

Photoactive and colored anodic oxides on titanium for architectural and design applications

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ABSTRACT

Anodizing processes performed on titanium can lead to the formation of oxides with thicknesses ranging from a few nanometers to half micrometer, either amorphous or containing crystal phases, showing a wide range of interference colors with different hues and saturations: the results of this process strictly depend on the parameters imposed. Nanocrystalline oxides also present peculiar properties activated by UV light: these oxides act as substrates for photocatalytic reactions, and at the same time can undergo surface changes that modify their hydrophilic state, which lead to the formation of self-cleaning surfaces. Therefore, the use of anodized titanium can add to the aesthetical side granted by its fascinating colors a more practical purpose conferred by the photoactivated self-cleaning properties, which involve lower maintenance efforts for indoor and outdoor cleansing of the surfaces.

Keywords: anatase, anodizing, interference color, photocatalysis, self-cleaning.

1 INTRODUCTION

Titanium has always attracted the attention of both researchers and industries thanks to its variety of applications, from oil industries and heat exchangers, to biomedical prostheses, automotive components, or architectural applications [1].

Concerning the fields of architecture and design, what most catches the attention of scientists as well as artists is the coloring of titanium. This metal, when exposed to the atmosphere, is covered by a transparent passive film few nanometers thick; by increasing the thickness of the native oxide up to a few hundreds nanometers the surface acquires particular colors, which are due to interference phenomena. In fact, when irradiated with white light, only a part of the incident photons are reflected by the oxide surface; the remaining part enters the oxide and is reflected by the metal surface. Interference phenomena taking place between the two exiting light waves result in the appearance of colors on the surface, whose hues are determined by the light components that happen to exit the oxide in phase (constructive interference). The in-phase wavelengths depend, in turn, on the optic path, that is, on the oxide thickness: therefore oxides with different thicknesses generate different colors.

This course of action can be exploited to obtain a desired color on the anodized surfaces: this can be achieved by controlling accurately the oxide thickness [2]. Actually, both hue and saturation depend strictly on the steps and parameters adopted in the anodizing process. A deep understanding of the anodic oxidation is therefore fundamental in order to grant the best control of morphology, crystal arrangement and homogeneity of the nanostructured layer, which in turn determine the properties of the product, from its aesthetic qualities to the resistance to either atmospheric or indoor exposure, to the possibility of developing photoinduced properties [3]. The parameters which mostly affect the resulting color are electrolyte and cell potential; in particular, the oxide thickness is directly proportional to the potential applied. Surface preparation and roughness also have an important influence, as they determine the surface behavior for what concerns light scattering and therefore the brightness of colors [4, 5].

Anodizing in sulfuric acid with suitable current densities and potentials also grants the partial conversion of the oxide to the crystalline phases of TiO_2 , that is, anatase or rutile: nanocrystals of anatase or rutile nucleate inside the amorphous matrix. The obtaining of a semicrystalline oxide confers to the surface photoactivated properties such as superhydrophilicity and photocatalytic activity whenever the surface is irradiated with UV light, thus leading to the production of a material which has self-cleaning attitude and at the same time contributes to the decomposition of organic and inorganic polluting substances present on the material surface; the most photoactive phase of TiO_2 is anatase [6]. These oxides can still present interference color, and therefore combine both aesthetic and functional interest.

In this research, the anodic coloration of titanium was studied; particular attention was paid to the photoactivity of these oxides, where present.

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, aimed cleaning the surface to avoid a partial shielding of some areas of the sample, which would alter the current distribution and therefore the color. To evidence

the effect of different roughness on the obtained color, two samples were prepared in different ways: one was previously sandblasted, while the other one was chemically etched in a HF/HNO₃ mixture [8].

Samples were anodized in sulfuric acid 0.5 M with cell potentials ranging from 10 V to 120 V (anode-to-cathode potential differences, being the cathode a titanium net). Anodizing was performed by applying a constant current density of 40 mA/cm² by means of a galvanostat; the effect of different current densities on the formed oxides was analyzed in previous work [3].

2.2 Oxides characterization

The characterization of the oxide layer was aimed at a full understanding of the chromatic and photoinduced properties. The former ones were determined by spectrophotometry, which allowed the precise and objective definition of the surface color (CIELab standard), and by reflectance curves, which were used to measure the oxide thickness. In fact, the 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.

