

Morphological variations on titanium by AC anodizing

M.V. Diamanti, M. Ormellese, and MP. Pedeferri

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering

Via Mancinelli 7, 20131 Milan, Italy

mariavittoria.diamanti@polimi.it

ABSTRACT

Titanium anodizing can induce various benefits, thanks to the generation of an oxide layer a few nm to a few μm thick: *e.g.*, an increase of the metal corrosion resistance, or its biocompatibility and osseointegration ability. Moreover, the formation of TiO_2 crystal phases confers to titanium dioxide surfaces photoactivated properties, such as the ability to degrade harmful inorganic and organic compounds simply by means of light absorption. For most TiO_2 applications, the obtaining of a high specific surface area, and a good control of its roughness, is crucial.

Tuning titanium surface morphology on the basis of the required application would therefore play an essential role in titanium functionalization. Thus, a new anodizing treatment was adopted: a first anodizing step in alternating current, aimed at modifying titanium roughness and preparing the surface for the second treatment in direct current, aimed at producing a photoactive oxide.

Keywords: alternating current, anatase, anodizing, pitting, titanium dioxide

1 INTRODUCTION

Titanium is a particularly fascinating metal, since it shows excellent mechanical performances combined with low density (and therefore lightness) and a noticeable corrosion resistance. The latter property is ascribed to the passive behavior of the metal, due to the presence of a few nanometers thick oxide film that spontaneously form on its surface: its presence protects the metal from further oxidation. Anodizing is a widely diffused process of surface alteration aimed at increasing the thickness of the passive oxide, which leads to engineered properties of the TiO_2 surfaces due to deep structural, chemical and morphological modifications.

The parameters that most affect the oxide characteristics are the electrolytic solution (concentration of reagents, pH and temperature), the feeding voltage imposed between cathode and anode and the anodic current density imposed to reach the value of feeding voltage; the dependence of the thickness of the so generated oxide layer on cell voltage is almost linear, with a thickness increase per unit voltage ratio ranging from 1.5 to 3 nm V^{-1} [1-3].

Feeding voltage and current density can vary within a wide range of values, being the polarization voltage approximately between few volts and hundreds of volts depending on the required oxide characteristics. In fact, low

voltages (1 to 130 V) allow the obtaining of a smooth, amorphous oxide, about 3 to 300 nm thick, whose color changes as a function of thickness and, consequently, of applied voltage (interference color) [4, 5]. On the contrary, high voltages (100 V up to 500 V), combined with high current densities, are used in anodic spark deposition (ASD) processes, which lead to a crystalline or semicrystalline oxide from a hundred nanometers to a hundred micrometers thick, showing the presence of either anatase or rutile TiO_2 crystal forms [6, 7]. In the last years, a new class of anodizing techniques has developed, consisting of the electrochemical oxidation of titanium in fluoride containing electrolytes, which grants the achievement of a nanotubular surface structure with enhanced surface area [8, 9].

The anodizing techniques hereby described, as well as most anodizing processes currently used to modify and functionalize the surface of metallic titanium, are generally performed in direct current (DC); almost no information is available on titanium anodizing in alternating current (AC). Nevertheless, if an enhancement of surface area is desired, AC can lead to surprising results. A peculiar amplification of localized corrosion processes was noticed on active-passive metals, caused by the simultaneous presence of chlorides in the environment and AC interfering the metallic structure [10]. In fact, the concomitant action of Cl^- and AC to weaken the protective passive film of the metal had a synergistic effect on the aggressiveness of pitting phenomena, leading both to the decrease of the Cl^- concentration threshold for pitting activation and to the increase of single pit dimensions in a given environment.

According to these studies, and being titanium itself an active-passive metal possibly subjected to pitting corrosion, the modification of titanium surface area by AC anodizing was considered promising, and was explored with particular reference to the aggressiveness of the electrolytic solution.

