Mechanical Behaviour of Heat Treated Al 2024 Alloy Using R-2,C-6-Diphenyl-T-3-Ethylpiperidin-4-one Semicarbazone Compound in 3.5% Nacl Solution

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Abstract

In the present research work, corrosion behavior of heat treated Al 2024 alloy in 3.5% NaCl with and without heat treatment in different concentration of inhibitors is studied. Rectangular specimen 2cm X 1cm X 1mm was subjected heat treatment for 2h, 4h and 6 hours in Muffle furnace at 550^{0}C. The specimen were tested for corrosion characterization of Electrochemical studies test. The result obtained is compared with heat treated and non-heat treated specimen. It was found that the heat treated specimen exhibits excellent corrosion Resistance when compared to non-heated specimen.

Keywords: Al 2024 alloy, Muffle furnace, potentiodynamic polarization, impedance.

Introduction

Aluminum remains as one of the most desired metallic materials because of its numerous application areas which include automobiles, aerospace, constructions etc. It is also the third most abundant element constituting about 8.13 % in the earth's crust and it mainly exists in very stable combinations with other materials (particularly as silicates and oxides) in nature. Metals and alloys are the most important sources of engineering materials, and the demand for these materials with improved properties (i.e. strength, ductility, light weight) is always on the increase with the ever advancement of science and technology.

The advantages are such as light weight with acceptable strength, high conductivity and good corrosion resistance due to the presence of barrier oxide film layer. For instance, aluminum's light weight performances are highly benefitted in transport applications that are related to aerospace industry. The metal has been widely used as construction materials, heat exchangers, catalyst, combustion processes, and power lines.

This research aims to investigate the corrosion resistance of 356 Al alloy of the heat treated specimens of peak age and over age tempers in 3.5% NaCl solution and compare the corrosion resistivity of different concentration of inhibitors. The surface morphology was also investigated to observe any change in the microstructure of the heat treated specimens produced after corrosion immersion test in an aggressive 3.5% NaCl medium. These alloys show specific behavior in Retrogression and Re-aging (RRA) heat treatments. The most important feature of the aluminium alloy is to form oxide on surface which acts as a barrier. This barrier oxide breaks due to aggressive environments and thus study of the corrosion parameters of any alloy is required to understand to estimate the current and its reaction with a metal surface.

Material and Methods

The alloy selected for the work is Al 2024alloy which is commercially available. Its composition is given in table 1.

Al 2024 ingots which are available commercially were melted in a furnace to a temperature slightly above melting point. Then the melt is poured into preheated cast iron moulds. Cylindrical castings are subjected to machining to get specimens of size 2cm x 1 cm x 1 mm. The specimens were abraded with silicon carbide papers of different numbers 400, 800, 1200 and 2500 grade and then polished with the help of polishing wheel. Before immersing in the corrosion media, the specimens were cleaned using double distilled water, acetone and dried at room temperature.

Muffule furnance for heat treatment

specimens for mechanical behaviour

Synthesis of Inhibitors

Synthesis of *r-2, c*-6-diphenylpiperidin-4-one semicarbazone

The method of Balasubramaniam and Padma[10] was followed for the preparation of the compound *r*-2, *c*-6-diphenylpiperidin-4-one (P1). To the solution of *r*-2, *c*-6-diphenylpiperidin-4-one (1.2g in 15 ml ethanol), ethanolic solution of semicarbazide hydrochloride (0.5g) and sodium acetate (0.5g) were added. The resulting mixture was stirred by use of magnetic stirrer till the precipitate was formed. The product formed was filtered off and washed with water. Crystallization from ethanol gave 62% yield with an m.pt range of 176-178^0 C

Characterization details:

Appearance; white color; MS (ESI, Positive): m/z; $(M+H)^+$: 188; ^{1}H-NMR (800MHz, $CDCl_3$-d); δ= 10.91 1H(s, NH), 8.82-8.51 2H(d, ArH_2, ArH_6), 8.35 1H(s,-N-CH=N-), 7.72 2H(d, ArH_3, ArH_5), 7.36-7.38 2H(s, NH_2), 7.1.6-7.18 1H(ArH_4), 13C-NMR (800MHz, CDCl3-d);158.46, 136.65, 129.25, 125.35, 122.25, 40.22, 40.11, 39.91, 39.80;analytical calculated for; $C_9H_8N_4$; C, 62.78, H, 4.28, N, 32.54; found; C, 62.54, H, 4.11, N, 32.11.

