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THERMAL POST-TREATMENT OF TiO_2 FILMS VIA SOL-GEL FOR ENHANCED CORROSION RESISTANCE

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ABSTRACT

Titanium oxide (TiO_2) coatings were deposited on the surface of 316L stainless steel substrates by sol-gel methods. Gel titania was prepared by hydrolysis of a titanium butoxide through a sol–gel process. Uniform TiO_2 coatings have been prepared on stainless steels using a dipping technique and thermal post-treatments at 300, 500 and 700 ^oC. The temperature dependence of the coatings morphology and structure were analysed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The corrosion behaviour of 316L stainless steel substrates coated with densified TiO_2 coatings was studied in 3.5% NaCl by potentiodynamic polarization curves at room temperature. The result shows that as the thermal post-temperature increased, the corrosion rate increased and the corrosion current density decreased gradually. The effect of withdrawing speed of the coatings on the corrosion parameters is also reported.

Keywords: TiO_2, stainless steel, sol-gel, corrosion protection.

INTRODUCTION

Advanced materials have been recognized as crucial factors to the growth of any industry, especially nanomaterials, having potentially the greatest market due to a wide range of product applications. There is a growing need for lighter, stronger and more corrosion-resistant materials, as well as reproducible methods for producing such materials (Šegota *et. al.,* 2012; Shapiro *et. al.,* 2007).

An increased resistance of metals and alloys to corrosion is generally obtained by the formation of a protective layer isolating the substrate from the surrounding oxidant atmosphere. A variety of protective ceramic coatings, such as nitrides, carbides, silicides or transition metal oxides, have been deposited on steel (Bamoulid *et. al.,* 2008). TiO_2 thin coatings possess properties, such as: hardness, chemical stability, resistance to oxidation and wear, biocompatibility, high refractive index, high dielectric constant, good photocatalytic and antibacterial properties (Ćurković *et. al.,* 2013; Hamid *et. al.,* 2003). Thus, TiO_2 are widely applied in electronics, optics, photocatalysis and could be applied in wear and corrosion protection. TiO_2 has three phases: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Anatase and rutile are of engineering importance because their properties are unique. Formation of each crystalline phase depends on deposition method, thermal treatment and sol composition (Hanaor and Sorrell, 2011).

The sol–gel techniques have distinct advantages over the other procedures due to the excellent control over the composition, homogeneity on the molecular level caused by the mixing of liquid precursors, and lower temperature of crystallization. Moreover, the microstructure of the films deposited by the sol-gel process, i.e., the sizes, volume, and surface area of the pores, can be tailored by the control over the variables of the process (Naghibi *et. al.,* 2014; Shanaghi *et.al.*, 2008; Bamoulid *et. al.,* 2008).

Currently, stainless steel is widely used in many applications such as furnace parts, heat exchangers, and tubing that related to heat and also for marine application. There are a highly demands for stronger, more corrosion resistant and lighter materials as well as reproducible methods for producing such materials. But, fouling deposition and localized corrosion on the heat-transfer surfaces or marine application of the stainless steel equipment often simultaneously exist, which can introduce additional thermal resistance to heat-transfer and damage equipment surfaces (Ahmad, 2006). A protective coating deposited to act as a barrier between the surfaces of the component and the aggressive environment that it is exposed during operation is now globally acknowledged to be an attractive means to significantly reduce damage to the actual component by acting as the first line of defense (Satapathy, 2005). Type 316L stainless steel was chosen taking into account the heat treatment necessary for the densification of the coatings. Therefore, low carbon content steel was judged more convenient since it is less susceptible to sensitization which might promote an enhanced corrosion. In addition, 316L stainless steel is a material widely used in chemical industry environments.

The present work had two objectives: (i) to study the influence of the thermal post-treatment on the morphology; (ii) to evaluate the corrosion resistance of titanium dioxide deposits on 316L stainless steel. Structural and micro-structural characterizations of thin films have been realized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The Tafel polarization curves were employed to measure anticorrosion performance of the TiO_2 coatings in 3.5% NaCl solution and to discuss the mechanism of corrosion resistance for the coatings.

