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Effect of thermal oxidation on titanium oxides' characteristics

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Nanocrystalline TiO₂, in the form of anatase or rutile, is one of the most important and used photocatalysts because of its excellent conversion efficiencies and its chemical stability. TiO₂ layers can be grown on titanium by means of anodising processes: the so-obtained oxides present either amorphous or semicrystalline structure, depending on process parameters. When a homogeneous oxide with maximum thickness of the order of hundreds of nanometres is formed, a wide range of interference colours appear on the oxide surface, showing different hues and saturations. Similar effects are obtained when the oxidation process consists of a thermal treatment. 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 its thickness and the contingent generation of crystal phases (anatase and rutile) responsible for photoinduced properties. Oxide characteristics are investigated by means of reflectometry and X-ray diffraction. Thermal treatments proved to be an efficient way to tune oxide thickness and structure, in order to achieve the formation of oxides showing photoactivated properties both in the UV and in the visible light range, as well as to tune their chromatic properties.

Keywords: anatase; anodising; reflectometry; thermal treatment; titanium dioxide

1. Introduction

While the exploitation 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 20 years [1,2]. Titanium dioxide, in the crystalline form of anatase or rutile, is the focus of the most part of those studies concerning photocatalysis, especially 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].

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Titanium dioxide films with controlled morphology and structure at the micro and nanometric scale can be obtained by means of anodic polarisation; 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 nanometres, the surface acquires particular colours due to interference phenomena taking place at the metal–oxide and oxide–air interfaces; colours are determined by the oxide thickness [4].

While the oxides produced by anodising have been extensively studied [5,6], less information is available concerning thermal oxidation. Titanium oxides obtained by techniques alternative to anodising, 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 consists of TiO_2 , but non-stoichiometric phases ($\text{Ti}_{1+x}\text{O}_{2-y}$) and sub-stoichiometric phases (Ti_2O_3 , TiO , Ti_2O , Ti_6O) may also form. In the case of conspicuous alteration of the oxide structure from amorphous to crystalline, the interference colour 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_2 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 anodised titanium will be investigated, and air and nitrogen atmospheres will be used. Investigations will focus on the oxide colour and thickness and on the different structures achievable in the tested atmospheres.

2. Materials and methods

2.1. Materials preparation

Rectangular specimens (20×30 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 to 700°C and treatment time ranging from 0.5 to 6 h. A first series of tests was performed on non-anodised titanium; subsequently, the same treatments were repeated on specimens anodised either in sulphuric acid 0.5 M or with a two-step anodising process described elsewhere [10], with cell potentials of 10, 20, 90 and 100 V (anode-to-cathode potential differences, being the cathode a titanium net). These values were chosen in order to investigate the behaviour of oxides with different initial thicknesses (Table 1). Anodising was performed by applying a constant current density (20 mA cm^{-2}) by means of a galvanostat.

2.2. Oxides characterisation

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

Table 1. Oxide thickness after anodising, measured by reflectance.

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

Note: A: anodised in H₂SO₄; 2A: two-step anodising (nm).

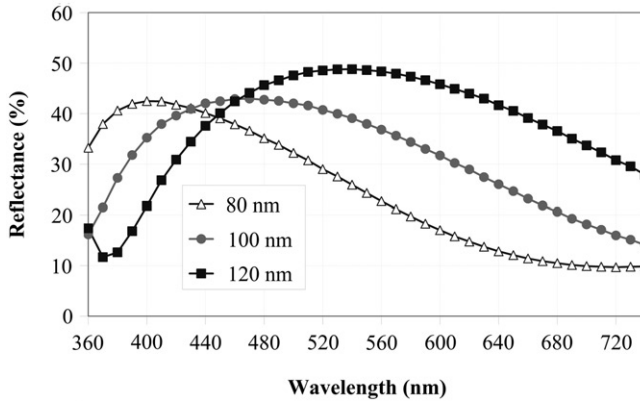


Figure 1. Reflectance spectra for 80, 100 and 120 nm thick oxides: as thickness increases reflectance peaks increase in number and shift towards higher wavelengths.

spectrum (Figure 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 TiO₂ necessary to interpolate the reflectance curves. The evolution of colours with oxidation was also considered.

Concerning oxides photoactivity, X-ray diffraction patterns were acquired in order to evidence any crystal phase formed during treatments. Titanium oxides anodised with a two-step procedure proved to be amorphous for any anodising potential and current density applied; on the contrary, high anodising potentials (90 and 100 V) reached in H₂SO₄ electrolytes led to a partial crystallisation of the oxide, with the formation of anatase nanocrystals in the amorphous matrix (Figure 2) [5]. Therefore thermal oxidation was performed on oxides which had not only different thickness, but also different structure.

