

# Effect of thermal oxidation on titanium oxides characteristics

M.V. Diamanti\*, S. Codeluppi\*, A. Cordioli\*, MP. Pedferri\*

\*CMIC Dept, Politecnico di Milano

Via Mancinelli 7, 20131 Milan, Italy, [mariavittoria.diamanti@polimi.it](mailto:mariavittoria.diamanti@polimi.it)

## ABSTRACT

Nanocrystalline TiO<sub>2</sub>, in the form of anatase or rutile, is one of the most important and used photocatalysts because of the excellent efficiencies of conversion of chemical species, and its stability in a wide range of environments and conditions. TiO<sub>2</sub> layers can be grown on titanium surfaces by means of anodizing processes: the so obtained oxides have thickness ranging from a few nanometers to tenths of micrometers, and present either amorphous or semicrystalline structure, depending on process parameters. When a homogeneous oxide with maximum thickness of the order of hundreds of nanometers is formed, a wide range of interference colors can appear on the oxide surface, showing different hues and saturations. Similar effects are obtained when the oxidation process consists of a thermal treatment, which can be performed at different temperatures in various atmospheres. This work is aimed at the exploration of the parameters involved in thermal oxidation and of their influence on the growing oxide characteristics, with particular reference to the surface thickness that can be achieved and the contingent generation of crystal phases, in particular anatase and rutile, which are responsible for photoinduced properties.

**Keywords:** anatase, anodizing, reflectance, thermal treatment, X-ray diffraction.

## 1 INTRODUCTION

While the exploiting of solar radiation has been extensively studied together with its applications in supplying energy and promoting chemical reactions (photoinduced processes), the role of semiconductor materials, such as titanium dioxide, only gained importance both for research studies and for industrial applications in the last twenty years [1, 2]. Titanium dioxide, in the crystalline form of anatase or rutile, is the focus of the most part of studies concerning photocatalysis, specially because of the high redox power of its electron-hole pair, which grants good efficiencies of conversion of chemical species, but also because of its commercial availability and its stability in many solvents under irradiation. The main drawback of titanium dioxide is the band gap, equal to 3,02 eV for rutile and 3,20 eV for anatase: therefore, photocatalytic performances are achieved only if the semiconductor is irradiated with UV light [3].

TiO<sub>2</sub> films with controlled morphology and structure at micro and nanometric scale can be obtained by means of anodic polarization: oxides can present smooth surface, or peculiar morphological features such as nanotubes. By increasing the thickness of the native oxide up to a few hundreds of nanometers, the surface acquires particular colors due to interference phenomena taking place at the metal-oxide and oxide-air interfaces: colors are determined by the oxide thickness [4].

While the oxides produced by anodizing have been extensively studied [5, 6], less information is available concerning thermal oxidation. Titanium oxides obtained by techniques alternative to anodizing, e.g. by thermal treatment or by pulsed laser, may present either an amorphous structure or the presence of crystal phases: the oxide stoichiometry principally consist of TiO<sub>2</sub>, but non-stoichiometric phases (Ti<sub>1+x</sub>O<sub>2-y</sub>) and sub-stoichiometric phases (Ti<sub>2</sub>O<sub>3</sub>, TiO, Ti<sub>2</sub>O, Ti<sub>6</sub>O) may also form. In case of conspicuous alteration of the oxide structure from amorphous to crystalline, the interference color is lost and consequently the aesthetical qualities of the surface [7, 8]. Nevertheless, the formation of a small fraction of nanocrystals with non-stoichiometric composition in oxide containing prevalently anatase or rutile may enhance to some extent the photoactivity of the oxide, since these phases can modify the electronic structure of the resulting complex oxide by creating accessible energy levels in the oxide band-gap, therefore reducing the energy necessary to activate the semiconductor. This principle is also exploited when TiO<sub>2</sub> is doped with chemical elements (e.g. nitrogen or carbon) which enter the crystal structure in interstitial or substitutional positions, thus altering the electronic structure and reducing the band-gap: this method is used to shift light absorption from UV towards visible light [9].

