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Coating of Titania Nanoparticles on Stainless Steel Using an Alkoxide Precursor

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ABSTRACT

Uniform nanostructure coating of TiO_2 was prepared on 316L stainless steel by sol-gel method using Tetra-n-Butyle Titanat (TBT) as alkoxide material. 316L specimens were coated with the mentioned sol by dip coating method. The influences of preparation condition, pH of sol on TiO_2 nanostructure coating were investigated. Their structural properties were examined at various calcination temperatures. The effect of drying cycle and solvent bath on crack reduction and the influence of withdrawal speed on thickness of the film was evaluated. Choosing of alcohol as a drying atmosphere could hinder the cracks formation. 400°C was desirable temperature to obtain nanoparticles from anatase phase. At this temperature it was found that TiO_2 films exhibited a uniform anatase structure with particle size of about 15 nm. Prog. Color Colorants Coat. 2(2009), 71-78. © Institute for Color Science and Technology.

1. Introduction

Recently titanium oxide (TiO_2) thin films have been investigated with regards to their remarkable optical, electrical and photo electrochemical properties.

A number of methods have been employed to fabricate TiO_2 films, including e-beam evaporation [1], sputtering [2], chemical vapour deposition [3] and sol-gel process [4]. Among these methods the sol-gel process is one of the most appropriate techniques to prepare thin film. The preparation of TiO_2 film on different substrates using several deposition techniques have been studied in [5, 6]. Different applications of these coatings are related to photo catalytic property, band gap and electrical structure of titanium oxide.

Crystalline TiO_2 exists in three phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [7]. In case of photo catalytic efficiency, anatase is superior to the rutile [8].

In this work, uniform and nanocrystalline TiO_2 thin films were prepared on 316 L stainless steel by sol-gel method. To hinder micro cracks and to achieve uniform coating, the drying process of coatings was controlled. Effects of pH value of sol, calcinations temperature and withdrawal speed on structural properties were investigated.

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2. Experimental

TiO_2 sol was prepared from Tetra-n-Butyle Titanat (TBT) ($C_{16}H_{36}O_4Ti$, Merck, ~ 99% purity) as starting material according to the following process: 91 mole % of ethanol (C_2H_5OH, Merck, ~ 98% purity) and 2 mole% of ethyl aceto acetate (EAcAc) ($C_6H_{15}O_3$, Merck, 99.8% purity) were mixed at room temperature and then 4 mole% of TBT was added. The solution was continuously stirred for 8 hours. Within the first 1 hour, 3 mole% of deionised water was carefully added to the obtained solution for hydrolysis. The solution was aged for 24 hours to complete the reactions. In order to achieve stable sol from TiO_2 nanoparticles and to avoid precipitation in the solution; the mixing condition was changed. To investigate the effect of pH on homogeneity and particle size, sols with different pH values were prepared by adding HCl and NaOH.

The 316 L stainless steel specimens (20×15×5 mm^3) were prepared before dip-coating. The specimens were ground with No. 80 to 1500 emery papers, and then polished with 0.3 and 0.05 µm Al_2O_3 powder. Finally the surface of specimens were cleaned by ethanol and acetone. The TiO_2 coatings were formed on the steel substrate by the dip-coating method at room temperature. Coating of specimen was performed at different withdrawal speeds (about 3, 10, 15, 25 cm/min) using dip-coater to investigate its effect on the thickness of coating. After natural drying in air flow, the samples were heated in an oven at 150°C for 30 minutes. Then the specimens were heat-treated in the temperature range of 350-550°C for 1 hour in a programmable furnace with increasing temperature rate of 5 °C/min to remove organic residuals. During the drying process, removal of solvent led to formation of crack defects. In order to eliminate crack defects in coatings, samples after dipping were dried in solvent bath to reduce the rate of solvent removal. Solvent bath was prepared using ethanol as a solvent, and samples were dried at the top region of the bath, under the pressure of ethanol vapour atmosphere.

