for the formation of self-organized (template-free) oxide structures on Ti, Nb and Ti–Nb alloys.

Ordered TiO2-based nanoscale structures are particularly interesting in terms of applications in catalysis,[24] solar cells,[25] photolysis,[26] sensing,[27] and electrochromic devices.[28] Nb is an important element in combination with Ti, since composite oxides can be formed, or TiO2 can be Nb-doped for an alteration of the electronic properties.[29] For TiO2 nanotubes, it has been shown that in large concentrations the incorporation of Nb leads to lattice widening[16] and is, therefore, beneficial in ion insertion devices (e.g., electrochromic applications and ion intercalation batteries). In smaller concentrations, Nb acts as a donor species to enhance the performance of TiO2-based solar cells and water splitting reactions.[28–30] Herein, we demonstrate that anodization in nitrate-based electrolytes can be tuned to form ordered, nanoporous oxide structures, not only on Ti, but also on Nb and Ti–Nb alloys. Moreover, in contrast to any other previously reported electrolyte types, this nitrate-based anodization leads directly to a through-hole morphology for all investigated structures, i.e., where the pores are open at the top and bottom.

A series of preliminary anodization experiments for all the metals in various aqueous and ethylene glycol-based nitrate electrolytes were carried out, screening parameters being concentration, pH, and water content. The results showed that on Ti, Nb and Ti45–Nb, ordered porous layers could be grown (Figure 1). In aqueous electrolytes, a sufficiently high anodization voltage had to be applied to initiate the growth of a porous layer with an aligned pore structure. For the three investigated materials, the conditions to achieve a defined layer growth are different in each case. For Ti, well-ordered pores could be observed for anodization in HNO3. The example shown in Figure 1 a resulted in an oxide-layer thickness of approximately 10 μm. The inset pictures in Figure 1 show that regular pore channels with a diameter of 10–20 nm and a through-hole morphology could be obtained. Using Nb, a stable compact oxide film, instead of a porous oxide layer, was formed in all explored aqueous nitric acid electrolytes. However, when anodization was carried out in an organic nitrate electrolyte, well-defined porous layers could be grown. Figure 1 b shows the cross section of a self-organized nanoporous Nb oxide layer formed in an ammonium nitrate electrolyte. The resulting layer thickness was approximately 4 μm, and the pore diameter of the through-hole morphology was approximately 10–15 nm.

A defined and self-organized pore morphology was obtained for the Ti45–Nb alloy in both types of electrolytes—
aqueous and organic nitrate. Examples of the highly aligned pore channels and the through-hole morphology for aqueous and organic electrolytes are shown in Figure 1 c and d. Whereas a pore diameter of 10–20 nm, comparable to Ti, was found in the aqueous electrolyte, a pore diameter of 20–50 nm was measured in the organic electrolyte. Compared to pure Ti, a thinner layer of approximately 4 μm was obtained with the alloy in the aqueous electrolyte, which indicates that the alloyed Nb reduces the oxide growth rate. The oxide layer thickness (~10 μm) grown in the organic electrolyte under the same conditions, on the other hand, is comparable to pure Nb (Figure 1 b and d).

Figure 2 shows current density–time curves observed during anodization, illustrating the different anodizing behaviors of the various substrates in aqueous and organic electrolytes. In general, the current density in the organic electrolyte is lower than in the aqueous electrolyte by an order of magnitude. In the aqueous electrolyte, very high current densities are directly observed with a gradual decay for Ti and the Ti–Nb alloy. Ordered porous layers were formed with both substrates with the thickness increasing with time. This type of behavior was seen for applied voltages in the range of 15–40 V. However, when anodization was carried out in ethylene glycol electrolytes, much higher currents were observed, and self-organized porous oxide layers could be grown in the voltage range of 15–60 V. In the organic electrolyte, the alloy showed an increase in current up to 10 mA cm⁻², followed by a decay. A similar trend was observed in the aqueous electrolyte, where highly self-organized nanoporous Ti–Nb oxide layers could also be observed in a potential range of 20–40 V. Overall, regarding the electrochemical conditions under which ordered, porous layers were formed, it may be deduced that in NO₃⁻-based electrolytes and under the investigated conditions, a mechanism lying between the high-field case, [7, 31–33] which is responsible for self-ordered nanoporous structures on Al in oxalic acid or fluoride-induced self-ordered structures, and the breakdown mechanism, which forms RBA tubes, [15] is responsible for order and oxide growth.

