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Deposition of TiO_2 Film on Duplex Stainless Steel Substrate Using the Cathodic Cage Plasma Technique

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This research used the "cathodic cage (CC)" technique for TiO_2 film deposition on duplex stainless steel substrate. This technique uses a multiple hollow cathode effect. Duplex stainless steel substrates were treated at temperatures of 300ºC, 350ºC and 400ºC, giving a temperature value ratio (T_s/T_m) of 0.27 to 0.31 (Ts being the substrate temperature and Tm the melting temperature of the deposited material). Treatment times of 1, 2 and 4 hours were administered and polycrystalline TiO_2 films were obtained. The films were analyzed by optical microscopy (OM), X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM). During analysis, the formation of uniform films and the possibility of controlling the TiO_2 phase were observed. It was also shown that with longer treatment times and higher temperatures the rutile phase predominates. For treatment times of 4 hours at all temperatures, the rutile structure was present. With treatment times of less than 4 hours, anatase was present. In addition, results showed that this simple, low cost technique can be an alternative method for depositions of TiO_2 films, with the advantage of high levels of control over porosity, thickness and phase composition (anatase and rutile).

Keywords: *Cathodic Cage; titanium dioxide; duplex stainless steel; TiO_2 thin films*

1. Introduction

TiO_2 is a transition metal oxide which has been studied extensively, mainly because of its excellent dielectric, optical and electronic properties. TiO_2 has wide range applications, including environmental purification, self-cleaning surfaces, and photo induced hydrophilicity[1-5], in addition to being an important biocompatible material[1,4]. TiO_2 crystallizes in anatase, rutile or brookite structural phases. The properties of TiO_2 films are known to be related to the amount to which the phases are present in the deposited layer[3]. Many studies have focused on the dependence of the obtained phase on preparation methods, deposition parameters, substrate type, doping of metallic and nonmetallic species[3,6]. Anatase TiO_2 is considered one of the best photocatalysts with high activity and non-toxic properties[5], furthermore, it exhibits high chemical reactivity and stability under UV illumination[2], which leads to greater possibilities for practical application as antibacterial agents[2-5], self-cleaning surfaces[7], organic photo degradation[8,6], and hydrogen generation by the splitting of water, termed solar-hydrogen[6,9,10]. In addition, depending of phase and preparation conditions, anatase TiO_2 has high durability, high refractive index (n = 2.3), high resistivity and dielectric constant[11] k, with values from 30 to 100, so it is suitable for applications in optical wave-guides[12], antireflection coatings[13], photochemical solar cells[14,15] and gas sensors[11,12]. Photons with energy equal or higher than the energy band gap (~3.2eV) are able to generate electron/hole pairs[7] and have energy high enough to initiate redox and oxidation reactions[16]. For example, excited electrons can reduce oxygen to superoxide radicals, whilst the holes oxidize water molecules into hydroxyl radicals[5,13]. These intermediate species induce the decomposition of various molecules such as those which are organic or microbes, which leads to the self-cleaning ability and anti-microbial applications of a TiO_2 surface[17]. In order to improve and expand upon the range of applications some modifications have been studied and several approaches have been proposed: First, to reduce the band gap of TiO_2 with the intention of improving the light absorption in the visible region, studies have been conducted involving doping with metallic and non-metallic impurities[4-6,18].

Second, to elucidate the influence of synthesis techniques, as well as film deposition methods and substrate type, many chemical and physical processes and techniques have been carried out and great advances have emerged[2,9,14,17].

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Recent investigations have included the use of practical and economical substrates such as metallic materials[5,15,16,20]. The particular properties of metals, such as its conductivity, flexibility, mechanical robustness and capacity to be shaped easily can change the photocatalytic characteristics and expand the possibility for practical application[7,16], such as self-cleaning surfaces, antibacterial agents, photo degradation of organics, use in the manufacture of components introduced in hospital equipment, utensils for food preparation and air conditioning[11,14].

