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TiO_2 nanotubes produced on thin titanium wires using aqueous electrolytes

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ABSTRACT

In this experimental work, homogeneous nanotube layers were successfully formed by anodization on titanium wires with diameters lower than 200 µm employing an aqueous anodizing solution composed of carboxymethylcellulose and sodium fluoride. Homogeneous nanotube layers were formed only when the titanium wires were electropolished. After heat treatment at 350 and 600°C, the nanotubes were transformed from amorphous phase into anatase phase or a mix between anatase and rutile phases. After both heat treatments, the nanotube coatings remained uniform; namely, no apparent cracks, critical defects, or coating delamination were seen. To the best of our knowledge, a homogeneous nanotube coating composed of anatase or a mix between anatase and rutile phases on titanium wires with diameters lower than 200 µm has not been reported. These coatings may be potentially useful in a variety of fields, including biomedicine, sensing, and catalysis.

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Introduction

Several mechanical and chemical properties have been observed on titanium-based materials, such as low density, chemical stability, and high mechanical properties.[1,2] Besides those characteristics, the titanium can spontaneously form a layer of TiO_2; however, this coating could be modified using an electrochemical process called anodization.[3,4] The anodization process allows the growth of TiO_2 layers with controlled morphological physical characteristics, namely, pores,[5] grooves[5] and nanotubes.[6,7] The TiO_2 nanotubes have been attractive to scientists due to the combination of the commonly known properties of TiO_2 combined with the higher specific area of the nanotubular geometry.[8–10] Through the anodizing technique, it is possible to coat pieces with complicated geometries; thus, TiO_2 nanotubular structures can be produced on the surface of thin titanium wires. From the literature review, several authors[11–16] recently reported non-homogeneous nanotubular structures made on titanium wires; namely, coatings with apparent cracks, important defects, and coating delamination. Most of those papers employed titanium wires with diameters higher than 300 µm. In a previous work,[17] we produced homogeneous TiO_2 nanotubes in titanium wires with diameters around 800 µm. However, additional research is necessary to produce homogeneous nanotubular structures on titanium wires with diameters lower than 200 µm. This experimental work aimed to evaluate the relationship between the electropolishing procedure and pH value with the morphologic characteristics of TiO_2 nanotubes produced on titanium wires with diameters lower than 200 µm, using an anodizing solution of sodium fluoride (NaF), carboxymethylcellulose (CMC) and distilled water. Furthermore, to analyze heat treatment effect on TiO_2 nanotubes to convert the amorphous phase into TiO_2 polymorphs as anatase or rutile phases without affecting their homogeneity. It is worth highlighting that homogeneous TiO_2 nanotubes on titanium wires with diameters lower than 200 µm were produced in this research work. As far as we are aware, homogeneous TiO_2 nanotubes on titanium wires with diameters lower than 200 µm composed of anatase or a mix between anatase and rutile phases have not been reported. A possible application of these homogeneous nanotubular layers composed of anatase or anatase/rutile mix is photocatalysis; due to the high specific area of TiO_2 nanotubes combined with high photocatalytic properties of anatase and rutile phases. Another possible application is in the biomedical field, specifically in biomedical devices such as stems or controlled drug release devices.

Materials and methods

The electropolishing process consisted of submerging wires of titanium grade 1 (ø:0.2032 millimeters) in a solution made of CH_3COOH, HF, and H_2SO_4 (60:25:15 volume/volume %) utilizing a current of 200 milliamperes per square centimeter for 160 s. Wires both electropolished and without electropolishing, were anodized by employing the exact procedure utilized during our earlier paper.[18] Titanium wires were immersed in an aqueous solution containing NaF and CMC; the anodization solution pH was established using phosphoric acid. The anodization procedure was implemented for 5 h at 20 V, utilizing platinum netting as a cathode and the titanium wires as the anode. After completing the anodization, the titanium wires were washed with filtered water and dried up with air. A scanning electron microscopy equipment (JEOL JSM 6940 LV) was employed to evaluate the anodic coatings; the cross-view images were captured by scraping the surface and sloping

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Table 1. Anodizing conditions of produced layers.