Corrosion media: A standard 3.5% NaCl solution was prepared in distilled water using research grade salt. The inhibitor was dissolved in standard 3.5% NaCl solution to estimate corrosion inhibition efficiency and corrosion resistance on Al 2024 alloy. Inhibitors from 50ppm to 200ppm were added in NaCl solution to conduct experiments at temperatures of 550°C with different time intervals of heat treatment. Analyses were carried out using Muffle furnace.

Experimental details: Heat treatment was carried out at 550°C for 2h, 4h, and 8h. Primarily, the specimens were positioned in the Muffle furnace and slowly heated up to 550°C. The samples after various intervals of time were taken out from the Muffle furnace and afterwards quenched in water and carried out (after and before heat treatment) using Electrochemical workstation of CH-instrument (CHI606E). All the specimens were metallographically polished by using various grades of emery papers monitored by alumina polishing and then finally washed with acetone. Electrochemical studies were carried out for as cast and heat treated specimens in 3.5% NaCl solution containing different amounts of inhibitor.

Electrochemical measurements: The electrochemical corrosion cell was arranged in a glass beaker with a conventional three electrode system. Al 2024 alloy was the working electrode. Platinum was used as the reference and Silver/Silver chloride (3.5mol/L KCl) is a counter electrode. The potentiodynamic polarization and electrochemical impedance studies tests were conducted in 3.5% NaCl solution.

Potentiodynamic polarization studies: Potentiodynamic polarization and EIS tests were conducted after measuring the open circuit potential and to study the intergranular corrosion of the specimens. Potentiodynamic polarization measurements were carried out starting from -100 mV (OCP) to +300 mV (OCP) at a sweep rate of 0.5mV/s. In order to assess the reproducibility, potentiodynamic polarization measurements were conducted for triplicate specimens in each experimental condition. The corrosion parameters such as corrosion current density (Icorr), corrosion potential (Ecorr) and passivation current density (Ipass) were involved in quantitative information which were obtained to understand the effect of heat treatments on passivation and corrosion characteristics of Al 2024 alloy.

Corrosion of Aluminium in chloride solution: Pitting corrosion is the most dangerous type of aluminum corrosion. It

Occurs as holes and pits of irregular shapes on the surface of the metal. The diameter and depth of the pits are dependent on the type of material, the corrosive medium, and the properties of the environment that the aluminum and its alloys are exposed to pitting corrosion of aluminum taking place frequently in aerated chloride solutions.

Chloride ions attack the natural oxide layer damaging it in the weakest parts. On the anodic sites, two main reactions occur:

$Al \longrightarrow Al^{3+} + 3e^-$ (1)

$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$ (2)

Equation (1) shows that at anodic sites, a more acidic (pH = 3–4) environment is created. The chloride ions facilitate the anodic dissolution of aluminum forming aluminum chloride. The later hydrolyzes to form the hydroxide and acid which shifts the pH to acidic values.

Equations (3) and (4) show the possible reactions at the cathodic sites:

