

On the Growth of Thin Anodic Oxides Showing Interference Colors on Valve Metals

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1. INTRODUCTION

In atmospheric environment, all metals - except Au and Pt - are naturally oxidized through a spontaneous process, with the formation of nanometric oxide or hydroxide layer. In the case of passive metals, such film is in the order of ~1-10 nm and is responsible for corrosion kinetics, as well as of any interaction with the external environment (Fig. 1) [1, 2]. The response of the surface to these interactions, and more generally to external stimuli, depends on the oxide film morphology, degree of crystallinity, thickness and chemical composition. Clearly, the chemical nature of the film strongly influences its features, e.g., changing the oxide character from semiconductive to insulating, or modifying its effectiveness as barrier against corrosion, or switching from a bioinert surface to a bioactive one thanks to an enhanced similarity with surrounding tissues: therefore, different interactions can take place on different metal oxides, leading to a variation in the response to an external stimulus. As a consequence by controlling the artificial formation of an oxide layer on the metal surface it is possible to engineer a wide variety of surface properties [3-8].

For these reasons, in the last years, research on metal surface engineering has been oriented to the obtaining of

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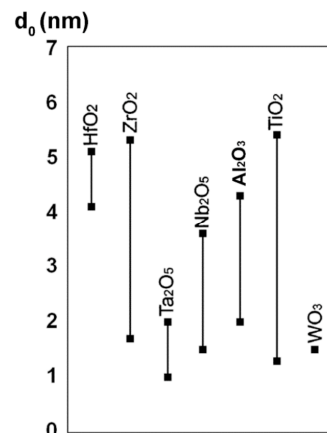


Fig. (1). Thickness d_0 of the passive film on a selection of valve metals and related range of variation. Values extracted from [2].

compact thin films as well as of more complex nanostructures and architectures, for applications ranging from corrosion resistance to bioengineering, from optical devices to environmental and energetic applications, bipolar resistive switching memories and electrochromic devices [9-15]. In this scenario, anodic oxidation can be a very effective technique in the controlled production of oxide films with high bond strength on valve metals, tuning growth kinetics and oxide properties as a function of process parameters. In fact, it is possible to relate the controlling electrochemical pa-

rameters (cell voltage, chemical composition of the electrolytic solution, process time) to the thickness, morphology, chemical and structural composition of the growing oxide layer [7, 8, 16].

The technique consists of polarizing the metal by imposing a current flow between the specimen and a counter electrode; this causes the metal atoms oxidation to cations, which combine with oxygen (or oxygen-containing) anions from the electrolyte to progressively form an oxide layer on the surface of the metal. The growth mechanism involves both an inward and outward growth due to field-assisted ions migration, with a slight predominance of O^{2-} charge carriers moving through the oxide to reach the metal surface where metal cations are produced [8, 17, 18].

The main parameters determining the oxide characteristics are:

- Electrolytic solution composition, concentration, and temperature;
- Feeding voltage imposed between cathode and anode, and possible imposition of a stabilization time in which the voltage is maintained constant;
- Anodic current density imposed to reach the value of feeding voltage;
- Metal composition and surface preparation.

1.1. Anodizing of Titanium

Concerning the metal substrate, most studies that can be found in literature refer to the anodic oxidation of titanium and its alloys [7, 8, 19, 20]. Both titanium itself and its oxide, TiO_2 , possess peculiar properties that make titanium anodizing of particular scientific and technological relevance. For instance, its lightweight and mechanical resistance make the metal particularly suitable for applications in bioengineering, where a large part of osteosynthesis devices and prostheses consist of titanium anodized in suitable conditions in order to improve its biocompatibility and reduce possible wear and metal ion release [7, 12, 21, 22]. Moreover, the semiconductive nature of crystalline titanium oxides has raised important applications as photoactive material, and in particular as anode in dye-sensitized solar cells, as photocatalyst in environmental cleanup technologies, and as sensor in environmental applications [23-29]. Anodic oxidation allows to modify oxide characteristics in order to meet the requirements of each of these applications, as a function of the surface property needed: oxides can be either crystalline – to have photo activated properties – or amorphous – to guarantee transparency, or the production of interference colors; thickness and porosity can be tuned in order to maximize the surface area, which is a key parameter in photocatalytic and energy applications; chemical composition can be changed with respect to stoichiometric TiO_2 to promote cell adhesion, or to induce sensing abilities or memrisitive behavior [7, 12, 13, 19, 30, 31].

