

Improvement of Oxidation Resistance of Mild Steel by SiO₂-Al₂O₃ Sol Gel Coating

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SiO₂-Al₂O₃ 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 (C₉H₂₀O₅Si) and Aluminium triisopropylate (C₉H₂₁O₃Al). 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. i_{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 SiO₂ [3], TiO₂ [4], Al₂O₃ [5] ZrO₂ [6], borosilicate [7], or mixed oxides coating of these, have been reported in the literature.

In this study, steel specimens were coated with SiO₂-Al₂O₃-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 SiO₂-Al₂O₃-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 (C₉H₂₀O₅Si, Glymo, Merck 841807), Aluminium triisopropylate (C₉H₂₁O₃Al, Merck 801079) were used as sources of SiO₂ and Al₂O₃ respectively. The chemical composition of the sol was as follows: 31.5 wt.% of C₉H₂₀O₅Si, 50.5 wt.% of C₂H₅OH, 8.8 wt.% of H₂O, 0.09 wt.% of HNO₃, and 9 wt.% of C₉H₂₁O₃Al. The preparation of the solutions was carried out as follows:

- 100 g of Glymo, 100 g of C₂H₅OH, 8 g of H₂O and 0.3 g of HNO₃ were stirred for 8 minutes at room temperature using magnetic stirrer in a beaker.
- 28.5 g of C₉H₂₁O₃Al 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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- Mixture of 20 g of distilled H₂O and 60 g of C₂H₅OH was added and the solution was stirred for 60 minutes at 85 °C.

Samples were cut to dimensions of 10 × 40 mm². Prior to coating process, in order to clean the surfaces, samples were placed in a beaker, which contained 1:1 mixture of HCl and water at 80 °C and held there for 30 minutes. After this period, the samples were cleaned with distilled water and preserved in acetone to prevent oxide formation.

A computer-controlled KSV type dip coating apparatus was used to coat the samples using withdrawing speeds of 250, 500, 750 and 1000 mm/min. Samples were dipped vertically in order to achieve coating on both sides and held for 200 seconds in the solution. After the coating process was finished, samples were dried at 60 °C in an incubator for 15 minutes and subjected to heat treatment at 200 °C for 1 hour in Protherm PID-controlled furnace. The samples were taken out from the furnace to cool to room temperature. In order to determine the corrosion properties of the coated specimens, corrosion tests of uncoated samples were also carried out for comparison.

The electrochemical measurements of both the coated and the uncoated specimens were done by measuring the variation of open circuit potential (E_{OCP}) with time, and then Tafel plots in 3.5 wt.% NaCl solution, using Gamry PCI4G750 potentiostat, were plotted. The analyses were carried out at room temperature in a standard electrochemical cell, equipped with a frequency response analyzer module. A three-electrode cell, including a saturated calomel electrode, as a reference electrode, graphite bar, as a counter electrode and the specimen, as the working electrode, was used in the experiments. The Tafel polarization curves were obtained using potentiodynamic polarisation at a constant scan rate of 1 mV/s, by sweeping the potential between +250 mV and -250 mV relative to the open circuit potential (OCP). Free corrosion potential measurements were completed after 2 hours and then the polarization resistance was measured. Different parameters, related to potentiodynamic polarization, were derived by curve fitting method using Gamry Echem. Analyst software.

Gelation process was carried out at room temperature. Gels were ground and heat treated at 100, 200, 300 and 400 °C. The presence of functional groups in the gel was analyzed using FTIR (Perkin Elmer Spectrum 100) in a frequency range of 4000–350 cm⁻¹.

3. Results and discussions

Figure 1 presents the polarization curves for the SiO₂-Al₂O₃-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}

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).