MATERIAL AND METHODS

Titanium (IV) n-butoxide ($Ti(O\text{-}n\text{-}Bu)_4$, 95%), absolute ethanol (EtOH), and ethyl acetoacetate (EAcAc) were used as received. EtOH was purchased from HmbG Chemicals and the other chemicals were from Kanto Chemical Co. Inc., Japan. To prepare homogeneous TiO_2 sols, the molar ratio of Ti(O-n-Bu)4/EtOH/EAcAc used was 1:20:1. The solution was stirred at room temperature for 1 h to allow hydrolysis process complete. Sols was kept for 24h before coating.

Plate samples (10 x 10 x 0.5 cm^3) of type 316L stainless steel were used as substrates in this study. Before the deposition of coatings, steel substrates were ground with SiC abrasive discs (240-1200 grit) and then polished with diamond paste (25 μm). Substrates were then ultrasonically cleaned in acetone and subsequently dried. TiO2 thin films were deposited on substrates by dip coating method with different withdrawing speeds. The films coated on the substrates were placed in an oven and dried at 100 ^oC for 30 min. The films were then annealed at various temperatures: 300, 500 and 700 for 1 hour at the heating rate 5 °C/min in an atmosphere. The flow chart of the whole procedure is shown in Figure-1.

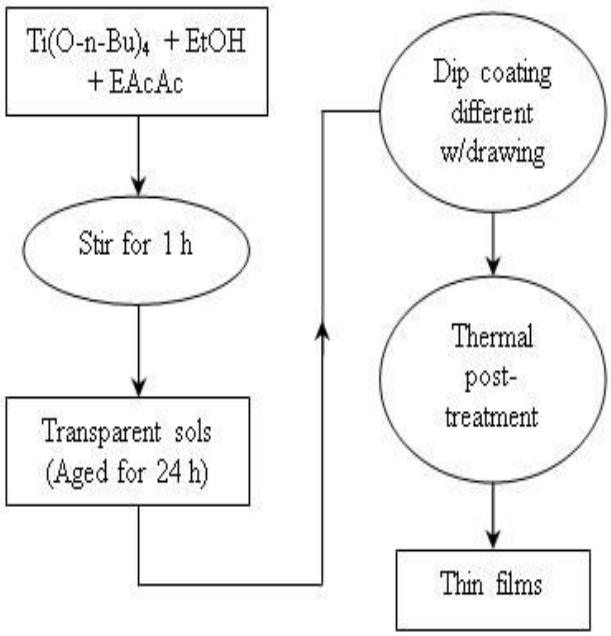

Figure 1. Schematic preparation diagram for sol-gel derived TiO2 films coated on 316L stainless steel.

The crystallinity and phases of the TiO_2 films were characterized by an X-ray diffractometer (XRD, Bruker D8 Advance) using Cu-Kα radiation in the range of 20 to 80^o while the surface morphologies were characterized by scanning electron microscope (SEM, JEOL JSM-6380LA). The corrosion resistance of the coatings was assessed by Tafel polarization tests carried out in 3.5% NaCl solution at room temperature using a potentiostat instrument and IVMAN software in order to analysis. The Tafel curves were measured from 0.5 V below the open circuit potential (E_{oc} −0.05 V) to a potential of up to 1.2 V at the rate of 0.1 mV/s and were started after 5 min immersion of samples in the solution.

RESULT AND DISCUSSIONS

Phase Analysis on TiO_2 films coated 316L stainless steel

Figure-2 illustrates XRD patterns of the TiO_2 coating prepared by dip coating under various withdrawing speeds and thermal post-treatment. The sharp diffraction peaks are in good agreement with those given in JCPDS data cards (JCPDS No.78-2485 and 78-2486) for TiO_2 anatase and rutile phase.