Sample	Anodizing Conditions	Electropolish
S1	20 V,5 hr, pH 4, 0.5 wt% NaF and 0.5 wt.% CMC	No
S2	20 V, 5 hr, pH 2.5, 0.5 wt% NaF and 0.5 wt% CMC	No
S3	20 V, 5 hr, pH 4, 0.5 wt% NaF and 0.5 wt% CMC	Yes
S4	20 V, 5 hr, pH 2.5, 0.5 wt% NaF and 0.5 wt% CMC	Yes
S5	20 V, 5 hr, pH 3.5, 0.5 wt% NaF and 0.5 wt% CMC	Yes

the sample holder (about 30°) until taking the chosen image. The measurements for internal diameter and thickness of TiO_2 nanotubes were estimated utilizing two SEM micrographs for every kind of sample; 10 measurements were done for each image. The heat treatment temperatures selected were 350 and 600°C, and the ramps employed will be presented later on. Once the heat treatment finishes, the samples were gradually cooled inside the furnace. The experimental conditions for every sort of anodic sample obtained are displayed in Table 1.

Results and discussion

Morphologic characterization of as anodized anodic coatings

Figure 1 reveals the SEM micrographs of anodized Ti wires with and without electropolishing, employing anodizing solutions with pH values of 2.5 and 4. From Fig. 1, it is observed that TiO_2 nanotubes were obtained only in the electropolished samples. The SEM pictures at low magnifications (below 10000X) of S3 and S4 samples revealed a higher homogeneity in the coatings; namely, no apparent cracks, important defects, or coating delamination were perceived. From the SEM images at higher magnifications (above 10000X) of S3 and S4 samples, it is observed that the nanotubes produced have high packability; no cracks or spaces between nanotubes can be seen. From Fig. 1, it is clear that the titanium wires without electropolishing, after anodization reduced their diameter to approximately 150 µm. On the other hand, the diameter of the electropolished titanium wires after anodization was in the range of 100–130 µm. Furthermore, the nanotubes internal diameter value was 101,87 ± 13,67 and 107,39 ± 9,05 nm for the S3 and S4 samples, respectively. Figure 2 displays the SEM images (transversal view) of the electropolished titanium wires after anodization (S3 and S4 samples). From Fig. 2, the length of the nanotubes was 2037,19 ± 31,75 and 1551,21 ± 49,67 nm for the S3 and S4 samples, respectively.

Recently various authors[13,14,19–23] reported that TiO_2 nanotubes produced on titanium wires presented defects such as delamination, cracks, coral like structures among others. Delamination could be a critical drawback for the real