Among the most important features of anodic oxides, it is important to describe how the cell voltage affects the growing oxide, since this parameter is the main responsible for the oxide thickness achieved. In fact, the thickness-voltage relationship has been proved to be linear in the range of for-

mation of barrier-type oxides, which is generally performed with voltages ranging from 0 to 100 V. The anodizing ratio, i.e., the oxide nanometers generated per Volt applied of cell tension, has an average value 2 nm/V which can vary slightly as a function of the electrolyte composition or of the composition of the substrate itself [32-34]. As will be described in section 3, the peculiar feature of barrier oxides is the appearance of an iridescent color, which is created by the interference of light at the metal-oxide and oxide-air interfaces.

There is almost no limit to the range of electrolytes that may be found in literature, from acid (most common), to neutral, to alkaline ones. The electrolyte features that exert an influence on the growing oxide are the amount of oxygen-containing species available to oxide formation, the incorporation of electrolyte ions in the film and the tendency to dissolve the oxide itself. Based on these observations, it is possible to identify the peculiarities of common electrolyte anions: phosphate ions tend to be incorporated in the oxide and delay its crystallization, while sulfur accelerates oxide breakdown and crystallization; halides (in particular, chloride and fluoride ions) induce a localized oxide dissolution, creating peculiar nanostructures [8, 23].

On the other hand, for higher voltages anodic spark deposition (ASD) conditions onset, which leads to the formation of crater-like porous ceramic layers some micrometers thick; for a more detailed explanation of the ASD mechanism – also called plasma electrolytic oxidation, PEO – and of the characteristics of the resulting oxides, we recommend to refer to the related research articles and reviews [7, 13, 35-37]. The linear thickness-voltage relationship is lost also in the case of anodic oxidation in the aforementioned halide-containing electrolytes, where the formation of a nanotubular oxide is achieved due to an equilibrium between the oxide growth and its localized dissolution induced by fluoride ions (or, less frequently, by chloride ions) [19, 38]. Different morphologies are often associated with different crystal structures, being the majority of the described anodic oxides prevalently amorphous: only ASD, or post-processing such as thermal annealing, allow to induce a conspicuous crystallization of the oxide to either anatase or rutile, or a mixture of the two (Fig. 2) [13, 37-39].

1.2. Anodizing of other Valve Metals

Analogous considerations can be drawn on other valve metals subjected to anodic oxidation. The process is carried out in an analogous fashion, and with similar results: in fact, either thin, compact films, or nanotubular oxides, or thick ceramic films can be produced at the surface of metals such as zirconium, aluminum, niobium, tungsten, hafnium and tantalum. Each oxide has peculiar characteristics that drive the development of the most suitable anodic oxidation techniques. For instance, aluminum anodizing has mostly focused on the production of amorphous nanoporous honeycomb oxides, which find applications as barriers to corrosion [40], or as template for the large scale production of nanostructures with tailored dimensions (e.g., nanodots and nanorods) [41-44], or as membranes [45], owing to their properties of chemical and mechanical stability [46]. To achieve such nanoporous structures, acid electrolytes are employed

