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Morphology evaluation of ZrO₂ dip coating on mild steel and its corrosion performance in NaOH solution

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Abstract. In this work, the morphology of ZrO₂ thin film from dip coating process on mild steel has been investigated. Mild steel was dip-coated on solution made of zirconium butoxide as a precursor, ethanol as solvent, acetylacetone as chelating agent and water for hydrolysis. Number of dipping was adjusted at 3, 5 and 7 times. The dipped sample then annealed at 350°C for two hours by adjusting the heating rate at 1°C/min respectively. The optical microscope showed that micro-cracks were observed on the surface of the coating with its concentration reduced as dipping sequence increased. The XRD result showed that annealing process can produce polycrystalline tetragonal-ZrO₂. Meanwhile, SEM image showed that the thicknesses of the ZrO₂ coatings were in between 400-600 nm. The corrosion resistance of uncoated and coated substrates was studied by polarization test through potentiodynamic polarization curve at 1mV/s immersed in with 3.5% NaCl. The coating efficiency was improved as the number of layer dip coated increased, which showed improvement in corrosion protection.

1. Introduction

Mild steel has been used in many engineering fields such as tooling, construction and transportation. It has an important role as it shows characteristics of high mechanical strength and ductility. However, mild steel do exhibit disadvantages, such as chemically unstable and corrosion happened on it easily. This deterioration may effect on premature and sudden failure with the risk of maintenance cost, unscheduled downtime, and lifetime. Several methods have been used for to protect mild steel from corrosion, such as coatings, cathodic protection, and inhibition [1-4].

Ceramic based coating was known as type of coating, which not only can improve corrosion resistance of metals, but also it can increase wear and erosion resistance and also provide thermal insulation [5,6]. Zirconium oxide is a type of ceramics materials that used largely for its excellent properties such as high hardness and good chemical stability and inertness [7-10]. It also known as ceramic material with thermalexpansion coefficient close to steel, which can reduce cracking during thermal treatment [11]. Furthermore, sol-gel technique was chosen to deposit ceramic coatings as it



provide several advantages, such as produce good homogeneity coating, can accommodate complex shape and low annealing temperature [12,13].

In this work, ZrO_2 coating was prepared using zirconium butoxide as a precursor. The coating was applied on mild steel substrate through dip-coating method at different dipping sequence followed by annealing at $350^\circ C$. The structure of the coating was characterized by optical microscope, XRD, and SEM/EDX. The corrosion test for the coated substrates were carried out to find out their performance as protection against corrosion using potentiodynamic polarization in 3.5% NaCl. It is expected that ZrO_2 sol-gel dip coating can improve the corrosion performance of mild steel.

2. Experimental Procedure

2.1 Sample and solution preparation

Figure 1 shows the mild steel sample used in this experiment. The steel was mechanically cut into half-rounded shape using electrical discharge machining (EDM) with thickness of 5 mm and diameter of 16 mm. For dip-coating purpose, 1 mm hole was drilled on the top of the sample. After that, the sample was polished by emery paper until 800 grit and ultrasonically cleaned by acetone.

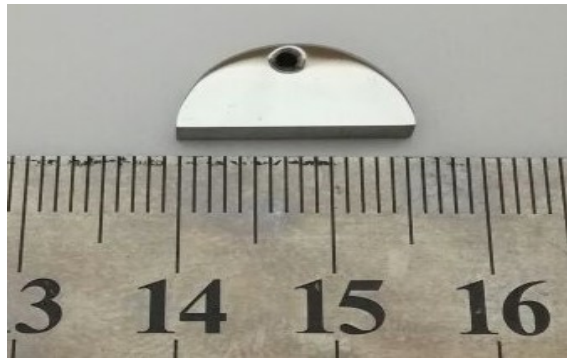


Figure 1. Mild Steel Substrate.

For sol-gel solution, zirconium (IV) butoxide, ethanol, acetylaceton, and distilled water were prepared at fixed molar ratio of: 1.25:20:1:3.2. Zirconium (IV) butoxide is a precursor, ethanol act as solvent, acetylaceton act as chelating agent, and distilled water for hydrolysis. First, zirconium (IV) butoxide and ethanol were mixed and stirred at room temperature using magnetic stirrer for 30 minutes. Then acetylaceton was added to the mixture continued to stir for another 30 minutes. Distilled water then added to continue the for another 30 minutes.

