



## **Influence of the Ti Microstructure on Anodic Self-Organized TiO<sub>2</sub> Nanotube Layers Produced in Ethylene Glycol Electrolytes**

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### **Abstract**

The relationship between the microstructure of Ti substrates and the anodic growth of self-organized TiO<sub>2</sub> nanotube layers obtained upon their anodization in the ethylene glycol based electrolytes on these substrates is reported for the first time. Polished Ti sheets with mirror-like surface as well as unpolished Ti foils were considered in this work. Grains with a wide range of crystallographic orientations and sizes were revealed by Electron Backscatter Diffraction (EBSD) and correlated with nanotube growth on both types of substrates. A preferred grain orientation with (0001) axis perpendicular to the surface was observed on all substrates. Surfaces of all substrates were anodized for 18 hours in ethylene glycol electrolytes containing 88 mM NH<sub>4</sub>F and 1.5% water and thoroughly inspected by SEM. By a precise comparison of Ti substrates before and after anodization, the uniformity of produced self-organized TiO<sub>2</sub> nanotube layers was evaluated in regard to the specific orientation of individual grains. Grains with (0001) axis perpendicular to the surface turned out to be the most growth-promoting orientation on polished substrates. No orientation was found to be strictly growth-retarding, but sufficient



anodization time (24 hours) was needed to obtain uniform nanotube layers on all grains without remnant porous initial oxide. In contrast with polished Ti sheets, no specific orientation was found to significantly promote or retard the nanotube growth in the case of unpolished Ti foils. Finally, the difference between the average nanotube diameters of nanotubes grown on various grains was investigated showing non-negligible differences in the diameter for different grain orientations and substrates.

**Keywords:** Titanium, Anodization, Titanium dioxide, Nanotubes, EBSD

## 1. Introduction

Lots of effort was carried out in the past to investigate the electrochemical behaviour of Ti in different electrolytes, including those containing chloride, fluoride and bromide anions [1-8]. Thus, the growth of an anodic barrier type TiO<sub>2</sub> layer is now well understood and described in the literature. About a decade ago, Ti anodization had attracted considerable attention due to the fact that by anodization of Ti in different electrolytes under tailored conditions, several distinct generations of TiO<sub>2</sub> nanotube layers were developed [9]. In turn, many interesting applications have been shown for the nanotube layers that stem from exploitation of unique TiO<sub>2</sub> properties combined with fascinating nanotubular architectures [10, 11].

However, comparably much less effort has been devoted to understand the role of the Ti substrate in the growth of anodic self-organized TiO<sub>2</sub> nanotube layers. Ti used for nanotube growth is typically a polycrystalline metal with hexagonal close packed (hcp) structure ( $\alpha$ -Ti) consisting of grains with different crystallographic orientations and sizes [12]. Depending on the processing route and desired properties, Ti substrates are made with various microstructures and chemical grades that are available on the market [13]. As any other solid substance, Ti substrate



contains crystallographic defects and impurities that accordingly influence its physical, chemical and electrochemical properties [14, 15]. Several reports investigating the relationship between the Ti-grain orientation and the electrochemically assisted flat TiO<sub>2</sub> or nanotube TiO<sub>2</sub> growth have already been published.

The pioneering work of König and Davepon et al. introduced great asset of EBSD analyses for investigation of the relation between the Ti crystallographic orientation and electrochemical behaviour [15, 16]. Crawford and Chawla first showed an influence of the orientation of the hexagonal  $\alpha$ -Ti on the oxide growth kinetics of the flat as well as nanotubular TiO<sub>2</sub> layers prepared by anodization in an aqueous electrolyte consisting of H<sub>2</sub>SO<sub>4</sub> - NaF [17] and leading to very thin tube layers (few hundreds of nm). They concluded that the growth of TiO<sub>2</sub> nanotubes is dependent on the crystallographic orientation of the Ti grains, with (0001) plane being the most growth-retarding orientation. Similarly, Leonardi et al. have shown that grain orientation has a dramatic influence on the nanotube characteristics [18] in terms of differences in the nanotube layer uniformity (demonstrated for (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> - NH<sub>4</sub>F electrolyte) and the growth rate at grains with different orientations [19] (demonstrated for glycerol - NH<sub>4</sub>F electrolyte).