2 EXPERIMENTAL

Titanium sheets 0.5 mm thick were cut into 15 mm diameter disks (commercial purity titanium, grade 2 ASTM B265). Four hydrochloric acid dilutions were prepared: 0.7 mol/L, 1.4 mol/L, 2.1 mol/L and 2.8 mol/L. A carbon steel rod (diameter: 5 mm, length: 50 mm) was used as counter electrode. Both electrodes were cleaned with acetone before use.

AC current was supplied by a Variac autotransformer, working with a 50 Hz frequency; current density was not

regulated. Two values of alternating feeding voltages were applied, *i.e.*, 5 V and 7 V: these values were maintained constant for three time intervals, 2, 5 or 10 minutes.

To prove the need for the synergistic effect of both chloride ions and alternating current to induce a significant surface alteration, tests were also performed by supplying AC in diluted sulfuric acid, 0.5 mol/L, and by supplying only DC in all considered hydrochloric acid solutions. Anodizing conditions are reassumed in Table 1.

Specimens treated by AC were then characterized through microscope observation (optical microscope, Scanning Electron Microscope), to evidence the achieved alterations of surface roughness. An image analysis software (Image ProPlus) was used to evaluate the percentage of pitted area with respect to smooth surface from optical micrographs. These evaluations were compared with weight loss data, obtained by accurately weighting samples before and after the anodizing process, in order to estimate the extent of localized corrosion as a function of process parameters.

AC anodizing was only aimed at obtaining a remarkable surface roughness modification by using a simple technique, involving low feeding voltages, short process times and basic instrumentation, since it exploits the electric system voltage without transforming it in a direct signal, as needed in DC anodizing. Nevertheless, in all major applications of anodized titanium a crystalline, or at least partially crystalline, oxide is required, *e.g.*, for photocatalytic applications as well as biomedical applications, where the presence of anatase improves the surface osseointegration properties.

Hence, a double treatment was also proposed: a first anodizing in AC in halogen acids bath, in order to enhance specific surface area, and a second anodizing step in DC, and precisely in ASD conditions in H_2SO_4 , to induce the formation of a thick, semicrystalline oxide over the roughened surface.

Electrolyte	Supplied current	Maintenance time	Cell voltage
HCl 0.7 mol/L	AC	2, 5, 10 min	5, 7 V
	DC	2, 10 min	
HCl 1.4 mol/L	AC	2, 5, 10 min	5, 7, 10 V
	DC	2, 10 min	
HCl 2.1 mol/L	AC	2, 5, 10 min	5, 7 V
	DC	2, 10 min	
HCl 2.8 mol/L	AC	2, 5, 10 min	5, 7 V
	DC	2, 10 min	
H_2SO_4 0.5 mol/L	AC	2 min	10, 15 V
	DC		

Table 1: Process parameters explored in AC anodizing, and test conditions applied in DC in comparison with AC.

3 RESULTS AND DISCUSSION

3.1 Hydrochloric acid electrolytes

Figure 1 shows optical micrographs (100 X) of titanium surfaces after anodizing in AC (5 V) in different HCl dilutions. Once reached the required feeding voltage between the two electrodes, the value was maintained for 2 minutes. The clearly visible black spots on the surface are deep, wide holes, ranging from hundreds of nanometres to tenths of micrometres in diameter, occurring because of the establishment of pitting corrosion.

The average external holes diameter increased with applied voltage and with HCl concentration, as expected: in fact, a higher amount of Cl^- ions in the electrolyte generated a higher aggressiveness and therefore increased pitting phenomena.

Same considerations arise from AC anodizing process in which cell voltage was maintained for 10 minutes (Fig. 2). The longer the cell voltage was maintained and the more concentrated the electrolyte, the higher the extent of surface area affected by pitting.

By increasing HCl concentration not only the roughened area increased in extension, but also the whole surface was more uniformly attacked by chlorides; for highly diluted HCl electrolytes, pitting concentrated in some areas, while leaving part of the surface intact. This was particularly true when anodizing process lasted only few minutes; for 10 minutes long processes the aggressive species had enough time to initiate homogeneous pit formation on the whole surface even in the case of low HCl concentrations.