Several methods have been used successfully to deposit TiO_2 thin films, including the sol–gel[21] method by hydrolysis of $Ti(OiPr)_4$, followed by calcination at 500–600°C, chemical vapor deposition[2,4,10] (CVD), physical vapor deposition (PVD), chemical bath deposition (CBD), reactive sputtering and atomic layer deposition (ALD)[8,14,19,22,23]. Low-pressure chemical vapor deposition (LPCVD) routes have been used to grow TiO_2 on a diverse range of substrates[14]. It has been shown[8,25] that, with a deposition temperature greater than 400°C, TiO_2 films are polycrystalline, whilst temperatures lower than 400°C lead to an amorphous structure and that the structural phase grown depends on the physical and chemical characteristics of the substrate. It was found that films grown on glass substrates present a rutile tetragonal structure, while on ITO-coated glass substrates films grow in an anatase structure[8,25].

According to Movchan and Demchishin[26], the microstructure of metal and oxide thin films is related to the homologous temperature, *i. e.* T_s/T_m (T_s is the temperature of the substrate and T_m is the melting temperature of the deposited material). The structural morphologies have three well-defined structural zones[26,27,28]: The first zone - T_s/T_m <0.3 - is characterized by small, elongated grains, with a columnar structure and a porous morphology, where there is a weak binding between the grains. The columnar structure is produced by low diffusion of surface adsorbed atoms through the substrate and atomic shadow effects that are dependent on the speed of growth of the columns and on the various incidence angles when the atoms reach the substrate surface. In the present work, TiO_2 thin films were produced using the so-called cathodic cage[24,29] (CC) method. The CC method is a hybrid technique, which promotes both the deposition and diffusion of chemical elements on the surface. The method used is such that the homologous temperature falls in the range $0.27 \leq T_s/T_m \leq 0.31$, where the microstructure of the film is characterized according to descriptions of 'first zone' described earlier by Movchan et al.

2. Experimental

The system was the same as that used in plasma nitriding[24], with a vertically mounted cylindrical vacuum chamber (40 cm in diameter and 40 cm in height, made of stainless steel) was used, but with a cathodic cage as shown in Figure 1, with a power source having a maximum output voltage and DC current of 1500 V and 2 A, respectively. During the treatment there was a variation in the current and voltage of 0.75 to 0.78 mA / 522 to 535 V, 0.55 to 0.59 mA / 455 to 464 V and 0.55 to 0.58 mA / 455 to 462 V, for treatment temperatures of 300°C, 350°C and 400°C respectively. The gas mixture was introduced and its flow rate adjusted using a four channels mass flow controller MKS /247D. The treatment pressure was measured by a BARATRON® Model 627D with a multichannel PDR 2000 / Mks.

Duplex stainless steel (UNS S31803) sheets, measuring 15x10x2 mm^3 with a nominal composition of 22Cr-6Ni-3Mo-N were used after metallographic preparation and ultrasonic cleaning, as a substrate for titanium dioxide films deposition[24]. A double cage was adapted in order to increase the deposition rate and involved the simple use of two concentric tubes of 75 mm x 55 mm and 45mm x 35mm (diameter x height) which formed the external and internal cages, in the configuration shown in Figure 1.

The cages were manufactured using grade 2 titanium sheets with a 2 mm thickness. The tubes were covered on top by discs also made of titanium. Holes, 8 mm in diameter, with a distance of 9 mm from each other, were made in the cages walls. The substrate was then placed on top of an insulated disk and sample holder. The substrate, insulated disk and sample holder were placed inside the internal cage in order to keep them at a floating potential. The shortest distance between the sample (substrate) and the cage wall was 25 mm. The chamber cleaning was performed by injecting and evacuating argon gas three times before deposition.

The deposition was performed under conditions shown in Table 1, at temperatures of 300°C, 350°C, 400°C and deposition times of 1h, 2h and 4h for treatments performed under a flow of 6 sccm of Ar + 6 sccm of H_2+ 3 sccm of O_2 under a working pressure of 150Pa. The flow rate and composition were optimized to produce a uniform layer of TiO_2 deposited on the substrate. Hydrogen (H_2) was introduced in order to control the oxidation process, thus avoiding the presence of some undesired oxides. This did not result in any significant change in the phase, and it is a common method to improve the surface properties of TiO_2, creating some defects (oxygen vacancies (OV) and Ti^{3+}), which are important for applications in photocatalysis[30,31].

