Rassegna

Tuning of anodic oxidation parameters for the production of nanostructured TiO$_2$ films

M.V. Diamanti, M. Ormellese, B. Del Curto, M.P. Pedeferri

Titanium dioxide is the most common among titanium oxides and minerals. It can be either synthesized by chemical routes or generated by anodic oxidation of titanium. The latter way allows to tune oxide properties by modulating process parameters, and it has gained much attention thanks to the wide variety of thicknesses, morphologies, structures and compositions of the oxide produced. The peculiar engineered properties of anodized titanium find applications in biomedical industry, automotive field, architecture and design, as well as in photovoltaic cells and in photocatalytic purification devices.
This article provides an overview of anodic oxidation treatments currently applied to form nanostructured oxide layers on titanium, paying special attention to their applications.

INTRODUCTION

Titanium and its alloys are light-weight metals that find applications in the most diverse fields:
- architecture (roofing and cladding sheets, such as in the Guggenheim Museum, in Bilbao) and design (glasses, watches, seminoble jewels, computer cases)
- biomedical components such as prostheses and osteosynthesis devices, dental implants and pacemaker cases
- aerospace: gas turbine engines, land gears, compressor blades, and any other element that takes advantage of weight reduction and increased durability (for instance, in Boeing 777 and 747, or in the Sikorsky helicopter)
- high performance automotive (pins, springs, valves, camshafts and more): the first example dates back to 1950s, with the Titanium Firebird II by General Motors
- chemical and petrochemical industry: tubing, pipes, pumps, heat exchangers, tanks
- military equipment: special artillery, body and vehicle armors
- sports equipment: golf clubs, bicycle frames, trekking and scuba diving equipment

This variety of application fields gives rise to an annual

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consumption of over 70 000 tons of titanium, with a projection of demand increase close to 40% within 2015 [1-6]. Structural applications are driven by its high strength combined to a low density, together with the low thermal expansion coefficient and thermal conductivity – which make it compatible with typical ceramic materials and construction materials – and its outstanding corrosion resistance [1,7]. Finally, its non-toxicity, osseointegration ability and biocompatibility, which can be easily improved by several surface treatments, together with its non-magnetic nature provide more than sufficient reasons for its use in bioengineering and medical devices [2]. Other side properties donate to this metal further added value, and in particular the appealing aesthetics given by its shiny silver surface and subtle reflectivity, and by the possibility to color the metal by oxidation due to interference phenomena that arise at the metal surface in presence of nanometric transparent films [8].

The main surface-related properties of this metal and its alloys, from corrosion resistance to aesthetic appearance, can be tuned as a function of the desired surface properties by oxidizing the metal, which is generally performed by anodic oxidation. The process consists of polarizing titanium by imposing a current flow between a titanium specimen and a counterelectrode inside a suitable electrolytic solution. Ti atoms are then oxidized to Ti^{4+} ions, which combine with oxygen (or oxygen-containing) anions from the electrolyte and progressively form an oxide film on the metal. Such process is generally applied to oxidize the so-called valve metals: Al, Nb, Ti, W, etc., i.e. metals that form ionically conductive oxides [9].

The following paragraphs will illustrate the most common experimental procedures for titanium anodizing, and the oxide features that can be achieved as a function of process parameters.

EXPERIMENTAL METHODS

As abovementioned, titanium anodizing is performed in suitable electrolytic solutions by forcing a current flow between the titanium anode and a counterelectrode, or cathode, commonly consisting of a highly conductive material – e.g., platinum wires, carbon rods, or activated titanium. This is achieved by imposing a potential difference between anode and cathode, being both electrodes immersed in the solution. As for the electrolyte, an important requirement is a low aggressiveness towards the growing oxide, to avoid a faster dissolution compared to its growth rate during the process. The most commonly used electrolytes in titanium anodizing are phosphoric, sulphuric, acetic and tartaric diluted acids, ammonium sulphate, sodium hydroxide, phosphate or bicarbonate solutions (1 to 15 wt %), aqueous or organic solutions containing fluoride ions and several more [10,11].

Nevertheless, anodizing may also be confined on specific portions of the metal surface. This technique resembles a pictorial means, and is in fact defined electrochemical painting; Figure 1 reports examples of electrochemical brushes that can be employed [12]. Anodizing is often performed in galvanostatic conditions, with current densities ranging from 1 A/m^2 to 1000 A/m^2, and less frequently through the application of a voltage ramp, from 1 V/s to 1 V/min. 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: as explained in more details in previous publications, the hue of interference colors arising at the anodized titanium surface change in a periodic fashion with the applied voltage, as described by the example in Figure 2 [8,13]. On the contrary, high voltages (100 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 few micrometers to a hundred micrometers thick [14]. In both cases, the techniques derive from several decades of experimental developments. On the other hand, in the last decade a new class of anodizing processes has emerged, consisting of the electrochemical oxidation of titanium in fluoride containing electrolytes, which grants the achievement of a nanotubular surface structure with enhanced surface area [15].