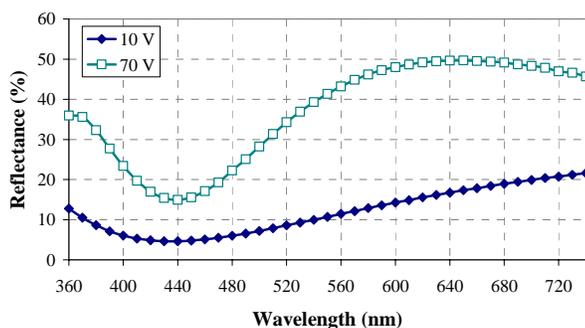


Figure 1: Example of reflectance spectra for samples anodized with cell potentials of 10 V and 70 V: samples show similar yellow hue but present different spectra (periodicity of interference colors).

Photoinduced properties were evaluated either in the mineralization of a solid organic compound, i.e stearic acid, or from the variation of the contact angle formed by water on the oxide surface after irradiation with UV lamps (300 W, 2 mW/cm²). For photocatalytic tests, a thin layer of stearic acid (approximately 90 µg) was deposited on the specimen surface; its mineralization was monitored during UV exposure by means of FT-IR analyses [7]. Tests lasted a maximum of 144 hours for each sample. Contact angle measurements were performed by placing a water drop (volume of 10 µL) on the sample surface with a precision pipette: the drop image was acquired through a CCD camera and then elaborated with an image analysis

software, which allowed a precise measurement of the contact angle. Measurements were performed before and after irradiation with UV light.

3 RESULTS AND DISCUSSION

3.1 Color

Colors shown by samples can be easily represented on the chromaticity diagram proposed by CIE (Commission Internationale de l'Eclairage), which associates each color to a set of three chromatic coordinates: a* indicates colors ranging from green to red, b* indicates variations from blue to yellow, and L represents brightness.

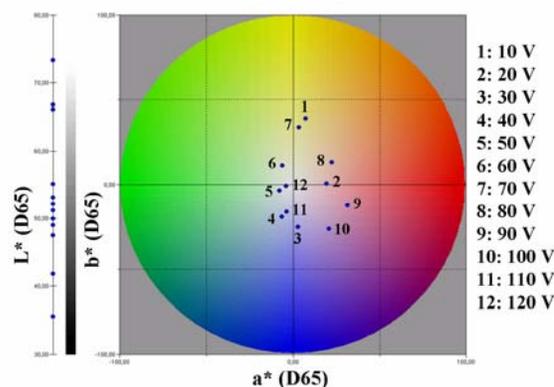


Figure 2: Chromaticity diagram for samples anodized in sulfuric acid 0.5 M; cell potentials range from 10 to 120 V.

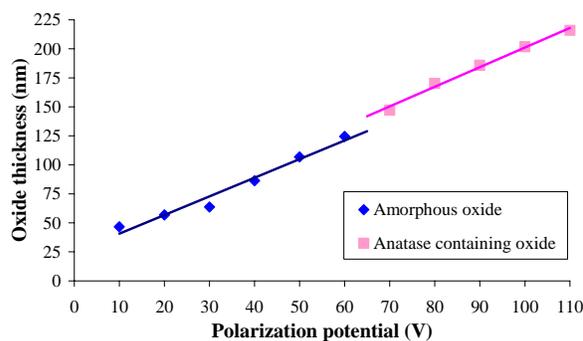


Figure 3: Oxides thicknesses measured by reflectance: for cell potentials higher than 110 V reflectance spectra didn't allow any calculation.

Anodized samples can assume almost any hue (Fig. 2); a periodic repetition of colors can be noticed whenever the interference process is given by oxide layers whose thickness is integer multiple of one another.

This is the case of samples anodized by applying cell potentials of 10 V and 70 V, which generated oxide thicknesses of 46 nm and 147 nm, respectively (Fig. 3), and

at the same time a similar yellow hue. It was also observed that reflectance measurements showed a linear relationship between oxide thickness and applied potential.

The limit of reflectance analyses lies in the scarce reliability in determining thicknesses when interference is weak. In fact, the oxide obtained with a cell potential of 120 V is partially opaque, due to crystallization processes, which cause the weakening of interference phenomena happening on the rest of the surface: for this reason reflectance peaks are particularly flattened and thickness cannot be estimated.

The color was demonstrated to be unaffected by surface finishing, as far as hue is concerned: only the color intensity, and therefore its saturation, is influenced, since it depends on the scattering and light diffusion processes happening on the surface. Therefore, the higher the roughness, the lower the component reflected by the surface which is perceived by the eye, and the lower the saturation (Fig. 4). The absence of influence of surface finishing on hue confirms the robustness and repeatability of the coloring treatment, which is fundamental when a precise tint is desired on a manufact, and thus when the aesthetic properties are the basis of a manufact possible applications, as in the case of architectural and design applications.