Based on Figure-2, the XRD patterns for temperature 300 °C does not show any peak and indicates that the TiO_2 were amorphous at this temperature (Yan and Chunwei, 2006). There is an anatase peak observed at temperature 500 °C. It is commonly accepted that high temperature calcination, at least at 400 °C is required to obtain anatase TiO_2. It is also had been acknowledged that TiO_2 had been known to have the existence of the crystalline phases of anatase and rutile. Thus, by studying the characteristics of the TiO_2 through XRD, the TiO_2 thin film possessed evident diffraction peaks characteristics of anatase. It showed the major anatase peaks at 26.5°, 44.1° and 75.6°. There is also some rutile peaks started to grow at peak 64° and 65.5°. Anatase phase has good stability and corrosion protective characteristic on metals. In addition, quality control of anatase phase was easier compared with rutile phase at 700°C. In general, the crystallization of TiO_2 films followed as: anatase → anatase + rutile → rutile, when thermal post-treatment temperature was increased from 300 to 700 °C (Naghibi *et. al.,* 2014; Yan and Chunwei, 2006).

In addition, the thermal post-treatment temperature obviously influences the crystallization and phase composition of the TiO_2 thin film. The intensities of the anatase peaks increases, implying an improvement in crystallinity. This had been proven by Wang, *et. al.* (2012), as the thermal post-treatment temperature is increasing, XRD reflections corresponding to both the anatase and rutile phase become narrower, which indicates the increase of crystallite size. However, when increased to higher temperature (600°C to 800 °C), anatase to rutile transformation could be seen clearly. The intensity of the peaks was decreases with the increase of withdrawal speed. It is because of more nucleation growth on the surface when the withdrawal speed increased (Wang, *et. al.* 2012). Therefore, it can be conclude that the rutile phases exist at a higher calcined temperature but with lower intensity range.

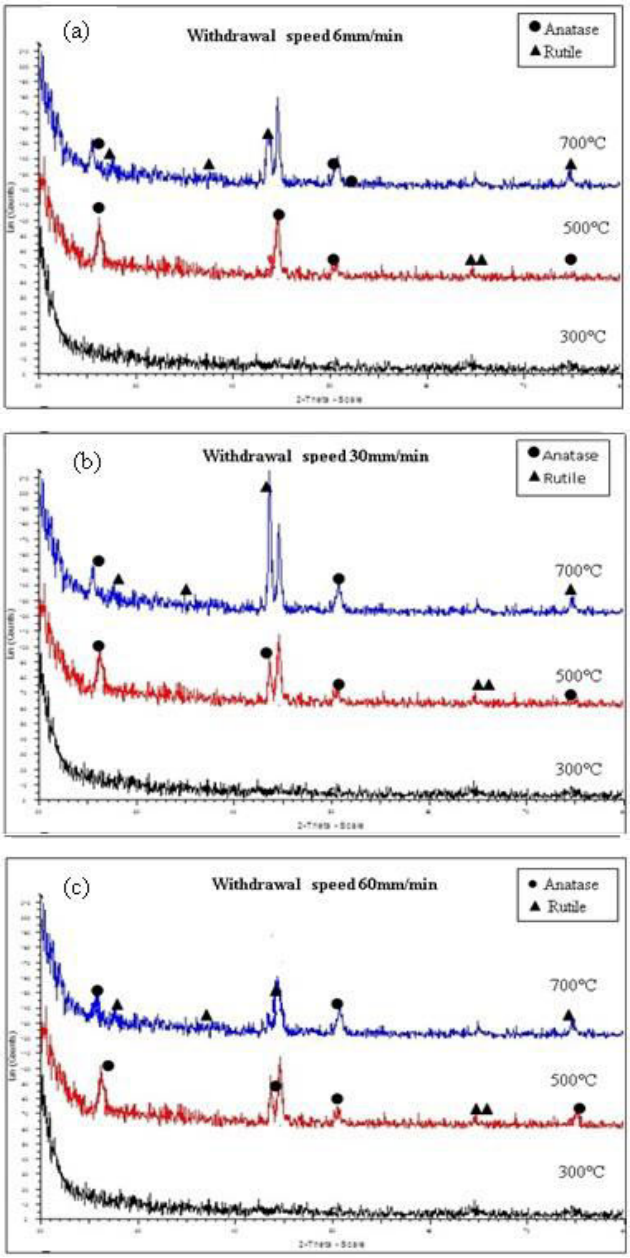

Figure-2. Illustrates XRD patterns of the TiO_2 coating prepared by dip coating under (a) 6 mm/min, (b) 30 mm/min, (c) 60 mm/min withdrawing speeds and various thermal post-treatment.