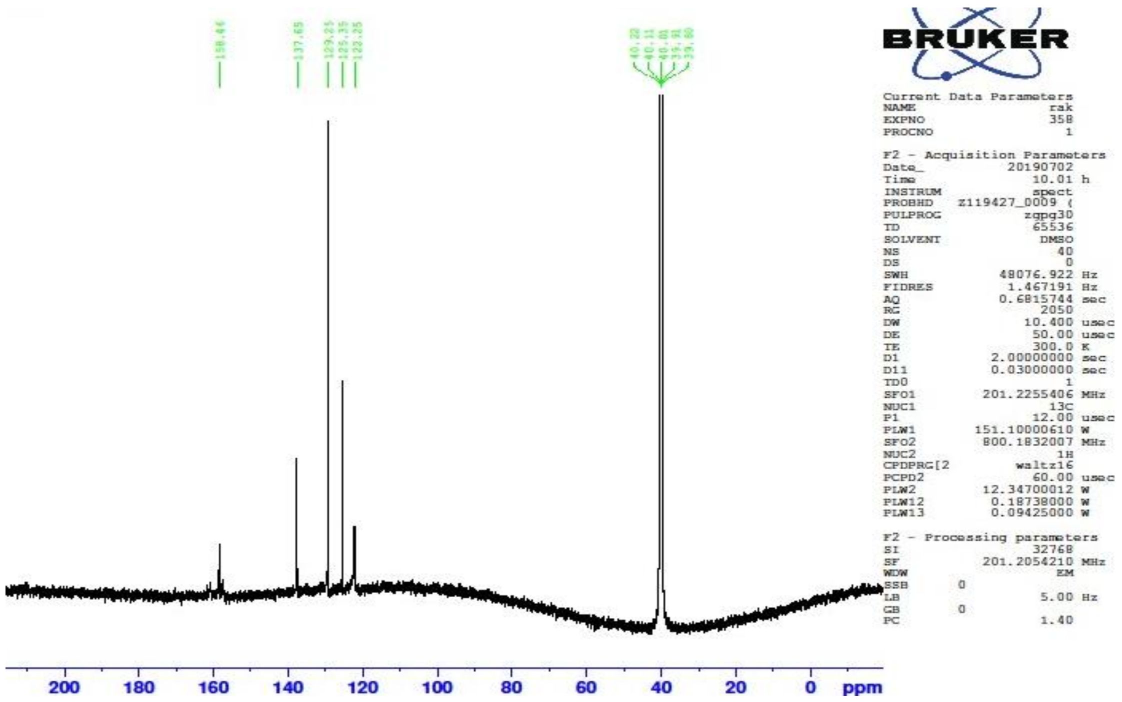

Figure 2: ^{13}C NMR spectra of r-2,c-6-diphenyl-t-3-ethylpiperidin-4-one semicarbazone

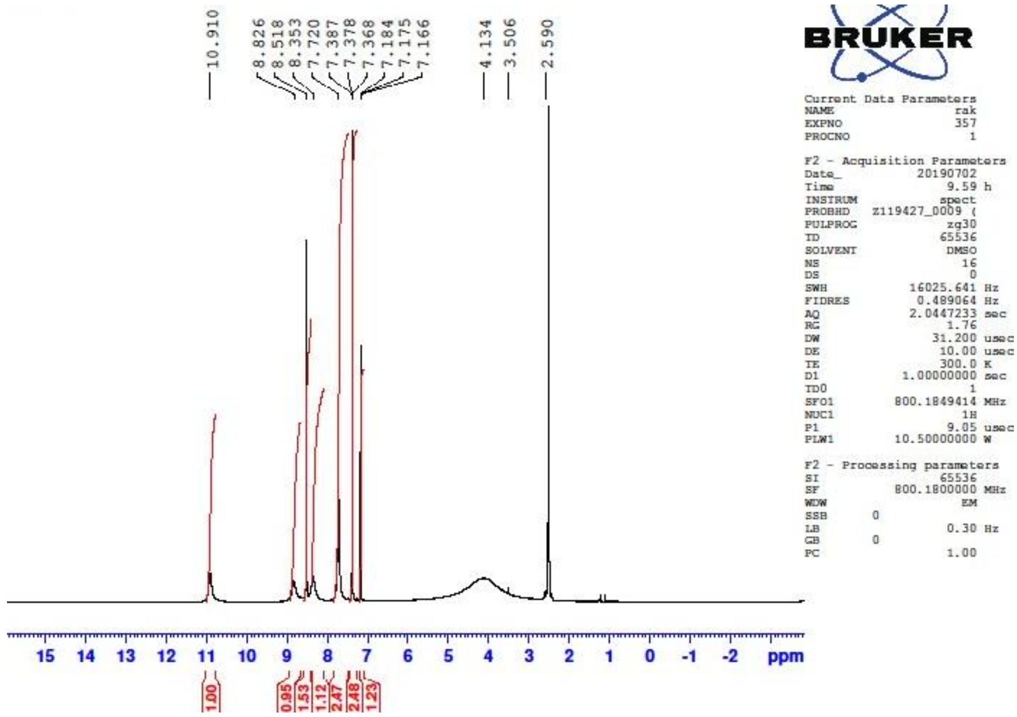

Figure 3: ^{1}H NMR spectra of r-2,c-6-diphenyl-t-3-ethylpiperidin-4-one semicarbazone

$AlCl_3+3H_2O \rightarrow Al(OH)_3+3HCl$ ----(3)

$3H^{+}+3e \rightarrow 3/2H_2$---------------------- (4)

$1/2O_2+H_2O+2e \rightarrow 2OH^{-}$ -----------(5)

As seen in equation (5), the cathodic sites are more alkaline due to the local hydroxide formation. The presence of oxygen is crucial for pitting. Cone-shaped accumulations of corrosion products are formed at the mouth of the pits due to the precipitation of aluminum hydroxide pits.