To the best knowledge of authors, no report has investigated the relationship between the Ti microstructure and TiO<sub>2</sub> nanotube layers obtained upon anodization in the ethylene glycol based electrolyte – the most widely employed electrolyte for the nanotube growth. In addition, no report has pointed out that the size and size distribution of the grains may influence the overall uniformity of the produced self-organized nanotubes. Therefore, in the present communication we focus on the relationship between the crystallographic orientation of individual Ti grains (and their size distribution) and the TiO<sub>2</sub> nanotube growth for different grain orientations upon the



anodization of Ti in ethylene glycol electrolyte. We also discuss the difference between average nanotube diameters of nanotubes grown on various grain orientations).

## 2. Experimental

Ti sheets (2 mm thick, 99.6+% purity, as-rolled) and Ti foils (0.125 mm thick, 99.6+% purity, non-polished) were purchased from Goodfellow. In order to obtain smooth, flat and mirror-like surfaces, that can be efficiently and quantitatively analysed by Electron Backscatter Diffraction (EBSD), the sheets were lapped using diamond suspensions (first 6  $\mu\text{m}$  particles, afterwards 1  $\mu\text{m}$  particles) and polished using colloidal silica (OPS). The as-polished Ti sheets with a mean roughness of  $\approx 3$  nm (based on an AFM investigation, not shown here) were thoroughly degreased by sonication in isopropanol and acetone, then rinsed with isopropanol and dried in air. The grain orientation maps and inverse pole figures (IPF) of polycrystalline Ti sheets (prior to anodization) were obtained by EBSD technique using a Microprobe JEOL 733 with an EBSD detector and EDAX software. EBSD maps of size 120 x 120  $\mu\text{m}$  were recorded over the Ti surface of each sample with an acceleration voltage of 25 kV and a beam current of 4 nA under 70° sample tilt. Further details about the EBDS technique can be found in literature [15, 16, 20]. The grain tolerance angle for the recognition of neighbouring grains was set to 5°. The grain size of each grain was evaluated using the EDAX software as a diameter of the circle that occupies the same area as the grain itself.

Ti foils were locally polished with focused ion beam (FIB) attached to scanning electron microscope (SEM) FEI Quanta 3D FEG to reveal a surface quality sufficient for EBSD analysis. EBSD was performed on the same microscope using EDAX Hikari EBSD detector. An area of  $\sim 70 \times 70 \mu\text{m}^2$  with depth of  $\sim 1 \mu\text{m}$  had to be removed to get reliable EBSD signal.



Anodizations of the Ti sheets and foils pre-screened by EBSD were carried out at 60 V (the sweep rate from 0 V to 60 V was 1 V/s) for 18 hours (if not denoted otherwise) at room temperature. The electrolytes consisted of ethylene glycol solution containing 88 mM NH<sub>4</sub>F (both Sigma-Aldrich, reagent grade chemicals) and 1.5 vol% deionized water. Electrolytes were aged prior to the main anodization runs (for 9 hours by anodization of blank Ti substrates at 60 V, for details see previous work [21]). The electrochemical setup consisted of a high-voltage potentiostat (PGU-200V, IPS Elektroniklabor GmbH) in a 2 electrode configuration using a Pt foil as the counter electrode, while the Ti sheets (working electrodes) were pressed against an O-ring of the electrochemical cell, leaving 1 cm<sup>2</sup> open to the electrolyte. After anodization, the Ti sheets were rinsed and sonicated in isopropanol and dried. The structure and morphology of the TiO<sub>2</sub> nanotubes were characterized by a field-emission scanning electron microscope (FE-SEM JEOL JSM 7500F). Locations on the Ti sheets, originally screened by EBSD and SEM were of interest for the nanotube analyses. Dimensions of the nanotubes were measured and statically evaluated using proprietary Nanomeasure software. For each grain orientation of interest in this work (6 different orientations), we calculated average values and standard deviations of nanotube diameters from a high number of nanotubes ( $n \geq 200$ ).

