Improvement of Oxidation Resistance of Mild Steel by SiO$_2$-Al$_2$O$_3$ Sol Gel Coating

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SiO$_2$-Al$_2$O$_3$ sol gel coating solution was used for coating of mild steel substrate by dip coating technique with withdrawing speeds of 250, 500, 750 and 1000 mm/min. The coatings were subsequently heat treated at 200 °C for 1 hour in order to improve their corrosion resistance properties. The coating sol was synthesised using Glycidoxypropyltrimethoxysilane (C$_3$H$_7$O$_3$Si) and Aluminium triisopropylate (C$_9$H$_5$O$_3$Al). The corrosion resistance of the both coated and uncoated samples was evaluated by the Tafel polarization in NaCl solution. Fourier-transformed infrared (FTIR) and energy dispersive spectroscopy (EDS) analyses were used to identify the presence of various functional groups in the coating solution. A comparison of the corrosion resistance of the coated and uncoated mild steel is presented. Variation of corrosion potential (\(E_{corr}\)) has increased and corrosion current density (\(i_{corr}\)) has decreased in the coated samples. \(E_{corr}\) values of coated specimens, heat treated at 200 °C, were 12 to 14 times smaller than those of uncoated specimen. The measured electrochemical parameters indicate that the corrosion resistance was improved by the coating.

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1. Introduction

Corrosion causes negative effects on the properties of metals and alloys. These effects are important in dealing with structural materials such as ferrous alloys. Various surface techniques have been developed to avoid or alleviate corrosion, such as temperature reduction, removal of oxygen or oxidizing materials and changing the concentration of the working environment. There are also anodic and cathodic protection methods that can be applied to improve corrosion resistance [1].

In recent years, methods of coating of metal surfaces with ceramic materials have been widely used for protection from corrosion. There are lots of methods for preparing the coatings on metal surfaces, such as PVD, CVD, sol gel and electro-deposition processes. Sol gel process has many advantages amongst these methods. Easy composition control, fabrication of large area thin films, film homogeneity, low cost and simple fabrication cycle can be listed as beneficial features of this method. In addition, the sol-gel method allows the deposition of vitreous, ceramic and organic-inorganic hybrid dense layers on different substrates, below 500 °C [2]. Corrosion-resistant coatings of steel, produced by different methods, using such material as SiO$_2$ [3], TiO$_2$ [4], Al$_2$O$_3$ [5] ZrO$_2$ [6], borosilicate [7], or mixed oxides coating of these, have been reported in the literature.

In this study, steel specimens were coated with SiO$_2$-Al$_2$O$_3$-based solution by applying sol-gel dip coating method. This was followed by low temperature heat treatment at 200 °C. In order to study performance of coating and its behaviour, as a barrier against wet corrosion, the samples were tested in 3.5 wt.% NaCl solution. Corrosion characteristics were assessed through the use of potentiodynamic polarisation curves with the analysis of electrochemical parameters. EDS analysis was made using Jeol JSM 5600 Scanning Electron Microscope (SEM). The remaining sols were allowed to gelify at room temperature and then were ground, to obtain suitable samples for the FTIR analysis.

2. Experiment

Mild steel samples (AISI 1005), 0.8 mm thick, were coated with SiO$_2$-Al$_2$O$_3$-containing solution. Samples were withdrawn from the coating solution at various speeds to obtain different coating thicknesses. The result of spectral analysis of mild steel used in the experimental studies showed that the composition consisted of 0.03% C, 0.01% Si, 0.17% Mn, 0.04% Cu and 0.05% Al. Glycidoxypropyltrimethoxysilane (C$_3$H$_7$O$_3$Si, Glymo, Merck 841807), Aluminium triisopropylate (C$_9$H$_5$O$_3$Al, Merck 801079) were used as sources of SiO$_2$ and Al$_2$O$_3$ respectively. The chemical composition of the sol was as follows: 31.5 wt.% of C$_9$H$_5$O$_3$Si, 50.5 wt.% of C$_2$H$_3$OH, 8.8 wt.% of H$_2$O, 0.09 wt.% of HNO$_3$, and 9 wt.% of C$_3$H$_2$O$_3$Al. The preparation of the solutions was carried out as follows:

- 100 g of Glymo, 100 g of C$_2$H$_3$OH, 8 g of H$_2$O and 0.3 g of HNO$_3$ were stirred for 8 minutes at room temperature using magnetic stirrer in a beaker.
- 28.5 g of C$_3$H$_2$O$_3$Al were dissolved in the ethanol and slowly added to the mixture. After this stage, all the solutions were stirred for 15 minutes.