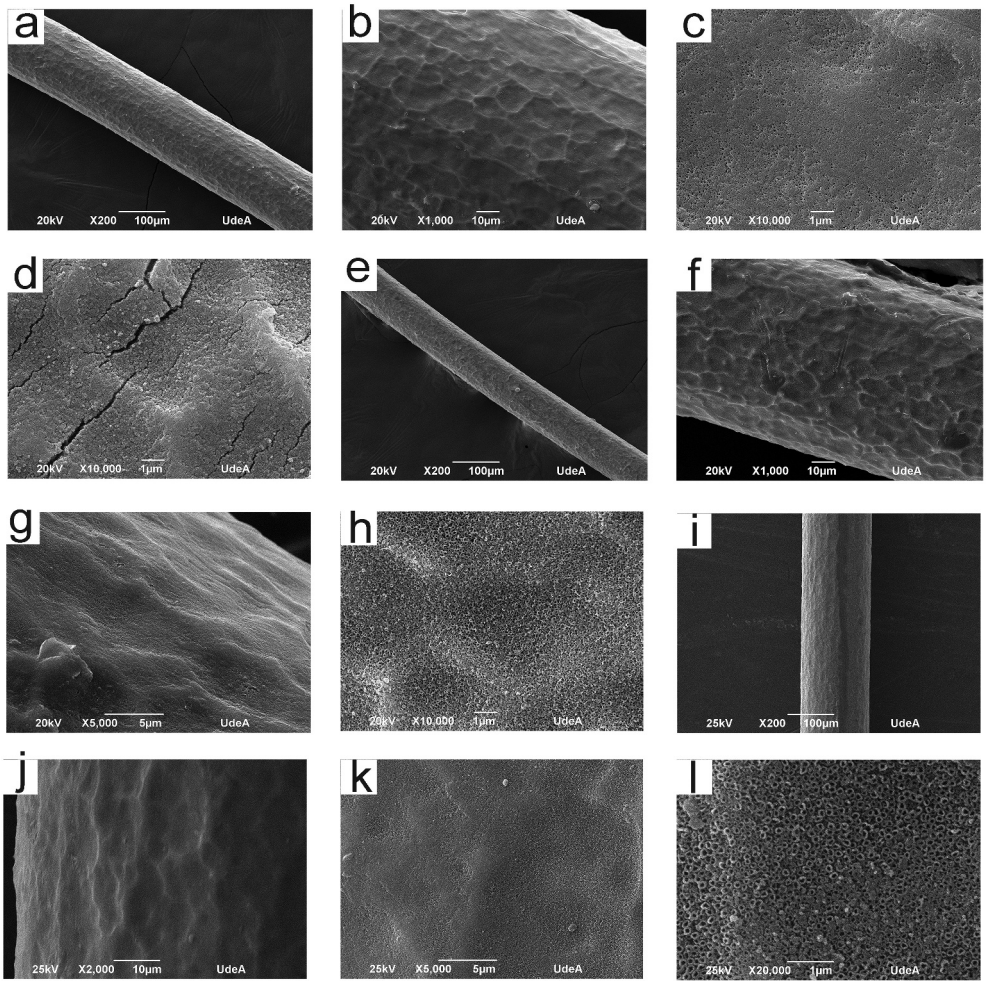


Figure 1. SEM micrographs of anodized titanium wires. S1 (a)-(c), S2 (d), S3 (e)-(h), S4(i)-(l).

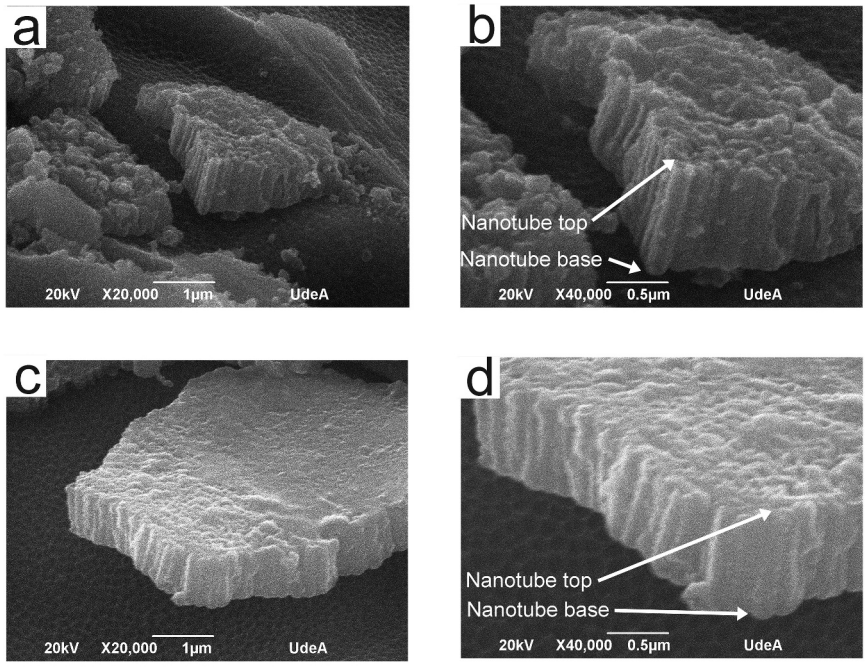


Figure 2. SEM micrographs (transversal view) of anodized titanium wires. S3 (a) and (b), S4 (c) and (d).

application of TiO_2 nanotubes created on titanium wires by anodization as the properties added to the Ti surfaces by the nanotubes would be lost. Isa et al.[14] made TiO_2 nanotubes onto titanium wires using an electrolyte of ethylene glycol and NH_4F for photocatalytic applications. These authors stated that reusability and stability are important characteristics of a catalyst in real situations. They also reported that photocatalytic properties dramatically decreased due to delamination after a second cycle of reuse; after a third cycle of reuse, the coating was peeled off and the photocatalytic properties were very low.

