Short Communication

An investigation on titania multilayer coatings for enhanced corrosion resistance of carbon steel in simulated seawater by sol–gel dip coating

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\begin{abstract}
A TiO\textsubscript{2} multilayer was investigated to be a low cost and high protection efficiency for carbon steel in simulated seawater. This study applied group theory for crystalline materials in a combination with DFT + U simulation to predict Raman spectra of TiO\textsubscript{2} – anatase and rutile phases. The simulated spectra were used as a peak-search-match reference for experimental Raman spectra. It also indicated that the coatings produced out of polycrystalline structures including anatase and rutile phases with large grain sizes and boundaries. Furthermore, the electrochemical measurements including potentiodynamic polarization and electrochemical impedance spectroscopy for the 1–8 TiO\textsubscript{2} layers were performed to reveal the anticorrosion properties of the coatings and the optimal values were pointed out. Based on those results, the protection mechanism of the TiO\textsubscript{2} multilayer coating was also suggested in the manuscript.

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\end{abstract}

1. Introduction

Corrosion (of metals and alloys) always have a significant effect on the economy, they pollute the environment and are also hazardous to human health and life. This is one of the main factors which can lead to premature failure of infrastructure in critical sectors. Despite of the developments in corrosion resistant alloys over the past few decades, carbon steel still constitutes 99% of the material used in the oil and gas, aviation, building industries as well as in chemical plants and also in water treatment systems due to the most cost-
effective option and easier processing than other alloys such as stainless steel. However, due to poor corrosion resistance in such aggressive environments, the cost savings can only be realized by adding a corrosion inhibitor to the environment [1–3] or by applying a protective coating to the steel [4,5] or using alloying element [6–8]. To prevent the steel corrosion, protective coatings provide the benefits of abrasion resistance, non-stick performance and chemical protection as well as the most widely used corrosion protection coatings in the industry to extreme chemical applications for maximum run life.

Titania has several remarkable properties in different fields. One notable use involves its wide band gap that allows absorption of near ultraviolet light [9]. This absorption is particularly useful when coupled with typically good stability of metal oxides to be the main constitution of sunscreen cosmetic [10]. Titania is also proved to have photocatalytic activities when exposed to UV light by various works on, for example, self-cleaning coating [11–13]. Other uses include pigment, opacifier, decorative coating and more optical applications, notably, with nanofibers [14]. As for functional coating, titania has been a popular material as nanocrystal to create a thin film of possible doping, possibly also doped for more functionality, or as nanoparticle to be incorporated into a composite film. One prominent technology to synthesize titania coatings is chemical vapor deposition (CVD). This method has the advantage of good control over the thickness and composition of the deposited film. Evans et al. [15] found that by varying the precursors and conditions of the deposition process, the phase, thickness and grain sizes can be well determined. Dunnill et al. [16] investigated various dopants on titania thin film for a wide variety of applications. However, for the purpose of this study, the effects of multilayers on roughness are the focus, which does not translate well in CVD where the deposition is done one at a time.

Sol–gel technology is another well-developed approach for titania coatings. Wang and Ying explored the effects of sol–gel synthesis and hydrothermal method on the crystallinity and purity of the obtained titania [17]. In terms of biocompatibility, titania has been shown to be safe with sol–gel synthesis, in combination with calcium phosphate [18] and hydroxyapatite [19,20]. Unexpectedly, titania coatings by sol–gel can be tuned to have hydrophobicity [21] (under the effect of alumina) or hydrophilicity [22] (under the hypothesis of oxygen vacancies). There are various reports on the use of inorganic, organic, and composite coatings to prevent corrosion of steel in various environments, for various purposes [23–25]. Therefore, this work focuses on the effect of TiO2 multilayer coatings on the corrosion protection of carbon steel in simulated seawater using electrochemical and surface analysis.