The sample surface microstructure was examined with a scanning electron microscope (SEM; JEOL, Japan, JSM-6060LV) and an optical microscope (Olympus BX60M). The phase structures of the deposited films were determined by theta-2theta X-ray diffraction (XRD), RIGAKU, Japan, RINT-2550V). To characterize the phase (rutile and anatase) present in the films, Raman spectroscopy (laser 785nm – Perkin Elmer) was used.

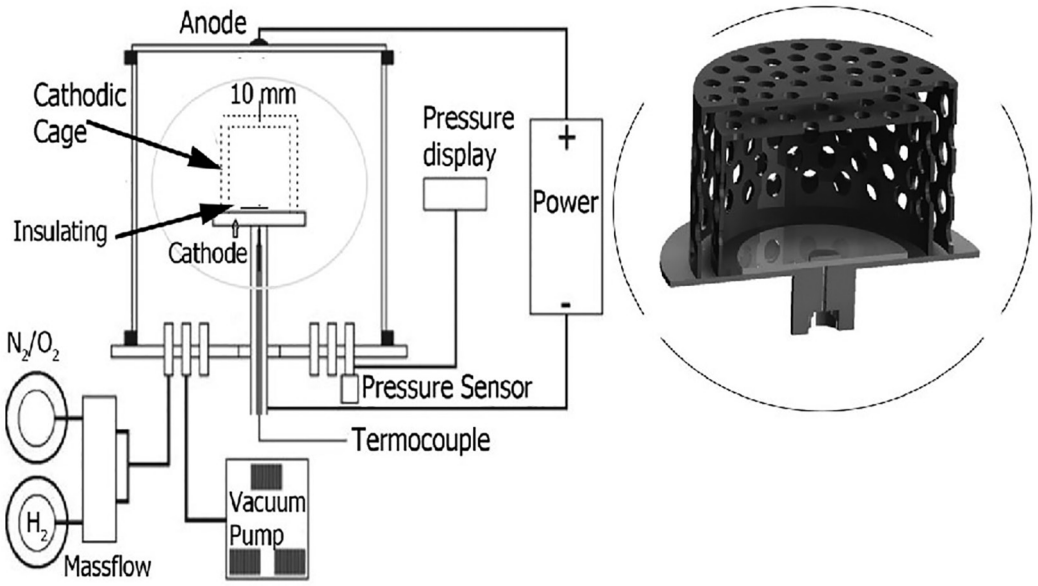

Figure 1: Schematic view of the ion nitriding reactor showing the spatial arrangement of the double cathodic cage.

Table 1: Temperature, deposition time and homologous temperature for treatments performed under a flow of 6sccm of Ar + 6 sccm of H2 + 3 sccm of O_2, and working pressure of 150 Pa.

Substrate	Temperature (°C)	Deposition time (h)	T_s/T_m
Inox300T1H	300	1	0.27
Inox300T2H	300	2	0.27
Inox300T4H	300	4	0.27
Inox350T1H	350	1	0.29
Inox350T2H	350	2	0.29
Inox350T4H	350	4	0.29
Inox400T1H	400	1	0.31
Inox400T2H	400	2	0.31
Inox400T4H	400	4	0.31

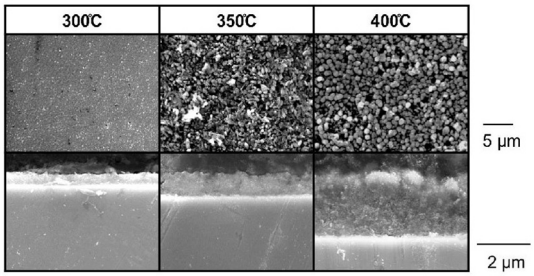

Figure 2: Surface microstructure of deposited films showing the increase of roughness and thickness when the ratio T_s/T_m change from 0.27 to 0.31.

3. Results and Discussion

Figure 2 shows the microstructure of both the surface and the cross section of the films deposited for 4h at different deposition temperatures. The roughness and thickness of the films increased with the increase of deposition temperature from 300°C to 400°C. These results are in accordance with the growth model proposed by Thornton[27] that for 300°C and 400°C (T_s/T_m is 0.27 and 0.31, respectively), TiO_2 films should present a columnar structure with porous morphology. Grains are produced by low diffusion and low mobility of the atoms absorbed at the substrate surface.

