Electrochemical characteristics of micro and nano metre sized mixtures of cerium oxide incorporated aluminium

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Received 26 June 2012 ; accepted 3 June 2013

The present study is aimed at investigating the electrochemical characteristics of aluminium due to the incorporation of nano metre and micro metre sized cerium oxide mixture. Treated aluminium exhibits higher corrosion resistance as evidenced by lower corrosion current density and corrosion rate and improved morphologies. Impedance spectra of aluminium subjected to long term exposure to 3.5% NaCl (w/v) show that the corrosion resistance of surface and internal matrix increases significantly and the corrosion is occurred in the $\beta$ spaces of the aluminium. Smaller grain size and increased electronic conductivity improve the corrosion resistance of aluminium.

Keywords: Aluminium, Corrosion, Electrochemical characteristics, Micro cerium oxide, Nano cerium oxide

Nano technological application in material science has got vast potential for the development of new metal matrix composites with improved properties. Frequent demands from the stake holders also instigated development of materials with higher toughness and low degradation. The major focus in recent years is on the development of materials by exploiting the potential of nanotechnology. Aluminium is extensively used by the industry for various applications. However the major disadvantage is that the materials undergo degradation very easily, especially under chloride environments. The immediately formed protective surface oxide film mainly consists of $\text{Al}_2\text{O}_3$, $\text{Al(\text{OH})}_3$ and $\text{AlO(OH)}$ phases. Chloride ion adsorption over the defective film results in the penetration and accumulation, which further leads to the destruction of the protective layer and thereby nucleation of pitting processes $^{1-3}$.

Chromium is extensively used for the surface modification of aluminium which enhances its corrosion resistance $^4$. The environmental concern over the toxicity of chromium results in its ban and the researchers suggest many alternatives. Among them, ecofriendly rare earth oxide based surface modification is found to be satisfactory$^5-11$. The cerium oxides are responsible for corrosion inhibition by forming cerium oxide islands on the surface of the matrix and it diffuses into the defects of the surface layer$^{12,13}$. The cerium oxide or rare-earh oxide conversion coatings are generally prepared by chemical conversion or electro-deposition methods and it has major disadvantages like shorter stability, difficulty in applying over larger surfaces and instability due to the chemical used for the above process$^{14}$. More efficient and corrosion resistant aluminium metal matrix composites are developed by incorporating cerium oxide in the aluminium matrix to produce more corrosion resistant aluminium$^{15}$.

The nanotechnology opened up the potential application of nano materials in the material science research. Introduction of nano metre sized particle in the aluminium matrix instead of macro or micro metre sized particles will increase the number of particles per unit area and result in less quantity of materials with maximum efficiency. The nano metre sized cerium oxide exhibits electronic conductivity and the micro metre sized shows ionic conductivity$^{16}$. The nano metre sized cerium oxide having higher charged cations in the aluminium matrix will interact electrostatically with the mobile cation vacancies, which results in enhanced electronic conductivity of oxide films of aluminium. This is considered to be an effective method to make corrosion resistant aluminium for use in aggressive environments$^{17}$. The deposition of micro metre and nano metre sized SiC in copper pyrophosphate bath leads to a significant increase in micro hardness, abrasion resistance,
uniform and localized corrosion resistance\textsuperscript{18}. Not much work has been carried out to study the impact of incorporation of micro metre and nano metre sized cerium oxide in aluminium. In the present study, an attempt has been made to incorporate micro metre sized and nano metre sized cerium oxide mixture in the aluminium for its corrosion resistance in aggressive chloride environments.

**Experimental Procedure**

Electrolytic grade pure aluminium (99.80\%) ingots were used for fabrication of metal matrix composites. The aluminium ingots contained Cu (0.0031\%), Fe (0.1069\%), Mg (0.0411\%), Mn (0.0024\%), Ti (0.0001\%), and Zn (0.0016\%) while chromium and nickel was absent. The cerium nitrate, cerium oxide (both from CDH, Mumbai) and ammonium hydroxide and sodium chloride from Merck were used for the experiment. Nano metre sized cerium oxide was prepared by precipitation method\textsuperscript{19} using cerium nitrate and ammonium hydroxide. Ammonium hydroxide solution was added to cerium nitrate solution at 80°C (pH 8) with constant stirring by a magnetic stirrer. The mixture was kept at that temperature for 2 h. The precipitate was collected by filtration and calcined at 350°C in a muffle furnace in presence of air.

