Nanoporous Titanium Oxide Morphologies Produced by Anodizing of Titanium

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ABSTRACT

A quick and dependable technique has been developed that allows us to selectively produce anodized TiO\(_2\) in the form of nanotubes. The process employs mild chemical conditions and ambient temperature. The method can consistently produce nearly 100% surface coverage of nanotubes within 10 min of anodizing. Anodizing in relatively high pH electrolytes for 1 hour permitted us to produce nanotubes of 2\(\mu\)m length. We attribute the repeatability of our results to a brief pre-anodizing etching step that consistently leads to excellent anodizing results. Without this etching step, we experienced very poor consistency in that only small patches of titania nanotubes were formed.

INTRODUCTION

Titanium anodizing is an industrial process that has been used for more than half a century. Until recently, the improved corrosion resistance, anti-galling properties, increased fatigue strength, or improved bondability imparted by anodizing that was of primary interest. The oxide coatings formed are rough, non-porous barrier films, or, have a random pore structure if anodized above the breakdown voltage. Recently, it has been shown that titanium anodizing can provide a surface covered with titanium oxide nanotubes (TNTs). A good sense of the current state of this area of study can be found (for example), in [1-6]. These nanotubes are a self-assembled structure which may be of use for a variety of applications requiring nanometer scale features.

BACKGROUND

As introduced above, there is presently a growing interest in anodizing titanium. A selection of other reported efforts are briefly summarized below.

HF, low pH

Gong et al. [1] studied voltage variations and the influence on anodizing of TiO\(_2\) using 0.5 wt% HF. They reported that a 20 VDC anodizing voltage produced the best results for the formation of nanotubes. They reported virtually no increase of TNT lengths after approximately 20 minutes. They examined the process at 1.5 wt% HF and 20 VDC and observed the uniform TNT structure after only 8 minutes of anodizing. No mention was made of the percentage of the surface area that was successfully covered with TNTs.
H$_2$SO$_4$—HF, low pH

Beranek et al. [2], reported successful anodizing of TNTs using 20VDC in 1M H$_2$SO$_4$, 0.15 wt% HF, but the process required upwards of 24 hours to develop a uniform structure. No mention was reported of the percentage of the surface area that was covered.

CrO$_3$—HF, low pH

Zwilling et al. [3] reported on their studies of TiO$_2$ anodizing using 0.5M CrO$_3$, 0.095M HF. They concluded that a porous TiO$_2$ layer can be formed in a chromic acid solution in the presence of a small amount of HF and the TiO$_2$ barrier oxide thickness is time independent whereas the thickness of porous TiO$_2$ increases with anodizing time. This contrasted with the results of Gong et al. [1], but was conducted in a different electrolyte.

KF, NaF, higher pH

Cai et al. [4] reported on their studies of TiO$_2$ anodizing using electrolyte solutions containing potassium or sodium fluoride with pH ranging from less than 1 up to 6.4. They reported that their higher pH solutions allowed for the TiO$_2$ nanotubes to grow to longer lengths (4.4 µm over 20 hours) because the already-grown material was not subject to the same dissolution as in systems at lower pH. In this report, the first (known) mention of the importance of surface coverage is introduced.

NaF,NH$_4$F, higher pH

Macák et al. reported on their studies using (NH$_4$)$_2$SO$_4$/NH$_4$F [5] and Na$_2$SO$_4$/NaF [6], also reporting that the higher pH electrolyte (with F$^-$ present) permitted longer TNTs, as did Cai et al. [4]. They anodized for 6 hours in the sodium system to produce ~2.4 µm long nanotubes [6]. In the ammonium system [5] they also reported ~2.5 µm of growth.

EXPERIMENTAL DETAILS

The long-term goal of our research program is to develop methods for efficient production of TiO$_2$ nanotubes or other nanostructures. As a first step, we attempted to implement the methods of Gong et al. [1] to provide a reference for comparisons with our subsequent efforts.

Sample Preparation

High-purity (99.97 %) titanium, 0.2-1 mm thick, 1.6 cm diameter specimens, were punched out of a sheet. A titanium disc is loaded into a Teflon specimen holder (stainless steel inner body) which exposes 1 cm$^2$ of the sample (1 side), provides even electrical contact over the sample, and minimizes contamination of the electrolytes from metal fixtures.
Anodizing

Our first set of anodizing experiments was conducted using HF in a manner to duplicate the work of Gong et al. [1]. We used a constant 20 V with 0.5 wt% and 1.5 wt% HF at ambient temperature. We encountered difficulty in reproducing the reported results (discussed below), leading us to adapt our methods to better study the formation process.

Our later experiments (discussed more below) used voltage sweeps (ramping) rather than a steady 20 VDC. Voltage sweeps from 1 to 20 V at a rate of 1-5 V/min. Ramping (sweeping) the voltage allowed us to monitor the current response as the voltage was ramped, and use the information gained to better control the process.

Finally, we discovered that a brief initial pause with the sample in the 0.5 wt% HF solution prior to anodizing (application of voltage) served to etch the initial surface and led to more repeatable and desirable anodizing of TiO$_2$ nanotubes.