Electrochemical impedance spectroscopy (EIS) measurements: EIS measurements were conducted at open circuit potential using Electrochemical Work station (CH Instruments) in the frequency range from 0.01 Hz to 100 kHz by superimposing an AC voltage of 10 mV amplitude. The EIS outcome could be interpreted by simple “equivalent circuit model” shown in figure (2).

Microstructure analysis: The microstructures and corrosion morphology of Al 2024 alloy were investigated by Scanning electron microscopy (SEM). The work specimens surface after the electrochemical tests were observed by SEM and XRD analysis.

Results and Discussion

Potentiodynamic polarization measurements: Fig.1 to 3 show the Tafel plots of Al 2024 alloy immersed in 3.5% NaCl solution. The potentiodynamic polarization studies were conducted to Al 2024 alloy with 50ppm, 100ppm, 150ppm and 200ppm of inhibitors solution and different time period of heat treatment. In the initial process, the potential was applied at 650 V. The inhibitor concentration was increased with decreases in current density value of the materials. This represents that the heat-treated Al 2024 alloy with 200ppm of inhibitor solution has the least tendency to corrode in 3.5% NaCl solution. These suggest that the heat treatment process increases the corrosion resistance of the inhibitor in 3.5% NaCl solution.

It may also be noted that the pitting corrosion with inhibitor of Al 2024 alloy shifts more towards the negative values than without inhibitor concentration of Al 2024 alloy. The investigation confirms that inhibitor heat treated specimen maintains structural stability and resists corrosion better than the without inhibitor heat treated specimen in 3.5% NaCl solution.

This is a good pointer that even after heat treatment up to a maximum temperature of 550^0C, corrosion rate decreases. The quantitative values for corrosion parameters of Al 2024 alloy heated 550˚C for different times were determined and are mention in table. With heated time increasing, I_{corr} and I_{pass} for Al 2024 heated at550˚C also increased. A similar trend could be observed in the polarization parameters obtained. When heated time is increasing, I_{corr} and I_{pass} for Al 2024 alloy heated at 550˚C decreased.

Impedance spectroscopy plots

Electrochemical impedance spectroscopic (EIS): For Al 356 alloy dipped in 3.5% NaCl without inhibitor heat treated, the capacitive curve diameter is observed to be smaller than with inhibitor heat treated Al 2024 alloy. The concentration of inhibitor increases as the diameter of the capacitive curves seems to increase. The capacitive curves of the heat-treated composites seem to have a very large diameter. The outcome of electrochemical impedance spectroscopy test was conducted to explain the electrochemical and passive film properties. The higher frequency capacitive curve can be accounted for the charge transfer reaction through the corrosion process occurring at the metal/oxide/electrolyte interface. The charge transfer occurs during the formation of Al^{3+}, OH^- and O^{2-} at the metal/surface layer/electrolyte interface.

The second capacitive curve at the lower frequency region could be due to the division of ions entrance through the corrosion product inhibitor layer. The fitted impedance parameters RS, Rf, CPEa-T, CPEa-n, CPEb-T and CPEb-n and Rct[obtained from figure 2 are shown in table 3. The value obtained for RS was very small when compared to Rct and no specific trend was noticed. The higher Rct value implies good corrosion resistance.

Table 2
Potentiodynamic Polarization parameters obtained in 3.5% NaCl at 550˚C for Al 2024 alloy heated at 2hr, 4hr and 6hr for different time internals

Temperature at various time	ba /(mV)	bc /(mV)	I_{corr} /(A/cm^2)	E_{corr} /(V)	I_{pass} /(A/cm^2)
0hr	261.29	93.759	1.38E-06	0.95968	1.98E-06
2hr	358.26	132.29	3.50E-06	0.96242	4.31E-06
4hr	349.88	76.283	3.33E-06	0.95982	4.88E-06
6hr	309.82	114.67	3.71E-06	0.94149	5.48E-06

