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ANODIZATION PARAMETERS AND APPLICATIONS OF TIO_2 NANOTUBES: A REVIEW

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RESUMO

Os nanotubos de TiO_2 (TNT) são estruturas óxidas tubulares de escala nanométrica crescidos sobre alguma superfície de titânio, geralmente pelo processo de anodização eletroquímica na presença de íons de flúor. Essas nanoestruturas são frequentemente estudadas pela ciência de materiais devido às suas propriedades específicas, que são bastante vantajosas para aplicações, sejam elas biomédicas ou fotocatalíticas. Em suma, o presente trabalho de revisão bibliográfica visa fazer um estudo na literatura de alguns dos mais importantes tópicos sobre o crescimento, os parâmetros de anodização e aplicações dos nanotubos de TiO_2, utilizando-se de publicações recentes com alto fator de impacto.

Palavras-chave: Anodization Parameters; Applications; TiO_2 Nanotubes.

INTRODUÇÃO

TiO_2 nanotubes were intensely studied for the first time by Zwilling et al. in 1999 (ZWILLING et al., 1999), since then, it has been getting more attention from materials researchers, due to its properties that allows applications in a wide range of industries,

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such as, biomaterials, solar cells, photocatalysis, biodegradation of pollutants and water splitting. In this context, the present work reviews with the main topics regarding the formation and application of TiO_2 nanotubes.

METODOLOGIA

The literature review here presented was made in academic journals linked to the Periódicos Capes and Google Scholar database, mainly in publications with an impact factor greater than 4 that were published from 2010. The search at these databases used the following keywords: TiO_2 nanotubes, parameters of anodization and TiO_2 nanotubes applications. Related works that were cited in the results of this initial search were also considered for this review. From the papers found, 21 articles were selected, which presented the necessary data for this review. The information analysis was carried out by means of exploratory reading of this material.

RESULTADOS E DISCUSSÕES

FORMATION OF TiO_2 NANOTUBES

Currently, there are different ways to grown TiO_2 nanotubes over titanium substrates, however, the electrochemical anodization is the more promising method, due to its high degree of manipulation, low cost and possibility to apply on large scale. The formation of TNTs is ensured by the oxidation of Ti allocated in an anode into an electrolyte, generally under potentiostatic condition, forming a thin and compact layer of TiO_2, which must be partially dissolved in localized regions by the presence of fluoride ions, generating nanoporous oxide layer. The simultaneous growth and localizes dissolution of the TiO_2 can be controlled, promoting the growth of the nanotubes (ROY; BERGER; SCHMUKI, 2011). This process could be better explained by a curve of current density

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over time, divided in three phases, as schematically illustrated in Figure 1. The first phase is marked by the fall of current density, which means that the thickness increase of compact layer is followed by the increase of electrical resistance, resulting the decrease of ionic mobility and consequently, the fallen of density curve (MINAGAR et al., 2012). The second phase occurs due to the presence of fluoride ions, that acts reacting with TiO_2, generating fluoride compounds ($[TiF_6]^{2-}$) and starts the nucleation along the oxide layer (KANG, S. H. et al., 2008). Due to the presence of these craters, there are an increase of current density and consequently, increasing the ionic mobility, allowing to O^{2-} ions penetrate through oxide layer and continue to react with Ti, aiding the thickening of TiO_2 layer and more uniform spreading of pores (ZHANG et al., 2010).

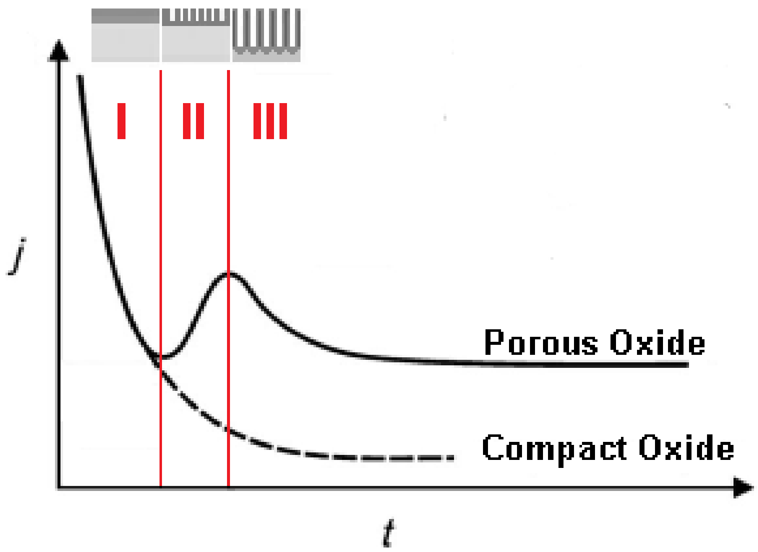

Figure 1: Schematically illustration of the current density (j) over time (t)

When the third phase is reached, is observed a constancy of current density, which could be attributed to the theory of Field Assisted Dissolution, that proposes the equal rates of dissolution and formation of new TiO_2 oxide layer, both at the base of each pore (REGONINI et al., 2012).

