Development of a new treatment to induce anatase growth on Ti

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ABSTRACT

The work deals with the evaluation of the application of a novel treatment of the titanium surface in order to increase anatase growth. Two different anodizing methodologies, previously developed [6] were considered, followed by a thermal post treatment able to convert the amorphous oxide film, obtained by anodizing, in a crystalline anatase structure. X ray thin film diffractometry and Raman spectroscopy have been used to identify anatase on the treated titanium surface. Combining the information obtained by the two analysis techniques allowed to verify that the best anatase crystallinity could be obtained by the treatment 1A followed by heat treatment.

Keywords: titanium, anatase, anodizing, spectroscopy, diffraction

1 INTRODUCTION

Titanium is a corrosion resistant and biocompatible material due to the titanium oxide film (about 2 nm thick) formation. The oxide film thickness can be increased by anodic oxidation techniques (anodizing) to hundreds of nanometers. Anodized titanium can assume different brilliant colors due to light interference phenomena. Colored titanium is appreciated for its aesthetical properties and has found many applications in design.

The anodizing treatment is already well known in the scientific background and is going to be transferred as industrial process for the treatment of bi- and tri-dimensional pieces as well as of tapes.

Titanium oxide produced during anodizing is essentially an amorphous oxide, but it can be transformed into crystalline TiO_2. Among the crystalline types the allotropic structure anatase is the most interesting one because of its photocatalytic and antibacterial properties [1,2]. Many works in the latest years have dealt with the studies of different treatments to utilize titanium dioxide as an agent to reduce environmental pollution [3], obtain sterilized surface [4] and inducing osteointegration of orthopedic and dental devices [5]. These not completely studied properties have enhanced titanium dioxide employment in the fields of environmental health and bioarchitecture. Aim of the work has been the evaluation of the application of a novel treatment of the titanium surface in order to increase anatase growth.

2 MATERIALS AND METHODS

After preliminary tests, two different anodizing methodologies, previously developed [6] were considered, followed by a suitable post treatment able to convert the amorphous oxide film, obtained by anodizing, in a crystalline anatase structure. The adopted methodology consist in two different types of titanium surface pretreatment named 1A and 2A followed by anodizing in a phosphoric acid solution at a potential of 130 V and a post heat treatment at 400 °C for two hours. X ray thin film diffractometry (PHILIPS PW 3020 Cu K_α radiation, parallel beam configuration) and Raman spectroscopy were used to characterize six sample conditions:

- NA-NT not anodized not heat treated (Ti as received);
- NA-YT not anodized heat treated;
- 1A-NT type 1 anodizing not heat treated;
- 1A-YT type 1 anodizing heat treated;
- 2A-NT type 2 anodizing not heat treated;
- 2A-YT:type 2 anodizing heat treated.

3 RESULTS AND DISCUSSION

As already mentioned the anodizing treatments produce a colored surface and the post treatment only slightly modifies the colors. This is an important result because of the possible aesthetic application of titanium products treated by the developed methodology.

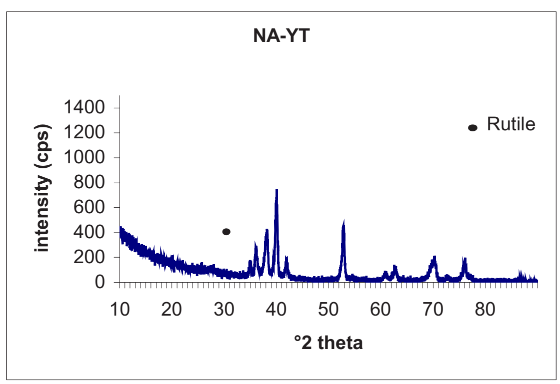

Figure 1: X ray thin film diffraction pattern.

NSTI-Nanotech 2005, www.nsti.org, ISBN 0-9767985-1-4 Vol. 2, 2005

The growth of titanium dioxide in the anatase allotropic form has been evaluated by X ray thin film diffraction and Raman spectroscopy, the results of the analysis are shown in the following sections.

3.1 X ray Thin Film Diffraction

In the figures from 1 to 3 the thin film X ray difraction patterns are showed. Diffraction pattern shows that no peaks other than titanium ones are present on the sample not treated, that is on the titanium strip. A small peak, corresponding to the most intense peak of rutile, appears in the diffraction pattern of the sample not anodized, but thermal treated (fig. 1).