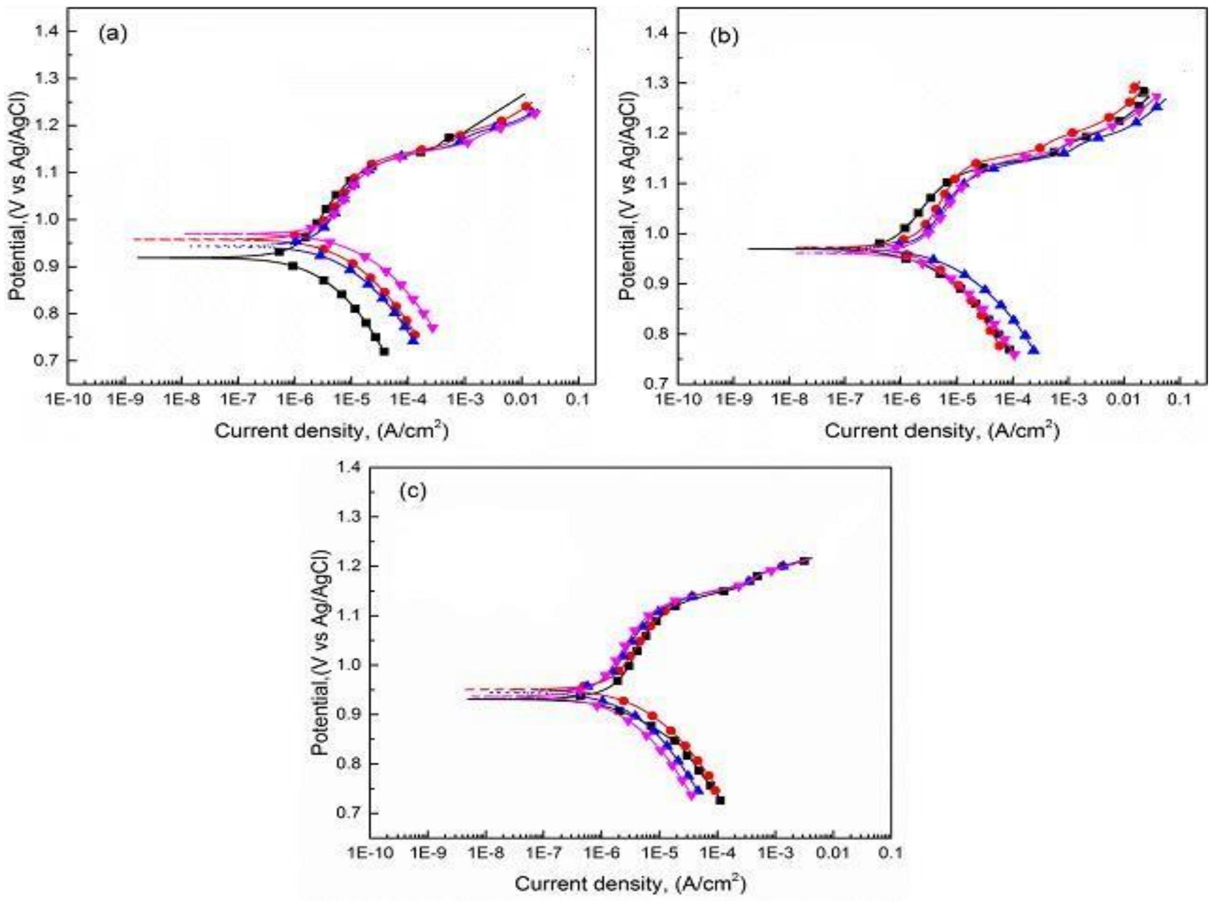

Figure 4: Potentiodynamic polarization plots obtained in 3.5% NaCl at 550◦C for the Al 2024 alloy aged at various time period like 2hr, 4hr and 6hr.

Table 3
Electrochemical impedance spectroscopic (EIS) fixed value of Al 2024 alloy heated at various temperature for 400second measured under OCP condition in 3.5% NaCl at 550°C.

Temperature at 350^0C	Rs /$\Omega \cdot cm^2$	CPEa-T /$F \cdot cm^{-2}$	CPEa-n	Rf /$\Omega \cdot cm^2$	CPEb-T /$F \cdot cm^{-2}$	CPEb-n	R_{ct} /$\Omega \cdot cm^2$
0	0.64057	3.04E-05	0.94228	3104	2.52E-05	0.68325	31475
2hr	0.6907	2.87E-05	0.96003	2389.1	2.32E-05	0.5768	32289
4hr	0.77537	3.28E-05	0.93739	2230.7	2.66E-05	0.65094	32465
6hr	0.9015	3.92E-05	0.92294	2177	6.17E-05	0.60614	19291