3. Results and discussion

3.1. Oxide thickness

The thermal treatment performed in air on bare titanium led to the formation of nanometric oxides of different thicknesses, depending on temperature and duration of the treatment itself (Figure 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.

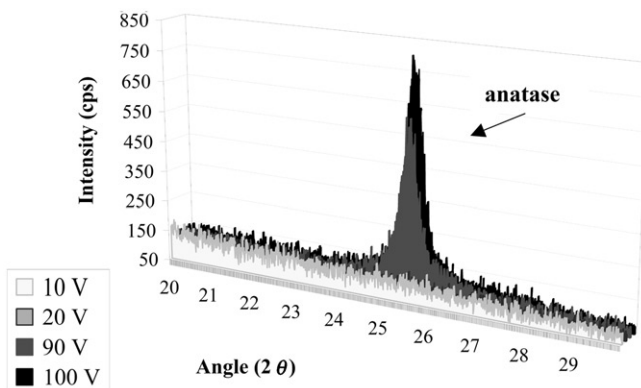


Figure 2. X-ray diffraction peak of anatase (25°) for the oxides obtained in H_2SO_4 0.5 M.

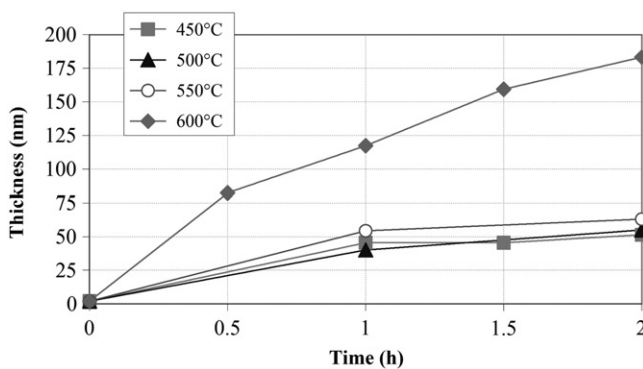


Figure 3. Relationship among treatment temperature, time and thickness achieved on bare titanium.

Table 2. Oxide thickness after thermal treatment in air of titanium anodised in H_2SO_4 with cell potential of 100 V, as a function of time and temperature (nm).

Temperature ($^\circ\text{C}$)	Time			
	0.5 h	1 h	1.5 h	2 h
400	170	170	173	170
450	173	176	184	184
500	185	187	185	189
550	191	197	200	206
600	203	233	233	237

On anodised titanium, the oxide thicknesses achieved at the different temperatures and durations after anodising at 100V are reported as an example (sulphuric acid anodising: Table 2; two-step anodising: Table 3). At the other applied cell potentials, analogous trends were observed.

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

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

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 and 20 V), the percent increase was even more pronounced, exceeding 100%.

Thermal treatments were also performed at 650 and 700°C. In these cases the conspicuous conversion of the amorphous structure to crystal phases led to the loss of the interference colour. 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 anodising processes (Figure 4). A first observation concerns the initial thicknesses of anodic oxides; for any applied potential, two-step anodising generated thicker oxides. This is due to the higher homogeneity of the oxide on the whole surface, in fact, oxides grown in H₂SO₄ are not perfectly uniform in colour and thickness at the microscale [5].

The effect of temperature is the same in the two anodising conditions, that is, a non-linear increase of thickness, more pronounced as the temperature increases; nevertheless, the oxides grown with two-step anodising 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.

Thermal treatments performed in N₂ 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 O₂ impurities present in the N₂ gas used in these tests. A higher purity atmosphere was not considered since a further oxidation was not 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 <20% in same conditions (Table 4). 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