RESULTS OF ANODIC OXIDATION PROCESSES

The importance of having a clear understanding of the anodizing process and its parameters lies in their substantial influence on all oxide properties, from its crystal structure to its thickness, from chemical composition and stoichiometry to morphology and porosity.

First of all, it is important to underline the well-known dependency of oxide thickness on applied voltage. The re-

Fig. 1 – Instruments of electrochemical painting: a) brush; b) galvanic pad

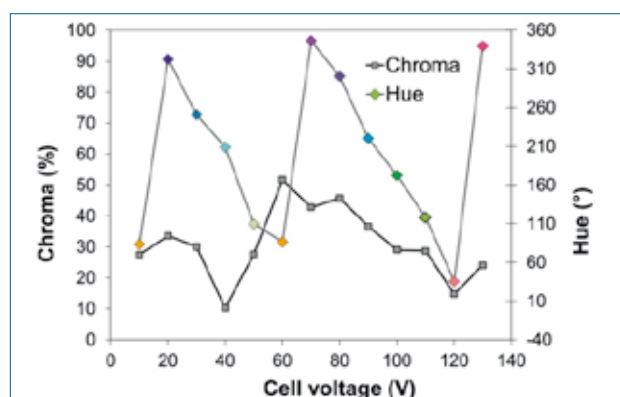*Fig. 1 – Strumenti di pittura elettrochimica: a) pennello; b) tampone per galvanica*

Fig. 2 – Trend of chroma and hue of interference colors produced by anodizing titanium in 0.5 M H$_2$SO$_4$

Fig. 2 – Andamento di croma e tinta dei colori di interferenza prodotti mediante anodizzazione del titanio in in 0.5 M H$_2$SO$_4$

lationship between these parameters is linear in the approximate range 0-100 V (and more in some electrolytes where crystallization is delayed or hindered). Depending on the composition of the electrolyte, anodizing ratios of 1.5 to 3 nm/V can be calculated. This applies to compact amorphous oxides, on account of the increase in the dielectric barrier opposed by increasingly thick oxide films to the electric field acting on the oxide itself, and regulated by the potential difference (cell voltage) applied between anode and cathode. On the contrary, when the dielectric breakdown is reached and crystallization occurs the linearity is lost, and small increases in voltage can cause major oxide thickening: in this case, the parameter that most affects oxide thickness is time, i.e., how long the required voltage has been maintained between electrodes to induce oxide buildup [16]. Same considerations can be drawn in the case of porous oxides, such as nanotubular ones, where the height of TiO$_2$ nanotubes is governed by two effects: the maintenance time and the asymptotic thickness, which is defined by the equilibrium between electrochemical oxide growth and oxide dissolution due to electrolyte aggressiveness [15].

Concerning oxide composition, a perfect oxide should present a TiO$_2$ stoichiometry; this condition, which is typical of

oxides produced by chemical synthesis or physical deposition, is usually not complied with by anodic oxides, which present several possible deviations from TiO_2. Low voltage anodizing – traditional anodizing – often produces sub-stoichiometric TiO_{2-x} as a consequence of the oxidation mechanism, which involves the migration of Ti^{4+} from the metal surface across the oxide and towards the outer surface in contact with the electrolyte, and of O^{2-} ions along the opposite path. The oxide generally builds up in between the two interfaces, on account of the mobility of both ions. The inner surface in contact with the metal accounts for the most pronounced sub-stoichiometry. This compositional defect, rather than being detrimental, generates unexpected properties of ionic conductivity that find application mainly in gas sensing devices, especially for the detection of oxygen – such as in lambda probes – and volatile organic compounds (VOCs) [17,18]. Moreover, oxygen vacancies at the metal/oxide interface can introduce a memristive behavior (Figure 3), i.e., resistivity becomes a function of current previously travelled through the oxide in the past, showing a bias-dependent switching response to current [19,20]. Memristive devices are seen as the future generation of non-volatile memories with fast access and improved data density, and are expanding their applications in the development of artificial neural networks [21].

