

## Corrosion Behavior of Cenosphere - Aluminium Metal Matrix Composite in Seawater Condition

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**Abstract:** Aluminium Alloy (AA) 6063 has been widely used in the fabrication of light-weight structures requiring high strength-to-weight ratios with better corrosion resistance. The corrosion behavior of cenosphere re-inforced AA 6063 with different compositions of cenosphere volume percentages (5%, 10% and 15%) were monitored in this study. To analyze the corrosion behavior of aluminum composite in seawater condition, the electrochemical behavior of the composite was experimented, using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Results obtained from Nyquist and Bode plots were compared with pure aluminium alloy and inferred that cenosphere-aluminium composite has better corrosion resistance. The surface morphology was investigated by recording the scanning electron microscopy (SEM) images of AA6063 and composites.

**Keywords:** Corrosion; Aluminium; Cenosphere; Seawater.

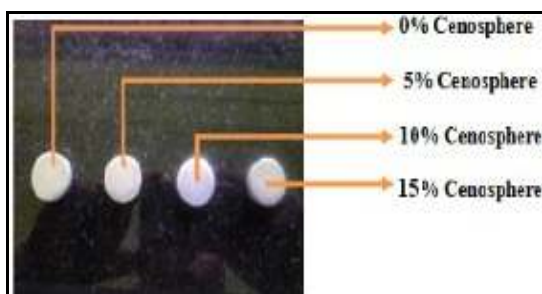
### 1. Introduction

The good corrosion resistance property of AA6063 makes it one of the commonly used aluminium alloy in seawater conditions. The oxide film, that develops on aluminum when exposed to the atmosphere or aqueous solutions will resist corrosion but is amphoteric and dissolves substantially when the metal is exposed to high concentrations of acids or bases [1]. Various methods like inhibitors and coating have been employed to reduce corrosion. The fresh oxygen and moisture brought in by air circulation becomes a disadvantage in case of inhibitors. Immersion time or the inhibitor addition to seawater will not affect corrosion drastically. Inhibition efficiency increases with increase in the concentration of the organic compound but decreases with rise in temperature [2]. Coating can be used to protect from corrosion but not permanently [3-6]. Nanostructured coating can be used to improve the corrosion resistance [7]. Metal matrix composites reduce corrosion in addition to bringing in other mechanical properties. Alumina with aluminium alloy 6063 has good corrosion resistance property in NaCl environment [8]. In the present investigation cenosphere re-inforced aluminium alloy was investigated in seawater conditions to observe the extent of corrosion resistance.

### 2. Raw Materials

The matrix material used in the experiment was AA6063. It has good mechanical properties and is heat treatable and weldable. It has a specific gravity of 2.6 g/cc (0.097 lb/cubic inch). Metallurgical properties of AA6063 highly depend on their chemical composition. AA6063 was bought from the market in bar and wire forms. To check its chemical composition spark test specimen was made and tested. The major elements of

AA6063 are Si (0.42%), Fe (0.28%), Cu (0.034%), Mn (0.07%), Mg (0.27%), Zn (0.055%), Ti (0.16%), Pb (0.16%) and Al (98.66%). The reinforcement material is the cenosphere particles, which are generally spherical in shape and range in size from 1  $\mu\text{m}$  to 500  $\mu\text{m}$ . They mainly consist of silicon dioxide in two forms (amorphous and crystalline), aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and iron oxide ( $\text{Fe}_2\text{O}_3$ ). The mixture of glassy crystalline particles like quartz, mullite and various oxides forms cenosphere making it heterogeneous. The characteristics of the particulate composite greatly depend upon the nature, size, density and its distribution. The composite produced possess good dispersion and reinforcement due to the size range of cenospheres. Particles were separated into size range 1-100 micron and used to prepare the specimens. The chemical compositions of cenosphere are  $\text{SiO}_2$  (55 %),  $\text{Al}_2\text{O}_3$  (31%),  $\text{Fe}_2\text{O}_3$  (5%),  $\text{K}_2\text{O}$  (5%),  $\text{Na}_2\text{O}$  (1%),  $\text{TiO}_2$  (1%) and  $\text{CaO}$  (0.5%). The cenosphere particles used for dispersion were 5%, 10% and 20% in volume. AA6063 was melted in a resistance furnace at 730° C and stirred using a turbine type stirrer. It was stirred up to 5-7 minutes at an impeller speed of 480 rpm. The cenosphere particles were dispersed in the melt using vortex method while the temperature was maintained at 700° C. The melt with reinforced particulates were poured into sand mould and allowed to solidify. Casted specimens were machined with diameter of 30 mm and length of 50 mm by using wire cut Electric discharge Machining (EDM). Wire cut EDM was used to get a less stressed surface which was exposed to the solution for corrosion testing. The specimen was polished using SiC grit sheets of five different sizes and velvet buffing wheel by dipping the specimen in kerosene to reduce pitting. The prepared specimens are shown in figure 1.