Microstructure analysis: The microstructure analysis of Al 2024 alloy after corrosion was analyzed by a Scanning electron microscope (SEM) (Fig. 3). From the SEM analysis, it may be observed that without heat treatment, Al356 alloys had undergone more dissolution than with inhibitor heat treated compounds of Al 2024 alloy. Various deep pitting sites can be seen along the granule limitations. Upper concentration of inhibitor exhibited lesser pits dispersed throughout the surface resulting in homogeneous and lower corrosion rate compared to without inhibitor concentration of Al alloy. An intermediate phase is formed between the atoms of Al356 alloy due to the chemical reaction between Al alloy and inhibitor. This intermediate

phase protects the surface of Al356 alloy from getting corroded.

The inhibitor acted as a protective layer of specimens' surface and preventing the alloy from being corroded. Corrosion can only be seen on the surface of the inhibitor concentration of alloys, but in the case of without inhibitor concentration of Al alloy, corrosion can also be observed in the intergranular spaces. N2-phenyl-1,3,5-triazine-2,4-diamine will act as a remarkable anticorrosion agent in Al356 alloy.

X-ray diffraction studies: The XRD study is used to find out layer formation of Al 2024 alloy in different test solutions. Peaks due to aluminum chloride appear at 2θ= 37.89°, 44.08°, 77.62o and 64.9° (Fig. 4). This represents that in the 3.5% NaCl, Al 2024 alloy specimen has undergone corrosion leading to the formation of oxide. The XRD pattern of the surface of the Al 2024 alloy immersed in 3.5% NaCl solution containing 200ppm of inhihibitor

shown in fig. 5. The Al peaks appear at 2θ = 38.22°, 44.46°.77.99° and 82.2°. It is observed that the peaks are due to hydroxides of Al such as $Al(OH)_3$. This confirms that the metal is completely protected from corrosion and also the protective layer does not consist of any oxide of Al.

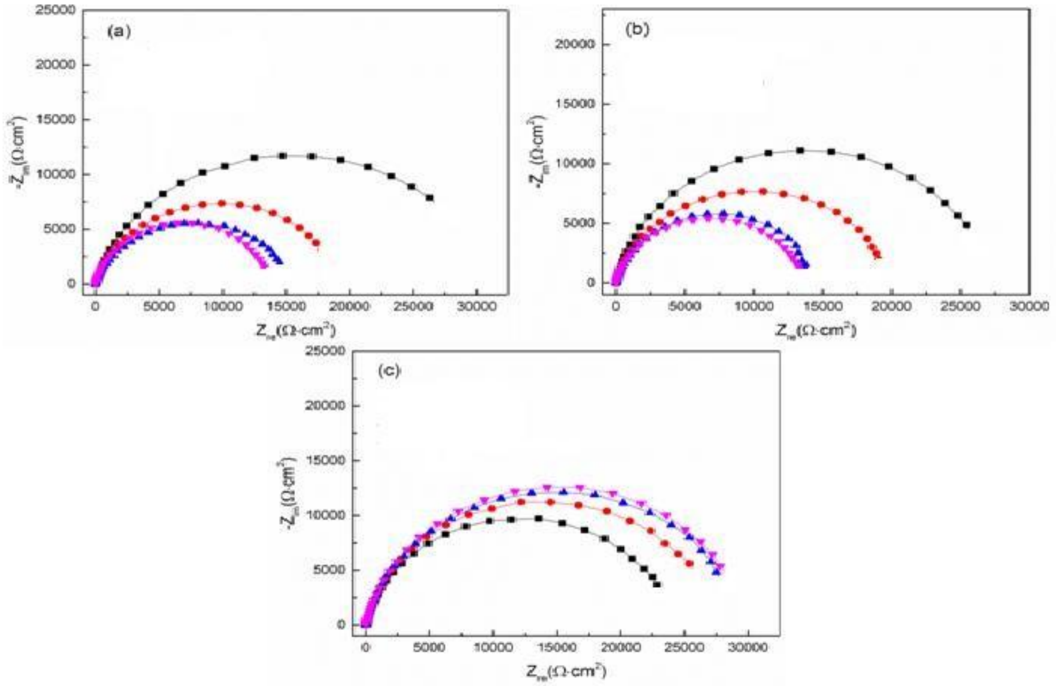

Figure 5: Electrochemical impedance spectrum of the Al 2024 alloy heated at (a) 2hr, (b) 4hr and (c) 6hr for different times obtained under OCP in 3.5% NaCl at 550°C.

