Corrosion resistance study of UNS A93105 aluminum alloy in neutral chloride and acid chloride solution

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Abstract: The corrosion resistance of UNS A93015 aluminum alloy (A93015) was studied in neutral chloride solution at specific chloride concentration and in 3.5% neutral chloride solution at specific sulphate concentration by potentiodynamic polarization technique, open circuit potential measurement (OCP) and optical microscopy characterization. The presence of sulphate ions in the neutral chloride solution significantly increased the corrosion rate of A93015 compared to the solutions with chloride ions. At 0.5% NaCl concentration, the lowest corrosion rate of 0.255 mm/y was obtained in the neutral chloride solution which corresponds to polarization resistance of 1121 Ω. The corrosion rate value increased to 0.295 mm/y at 3.5% NaCl with significant cathodic shift in corrosion potential. The presence of sulphate ion in the neutral chloride solution significantly increased the corrosion rate of A93015. At 0.00625M sulphate ion concentration the corrosion rate is 4.739 mm/y while at 0.1M concentration, the corrosion rate is 22.176. OCP curves of A93015 at 0.5% and 3.5% NaCl concentration transited anodically to -0.651 V and -0.703 V with relative thermodynamic stability. A93015 OCP plots from 3.5% NaCl solution at 0.00625 M and 0.1 M SO$_4^{2-}$ ion concentration shifted the OCP plots cathodically with absence of potential transients which signifies improved thermodynamic stability.

1. INTRODUCTION

Aluminum alloy has extensive industrial application in most industries due to its excellent strength to weight ratio, formability and corrosion resistance [1, 2]. Aluminium properties can be tailored to meet the demands of specific applications through the addition of alloying elements, its processing types and conditions etc. [3]. Purely refined aluminium from its ore has appreciable resistance to corrosion, however, it application is limited due to its weak structural strength. The heterogeneous microstructural properties of aluminium with the addition of other elements for improved performance expose the substrate aluminium to corrosion [4-8]. The high corrosion resistance of aluminium alloys compared to carbon steels is due to the formation of a protective oxide film on the alloy surface which shields it from aggressive anion attack. Under certain corrosive conditions the protective oxide is partially stable. However, at higher concentrations of chlorides, sulphates, thiosulphates etc the protective oxide breaks exposing the aluminium alloy to localized corrosion deterioration [9]. A number of factors determined the operating lifespan and corrosion resistance of aluminium alloys. In industry, the operating environment is hugely important. However, appropriate selection of aluminium alloy series for the specific environment improves the operating lifespan of aluminum. Marine environment is highly corrosive to aluminum alloys due to its chloride ion content [10]. Some other environments contain sulphur and nitrogen oxides from the combustion of fossil fuels which combine with atmospheric water to form acids. The acids corrode the aluminum surfaces which come in contact with it [11]. Effective utilization of aluminum alloy is directly linked to the appropriate condition under which it performs optimally with minimal risk of corrosion. A93015
aluminum alloy is a 3000-series aluminum alloy whose main alloying addition is manganese, which it is processed primarily into wrought products for application in environments that exposes them to chlorides and sulphates. This paper focuses the corrosion resistance of A93015 aluminum alloy in neutral chloride solution at specific chloride concentration and in 3.5% neutral chloride solution at specific sulphate concentration.

2. MATERIAL AND METHODS

UNS A93015 aluminum alloy (A93015) was cut, sectioned and subsequently encased in resin mounts with visible surface area of 1 cm². The exposed surface was grinded with coarse silicon carbide papers. Analar grade NaCl was formulated in volumetric concentrations of 0.5%, 1%, 1.5%, 2%, 2.5%, 3% and 3.5% NaCl in 200 mL of H₂O. Analar grade H₂SO₄ (98% purity) was prepared in molar concentration of 0.00625 M, 0.0125 M, 0.025 M, 0.05 M and 0.1 in neutral chloride solution at 3.5% NaCl concentration. Potentiodynamic polarization test on A93015 was done with Digi-Ivy Potentiostat. A triple electrode configuration linked the aluminium working electrode with the Potentiostat. The electrodes were submerged in 200 mL of the neutral chloride and acid chloride solution inside glass container. Open circuit potential measurement of A93015 was done at step potential of 0.1V/s for 5400 s in neutral chloride solution (0.5% NaCl and 3.5% NaCl), and 3.5% NaCl solution at 0.00625 M and 0.1 M H₂SO₄ concentration) with the aid of Digi-Ivy 2311 potentiostat.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization studies