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3. Results and discussions

Figure 1 presents the polarization curves for the SiO$_2$-Al$_2$O$_3$-coated and the uncoated specimens, heat treated at 200°C for 1 h. The open circuit potential of the uncoated specimen was measured as $-685.9$ mV. The corresponding values for the coated specimens were between $-534.2$ mV and $-541.3$ mV. OCP decreased gradually with time, for up to 2 hours, after the immersion, and then attained a steady state value. The higher $E_{corr}$ higher correspoding values for the coated specimens were between $-534.2$ mV and $-541.3$ mV. OCP decreased gradually with time, for up to 2 hours, after the immersion, and then attained a steady state value. The higher $E_{corr}$ and lower $i_{corr}$ values indicate a better corrosion resistance [8, 9]. In this work, it was found that $E_{corr}$ values were in the range of 144.6–151.7 mV, and were higher in the coated specimens in comparison with the uncoated specimen (Fig. 1).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$E_{corr}$ [mV]</th>
<th>$i_{corr}$ [$\text{A cm}^{-2}$]</th>
<th>Corr. rate [$\text{mm/year}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncoated</td>
<td>-685.9</td>
<td>14.19</td>
<td>0.149</td>
</tr>
<tr>
<td>coated at 250 mm/min</td>
<td>-534.2</td>
<td>1.18</td>
<td>0.012</td>
</tr>
<tr>
<td>coated at 500 mm/min</td>
<td>-541</td>
<td>1.16</td>
<td>0.012</td>
</tr>
<tr>
<td>coated at 750 mm/min</td>
<td>-541.3</td>
<td>1.02</td>
<td>0.010</td>
</tr>
<tr>
<td>coated at 1000 mm/min</td>
<td>-539.6</td>
<td>1.08</td>
<td>0.011</td>
</tr>
</tbody>
</table>

It was observed that values of corrosion currents of the coated specimens were all very close. This shows that the critical coating thickness for protection was achieved. Similar polarization tests have been used for the SiO$_2$ and boehmite sols on the galvanized steel [12], ormosil-based silica on the austempered ductile iron [13] and yttrium-stabilized zirconia-on-carbon steel sheets [8]. The corrosion behaviour of the specimens examined in this study is in good agreement with the literature.
Figure 2 illustrates the FTIR spectra of SiO$_2$-Al$_2$O$_3$ gel heat treated at 100, 200, 300 and 400°C. The absorption bands shown in Fig. 2, due to the OH, CH$_2$, H-OH (free water), C-H and Si-O bonds, are positioned at 3300–3600, 2800–3000, 1650, 1420 and 1120 cm$^{-1}$, respectively. The absorption bands at 925–950 cm$^{-1}$ correspond to Si-O-Si. The characteristic peak for Si-O-Si bond is at 1000–1200 cm$^{-1}$ and the characteristic peak for Si-OH bond is at 940–950 cm$^{-1}$ [14, 15]. In this study, the peaks due to Al-OH and Si-O-Al absorption bands are positioned at 700 and 560 cm$^{-1}$, respectively. The FTIR spectra clearly show that the organic groups, Si-O-Al and Si-O-Si bonds form in the gels heat treated at 200°C. As is shown by the FTIR analyses, the organic groups are still present on the surface substrate after sintering at 200°C. FTIR spectra of SiO$_2$-Al$_2$O$_3$ gel, heat treated at 300 and 400°C indicate the removal of organic groups from the gel. The elasticity of the coating can be improved by the presence of organic groups, which reduce the stress and crack formation during sintering [16].

4. Conclusions

SiO$_2$-Al$_2$O$_3$ coatings on mild steel were prepared by sol-gel dip coating method. This study showed that specimens coated with SiO$_2$-Al$_2$O$_3$ sol have a higher corrosion resistance than that of the uncoated specimen. $i_{corr}$ values for the coated specimens were 12 to 14 times smaller than those of the uncoated specimen. The FTIR spectra revealed that the organic groups, Si-O-Al and Si-O-Si bonds form in the gels heat treated at 200°C. The elasticity of the coating can be improved by the presence of organic groups, which reduce the stress and crack formation during the sintering.

Acknowledgments

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References