Figure 3 shows the XRD pattern for films deposited for 4h at different deposition temperatures. Compared to the untreated substrate, it shows that TiO_2 was formed for all treatment conditions. Further observation also shows that the peak positions corresponding to the α and γ phases of the steel substrate with a shift towards higher angles(2θ), showing that there was a modification at the substrate/film interface, probably due to oxygen diffusion, with the substrate forming a sub-layer or an interface layer between the substrate and the film (Figure 3b).

Analysis of the XRD spectra shows the onset of rutile phase formation at temperatures above 300°C for surface treatment times of 2h (Figure 4), although, for other conditions, the sensitivity of the XRD technique was not sufficient to distinguish the two distinct structures with a good enough resolution. Using Raman spectroscopy (Figure 5) we can verify the change of the film structure from anatase to rutile as a function of sample temperature and treatment time. Even a very low amount of anatase TiO_2 can be detected using Raman spectroscopy, because of the high scattering factor of such a phase[32]. We have found the presence of anatase and rutile in the films with high accuracy. A dependency, mainly related to treatment time was found, where it was observed

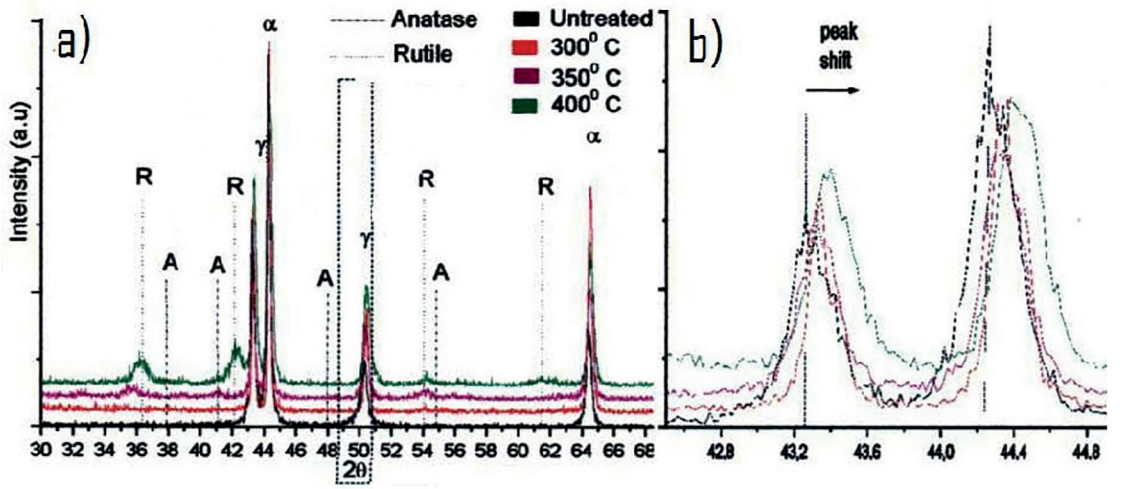

Figure 3: (a) XRD pattern for films deposited at different temperatures during 4 hours and (b) peak shift detail for α and γ phase of the substrate.

that with a treatment time of 4 hours, for all temperatures, there is a predominance of rutile structure in the films. The case of a treatment at 400°C the rutile phase is found to be the predominant phase, and a very low amount of anatase (not detected in XRD) is present. For a treatment time of 2 h, rutile is found to be the majority phase confirming the onset predicted by XRD. At 300 ºC, anatase is the majority phase for up to 2 h of treatment (there is no sign of rutile phase at 1 and 2 h). After that, rutile is predominant with a very low amount of anatase phase present.

4. Conclusions

Our research shows that the use of the low cost cathodic cage (CC) technique, based on a multiple hollow cathode effect, allows TiO_2 coatings on duplex stainless steel (UNS S31803) substrates, to be obtained with a regular microstructure. It is also seen that, by controlling the treatment temperature and the treatment time it is possible to control the amount of phases (anatase and rutile) present in the grown layer. Research also shows that the best conditions for the rutile phase to occur are at a deposition temperature of 400ºC and for the anatase