The internal diameter values of the TiO_2 nanotubes produced in this experimental work were similar to those measured in our previous papers on flat surfaces[18] and titanium wires with diameters around 800 μm,[17] at identical anodizing conditions. However, the length of TiO_2 nanotubes produced in this experimental work was shorter than those made on flat surfaces[18] and bigger than those grown on titanium wires with diameters around 800 μm.[17] The TiO_2 nanotube length differences between S3 and S4 samples are related to the electrolyte pH effect. The relationship between electrolyte pH value and nanotube length has been reported in preceding

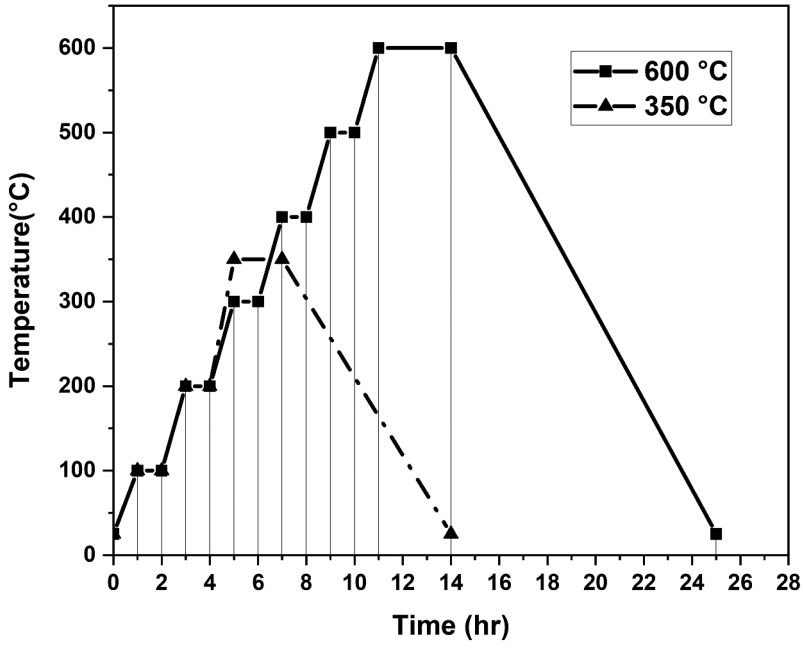


Figure 3. Ramps of temperature for every heat treatment (350 and 600 °C).

experimental works,[18,24–26] and our results are congruent with those articles.

Heat Treatment

To obtain nanotubular coatings composed of anatase or rutile phases or a mixture of them, on the surface of titanium wires, two heat treatments were employed using temperatures of 350 and 600°C. Figure 3 shows the ramp used for the heat treatments utilizing temperatures of 350 and 600°C for S3 and S4 samples. From Fig. 3, the ramps used slowly increased and the temperature was maintained at specific values for about 1 hour; however, the final temperature (either 350 or 600 °C) was held for 2 h. This ramp was designed to prevent the nanotube coating delamination and the appearance of cracks or defects in the nanotube layer. Figure 4 displays the Raman spectra of S3 and S4 samples both heat-treated (350 and 600 °C) and in the absence of heat treatment. From Fig. 4(a), the coatings without heat treatment have a distinctive Raman spectra form with wide peaks nearly at 152, 451, and 610 cm^{-1} as described in earlier research papers for amorphous TiO_2 nanotubes.[7,27,28] Since Fig. 4(b), the predominant phase in the 350°C heat-treated samples S3 and S4 was anatase. Samples S3 and S4 heat-treated at a temperature of 600°C were composed of rutile and anatase, as shown in Fig. 4(c). Images of anodized titanium wires (S3 and S4 samples) later heat treatment at 350°C are shown in Fig. 5. The uniformity of the coatings is preserved in both S3 and S4 samples heat-treated at a temperature of 350°C. Furthermore, the nanotubes preserve the high packability observed in the nanotube coatings without heat treatment. Figure 6 displays the SEM micrographs of anodized titanium wires (S3, S4 and S5 samples) later heat treatment at 600°C. Coating delamination has been seen in the heat-treated S3 samples at a temperature of 600°C since Fig. 6 (a)-(6). Heat-treated S4 samples at a temperature of 600°C maintained the coating uniformity found in the nanotube coatings without heat treatment, as shown in Fig. 6 (f)-(6); thus, cracks, defects or delamination was not seen in these samples. From Fig. 6 (j)-(6), S5 samples heat-treated at 600°C retained the coating homogeneity, noted in the same nanotube coatings in the absence of heat treatment.