2. Experimental details

2.1. Chemicals and procedure

All chemicals used in the manuscript were analytical grade, purchased from Merck Millipore Singapore and used directly without purification, all experimental processes were taken in a glove box under ambient nitrogen. From the beginning, the appropriate amounts of tetraisopropyl orthotitanate (TIP, 98% min. purity), diethanol amine (DEA, 99.5% min. purity) and isopropanol alcohol (IPA, 99.5% min. purity) were mixed together to form the 1.0 M precursor solution A, with the TIP:DEA molar ratio in solution A being 1:1. The role of DEA in solution A is to reduce hydrolysis rate of TIP due to the formation of complexes. Besides, the appropriate amounts of deionized water (DIW from Purelab Ultra system) and IPA were also mixed together to form the solution B. Solution A was stirred at 400 rpm for 2 h before being added dropwise to solution B under vigorous stirring of 400 rpm for 2 h forming the sol C, with the final TIP:DEA:DIW:IPA molar ratio being 1:1:2:75. Finally, the sol C was then aged for 24 h in a close beaker under ambient nitrogen to form a gel for the dipping process. TiO2 films were deposited on steel substrates by dip coating method (Holmarc dip coating unit). Dipping process was as following: withdrawal speed (in and out) 18 cm/min, immersion time of 5 s in the gel, drying time of 5 min at 150 °C in open air. The process was iterated for a variable of times, from 1 to 8, on different substrates to form different multilayer TiO2 films. Steel coupons are 15 mm × 15 mm × 5 mm in dimensions, the compositions of the carbon steel were determined by optical emission spectroscopy (OES) reported in our previous study [26].

The electrochemical measurements were taken on the TiO2 multilayer coating specimens (denoted numerically as 1L-TiO2 to 8L-TiO2) and a blank substrate in simulated seawater (NaCl 3.5 wt.% in DIW). All electrochemical measurements were performed in a 250 mL cell vial, with a silver/silver chloride reference electrode and a platinum mesh as counter electrode. The electrochemical impedance spectroscopy (EIS) and potentiodynamic measurements (PD) were taken by VSP system (Bio-Logic Science Instruments) following these settings: the EIS peak-to-peak amplitude of 10 mV, frequency range from 10 kHz to 10 mHz, the PD sweep rate of 0.166 mV/s, PD scan range from −250 mV vs. open circuit voltage to 800 mV (vs. VAg/AgCl). The EIS and PD fitting was performed by the EC-Lab program belonging to VSP system. Surface mapping was captured by the scanning electron microscope (SEM) Hitachi S-4800 system. Raman spectroscopy was recorded by Horiba Jobin Yvon–Raman Spectrometer.

2.2. Computational method

Theoretical prediction of Raman peaks of TiO2 (anatase and rutile phases) was investigated by group theory for crystalline materials and simulated with DFT+U approach by the CASTEP module packaged in Materials Studio 2017 program. All TiO2 original crystal structures were extracted from the program’s library and optimized using following parameters, generalized gradient approximation (GGA) functional, Perdew–Wang 1991 (PW91) exchange–correlation, OTFG ultrasoft pseudopotentials, Koelling–Harmon relativistic treatment, BFGS mixing density, energy and force convergence tolerance below 5.0 × 10−6 eV/atom and 0.01 eV/A, cut-off energy 630 eV, max scf tolerance 1.0 × 10−7 eV/atom, Hubbard potential applied to Ti-3d orbital, optimal values are U_{anatase} = 7.8 eV for anatase and U_{rutile} = 7.1 eV for rutile. The geometrically optimized anatase and rutile structures then
were used to simulate Raman spectrum at 300 K with the same of previous settings.

3. Results and discussion

Anatase crystal belongs to ditetragonal dipymidal class, space group I41/amd (space group no. 141), Wyckoff sites for Ti (a) and O (e). Rutile crystal has the same class, space group P42/mnm (space group no. 136), Wyckoff sites for Ti (a) and O (f). Based on group theory for crystalline materials [27], one can render the irreducible representation for vibration modes of anatase and rutile as shown in (1.1) and (1.2), where R, IR and X represent Raman, IR and forbidden modes, respectively.

\[
\Pi_{\text{anatase}} = A_{1g}^{[R]} + A_{2u}^{[R]} + 2B_{1g}^{[R]} + F_{2u}^{[R]} + 3E_{g}^{[R]} + 2E_{u}^{[R]} \\
(1.1)
\]

\[
\Pi_{\text{rutile}} = A_{1g}^{[R]} + A_{2g}^{[R]} + B_{1g}^{[R]} + B_{2g}^{[R]} + A_{1u}^{[R]} + 2B_{2u}^{[R]} + E_{g}^{[R]} + 3E_{u}^{[R]} \\
(1.2)
\]

Theoretical calculation for vibration modes of anatase and rutile extracted from DFT + U approach in this study and from other researches are listed in Table 1. The Raman peaks from our calculation are well matched with other studies including experimental and simulated research [28–31], resulting in a highly believable references using for peak-search-match of the experimental Raman spectroscopy discussed afterward.