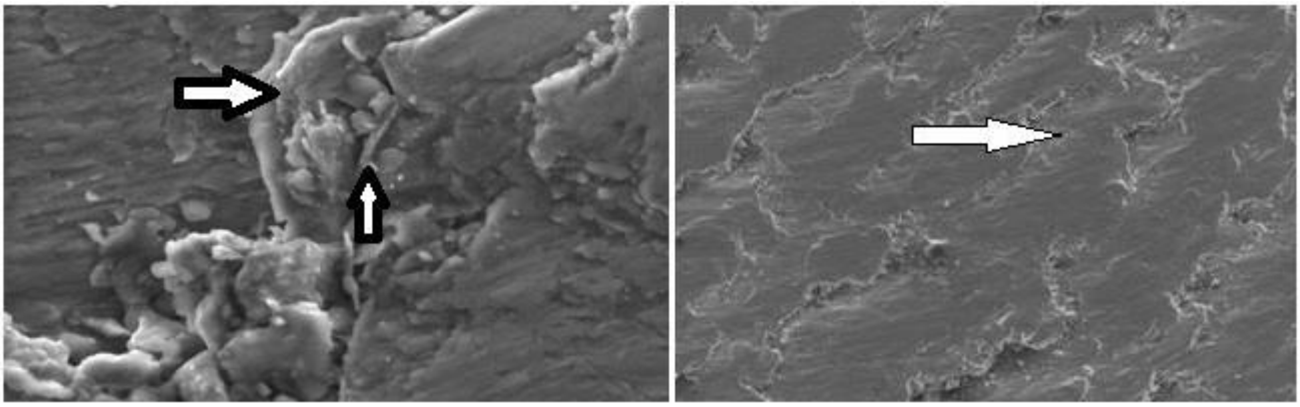

Figure 6: SEM images of Al 2024 alloy in 3.5% NaCl at 550°c (a) without inhibitor (b) with 200ppm inhibitor.

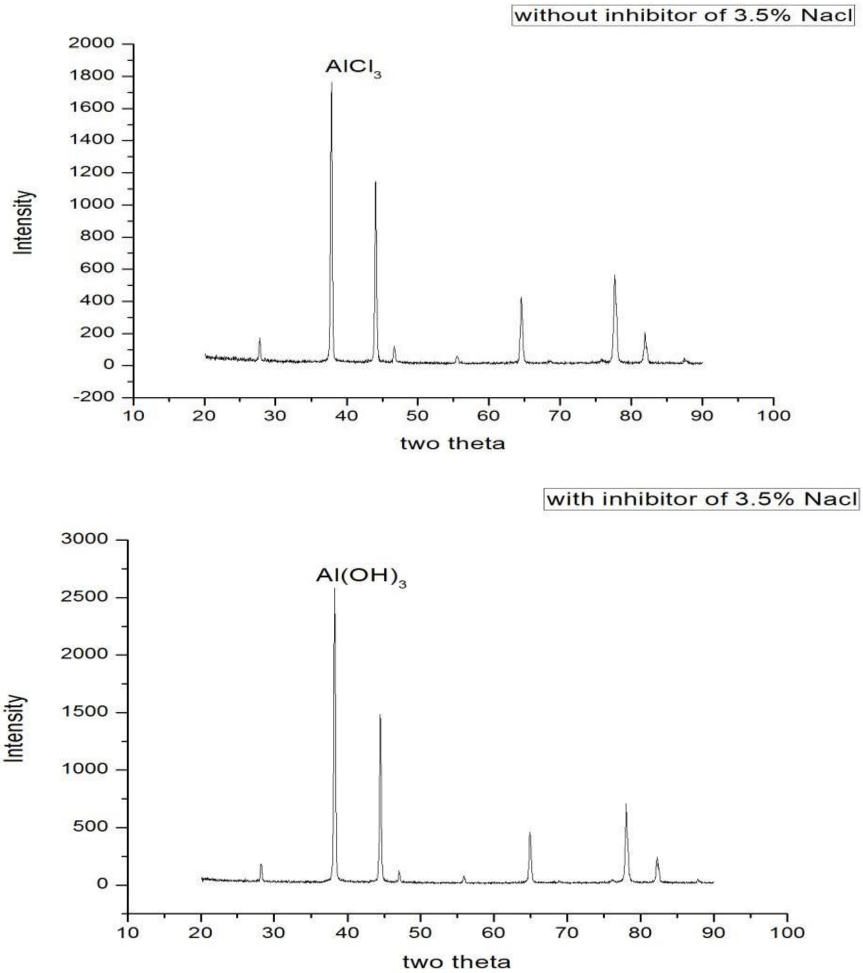

Figure 7: XRD spectrum of Al 2024 alloys corrosion in the A) without inhibitor B) With inhibitor