### 3. Results and discussion

Fig. 1 shows results of the EBSD analysis of the polished Ti sheet before anodization. Fig. 1a shows an example of the IPF map recorded at the specific region of the Ti surface (marked by a scratch prior to the EBSD characterization for better traceability), which was also examined by SEM after the anodization process for comparison. The IPF map is a graphical representation of microstructures showing the relationship between orientation of the crystallographic axes of



the grains and a sample surface. As one can see from the colour palette (Fig. 1b), there are grains with wide range of orientations exposed at the surface of the Ti sheet. However, some preferential orientation of the grains (so called texture) can be traced in Fig. 1d. Higher density of orientations observed around (0001) axis indicates that the c-axis of the grains tend to be perpendicular to a surface (i.e. plane of EBSD mapping). The EBSD maps were recorded at various locations of the polished substrate, yielding similar results with no or negligible differences in the distribution of the grain orientations. Figs. 1c and 1d highlights the grains selected for further nanotube growth examination.

Fig. 2 shows an equivalent EBSD analysis of unpolished Ti foil. In comparison with Fig.1, the average grain size is significantly smaller. Furthermore, Fig. 2d depicts an obvious texture, where the (0001) axis of grains is preferentially perpendicular to the surface. In this case, the texture is more pronounced than for the polished Ti sheet.

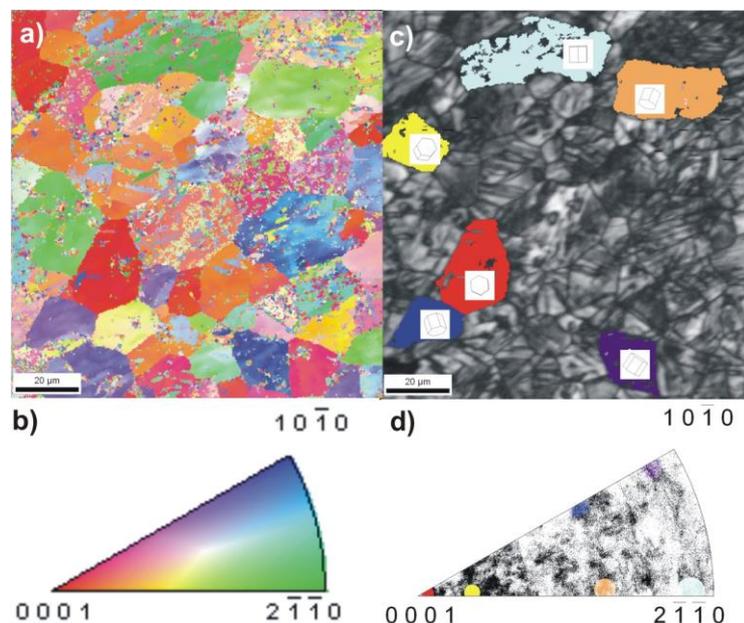


Figure 1 (a) IPF map recorded at a specific region of the polished Ti sheet; (b) colour-coding of the IPF map; (c) Image quality map of the same region as in (a) showing selected grains with



specific orientation marked by different colours and respectively oriented hexagonal unit cell placed on each corresponding grain; (d) IPF pointing out the orientation of specific grains selected in (c).