RESULTS AND DISCUSSION

During our initial experiments, we experienced considerable difficulty in achieving good and uniform coverage of the surface with the desired TNT morphology when using the methods reported in the literature for HF anodizing [1]. Figure 1 shows a representative micrograph of an attempt to reproduce the 0.5 wt% HF conditions reported in [1]. A TiO$_2$ film has formed, but no (significant) TNTs were observed. When we increased the HF concentration to 1.5 wt% (as also reported in [1]), nanotube growth was observed. Figure 2a shows a low magnification view of such a sample with a “patch” or “island” of TNTs on the upper right, but with only porous oxide on the lower left (no nanotubes). Figure 2b shows a higher magnification view of the nanotubes. Whereas the stronger HF solution had the desired effect (creating nanotubes), we anodized under these conditions ~10 times, obtaining 90% nanotube coverage of the surface only once. All other attempts yielded only ~25% coverage in “patches”.

Figure 1. In numerous attempts, anodizing in 0.5 wt% HF @ 20V did not produce nanotubes.

Figure 2. When using 1.5 wt% HF, TiO$_2$ nanotubes were observed, but typically only covered ~25% of the surface in localized islands.
**Voltage Ramping**

To better understand the reasons for the inconsistent TNT formation and coverage, we studied the process in a more controlled manner. Anodizing in a 0.5 wt% HF solution commenced at 1V (at \( t \approx 35s \)), increasing at a steady rate of 3 V/min until it reached 20 V. A plot of the voltage and current response is shown in Figure 3. Initially, as the voltage ramps upwards from 1V, the current responds by increasing in a linear manner (\( t = 35 \) to \(~120 \) seconds) starting at 12 mA/cm\(^2\) and rising to 36 mA/cm\(^2\). At this point, the current drops rapidly to \(~8 \) mA/cm\(^2\), and then begins to slowly rise again.

The surface morphologies during the initial rise (points A-B) in the process are depicted in Figures 4A-B. After the process begins, small (nanoscale) rods of TiO\(_2\) begin to appear. As time progresses, the nanorods increase in number density, until they reach a maximum (Figure 4C-D). A short time later (Figure 4E-F), the nanorods disappear as the current drops dramatically. A nanoporous begins to appear (Figure 4G) as the current climbs again, evolving into surfaces with TNT coverage approaching 100% (Figures 4H-J).

**Etching**

The current response behavior and morphological development depicted in Figures 3 and 4 are considered our “optimal” product. However, after repeated experiments, we found that we could not (at first) reproducibly produce the uniform TNT coverage of Figures 4H-J. In the unsuccessful experiments, even though the voltage was ramped from 1 to 20 V, the current response differed greatly from that depicted in Figure 3. Instead, the current increased initially, (Figure 5), and settled into a relatively steady value of \(~8\) mA/cm\(^2\). The morphology of the anodizing resulting from such a run typically appeared as

![Figure 3](image-url)  
**Figure 3.** Anodizing current response during voltage ramping. Micrographs of the surface morphology at each of the indicated times are depicted below.

![Figure 4](image-url)  
**Figure 4.** Time sequence of surface morphology for times corresponding to those identified in Figure 3.
shown in Figure 6—i.e., there are no TNTs produced.

It was eventually noticed that the success of the anodizing appeared to be dependent on whether (and how long) we permitted the sample to sit in the 0.25-0.5 wt% HF electrolyte prior to applying the anodizing voltage. We found that letting the sample sit in the HF bath for a brief period prior to anodizing allowed time for chemical etching to occur. Etching appears to replace the native oxide layer, preparing the surface for anodizing in a manner that favors the TNT structure we desire. We studied variations in the etching step, and attempted to correlate the final TNT structure with the pre-etch parameters. We observed in our work, that as the voltage between the rectifier terminals (Ti, Pt) reaches -1.7V (rectifier off), gas bubbles start to become evident to the unaided eye after approximately 30 seconds. The surface, at this point, appears much as depicted in Figure 4A. If we then begin anodizing, the process consistently proceeds in the manner depicted in Figure 3, producing the desired uniform TNT coverage depicted in Figures 4I-J.

**Titania Nanotube (TNT) Length**

As many potential applications of TNTs would benefit from long tube lengths, we conducted a preliminary study of the tube lengths which we could produce using our methods. As summarized above, Macák et al. recently reported production of TNTs of ~2.5 µm length in 6 hours [6]. Thus far, we have produced ~2 µm TNTs (Figure 7) in ~1 hour using 1M Na₂SO₄ with 0.5 wt% NaF at pH 5 (at ambient temperature). As this was a preliminary study, we have not yet attempted longer growth periods. Examination of our current response over the 1 hour anodizing, shows no behaviors that would indicate that the growth had significantly slowed or stopped prior to the end of the hour. Macák et al.
presented data (Fig. 3 in [6]) that suggested that the slowing of the growth process begins at about 2 µm in TNT length. Cai et al. observed lengths up to 4.4 µm, taking 20 hours [4]. The longer lengths are attributed in the respective literature as being primarily due to the use of higher pH electrolytes.

CONCLUSIONS

We reported here on our efforts to produce nanostructured TiO$_2$ nanotubes using anodizing methods. We were able to achieve very high surface coverage, with uniform TNT morphologies in relatively short anodizing periods (within 10 min). In one hour anodizing experiments, we were able to produce 2 µm long TNTs when a higher pH electrolyte (compared to HF) was used. Finally, a key conclusion of this work was the development of the initial etching process, which, when combined with gradual voltage ramping to 20 V, helps the anodizing process to quickly develop a consistent TNT morphology, with surface coverage approaching 100%.

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REFERENCES