In this research, the effect of thermal treatment both on bare titanium and on anodized titanium will be investigated: air and nitrogen atmospheres will be used. Investigations will focus on the oxide color and thickness and on the different structures achievable in the tested atmospheres.

## 2 MATERIALS AND METHODS

### 2.1 Materials preparation

Rectangular specimens (20 x 30 mm) were cut out of a sheet of commercial purity (grade 2) titanium, 0.5 mm thick. Surface preparation involved only a degreasing step

with acetone. Samples were thermally treated in air and in nitrogen atmospheres, with temperatures ranging from 400°C to 700°C and treatment time ranging from 0.5 hours to 6 hours. A first series of tests was performed on non-anodized titanium; subsequently, the same treatments were repeated on specimens anodized either in sulfuric acid 0.5 M or with a two-step anodizing process described elsewhere [10], with cell potentials of 10 V, 20 V, 90 V and 100 V (anode-to-cathode potential differences, being the cathode a titanium net). These values were chosen in order to investigate the behavior of oxides with different initial thicknesses (Table 1). Anodizing was performed by applying a constant current density (20 mA/cm<sup>2</sup>) by means of a galvanostat.

Cell potential (V)		10	20	90	100
Thickness (nm)	A	37	51	161	169
	2A	40	58	196	218

Table 1: Oxide thickness after anodizing, measured by reflectance. A: anodized in H<sub>2</sub>SO<sub>4</sub>; 2A: two-step anodizing.

## 2.2 Oxides characterization

The thickness of the oxide layer was derived from reflectance curves: in fact, thickness can be calculated on the basis of the position of maxima and minima in the reflectance spectrum (Fig. 1), which in turn are determined by Bragg's law for constructive and destructive interference. Reflectance data were elaborated with the FTM (Film Thickness Module) software; the software provided the refractive index dispersion curve for TiO<sub>2</sub> necessary to interpolate the reflectance curves. The evolution of colors with oxidation was also considered.

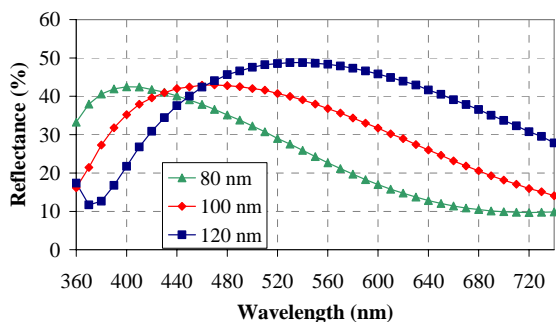


Figure 1: Reflectance spectra for 80, 100 and 120 nm thick oxides: as thickness increases reflectance peaks increase in number and shift towards higher wavelengths.

Concerning oxides photoactivity, X-ray diffraction patterns were acquired in order to evidence any crystal phase formed during treatments. Titanium anodized with a two-step procedure proved to be amorphous for any anodizing potential and current density applied; on the

contrary, high anodizing potentials (90 V and 100 V) reached in H<sub>2</sub>SO<sub>4</sub> electrolytes led to a partial crystallization of the oxide, with the formation of anatase nanocrystals in the amorphous matrix (Fig. 2) [5]. Therefore thermal oxidation was performed on oxides which had not only different thickness, but also different structure.

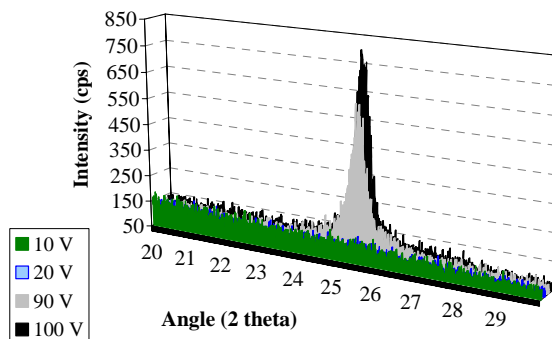


Figure 2: X-ray diffraction peak of anatase (25°) for the oxides obtained in H<sub>2</sub>SO<sub>4</sub> 0.5 M.