2.2 Sol-gel dip coating process

The sol-gel dip coating process was conducted on PTL-MM01 Dip Coater. The substrates were dip coated for 3, 5 and 7 number of coatings. The parameters of the dip coater was set as followed; travel distance of 35 mm and immersion speed of 20mm/s at room temperature. The substrates were fully immersed in zirconium oxide solution for 1 minute after which air dried for another 2 minutes. These steps were repeated according to the number of coatings of each substrate. Once the deposition of the coating was completed, the substrates were thermally treated. During this phase, excess organic compounds found on the surface of coated substrates will evaporate. The substrate then annealed at $350^\circ C$ for two hours by adjusting the heating rate at $1^\circ C/min$.

The morphology and thickness of coated substrates were examined using optical microscope and SEM (back scattered emission gun), while the chemical composition was studied using EDX. The SEM was equipped with a detector for energy dispersive X-ray analysis (EDX) and conducted at 15 kV. The X-ray diffraction (XRD) Rigaku Miniflex using detector $CuK\alpha$ amp radiation at 30 kV and 15 mA. The diffractogram was obtained at scanning range 20 -70 degrees at scan step of 0.02 degree.

2.3 Corrosion testing

The rates of corrosion of the coated substrates were tested using electrochemical corrosion test. Electrochemical corrosion behaviours of ZrO_2 films were investigated using potentiostat to determine the corrosion protection efficiency of ZrO_2 coating in 3.5 % NaCl solution. Three electrodes were used to setup the electrochemical reaction, namely; platinum foil as a counter electrode, saturated calomel electrode (SCE) as a reference electrode and substrate as working electrode. At a scan rate of 1mV/s, the experiment was carried out to reach the required equilibrium. The scanning range for voltage was set between -1.0 to 1.5 volt. The open circuit potential (OCP) was measured for 2 minutes to confirm the condition equilibrium prior to obtaining the potentiodynamic polarization curve.

3. Results and Discussion

The surface morphology and quality of the resulting ZrO_2 coatings was investigated using an optical microscope. Minor cracks were observed on the surface of the substrates under the microscope, as shown in Figure 2. More cracks were observed in the area close to the hole of the sample, meanwhile, less visible cracks were observed in the substrate with 7 times coatings compared to 3 times coating. These cracks may come from contamination of the solution due to environmental impurities and undeveloped dip coating technique which lacks control and consistency [14, 15].

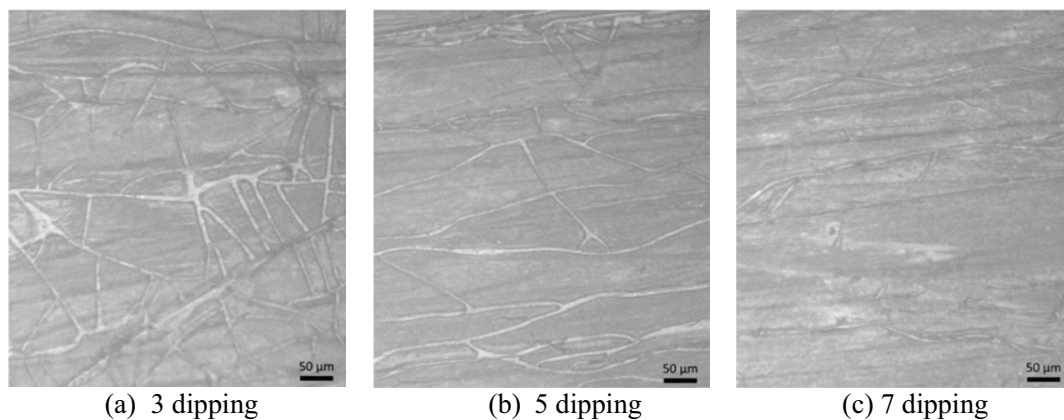


Figure 2. Optical microscopic images of the coated substrates at different number of dipping.