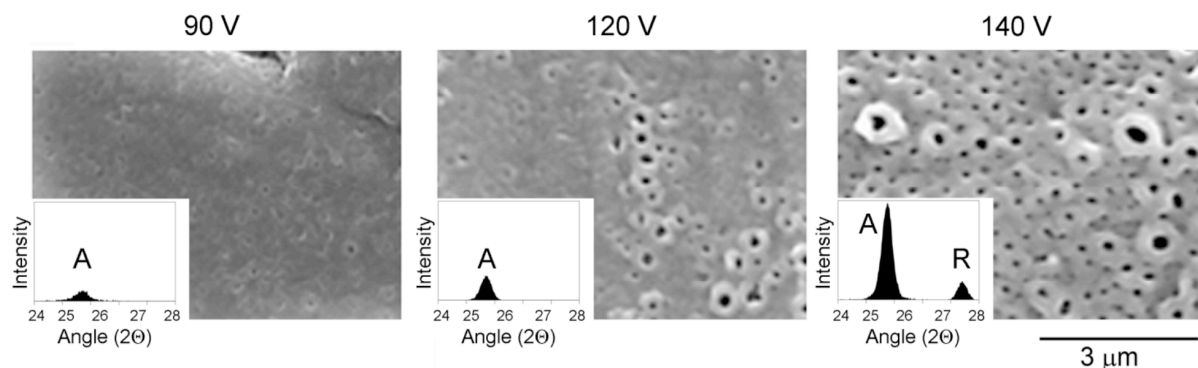


Fig. (2). SEM images of nearly flat TiO_2 oxide (90 V, incipient ASD) and of oxides produced at intermediate voltage (120 V) and high voltage (140 V, complete ASD). Craters are clearly visible at the intermediate and high voltages. The insets represent the XRD peaks measured on the oxides in the range of diffraction angles $24\text{--}28^\circ$, where A = anatase, R = rutile: intensity scales are proportional to the actual content of crystal phases. Data extracted from [37].

of extremely varied compositions; in the majority of cases oxalic, phosphoric and sulfuric acids are used, giving rise to nanopores of diameter ranging from 10 to 240 nm [46]. In the following, a more detailed view of the main characteristics of anodized zirconium, niobium and tantalum are reported, on account of their technological interest in different fields, from bioengineering to electronics; a similar response to the anodic oxidation process could be identified in the other valve metals that are not described here.

As regarding zirconium, it finds applications as structural component in chemical reactors and in water-moderated nuclear reactors, as well as bioprosthetic implant, thanks to a good workability combined with high strength also at high temperature, and good corrosion resistance, which can be further improved by anodic oxidation [47, 48]. ZrO_2 coatings are commonly employed to further reduce corrosion rate, and especially in the production of biomedical implants the ASD process can be applied to produce crystalline films with tunable composition [14]. On the other hand, its oxide exhibits peculiar functional properties, including high dielectric constant, luminescence and the possibility to obtain ionic conductivity – and related gas-sensing ability and suitability as solid electrolyte: therefore, ZrO_2 films gained interest in the production of optical and electronic devices [49–53]. Common electrolytes used in zirconium anodizing process are sulfate-based ones (H_2SO_4 , Na_2SO_4 , K_2SO_4), borate based ones (ammonium borate), carbonate based ones, caustic solutions (NaOH , KOH). Owing to the incorporation of electrolytic anions into the anodic films, oxidation kinetics and resulting optical and electrical properties of ZrO_2 mainly depend on the chemical nature of the electrolytic anions [17, 54, 55]. As in the case of titanium anodizing, all possible anodic oxides can be produced – barrier-type ZrO_2 , thick ceramic layers by ASD, and nanotubular oxides in presence of fluoride containing electrolytes (Fig. 3a, b) [14, 55–57]. The crystal structure can also be tuned as a function of the electrolyte composition, being the cubic and monoclinic lattices the preferred crystal arrangements occurring [14, 49, 58, 59].