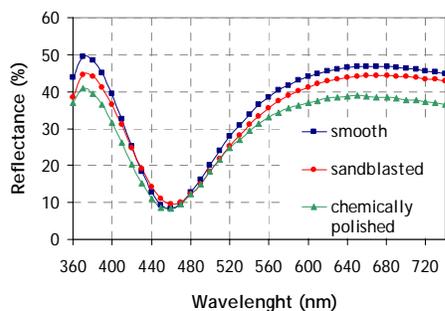


Figure 4: Different reflectance spectra of samples anodized in same conditions but having different surface preparation.

3.2 Photoactivity

X-ray diffraction was used to characterize the oxide structure; data presented are referred to the diffraction angles ranging from 20° to 30°, since this interval includes the principal diffraction peaks for both anatase and rutile, and is therefore useful to investigate the presence of these phases.

While for low potential differences applied the oxide results completely amorphous, when a certain potential threshold is overcome (in this case, 70 V) anatase nanocrystals start to form inside the amorphous matrix. The crystalline portion increases with applied potential (Fig. 5).

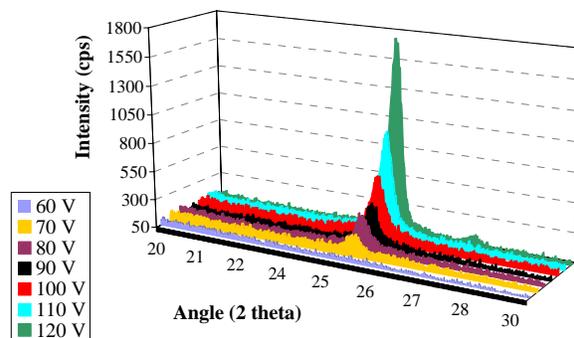


Figure 5: X-ray diffraction peak of anatase (25°) for the obtained anodic oxides.

The presence of the anatase phase is indeed a first proof of a possible photoactivity of the oxides: to prove the actual efficiency of the oxides, the TiO₂-assisted photodegradation of stearic acid was analyzed using four substrates: one bare titanium specimen, one sample presenting an amorphous oxide and two samples with semicrystalline oxides. Samples are identified with the cell potential applied during anodizing: 0 V, 40 V, 90 V and 120 V, respectively (Fig. 6). A further investigation was performed on a sandblasted sample anodized with cell potential of 90 V, in order to evidence the possible influence of surface finishing on the photocatalytic process (sample label: 90V S).

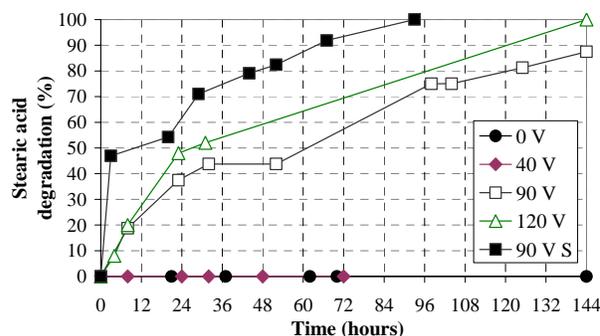


Figure 6: Stearic acid photocatalytic degradation assisted by differently anodized titanium substrates.

Stearic acid mineralization was achieved only when an anatase-containing substrate was used. Concerning the degradation kinetics, it is interesting to notice an increase in photoactivity both with anatase content and with surface area. Nevertheless, the latter parameter has a stronger influence on photoefficiency, since the sandblasted sample, though containing a lower fraction of anatase with respect to sample anodized to 120 V, promoted the total degradation of stearic acid in only 93 hours, compared to the 144 hours needed by the system using as photocatalytic substrate the more crystalline oxide. This is explained by the higher number of active sites available for

photocatalysis present on the surface of the sandblasted sample, which could therefore absorb UV light more efficiently and offer a better substrate to the adsorption of the organic contaminant.

Finally, contact angle was measured to evaluate the hydrophilicity of the surfaces. Titanium oxide is basically hydrophobic, being the contact angle of water approximately 70°. Specimens were irradiated with UV light for 67 hours and contact angle was measured repeatedly; subsequently, the inverse process of deactivation of superhydrophilicity was studied by storing the irradiated samples in the dark and monitoring the contact angle variations in time.