The X-Ray Diffraction (XRD) traces for TiO_2 coatings at different calcination temperatures and pH values were obtained. The used X-Ray diffraction system was with CuK_α crystal radiation (λ= 1.5406 °A) scanning at a rate of 1° min^{-1} for 2θ ranging from 10° to 70°. The effect of calcination temperature and pH values on microstructure and morphologies of the TiO_2 films were analyzed by the scanning electron microscopy (XL30, Philips). Thicknesses of the films at different withdrawal speeds were taken by AFM and the thickness analyzer (elcometer 355).

3. Results and discussion

Figure 1(a) shows the Optical Microscopy (OM) image of TiO_2 coating surface after dipping and natural drying under flow of air. The image of this specimen after drying in oven is showed in Figure 1(b). In both of these images, cracks are evident, which indicate that the cracks formed before drying up the specimens in the oven. this might occur during natural drying, due to removal of solvent at high speeds. In order to prevent crack formation and achieve uniform and homogenous TiO_2 films, the specimens were dried in the solvent (ethanol) bath to reduce the rate of solvent removal.

Figure 2 shows the optical microscopy image of TiO_2 film after drying under controlled conditions. From this image it is clear that crack defects can be eliminated by drying in solvent bath. In this case, increasing solvent vapour pressure in the bath, would lead to reduction in the rate of solvent removal.

Figure 3 illustrates the XRD trace of the TiO_2 thin films calcined for 1 h in air at various calcination temperatures; from 350 to 550°C (all samples prepared using natural sol). As shown in the XRD peaks, the anatase phase is forming in the TiO_2 thin films at 350°C. From the results; as the temperature is raised up to 550°C, the intensities of the anatase peaks increases, implying an improvement in crystallinity. The crystallite size of TiO_2 thin films can be deduced from scherrer equation [9].

$$D = \frac{k\lambda}{\beta Cos\theta} \qquad (1)$$

Where D is the crystallite size of TiO_2 thin films, k, is a constant (0.94), λ is the wavelength of x-ray (CuKa=1.5406 A°), β is the true half-peak width, and θ is the half diffraction angle of the centred of the peak in degree. The results are shown in Figure 4 that as temperature increases, the TiO_2 crystallites grows.

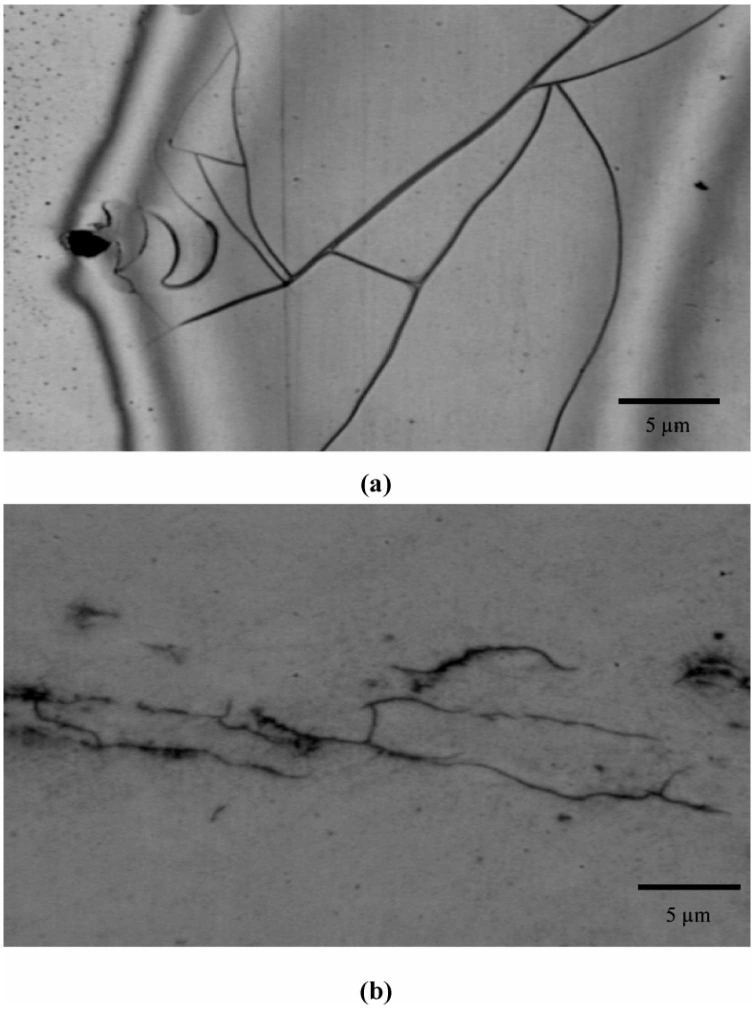


Figure 1: OM images of coated samples after drying up under air flow, (a) before drying in oven (b) after drying at oven (150°C).