Also anodized niobium has attracted large attention, especially on account of the high dielectric constant and high breakdown potential of the anodic oxide [60–62]. In the early stages of research, Nb_2O_5 was mostly studied as catalysts,

sensors and electrochromic layers [63–66], while more recently the path was opened for applications in photocatalytic purification devices, batteries, solar cells and other electronic devices such as memristors [67–69]. Anodizing is mainly performed in acid aqueous solutions (H_2SO_4 , HNO_3 , H_3PO_4 , HClO_4 , HF) and, more generally, in phosphate or fluoride based electrolytes: as in the previously described anodizing processes, also on niobium the choice of electrolyte strongly affects the oxide morphology, with the formation of either compact barrier-type layers, or nanostructured porous layers (Fig. 3c) [60, 66]. Conversely to anodic ZrO_2 , which is mostly crystalline, anodic Nb_2O_5 films maintain in a wider range of conditions an amorphous structure, as a result of the high breakdown potential: field crystallization is generally achieved only at high voltages, as in the case of titanium anodizing [70–72]. Once again, electrolyte ions such as phosphates or sulfates may be incorporated in the oxide during anodizing [73, 74].

Finally, anodized tantalum oxides present high relative permittivity and greater storage capacitance for the same thickness with respect to SiO_2 , which makes them particularly attractive to produce dielectric films for electronic industries [75–77]. Typical anodic processes for Ta are similar to those related to Nb anodizing, and also the results have close similarities, with a mostly amorphous nature and the possibility to produce self-ordered nanotubular structures in electrolytes containing fluoride ions (Fig. 3d) [77–80]. Taking into account the oxide composition, only high voltage anodizing usually leads to the modification of stoichiometry by incorporation of electrolyte ions; in the low voltage production of barrier films, the oxides can experience slight deviations from their original chemistry, but to a negligible extent. Conversely, Ta anodizing in H_3PO_4 [80, 81] causes the incorporation of a substantial quantity of phosphate ions, with the peculiar formation of a double layered barrier-type structure with a more stoichiometric oxide close to the metal interface and one richer in phosphates close to the electrolyte [81, 82]; similar considerations were drawn in experimental works on zirconium anodizing in phosphate electrolytes [83].

As emerges from the quick overview given, valve metals behave similarly, and many features are repeated – for instance, the production of nanostructures in aggressive electrolytes that give rise to localized oxide dissolution, or the

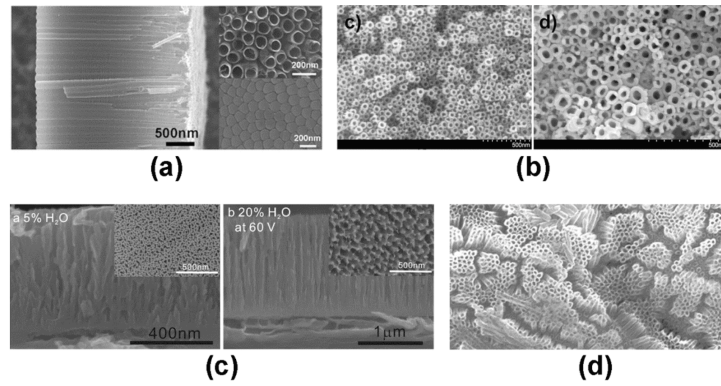


Fig. (3). Anodic oxides with nanotubular morphology obtained on: **a)** titanium [27], **b)** zirconium [57], **c)** niobium [66] and **d)** tantalum [78]. Adapted with permission from [27, 57, 66] and [78].

onset of plasma anodizing (ASD) at high voltages. Still, it is essential to understand how to modulate the oxide properties at the nanoscale, not (or not only) in the formation of nanoporous structures, but most importantly in oxide films with thickness ranging from few nanometers up to few tens of nanometers. In fact, it is in this range of dimensions that oxide properties can be changed radically, giving rise to new applications. The next section will therefore focus more specifically on the production of thin barrier oxides on the surface of Ti, Zr, Nb and Ta, and on their engineered applications in optical and electronic devices.

2. OPTICAL AND ELECTRONIC PROPERTIES OF ANODIC COATINGS

Thin anodic films produced on valve metals lie in the field of engineering coatings, whose properties can be tuned as a function of the desired application – be it a gate dielectric, a gas sensor, or an electrochromic display. In such applications, the key characteristics to be carefully controlled are oxide thickness and crystal structure; the presence of a small quantity of impurities can be vital to induce peculiar semiconducting features, as will be discussed in the following.

