Corrosion behaviour of sol-gel Al₂O₃ coated Al-Si alloy in 3.5% NaCl solution

I B Singh*, M Singh, S Das & A H Yegneswaran
Advanced Materials and Processes Research Institute, Hoshangabad Road, Bhopal 462 026, India
*Email: ibsingh58@yahoo.com

Received 6 January 2010; revised 6 August 2010

Alumina sol was synthesized and coated on Al-Si alloy. The coated substrates were heated at 300°C for sintering and precursor removal purposes. The cross-sectional examination of the coated specimens in SEM showed the presence of around 7 µm thick non porous and compact coating. XRD analysis confirmed the presence of αAl₂O₃ in the coated layer. The corrosion characteristics of the coating were evaluated in 3.5% NaCl solution by electrochemical measurements. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) analysis indicated that the coated substrate possesses an order of magnitude higher corrosion resistance as compared to uncoated substrate. EIS study has also indicated a significant decrease in diffusion phenomena of chloride ions through the coating/metal interfaces. The effect of heat treatment of Al-Si alloy on its corrosion properties has also been investigated.

Keywords: Al-Si alloy, Composite, Alumina coating, Sol-gel process, Corrosion

Al-Si alloy make composites have become a substitute material in automobile industries especially in making of piston, cylinder blocks etc. They are also being considered as a potential material in making of impellers, agitators etc in marine structural applications because of their enhanced physical, mechanical and tribological properties. However, service life of any material mainly depends on its corrosion resistances in the surrounding environment. For example, if Al-Si alloy make AMC are used in marine environment, their susceptibility to pitting corrosion is likely to be increased in the presence of chloride ions. Chloride ions adsorb on the metal surfaces and destroy the existing passive oxide film that leads a localized attack in the form of pitting corrosion. Since pitting corrosion is a main problem of AMC, different approaches have been made to control pitting corrosion by halide ions.

Development of sol-gel coatings on metals is rather a recent approach. The hydrolysis and condensation reactions of metals alkoxide are main chemical reactions involved in the sol-gel processing. This method of coating development has many advantages. The coatings are generally amorphous or microcrystalline and stoichiometrically homogeneous. Development of uniform coatings even on a complex shaped structure is another advantage of sol-gel method of coatings development. Schmidt et al. reported that formation of alumina-silicate compound decreases Gibbs free energy lower than the boehmite {AlO(OH)}, which is the first stage of aluminum oxidation in the presence of moisture. The decrease in Gibbs free energy leads a thermodynamic stability at silica/aluminum interfaces in corrosive atmosphere. The chemical bonding of the sol-gel film with aluminum substrate makes a major contribution in increasing of the adherence of the coating. In addition, an excellent coating is obtained when bonds between the film and the substrate is produced before a strong bond within the film is formed. But delamination due to mismatch in thermal expansion coefficients between the coating materials and the substrate is one of the major disadvantages of sol-gel based ceramic coatings. In Al-Si alloy presence of Si-O-Al bond may likely to make a strong adherence with alumina coating. In a recent review a detailed description have been given about different types of sol-gel ceramic coatings on different substrates. However, no report has been given on the development of sol-gel alumina coating on Al-Si alloy. In view of above alumina coating through sol-gel route on Al-Si alloy was developed. Thereafter, its various corrosion resistance properties were evaluated in 3.5% NaCl solution using different electrochemical measurements.

Experimental Procedure

Materials
The composite was prepared by using an oil fired furnace. Al-Si (2014) alloy (composition: Al- 13; Si-0.6; Fe-0.5; Mn-0.1; Mg-0.1% Cu) ingot pieces were
heated in a graphite crucible. The degassing of the molten alloy was carried out by passing nitrogen gas through the melt after covering the melt with a flux, Coveral-11 supplied by Greece Foseco, Pune, India. The melt was cleaned by taking out the dross collected on the melt surfaces with a perforated flat spoon. The metal was cast in the shape of disc (thickness 12 mm; dia 120 mm).

Specimens preparation

The specimens used for electrochemical measurements were cut from the prepared disc in the cubical shape of dimension 1 x 1 x 1 cm. For making of electrical contact specimens were screwed at its one end and fitted with copper rod. Before carrying electrochemical measurements specimens were metallographically polished till the attainment of mirror finish using emery paper of different grades. The polished samples were degreased properly with trichloroethylene.