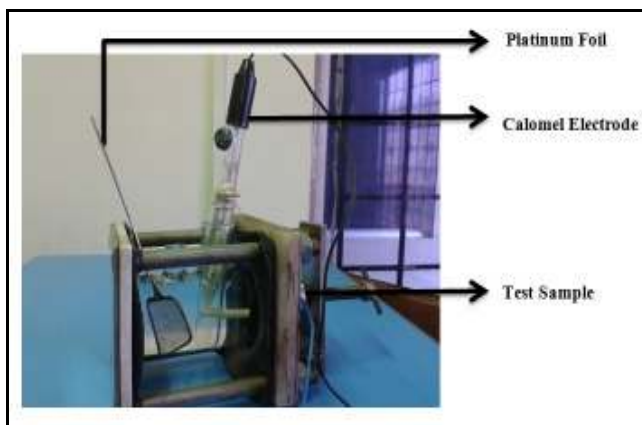


**Figure 1.AA6063 and Composite Specimen**

### 3. Experimental

Experiment was conducted on specimens using electrochemical impedance spectroscopy (EIS) and DC polarization techniques when immersed in seawater solution open to air and at room temperature of 25° C for one day. Seawater environment maintained a salinity of about 3.5% (35 g/L, or 599 mm). A three-electrode set-up was used with impedance spectra being recorded at the corrosion potential ( $E_{\text{corr}}$ ). EIS was performed between 0.01 Hz - 65 kHz frequency range using a frequency response analyzer. The frequency response analyzer was used for impedance data analysis and to fit parameters. The response of electrochemical systems was very nonlinear. The impedance was interrogated in a perturbative manner by small amplitude (~10 mV) AC ripple on top of the controlled DC polarization potential. Potentiodynamic polarization technique was performed to find the behavior of composite material in an environment which was made by forcing the material from its steady state corrosion rate. This was done at a constant voltage scan rate. The response of the current to the application and removal of the voltage force was observed. Potential was applied in a controlled manner to an electrode which was made by the composite under study. The experiment was conducted based on ASTM Standard G61. The potential was ramped at a continuous, often slow rate relative to a reference electrode using an instrument called potentiostat. The potential was first increased at a constant rate in the anodic or noble direction (forward scan). The scan direction was reversed at some chosen maximum current or voltage and progressed at the same rate in the cathodic or active direction (backward or reverse portion of the scan). The scan was terminated at another chosen voltage either the original corrosion potential or some voltage active with respect to that corrosion potential. The voltage at which the scan started was the corrosion potential as measured after the corrosion reaction has reached a steady state. The corrosion behavior was predicted from the structure of the polarization scan. The potentiodynamic polarization tests were performed with a potentiostat (Gill AC) of ACM Instruments, UK. The electrochemical cell consists of three electrodes out of which sample being interrogated was taken as working electrode. A saturated calomel electrode (SCE) formed the reference electrode which provided a stable "reference" against which the applied potential could be accurately measured.

A platinum electrode served as the counter electrode which provided the path for the applied current into the solution. The design of the cell was such that only an area of  $1 \text{ cm}^2$  of the composite surface was exposed to the electrolyte. The potentiostat was controlled through a PC which also captures the polarization data. The polarization plot was obtained from the Power Suite software, which also possesses a special tool in order to manually extrapolate the values of  $E_{\text{corr}}$  (corrosion potential) and  $I_{\text{corr}}$  (corrosion current density) from the plot. The Test sample was experimented to find the corrosion resistance in it. The experimental setup used for current study is shown in figure 2.