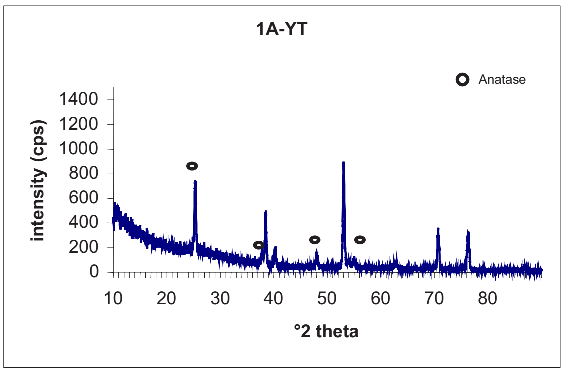

Figure 2: X ray thin film diffraction pattern.

The diffraction patterns, obtained from the samples anodized but not thermally treated (1A-YT, 2A-YT), show a small and broad peak in the angular range 25-30 °2Theta, suggesting the presence of an amorphous compound. The thermal treatment produces anatase growth on the samples anodized (1A-YT e 2A-YT) as can be seen from the diffraction patterns of figures 2 and 3. The main anatase peak is narrower and more intense in the case of treatment 1A than 2A, suggesting the presence of crystalline anatase.

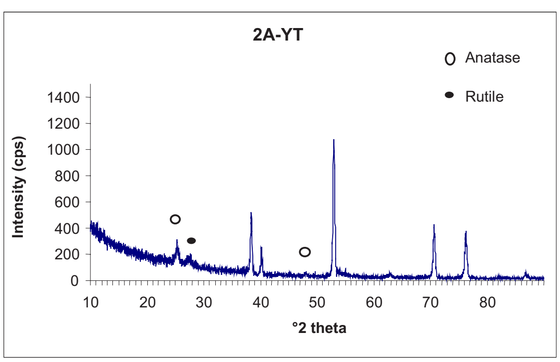

Figure 3: X ray thin film diffraction pattern.

3.2 Raman Spectroscopy

In figure 4 the Raman spectra of not anodized samples, before and after post treatment (NA-NT and NA-YT), are compared. As can be seen NA-NT is an essentially metallic sample. In the spectrum of sample NA-YT rutile peaks (442 and 611 cm^{-1}) are evident. The broad band at 200-300 cm^{-1} is typical of defective and/or substoichiometrics structures.

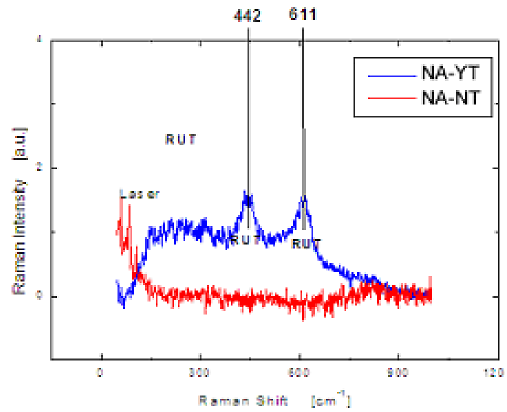

Figure 4: comparison of Raman spectra.

From comparison of Raman spectra of 1A anodized samples, before and after heat treatment (fig. 5), it can be noted that the spectrum of the not post treated sample is typical of an amorphous material, as demonstrated by the broad bands, while the five peaks present in the spectrum of the heat treated sample are proper of anatase. The peaks position is in good agreement with literature.

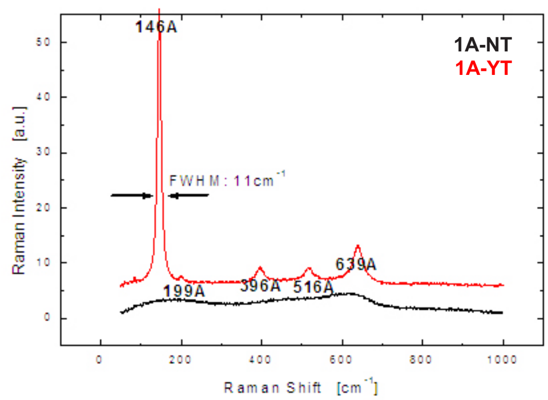

Figure 5: comparison of Raman spectra.