The crystallite size of TiO_2 thin films can be deduced from Scherrer equation:

$$D = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

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 centered of the peak in degree (Ainuddin and Idris, 2015). The results are show in Figure-3(a) that as the temperature increases (Kaewwiset *et. al.,* 2008; Yan and Chunwei, 2006) and Figure-3(b) as the withdrawing speed increases (Barati *et. al.,* 2009) the TiO_2 crystallite grows.

Morphology observation

To evaluate the corrosion resistance of the TiO_2 films coated on the 316L stainless steel, the test in 3.5% NaCl solution was carried out. The SEM micrographs of the TiO_2 thin films thermal post-treatment at various temperatures and withdrawal speed before corrosion are shown in Figure-4; where all the fabricated films were uniform and prepared using natural sol. The SEM images at 300 °C do not show any crystallinity growth since at this temperature films still in amorphous phase.

However, as the temperature increased to 500 °C, the film shifted into the agglomerated state as a result of the densification. It is also recognized that 500 °C is the best thermal post-treatment temperature in achieving crystalline anatase phase. It is observed that at temperature 500 °C, the particles formed in different shape and size. This may due to the insufficient temperature for its homogenation. Whereas, when the thin film thermal post-treatment at 700 °C, it can be seen that larger crystallite are broken down to a smaller one. This causes relatively homogeneity. The particles are also finely divided at temperature 700 °C. This has be proven by Shailesh *et. al.* (2011), as the temperature increased, the crystallite will result in better homogeneity and fine grains. The crystallite grain size also increased as the thermal post-treatment temperature increased that matches with previous studied investigated by Barati, *et al.* (2009).

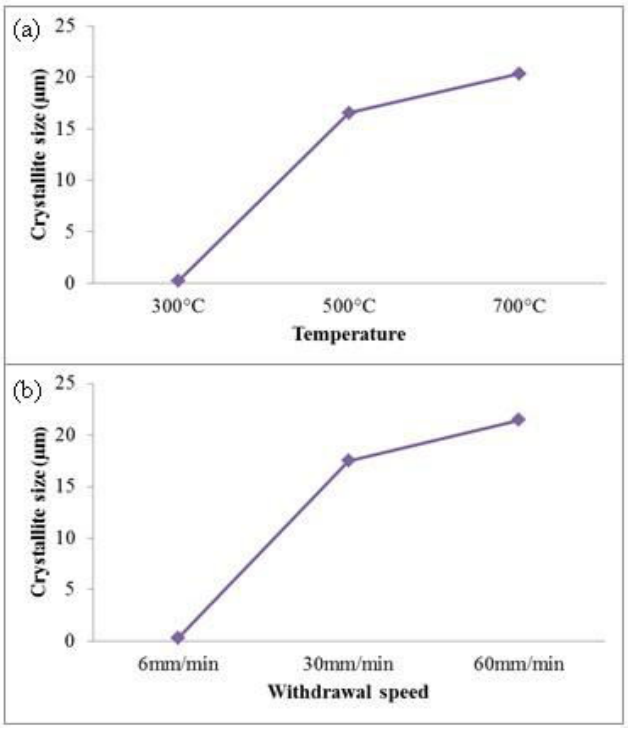

Figure-3. Crystallite size of TiO_2 films at different (a) post-treatment temperature and (b) withdrawal speed.