To confirm the need for the synergistic effect of chlorides and AC to create such a complex pitted morphology starting from a smooth surface, AC anodizing in HCl was compared with anodizing either in AC or in DC in 0.5 M H_2SO_4 , and with DC anodizing in HCl. In the former cases, no morphological effect was obtained: after anodizing the surface was unaltered.

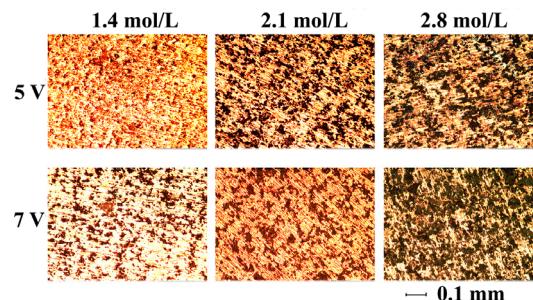


Figure 1: Surface morphology of samples anodized in AC in HCl solutions (100 X magnification): process lasted 2'.

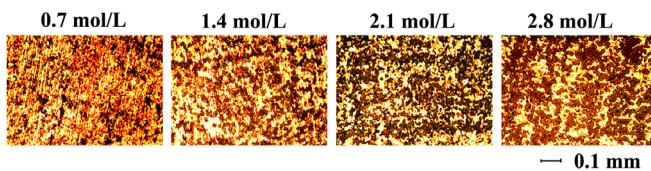


Figure 2: Surface morphology of samples anodized in AC in HCl solutions (100 X magnification): process lasted 10'.

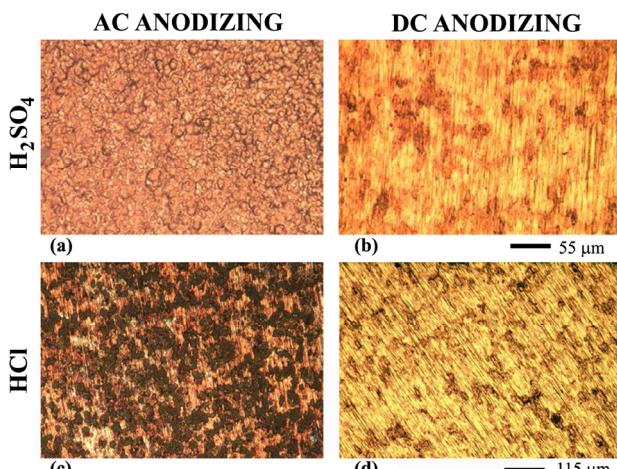


Figure 3: Optical micrographs of specimens anodized a) in H_2SO_4 (10 V, AC); b) in H_2SO_4 (10 V, DC); c) in HCl (10 V, AC); d) in HCl (10 V, DC).

On the other hand, the presence of chlorides in the anodizing environment produced a small pitting effect on the surface of samples when DC anodizing is performed; nevertheless, this effect was negligible (few pits, apparently very shallow ones) if compared to the massive surface modifications obtained in the case of AC anodizing (Fig. 3).

SEM micrographs of the treated surfaces were obtained in order to achieve a more detailed analysis of pits topography (Fig. 4). It is possible to notice the real structure of the holes observed with optical microscopy: these surface features were actually proved to be constituted by clusters of pits, originated by chlorides attacking titanium passive film. Number and diameter of pits clusters increased with increasing HCl concentration, as well as the average dimension of the inner, smaller pits which created a double morphological texture, and the borders of these pits became more defined: as an example, the diameter of inner pits increased by almost 30% by doubling the concentration of HCl from 1.4 to 2.8 mol/L.

To quantify the morphological variations induced by pitting corrosion two analytical methods were combined: weight loss measurements and the determination of the percentage of pitted area as a function of HCl concentration and AC voltage.