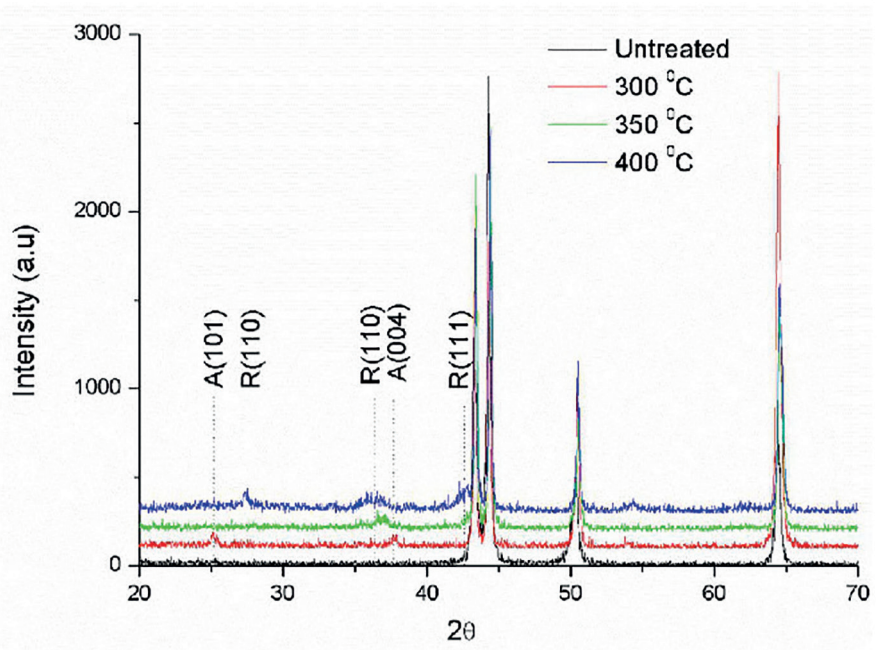

Figure 4: XRD pattern for films deposited during 2h and different deposition temperatures showing the change of anatase to rutile phase.

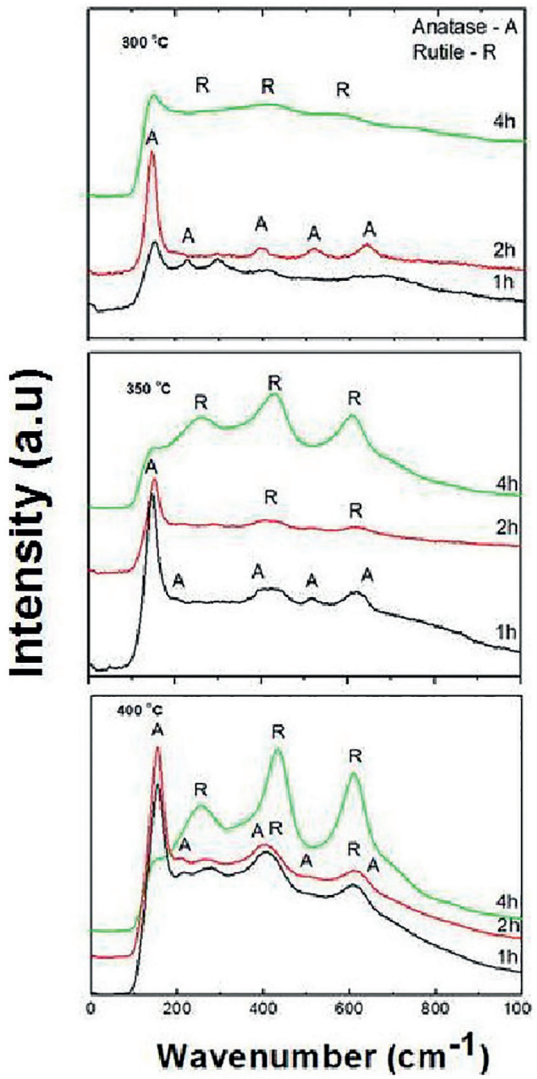

Figure 5: Raman spectroscopy pattern for films deposited at 300ºC, 350ºC and 400ºC for different treatment times showing the change of anatase to rutile phase.

phase to be present are at temperatures lower than 300ºC. The results show that this simple and low cost technique can be applied over wide range of deposition parameters and is a good alternative for obtaining TiO_2 films with the advantage of a high degree of control of the properties and phases of the films. Furthermore, it is possible to obtain films on an economical, practical and versatile substrate, presenting elongated grains, with a columnar structure and a porous morphology which should increase greatly the possibility of its technical applications.

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