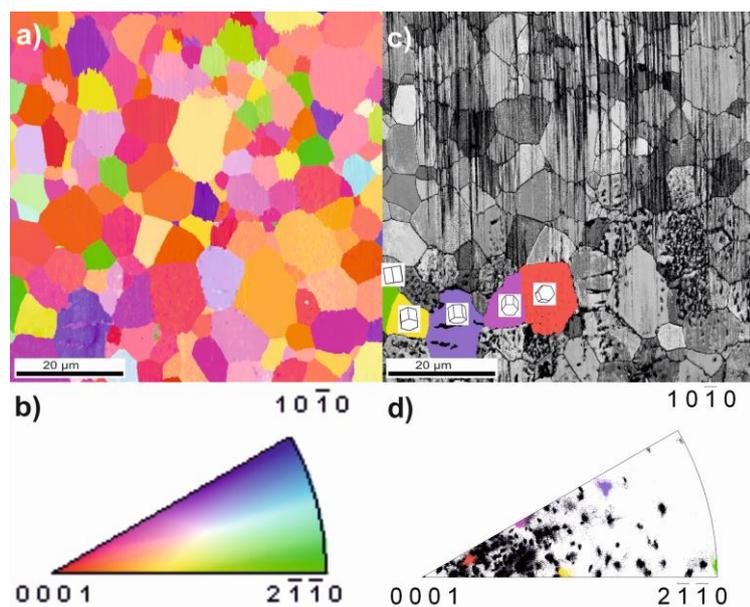


Figure 2 (a) IPF map recorded at a specific region of an unpolished Ti foil; (b) colour-coding of the IPF map; (c) Image quality map of the same region as in (a) showing selected grains with specific orientation marked by different colours and respectively oriented hexagonal unit cell placed on each corresponding grain; (d) IPF pointing out the orientation of specific grains selected in (c).

After the initial EBSD analyses and subsequent anodization, differences between the nanotube growth on selected grains with different orientations were studied for both Ti substrates by means of SEM characterization. This characterization was in particular carried out to compare the nanotube growth with the previously published results for the nanotube layers grown in aqueous or glycerol based electrolytes [17-19], which strongly pointed to some nanotube-growth-promoting and nanotube-growth-retarding grains.



However, at a low SEM magnification and also with naked eye, considerable differences between both anodized substrates were observed (images not shown here). Distinct patterns could be observed on the anodized surface of Ti polished sheets suggesting some variations in the morphology, while anodized unpolished Ti foils had a uniform appearance. Therefore, a closer look by SEM at high magnifications (5k and more) was needed to investigate the morphology of the nanotube layers.

In order to link a grain orientation with the nanotube growth, grains with particular orientations located in the IPF were identified in the substrate, as shown in Fig. 1c and 2c. The orientation of five and six selected grains for the Ti foil and the Ti sheet, respectively, is depicted by the images of hexagonal cells corresponding to  $\alpha$ -Ti structure. The grains were selected to cover a wide range of possible orientations (close to the vertices and on the sides of the IPF triangle, as marked in Fig. 1d and Fig 2d using the same colours as in Fig. 1c and Fig 2c).

At a first glance, it appeared that on some grains (such as for example those with (0001) orientation, red grain in Fig. 1c) uniform and ordered nanotube arrays were grown in line with our expectations, while on other grains the nanotube growth was hindered. Nevertheless, by a closer look it turned out that nanotube layers were grown on all grains, regardless their orientation.

Fig. 3 shows the SEM images of the  $\text{TiO}_2$  nanotube layers grown on polished Ti sheet (Fig. 3a) and an unpolished Ti foil (Fig. 3b). Both images represent illustrative examples of nanotube layers on regions of the substrates that have grains with (2 -1 -1 0) orientation, shown in the IPFs (Fig. 1d and 2d) in the right lower corners. As one can see, both layers were different in terms of their uniformity. The nanotube layer grown on the polished Ti sheet (Fig. 3a) had apparent remnants of the initiation  $\text{TiO}_2$  layer from the early stage of the anodization, which is



described in the literature [9]. The degree of remnants was different between various grains on the polished substrates. In contrast, the nanotube layers grown on an unpolished Ti foil (Fig. 3b) did not show even traces of the initiation layer. Essentially the whole nanotube layer was uniform and no apparent differences between different grains were revealed.

According to our investigation, on the polished Ti sheet the grains whose orientations were within the (0001) orientation or were close to this were the most ideal grains in sense of the nanotube uniformity. In other words, there were no remnant porous layers on the nanotube tops and the nanotubes were comparably well ordered. On the other hand, the grains that were on the other side of the IPF, i.e.  $(2 -1 -1 0)$  and  $(1 0 -1 0)$ , as shown in Fig. 1d, showed a degree of coverage by the porous layer that originates from the initial period of the nanotube growth [9]. This fact was especially strongly apparent for the grains that were close to the  $(1 0 -1 0)$  orientation in Fig. 1d.