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RELEVANT PARAMETERS FOR THE GROWTH OF TNTs

Some alterations can be made in anodization parameters in order to modify some properties of TNTs, as its thickness, tube diameter, homogeneity or crystalline structure. The following topics will discuss each of these parameters and their influence on the TNT's properties.

ELECTROLYTE

There are three generations of electrolytes that could be used to grow TNTs. The first generation is marked by the utilization of HF and other acid mixtures as fluoride ions in water, for example 0.5 to 3.5 wt% hydrofluoric acid in water presence. However, this HF based electrolytes usually are very aggressive, which promotes a very fast formation of nanotubes. This kind of electrolyte typically didn't allow the auto-ordering and thickening of TNT's, resulting in unordered array of TNTs with small thickness (0.5-0.6 μm) (BERGER et al., 2010). By other hand, the second generation of electrolyte used solutions of neutral fluoride salts in water as electrolyte, for instance, 1M Na_2SO_4 + 0.3 to 1% wt. of NaF. This kind of electrolyte lead to an increase of the environment pH and a reduced oxide dissolution rate, consequently, thickening nanotubes layer (2-4 μm), with a higher degree of self-ordering (CAI et al., 2005). Finally, the third generation of electrolytes uses organic solutions and fluoride salts under neutrals pH, for instance, ethylene glycol, with 0.3 wt% NH_4F and 2 vol.% water could be used to generates improved TNTs. This type of electrolyte allows a slower and more controlled anodization. Nanotubes layers obtained in those conditions have much higher thickness (100-1000 μm) and higher degree of self-ordering. Besides that, nanotubes formed with organic electrolyte does not have lots of rips over its walls, like those occurring in inorganic electrolytes, which can improve its functional properties (REGONINI et al., 2009).

FLUORIDE IONS CONCENTRATION

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The fluoride ions concentration must be moderate (0.05-1.5 wt%), as its absence can keep the TiO_2 compact layer virtually intact, and its excess cause the retarding of TiO_2 growth, or even, the total dissolution of oxide layer, maintaining only the metal substrate exposed to electrolyte. Wang et al., found a good range for TNTs formation using fluoride concentration between 5 to 150 mM (WANG et al., 2016).

ELECTROLYTE pH

Electrolyte pH is also a very important parameter as previously mentioned. The electrolyte pH directly influences the ionic mobility in the dissolution process of TiO_2. Commonly, the most appropriate pH to get taller and ordered tubes is higher than 5. However, neutral pH solutions can make the process slower due to reduction of ionic mobility. For instance, nanotubes anodized over 12 hours, obtained by glycerol + 0.5 wt % NH_4F reach a higher pH than 1M $(NH_4)_2SO_4$ + NH_4F, and consequently higher rates of growth (MACAK, Jan M.; SCHMUKI, 2006).

TEMPERATURE

In organic electrolytes it is observed a directly proportional relationship between temperature and nanotube diameter due to the increased ionic migration, and consequently, dissolution of TiO_2 layer (MOHAN et al., 2020). Also, the ideal anodization temperature selection will depend on the electrolyte in use. For aqueous electrolytes, lower temperatures (~2ºC) can lead to inhibition of TiO_2 growth, while in organic environments, the temperature range of 0 to 40ºC has been successfully applied, for instead, in glycerol + 0.5 wt.% NH_4F there is a directly relationship between thickness and diameter along the time (MACAK, Jan M.; SCHMUKI, 2006; REGONINI et al., 2013).

ANODIZATION TIME

As mentioned before, the anodization time of Ti depends on the rates of growth and dissolution of TiO_2, which could take some minutes in aggressive medium (inorganic) to several hours in organic medium. In the first case, typically leading to smalls, unordered

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and ripped tubes, while in the second case led to high ordered, unripped and taller tubes (REGONINI et al., 2012). Besides that, TNTs can present higher thickness for longer anodization times, for instance, H_2SO_4 1M + HF 0.15 wt % reach higher thicknesses if anodized over 12 hours compared to lesser times. However, there is a limit where a the anodization starts to decrease the tubes size and an intense dissolution of tubes walls could lead the tube to a collapse (ROY; BERGER; SCHMUKI, 2011).