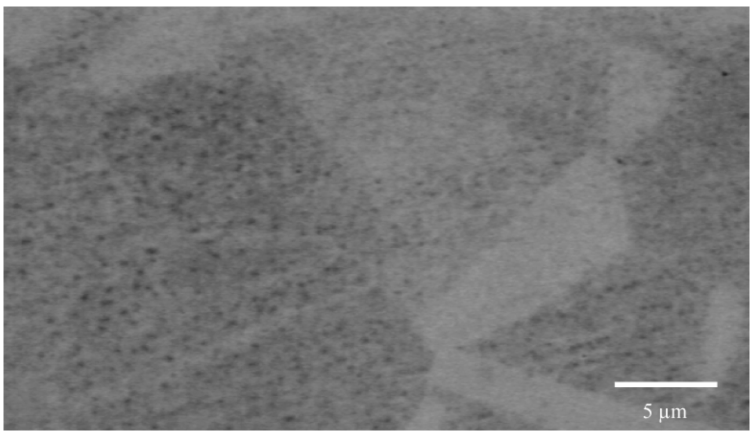


Figure 2: OM image of coated sample after drying in controlled conditions (solvent bath).

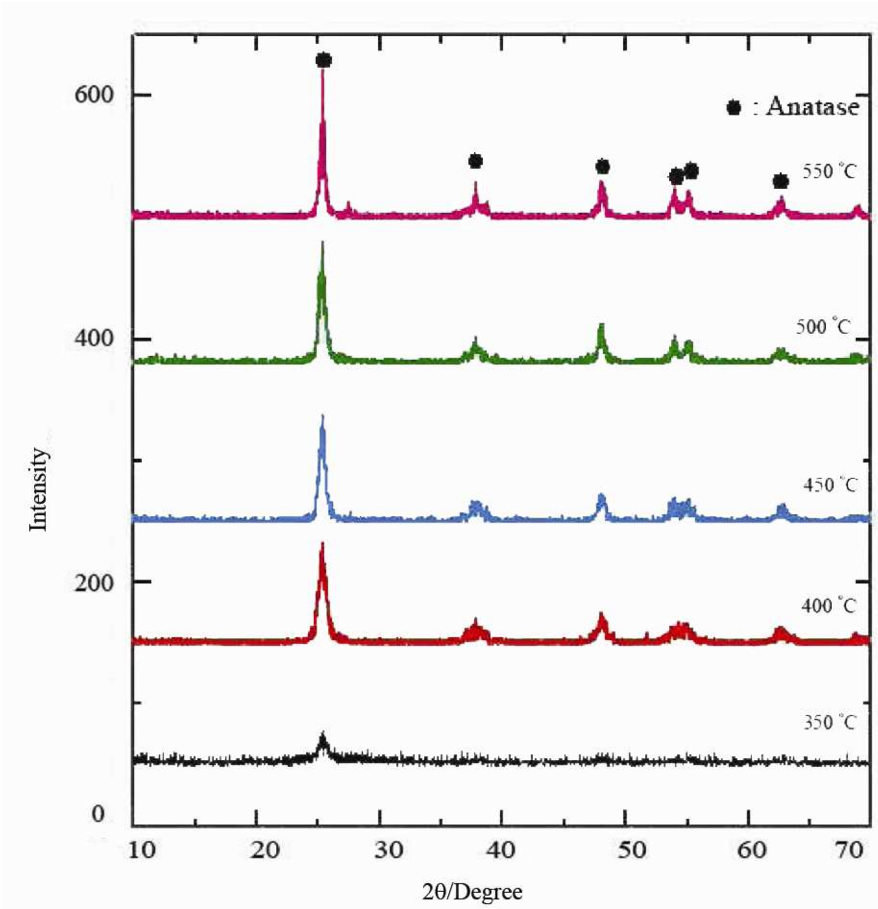


Figure 3: XRD traces of the TiO_2 thin films calcined at different temperatures.