From this point of view, a first consideration must concern the optical and electronic properties of the anodic oxide. Fig. (4) reports the band gap and permittivity of most commonly used valve metal oxides, extracted from [2]. Permittivity values for TiO_2 are highly scattered, and it is possible to find several discrepancies in literature reviews:

still, the most utilized dielectric oxides are Nb_2O_5 and Ta_2O_5 ; on the other hand, it is more important to have reliable information on titanium dioxide band gap, given its applications in photocatalysis [23, 84-86]. Several studies have been performed, aimed at defining properties such as band gap, donor concentration, specific capacitance, as a function of production processes and of the application envisioned [87-93]. For instance, as reported in [83] and references therein, passive ZrO_2 films may change from the usual pure dielectric behavior to *n*-type semiconduction when in contact with diluted sulfuric acid, or in the case of very thin films [94-96]; donor density was observed to depend on cell voltage applied during anodizing, which was correlated with a decrease in donor concentration with increasing film thickness [83, 94]. Furthermore, ZrO_2 films with similar thickness may show substantially different dielectric constants as a function of the electrolyte where the oxides were produced, in terms both of chemical composition and of pH [97]. Similar effects are evidenced in niobium anodizing [98-100]: as previously mentioned, this is often used – as alternative to tantalum – to produce solid electrolyte capacitors, where the anodized metal provides both the contact (metallic substrate) and the dielectric (oxide). In this context, field-assisted crystallization is an undesired effect, as it decreases the film permittivity: the incorporation of silicon has been suggested to hinder oxide crystallization [98, 99]. Losses in the dielectric capability are also related to the onset of *n*-type semiconduction, which is ascribed to the formation of an oxygen-deficient oxide; in this case, annealing treatments have been demon-

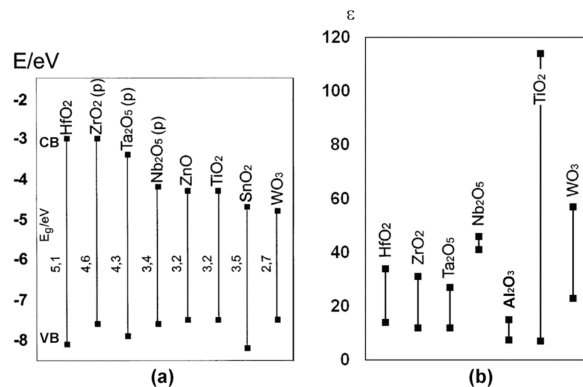


Fig. (4). **a)** Band gap and **b)** permittivity of a selection of valve metal oxides and related range of variation. Values extracted from [2].

strated to increase the oxide specific capacitance [99 and references therein].

On the other hand, the memristive ability of some valve metal oxides (TiO_2 , Nb_2O_5 , Ta_2O_5) is strictly related to their semiconductive nature and to the presence of a sub-stoichiometric oxide [101-107]. Under the effect of an external voltage, oxygen vacancies build up a conductive filament within an insulating oxide, reducing its resistance: this low resistance state can be reversed by applying an opposite voltage, which redistributes oxygen vacancies throughout the oxide volume, causing the oxide resistance to increase to its initial value. Such effect is of great interest in the field of non-volatile memories, and the use of anodic films is particularly promising, given the low cost of the production process compared with techniques typical of the electronic industry (ALD, sputtering...), although printing techniques have experienced strong improvements and are now starting to produce sufficiently efficient oxide films [30, 31, 108-111]. The most important feature to be controlled, together with the deviations from stoichiometry, is oxide thickness: in fact, the memristive behavior is lost in presence of exceedingly thick films – generally the range of suitability is limited at few tens of nanometers [112, 113].