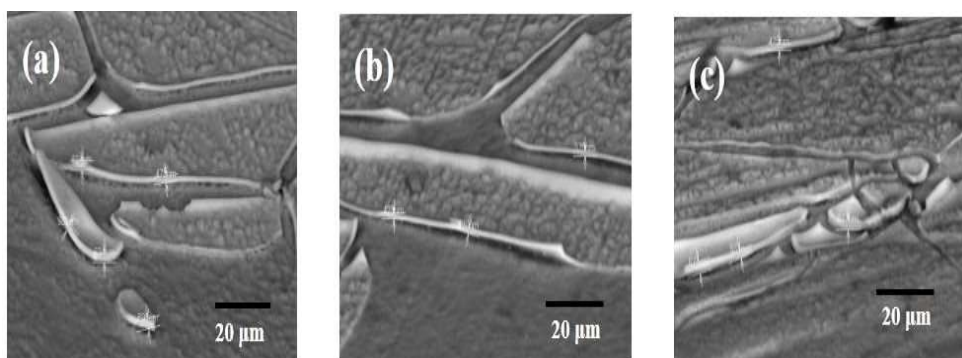


Figure 3. Thickness of ZrO_2 from different dipping time: (a) 3 dipping, (b) 5 dipping, and (c) 7 dipping.

Figure 3 shows the SEM images of ZrO_2 thin films from different dipping time. Cracks were clearly observed from all dipped sample, as has been shown in optical microscope. Thicker ZrO_2 was clearly shown by 5 and 7 dipping, as compared to 3 dipping. The thicknesses of coating were measured at several points and the average thickness of the coating was shown in Figure 4. From the

graph, it was understood that the thickness was almost proportional to the number of coatings. Somehow, the change from 5 dipping to 7 dipping was not significant. The thickness for each dipping time are: 3 dip = 409 ± 35 nm, 5 dip = 571 ± 107 nm, and 7 dip = 623 ± 18 nm. The EDX results shows the compositions of the element in all coated substrates consist of Fe, O and Zr. Fe was came from the mild steel substrate, since the ZrO_2 films was very thin, so electron can penetrate to the substrate area.

The characterization of thin film was continued by analysing ZrO_2 powder which were obtain by heating the sol-gel solution at 350°C at rate of $1^\circ\text{C}/\text{min}$ for 2 hours. This work was conducted since ZrO_2 films was too thin so it will be difficult to get the XRD peak for the coating materials. From the XRD result in Figure 5, it was found that the annealing of ZrO_2 was successfully transformed amorphous ZrO_2 into polycrystalline tetragonal ZrO_2 (t- ZrO_2). This result was in a good agreement with the work done by Soo et.al [16].

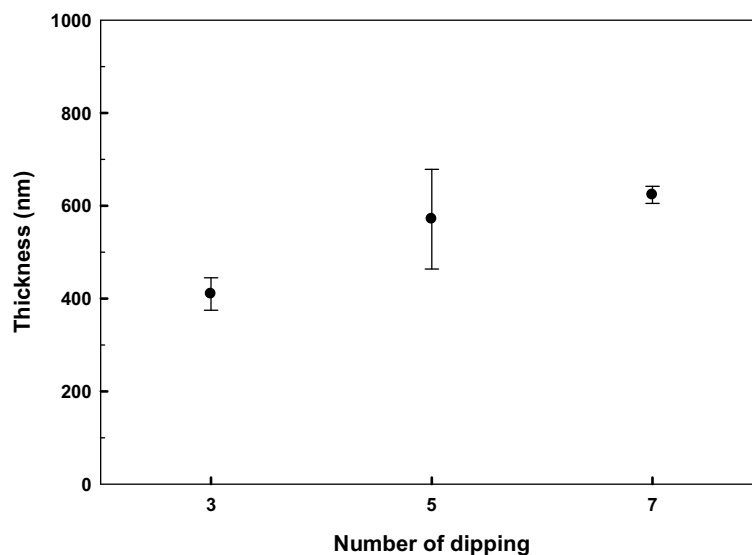


Figure 4. Average thickness of ZrO_2 thin film at different number of dipping.

Figure 6 shows a comparison of potentiodynamic polarization curve between uncoated substrate and coated substrates with different number of coating. It can be observe that all the substrate shows a plateau state for the cathodic reaction, this might be limiting current controlled by O_2 diffusion in the NaCl solutions.

The corrosion current density I_{corr} decreases. Normally E_{corr} can be used to estimate the tendency of the substrates. Based on the data summarized the corrosion current density decreases while polarization resistance increases as the number of coating increases. Based on the discussion can it can be conclude that corrosion resistance of zirconium oxide coating was gradually improved with increasing of number of coatings.