**Figure 2.**Three electrode systemsetup

#### 4. Results and Discussion

In this study, the corrosion behavior of AA6063 specimens containing different amount of cenospheres were investigated using electrochemical impedance spectroscopy (EIS) in seawater conditions. The measured impedance spectrum is displayed in the form of a Nyquist diagram and Bode diagrams in figure 3. The Nyquist plot displays the impedance data by the complex variables separated into real ( $Z_{\text{re}}$ ) and imaginary ( $Z_{\text{im}}$ ) parts, expressed in  $\Omega \text{ cm}^2$ . But in the Bode diagram the frequency dependence of the absolute magnitudes of the impedance modulus ( $|Z|$ ) and the phase angle are plotted. The advantages of this procedure are that the data for all measured frequencies and a wide range of impedance values can be displayed simultaneously.

The changes in the impedance characteristics as a result of the exposure of the specimens to the corrosive environments could be detected from the comparison of the spectra. These variations are related to the different percentage of cenosphere reinforcement on AA6063. In 5% and 15% cenosphere reinforcement, there was no effective protection to AA6063 against corrosion in seawater condition, whereas in 10% reinforcement an effective corrosion resistance was provided. The corrosion resistance of AA6063 without cenosphere is less than  $4 \times 10^3 \Omega \text{ cm}^2$ . The resistance increased after addition of 10% cenosphere which is more than  $6 \times 10^3 \Omega \text{ cm}^2$ . Bode plot showed that the pitting resistance of the AA6063 improved with the addition of 10% cenosphere content which was confirmed by the relaxation of the impedance spectra. This may be attributed to formation of rich oxide films with Si and Al. Low impedance modulus values in the order of  $105 \Omega \text{ cm}^2$  were measured. The response of the system must be described as resistive over all the frequency range (as characterized by phase angles smaller than 70 degrees). The experiments showed that 5% and 15% cenosphere reinforcement could not provide a better corrosion resistance compared with AA6063. A better situation was observed with the 10% reinforcement, shortly after immersion in the test electrolyte. For 10% reinforcement, even at small frequency range, phase angle is equal or excess to pure AA6063 phase angle.

Polarization measurements were performed for the AA6063 and composites after 30 minutes of immersion in seawater solution. AA6063 with 5% cenosphere reinforcement showed a better polarization resistance than the AA6063. But AA6063 with 10% cenosphere reinforcement showed even better polarization resistance than the AA6063 and 5% reinforcement. The corrosion potential of 5% and 10% reinforcement were shifted towards the passive direction compared with the pure AA6063. Composite with 15% reinforcement did not show improvement when compared with pure AA6063. The results obtained from polarization measurements are displayed in figure 4.