## 3 RESULTS AND DISCUSSION

### 3.1 Oxide thickness

The thermal treatment in air of bare titanium led to the formation of nanometric oxides of different thicknesses, depending on temperature and duration of the treatment itself (Fig. 3). In particular, the applied temperature is more relevant than the treatment time: in fact, treatments performed at 450, 500 and 550°C all cause the growth of an oxide with thickness ranging from 30 to 60 nm, while at 600°C the oxide thickness increases more evidently, and also the effect of time becomes more relevant.

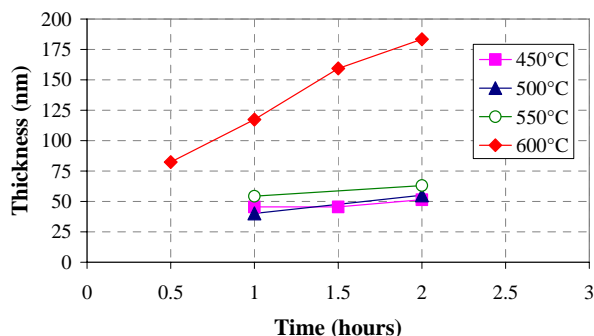


Figure 3: Relationship among treatment temperature, time and thickness achieved on bare titanium.

On anodized titanium, the achieved oxide thicknesses for the different temperatures and durations, for specimens anodized with cell potential of 100 V both in sulfuric acid and with a two-step anodizing, are reported as example; for

the other applied cell potentials, analogous trends were observed (Table 2, 3).

	0.5 h	1 h	1.5 h	2 h
400°C	170	170	173	170
450°C	173	176	184	184
500°C	185	187	185	189
550°C	191	197	200	206
600°C	203	233	233	237

Table 2: Oxide thickness after thermal treatment in air of titanium anodized in H<sub>2</sub>SO<sub>4</sub> with cell potential of 100 V, as a function of time and temperature.

	0.5 h	1 h	1.5 h	2 h
400°C	217	222	218	218
450°C	222	219	225	226
500°C	232	239	245	243
550°C	261	269	252	263
600°C	283	279	286	279

Table 3: Oxide thickness after thermal treatment in air of titanium treated with two-step anodizing, with cell potential of 100 V, as a function of time and temperature.

It is easily noticed that the influence of the treatment duration on oxide growth is almost negligible, compared to the effect of temperature, which allows an increase in oxide thickness of more than 20% with respect to the anodic oxide. For thin anodic oxides (10 V and 20 V), the percent increase was even more pronounced, exceeding 100%.

Thermal treatments were also performed at 650°C and 700°C: in these cases the conspicuous conversion of the amorphous structure to crystal phases led to the loss of the interference color. Reflectance spectra attested the degradation of the interference characteristics, with the disappearance of reflectance peaks; for this reason the oxide thickness could not be calculated for temperatures higher than 600°C.

The relationship between oxide thickness and temperature of thermal treatment is reported for both anodizing processes (Fig. 4). A first observation concerns the initial thicknesses of anodic oxides: for any applied potential, two-step anodizing generated thicker oxides. This is due to the higher homogeneity of the oxide on the whole surface: in fact, oxides grown in H<sub>2</sub>SO<sub>4</sub> are not perfectly uniform in color and thickness at the microscale [5].

The effect of temperature is the same in the two anodizing conditions, that is, a non-linear increase of thickness, more pronounced as temperature increases; nevertheless, the oxides grown with two-step anodizing exhibit a lower tendency to a further oxidation as temperature increases. This is attributed to the higher barrier effect performed by these oxides towards oxidation, which in turn is imputable to the superior homogeneity.