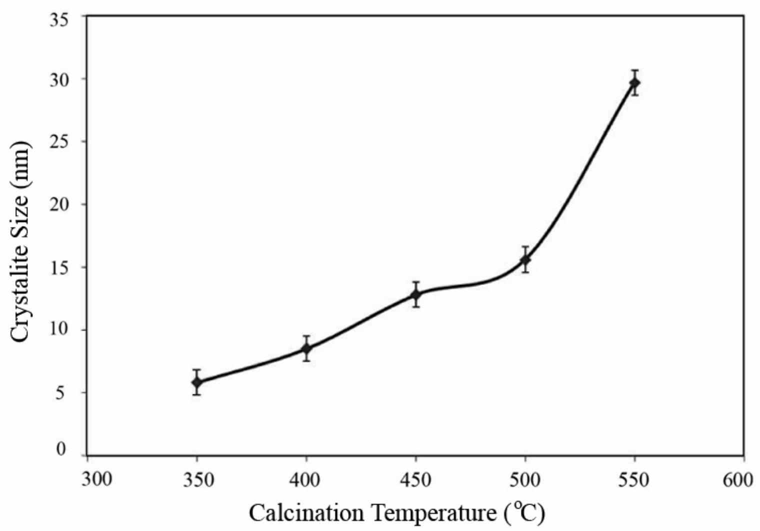


Figure 4: Crystallite size of TiO_2 films at different temperatures.

SEM micrographs of the TiO_2 thin films calcined at various temperatures are shown in Figure 5; where the all fabricated films were uniform and prepared using natural sol. Even though the film calcined at 350°C was in anatase phase according to the crystallite size obtained from XRD trace. In Figure 5(b) the degree of crystallinity of the film calcined at 400°C can be seen. In Figure 5(c) the film calcined at 450°C is composed of particles of about 90-100 nm in size. As the calcination temperature increased to 550°C, the films shifted into the agglomerated state as a result of the densification. It is recognized that 400°C is the best calcination temperature in achieving nanocrystalline anatase phase.

Figure 6 illustrates the SEM images of TiO_2 thin films which are grown on 316 L stainless steel substrates at different pH values with the same calcination temperature (400°C) In Figure 6(a) the pH value of the sol is about 2.3; in this image it is difficult to identify the particles in the film, because of existence of small crystallite sizes. As increasing pH values up to 7, from SEM images it is observed that the crystallite size in TiO_2 thin films will be increased.

The phase transformation from $Ti(OH)_4$ to anatase TiO_2 is assumed to be inhibited by excessive adsorption of OH^- ions to the TiO_2 clusters. Here, it is noteworthy that the excessive adsorption of OH^- may inhibit the nucleation of anatase TiO_2 crystalline particles rather than their growth, since the final particle size of anatase TiO_2 increases with increasing pH. Increasing the pH value reduces the precursor which in turn decreases the nucleation rate.

A thickness analyzer (elcometer 355) was used to evaluate the thickness of the prepared films. The relation between the thickness and the withdrawal speed has been investigated. The thicknesses of TiO_2 films versus withdrawal speed graph are given in Figure 7. It is found that the thicknesses of prepared TiO_2 films increase with increasing the withdrawal speed.