Figure 6 shows Raman spectra of 2A anodized samples before and after heat treatment. The spectrum of the not post treated sample consists of broad bands and a low intensity peak at 148 cm^{-1} corresponding to anatase. This suggest that the material is mainly amorphous with inclusions of anatase mono crystals. In the spectrum of the post treated sample four anatase peaks are present. The most intense peak is shifted toward the highest frequencies and broadened, this can be related to the phononic entrapping typical of a crystalline phase constituted of crystals whose dimension are of about tens nanometers. As a consequence it can be assumed that the analyzed material is composed by anatase nanocrystals.

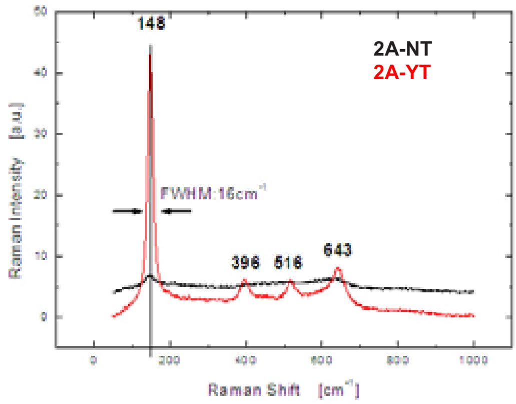

Figure 6: comparison of Raman spectra.

From the results obtained by Raman analysis of the not heat treated samples it can be summarized that:

- in the spectrum of the NA-NT sample no broad bands nor peaks are present as can be expected from metallic material, on the contrary both 1A-NT and 2A-NT spectra show broad bands related to amorphous phases (fig. 7);
- the 2A-NT spectrum shows one peak related to anatase: it could be an amorphous phase with nanocrystals of anatase. This result is partially in agreement with X ray diffraction analysis.

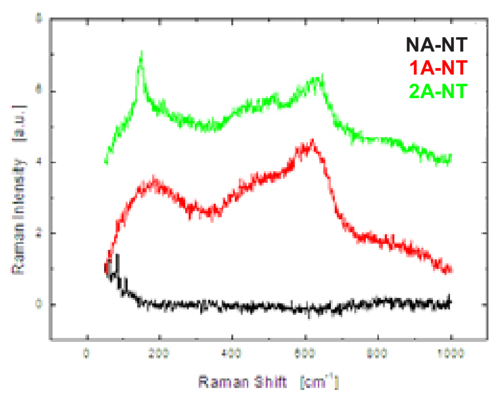

Figure 7: comparison of Raman spectra.

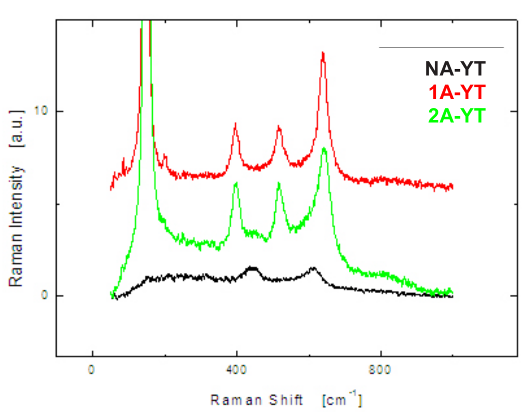

Figure 8: comparison of Raman spectra.

From the results obtained by Raman analysis of the heat treated samples it can be summarized that the difference in the position and width of the more intense anatase peak between the 1A and 2A anodized samples is due to different size of the crystalline domains in the anatase phase. Raman spectroscopy indicates that anatase crystalline domains of sample 2A-YT have a smaller dimension than those of sample 1A-YT.

4 CONCLUSIONS

Raman spectroscopy could give complementary informations to X ray diffraction analysis. Both the analysis techniques indicate that the anodizing 1A treatment followed by an appropriate heat treatment give rise to the formation of crystalline anatase. As a matter of fact the two analysis techniques equally indicate that the treatment 1A followed by heat treatment could be applied to improve anatase growth on titanium surface.

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