The temperature ramp was designed based on our previous works[7,17,27] to prevent the occurrence of delamination, cracks or imperfections in the nanotube coatings. However, the coating stability after heat treatment depends on the layer characteristics in some cases. From the results section (Fig. 6), the S3 samples later heat treatment at 600°C presented coating delamination and cracks; however, the S4 samples after the same heat treatment maintained the coating uniformity observed in the nanotube coatings without heat treatment. An explanation of this behavior can be based on the nanotube length; from Fig. 2, the length of TiO_2 nanotubes of S3 samples is about 2000 nm compared with 1500 nm of those in the S4 samples. Thus, the integrity of the TiO_2 nanotubes heat-treated at a temperature of 600°C depends on the length of the nanotubes. The length of the TiO_2 nanotubes in the S5 samples (pH 3.5) was smaller than those in the S3 samples (pH 4) but larger than the nanotubes in the S4 samples (pH 2.5). From Fig. 6, the S5 samples show a higher coating uniformity than the S3 samples after heat treatment; thus, from our results, nanotubes with lengths shorter than 2000 nm maintain the coating uniformity after heat treatment at 600°C. Shivaram et al[29] produced TiO_2 nanotubes in flat surfaces with different lengths (300 and 950 nm) to study the heat treatment effect on the

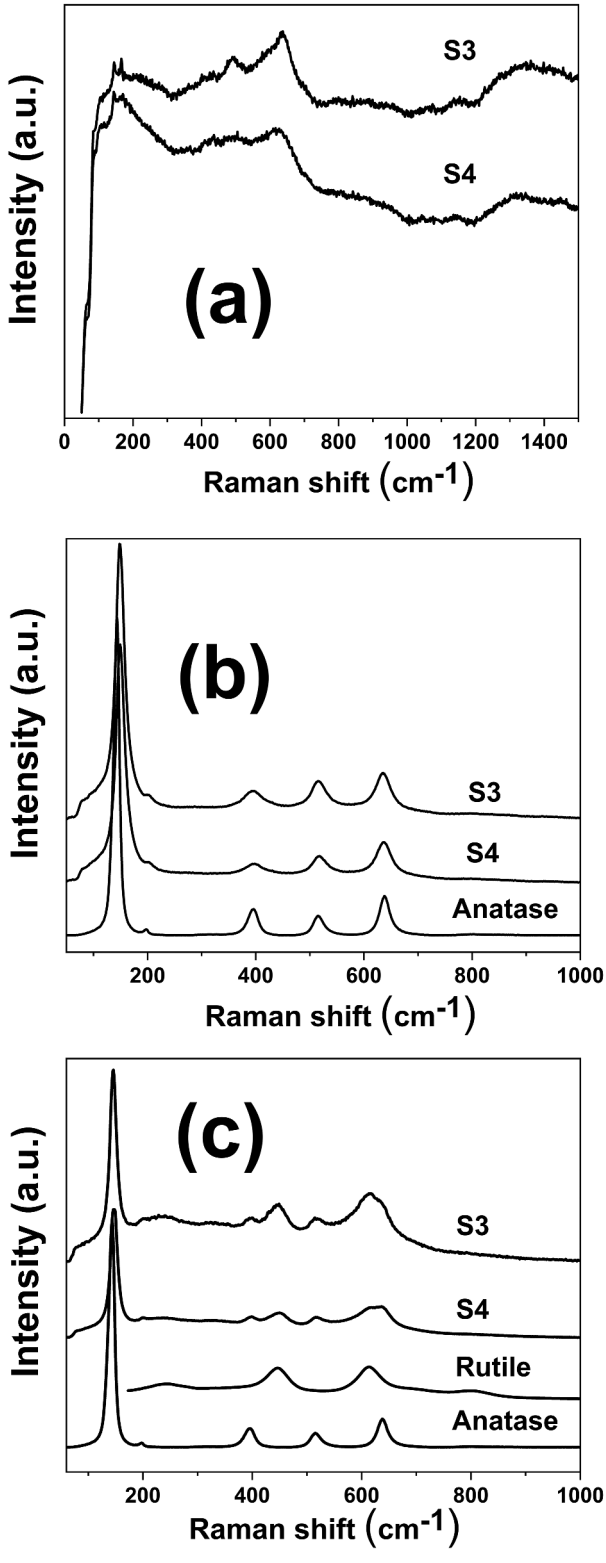


Figure 4. Raman spectra of anodized titanium wires (S3 and S4 samples) before heat treatment (a), with heat treatment at 350°C (b) and with heat treatment at 600 °C (c).

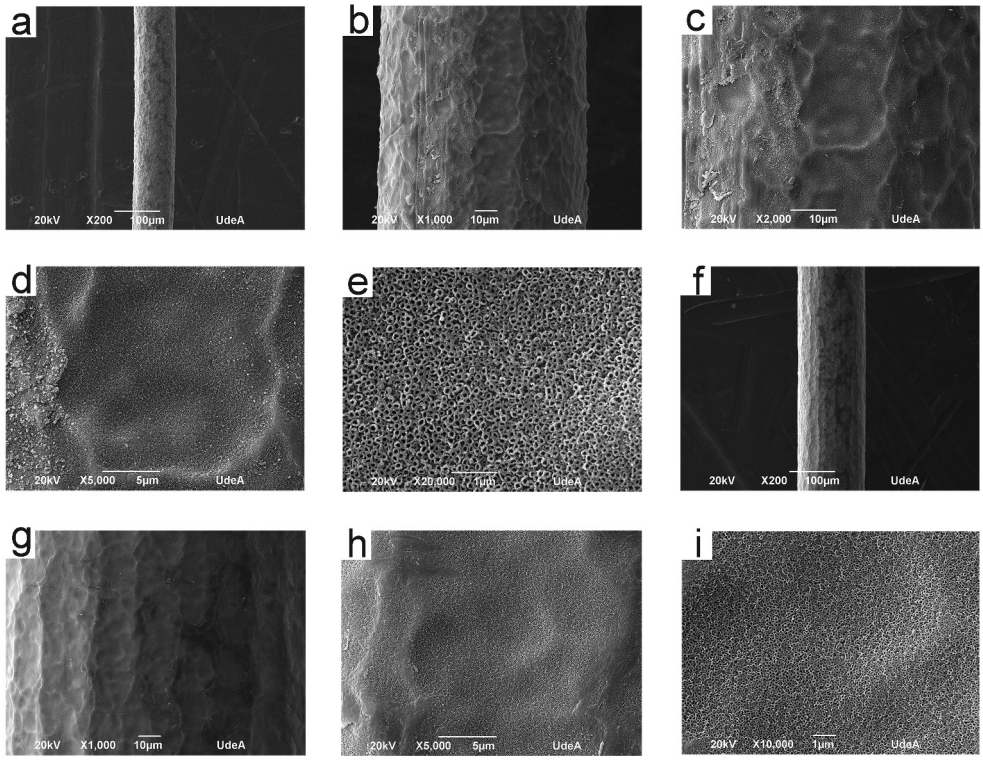


Figure 5. SEM micrographs of heat-treated at 350°C anodized titanium wires. S3 (a)-(e), S4 (f)-(i).

