

EXPERIMENTAL CORRELATION BETWEEN HEAT TREATMENT PARAMETER AND CORROSION BEHAVIOUR OF 800 SERIES Ni-Fe SUPERALLOY IN HCl SOLUTION

C.C. Nwogbu¹, B.A. Okorie^{1,2}, and V. S. Aigbodion²

¹*Department of Metallurgical and Materials Engineering,
Enugu State University of Science and Technology, Enugu, Nigeria.*

²*Department of Metallurgical and Materials Engineering,
University of Nigeria, Nsukka.*

ABSTRACT

Experimental correlation between heat treatment parameter and corrosion behaviour of 800Ni-Fe superalloy in HCl solution has been investigated. The sample was produced by spark plasma sintering (SPS) and was heat treated at temperatures of 800 and 1000°C and time of 1 and 2 hours at each temperature. Electrochemical studies were carried out in HCl medium, using potentiodynamic anodic polarization technique. From the results the heat treated alloy showed better corrosion resistance than the untreated alloy. Heat treatment temperature and time have great influences on the corrosion behaviour and morphology of the alloy. The sample heat treated at 800°C for 1 hour gave a high protection efficiency of 75.33%. It has been established that heat treatment can be used to improve the corrosion resistance of the alloy.

Keywords: *Ni-Fe alloy, Microstructure, Corrosion and Heat treatment*

1.0 INTRODUCTION

Nickel-iron base alloys appear to be a promising alternative to austenitic stainless steels because of their better corrosion resistance, thermal conductivity and mechanical properties. Using these alloys, complex processes and waste streams can be handled safely due to their high corrosion resistance. [1,2]. These alloys possess higher tolerance for alloying elements in solid solution than stainless steels and other iron base alloys[3]. The good metallurgical stability of the nickel base alloys make them a better alternative to stainless steel[4,5]. Owing to the excellent mechanical and physical properties, nickel base superalloys are extensively employed in nuclear power plants[6].

The 800 nickel base solid solution strengthened superalloy with major elemental composition as Ni-Fe-Cr; is a non-magnetic, corrosion and oxidation resistant alloy. The major elements nickel and chromium, provide good resistance to oxidizing environments. In nuclear power plants. Alloy 800 is used as steam generator tubes [7]. The selection of this material is because of its good mechanical strength,

thermal conductivity, high formability and corrosion resistance.

The high temperature performance of the Ni-base superalloy Superni-75 has been evaluated under cyclic conditions for 1,000 h in real service environment of the waste incinerator based upon medical waste as fuel. The performance has been characterized via surface morphology, phase composition and element concentration using the combined techniques of XRD, SEM/EDX, BSEI and EPMA. Initially, due to chlorine-based corrosion attack on the Superni-75 alloy, there was inner penetration of the corrosive species. However, with the growth of a thin Cr₂O₃ interface layer along the scale/surface boundary, the performance of the alloy improved against the attack by the flue gases in the real service conditions of the medical waste incinerator. Boiler tubes made of Superni-75 were estimated to have an erosion-corrosion rate of about 65 mils/year.

Paula Rojas [8] reported on the electrochemical behaviour and corrosion resistance of glassy Fe68.6-Ni28.2-Mn3.2 (at%) specimens which were studied in

different concentrations of HCl solutions. The results indicated that the corrosion rate increased with increasing concentration of the HCl solutions. Electrochemical impedance spectroscopy results were analysed by fitting the experimental data to an equivalent circuit using the ZSim Demo program, and suitable equivalent circuit models were determined. The results obtained from the impedance and polarization measurements are in good agreement. The thermodynamic parameters were evaluated for the corrosion process and discussed. In order to further research in this novel area for better service condition, the present work has been undertaken.

2.0 MATERIALS AND METHOD

A spark plasma sintering machine (model SPS 10-3), manufactured by Thermal Technologies LLC, was used to produce the alloy samples. Specimens of diameter 100 mm, were produced using dies and punches of graphite. The samples were produced at a temperature of 1150°C temperature and a pressure of 5MPa with heating and cooling rate of 10°C/min. The thermocouple inserted into the bottom punch was used to measure the temperature. All the samples were produced in a closed furnace where 10⁻² torr vacuum was maintained throughout the experiment. A standard Ni-Fe base superalloy (Incoloy 800) with composition shown in Table 1a below was used.