Sol-gel alumina coatings

Alumina sol was prepared by using Al-isopropoxide and water in their molar ratio of 1:100. A small amount of nitric acid was added to maintain the pH (~ 4) of the suspension. The suspension was refluxed and stirred vigorously at 82-85°C for several hours till it converted into a clear sol. Once sol cooled, its viscosity was measured by using Brookfield make Rheometer. The viscosity was found to be 5.13 mPas. Afterwards alumina coating was made on the composite specimens by dip coating method at a constant withdrawal speed of 1 cm/s. After air drying, the sol-gel coated specimens were heated at 300°C in inert nitrogen atmosphere to obtain an alkoxide free alumina coating. The details of the synthesis of alumina sol-gel, coating development, heating etc are available elsewhere.

Surface characterization

The plane surface morphology and cross-sectional views of the specimens were examined by Scanning Electron Microscope (JEOL, Japan make JSM 5600). For the cross-sectional analysis specimens were cut carefully with the help of high precision diamond cutting saw in presence of a coolant. The transverse section of the coated specimens were mounted and polished metallographically to view in SEM. The phase analysis of the coated specimens was performed by X-ray diffraction using X-ray diffractometer (D8 Bruker model) under Cu Kα radiation.

Electrochemical measurements

Open circuit potential (OCP) variation with time, Tafel plots and impedance measurements were performed using a conventional three electrodes (a saturated calomel electrode as reference electrode, platinum foil as counter electrode and test specimen as working electrode) electrochemical cell in 3.5% NaCl solution at room temperature (30±2°C) using computer controlled Solatron 1280 Z corrosion system equipped with software Corrware and Zplot. The Tafel plots were obtained by carrying potentiodynamic polarisation at a constant scan rate of 1 mV/s by sweeping the potential between ±150 mV from OCP. Impedance measurements were carried out in a frequency range of 0.02 Hz to 20 kHz at OCP by applying a sine potential signal of 10 mV. The different parameters related to electrochemical polarisation and impedance measurements were derived by curve fitting method using Corrview and Zview softwares, respectively. Each experiment has been repeated two to three times in order to obtain reproducible results.

Results and Discussion

XRD analysis

Phase analysis of the alumina sol gel coated specimen was carried out by XRD (Fig. 1). The XRD spectrum revealed the presence of distinct peaks of aluminum (Al) and silicon (Si). The dominant peaks positioned at 2θ value of 38.52°, 44.70° and 65.15° correspond to Aluminum. The XRD peaks occurred at 2θ value of 29.43°, 47.43°, 51.62 belong to Si. The

![Fig. 1—XRD pattern recorded on the surface of sol-gel derived alumina coating on Al-Si alloy](image-url)
presence of peaks, at 28.54°, 36.02°, 43.23° and 57.51° are relatively small in intensity that corresponds to $\alpha Al_2O_3$. Recently Singh and co-worker\(^2\) have made detailed studies on the effect of heat treatment on the removal of precursor (alkoxide group) from the alumina gel by carrying out FTIR and XRD analysis. A complete removal of alkoxide precursor from the alumina gel was found after heating at 300°C. In view of this observation, it may therefore be assumed that alumina coating heated at 300°C in the present study is free from the organic precursor.

**Microstructural studies**

SEM micrograph depicting the structure of the alloy, is shown in Fig. 2a. It can be noticed from the Fig. 2a that Si is present in dendrites form and mixed homogeneously in Al matrix. A number of voids and cavities can be seen in the microstructure of the alloy. In heat treated alloy the Si dendrites transformed to elongated form (Fig. 2 b). The morphology of sol-gel derived alumina coating is depicted in Fig. 2c. In photomicrograph one can see the presence of a homogeneous and compact coating present on the surface. The cross-sectional views of the coated specimens is demonstrated in the Fig. 2 d. The coated layer appears to be completely whitish and compact in nature of having ~7 µm thickness. The Si dendrites of the alloy are observed to be fully covered with coating at the outer edge of the coated specimen. Due to this a strong bonding of Si-O-Al at the metal/coating interfaces is presumably developed. This may be the reason that coating was observed adherent in nature.