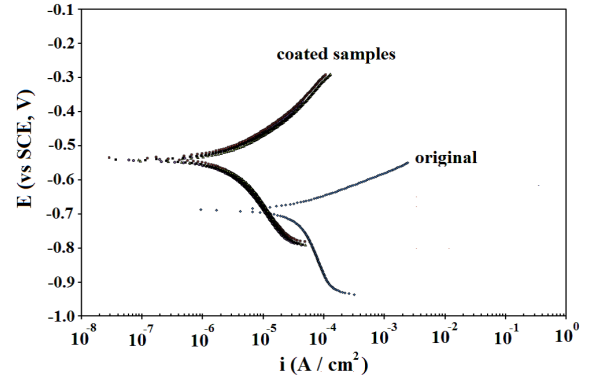


Fig. 1. Polarization curves for the SiO₂-Al₂O₃-coated and the uncoated (“original”) specimens, heat treated at 200 °C for 1 h.

The corrosion potential was calculated from the intersection of cathodic and anodic Tafel curves, using Tafel extrapolation method. The corrosion rates were determined by Stern-Geary equation from the polarization measurements [10]. Electrochemical parameters obtained from Tafel extrapolation are given in Table. This shows that i_{CORR} values of the coated specimens, heat treated at 200 °C, are 12 to 14 times smaller than those of the uncoated specimen. The corrosion rate (r_{CORR} , in mm per year) was calculated using the following equation [11]:

$$r_{CORR} = \frac{3272 i_{CORR} E_w}{d}, \quad (1)$$

where i_{CORR} is the corrosion current, E_w is the equivalent weight and d is the density of tested metal.

TABLE

Electrochemical parameters of mild steel, uncoated and SiO₂-Al₂O₃-coated, obtained from Tafel extrapolation.

Electrode	E_{CORR} [mV]	i_{CORR} [A cm ⁻²] × 10 ⁻⁶	Corr. rate [mm/year]
uncoated	-685.9	14.19	0.149
coated at 250 mm/min	-534.2	1.18	0.012
coated at 500 mm/min	-541	1.16	0.012
coated at 750 mm/min	-541.3	1.02	0.010
coated at 1000 mm/min	-539.6	1.08	0.011

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 SiO₂ and bohmite 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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].

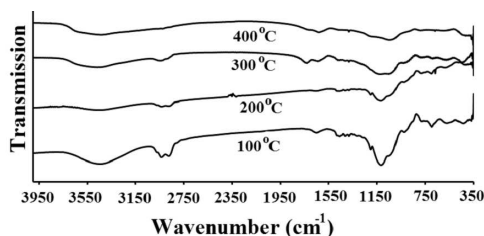


Fig. 2. FTIR analysis of $\text{SiO}_2\text{-Al}_2\text{O}_3$ gel, heat treated at different temperatures.

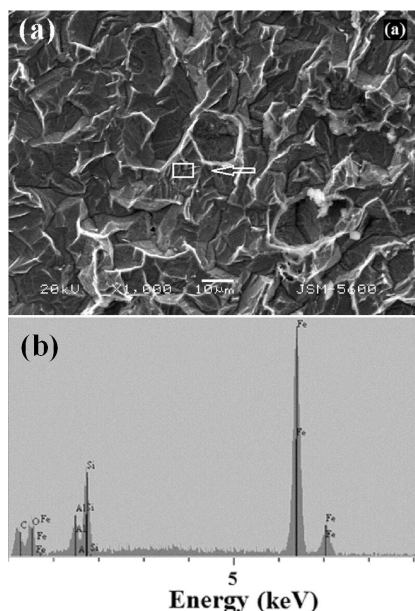


Fig. 3. (a) SEM image of $\text{SiO}_2\text{-Al}_2\text{O}_3$ -coated sample, heat treated at 200 °C, (b) EDS analysis of the sample.

Figure 3a shows the SEM image of $\text{SiO}_2\text{-Al}_2\text{O}_3$ -coated sample, heat treated at 200 °C. Figure 3b shows the EDS

analyses of the area indicated in Fig. 3a, where the presence of Si and Al peaks can be seen. It is important to note that Fe peaks are resulting from the substrate.

4. Conclusions

$\text{SiO}_2\text{-Al}_2\text{O}_3$ coatings on mild steel were prepared by sol-gel dip coating method. This study showed that specimens coated with $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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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