To obtain information on the structure and composition of the oxide layers, X-ray diffraction (XRD) and energy dispersive X-ray (EDX) measurements were carried out. The XRD patterns in Figure 3 a–c show the as-formed nanoporous oxide layers on Ti, Nb and the Ti–Nb alloy to be amorphous. EDX measurements confirmed the as-formed layer on Ti to correspond to
TiO$_2$, and the layer on Nb to correspond to Nb$_2$O$_5$. The structures could be crystallized by an appropriate annealing treatment. Crystallization was carried out at 450°C in air for TiO$_2$ and at 550°C in an N$_2$ atmosphere for Nb$_2$O$_5$.[34, 36] As seen from the XRD measurements, after annealing, the nanoporous oxide layers were present as anatase TiO$_2$ with small amounts of rutile TiO$_2$ in the case of Ti,[34] and as monoclinic Nb$_2$O$_5$ for pure Nb.[35] Upon annealing, the layer on the alloy showed conversion to a composite oxide (Figure 3 c), that is, individual anatase TiO$_2$ and monoclinic Nb$_2$O$_5$ phases could be detected. EDX measurements of the annealed layer grown on the Ti45–Nb alloy in the aqueous or organic electrolyte yielded a composition of approximately 14% Ti, 33% Nb, 48% O, 5% C and 0% N in both cases (Figure 4 a and b). The results are in line with the formation of a TiO$_2$/Nb$_2$O$_5$ layer on top of the Ti–Nb substrate. It must be mentioned that the substrate is clearly contributing to the EDX signal. From this result, it becomes apparent that in the oxide structures, Nb$_2$O$_5$ is enriched compared with TiO$_2$. This is in line with the electrochemical behavior observed in Figure 2 and literature reports that state TiO$_2$ to be much more prone to dissolution in NO$_3$-based electrolytes than Nb$_2$O$_5$.[30]

Overall, the finding that nitrate-based electrolytes can be used to achieve self-organized oxide growth on metals with a very different electrochemical behavior, such as Ti and Nb (and their alloys), indicates that these electrolytes are very versatile. It is therefore likely that this approach can be applied to a wide range of metals to form ordered, through-hole morpholo-
H2O at potentials of 10–60 V. For the electrochemical experiments, solutions of TiO2 and doped TiO2 nanoscale structures in particular, metals can be anodized to form self-organized, through-hole nanostructures. These findings suggest that, based on nitrate electrolytes, a wide range of metals can be anodized to form self-organized, through-hole porous oxide structures. Considering the plethora of applications of TiO2 and doped TiO2 nanoscale structures in particular, we believe that the present finding represents a novel platform for the fabrication of doped and well-defined metal oxide nanostructures.

**Experimental Section**

Titanium and niobium foils (0.1 mm, 99.6% Ti, 99.9% Nb purity; Advent Materials, Oxford, UK) and a Ti–Nb alloy with a composition of 55 wt% Ti and 45 wt% Nb (ATI Wah Chang, Albany, USA) were used as substrates for anodization experiments. Prior to electrochemical treatments, the samples were degreased by sonication in acetone and ethanol, subsequently rinsed with deionized water and finally dried in a nitrogen stream. The samples were contacted with a copper plate and pressed against an o-ring in an electrochemical cell (1 cm² exposed to the electrolyte). Anodization was carried out in 0.1 M HNO3, in a potential range of 10–40 V, or, alternatively, in ethylene glycol containing 0.2 M NH4NO3 with 3 % (v/v) H2O at potentials of 10–60 V. For the electrochemical experiments, a high-voltage potentiostat (Jaisle IMP 88) was used in a conventional three-electrode configuration with a platinum sheet as a counter electrode and a platinum wire as the pseudo reference electrode. All electrolytes were prepared from reagent grade chemicals.

A scanning electron microscope (Hitachi FE-SEM S4800) was employed for the morphological characterizations. The composition of the porous anodic oxide layers was investigated by energy dispersive X-ray (EDX) spectroscopy (Genesis system from EDAX). For structural characterization, X-ray diffraction (XRD) measurements were performed (X’Pert XRD system from Philips). Annealing of the samples was carried out in a furnace at 450 °C in air for Ti and at 550 °C in an N2 atmosphere for 1 h for Nb and the Ti45–Nb alloy.

**Keywords:** nanotubes · niobium pentoxide · self-organization · through-hole morphology · titanium dioxide

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