Conclusion

- Inhibitor was synthesized, recrystallized and melting point was determined
- Al356 alloy was casted in preheated cast iron moulds.
- Specimens were machined from the castings as per ASTM standards
- Specimens were subjected to heat treatment for 2,4 and 6 hours at 550^0C in Muffle furnace
- Both cast and heat treated specimens were subjected to polarization studies and EIS using electrochemical workstation
- Heat treated specimens exhibited increased corrosion resistance when compared with that of as cast Al 2024.
- As the concentration of the inhibitor increases, the arc of the curve was also increased.
- Heat treated specimens exhibited increased charging when compared with that of as cast Al 2024.
- Hence heat treated Al 2024 alloy is more suitable than the as cast specimen for applications in saltish environment.

Reference

1. *Miller W.S., Zhuang L., Bottema J. and Wittebrood A.J., Mater. Sci. Eng. A,* ***280****, 37* ***(2000)***

2. *Masami S., Mater. Sci. Forum,* ***519****, 11* ***(2006)***

3. *Guillaumin V. and Mankowski G., Corros,* ***56****, 12* ***(2000)***

4. *Svenningsen G., Larsen M.H., Nordlien J.H. and Nisancioglu K., Corros. Sci.,* ***48****, 258* ***(2006)***

5. *Zheng C., Cai L., Tang Z. and Shen X., Surf. Coat. Tech.,* ***287****, 153* ***(2016)***

6. *Feng C., Liu Z., Ning A., Zeng S. and Cent J., South Univ,* ***37****, 1054* ***(2006)***

7. *Liu J., Li D., Liu P., Guo B. and Zhu G., Trans. Mater. Heat Treat.,* ***23****, 50* ***(2002)***

8. *Chen K., Chao H., Fang H., Xiao D., Chen S., J. Central South Univ.,* ***41****, 1730* ***(2010)***

9. *Li Z., Xion B., Zhang Y., Zhu B., Wang F. and Liu H., Chin. J. Rare Metals,* ***32****, 794* ***(2008)***

10. *Stansbury E.E. and Buchanan R.A., Fundamentals of Electrochemical Corrosion ASM, International Materials Park, USA* ***(2000)***

11. *Christian Vargel, Corrosion of aluminium Elsevier Ltd., New York* ***(2004)***

12. *Kosting P.R. and Heins C., Ind. Eng. Chem.,* ***23****, 140-150* ***(1931)***

13. *Badaway W.A., Al Kharafi F.M. and El-Azab A.S., Corro. Sci.,* ***41****, 709-727* ***(1999)***

14. *Desai P.S. and Kapopara S.M., Ind. J. Chem. Tech.,* ***16****, 486- 491* ***(2009)***

15. *Paul and Sigwalt Juniere M., Aluminium in the Chemistry and Food Industries, British Aluminium Co. Ltd., London, 46* ***(1964)***

16. *Ating E.I., Umoren S.A., Udousoro I.I., Ebenso E.E. and Udoh A.P., Green Chemistry Letters and Reviews,* ***3****, 61-68* ***(2010)***

17. *Umoren S.A., Obot I.B., Ebenso E.E. and Obi-Egbedi N.O., Desalination,* ***247****, 561-572* ***(2009)***

18. *Si Y.J., Xiong Z.P., Zheng X.W., Li M.J. and Yang Q.H., Int. J. Electrochem. Sci.,* ***11****, 3261* ***(2016)***

19. *Padhy N., Paul R., Kamachi Mudali U. and Raj B., Appl. Surf. Sci.,* ***257****, 5088* ***(2011)***

20. *Jinlong L. and Hongyun L., Appl. Surf. Sci.,* ***263****, 29* ***(2012)***

21. *Fauvet P., Balbaud F., Robin R., Tran Q.T., Mugnier A. and Espinoux D., J. Nucl. Mater.,* ***375****, 52* ***(2008)***

22. *Robin R., Miserque F. and Spagnol V., J. Nucl. Mater.,* ***375****, 65* ***(2008)****.*