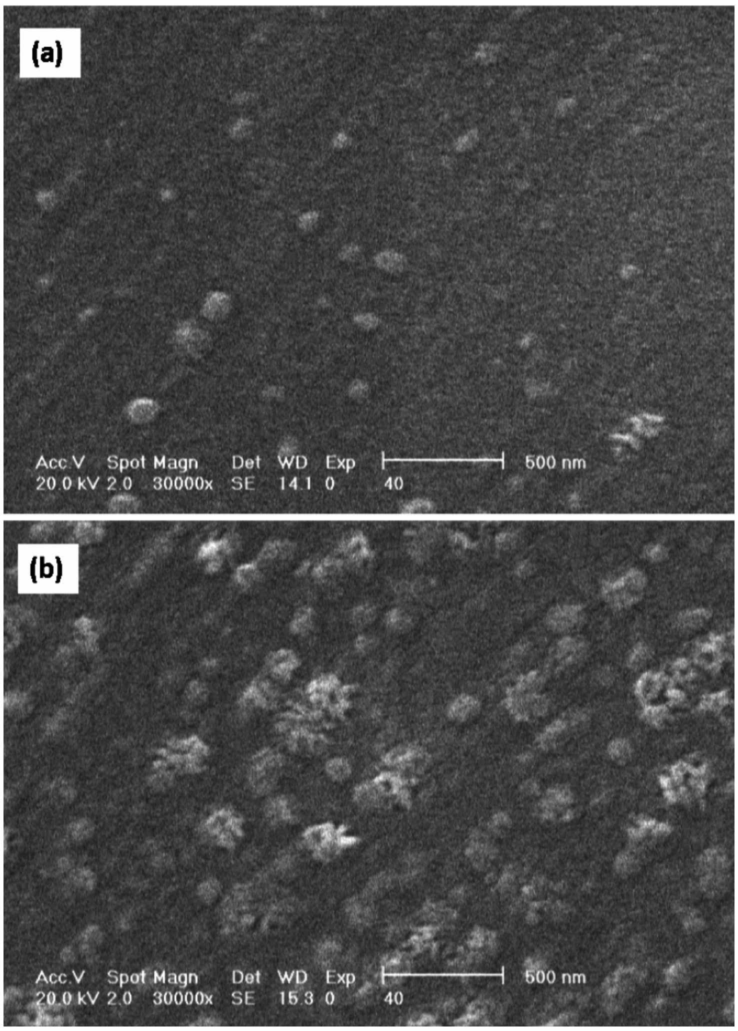


Figure 5: SEM micrographs of TiO_2 thin films calcined at various temperatures for 1 h: (a) 350 °C; (b) 400°C; (c) 450°C; (d) 500 °C; (e) 550 °C.