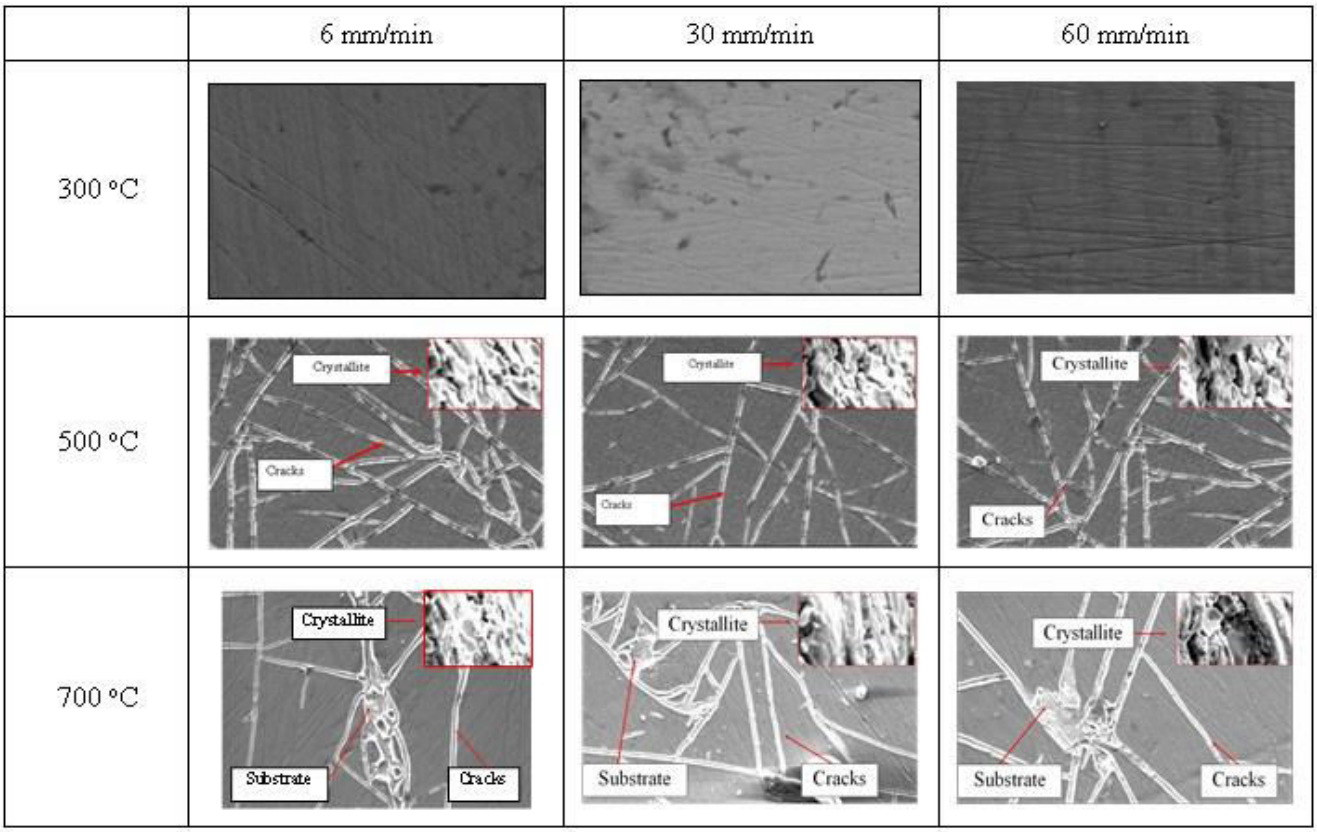

Figure-4. The microstructure of SS 316L coating with TiO_2 before thermal post-treatment.