The ingots of pure aluminium were melted at 850±10°C in a muffle furnace. The required amount of micro metre and nano metre sized cerium oxide powder was pre heated to 850±10°C, added into the melt and stirred using a SiC rod. The melt was again kept in the muffle furnace for another 15 min at the same temperature and poured into a red brick mould. The cast aluminium coupons were sliced to appropriate shape and ground using a series of silicon carbide papers up to 1000 grits. The coupons were cleaned by using ultrasonic cleaner, wiped with acetone and rinsed with distilled water (MilliQ Gradient). Five batches of aluminium composites incorporating micro metre and nano metre sized cerium oxide (1:1) at percentages of 0.00 (T1), 0.01 (T2), 0.02 (T3), 0.05 (T4), 0.10 (T5) and 0.20\% (T6) were prepared for the study.

Electrochemical measurements like electrochemical impedance spectroscopy and linear sweep voltammetry were carried out by using an Autolab PGSTAT 30 plus FRA2 electrochemical analyzer. Electrochemical impedance spectroscopy (EIS) analysis was carried out in 3.5\% (w/v) NaCl as electrolyte. Ag/AgCl (3M KCl), Pt and the coupon having 1 cm\textsuperscript{2} exposed area was used as reference, counter and working electrodes respectively. The frequency range used for scanning was 1 MHz to 0.1 Hz with reference to the open circuit potential (OCP) after 30 min of exposure of the coupon in the electrolyte. The impedance data were fitted with simple Randle’s equivalent circuit model and the impedance parameters like polarization resistance, constant phase element were derived by using the Autolab FRA 2 software. The coupon having 1cm\textsuperscript{2} exposed area was immersed in 3.5\% NaCl for 1 h prior to potentiodynamic polarization experiment at a scan rate of 0.010V/s. Potential sweep was carried out from cathodic to anodic region (+0.500V and -0.500V from OCP). The Ag/AgCl (3M KCl) and Pt were used as reference and counter electrode. The Tafel slope parameters were derived by using Autolab’s GPES software. Weight loss measurements were made after exposing the pre weighed coupons in 3.5\% NaCl for a period of 40 days as per ASTM G31-72. All analyses were carried out with at least three replicates. The coupons were cleaned using a hot pickling solution of phosphoric acid (50 mL l\textsuperscript{-1}) and potassium dichromate (20 g l\textsuperscript{-1}). The coupons were rinsed with distilled water, dried, weighed and calculated the corrosion rates.

The surface of fresh micro and nano cerium oxide incorporated aluminium coupons were ground using a series of silicon carbide papers up to 2000 grit followed by etching with 1\% (w/v) NaOH solution and their surface morphology was studied using Hitachi scanning electron microscope at 15 keV. General statistical analysis was carried out using Microsoft Excel software.

**Results and Discussion**

**Nano metre sized cerium oxide**

Nano metre sized cerium oxide was synthesized by precipitation reaction\textsuperscript{19} using the reaction mechanism described by Liao et al\textsuperscript{20}. Transmission electron micrograph (TEM) of nano metre sized cerium oxide (Fig. 1a) shows that the synthesized cerium oxide is composed of two types of nano particles, viz spherical and rod shaped. The size of cerium oxide is about 50 nm and the length of rod shaped cerium oxide is about 265 nm.

**Surface morphology**

The scanning electron micrographs of micro metre and nano meter sized cerium oxide incorporated aluminium are shown in Fig. 1 (b). Addition of micro
metre and nano metre sized cerium oxide mixture into the pure aluminium improves the morphology substantially and the smaller grain boundaries. Addition of nano metre sized crystalline rare earth oxide on silicon crystals improves the characteristic of the material by changing star shape to polyhedron state\textsuperscript{21}. Cerium is known for its surface activity with large atomic radius and low electronegativity. This implies that cerium can form positive ions easily and react simply with other elements. During the solidification of aluminium along with cerium oxide from melt, the cerium would distribute in front of the solid /liquid interface or at the given boundary, since it has low surface energy. In the grain boundary the atomic arrangement is irregular and this increases the tendency of composition under-cooling. Increase in the under-cooling and nucleation rate will suppress the growth of grain\textsuperscript{22}.

**Linear sweep voltammetry**

The coupons were subjected to linear polarization studies and the results are shown in Fig. 2. The Tafel slope analysis shows that the corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and polarization resistance ($R_p$) vary from -0.780 to -0.687V, from $2.83 \times 10^{-7}$ to $1.25 \times 10^{-6}$ Acm$^{-2}$ and from $3.65 \times 10^{-4}$ to $2.30 \times 10^{-5}$ $\Omega$ cm$^2$ respectively (Table 1). Lowest mean corrosion current is exhibited by the coupons with 0.20% each of micro metre and nano metre sized cerium oxide incorporated aluminium. Comparative evaluation of pure aluminium vs mixed micro metre and nano metre sized cerium oxide incorporated aluminium shows that the latter has excellent corrosion resistance characteristics. The coupons exhibit a current plateau beyond corrosion current; this can be associated with a passivation process\textsuperscript{15,23-28}.