Fig. 1 shows the Raman spectroscopy of the blank substrate and the TiO₂ multilayer coatings, specifically 1, 4 and 7 layers, deposited by dip coating method on steel substrates. While steel substrate expectedly has no Raman activity, the TiO₂ peaks are not recognized on the specimens until the 4th layer because of the low thickness and low crystallinity of the TiO₂ films. The 7-layer specimen has good thickness that shows both anatase and rutile vibration modes. There is only one A-Eg mode in the 4L-TiO₂, it turns to several modes of both anatase and rutile phase, indicating that anatase phase is easier to form than rutile phase. There are 3 anatase and 2 rutile peaks detected in the 7L-TiO₂ sample. Except for a small shift to higher wavenumber of the R-B₂g and A-Eg peaks, the rest are well fitted to calculated position listed in Table 1. The origin of the peak shift is phonon scattering in the TiO₂ lattice, taken place at the point defects in crystal structures, as pointed out by Lukačević, Wu and Prasai [32–34]. From Raman spectra result, one can expect the more the layers of TiO₂ the higher the protection of the film, an expectation to be revisited later in this study.

A protective coating must have a smooth, dense and highly crystalline surface that needs to be verified. While the crys-

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Table 1 - Raman peak positions from theoretical and experimental studies.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Modes</th>
<th>This study</th>
<th>Experimental results [28,29]</th>
<th>Simulated results [30]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>A₁g + B₁g</td>
<td>515.29</td>
<td>514</td>
<td>506 and 528</td>
</tr>
<tr>
<td></td>
<td>B₁g</td>
<td>381.10</td>
<td>399</td>
<td>390.7</td>
</tr>
<tr>
<td></td>
<td>E₁g</td>
<td>139.49</td>
<td>144</td>
<td>140.8</td>
</tr>
<tr>
<td></td>
<td>E₂g</td>
<td>201.33</td>
<td>187</td>
<td>164.1</td>
</tr>
<tr>
<td></td>
<td>E₄g</td>
<td>636.50</td>
<td>639</td>
<td>650.4</td>
</tr>
<tr>
<td></td>
<td>B₂g</td>
<td>159.21</td>
<td>143</td>
<td>169</td>
</tr>
<tr>
<td></td>
<td>E₅g</td>
<td>448.26</td>
<td>447</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>A₁g</td>
<td>574.89</td>
<td>612</td>
<td>558</td>
</tr>
<tr>
<td></td>
<td>B₁g</td>
<td>783.49</td>
<td>826</td>
<td>803</td>
</tr>
</tbody>
</table>

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**Fig. 1 - Raman spectroscopy of TiO₂ multilayer coatings on steel substrate.**
Table 2 – Electrochemical properties from EIS measurement of TiO₂ multilayer coatings immersed in simulated seawater.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$ (Ω)</th>
<th>$CPE_1$ (µF)</th>
<th>$\alpha_f$</th>
<th>$R_t$ (kΩ)</th>
<th>$CPE_{dl}$ (nF)</th>
<th>$\alpha_{dl}$</th>
<th>$R_{ct}$ (kΩ)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>15.56</td>
<td>641.85</td>
<td>0.647</td>
<td>0.696</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>7845</td>
</tr>
<tr>
<td>1L-TiO₂</td>
<td>17.84</td>
<td>437.11</td>
<td>0.754</td>
<td>1.572</td>
<td>547.63</td>
<td>0.734</td>
<td>0.552</td>
<td>10,000</td>
</tr>
<tr>
<td>2L-TiO₂</td>
<td>19.82</td>
<td>71.52</td>
<td>0.781</td>
<td>4.430</td>
<td>69.26</td>
<td>0.940</td>
<td>13.697</td>
<td>93,706</td>
</tr>
<tr>
<td>3L-TiO₂</td>
<td>19.79</td>
<td>48.83</td>
<td>0.751</td>
<td>10.972</td>
<td>58.73</td>
<td>0.954</td>
<td>53.199</td>
<td>119,656</td>
</tr>
<tr>
<td>4L-TiO₂</td>
<td>21.71</td>
<td>36.71</td>
<td>0.785</td>
<td>17.217</td>
<td>35.62</td>
<td>0.946</td>
<td>71.217</td>
<td>140,149</td>
</tr>
<tr>
<td>5L-TiO₂</td>
<td>25.58</td>
<td>35.22</td>
<td>0.768</td>
<td>22.884</td>
<td>37.15</td>
<td>0.989</td>
<td>80.340</td>
<td>151,944</td>
</tr>
<tr>
<td>6L-TiO₂</td>
<td>30.88</td>
<td>29.62</td>
<td>0.756</td>
<td>30.945</td>
<td>24.43</td>
<td>0.974</td>
<td>209.866</td>
<td>176,252</td>
</tr>
<tr>
<td>7L-TiO₂</td>
<td>36.62</td>
<td>27.17</td>
<td>0.788</td>
<td>67.142</td>
<td>12.67</td>
<td>0.995</td>
<td>532.724</td>
<td>191,411</td>
</tr>
<tr>
<td>8L-TiO₂</td>
<td>31.24</td>
<td>28.65</td>
<td>0.728</td>
<td>47.124</td>
<td>22.69</td>
<td>0.966</td>
<td>467.142</td>
<td>211,397</td>
</tr>
</tbody>
</table>

Fig. 2 – SEM image of the as-prepared 1L-TiO₂ (a) and 7L-TiO₂ (b).