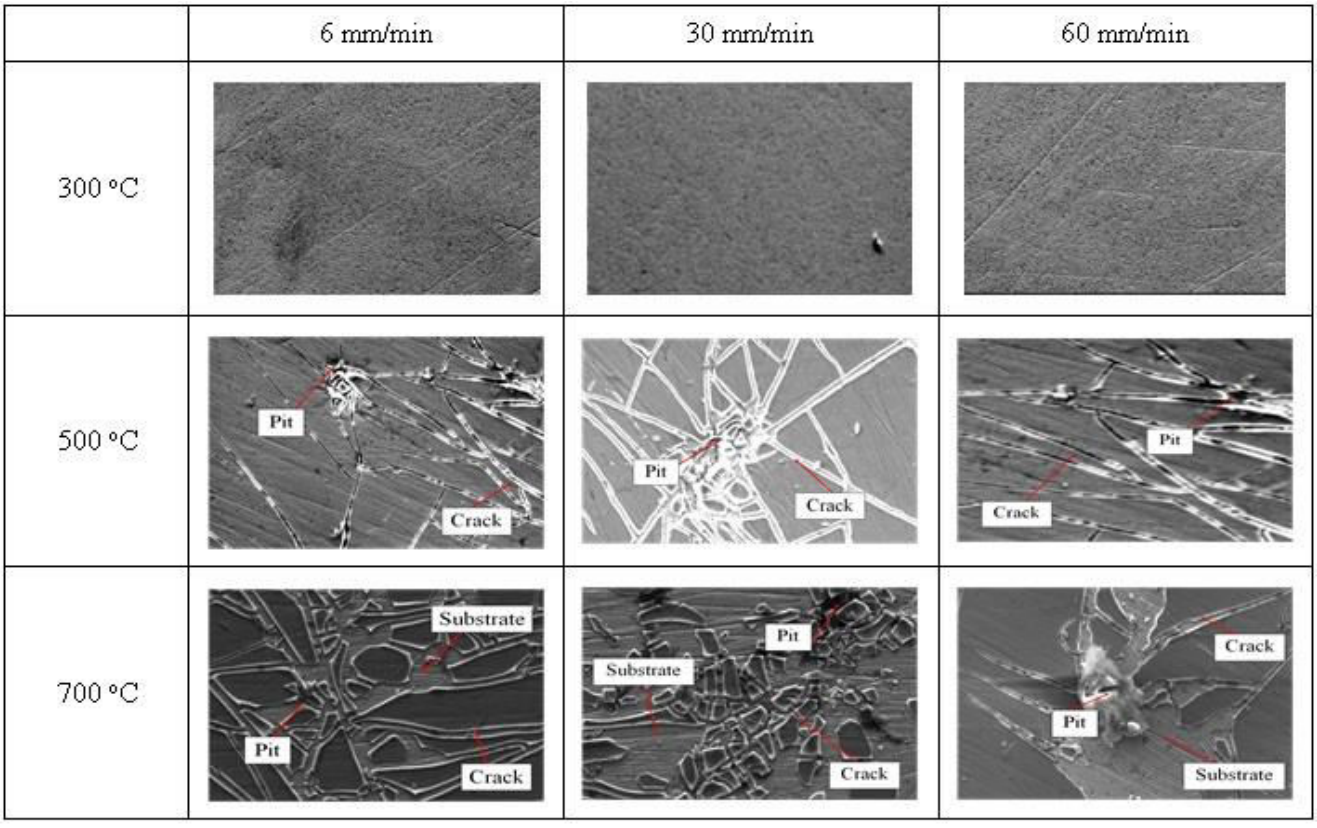

Figure-5. The microstructure of SS 316L coating with TiO_2 after thermal post-treatment.

Based on Figure-5, the specimen after corrosion shows that at temperature 500 °C, the thin film coating starting to crack at some area. Therefore, there are some pitting corrosion exist but not too much. The specimen at 700 °C shows that there are some cracks on thin films which exposed the sample to corrosion attack. The crack at sample thermal post-treatment at temperature 500 and 700 °C are due to the increasing of withdrawal speed that reduced the thickness of coating at this high annealed temperature (Shailesh *et. al.,* 2011). However, the corrosion rate of this SS316L still in outstanding condition.

Test of corrosion resistance

Table-1 shows the measured values of I_{corr}, E_{corr}, E_b, E_{pp} and corrosion rate indicating the pitting corrosion resistance of the films. Based on potentiodynamic plot, all samples gives outstanding in corrosion resistance under this condition. Value of I_{corr} and E_{corr} can be determined by extrapolated linear sections from the anodic and cathodic curves of potentiodynamic plot. The I_{corr} values impart the following data which is the higher value of I_{corr} indicates metal possesses less corrosion resistance under the polarization resistance status and lower values of I_{corr} show material had better corrosion resistance at certain condition (Shailesh *et. al.*, 2011). It can be seen that the position of polarization curves for TiO_2 coated shifts towards the positive direction.