A carbolite furnace was used for the heat treatment of the samples. The samples were placed inside the furnace and the following heat treatment programme was used.

- i. Hold at 1000°C for 1 and 2 hours; then rapidly cool by quenching in water.
- ii. Hold at 800°C for 1 and 2 hours; then air cool,

X-ray diffraction (XRD) analysis, with Cu-K α radiation, was conducted using a PANalytical X'Pert PRO. The XRD was operated at 45kV voltage and 40mA current.

The 2 θ angles between 1° and 90° were scanned and analyzed using the Bragg law. A Rietveld refinement software, TOPASTM, was used for quantitative analysis. A TESCAN Scanning Electron Microscope was used in the research. The polished and etched samples were firmly held in the sample holder using a double-sided carbon tape before putting them inside the sample chamber. The SEM was operated at an accelerating voltage of 20 kV.

Electrochemical measurements were carried out using an Autolab Potentiostat with the General Purpose Electrochemical Software package. The samples were cold mounted with epoxy leaving a working area of 0.785 cm². The working surface was ground with grinding papers from 600 to 1000 grit, and then cleaned with distilled water and ethanol. A conventional three electrode cell, consisting of Ag/AgCl, Platinum and samples was used as: reference, counter and working electrodes respectively. The medium used for the electrochemical measurement was 0.5M HCl. The measurement was carried out at room temperature. The potentiodynamic potential scan was fixed from -1.5 V to +1.5 V with a scan rate of 0.012 V/s.

3.0 RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of the untreated alloy, while Figures 1b-1e display the XRD patterns of the heat treated samples. From the XRD spectrum of the alloy, it is observed clearly that there is presence of Ni,Fe (Awaruite), Al_{0.3}Fe₃Si_{0.7} (Aluminum Iron Silicon), and Cr₇C₃ (Carbon Chromium) phases. After heat treatment it is observed that new phases appeared such as: FeSi (Fersilicite, syn [NR]), Manganese Carbide, Chromium Iron Carbide, Manganese Silicon Carbide. The presence of (Ni,Fe) (Awaruite) phase is common to all the samples; this is expected because the

Table 1a: Composition of the superalloy Incoloy 800 used

| Ni | Fe | Cr | Mo | Mn | Si | C | Al | Ti | Cu | Other |
|------|------|----|----|-----|-----|------|-----|-----|-----|-------|
| 32.5 | 44.5 | 21 | - | 0.8 | 0.5 | 0.05 | 0.4 | 0.4 | 0.4 | - |

