Cerium Sulfate Preparation from Egyptian Monazite's Rare Earth Cake for Its Application as Corrosion Inhibitor of Aluminum Alloy AA6061

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Abstract

Pure cerium sulfate was prepared from economic natural resources using Egyptian monazite rare earth cake. About 90% of the former was extracted by tri-butyl phosphate in kerosene at the optimum conditions: 15% solvent concentration, equilibrium pH of 1.7, equilibrium time 7 min and O/A ratio of 1/1. The aim of the present work was studying the corrosion inhibition properties of cerium sulfate towards aluminum alloy AA6061 in two solutions; 1.0 M disodium hydrogen orthophosphate and 3.5 % sodium chloride (simulation of sea water). The corrosion inhibition was evaluated using electrochemical techniques under different experimental conditions. The results showed that, in the presence of cerium sulfate, the AA6061 surface is well protected due to formation of passive film composed of Ce₂O₃/Ce(OH)₃ which precipitated on the electrode surface.

Keywords: Aluminum alloy AA6061, corrosion inhibitor, tri-butyl phosphate, sulfuric acid, cerium sulfate.

1. Introduction

The aluminum alloy AA6061(one of the most important alloys of aluminum) has good nuclear properties such as small cross section for neutron absorption, good corrosion resistance against coolant water, toughness even after long term exposure in a neutron field and short life-times of the radioactive nuclei produced by nuclear reactions [1]. Also, AA6061 is commonly used for construction of aircraft structures such as wings and fuselages, yacht construction, automotive parts and aluminum cans for the packaging of foodstuffs and beverages. In aluminum alloys, the alloying elements introduce heterogeneity into the microstructure, which is the main cause of localized corrosion that initiates in the form of pitting [2-4]. The electrochemical behavior of AA6061 in 3.5% NaCl in the absence and presence of some rare earth elements (REEs) has been studied by means of polarization curves and impedance measurements. The current–potential curves show that, the corrosion resistance of the alloy is greatly enhanced by addition of lanthanide salts especially cerium (Ce) ions which are effective environmentally friendly inhibitors to prevent pitting corrosion [5-8]. The former forms a passive layer on the alloy surface, whose protective properties are reinforced by ageing in solution [9-10].

Consequently; REEs exist in a variety of minerals, the most economic are Bastnasite (La, Ce) FCO₃ (60-70% RE₂O₃), Monazite (Ce, La, Y, Th) PO₄ and Xenotime, (Y) PO₄ [11-13]. Monazite in the black sands (North Delta) represents the main source of rare earth elements in Egypt; it contains about 60% of LREEs and 5-10% HREEs. According to Murthy and Gupta, [14] the reserves of RE₂O₃ from monazite in the Nile Delta are about 120-000 equivalent tons. Solvent extraction was reported to be one of the most effective technique to separate Ce (IV) from RE (III) because of high separation factor values of Ce(IV) to RE(III) (>600) [15-17]. In addition, several number of extractants such as: neutral and acidic organophosphorus extractants have been used for Ce

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separation [18-26]. However, tri-butyl phosphate (TBP) was considered as one of the most selective extractant of Ce especially in its oxidation state (IV) [27-29]. The present work is focusing on studying the corrosion inhibition properties of cerium sulfate prepared from Egyptian monazite cake against the corrosion of aluminum alloy AA6061 in 1.0 M disodium hydrogen orthophosphate and 3.5% sodium chloride solutions.

2. Experimental Work
2.1. Materials and Methods

Aluminum alloy (AA6061) specimens were purchased from Xintai Aluminum Industry Co., Ltd and were used as working electrodes throughout the study. The elemental composition (wt., %) of AA6061 is: Mg: 0.8; Si: 0.4; Cr: 0.35; Zn: 0.25; Cu: 0.15; Mn: 0.15; Ti: 0.15; Fe: 0.1; Al (remainder). Cerous sulfate was purchased from Merck and was used without further purification. Tri-butyl phosphate [Fluka] was used as a solvent for Ce (IV) extraction from Egyptian monazite REE-cake. The latter was analyzed for its rare earth contents using Inductively Coupled Plasma (Prism ICP) High Dispersion (Teledyne Leeman Labs. USA). Ce concentration in its oxidation state (IV) was analyzed by ultra violet-visible spectrometer (Shimadzu UV-160A). Scanning electron microscope (ESEM) EXL 130 attached by energy dispersive spectrometry (EDX) unit system and X-ray diffraction (XRD), a Phillips X- ray unit (PW3710) with a generator (PW1830), using Cu target tube (PW 223/20) and Ni – filter operated at 40 Kv and 30 mA were used during experimental work. Moreover, the potentiodynamic linear polarization experiments were conducted using a Potentiostat/ Galvanostat using an amplifier model 5210 and M 398 software from EG&G Princeton.