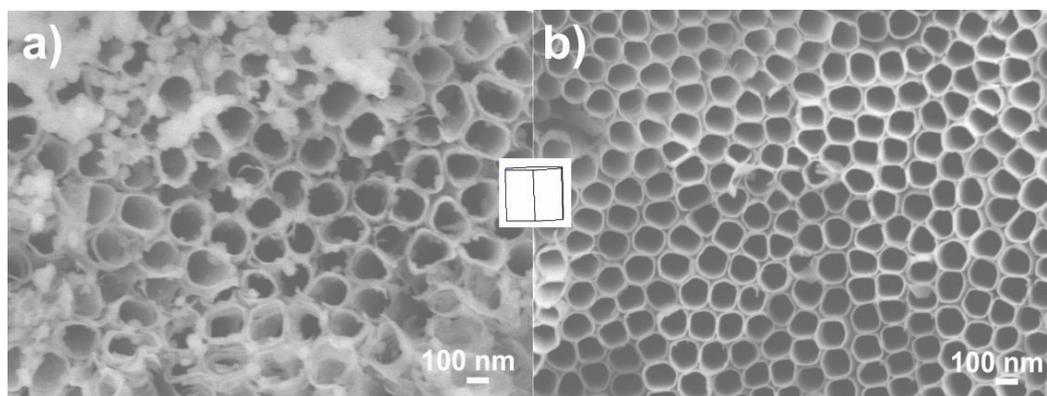


Figure 3 SEM images of  $\text{TiO}_2$  nanotubular layers grown on a) the polished Ti sheet and b) the unpolished Ti foil anodized in ethylene glycol electrolytes containing 88 mM  $\text{NH}_4\text{F}$  and 1.5% water for 18 hours yielding a growth of a self-organized  $\text{TiO}_2$  nanotube layer. The images were taken on grains with  $(2 -1 -1 0)$  orientation (as marked by a hexagonal unit cell in an inset).



It has to be pointed out that the previous literature reported that in aqueous and glycerol electrolytes, (0001) grain orientation is the most nanotube growth retarding one [17-19]. However, our experiments provided completely opposite results for the polished Ti sheets and no specific influence on the unpolished Ti foils. Such finding can be advantageous for the preparation of the nanotubes in the ethylene glycol electrolytes over other electrolytes, because Ti substrates prepared usually by rolling often exhibit texture in which (0001) axis of the grains in Ti sheets tend to be oriented perpendicular to the sheet plane [13]. Although exact reasons for preferential nanotube growth in (0001) direction remain unclear, the results can be specific for anodization in ethylene glycol electrolytes.

In order to further investigate the influence of the grain orientation on the nanotube growth, the differences in the nanotube diameters were thoroughly studied from grain to another grain for both substrates. At first, we discuss in the following text the polished Ti sheet. The statistically evaluated diameters were in the range of 142 to 163 nm (mean values) for all selected grains marked in Fig. 1c and 1d for the polished Ti sheet. Even though the standard deviation of the mean diameter values was non-negligible (some 12-15 % variation from the mean values), still the difference was not due to the measurement scatter. Considering that the anodization time of 18 hours was long enough to develop the nanotubes (i.e. to allow them to completely self-organize), this variation shows that the grain structure slightly influences also the nanotube diameter. It is known from literature, that the thickness of anodic TiO<sub>2</sub> films is directly proportional to the applied voltage [1-6]. The same rule also applies for the nanotube diameter vs. voltage used for the nanotube growth [9, 22, 23]. Presumably, these nanotube diameter differences observed among Ti grains with different orientation stem from slightly differing oxide growth rates of these grains. As a consequence, the field-aided growth and dissolution (that



are in dynamic equilibria during the nanotube growth) are set in different proportions for different grains. This assumption is strongly corroborated by the fact that on different grains, different amount of the remnant initiation  $\text{TiO}_2$  layer was present.