As-prepared 1L- and 7L-TiO₂ films are captured to explore its morphology, as presented in Fig. 2. It can be seen that there are differences in the morphology between the 1L-TiO₂ (Fig. 2(a)) and the 7L-TiO₂ (Fig. 2(b)) surfaces. The 1L-TiO₂ surface consists of many discreetly distributed oases (islands), while the 7L-TiO₂ surface is more condensed and continuous. In addition, one can conclude that the crystallinity of the 7L-TiO₂ sample is higher than the 1L-TiO₂, as greater grain size and smaller boundaries. SEM images have high agreement with Raman spectra, verifying the better crystallinity of the 7L-TiO₂ sample. From Fig. 2 one can suggest a fitting circuit for EIS as drawn in Fig. 3(b), whereas $R_s$, $R_t$ and $R_{ct}$ represent to, respectively, solution resistance, TiO₂ coating resistance and charge transfer resistance (of a very thin layer at the coating and substrate interface). Furthermore, $CPE_1$ and $CPE_{dl}$ represent the constant phase element of the TiO₂ film and of the double layer (a very thin layer at the coating and substrate interface), respectively [35]. In case of blank substrate, the fitting circuit in Fig. 3(b) was applied, wherein $CPE_1$ and $R_t$ represent the constant phase element and resistance of a rust layer formed on the steel surface.

All of the as-prepared TiO₂ multilayer coating and the blank substrate samples were soaked in simulated seawater and left unchanged for 2 h in order to stabilize the surface potential, before any EIS or PD measurements were taken place. Measured data are plotted in Fig. 3, specifically, the Nyquist plot (Fig. 3(a)) and the potentiodynamic polarization plot (Fig. 4). Fitting results from the Nyquist plots using an equivalent circuit shown in Fig. 3(b) are given in Table 2. Moreover, Tafel fitting results are presented in Table 3, by employing formulae (1.3) and (1.4) [36].

$$R_p = \frac{1}{i_{corr}} \times \frac{\beta_a \cdot \beta_c}{2.303(\beta_a + \beta_c)}$$

(1.3)

$$C_R = \frac{i_{corr} \cdot k \cdot EW}{d \cdot A}$$

(1.4)

In Eq. (1.3), $R_p$ and $i_{corr}$ are polarization resistance and corrosion current density, $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel constants, respectively. In Eq. (1.4), $C_R$ is the corrosion rate while $k = 3.27 \times 10^{-3}$, $EW = 28.25$ g/mol, $d = 7.85$ g/cm² and $A = 1$ cm² are, respectively, a constant that specifies the units for the corrosion rate, the equivalent weight of steel, the density of steel and the exposed area in the aggressive medium.

In Fig. 3(a), all experimental data are drawn by dotted lines while fitted data are drawn by solid lines. There are some noises in experimental curves especially in 7L- and 8L-TiO₂.
Table 3 – Corrosion properties from potentiodynamic polarization measurements of TiO$_2$ multilayer coatings immersed in simulated seawater.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ ($\mu$A)</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>$CR \times 10^{-3}$ (mm/yr)</th>
<th>$R_p$ (k$\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>-602</td>
<td>28.994</td>
<td>109.3</td>
<td>1465.9</td>
<td>341.405</td>
<td>1.52</td>
</tr>
<tr>
<td>1L-TiO$_2$</td>
<td>-582</td>
<td>15.168</td>
<td>80.3</td>
<td>481.6</td>
<td>178.604</td>
<td>1.97</td>
</tr>
<tr>
<td>2L-TiO$_2$</td>
<td>-448</td>
<td>1.853</td>
<td>57.1</td>
<td>363.4</td>
<td>21.819</td>
<td>11.56</td>
</tr>
<tr>
<td>3L-TiO$_2$</td>
<td>-483</td>
<td>0.291</td>
<td>56.7</td>
<td>255.1</td>
<td>3.422</td>
<td>69.21</td>
</tr>
<tr>
<td>4L-TiO$_2$</td>
<td>-498</td>
<td>0.252</td>
<td>59.0</td>
<td>144.2</td>
<td>2.965</td>
<td>72.14</td>
</tr>
<tr>
<td>5L-TiO$_2$</td>
<td>-498</td>
<td>0.179</td>
<td>59.5</td>
<td>391.6</td>
<td>2.106</td>
<td>125.29</td>
</tr>
<tr>
<td>6L-TiO$_2$</td>
<td>-474</td>
<td>0.073</td>
<td>54.3</td>
<td>271.7</td>
<td>0.859</td>
<td>269.18</td>
</tr>
<tr>
<td>7L-TiO$_2$</td>
<td>-497</td>
<td>0.030</td>
<td>74.0</td>
<td>121.9</td>
<td>0.353</td>
<td>666.47</td>
</tr>
<tr>
<td>8L-TiO$_2$</td>
<td>-560</td>
<td>0.056</td>
<td>131.0</td>
<td>94.3</td>
<td>0.659</td>
<td>425.14</td>
</tr>
</tbody>
</table>