2.2. Preparation of Rare Earth Elements Cake

The starting material of the present work is the Egyptian monazite REE-cake. It was prepared by digesting 200g of Rosetta monazite mineral concentrate (90% purity) ground to -300 mesh in 40% NaOH solution at S/L ratio of 1.0/1.5 for 4 h at 140°C [30]. After filtration and thoroughly washing, the obtained hydrous oxide cake was dried and was then treated with concentrated sulfuric acid at S/L ratio of 1.0/1.5 at 85°C for 2h for dissolving its contents of REEs, Th and U. A prior separation of the REEs and Th was carried out. From the mixed oxalate precipitate, it was possible to optimize the selective alkali dissolution of Th using a mixed Na₂CO₃/NaHCO₃ solution leaving behind pure REE-cake. This was carried out at the optimum dissolution conditions of 3/1 Na₂CO₃/Na HCO₃ in a total concentration of 200 g/L and using a solid/liquid ratio of 1/6 for 2h at 75-80°C [31].

2.3. Solvent Extraction of Cerium (IV)

The prepared Egyptian monazite REE-cake was first dissolved in 3M HNO₃ at 80°C for 1 h. An oxidation process upon the prepared nitrate solution was carried out using 1M Na₂S₂O₃ to oxidize Ce(III) to Ce(IV). A series of experiments affecting the extraction efficiency of Ce from the prepared nitrate solution were conducted. These factors included: the concentration of TBP, equilibrium pH, equilibrium contact time and organic/aqueous (O/A) ratios. Different stripping parameters such as: type and concentration of stripping agent, equilibrium contact time and A/O volume ratios were also studied to achieve maximum Ce stripping efficiency. Finally, Ce₂(SO₄)₃·5H₂O was prepared by crystallization and then was used as conversion coatings against the corrosion of the aluminum alloy AA6061.

3. Results and Discussion

3.1. Separation of Pure Cerium from the Prepared Monazite REE-Cake

The Egyptian monazite REE-cake was analyzed for its rare earth contents using Inductively Coupled Plasma (Prism ICP) High Dispersion (Teledyne Leeman Labs. USA) as shown in table (1). The prepared REE-cake was first dissolved in 3M HNO₃ at 80°C for 1 h and its Ce concentration was found to assay 2.4 g/L. An oxidation process upon the prepared nitrate solution was carried out using 1M Na₂S₂O₃ to oxidize Ce(III) to Ce(IV). The extraction of cerium as tetravalent nitrate complex from the aqueous solution using TBP proceeds according to the following equation, [32]:

\[(\text{Ce}^{4+} + 4\text{NO}_3^-)_{\text{aq}} + 2 \text{(TBP)}_{\text{org}} = [\text{Ce(NO}_3)_4\cdot2\text{TBP}]_{\text{org}}\]
3.1.1. Effect of TBP Concentration

Four equilibrium experiments were carried out using TBP concentrations ranging from 5 to 20% (v/v) in kerosene at O/A ratio of 1/1, 5 min equilibrium time and pH of 1.5. After separation, Ce was analyzed in the raffinate aqueous solution to calculate its extraction efficiency. The obtained data given in Figure (1-a) emphasized that, Ce extraction efficiency improved progressively from 36.7 to 84.8% as the concentration of TBP increased from 5 to 15%. However, further increase of the latter to 20% showed a decrease in Ce extraction efficiency to 77.8%; this may be attributed to extraction of other trivalent rare earth elements [33].

3.1.2. Effect of Equilibrium pH

The effect of equilibrium pH values was studied in the range from 1.5 to 2.2 while, the other parameters were kept constant at 15% TBP in kerosene, O/A volume ratio of 1/1 and 5 min equilibrium time. Data in Figure (1-b) revealed that, the extraction of Ce(IV) increased from 84.8 to 87.8% by increasing the equilibrium pH from 1.5 to 1.7. Beyond the latter, the extraction efficiency of Ce(IV) decreased to 79.9%; this may be attributed to the precipitation of Ce as Ce(OH)4 [34].

3.1.3. Effect of Equilibrium Contact Time

This effect was studied at different periods of time ranging from 3 to 12 min using 15% TBP in kerosene, equilibrium pH of 1.7 and O/A volume ratio of 1/1. Data illustrated in Figure (1-c) indicated that, maximum Ce(IV) extraction efficiency of 88.9% was attained at 7 min equilibrium contact time.