Memristors are not the only devices where the nanoscale control of oxide thickness is crucial to meet the characteristics required by the final application. In this respect, anodic oxides present an interesting property that helps monitoring the results of the oxidation process: in fact, the transparent oxide interferes with light and causes the appearance of interference colors at the metal surface. This phenomenon allows to check the oxide thickness on the basis of the color appearing, and simple reflectance measurements can provide information on surface color, which in turn provides an indirect evaluation of oxide thickness [4, 34, 55, 114-118]. As mentioned in section 1.1, several researches report growth kinetics of anodic oxide films on valve metals, identifying a linear correlation between cell voltage applied and oxide thickness. Still, it is difficult to perform a homogeneous comparison among the main properties – composition, structure, thickness – of different valve metal oxides, on account of the different anodizing conditions applied in different works. For this reason, the last section of this review presents an assessment of oxidation kinetics and resulting oxide structure and color on titanium, niobium, tantalum and zirconium anodized in same conditions, in order to investigate similarities and differences in the behavior of these materials.

3. THIN ANODIC FILMS ON TI, NB, TA, ZR: A COMPARISON

3.1. Experimental Conditions

Anodic oxidation was performed on four valve metals: Ti, Zr, Nb, Ta. Metal foils were purchased from Goodfellow and cut into square specimens, 2 cm x 2 cm. Table 1 reports information on the metals purchased. Samples were anodized in as-received conditions: only a degreasing step was performed with acetone, in order to remove possible organic residues from mechanical processing. Two electrolytic solutions were considered, i.e., 0.5 M H_2SO_4 and 0.5 M H_3PO_4 , obtained from pure reagents purchased from Sigma Aldrich,

Table 1. Degree of purity and thickness of the sheets used in the experimental section (data available on Goodfellow website).

Metal	Purity	Thickness (mm)
Ti	99.6%	0.125
Zr	99.2%	0.125
Nb	99.9%	0.25
Ta	99.9%	0.075

both utilized at room temperature. A PLH120 potentiostat by AIM & Thurlby Thandar Instruments was used to supply a direct current in galvanostatic conditions; in all anodic oxidation processes, a current density of 100 A/m^2 was applied between the sample and an activated titanium counter electrode. Cell voltages ranging from 10 V to 100 V were applied on each metal in order to record the growth kinetics of the four metal oxides in the indicated electrolytes.

Oxides structure was analyzed by means of X-ray diffraction spectroscopy (XRD). A Philips PW3020-Cu Ka instrument was used to collect XRD spectra in the range of diffraction angles $0-80^\circ$. Oxide thickness was measured indirectly by spectrophotometry: reflectance spectra were collected by using a Konica Minolta CM-2600d spectrophotometer, and the position of interference maxima and minima were used to determine oxide thickness as indicated by Bragg's law and reported in previous works [119]. Reference values of the oxides refractive indexes were taken to perform the calculation; the following values of refractive index at 550 nm were chosen: $n_{\text{Ti}} = 2.2$, $n_{\text{Nb}} = 2.3$, $n_{\text{Ta}} = 2.1$, $n_{\text{Zr}} = 2.1$ [34, 120-125]. Spectrophotometric measurements were also used to identify the oxide color hue.

3.2. Results

A selection of oxidation kinetics results are presented in Fig. (5), where the voltage increase in time on Ti in 0.5 M H_2SO_4 and in 0.5 M H_3PO_4 are compared, together with that of Nb in 0.5 M H_2SO_4 . While Nb shows an almost linear voltage increase with time, on Ti the oxidation kinetics clearly slows down with time and with oxide thickening. This effect is related to the relevant oxygen development

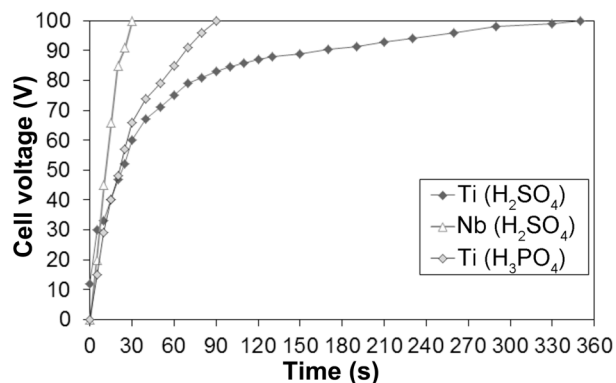


Fig. (5). Oxidation kinetics on the different valve metals in 0.5 M H_2SO_4 with current density 100 A/m^2 .

taking place at the titanium surface as parasitic reaction, which decreases process efficiency.