![SEM photomicrographs](image)

**Fig. 2**—SEM photomicrographs (a)-microstructural view of Al-Si alloy matrix; (b)-microstructural changes of Al-Si alloy after its heat treatment at 300°C; (c)-plane surface morphology of the sol-gel derived alumina coated Al-Si alloy heated at 300°C; (d)-cross-sectional view of the sol-gel derived alumina coated Al-Si alloy at lower magnification (X 500)
**Electrochemical measurements**

**OCP versus time behaviour**

Figure 3 presents the trend of the variations of open circuit potential (OCP) with exposure time of Al-Si alloy as such, Al-Si alloy after their heat treatment and sol-gel alumina coated Al-Si alloy in 3.5% NaCl solution. A lot of fluctuations in OCP for both, unheated and heated Al-Si alloy were recorded during initial 10 min of exposure. Afterwards, their OCP attained a steady state. The steady state values of OCP are given in Table 1. The heat treated alloy showed more than 250 mV positive OCP than unheated alloy. On the other side the alumina coated alloy showed a much more positive OCP over heat treated alloy. As shown in Fig. 3 and Table 1, the OCP of coated alloy occur -210 mV which is 310 mV more than heat treated alloy. Whereas the OCP of uncoated alloy occurs more than 300 mV more active than heat treated Al-Si alloy. The occurrence of a positive shift in the OCP of coated specimen indicates the existence of anodically controlled reaction.

**Tafel plots**

The partial potentiodynamic polarization curves of unheated, heated and sol-gel alumina coated Al-Si alloy specimens are presented in Fig. 4. The corrosion current density \( I_{corr} \) derived after the extrapolation of Tafel plots, is given in Table 1. The observed \( I_{corr} \) shows that the sol-gel alumina coated specimen possesses much better corrosion resistances. It exhibits more than an order of magnitude lower \( I_{corr} \) as compared to Al-Si alloy without any treatment. Heat treatment of the Al-Si alloy is appeared to improve the corrosion resistances noticeably. Because more than two times lower \( I_{corr} \) was measured for the heat treated alloy as compared to Al-Si alloy of without heat treatment.

**EIS analysis**

EIS analysis was carried out for all the three types of studied specimen at their steady \( E_{cor} \) in 3.5% NaCl. The observed EIS are presented in Bode plots in Fig. 5. Different parameters related to impedance measurement derived by curve fitting method, are given in Table 1. An equivalent circuit consisting of resistor connected in series to a parallelly connected resistor and capacitor has been used for data analysis. As expected, a very less charge transfer resistance \( R_{ct} \) and a higher double layer capacitance \( C_{dl} \) were obtained for untreated Al-Si alloy. In case of heat treated alloy \( R_{ct} \) value measured is slightly more but its \( C_{dl} \) reduced noticeably in comparison to Al-Si alloy. After coating its charge transfer resistance increases remarkably (Fig. 5 and Table 1). From the Table 1, it can be noted that the sol-gel alumina coated specimen shows two orders of magnitude higher

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Al-Si</th>
<th>Al-Si heat treated</th>
<th>Al-Si sol gel coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCP (mV, SEC)</td>
<td>-825</td>
<td>-520</td>
<td>-210</td>
</tr>
<tr>
<td>( I_{corr} ) (A/cm(^2))</td>
<td>3.2×10(^{-6})</td>
<td>1.02×10(^{-6})</td>
<td>122×10(^{-7})</td>
</tr>
<tr>
<td>( R_s ) (( \Omega )cm(^2))</td>
<td>9.35±8.2%</td>
<td>562±9.9%</td>
<td>4632±6.5%</td>
</tr>
<tr>
<td>( C_{dl} ) (F/cm(^2))</td>
<td>5.8×10(^{-6})±4.8%</td>
<td>5.2×10(^{-6})±5.4%</td>
<td>1.8×10(^{-7})±8.1%</td>
</tr>
<tr>
<td>( R_{ct} ) (( \Omega )cm(^2))</td>
<td>5313±10.1%</td>
<td>5890±6.1%</td>
<td>116670±7.3%</td>
</tr>
</tbody>
</table>
The $R_{ct}$ value as compared to uncoated specimen. The capacitance of coated specimen was found to be decreased an order of magnitude lower than that of Al-Si alloy of without any treatment. Measurement of a less charge transfer resistances and higher capacitance for Al-Si alloy indicates its pronounced corrosion tendency in NaCl solution. Observation of comparatively very less solution resistances ($R_s$) for Al-Si alloy of without any treatment indicates the existence of highly conducting surface film. A porous oxide film of having a higher double layer capacitance increases the diffusion of chloride ions through metal/solution interfaces. Any oxide film which possesses above properties makes a fast diffusion reaction. Capacitance of the coating is related to extent of water up take. Measurement of one order of magnitude low value of $C_{dl}$ for the alumina coated specimen as compared to uncoated specimen attributes the presence of less conductive film. Heat treatment of the Al-Si alloy does not make any noticeable improvement in charge transfer resistance and in reduction of capacitance of the surface film. The observed $R_{ct}$ and $C_{dl}$ values for all the three types of investigated specimens are well in accordance with the $I_{corr}$ measured by Tafel extrapolation (Table 1).