3.1.4. Effect of (O/A) Volume Ratios

Different O/A volume ratios ranging from 1/3 to 3/1 were studied by contacting the nitrate solution with 15% TBP in kerosene at pH of 1.7 and 7min equilibrium time. The obtained data in table (2) emphasized that, although the extraction efficiencies of Ce(IV) increased to 92.1 and 94.9% at O/A ratios of 2/1 and 3/1, respectively; but these ratios were not applied because the loaded Ce(IV) was diluted in the organic phase. On the other hand, the O/A ratios of 1/2 and 1/3 showed lower extraction efficiencies of Ce(IV). Indeed, the suitable O/A volume ratio of Ce extraction was 1/1.

Table (1). Chemical composition of REE-cake.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Ce₂O₃</th>
<th>La₂O₃</th>
<th>Nd₂O₃</th>
<th>Sm₂O₃</th>
<th>Pr₂O₃</th>
<th>Gd₂O₃</th>
<th>Dy₂O₃</th>
<th>Y₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>48.8</td>
<td>20.8</td>
<td>21.7</td>
<td>3.9</td>
<td>2.8</td>
<td>0.8</td>
<td>0.3</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Figure (1). Effect of TBP concentration (A), equilibrium pH value (B) and contact time (C) upon the extraction efficiency of Ce(IV).
Table (2). Effect of O/A ratios upon Ce(IV) extraction efficiency [15% TBP conc., pH of 1.7 and contact time 7 min].

<table>
<thead>
<tr>
<th>O/A</th>
<th>Ce(IV) extraction efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3</td>
<td>48.3</td>
</tr>
<tr>
<td>1/2</td>
<td>62.2</td>
</tr>
<tr>
<td>1/1</td>
<td>88.9</td>
</tr>
<tr>
<td>2/1</td>
<td>92.1</td>
</tr>
<tr>
<td>3/1</td>
<td>94.9</td>
</tr>
</tbody>
</table>

From the foregoing study, maximum Ce(IV) extraction efficiency (88.9%) from rare earth nitrate solution was achieved at the optimum conditions of: 15%TBP in kerosene, equilibrium pH 1.7, equilibrium time 7 min and O/A ratio of 1/1.

3.2. Optimization of the Stripping Process

Different stripping parameters were studied for Ce (back extracting) to the aqueous phase. These include the followings:

3.2.1. Effect of Stripping Agent Types

Different stripping agents such as: (cold water, hot water, 2.0M H$_2$SO$_4$ and 2.0M HNO$_3$) were studied at A/O volume ratio of 1/1 and equilibrium time 5 min. The obtained data in figure (2) revealed that, H$_2$SO$_4$ solution is the most effective agent for Ce stripping with efficiency of 82.2%.

3.2.2. Effect of Strip Solution Concentration

This effect was studied by contacting the loaded solvent with different H$_2$SO$_4$ concentrations ranging from 0.2 to 3.0M at A/O ratio of 1/1 and equilibrium time 5 min. Results represented by Figure (3-a) showed that, the maximum Ce stripping efficiency was obtained using 2.0M H$_2$SO$_4$ acid. Further increase in the strip solution’s concentration to 3.0M showed slight improvement in Ce stripping efficiency (85.4%). Therefore, 2.0M H$_2$SO$_4$ was chosen as the suitable concentration.

3.2.3. Effect of Equilibrium Contact Time

Four experiments were performed at A/O of 1/1 and 2.0 M H$_2$SO$_4$ to study the effect of contact time upon Ce stripping efficiency. Figure (3-b) showed that, the contact time of 5 min is sufficient for back extracting approximately 92% of Ce. Further increase in the contact time to 7 and 10 min led to decrease in Ce stripping efficiency to 70.4 and 65.2% respectively. This may be due to transition of some Ce again to the solvent by increasing time [35].

3.2.4. Effect of (A/O) Volume Ratio

The A/O volume ratio in Ce stripping from the loaded TBP with 2.0 M H$_2$SO$_4$ was varied from 3/1 to 1/3 at a contact time of 5 min. As can be seen in table 3, Ce was stripped with 92.4 and 97.2% efficiencies at A/O ratios of 2/1 and 3/1, respectively. At the A/O ratios of 1/2 and 1/3, Ce stripping efficiency decreased to 73.1 and 62.9%, respectively. Thus, the preferable ratio is A/O of 1/1 with 82.2% stripping efficiency to avoid Ce dilution in the aqueous solution.

Table (3). Effect of A/O ratios upon Ce (IV) stripping efficiency [2.0 M H$_2$SO$_4$ and 5 min contact time].