To explain this behavior, XRD analyses were performed on the anodized specimens. Only titanium and zirconium anodizing produced crystalline oxides, in the latter case in both electrolytes tested (Fig. 6a) while TiO_2 crystallized only in sulfuric acid (Fig. 6b), as already described in previous works [125]; on the other hand, on niobium and tantalum no crystal phase was observed. This explains the higher efficiency of anodizing on the latter metals, where crystallites – if present – are limited to such a small dimension that XRD cannot reveal them: therefore, the oxide electronic conductivity is limited and parasitic reactions take place to a less relevant extent. Yet, titanium oxides produced in phosphoric acid are amorphous, but a consistent oxygen evolution occurs: this shall be ascribed to the large incorporation of phosphate ions, which makes the oxide particularly defective and therefore opens conductive paths within the insulating oxide. On the other hand, on titanium anodized in sulfuric acid not only the production of crystalline oxides increases the favorability of oxygen evolution compared with oxide growth, but also sparking conditions heat up the surface, further slowing down the oxide buildup due to the elevated temperature. For this reason, two distinct kinetics are observed on Ti, in both cases less efficient than the growth of compact and amorphous oxides on Nb, depending on the onset of intense oxygen development and on the concurrent – but not consequent – oxide crystallization and related heating. This consideration also allows to determine the beginning of sparking, which attests around 60-70 V, coherently with our previous observations on the onset of TiO_2 crystallization due to sparking [37].

Examples of the linear trend of oxide thickness increase obtained as a function of cell voltage applied is reported in Fig. (7a). Results follow the trend of other works found in literature, with anodizing ratios included between 1.5 and 2.1 nm/V [4, 32-34]. It is interesting to notice how anodic oxidation in diluted phosphoric acid tends to produce slightly thinner oxides compared with diluted sulfuric acid (Fig. 7b). It is not possible to draw detailed considerations on the relative thicknesses of oxides produced on different metals, on account of the uncertainties on the oxide refractive index,

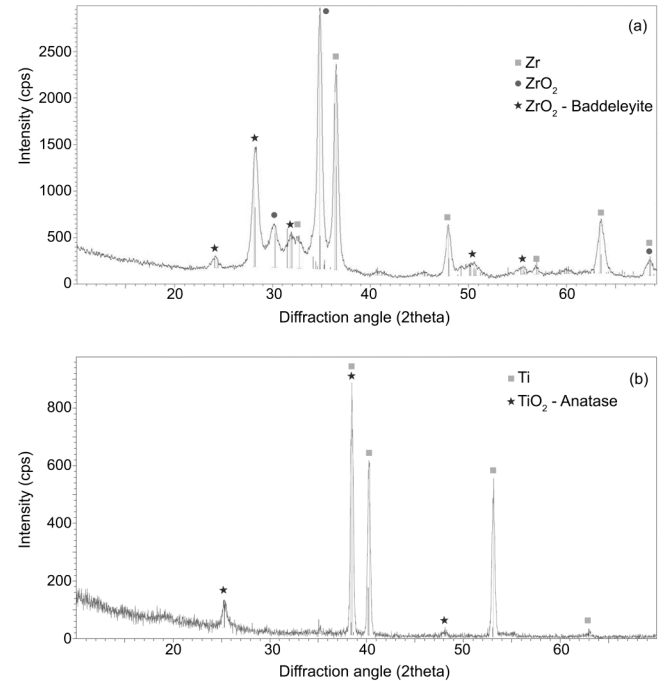
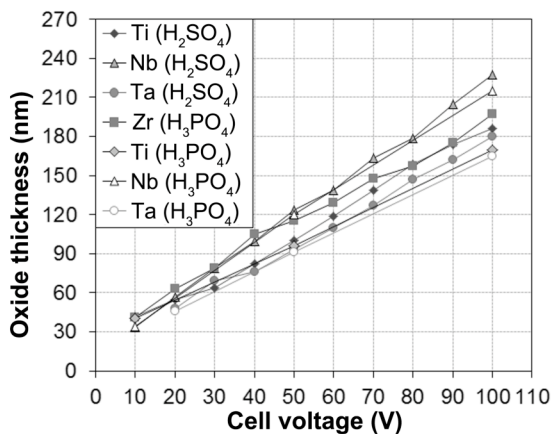