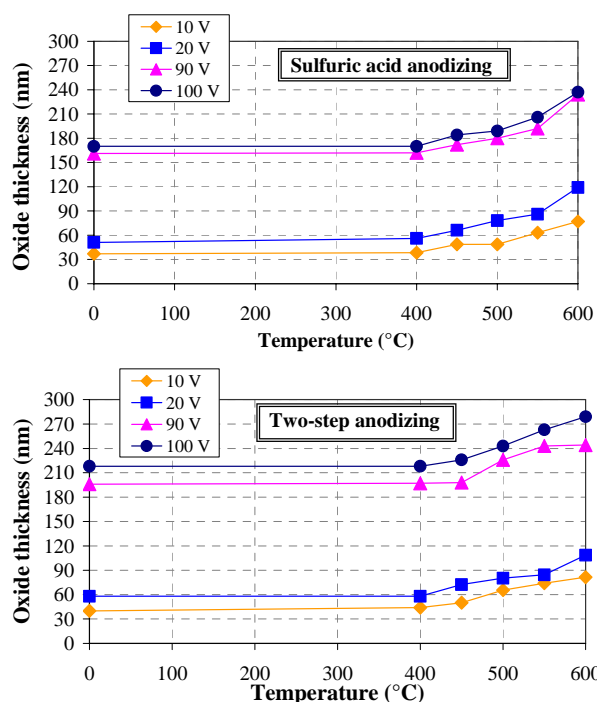


Figure 4: Oxide thickness variation with temperature for titanium anodized in H<sub>2</sub>SO<sub>4</sub> and with two-step anodizing, for 2 hour thermal treatments.

Thermal treatments performed in N<sub>2</sub> atmosphere led to a less pronounced increase in oxide thickness; yet, a variation was noticed though the chosen atmosphere was considered to be inert, and this is due to O<sub>2</sub> impurities present in the N<sub>2</sub> gas used in these tests. A higher purity atmosphere wasn't considered since a further oxidation wasn't considered to affect the tests negatively. Thickness of thin anodic oxides increased by 60% on average for treatments performed at 600°C; thicker oxides increased by less than 20% in same conditions. The oxidation kinetics are similar to those observed in air.

### 3.2 Crystal phases

Thermal treatments performed in air on bare titanium produced the formation of rutile at high temperature (600°C or more). Surfaces treated at lower temperature presented completely amorphous oxides, probably on account of the particularly low oxide thickness. On previously anodized samples the presence of crystal phases was noticed at lower temperatures: anatase starts to crystallize at 500°C in very thin amorphous oxides (10 V) while the temperature necessary to its formation drops to 400°C with the increase of oxide thickness. Rutile appears at 600°C as for bare titanium. At 700°C the anatase component decreases or even disappears and a very intense peak of rutile is displayed (Fig. 5). Results obtained for titanium anodized in H<sub>2</sub>SO<sub>4</sub> at 100 V are presented as example.

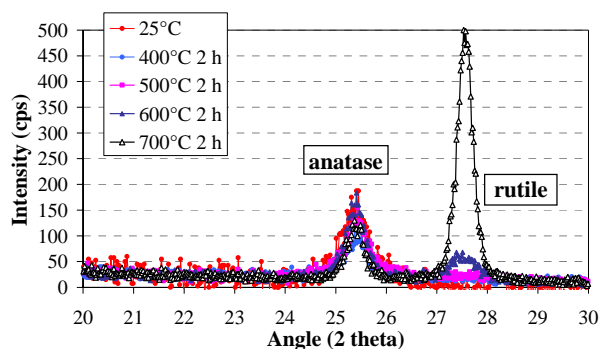


Figure 5: X-ray diffraction peaks of anatase (25°) and rutile (27.5°) for the oxide grown in  $H_2SO_4$ , cell potential: 100 V, thermally treated in air for 2 hours at various temperatures.

Macrocrystalline rutile is the thermodynamically stable structure of  $TiO_2$ , while anatase is a metastable phase which owes its stability at room temperature to the almost null transformation kinetics. However, thermodynamic stability is particle-size dependent, and at particle diameters below ca. 14 nm, anatase is more stable than rutile [3]. Therefore the observed behavior, i.e. the first appearance of anatase peak for low temperatures followed by the co-presence of the two structures and the final disappearance of anatase in favor of rutile phase, can be explained by considering the initial nucleation of nanocrystals, with average dimensions lower than 15 nm and thus with anatase structure, which increase in dimensions with increasing temperature, therefore gradually converting to rutile.