<table>
<thead>
<tr>
<th>A/O volume ration</th>
<th>Ce stripping efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/1</td>
<td>97.2</td>
</tr>
<tr>
<td>2/1</td>
<td>92.4</td>
</tr>
<tr>
<td>1/1</td>
<td>82.2</td>
</tr>
<tr>
<td>1/2</td>
<td>73.1</td>
</tr>
<tr>
<td>1/3</td>
<td>62.9</td>
</tr>
</tbody>
</table>
CERIUM SULFATE PREPARATION FROM EGYPTIAN MONAZITE’S RARE EARTH CAKE

It was important herein to mention that, hydrogen peroxide solution in concentrations ranged from 2-10% was used with H₂SO₄ acid as stripping agent. The H₂O₂ was used as a reducing agent to convert cerium from tetravalent to trivalent state to facilitate the stripping step and to improve the cerium stripping efficiency [36]. Data shown in Figure(3-c) proved that, the stripping efficiency of Ce was obviously increased to reach its maximum value of 99.8% as the concentration of H₂O₂ increased to 10% in the solution of 2.0M H₂SO₄.

From the above study, it could be concluded that, Ce was almost transferred to the aqueous solution with efficiency of 99.8% at the optimum conditions of: 10% H₂O₂ in 2.0M H₂SO₄ concentration, 5 min equilibrium time and A/O ratio of 1/1. The stripped cerium solution was crystallized as cerium sulfate [Ce₂(SO₄)₃·5H₂O] as was confirmed by using XRD and EDX instrumental techniques, (Figures 4 and 5). Moreover, The ICP chemical analysis of the prepared product of Ce₂(SO₄)₃·5H₂O showed a purity of 98.95% with the associated 0.3% Sm, 0.2% La, 0.3% Nd and 0.25% Pr.

However, the prepared Ce₂(SO₄)₃·5H₂O achieved 75% efficiency in comparison to the standard one which may be referred to the existence of some impurities on the prepared Ce₂(SO₄)₃.

Figure (7) displays the polarization E/log I curves for AA6061 in 3.5% NaCl solution devoid of and containing different concentrations (100–500 ppm) of Ce₂(SO₄)₃. As can be seen, the addition of Ce₂(SO₄)₃ to the blank chloride solution, decreases the cathodic current and shifts E_corr to more negative direction and causes a widening of the passive potential range between E_corr and E_pit (i.e., the passivity field).

It can be also seen from Figure (8) that, both the prepared and the synthetic (standard) cerium sulfate inhibits the corrosion of AA6061 in 1.0M Na₂HPO₄ due to formation of Ce₂O₃/Ce(OH)₃ conversion coat on the electrode surface which block the electrode surface from solution.

Figure (3). Effect of H₂SO₄ concentration (A), contact time (B) and H₂O₂ concentration (C), upon Ce stripping efficiency.

Figure (4). XRD analysis of the prepared crystallized cerium sulfate Ce$_2$(SO$_4$)$_3$.5H$_2$O.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>At %</th>
<th>K-Ratio</th>
<th>Z</th>
<th>A</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>31.99</td>
<td>67.28</td>
<td>0.1546</td>
<td>1.1348</td>
<td>0.4228</td>
<td>1.0071</td>
</tr>
<tr>
<td>CeL</td>
<td>68.01</td>
<td>32.72</td>
<td>0.6051</td>
<td>0.9104</td>
<td>0.9774</td>
<td>1.0000</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure (5). The EDX analysis of the prepared crystallized cerium sulfate Ce$_2$(SO$_4$)$_3$.5H$_2$O.

Figure (6). The potentiodynamic polarization curves of AA6061 in 3.5% NaCl solution without and with concentrations of Ce$_2$(SO$_4$)$_3$.5H$_2$O at 30ºC.
Figure (7). The potentiodynamic polarization curves of AA6061 in 3.5% NaCl solution without and with different concentrations of Ce$_2$(SO$_4$)$_3$ at 30°C.

Figure (8). The potentiodynamic polarization curves of AA6061 in 3.5% Na$_2$HPO$_4$ solution without and with 500 ppm of Ce$_2$(SO$_4$)$_3$.5H$_2$O at 30°C
4. Conclusion
An Egyptian monazite REE-cake was first prepared and used as natural economic source of Ce. The latter was separated with purity of 98.9% and extraction efficiency of 88.9% using 15%TBP in kerosene at equilibrium pH of 1.7. The Ce$_2$(SO$_4$)$_3$·5H$_2$O was prepared from the strip solution and was then used as green non toxic corrosion inhibitors for AA6061 alloy. The inhibition mechanism of Ce- salt is attributed to the formation of passive film composed of CeO$_2$/Ce(OH)$_3$ which precipitated on electrode surface. This film blocks the active cathodic sites and reduces the rate of cathodic reaction and consequently the uniform corrosion rate of the alloy.

Compliance with Ethical Standards
The present paper is an original work and all the authors declare that they have no conflicts of interest.

References
[14] Murthy T. S., Gupta C. K., Rare earth resources, their extraction and application; Bhabha Atomic Research Center, Trombay, Bombay, India, (1980).