**Table 1 — Linear sweep voltammetric parameters of nano and micro cerium oxide incorporated aluminium**

<table>
<thead>
<tr>
<th>Nano and micro cerium oxide, %</th>
<th>Corrosion potential ($E_{corr}$), V (Ag/AgCl)</th>
<th>Corrosion current density ($I_{corr}$), Acm$^{-2}$</th>
<th>Polarization resistance ($R_p$), $\Omega$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>-0.666</td>
<td>$2.41 \times 10^{-7}$</td>
<td>23670</td>
</tr>
<tr>
<td>0.01</td>
<td>-0.737</td>
<td>$6.99 \times 10^{-7}$</td>
<td>46455</td>
</tr>
<tr>
<td>0.02</td>
<td>-0.780</td>
<td>$1.25 \times 10^{-6}$</td>
<td>36533</td>
</tr>
<tr>
<td>0.05</td>
<td>-0.756</td>
<td>$8.27 \times 10^{-7}$</td>
<td>96260</td>
</tr>
<tr>
<td>0.10</td>
<td>-0.687</td>
<td>$4.15 \times 10^{-7}$</td>
<td>100700</td>
</tr>
<tr>
<td>0.20</td>
<td>-0.730</td>
<td>$2.83 \times 10^{-7}$</td>
<td>230843</td>
</tr>
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</table>
The current plateau is steadily extended up to -0.500V in the case of 0.10% and 0.20% each of mixed cerium oxide incorporated aluminium and then the current increases slowly with an anodic polarization. Introduction of micro metre and nano metre sized cerium oxide in aluminium decreases the corrosion current density by one order compared to pure aluminium. The polarization resistance increases with the increase in amount of mixed oxides in aluminium and is found to be the highest in the case of 0.20%. This is due to the presence of increased amount of cerium oxide in the matrix. Incorporation of nano metre and micro metre sized mixed oxide in aluminium accelerates the cathodic reaction and shifts $E_{\text{corr}}$ to more passive region. Shifting of $E_{\text{corr}}$ to more passive region is attributed to the property of cerium ions that acts as cathodic inhibitors against uniform and localized corrosion. This may be achieved mainly by the suppression of the oxygen reduction reaction\textsuperscript{29}. Zheludkevich et al\textsuperscript{30} introduced mixed oxides of cerium and zirconium in sol gel film where cerium played the role of nano reservoirs storing and slowly releasing cerium ions when a defect is formed in the sol gel film. Incorporation of micro metre and nano metre sized cerium oxide in the aluminium matrix experiences two types of conductivities, viz. ionic and electronic. The latter is stronger and its effect further enhances with the decrease in grain size\textsuperscript{16}. Smaller grain boundaries due to the incorporation of cerium oxide will lower specific resistance of the matrix\textsuperscript{31}. The combined effects of smaller grain size and higher electronic conductivity in the matrix may have resulted quick healing of the outer most aluminium oxide layer from chloride injuries, thus resulting in higher corrosion resistance.

**Electrochemical impedance spectra**

In order to evaluate the corrosion inhibition effect of micro metre and nano metre sized cerium oxide incorporated aluminium, electrochemical impedance spectra (EIS) of samples were taken and the results show that the diameter of the low frequency domain of Nyquist plot is larger with the increase in cerium oxide concentration. The spectral data are fitted to simple Randle’s equivalent circuit model $[R_i(C_1[R_i(C_2R_2)])]$ and the results are shown in Table 2. It is assumed that the high frequency ($R_iC_1$) loop indicates surface characteristics of the aluminium and the possible defects may be present in the surface layer of the matrix\textsuperscript{32}. The low frequency ($R_2C_2$) loop shows the double layer formed at metal solution interface and highlights the significance of internal matrix of the composites. Increased capacitance in the case of low frequency loop compared to high frequency loop shows the thin grain boundary layers perpendicular to the electric field. The results highlight the maximum $R_p$ values exhibited by the coupon with 0.2% each of nano and micro cerium oxide incorporated aluminium. Similarly, lowest constant phase element values are exhibited by the 0.2% each of micro metre and nano metre sized cerium oxide incorporated aluminium. According to Mansfeld\textsuperscript{32} the $C_2$ values show the real corroding region of the sample surface and a lower $C_2$ value is associated to a smaller real corroding area.

**Weight loss studies**

Weight loss studies were carried out by exposing the coupons in 3.5% NaCl for 40 days and the results are shown in Fig. 3. The corrosion rates of micro metre and nano metre sized mixed cerium oxide incorporated aluminium decrease significantly except in the case of T2, where the corrosion rate is

<table>
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<th>Table 2 — Electrochemical impedance parameters of nano and micro cerium oxide incorporated aluminium</th>
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</thead>
<tbody>
<tr>
<td>Cerium oxide%</td>
</tr>
<tr>
<td>High frequency region ($R_1$)</td>
</tr>
<tr>
<td>Pure Al</td>
</tr>
<tr>
<td>0.01</td>
</tr>
<tr>
<td>0.02</td>
</tr>
<tr>
<td>0.05</td>
</tr>
<tr>
<td>0.10</td>
</tr>
<tr>
<td>0.20</td>
</tr>
</tbody>
</table>

*Micro and nano metre sized cerium oxide (1:1).*
increased. There is not much difference found between the treatments, except in the case of coupons having 0.1% each of cerium oxide. There is slight variation in the corrosion rate by weight loss and electrochemical measurements.