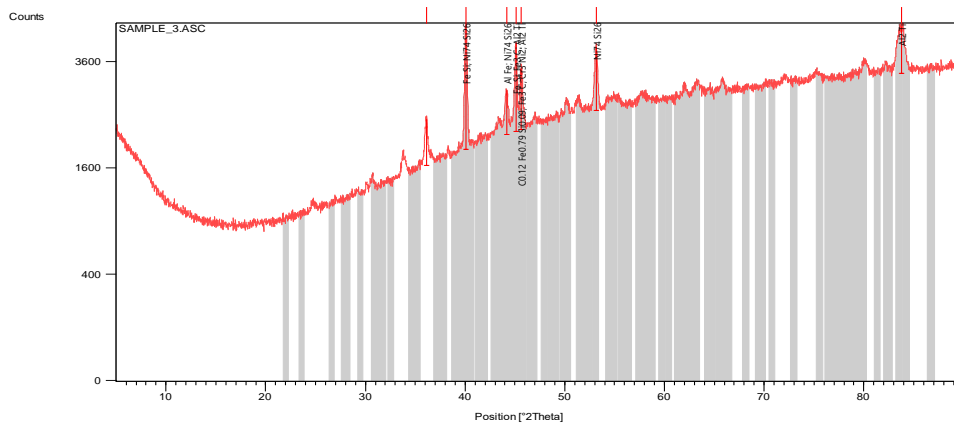


Figure 1d: XRD spectrum of the alloy heat treated at HT8001hr

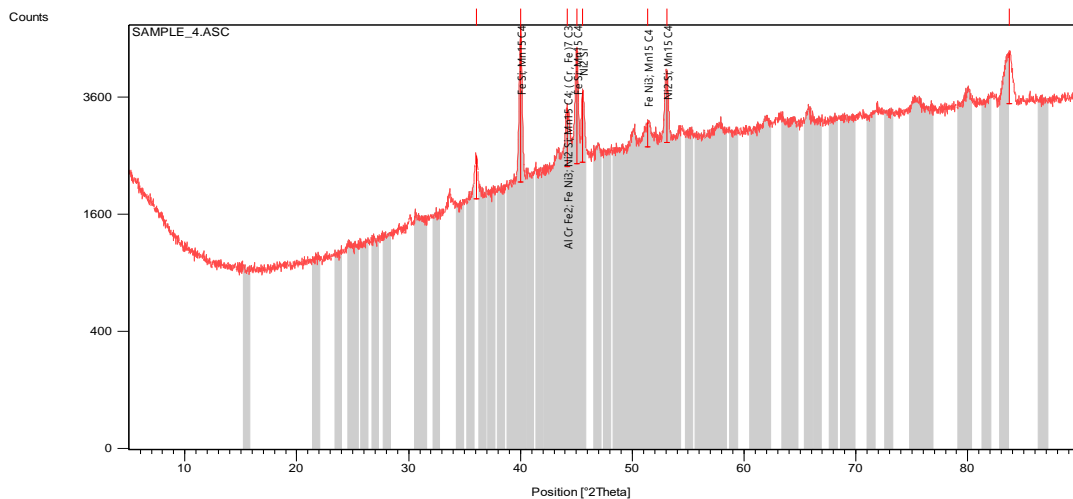


Figure 1e: XRD spectrum of the alloy heat treated at HT8002hrs

Table 1: Identified Patterns List

| Control | HT10001HR | HT10002HR | HT8001HR | HT8002HR |
|--|--|--|--|--|
| (Ni , Fe)(Awaruite) | (Ni , Fe) (Awaruite) | (Ni , Fe)(Awaruite) | (Ni , Fe)(Awaruite) | Al Cr Fe2 |
| Al0.3 Fe3 Si0.7(Aluminum Iron Silicon) | Mn5 C2 (Manganese Carbide) | Al Ni2 Ti(Aluminum Nickel Titanium) | Fe Si(Fersilicite, syn [NR]) | Fe Si(Fersilicite, syn [NR]) |
| Cr7 C3(Carbon Chromium) | Al0.5 Fe0.5(Aluminum Iron) | Al0.96 Ni1.04(Aluminum Nickel) | C0.12 Fe0.79 Si0.09(Carbon Iron Silicon) | Fe Ni3(Awaruite) |
| Ni3 (Al , Ti)("Udimet 500") | Mn Si(Manganese Silicon) | Fe7 C3(Iron Carbide) | Fe3 C(cementite) | Ni2 Si(Nickel Silicon) |
| | (Cr , Fe)7 C3(Chromium Iron Carbide) | Al0.4Fe0.6(Aluminum Iron) | Cr3Ni2(Chromium Nickel) | Mn15C4(Manganese Carbide) |
| | Ni2.67 Ti1.33(Nickel Titanium) | Cr22 C6(Carbon Chromium) | Al2 Ti(Aluminum Titanium) | (Cr , Fe)7 C3(Chromium Iron Carbide) |
| | Mn22.6 Si5.4 C4(Manganese Silicon Carbide) | | Ni74 Si26(Nickel Silicon) | |

From the Figures 2a-2e, one can observe a great difference between the morphology of the untreated alloy (see Figure 2a) and those of the heat treated samples (see Figures 2b-2e). Samples heat treated for 1hr have a more refined structure. The dark spots show the presence of some of the new phases developed during heat treatment.

The electrochemical potential of the alloy was investigated using HCl solution. Table 2 presents the corrosion data including the corrosion rate, while Fig. 3(a) and 3(b) present results of the polarization tests. From the results obtained in Table 2 and Figure 3, the corrosion rate of the samples generally decreases after heat treatment. The untreated sample has the higher corrosion rate.