Bode plots are quite informative in interpretation of diffusion process as it provides data related to the variation of impedance and phase angle with respect to frequency. As presented in Fig. 5 one can see the presence of three different frequency regions with respect to impedance ($Z$) and theta ($\theta$). In general, the high frequency region determines the properties of reference electrode and solution resistance. The medium frequency region describes capacitive properties of film and the low frequency region explains the charge transfer process occurring at solution/coating interfaces. The sol-gel alumina coated specimens show a wide capacitive resistive behaviour with the decrease of frequency. The values of the phase angle occur maximum (-30°) in the middle frequency region and decreased gradually with the decrease of frequency in the lower range. Finally, the phase angle occurred at -5° which is close to zero indicating the existence of a diffusion controlled process. It is reported that a high value of phase angle at lower frequency part is also associated with the presence of porosities and existence of diffusion process. A slight fluctuation in phase angle was noticed at 0.126 Hz for the sol-gel coated specimen.

The fluctuation in the phase angle at this particular frequency could be due to the start of diffusion of chloride ions through solution/coating interfaces. In Al-Si alloy of without any treatment the maximum phase angle (-65°) occurs at middle frequency region. The fluctuations in the phase angle were found to start in the middle frequency region itself. The start of fluctuation in phase angle for Al-Si alloy was found at 5.18 Hz. This frequency is quit higher than the start of fluctuation in the phase angle was noted for alumina coated specimen. In case of heat treated alloy the start of fluctuation in phase angle was noticed at 12.62 Hz which is unexpectedly quite high than the frequency at which fluctuation in phase angle recorded for Al-Si alloy without heat treatment. Since the fluctuation in phase angle is the result of start of diffusion phenomena of chloride ions through metal/solution interfaces, it can therefore be suggested that the susceptibility of pitting corrosion is likely to be more pronounced in the heat treated alloy. Though, heat treated alloy showed somewhat better corrosion resistances than unheated alloy in their $I_{corr}$ measurement (Fig. 4). Sensitizing the alloy by heat treatment is appeared to increase the susceptibility of localized attack. Microstructural studies of heat treated alloy (Fig. 2 b) showed enlargement of Si dendrites.
length in the matrix. This increases the active sites in the matrix which, in turn, enhances localized attack in presence of chloride ions. After alumina coating the pitting susceptibility is appeared to reduce maximum. The start of the fluctuations in phase angle process was noticed at very low frequency. The presence of non-porous alumina coating is likely to act as diffusion controlled barrier layer which minimizes the diffusion of chloride ions up to maximum level. Based on the above observations it can be concluded that alumina coating substantially improves the corrosion and pitting resistances of Al-Si alloy in NaCl solutions.

**Conclusion**

Different types of electrochemical measurements suggested that developed sol-gel alumina coating is quite effective in improving the corrosion resistance of Al-Si alloy in 3.5% NaCl solution. EIS measurement indicates that coated alumina layer is able to control the diffusion of chloride ions through the coating/metal interfaces up to maximum extent. Sensitizing the alloy by heat treatment is appeared to increase the susceptibility of localized attack. Because Si dendrites get elongated after heat treatment that increases the active sites in the matrix which, in turn, enhances the localized corrosion in the presence of chloride ions. However, heat treatment does not make any noticeable effect on the start of diffusion process on the alumina coated alloy surfaces. Microstructural and phase analysis of the coated specimen confirmed the presence of a compact coating of $\alpha Al_2O_3$.

**Acknowledgement**

Authors are thankful to the Director, Advanced Materials and Processes Research Institute for providing of laboratory facilities for carrying above work. The help rendered by T.V.S. Chakradhar Rao in SEM analysis, is also acknowledged.

**References**