On the other hand, it is possible to modify the oxide composition on purpose by adding desired elements to the film. This can be performed through the ASD process. The initial oxide layer formed in the first tens of Volts creates a compact dielectric barrier, which prevents ionic current from further flowing until the dielectric breakdown voltage is exceeded: this condition is verified thanks to the growing oxide defectiveness, as current concentrates in the oxide weak points reaching extremely high local electric field and inducing atom ionization and a localized microplasma state [14,22]. The dielectric breakdown is accompanied by a cracking noise and sparking, i.e., small electric discharges that last fractions of seconds and move along the whole surface, creating electric arcs as the microplasma state moves from one weak point to another. The resulting oxide presents a semicrystalline or crystalline structure, with TiO_2 crystals embedded in an amorphous matrix, a glossy surface due to the rapid quenching of the molten oxide, and – most importantly – an increased cationic mobility causes ions from the electrolyte to be incorporated into the oxide during plasma quenching [16,22]. This effect can be exploited to alter oxide composition even by several atomic percent, and is mostly employed in bioengineering to integrate Ca and P ions in the oxide: in fact, the presence of these elements favors the formation of a hydroxyapatite layer on the oxide surface, which in turn stimulates osseointegration and bone growth in prosthetic implants [23].

Finally, the oxide crystal structure firmly influences potential applications as functional coating. This is true in the already cited bioengineering field, where the production of crystalline oxides in the allotropic phase of anatase and/or rutile enhances hydroxyapatite formation, while amor-
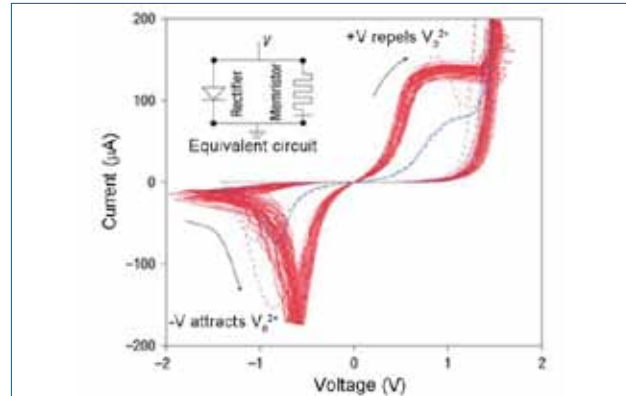

Fig. 3 – Experimental (solid) and modelled (dotted) switching I–V curves recorded on a 50-nm TiO_2 film with a near-stoichiometric TiO_2 outer layer and an oxygen-deficient inner TiO_{2-x} layer (50 experimental switching loops, which show a high degree of repeatability). Inset: The equivalent circuit model consists of a rectifier in parallel with a memristor. Adapted with permission from [20], published by Nature Publishing Group

Fig. 3 – Curve I-V sperimentali (continue) e teoriche (tratteggiate) registrate su un film di TiO_2 spesso 50 nm composto da uno strato esterno stechiometrico e uno interno substechiometrico TiO_{2-x} (50 cicli sovrapposti, a dimostrare l'ottima ripetibilità). Riquadro: Circuito equivalente modello costituito da un raddrizzatore in parallelo con un memristore. Adattamento autorizzato da [20], pubblicato da Nature Publishing Group

phous oxides don't present the same characteristics [24]. The same applies to the achievement of photoinduced properties, where anatase plays the role of favorite crystal structure. Photoinduced properties are a consequence of the semiconductive nature of crystalline TiO_2, with a bandgap of 3 to 3.2 eV depending on crystal structure: oxide irradiation with light of suitable energy (in the UV range, specifically with wavelengths of approximately 387 nm [25]) causes the promotion of an electron to the conduction band and therefore the formation of an electron/hole couple with high redox potential [26]. This principle is exploited in several fields, from water splitting to dye-sensitized solar cells, to the photocatalytic degradation of pollutants, where electron/hole couples and related reactive species accelerate the degradation of organic and inorganic substances adsorbed on the film surface [27].

In this respect, not only crystal structure plays a decisive role, but also the available surface area for adsorption as well as for light harvesting affects the oxide performances, and in particular the higher the number of available active sites, the higher the oxide efficiency in photoinduced processes. For this reason, TiO_2 nanotubes are having great resonance, since such a nanostructure can increase the specific surface area by orders of magnitude, ensuring both faster photocatalytic reactions kinetics and increased photogeneration efficiencies in dye-sensitized solar cells (Figure 4) [28,29].