**OCP evaluation**

The micro metre and nano metre sized cerium oxide incorporated aluminium were immersed in 3.5% NaCl and the open circuit potential was measured on long term basis. The open circuit variation during the exposure with standard deviation is given in Fig. 4. The average OCP varies from -0.804 to -0.760 V and lowest OCP is recorded by coupons having higher than 0.02% of cerium oxide. The coupons with 0.2% micro metre and nano metre sized cerium oxide incorporated aluminium exhibit lowest OCP and this is correlated with the finding of electrochemical studies. Lower amounts of cerium oxide in the matrix have created more anodic areas and this results in higher corrosion in the matrix.

**Evaluation of corroded aluminium**

The SEM micrographs of corroded specimens show (Fig. 5) the corrosion is minimum near to the cerium oxide and mainly it is in the β space of the matrix. The corrosion pattern is uniform. The results show the superiority of the micro metre and nano metre sized mixed cerium oxide incorporated aluminium.

**Impedance response**

The electrochemical impedance spectra of the corroded coupons were measured and the result are shown in Table 3. The polarization resistance is increased significantly in all the coupons after immersing 40 days in NaCl. Similarly, capacitance is also increased in comparison to the fresh coupons. When coupons are exposed to NaCl, the surface layers are continuously attacked by chloride ions; the micro metre and nano metre sized cerium oxides are exposed more to the surface; and the same acts as cathodic islands. This will slow down the degradation of aluminium. The capacitance in the high frequency region is somewhat uniform in all the coupons highlighting that the surface layer has undergone chloride attack and it is resisted by repairing the defects. The capacitance in the low frequency region exhibits irregular behaviour but the capacitance increases significantly than fresh coupons. The data show that the coupons exhibit higher corrosion resistance when exposed to the aggressive corrosive medium.

**Comparative evaluation**

A comparative evaluation based on linear sweep voltammetric data was carried out and the results are presented in Fig. 6. In our previous work, we have found that 0.2% cerium oxide incorporated aluminium and 0.1% nano cerium oxide incorporated aluminium have superior corrosion resistance.

<p>| Table 3 — Electrochemical impedance parameters of corroded nano and micro cerium oxide incorporated aluminium. |</p>
<table>
<thead>
<tr>
<th>Cerium oxide&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Polarisation resistance Ω cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Capacitance High frequency region (R&lt;sub&gt;1&lt;/sub&gt;)</th>
<th>Low frequency region (R&lt;sub&gt;2&lt;/sub&gt;), nF</th>
<th>High frequency region (C&lt;sub&gt;1&lt;/sub&gt;), µF</th>
<th>Low frequency region (C&lt;sub&gt;2&lt;/sub&gt;), µF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>27.07</td>
<td>77900</td>
<td>5.60</td>
<td>11.27</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>33.01</td>
<td>50633</td>
<td>5.78</td>
<td>3.83</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>32.90</td>
<td>120350</td>
<td>5.49</td>
<td>9.88</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>30.77</td>
<td>130400</td>
<td>5.68</td>
<td>11.10</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>32.27</td>
<td>162300</td>
<td>5.19</td>
<td>11.36</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>32.03</td>
<td>139833</td>
<td>5.23</td>
<td>10.78</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Micro and nano metre sized cerium oxide (1:1).
aluminium are optimum for highest corrosion resistance. The LSV graph of micro metre and nano metre sized cerium oxide incorporated aluminium highlights that the corrosion current density of micro metre and nano metre sized cerium oxide aluminium is significantly lower than that of the above-said cerium oxide incorporated aluminium. In view of the above results, the prepared matrix is a potential candidate for use in marine environment.

Conclusion

Micro and nano metre sized cerium oxide incorporated aluminium exhibits improved surface morphology and smaller grains. The material exhibits excellent corrosion resistance with lowest corrosion current density, higher polarization resistance, and steady and longer current plateau. Similar results are exhibited by EIS, weight loss and EIS of long term exposed panels. The corroded coupons exhibited corrosion in the β position of the matrix, and comparative evaluation with pure aluminium, micro sized cerium oxide incorporated aluminium and nano cerium oxide incorporated aluminium shows significant corrosion resistance character. The result highlights that the prepared matrix is a potential candidate for marine use.

References