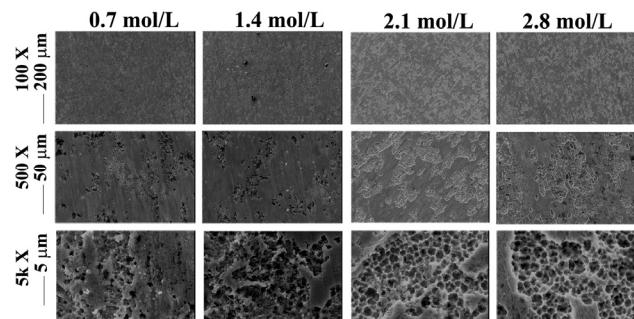


Figure 4: SEM micrographs of samples anodized by supplying AC in HCl solutions 0.7 to 2.8 mol/L with 5 V feeding voltage maintained for 2'.

The increase of both maintenance time and HCl concentration led to increasing weight loss of samples. As reported on the basis of morphological observations, it clearly emerged from weight loss data that in the case of DC anodizing the pitting extent was almost negligible compared to what could be achieved in AC (Fig. 5).

On the contrary, the effect of applied cell voltage was slightly controversial: the reason may lie in the higher thickness of the oxide formed on the surface during anodizing, even if the process is performed by applying AC; the actual formation of a thicker oxide was demonstrated by the change in the hue of the interference color displayed by the surface after anodizing.

Oxide thickening can be responsible for an increased protection of the surface: thus, Cl^- ions will have more difficulties attacking the surface, and the extent of pitted area will be lower, as confirmed by data presented in Fig. 6.

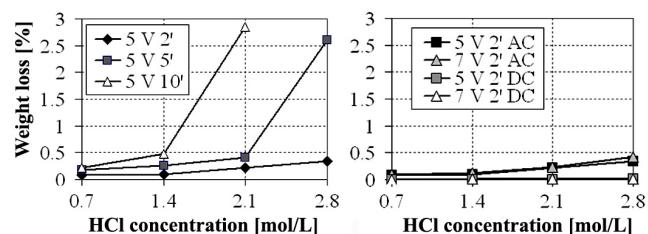


Figure 5: Weight loss as a function of HCl concentration and: maintenance time, 2, 5 and 10 minutes at 5 V in AC (left); feeding voltage, 5 V and 7 V, in DC and AC (right).

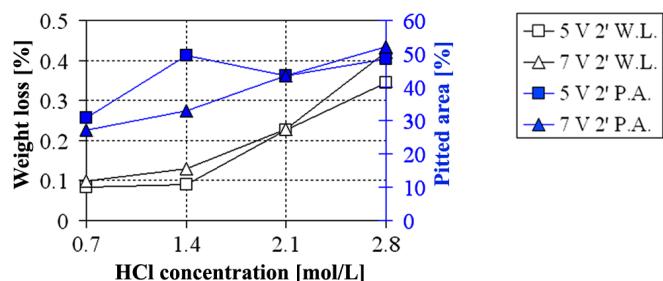


Figure 6: Comparison between weight loss (W.L.) and pitted area (P.A.) percentages.

3.2 AC anodizing combined with ASD

As mentioned in the experimental section, low-voltage AC anodizing was followed with a second anodizing treatment in ASD conditions (H_2SO_4 0.5 M, 140 V, 80 mA/cm²) in order to combine the effects of increased surface area given by the former process and of production of semicrystalline oxide given by the latter. In fact, as shown in previous work, the chosen ASD treatment allows the obtaining of anatase and rutile crystals in an amorphous TiO_2 matrix [11].

First, the overlapping of the two processes led to a remarkable morphology: in fact, the anodized surfaces resulted to have a threefold morphological texture, given by a micrometric roughness due to pit clusters, a sub-micrometric roughness due to single pits and a nanometric roughness due to ASD-generated craters (Fig. 7). This is of great importance, since not only the resulting surface area is noticeably increased, but also because each one of the three roughness levels can be tuned by choosing the suitable process parameters, *i.e.*, HCl concentration, feeding voltage and anodizing time of the AC process, and cell voltage of ASD. In particular, the variation of HCl concentration led to an easy variation of the average cluster dimension and single pit dimension, and of their distribution over the surface.