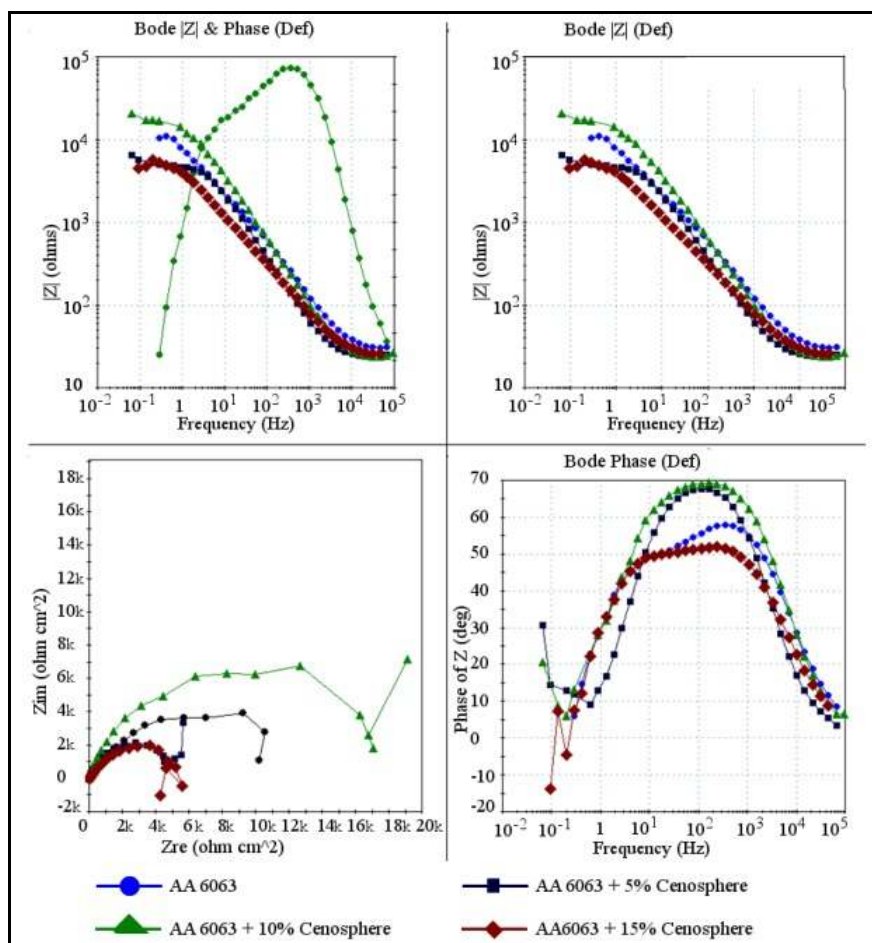


Figure 3. Experimental impedance spectra of aluminium 6063 with different volume % of cenospheres in seawater solution.

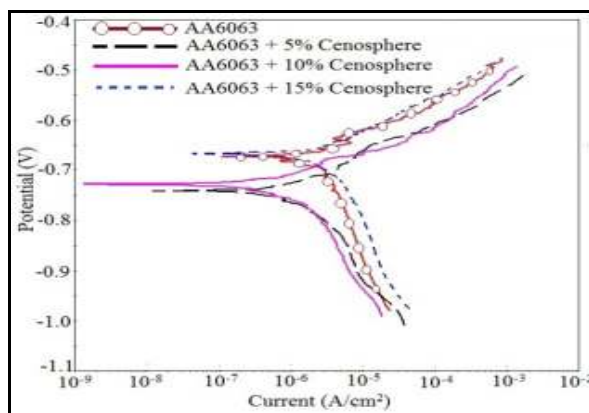


Figure 4. Potentiodynamic polarization in seawater solution

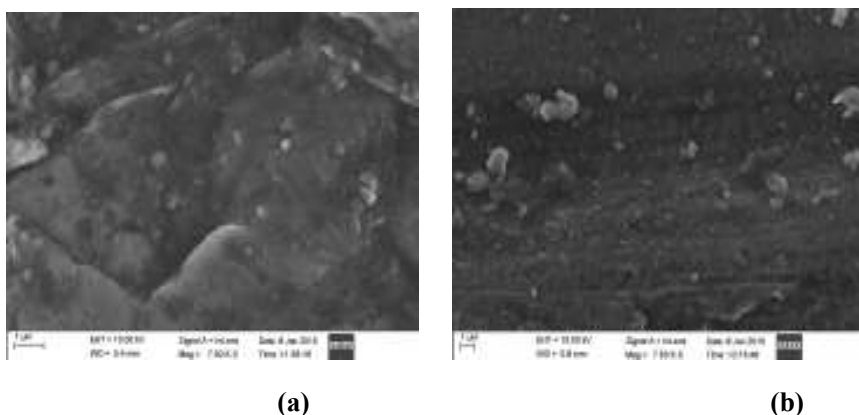
It was observed that, both cathodic ( $\beta_c$ ) and anodic ( $\beta_a$ ) current densities changed with the presence of cenosphere. This behavior indicates that cenosphere affects both anodic and cathodic reaction of corrosion process. The values for the corrosion potentials and corrosion current densities were estimated from the intersection of the anodic and cathodic Tafel lines. The corresponding corrosion potentials ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ), anodic Tafel slopes ( $\beta_a$ ), cathodic Tafel slopes ( $\beta_c$ ) and corrosion rate (CR) are listed in the table below.