Upon analyses of the nanotube layers grown under the same conditions (60 V, 18 hours) on different grains of unpolished Ti foils, marked in Fig. 2c and 2d, the nanotube diameters were in the range of 125 to 135 nm (mean values). Thus, comparably smaller differences between the grains were revealed than for the polished Ti sheets. This is an interesting observation which has also an implication on the total number of nanotubes per unit area. One can clearly see in Fig. 3 that the unpolished Ti foil contains more nanotubes per unit area than polished Ti sheet. It means that there is a larger number of nucleation sites for nanotube growth on the unpolished Ti foil that are later on, once the anodization process is finished, translated into a larger number of smaller diameter nanotubes.

In order to find reasoning for that, the surface roughness of the substrates needs be considered. The rolled Ti foils have a roughness on the scale of tens of micrometers [14, 24]. In contrast, polished substrates have a roughness on the scale of nanometers, as verified experimentally for this work by AFM. Thus, the active surface per unit area of the substrates is higher for unpolished Ti foils. On the other hand, both types of substrates contain some number of intrinsic defects (dislocations, vacancies, grain boundaries), whose amount is difficult to quantify, but in the first approximation can be considered similar, because both microstructures were obtained by rolling and they are fully recrystallized. It is therefore envisaged that the larger number of nucleation sites for the nanotube growth on the unpolished Ti foils may stem from a larger active surface area.



Prior to the experiments shown in Fig. 1 and 2, we performed anodizations of polished Ti sheets for shorter times, e.g. for 6 hours, which is an average time and completely sufficient time typically used for the unpolished Ti foils to yield uniform nanotube layers (without remnant initial porous oxide covering the nanotube layer). However, while nanotube layers were already developed at that time on the polished Ti sheets, we observed a very high degree of coverage by the remaining initial porous oxide layer, typically seen on unpolished Ti foils for anodization runs shorter than approximately 1-2 hours, depending on the fluoride concentration in the electrolyte. Since the TiO<sub>2</sub> nanotube growth proceeds with field-aided oxidation and dissolution of mainly defect areas on the surface [9], it therefore takes comparably longer time for very flat Ti sheets to achieve uniform nanotube layers without remnants of the porous oxide from the initial stage of the nanotube growth. While for the unpolished Ti foils it takes at most 6 hours to have uniform nanotube layers (under the same experimental conditions as used in this work), polished Ti substrates still bear even after 18 hours some porous oxide remnants that cover the opening of the nanotubes, as apparent in Fig. 3a (except some grain orientations close to (0001) orientation). To tackle this point, we performed longer anodization runs in order to see, how long it takes to obtain (under the same experimental conditions except the anodization time) uniform nanotube layers on the flat polished Ti sheets. After numerous trials, we came to the conclusion that 24 hours of anodization is sufficiently long time to achieve uniform layers. An example of the surface of a TiO<sub>2</sub> nanotube layer prepared by anodization of a polished Ti sheet for 24 hours is given in Fig. 4.



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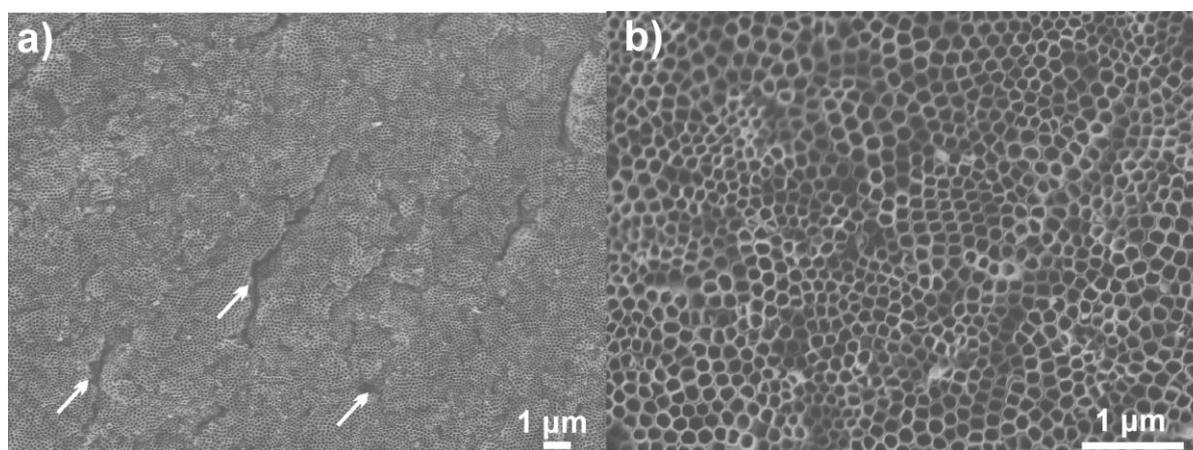