CONCLUSIONS

This review dedicated to the anodizing of titanium highlighted how an improved control of TiO_2 surface properties can boost the material efficiency in several applications, and further broaden its fields of use. All oxidation treatments described in this article have manifold purposes together with the production of an oxide layer, from the morphological alteration of titanium to produce the highest surface area possible, to the partial conversion of amorphous oxides into crystalline ones in order to achieve photoactivated properties, to the modification of their chemical composition by incorporating electrolyte ions. Given the wide range of properties obtainable and of current and potential applications, a huge number of characterization techniques can be employed, which has led to the boom of studies on anodic TiO_2 characteristics performed with the most diverse techniques, emphasizing always different aspects of these oxides.

Fig. 4 – FE-SEM cross-sectional (a,d), top (b) and bottom (c) views of TiO_2 nanotubes produced by anodizing in ethylene glycol + 2 wt% water + 0.25 wt% NH_4F. Reprinted with permission from [30], published by The Royal Society of Chemistry

Fig. 4 – immagini FE-SEM della sezione trasversale (a,d), vista superiore (b) e fondo (c) di nanotubi di TiO_2 prodotti mediante anodizzazione in glicole etilenico + 2% in peso d'acqua e 0.25% in peso di NH_4F. Riproduzione autorizzata da [30], pubblicato da The Royal Society of Chemistry

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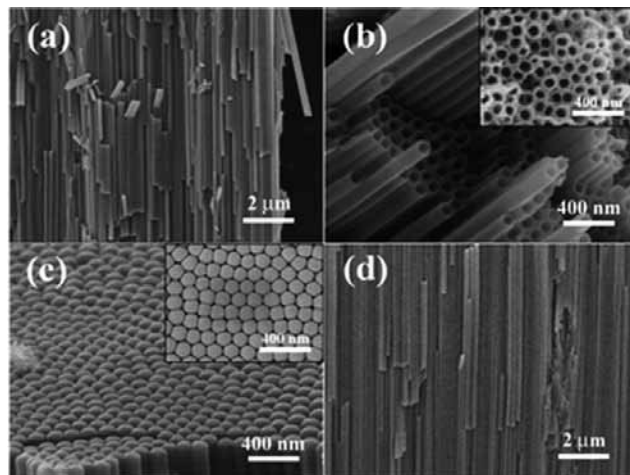[30] S. Lee, I.J. Park, D.H. Kim, W.M. Seong, D.W. Kim, G.S. Han et al., Energy Environ. Sci. 5 (2012) 7989-95.

Ottimizzazione dei parametri di anodizzazione per la produzione di film di TiO_2 nanostrutturati

Keyword: Titanio e leghe - Elettrochimica - Ossidazione - Trattamenti superficiali - Proprietà

Il titanio e i suoi ossidi rivestono un interesse scientifico e tecnologico sempre maggiore, grazie all'estensione dei campi di applicazione sia di questo metallo leggero e al contempo resistente meccanicamente e a corrosione, sia degli ossidi di titanio come rivestimento funzionale. I settori che maggiormente beneficiano degli sviluppi e della ricerca su questa tematica sono:
• l'architettura e il design, dove la possibilità di produrre colori d'interferenza attraverso la formazione di film nano-

metrici di ossido di titanio crea un notevole valore aggiunto;

- la bioingegneria, che da tempo sfrutta l'atossicità e la biocompatibilità del titanio e delle sue leghe per ridurre i rischi di infezione e rigetto di protesi e dispositivi di osteosintesi, anche grazie alla incorporazione nell'ossido superficiale di elementi benefici quali calcio e fosforo;
- l'automotive, settore in cui una riduzione di peso a fronte di una elevata resistenza meccanica è fondamentale per ridurre i consumi, soprattutto nelle fasce più alte del mercato; lo sviluppo di trattamenti di ossidazione anodica ad hoc ha permesso la riduzione dei problemi di usura e galling;
- le industrie chimiche e petrolchimiche, dove l'elevata resistenza a corrosione del metallo, ulteriormente migliorata dalla presenza di ossidi protettivi, permette di estendere la vita di servizio dei componenti e ridurre i rischi di cedimento o perdite.

Grazie allo sviluppo di trattamenti di ossidazione, e in particolare di ossidazione anodica, è possibile conferire alla superficie del metallo proprietà funzionali quali non solo le già menzionate biocompatibilità e resistenza a usura, ma anche proprietà fotoindotte: attività fotocatalitica, superidrofilia e autopulizia, che ne promuovono l'utilizzo come anodo di celle fotovoltaiche, come componente attivo di dispositivi fotocatalitici di purificazione, e per lo sviluppo di superfici autopulenti. Gli ossidi anodici devono le loro proprietà specifiche ai parametri del processo di anodizzazione, che possono essere modulati al fine di ottimizzare la struttura chimica e cristallina, la morfologia e la composizione degli ossidi risultanti.