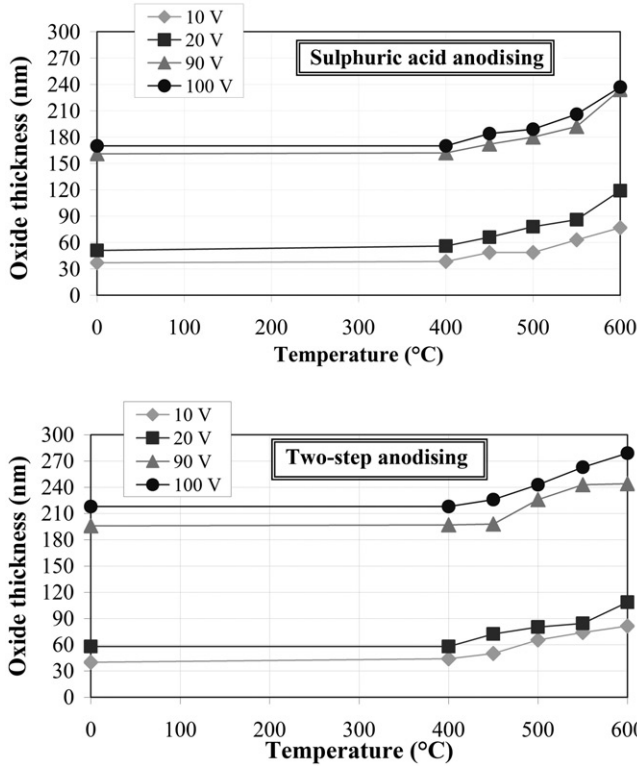


Figure 4. Oxide thickness variation with temperature for titanium anodised in H₂SO₄ and with two-step anodising, for 2 h thermal treatments.

Table 4. Oxide thickness after 2 h thermal treatment at 600°C of differently anodised titanium: comparison between air and nitrogen atmospheres with respect to initial thickness (nm).

	Non-treated	Air	Nitrogen
A, 10 V	37	77	63
A, 20 V	51	119	81
A, 90 V	161	234	204
A, 100 V	169	237	205
2A, 10 V	40	81	78
2A, 20 V	58	109	92
2A, 90 V	196	244	208
2A, 100 V	218	279	233

Note: A: anodised in H₂SO₄; 2A: two-step anodising (nm).

oxide thickness. On previously anodised samples the presence of crystal phases was noticed at lower temperatures; anatase starts to crystallise 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

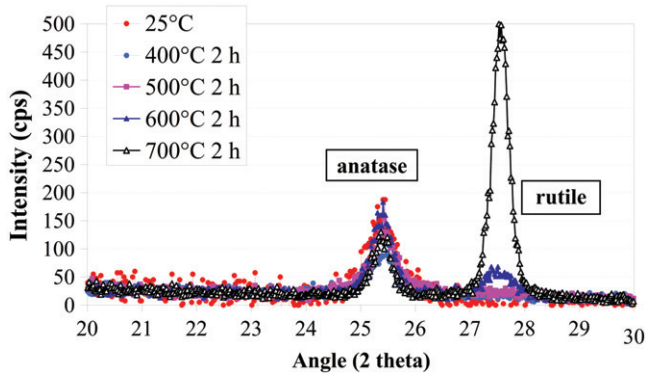


Figure 5. X-ray diffraction peaks of anatase (25°) and rutile (27.5°) for the oxide grown in H_2SO_4 , cell potential: 100 V, thermally treated in air for 2 h at various temperatures.

component decreases or even disappears and a very intense peak of rutile is displayed (Figure 5). Results obtained for titanium anodised in H_2SO_4 at 100 V are presented as example.

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 nil transformation kinetics. However, thermodynamic stability is particle-size dependent, and at particle diameters below *c.* 14 nm, anatase is more stable than rutile [3]. Therefore, the observed behaviour, 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 favour 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 anodising, 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.

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 (Figure 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 behaviour of titanium when

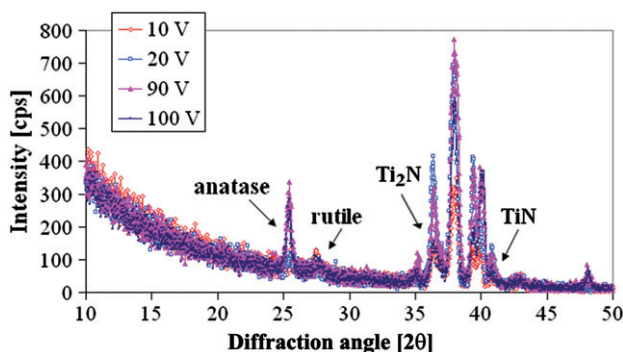


Figure 6. X-ray diffraction patterns of the oxides grown in H_2SO_4 thermally treated in N_2 at 700°C for 2 h: crystal phases observed are labelled on the pattern.

subjected to thermal treatment was predictable, a particular focus was placed on the analysis of the behaviour of anodised titanium to such treatments, since the presence of an oxide layer was supposed to slow down further oxidation. Any oxide layer, 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 crystallisation, 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.

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