Figure 4 (a) low magnification (5k) and (b) high magnification (20k) SEM images of a self-organized  $\text{TiO}_2$  nanotube layer grown on a polished Ti sheet during its anodization in ethylene glycol electrolyte containing 88 mM  $\text{NH}_4\text{F}$  and 1.5% water for 24 hours. No remnant porous oxide layer was present on the tube surface. For a better visibility, some locations of the grain boundaries with most apparent gaps in the tube layers were marked by white arrows in a).

Apparently, there are no traces of the initial porous oxide layer visible on the nanotube layer neither under low magnification, nor under high magnification. In regard to previously published work on the influence of Ti sheet pre-treatment for the uniformity of nanotube layers grown [14], we demonstrate by these results that very uniform nanotube layers can be produced on polished Ti substrates upon extensive anodization periods without remnant porous oxide layer.

However, small gaps are observed in the uppermost part of the nanotube layers at the locations of the grain boundaries, as apparent from the Fig. 4a. This is likely due to different energies of grain boundaries. As a consequence, due to the necessary dissolution reactions taking places in the nanotube growth, there can be some grain boundaries etched more than the others. In addition, as apparent from the zoomed image in Fig. 4b, there are some small ordering



imperfections – some nanotubes are comparably larger than the average size, some nanotubes are comparably smaller than the average size, some have rather round shape, some have rather hexagonal shape, etc. Nevertheless, these gaps or imperfections have not been found detrimental for any application.

Finally, in order to explore the distribution of the grain sizes and discuss possible effect on the nanotube growth (specific to the production [12] of the Ti sheet we used), we performed statistical evaluation of the EBSD maps collected in this study, as shown in Fig. 5. Even though there are some unindexed points and noise in the maps, still it is possible to evaluate the trends in the grain size of both substrates. As one can see from examples of this evaluation shown in Fig. 5a for the polished Ti sheet and Fig. 5c for the unpolished Ti foils, there is a whole range of grain sizes present on both substrates. Based on the obtained histogram shown in Fig. 5b, it is evident that polished substrate consists of grains that have an average size as small as  $\approx 2 \mu\text{m}$  or as large as  $\approx 26 \mu\text{m}$ . For the unpolished Ti foils, the grains are comparably smaller – in the range of  $\approx 2$  to  $\approx 14 \mu\text{m}$  (Fig. 5d). Grains of different sizes occupy different proportions of the surface of both types of substrate, as indicated by the percentages in both histograms. The grains have implications on the uniformity of the nanotube layers, as shown and discussed in Fig. 4. As a matter of fact, the larger the grains would be on the surface, the smaller the number of the grain boundaries would be present on the surface. In order to have as uniform nanotube surfaces as possible (i.e. no surface defects, extremely high degree of ordering), it is very likely that the single crystalline Ti substrates would be most efficient to work with. Based on the results of this work, the most ideal orientation of the single crystal would be (0001).