Fig. 3 – (a) Nyquist plot for steel substrate and multilayer TiO$_2$ coated-steel in simulated seawater and (b) equivalent circuit to fit the EIS data.

samples due to very high dielectric properties of the TiO$_2$ films. Fig. 3(a) points out that the electrochemical impedance of the protective layer is improved with the number of coatings on the substrate, reaching max values at 7 layers, indicating possible optimal structure arrangement in each layer and among the layers. Indeed, the layer thickness in dip coating method has a significant influence to the product’s properties, by supplying the desired amount of material to form crystal phases of the coating, the cases of an excess or a lack of material will lead to the formation of secondary phases that
disrupts the continuity of the structure, reducing its properties. EIS fitting results from Table 2 are in good agreement with the last inference and have reasonable low \( R^2 \) values, demonstrating the relevance of the proposed fitting circuit in Fig. 3(b). Additionally, the 7L-TiO\(_2\) sample has \( R_{ct} \), 965 times greater than that of the blank substrate. Notably, the \( R_{ct} \) values were dramatically increased when the number of layers reached 6, as a consequence of local values near the optimal value.

Potentiodynamic polarization measurements to help study corrosion properties of the TiO\(_2\) multilayer coating were applied on this research. The results are plotted in Fig. 4, along with fitting results shown in Table 3. From Fig. 4 one can divide Tafel plot into 3 groups, including i) the blank substrate and the 1L-TiO\(_2\) sample, ii) the 2L-TiO\(_2\) sample and iii) the other samples. Each group experiences a significantly increase in protective properties going to the next group, listed in ascending order of group i, ii and iii. The PD results are in good agreement with all above analyses, pointing out that the 7L-TiO\(_2\) sample has the best anticorrosion performance, reducing corrosion rate down to 967 times in comparison to the blank substrate. In addition, the 7L-TiO\(_2\) sample also has the lowest corrosion current density and highest polarization resistance among the surveyed samples.

Based on the above results and discussions, we propose the protection mechanism of the TiO\(_2\) multilayer coating for steel in simulated seawater as following. The TiO\(_2\) coatings in this study prefer polycrystalline morphology, with low crystallinity, large grain sizes and boundaries, facilitate aggressive agents to meet steel surface that causes corrosion. A thin TiO\(_2\) coating (i.e., 1 and 2 layers) cannot protect steel surface unless the coating has enough material (island growth) to form the crystalline phase (4 layers or higher). At 6 TiO\(_2\) layers or higher, the corrosion protection effect of the coatings is dramatically increased and reaches optimal values at 7 layers, due to the coating completeness, minimizing the diffusion of corrosion agents into the coating. Some minor assumptions include the effects of roughness and defects on the interface of the film-solution and the diffusion in the solution itself, interpreted from the EIS data.

4. Conclusion

This study investigated the protection ability of TiO\(_2\) multilayer coatings, prepared by sol–gel dip coating, for carbon steel in simulated seawater. Due to low crystallinity of the coatings, the Raman spectra and SEM images were suggested to explore their structural characteristic. The simulated Raman spectra were calculated and used as reference peak-search-match for experimental spectra, pointed out that the coatings had polycrystalline structures including anatase and rutile phases. The SEM images showed that the coatings had large grain sizes and boundaries. While the grain sizes increased with the increase in the number of coating layers, the boundary sizes decreased with the increase in the number of coating layers instead. The electrochemical measurements indicated that the coatings showed their best protective performance at 7 layers, reduced corrosion rate down to 967 times in comparison to the blank substrate. The improved corrosion protection could be attributed to the surface roughness, coating completeness and less defects within the coating.

Conflicts of interest

The authors declare no conflicts of interest.
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REFERENCES