Table Potentiodynamic polarization data for A93015 corrosion in neutral chloride and acid chloride solution are shown in Tables 1 and 2. A93015 corroded more significantly in the acid chloride solution due to the combined effect of sulphate and chloride ions within the electrolyte compared to chloride ions only within the neutral chloride media. Corrosion rate of 0.255 mm/y was obtained at 0.5% NaCl concentration (polarization resistance = 1121 Ω). At optimal NaCl concentration (3.5%) simulating seawater the corrosion rate is 295 mm/y (polarization resistance = 823.71 Ω). It must be noted that the corrosion rate of A93015 aluminium is increased with increase in chloride concentration. Variation in corrosion potential caused significant shift in the cathodic direction from 0.5%-1% NaCl concentration, signifying dominant cathodic reaction mechanism. Beyond 1% NaCl concentration, the corrosion potential of A93015 shifted to anodic values due to increase of Al³⁺ ion into the electrolyte [12, 13]. The presence of sulphate ions in the neutral chloride solution at 3.5% NaCl concentration significantly increased the vulnerability of A93015 to corrosion. Addition of sulphate ion at 0.00625M concentration increased the corrosion rate to 4.739 mm/y (polarization resistance = 57.55 Ω). At this concentration, the corrosion potential transited from -1.030 V to -0.691 V due to increase in anodic dissolution of the aluminum alloy and diffusion of Al³⁺ into the acid chloride solution. The sulphate ion destroyed the protective oxide on A93015 surface compared to the electrochemical action of chlorides which tends to be more localized. Significant increase in corrosion rate occurred at 0.0125M SO⁴⁻ ion concentration to 16.115 mm/y corresponding to polarization resistance of 16.92. Ω due to the higher concentration of sulphate ions. This indicates that sulphate concentration greater than 0.0125 M is not appropriate foe A93015 application. The optimal corrosion rate of 22.176 mm/y was attained at 0.1 M sulphate concentration.
Table 1. Potentiodynamic polarization data of A93015 corrosion in neutral chloride solution (0.5% to 3.5% NaCl)

| Sample | NaCl Conc. (%) | Corrosion Rate, $C_r$ (mm/y) | Corrosion Current, $C_i$ (A) | Corrosion Current Density, $C_j$ (A/cm²) | Corrosion Potential, $C_p$ (V) | Polarization Resistance, $R_p$ (Ω) | Cathodic Tafel Slope, $B_c$ (V/dec) | Anodic Tafel Slope, $B_a$ (V/dec) |
|--------|----------------|-------------------------------|-----------------------------|---------------------------------------------|-------------------------------|--------------------------------|--------------------------------|---------------------------------|
| A      | 0.5            | 0.255                         | 2.29E-05                    | -0.636                                      | 1121.00                       | -9.700                          | 4.880                           |
| B      | 1              | 0.263                         | 2.36E-05                    | -1.244                                      | 1088.00                       | -1.071                          | 2.108                           |
| C      | 1.5            | 0.269                         | 2.42E-05                    | -1.210                                      | 1025.00                       | -3.522                          | 1.728                           |
| D      | 2              | 0.273                         | 2.46E-05                    | -1.114                                      | 1001.00                       | -1.037                          | 1.420                           |
| E      | 2.5            | 0.278                         | 2.50E-05                    | -1.106                                      | 976.00                        | -1.052                          | 2.225                           |
| F      | 3              | 0.286                         | 2.57E-05                    | -1.076                                      | 922.00                        | -1.110                          | 2.161                           |
| G      | 3.5            | 0.295                         | 2.78E-05                    | -1.030                                      | 823.71                        | -1.664                          | 2.830                           |