The values of the I_{corr} of the thermal post-treatment coated samples at temperature 300 °C show the lowest value. This indicates that heat treatment at 300 °C obviously improve the pitting corrosion resistance of the TiO_2 coating. From the results of potentiodynamic polarization scans, it should be noted that the pitting corrosion resistance of TiO_2 coating heat treated at 300 °C is the best among the thermal post-treatment coatings. It can be predicted that improvement of the pitting corrosion resistance of TiO_2 may correlate to the microstructure of TiO_2 obtained after heat treatment at 300 °C. As can be seen on the XRD results, the surface topographies and phases of the thermal post-treatment coatings indicates that the amorphous microstructure of the coatings after heat treatment is beneficial for improving their pitting corrosion resistance in contrast to the crystallized TiO_2.

The obtained result can be conclude that as thermal post-treatment temperature increased, the corrosion rate increased and the corrosion current density decreased gradually. This was related to the reduction in porosity and better bonding between particles which led to the blocking of the penetration route to the corrosive solution. It can be seen that at heat treatment temperature 500 °C and 700 °C, the TiO_2 particles begin to crystallize and to lose its amorphous character. At higher temperature, the particles are conglomerate and had caused a severe reduction in corrosion resistance. Other than that, at high temperature the particles shrink and resulting in cracks through the coating which can expose the substrate to attack.

From the Table-1, it can be seen that the relationship between value of breakdown potential (E_b) and thermal post-treatment temperature. As the temperature of thermal post-treatment increased, the breakdown potential also increased. This indicates that at lower thermal post-treatment temperature, SS 316L have lower tendency to pitting (Shailesh *et. al.,* 2011).

Based on Table-1, corrosion resistance of the coatings was found to decrease with increase in withdrawal speed for all specimens from 6 mm/min to 60 mm/min. The increase in withdrawal speed involves a thickening of films and some cracks appear for the thicker coatings. Therefore, it will expose the substrate to corrosion attack.

Table-1. Comparison of corrosion rate SS 316L coating with TiO2 at different calcined temperature and withdrawal speed.

Temp.	With-drawal speed (mm/min)	*OCP*	E_{corr} (mV)	I_{corr} (mA)	E_b (V)	E_{pp} (V)	Corrosion rate (mpy)
300°C	6	-220	-215	0.4164	-0.06	-0.12	0.1708
	30	-310	-301	0.0064	-0.05	-0.14	0.0026
	60	-400	-399	0.0036	-0.01	-0.29	0.0015
500°C	6	-230	-229	0.4796	0.50	0.20	0.1967
	30	-300	-261	0.0089	0.55	0.40	0.0035
	60	-70	-64.9	0.0043	0.59	0.71	0.0018
700°C	6	415	409	0.5851	1.00	0.09	0.2399
	30	410	400	0.4273	1.05	1.10	0.1752
	60	100	99	0.0049	1.95	1.20	0.0020

CONCLUSIONS

The work presented in this research deals with experimental and theoretical studies related to titanium dioxide (TiO_2) thin films. The main purpose of this research is to prepare the TiO_2 sol gel coating on 316L stainless steel with the effect of withdrawal speed and heat treatment. The parameters used in this study are thermal post-treatment temperature (300, 500 and 700 °C) and withdrawal speed (6, 30 and 60 mm/min). The coatings were obtained by the sol-gel method. The characteristics of the TiO_2 sol-gel coating on 316L stainless steel were investigated using XRD and SEM. Then, corrosion behavior of the sample was obtained by electrochemistry test. The coating was examined in 3.5% NaCl at room temperature (25±0.2°C). The result shows that as thermal increased, the films particles become more compact and also the grain size become more distinct.

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