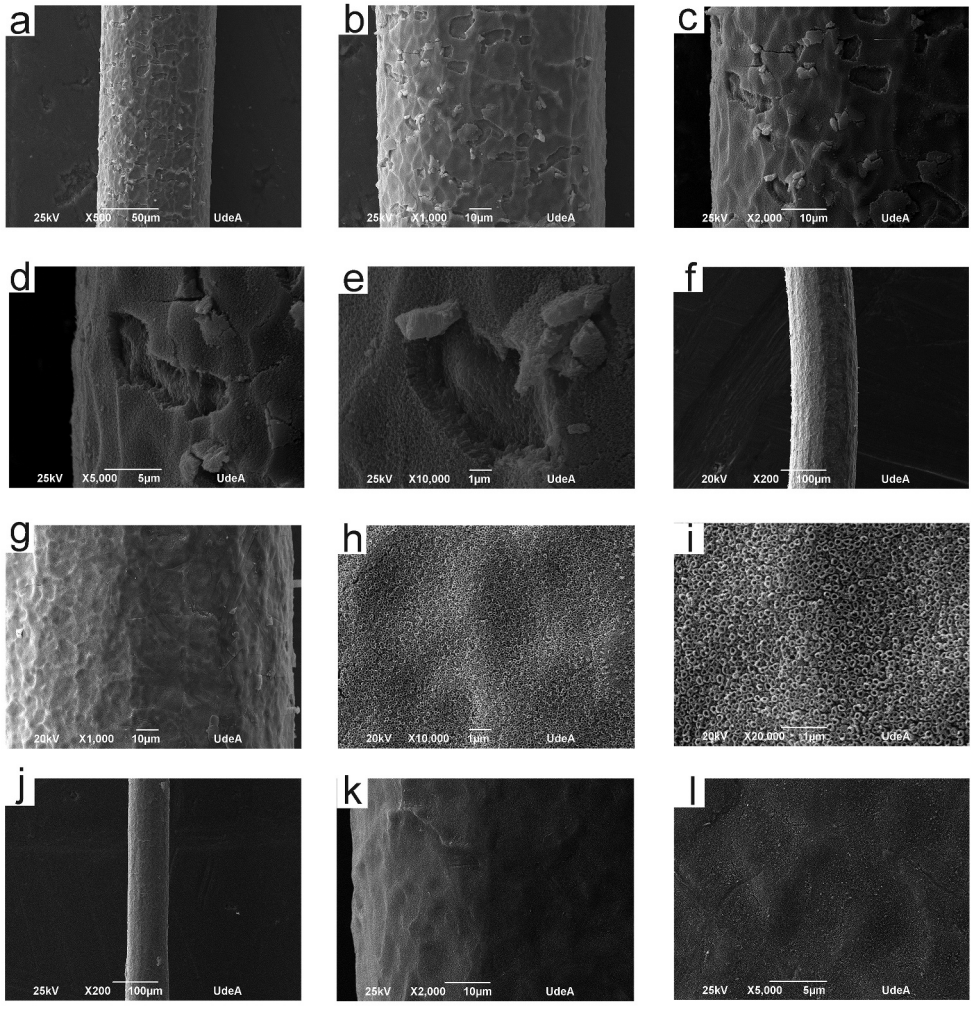


Figure 6. SEM micrographs of heat-treated at 600°C anodized titanium wires. S3 (a)-(e), S4 (f)-(i), S5 (j)-(l).

nanotube integrity. Shivaram et al. found that, after heat treatment, longer nanotubes were thermally more unstable than those with lower lengths. The results of Shivaram et al. are in accord with our results.

According to the literature review, some authors[11,30–32] reported TiO_2 nanotubes produced on titanium wires composed of anatase or anatase and rutile phases. However, those authors did not report the impact of heat treatment on the integrity of the nanotubular structures of TiO_2. Furthermore, the authors of those experimental works reported that TiO_2 nanotubes produced on titanium wires without heat treatment had problems such as delamination, cracks, and defects. Thus, the heat treatment could increase those problems by detaching a high percentage of the coating.

Some authors[11,33,34] reported that the photocatalytic properties are enhanced when the TiO_2 is constituted of a combination of anatase and rutile. Thus, the homogeneous TiO_2 nanotubes consisting of a mix of anatase and rutile produced in this work could be used in photocatalytic applications.

Conclusions

TiO_2 nanotubes were successfully produced on titanium wires with diameters smaller than 200 µm, employing an aqueous anodizing solution of NaF and CMC. Based on the results, the subsequent could be concluded:

- Homogeneous nanotube coatings were made only in the titanium wires with electropolishing pretreatment.
- The internal diameter values of TiO_2 nanotubes produced were similar to those measured in flat surfaces and titanium wires with diameters around 800 µm.
- The length of TiO_2 nanotubes produced was shorter than those made on flat surfaces and longer than those grown on titanium wires with diameters of around 800 µm.
- After both heat treatments, homogeneous nanotube composed of anatase or a mix between anatase and rutile phases were produced without apparent cracks, critical defects, or coating delamination.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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