The presence of crystal phases in the so-formed oxides was analyzed by means of X-ray diffraction. The intensity of the anatase diffraction peak (located at $2\theta = 25^\circ$) seems to decrease with HCl concentration, which was ascribed to a slight inhibition of chloride ions on anatase crystallization; conversely, the diffraction peak of rutile ($2\theta = 27^\circ$) didn't exhibit manifest variations. In any case, the quantity of anatase and rutile present in the anodic oxide after ASD was much lower than that exhibited by specimens subjected to sole ASD, thus confirming the inhibiting effect of chlorides on TiO_2 crystallization.

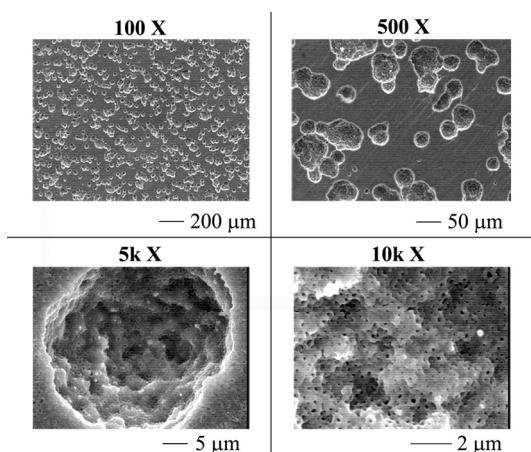


Figure 7: SEM micrographs of specimens anodized first in AC in HCl 1.4 mol/L, then in ASD conditions: highlighting of *micro* and *nano* morphological features.

4 CONCLUSIONS

The anodizing treatments hereby described had a twofold purpose, *i.e.*, the morphological alteration of titanium, as to produce the highest surface area possible, and the formation of at least partially crystalline oxides, in order to confer them the desired photoactivated properties for catalytic purposes or an enhanced biocompatibility and osseointegration characteristics.

AC anodizing proved to be an easy and extremely fast process for surface morphology alteration, whenever an enhanced substrate roughness is required. To achieve the desired TiO_2 crystal structure, a subsequent ASD treatment in H_2SO_4 was applied. Though spark discharges caused by ASD produced an aggressive modification of the surface characteristics, the enhancement of surface area achieved by AC anodizing wasn't affected. ASD was therefore proved to be helpful in increasing oxide thickness, creating a semicrystalline oxide and further enhancing surface roughness.

REFERENCES

- [1] J.L. Delplancke, R. Winand, *Electrochim. Acta* 33 (1988), 1539.
- [2] T. Shibata, Y.C. Zhu, *Corros. Sci.* 37 (1995), 253.
- [3] X. Liu, P.K. Chu, C. Ding, *Mater. Sci. Eng. R* 47 (2004), 49.
- [4] S. Van Gils, P. Mast, E. Stijns, H. Terryn, *Surf. Coat. Technol.* 185 (2004), 303.
- [5] M.V. Diamanti, B. Del Curto, MP. Pedeferri, *Color Res. Appl.* 33 (2008), 221.
- [6] S. Meyer, R. Gorges, G. Kreisel, *Thin Solid Films* 450 (2004), 276.
- [7] G.P. Wirtz, S.D. Brown, W.M. Kriven, *Mater. Manufact. Proc.* 6 (1991), 87.
- [8] D. Gong, C.A. Grimes, O.K. Varghese, W. Hu, R.S. Singh, Z. Chen, E.C. Dickey, *J. Mater. Res.* 16 (2001), 3331.
- [9] G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese, C.A. Grimes, *Nano Lett.* 5 (2005), 191.
- [10] S. Goidanich, L. Lazzari, M. Ormellesse, MP. Pedeferri, 16th International Corrosion Congress ICC, Beijing (China), Paper 04-03, September 2005.
- [11] M.V. Diamanti, MP. Pedeferri, *Corros. Sci.* 49 (2007), 939.