Finally, treatments performed in nitrogen atmosphere caused the formation of several crystal phases, besides anatase and rutile which are present as well. A non-stoichiometric oxide ( $Ti_6O$ ) was observed on bare titanium and for 10 V anodizing, that is, for very thin oxides, at 600°C or more. This is ascribed to the low oxidative power of the  $N_2$  atmosphere, which is only due to  $O_2$  impurities, and therefore the shortage of oxygen can lead to the formation of titanium oxides with lower oxygen content.

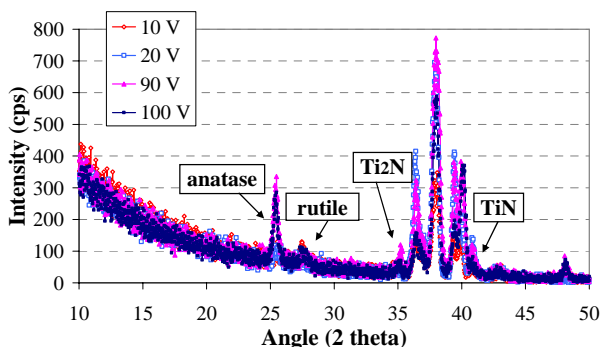


Figure 6: X-ray diffraction patterns of the oxides grown in  $H_2SO_4$  thermally treated in  $N_2$  at 700°C for 2 hours: crystal phases observed are labeled on the pattern.

The detection of titanium nitrides was considered particularly interesting: in fact, while the formation of a crystal phase containing nitrogen has no influence on band gap modification, it is surely indicative of the occurred adsorption of nitrogen in  $TiO_2$  (Fig. 6). As mentioned in the introductory part, nitrogen adsorption is the physical phenomenon responsible for generation of admitted levels in the prohibited band gap, and therefore for band gap decrease, which cause the shift of  $TiO_2$  light absorption from UV wavelengths towards visible light.

## 4 CONCLUSIONS

The presented research showed the possibility of creating oxides with different thicknesses and structures by means of thermal oxidation. While the behavior of titanium when subjected to thermal treatment was predictable, a particular focus was placed on the analysis of the behavior of anodized titanium to such treatments, since the presence of an oxide layer was supposed to slow down a further oxidation. Any oxide layer, either thin or thick, amorphous or semicrystalline, present on titanium surface actually restrains oxidation. While the duration of thermal treatment was proved to have a negligible influence on both oxide thickening and crystallization, the effect of temperature is definitely fundamental in determining thickness and structure, not only in terms of the quantity of a certain phase present in the oxide, but also (and mainly) for the type of crystal phases and the dimensions of the nanocrystals. Moreover, the presence of nitrogen in the atmosphere allowed the formation of titanium nitrides, which is considered as indicative of the adsorption of nitrogen atoms inside the oxide structure.

## REFERENCES

- [1] A. Fujishima, K. Honda, *Nature*, vol. 238 (1972), 37-38.
- [2] S.N. Frank, A.J. Bard, *J. Am. Chem. Soc.*, vol. 99 (1977), 303-304.
- [3] O. Carp, C.L. Huisman, A. Reller, *Prog. Solid State Chem.*, vol. 32 (2004), 33-177.
- [4] U.R. Evans, *Proceedings of the Royal Society of London. Series A*, vol. 107 (1925), 71-74.
- [5] M.V. Diamanti, M.P. Pedferri, *Corros. Sci.*, vol. 49 (2007), 939-948.
- [6] J.L. Delplancke, M. Degrez, A. Fontana, R. Winand, *Surf. Technol.*, vol. 16 (1982), 16.
- [7] P. Kofstad, *High temperature corrosion*. London and New York, Elsevier Applied Science (1988).
- [8] L. Lavisse, D. Grevey, C. Langlade, B. Vannes, *Appl. Surf. Sci.*, vol. 186, Issue 1-4 (2002), 150-155.
- [9] L. Wan, J.F. Li, J.Y. Feng, W. Sun, Z.Q. Mao, *Mat. Sci. Eng. B*, vol. 139 Issue: 2-3 (2007), 216-222.