Fig. (6). XRD spectra of Zr oxidized at 100 V in 0.5 M H_3PO_4 and Ti oxidized at 100 V in 0.5 M H_2SO_4 .

which may present values slightly different from those used to calculate oxide thickness. Still, it is possible to conclude that all valve metals examined present similar behavior to anodizing in diluted acids, with the formation of a barrier oxide of similar thickness as a function of applied voltage.

As a last consideration, the color hue of anodized specimens was plotted versus cell voltage. In spite of an oxide thickness comparable to that of titanium oxides, anodized tantalum seems to produce different hues, with a shift of colors appearing at the surface at higher voltages compared to the same hues produced on titanium. This effect is also noticed on zirconium, but only at voltages higher than 40-50 V. Such discrepancies can be attributed to the lower refractive indexes chosen for Ta and Zr, which lead to a mismatch in wavelengths that produce interfering effects for the same oxide thickness.

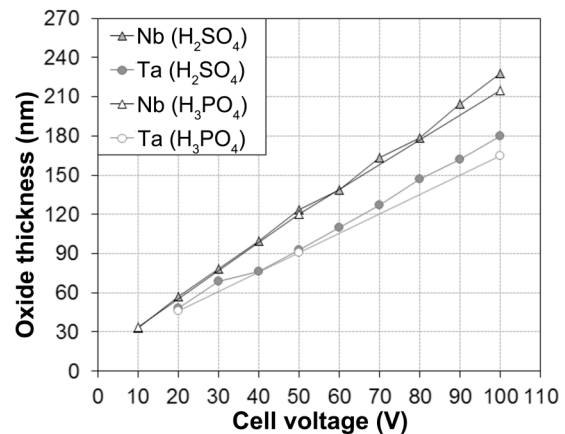


Fig. (7). Linear relationship between oxide thickness and cell voltage applied.

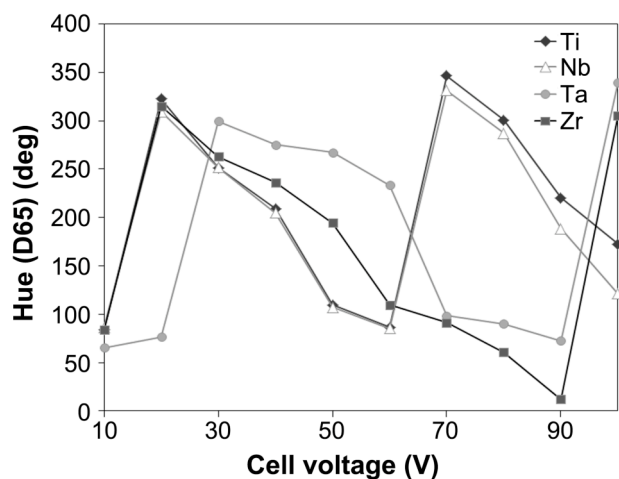


Fig. (8). Oxide hue as a function of cell voltage for oxides produced in 0.5 M H₂SO₄ with current density 100 A/m².

CONCLUSIONS

The review here presented was aimed at highlighting the importance of having a good know how and control over the anodic oxidation process, in order to have high process reliability. This could be of importance when anodic coloring is considered, for instance in design and arts applications, but it becomes crucial when a specific functionality is desired, and in particular in the field of electronics, where anodic oxidation may become competitive towards physical deposition systems only if high precision is reached in the control of oxide thickness and structure achieved.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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