**Table 1.**Corrosion parameters of AA6063 and composites

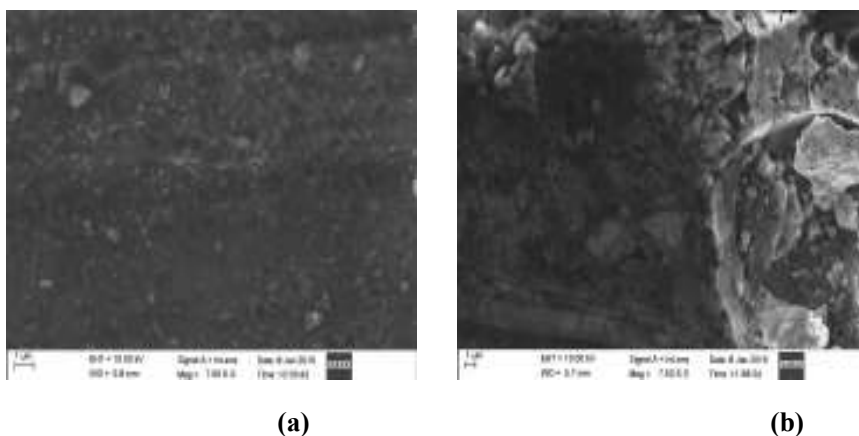
Parameters	AA6063	AA6063 with 5 % cenosphere	AA6063 with 10% cenosphere	AA6063 with 15% cenosphere
E <sub>corr</sub> (I=0) (mV)	-673.04	-741.08	-673.04	-673.04
I <sub>corr</sub> (μA)	3.11	1.39	1.109	1.41
β <sub>c</sub> (mV)	534.73	219.79	554.73	462.73
β <sub>a</sub> (mV)	95.46	97.51	95.465	97.46
CR (mpy)	2.38	1.89	1.63	1.93

#### 4.1. Surface Morphology

The morphology study of the surface of AA6063 and composites after corrosion tests was undertaken by field emission scanning electron microscope (FESEM). The SEM analysis was carried out for each specimen at magnification of 7500 X under an accelerating voltage of 10kV. The results of the SEM analysis are shown in the figure 5 and figure 6.



**Figure 5.**SEM images of corroded samples at 7500 X. (a) AA6063, (b) AA6063 with 5% Cenosphere



**Figure 6.**SEM images of corroded samples at 7500 X. (a) AA6063 with 10% Cenosphere, (b) AA6063 with 15% Cenosphere

The SEM images show the practical evidences of the corrosion protection ability of AA6063 and composites. The reinforcement of cenosphere particles into aluminium matrix was revealed by the presence of spherical shaped grains on the surface of composite samples. Pure aluminium alloy undergoes more dissolution than composites. Figure 5(a) indicates the easy dissolution of the crystals during corrosion.

The SEM images of pure AA6063 showed larger deep pits arising out of higher corrosion rate. The composites with 5% and 10% cenosphere showed in figure 5(b) and 6(a) exhibited small pits distributed throughout the surface and resulted in uniform corrosion with lower rate. But figure 6(b) implies that the

composite with 15% cenosphere showed more corrosion due to brittle fracture. The change in corrosion rate is due to the increase in brittleness caused by increase in cenosphere percentage.

## 5. Conclusion

From the analysis of the impedance spectra of cenosphere reinforced AA6063 specimens immersed in seawater solution at ambient temperature, the excellent anticorrosion characteristics of an AA6063 with 10% cenosphere reinforcement have been demonstrated. AA6063 showed less improvement for 5% reinforcement. AA6063 did not show improvement when the reinforcement is 15%. The SEM images revealed higher corrosion resistance property of composite with 5% and 10% cenosphere compared to pure AA6063. Hence the best among all the above mentioned compositions is AA6063 with 10% of cenosphere as it possesses high corrosion resistance property. The residues generated during the combustion of coal (Fly Ash-Cenosphere) can be effectively utilized for particulate reinforcement in Aluminium Metal Matrix.

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