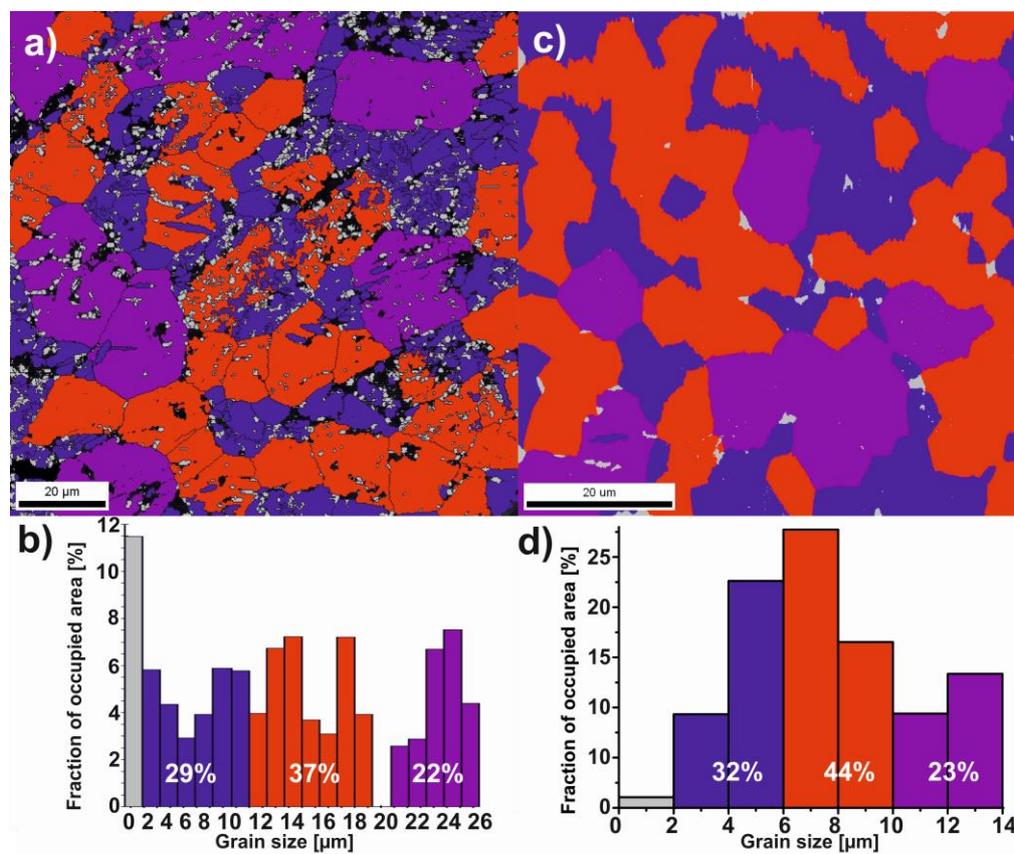


Figure 5 Grain size distribution (regardless of the grain orientation) on the (a) polished Ti sheet and (c) unpolished Ti foil marked by 4 different colours. The same colours are used in the histograms for the (b) polished Ti sheet and (d) unpolished Ti foil showing the presence of various grain sizes on the overall area. Gray regions represent the minor part of the surface that was mis-indexed by EBSD.

## Conclusions

In summary, we showed in detail an influence of the microstructure of polished Ti sheets and as-delivered (i.e. unpolished) Ti foils on the growth of anodic self-organized TiO<sub>2</sub> nanotube layers. In particular, by precise evaluation of the nanotube growth on grains with specific orientations (analysed by EBSD), we revealed that the nanotube growth in ethylene glycol based



electrolytes is not retarded compared to the case when aqueous electrolytes were used, as known from the literature. In addition, we showed that the smoothness of the sheets has an impact on the overall uniformity of nanotube layers. In order to have uniform nanotube layers, without any unwanted remnant porous oxide layers, it is necessary to carry on anodization runs for significantly longer times in comparison to rough Ti sheets or foils. The present results clearly suggest that utilization of well-oriented single crystalline Ti for the nanotube growth could be a step forward towards an improved degree of the nanotube uniformity.

### **Acknowledgements**

ERC and the Czech Science Foundation are acknowledged for financial support of this work through projects 638857 and 14-20744S, respectively. The authors also thank to project CZ.1.05/4.1.00/11.0251 „Center of Materials and Nanotechnologies“ cofinanced by the European Fund of the Regional Development and the state budget of the Czech Republic. Dr. Petr Knotek is acknowledged for AFM measurements. One of the authors (A.J) would like to acknowledge financial support of the Czech Science Foundation through project GBP108/12/G043.

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