Table 2. Potentiodynamic polarization data of A93015 corrosion 3.5% NaCl solution at 0 M to 0.1 M sulphate concentration

| Sample | $H_2SO_4$ Conc. (%) | Corrosion Rate, $C_r$ (mm/y) | Corrosion Current, $C_i$ (A) | Corrosion Current Density, $C_j$ (A/cm²) | Corrosion Potential, $C_p$ (V) | Polarization Resistance, $R_p$ (Ω) | Cathodic Tafel Slope, $B_c$ (V/dec) | Anodic Tafel Slope, $B_a$ (V/dec) |
|--------|---------------------|-------------------------------|-----------------------------|---------------------------------------------|-------------------------------|--------------------------------|--------------------------------|---------------------------------|
| A      | 0                   | 0.295                         | 2.78E-05                    | -1.030                                      | 923.70                        | -1.664                          | 14.83                           |
| B      | 0.00625             | 4.739                         | 4.46E-04                    | -0.662                                      | 57.55                         | -5.072                          | 0.669                           |
| C      | 0.0125              | 16.115                        | 1.52E-03                    | -0.682                                      | 16.92                         | -4.271                          | 0.165                           |
| D      | 0.025               | 17.155                        | 1.62E-03                    | -0.687                                      | 16.95                         | -4.562                          | 1.421                           |
| E      | 0.05                | 20.755                        | 1.96E-03                    | -0.651                                      | 13.45                         | -4.911                          | 1.454                           |
| F      | 0.1                 | 22.176                        | 2.09E-03                    | -0.664                                      | 10.30                         | -4.993                          | -1.647                          |

3.2 Open circuit potential measurement
Tables OCP curves for A93015 aluminium in neutral chloride solution at 0.5% NaCl and 3.5% NaCl, and in 3.5% NaCl solution at 0.00625 M and 0.1 M sulphate concentration are depicted in figure 1 and figure 2. The curve for A93015 in 0.5% NaCl and 3.5% NaCl transited anodically -0.703 V and -0.651 V at 405 s and 584.2 s. At this point the curves indicated relative thermodynamic stability due to formation of inert protective oxide of $Al_2O_3$ on the alloy surface. The curve for A93015 in 0.5% NaCl solution is relatively more anodic than at 3.5% NaCl due to higher concentration chlorides which increases the vulnerability of the alloy to corrosion. The visible presence of potential transients on the OCP curve at 3.5% NaCl concentration confirms this due to the collapse and reforming of the protective oxide on the alloy. The OCP curves from 3.5% NaCl solution at sulphate concentrations of 0.00625 M and 0.1 M concentration shifted to more negative values compared to the OCP curves at from neutral chloride solution at 3.5% NaCl concentration due to greater vulnerability to corrosion. However, the curves are more thermodynamically stable from the visible decrease in active-passive shift of the curves though 0.00625 M was more electronegative.
4. CONCLUSION

The corrosion behaviour of UNS A93105 aluminum alloy in neutral chloride and sulphate-chloride solution was studied. The corrosion rate of the aluminium alloy increased with increase in chloride concentration with 3.5% NaCl solution having the highest corrosion rate. Corrosion of the aluminium in the acid chloride solution were significantly higher than values obtained from neutral chloride solution due to the accelerated deterioration of the alloy in the presence of \( \text{SO}_4^{2-} \) and \( \text{Cl}^- \) ions compared to \( \text{Cl}^- \) ion only in the neutral chloride solution. Cathodic transition of the aluminium corrosion potential is proportional to increase in chloride concentration. Curves from open circuit potential measurement in neutral chloride solution transited anodically with visible potential transients and active-passive shift before attaining thermodynamic stability. Sulphate ions within the neutral chloride solution shifts the potential of the curves cathodically in addition to significant decrease in active-passive shift and thermodynamic stability.
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