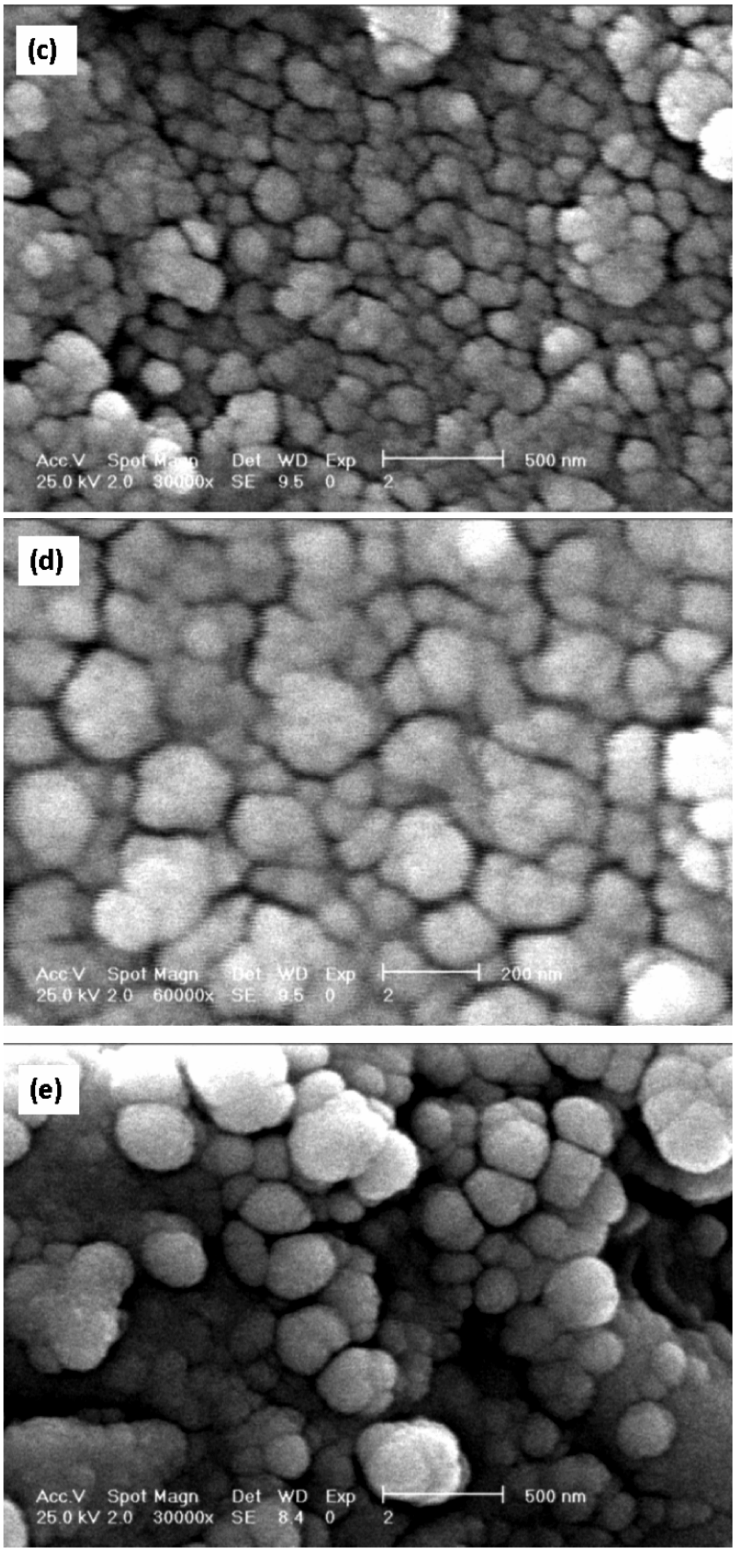
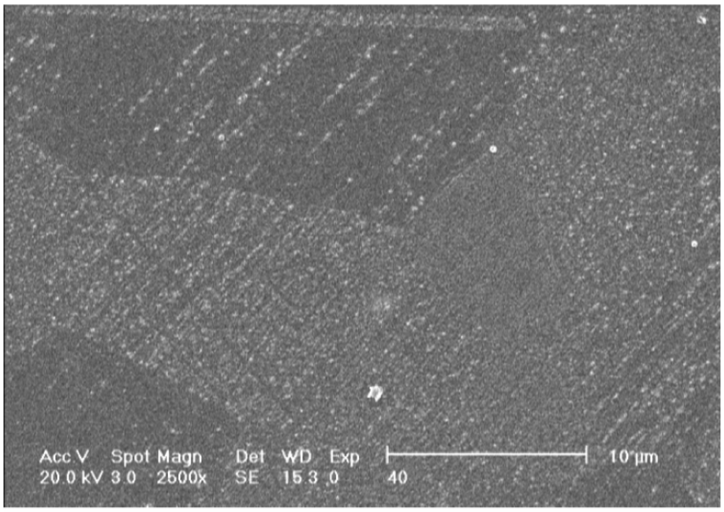
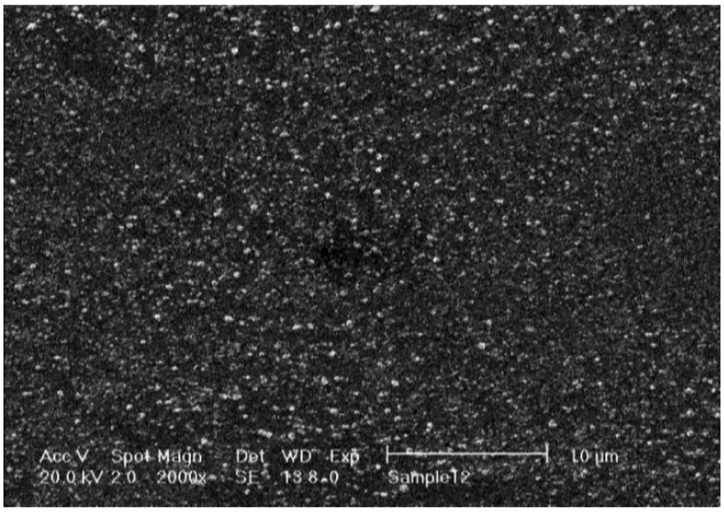