After irradiation with UV light a variation of contact angle was noticed only for samples which presented anatase on their surfaces (Fig. 6). This indicates the establishment of a superhydrophilic state, which is due to the formation of a highly hydroxylated layer on the crystals surfaces [6]. It is particularly interesting to observe that the backward process is not symmetrical: 300 hours are needed to return to a hydrophobic state, while superhydrophilicity was already achieved after less than 70 hours.

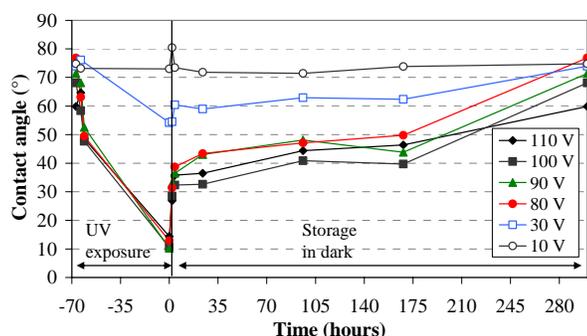


Figure 6: Contact angle values measured on differently anodized titanium: first samples were irradiated with UV lamps (67 hours) then stored in the dark (300 hours).

The photoactivation is faster than the deactivation of the superhydrophilic state: this is of great importance for the architectural applications of self-cleaning materials. In fact, self-cleaning is due to the combined effect of photodecomposition of chemical species coming from a polluted atmosphere and adsorbed on urban surfaces, and the easy removal of their reaction products ascribed to the enhanced wettability of the activated surface. Being sunlight the source of UV radiation, necessary for TiO₂ activation, the maintaining of superhydrophilicity during night as well as during cloudy and rainy hours, that is, when water is actually available for surface cleansing, is crucial to exploit the self-cleaning properties efficiently.

Anodizing in sulfuric acid allows the obtaining of colors with low saturation; nevertheless, the process doesn't require any pretreatment, is easily controlled and leads to the formation of anatase crystals in the oxide. More brilliant and saturated colors can be obtained by using a two-steps

anodizing process, which requires a first pre-anodizing step at low potential in HCl and a final anodizing in H₃PO₄; an initial etching of titanium surface is also performed to improve color homogeneity [8, 9]. The formed oxide is amorphous in any case; a partial conversion of the amorphous oxide to anatase can be achieved by means of thermal treatment. This procedure is more complicated, but involves lower current densities: therefore it can be applied to any titanium manufacture, even of large dimensions, and becomes specially attractive when photoactivated properties are desired together with particularly attractive colors.

4 CONCLUSIONS

The anodic oxidation process proved to be a strong and reliable method to modify the surface of titanium manufactures. Anodizing parameters are fundamental to determine the properties of the growing oxides: the good knowledge of the process consequently lead to the control of the oxide nanostructure and color.

Though the highest photocatalytic efficiency was attained by samples whose anodizing potential was particularly high, in which the saturation of the interference color is scarce, an interesting photoactivity was demonstrated by samples which still maintained an attractive surface tint.

From the presented data, it emerges that the use of anodized titanium, which is already known either for indoor applications as well as building coating and decoration, can add to the aesthetical side granted by its fascinating colors a more practical purpose conferred by the self-cleaning properties, which involve lower maintenance efforts for indoor and outdoor cleansing of the surfaces.

REFERENCES

- [1] Hanson B., A Selection and Use of Titanium. London: The Institute of Materials; 1995.
- [2] U.R. Evans, Proceedings of the Royal Society of London. Series A, vol. 107 (1925), 71-74.
- [3] M.V. Diamanti, M.P. Pedferri, Corros. Sci., vol. 49 (2007), 939-948.
- [4] J.L. Delplancke, M. Degrez, A. Fontana, R. Winand, Surface Technology, vol. 16 (1982), 16.
- [5] M.E. Sibert, J. Electrochem. Soc., vol. 1 (1963), 65.
- [6] O. Carp, C.L. Huisman, A. Reller, Prog. Solid State Chem., vol. 32 (2004), 33-177.
- [7] M.F. Brunella, M.V. Diamanti, M.P. Pedferri, F. Di Fonzo, C.S. Casari, A. Li Bassi, Thin Solid Films, vol. 515 Issue 16 (2007), 6309-6313.
- [8] EP 1 199 385 A2 - 19.10.2000 "Method of coloring titanium and its alloys through anodic oxidation".
- [9] M.V. Diamanti, B. Del Curto, M.P. Pedferri, Col. Res. Appl., accepted August 17 2007, in press.