The substrate with 7 number of coating shows excellent corrosion resistance. This is because the quality of the films has an important effect on their corrosion behavior. Structural defects such as major and minor cracks permits corrosion on substrates so that the corrosion was far more serious than the substrates with minimal cracks.

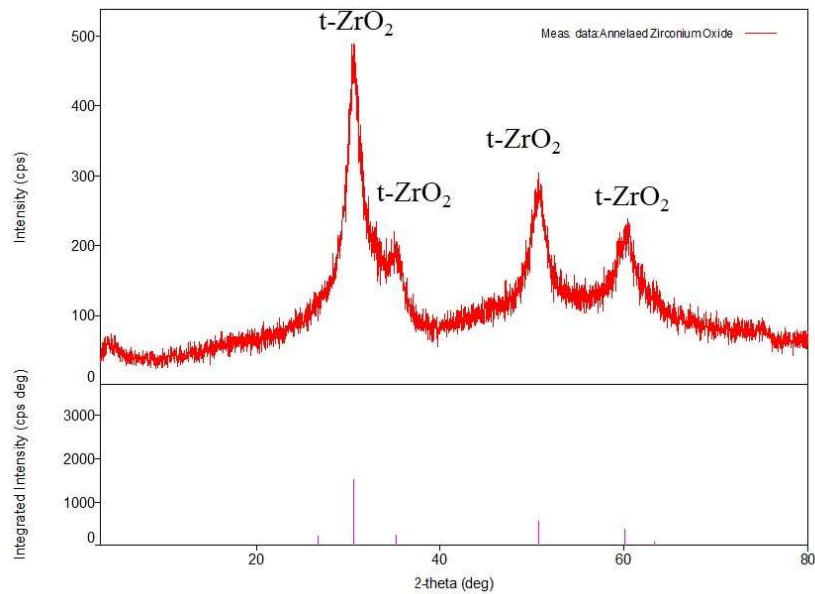


Figure 5. XRD analysis of ZrO₂ anneal at 350 °C with heating rate of 1 °C/min for 2 hours.

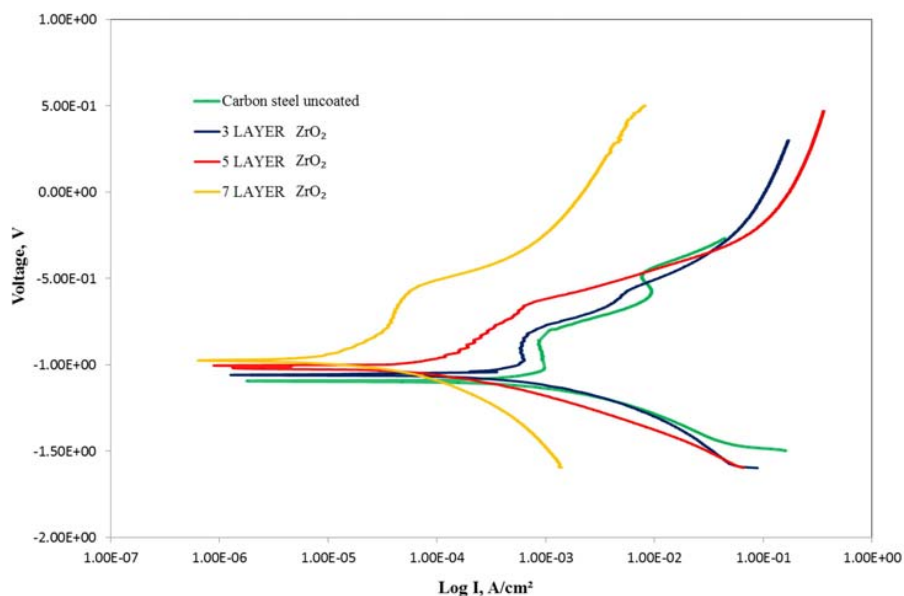


Figure 6. Potentiodynamic polarization curve of coated and uncoated substrates.

4. Conclusions

The morphology of ZrO₂ thin film produced by sol-gel dip coating techniques on mild steel has been studied. The performance of the coating on corrosion protection NaOH has also been investigated. It was found that number of dipping has a strong influence on the crack formation and film thickness. Higher dipping number produce thicker film with lower crack concentration. This properties effect on corrosion performance of the mild steel. The steel coated with higher dipping number produce better corrosion protection. These results confirmed that zirconium oxide coating can be applied as a barrier for the corrosion protection of mild steel.

Acknowledgements

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