Il processo di anodizzazione cosiddetto tradizionale prevede l'applicazione di poche decine di Volt ad un anodo in titanio, generalmente in condizioni galvanostatiche, utilizzando soluzioni elettrolitiche di varia composizione, solitamente acide (ad esempio, acido solforico o acido fosforico diluiti). Ne consegue la formazione di film sottili di TiO_2, da pochi nanometri a qualche centinaio di nanometri, compatti e prevalentemente amorfi. Questi film producono interferenza con la luce visibile, e di conseguenza la comparsa di colori sulla superficie, dovuti all'intensificazione dei colori associati alle componenti luminose in fase e viceversa l'annullamento di quelli in opposizione di fase. Questo effetto permette di studiare le cinetiche di ossidazione del metallo calcolando lo spessore dell'ossido attraverso tecniche ottiche (spettrofotometria, ellissometria); è inoltre di notevole interesse estetico ed artistico, al punto da aver portato allo sviluppo di tecniche pittoriche mediante anodizzazione (Figura 1).

Se effettuata in soluzioni contenenti fluoruri, l'anodizzazione a basso voltaggio può portare allo sviluppo di un ossido nanoporoso, costituito da tubi di diametro di poche decine di nanometri chiusi a contatto con il metallo sottostante e aperti verso la soluzione elettrolitica, che si auto-organizzano sulla superficie metallica creando una struttura nanotubolare con spessori che possono arrivare ai 100 μm (Figura 4).

L'anodizzazione ad alto voltaggio (superiore in genere ai 100 V, fino anche ad alcune centinaia di Volt) porta al fenomeno di Anodic Spark Deposition (ASD), in cui condizioni di elevate densità di corrente concentrate in pochi punti deboli, o difetti, dell'ossido in crescita portano alla formazione di microplasmi localizzati, con conseguente fusione locale dell'ossido e sua rapida solidificazione. I microplasmi portano livelli di energia talmente elevati da danneggiare anche l'ossido circostante, creando nuovi punti deboli lungo i quali il processo di ASD si diffonde a tutta la superficie anodizzata. In questo caso, l'ossido sarà spesso alcuni micrometri, avrà struttura parzialmente o prevalentemente cristallina e la composizione chimica potrà deviare anche consistentemente dallo stechiometrico TiO_2, a causa dell'incorporazione di ioni dalla soluzione elettrolitica durante il solidificarsi dell'ossido.

La scelta dei parametri di anodizzazione permette pertanto la definizione precisa e controllata delle caratteristiche dell'ossido. Questo è di fondamentale importanza per i numerosi risvolti ingegneristici imputabili al controllo microstrutturale e composizionale dei film di TiO_2. Nel seguito si riportano alcuni esempi di particolare rilevanza.

I colori di interferenza precedentemente descritti divengono meno intensi fino a scomparire quando l'ossido perde il suo carattere amorfo, a causa delle diverse proprietà ottiche del TiO_2 cristallino, in una delle sue forme allotropiche (anatasio, rutilo o brookite). Al contrario, per produrre ossidi fotoattivi utili per applicazioni nel campo della fotocatalisi o delle celle solari è necessaria un'elevata cristallinità, e la struttura cristallografica dell'anatasio è particolarmente favorevole all'ottenimento di elevate efficienze di fotoattivazione. Anche l'utilizzo nel campo della sensoristica ambientale, che si basa sul chemisorbimento di gas ossidanti o riducenti sulla superficie dell'ossido e sul conseguente cambiamento della conducibilità dell'ossido stesso, richiede lo sviluppo di materiali altamente cristallini. Per ottenere un'elevata biocompatibilità è invece d'aiuto alterare la composizione chimica dell'ossido, incorporando ioni adatti ad aumentare l'integrabilità dell'impianto con i tessuti circostanti. Infine, il drogaggio dell'ossido con altri ioni metallici (W, Zr, Fe, Cu) o non-metallici (C, N, F, S) può alterare le proprietà di semiconduzione del TiO_2, in particolare riducendo l'energia di band gap. Questo permette di spostare il range di fotoattivazione dell'ossido dalla sola luce ultravioletta alla luce visibile, aumentando la percentuale di assorbimento della luce solare e dunque l'efficienza di dispositivi di fotocatalisi e solari funzionanti in esterno, nonché estendendone il funzionamento indoor, dove la luce ultravioletta non è disponibile.