This was attributed to the high anodic potential reached by the sample. Meanwhile, as the sample was heat treated there was decrease in corrosion rate. This may be attributed to the formation of a hard thin film, which may have retarded the ingress of Cl^- ions. As the heat treatment time decreased from 2 to 1hr the corrosion rate of the alloy decreased. Heat treatment contributes immensely to the corrosion behavior of the alloy (see Figure 3) e.g corrosion rates of 0.471, 0.244, 0.358, 0.116 and 0.318mm/year were obtained for the untreated, heat treated at 1000°C for 1, 2hrs and 800°C for 1, 2hrs respectively. The various hard phases formed after heat treatment are the major factor responsible for the improvement in the corrosion behavior of this alloy

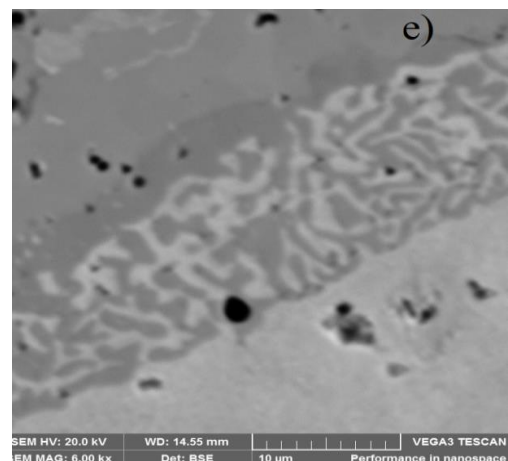
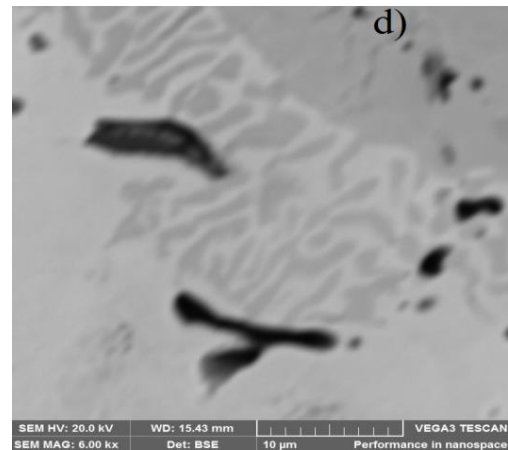
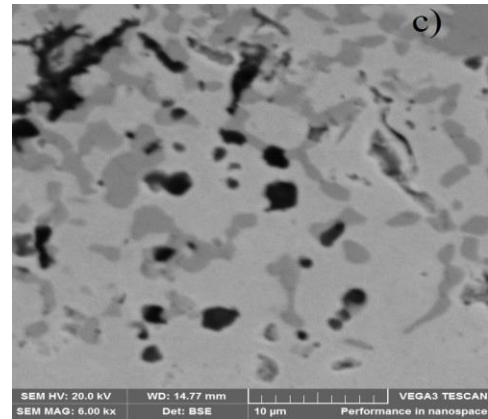
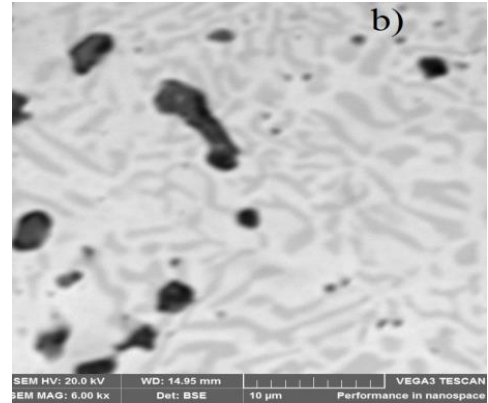
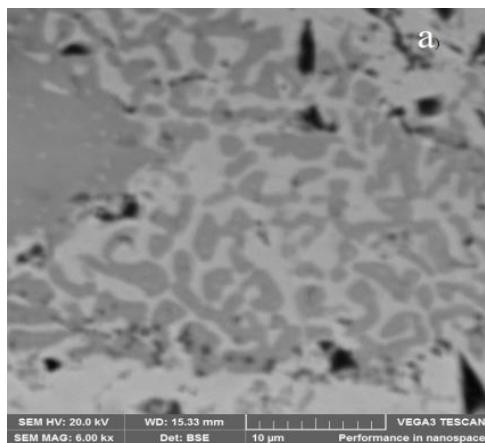


Figure 2: SEM image of a) Untreated alloy b) HT10001hr c) HT10002hrs d) HT8001hr e) HT8002hrs