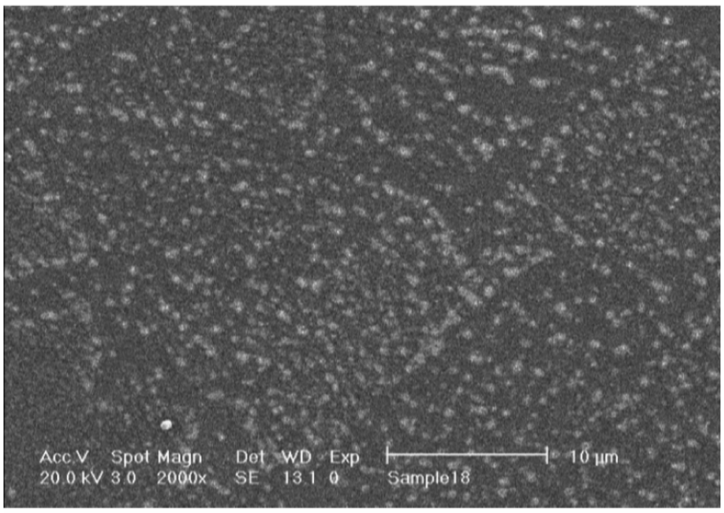
Figure 5: continued.



(a)



(b)



(c)

Figure 6: SEM images of TiO_2 films prepared on 316 L stainless steel substrates at 400°C with different pH values (a) 2.3; (b) 4.5; (c) 7.

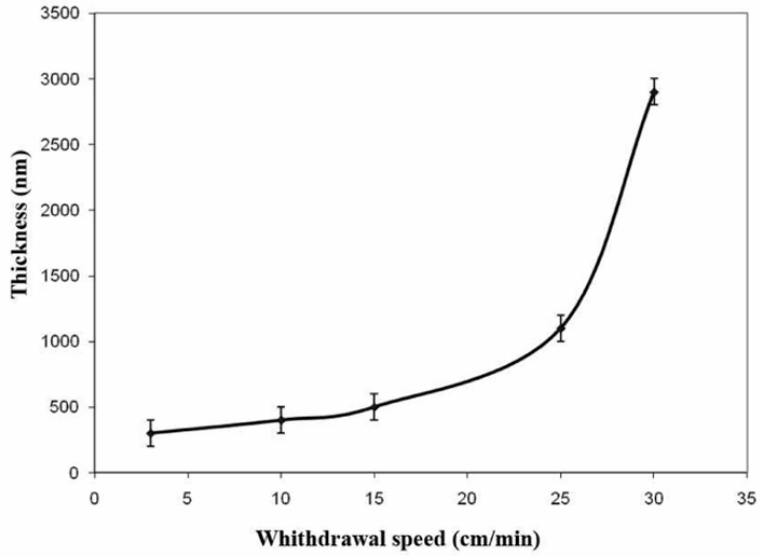


Figure 7: Effect of the Withdrawal Speed on the thicknesses of TiO_2 films calcined at 400°C.

4. Conclusions

We have prepared a uniform and homogenous TiO_2 nanostructure coating on the 316 L stainless steel by the sol-gel method.

In this process the crack formation could be avoided by drying films in a solvent bath. In this case, by the solvent bath the vapor pressure of solvent will be increased and then the rate of solvent removal will be decreased.

The physical properties of TiO_2 thin films are found to be dependent on the preparation condition.

The XRD traces of films which have been calcined at 350-550°C, are anatase.

The surface morphology and crystal structure of TiO_2 films are influenced by calcination temperature and pH values. In an acidic region, the crystallite size decreases by decreasing pH values. This effect can be explained by the change in the nucleation and growth rate which are affected by the amount of OH^- ions.

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