ANODIZATION POTENTIAL

The anodization is usually performed under potentiostatic conditions, and it is commonly observed a linear relationship between applied potential and TNTs diameter until 60V, and the inverse relationship for potentials over 100V (REGONINI et al., 2009). The correlation can be rationalized by the fact that the electric field is responsible for ions migration, as improved ions mobility leads also to high dissolution rates, the tubes diameters is enlarged by higher anodization voltages. Commonly applied potentials range from 5 to 30V in aqueous electrolyte, and 10 to 60V in organic electrolytes (MACAK, J M et al., 2007).

WATER CONCENTRATION AND AGING OF ELECTROLYTE

Water has two essential roles in the nanotubes formation, (i) it is responsible for providing oxide ions (O^{2-}) to titanium to form the compact TiO_2 film (REGONINI et al., 2013) and (ii) has also the role of conversion from pores to tubes, by dissolving the high concentration of $[TiF_6]^{2-}$ ions between two pores, thus generating distinct tubes. This way, water is always needed in the growth of TNTs, even on small scales (WEI et al., 2010). During the TNTs formation, the reuse of electrolyte can help in the synthesis of nanotubular arrays, as result of amplification of its electric conductivity, due to the large waste rate of $[TiF_6]^{2-}$ ions adsorbed over several other anodization cycles, and the high content of water acquired, for example, tubes grown into older electrolytes presents

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smaller thickness but higher self-ordering compared to those grown over fresh electrolytes (SOPHA et al., 2015).

APPLICATIONS OF TiO_2 NANOTUBES

BIOMEDICAL APPLICATIONS

There are a lot of applications of TNTs for biomedical purposes, mainly as coating for orthopedical implants. Due to its low elastic modulus, great fatigue and corrosion resistance, higher surface area and its biocompatibility properties, they can promote a better and faster osseointegration compared to the metals without any coating (KANG, C. G. et al., 2015). The mainly advantage to use thicker layers of highly ordered TiO_2 nanotubes for bones implantations is its larger surface area. The high surface area allows the high deposition of hydroxyapatite (HAP), that is the principal compound responsible by traffic of cells and cells compounds, consequently, promoting the growth of osteoblast cells and aiding the bone recovering (MELLO et al., 2017). Moreover, another important capacity of TNTs is its great degradation resistance into biological systems, what prevents that wastes be released into biological body (KANG, C. G. et al., 2015).

POLLUTANTS DEGRADATION

In photocatalysis field, TNTs have two important properties: (i) it has extremely high photocorrosion stability and (ii) it has a specific band edge, which ensure its application for water and gas photocatalysis organic pollutants degradation, converting those compounds (as aromatics pesticides) to H_2O and CO_2 (PARAMASIVAM et al., 2012). The mechanism driving this process of photodegradation is the photoexcitation, which rises the electron from valence band to conduction band, generating a “hole” with oxidant power into valence band of the TNT. After that, both electron and hole will diffuse through TiO_2 layer until reach its surface limit, where both will react with its suitable

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redox species, forming O^{2-} and OH^-, compounds with capacity to reduce virtually any organic pollutants (KUO, 2009).

DYE – SENTITIZED SOLAR CELLS

Other important application for TiO_2 nanotubes is for solar cells aiming to obtain higher conversion rates of photoelectricity. The fundamental mechanism works in a similar way to the pollutants degradations by photocatalysis. However, TNTs have a high band gap, reason of why it is used dyes to cover nanotubes, reducing band gap and favoring the injection of electrons to valence band of TiO_2 (ROY et al., 2010). The mechanism of light conversion is based on the electron excitation and its injection from dye valence band into conduction band of TiO_2, where the electron will travel through TiO_2 nanotube layer to back contact. The electron absence in dye generates a hole, that is promptly filled by another electron from electrolyte contained into solar cells, this way, the circuit is complete, generating electricity (ROY et al., 2010).

CONSIDERAÇÕES FINAIS

TiO_2 nanotubes could be formed over Ti substrate by the anodization process. During the anodization ions into electrolyte cause the nucleation of pores in the compact TiO_2 layer, those ions are usually fluoride ions. The competitive process of growing a compact TiO_2 layer and the simultaneous localized dissolution of this layer builds the TNTs. During the anodization process, several parameters can be altered in order to manipulate the formation of TNTs, namely, the electrolyte characteristics such as, fluoride ions concentration and pH; the bath temperature, the anodization voltage and time. Some of the more important of those parameters is electrolyte choice, which is commonly used the third generation, due to its better capacity to produce TNTs with higher thickness and

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self-ordering degree. Anodization potential and time must also receive attention, due to a directly correlation between these parameters in the morphology of the obtained TNTs. There are several important ways to apply TiO_2 nanotubes, and here it was highlighted the biomedical and photocatalytic applications. In this context, TNTs are nanostructures with promising technological application that can contribute to breakthrough in the use of nanotechnology in daily used products. Finally, a deeper understanding of the effects of different parameters involved in the TNTs formation can contribute to a faster application of this material in large scale.

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