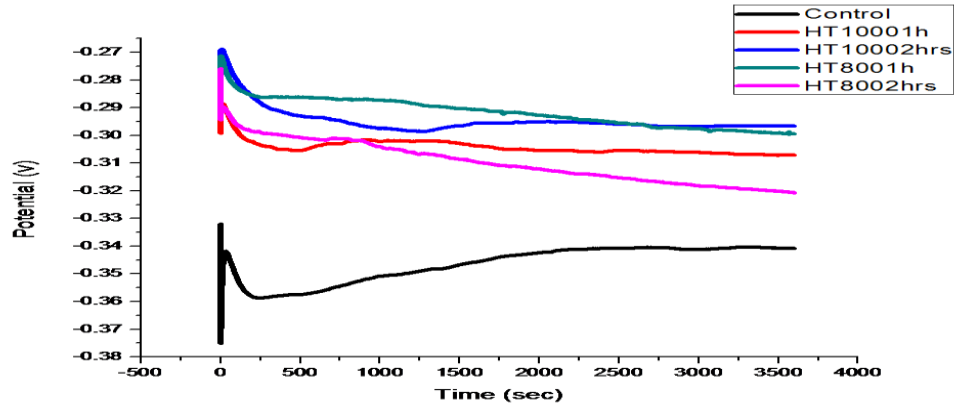


Figure 3a: Variation of the open circuit potential with time

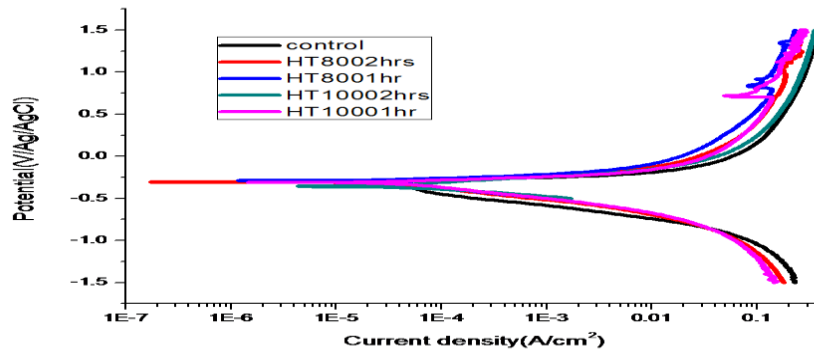


Figure 3b: Potentiodynamic polarization curve

Table 2: Electrochemical corrosion data

| N | SAMPLES | I_{corr} (A/cm ²) | b_a (v/dec) | LPR R_p (Ω cm ²) | $-E_{corr}$ (V) | CR (mm/yr) |
|---|------------|---------------------------------|---------------|--|-----------------|---------------|
| | Untreated | 4.398E-5 | 0.330 | 159.1 | -0.30 | 0.4710 |
| | HT10001hr | 2.275E-5 | 0.042 | 121.2 | -0.304 | 0.2437 |
| | HT10002hrs | 3.349E-5 | 0.046 | 102.1 | -0.289 | 0.3586 |
| | HT8001hr | 1.085E-5 | 0.043 | 180.2 | -0.322 | 0.1162 |
| | HT8002hrs | 2.977E-5 | 0.72 | 80.84 | -0.356 | 0.3180 |

Table 3a: Upper and lower levels used with their

| S/No | Temperatures(A) °C | Time(B) hrs | Corrosion rate(mm/yr) |
|------|--------------------|-------------|-----------------------|
| 1 | 800 | 2 | 0.3188 |
| 2 | 1000 | 2 | 0.3586 |
| 3 | 1000 | 1 | 0.2437 |
| 4 | 800 | 1 | 0.1162 |

The heat treated sample may act as a cathode, which prevents conductance of ions but allows electronic conductance to some extent. It should also be emphasized that the electrical potential in all the samples decreases in the direction from the anode to the cathode (positive ions move towards the cathode, negative ions towards the anode)(see Figure 3a). The surface of the anode in reality is much smaller than that of the

cathode, i.e. the electrolytic current density is much higher near the anode.

It is worthy to note in this present work that heat treatment temperature and time play a vital role in the electrochemical potential of all the samples. The optimum condition that led to the higher corrosion resistance is the sample heat treated at HT8001hr. This optimum condition gave a protection efficiency of 75.33%.

Two factors and levels of factorial design experiment were used to study the influences of heat treatment temperature and time on the corrosion behaviour of the materials. Table 3a, shows the upper and lower levels of each variable with their response values.

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Figure 4, shows the estimated response surface for the samples. It is observed that the corrosion behavior is highly influenced by temperature and time. The corrosion rate increases with increase in heat treatment temperature and time. For example as the temperature increases from 800 to 1000°C and time from 1 to 2hours the corrosion rate increased rapidly (see Figure 4). Equation 1 shows the dependence of corrosion rate on temperature and time.

$$\text{Corrosion rate} = -0.048750 + 1.82500\text{E-}004 * \text{Temperature} + 0.11160 * \text{Time} \quad (1)$$

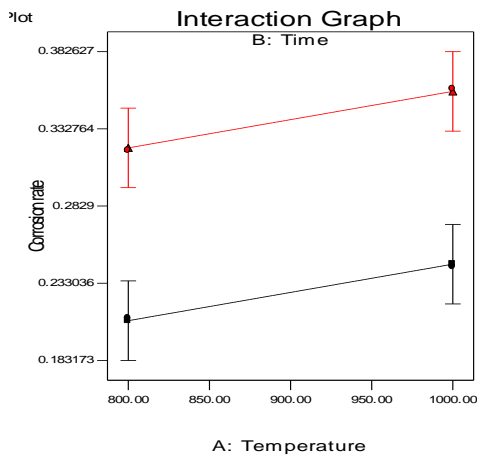


Figure 4a: Interaction curve for the corrosion behaviour

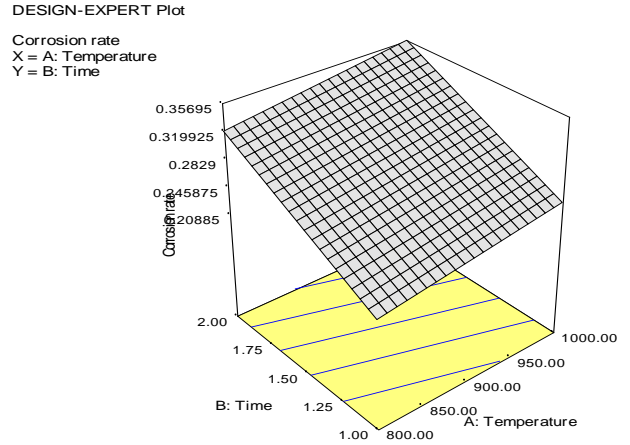


Figure 4b: 3-D plot for the corrosion behaviour

From equation 1, it can be clearly seen that the coefficients associated with temperature and time are positive. It indicates that as the temperature rises from 800 to 1000°C, the corrosion rate rises by 1.82500E-004. Also as the time increases from 1 to 2hours the corrosion rate rises by 0.11160. This further supports the earlier observation in Figure 4a and 4b.

Analysis of variance (ANOVA) was used to determine the design parameters significantly influencing the corrosion rate. Table 3b shows the results of ANOVA at 95% confidence level (significance level of $\alpha=0.05$). The last column of Table 3b shows the contribution (P) of each parameter to the response, indicating the degree of influence on the results.

The Model F-value of 633.00 implies that the model is significant. There is only a 2.81% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate that the model terms are significant. In this case B(time) is a significant model term.

Table 3b: ANOVA for Selected Factorial Model

| | | Hardness values | | | |
|----------|----------------|-----------------|-------------|--------------------|--------------------|
| Source | Sum of Squares | DF | Mean square | F _{value} | P _{value} |
| Model | 0.014 | 2 | 6.893E-003 | 633.00 | 0.0281 |
| A | 1.332E-003 | 1 | 1.332E-003 | 122.34 | 0.0574 |
| B | 0.012 | 1 | 0.012 | 1143.67 | 0.0188 |
| Residual | 1.089E-005 | 1 | 1.089E-005 | | |
| CorTotal | 0.014 | 3 | | | |

The "Pred R-Squared" of 0.9874 is in reasonable agreement with the "Adj R-Squared" of 0.9976.

| | | | |
|-----------|------------|----------------|--------|
| Std. Dev. | 3.300E-003 | R-Squared | 0.9992 |
| Mean | 0.28 | Adj R-Squared | 0.9976 |
| C.V. | 1.17 | Pred R-Squared | 0.9874 |
| PRESS | 1.742E-004 | Adeq Precision | 51.822 |

4.0 CONCLUSIONS

From the results and discussion above the following conclusions can be made:

1. The heat treated alloy showed better corrosion resistance than the untreated alloy
2. Heat treatment temperature and time have great influences on the corrosion behaviour and morphology of the alloy.
3. The sample heat treated at 800°C for 1 hour gave a high protection efficiency of 75.33% .
4. It has been established that heat treatment can be used in improving the corrosion resistance of the alloy.

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