THE EXPERIMENTAL CORRELATION BETWEEN HEAT TREATMENT PARAMETER AND CORROSION BEHAVIOUR OF 718 SERIES Ni-Fe SUPERALLOY in H₂SO₄ SOLUTION

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ABSTRACT

The correlation between heat treatment parameter and corrosion behavior of 718 Ni-Fe superalloy was investigated in H₂SO₄ solution. Spark plasma sintering (SPS) was used in producing the samples which were then heat treated at temperatures of 800°C and 1000°C and time of 1 and 2 hours for each temperature. Electrochemical studies were carried out in H₂SO₄ medium, using potentiodynamic anodic polarization techniques. It was observed from the results that the heat-treated alloy showed better corrosion resistance than the untreated alloy. Heat treatment temperature and time have great influences on the corrosion behavior and morphology of the alloy. An optimal protection efficiency of 55.29% was given by sample heat treated at 800°C for 2 hours. 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 makes 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].

INCONEL 718 alloy can be fabricated with ease, combined with its good tensile, fatigue, creep, and rupture strength, have resulted in its use in a wide range of applications. It has been widely used in the aircraft industry due to its high-strength, corrosion-resistant and excellent mechanical properties at elevated temperatures [7–9]. INCONEL 718 is strengthened mainly by the nano-scale γ'' (Ni₃Nb) and γ' (Ni₃(Al, Ti)) phases. The γ'' phase has a disc shape with a body centered tetragonal (bct) structure [10, 11]. The γ' phase has a cubic (fcc) structure and precipitates as a cube-to-cube relationship with the matrix [12]. There will be more γ'' than γ' in the alloy due to its composition. The γ'' phase is metastable and can transform into the δ (Ni₃Nb) phase at high temperatures [13–15]. Adequate amounts of δ phases at grain boundaries can refine the grain sizes and improve the resistance to grain boundary creep fracture [16–18].

The high temperature performance of the Ni-base superalloy Superni-75 has been evaluated under cyclic conditions for 1000h 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 Cr_2O_3 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 [19] reported on the electrochemical behavior and corrosion resistance of glassy Fe_{68.6}-Ni_{28.2}-Mn_{3.2} (at%) specimens which were studied in different concentrations of acid solutions. The results indicated that the corrosion rate increased with increasing concentration of the acid solutions. Electrochemical impedance spectroscopy results were analyzed 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 100mm were produced using dies and punches of graphite. The samples were produced at a temperature of 1150⁰C temperature and a pressure of 5MPa with heating and cooling rate of 10⁰C/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 (INCONEL718) with composition shown in Table 1 below was used.

Table 1: Composition of the superalloy INCONEL 718 used (wt%)

Ni	Fe	Cr	Mo	Mn	Si	C	Al	Ti	Other
53	18.5	18.6	3.1	0.3	0.4	0.4	0.4	0.9	5.0 Co

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 100⁰C for 1 and 2 hours; then rapidly cool by quenching in water.
- ii. Hold at 800⁰C 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 1⁰ and 90⁰ 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 surface was ground with grinding papers from 600 to 1000 grit, and

then cleaned with the 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 $0.5\text{MH}_2\text{SO}_4$. 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), $\text{Al}_{0.3}\text{Fe}_3\text{Si}_{0.7}$ (Aluminum iron Silicon), and Cr_7C_3 (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 expected because the specimen is a Ni-Fe base superalloy. By comparing the XRD of the control (Figure 1a) with the heat treated samples (Figures 1b- 1e), one can observe that there is a great change in the spectrum which resulted in more diffraction peaks, and a larger quantity of hard carbides with smaller inter-particle distance. In the heat treated samples, it is clear that the various phases formed after the heat treatment depends on the heat treatment condition as shown in Table 2.

Figure 1a: XRD spectrum of the untreated alloy

Figure 1b: XRD spectrum of alloy heat treated at HT10001hr

Figure 1c: XRD spectrum of alloy heat treated at HT10002hrs

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 1 hr 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 H_2SO_4 solution. Table 3 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 3 and Figure 3, the corrosion rate of the sample 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 SO_4^{2-} ions. As the heat treatment time decrease from 2 to 1 hr 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 2.55(untreated), 1.302, 3.59, 1.835 and 1.14mm/year were obtained for samples heat treated at 1000°C for 1, 2hrs and 800°C for 1, 2hrs respectively. The various hard phases formed after heat treatments are the major factor responsible for the improvement in the corrosion behavior of this alloy.

Figure 2a: SEM image of untreated alloy

Figure 2c: SEM image of alloy heat treated at HT10002hrs

Figure 1b: SEM image of alloy heat treated at HT10001hr

Figure 2d: SEM image of alloy heat treated at HT8001hr

Figure 2e: SEM image of alloy heat treated at HT8002hrs

Figure 3a: Variation of open circuit potential with time

Figure 3b: potentiodynamic polarization curve

Table 3a: Electrochemical corrosion data

SAMPLE	E _{corr}	I _{corr} (A/cm ²)	R _p (Ω)	β _a (V/dec)	β _c (V/dec)	CR(mm/Y)
Control	-0.359	2.35E-04	1.69E+01	0.064	0.112	2.55E+00
718HT1000C1HR	-0.316	1.199E-4	2.264E+1	0.059	0.083	1.302E+0
718HT1000C2HRS	-0.309	3.31E-04	1.71E+01	0.08	0.128	3.59E+00
718HT800C1HR	-0.366	1.708E-4	1.62E+1	0.054	0.093	1.853E+0
718HT800C2HRS	0.279	1.05E-04	7.25E+01	0.113	0.122	1.14E+00

Table 3b: Upper and lower levels used with their

S/No	Temperatures (A) 0C	Time (B) hrs	Corrosion rate (mm/yr)
1	800	1	1.853E+0
2	1000	2	3.59E+00
3	1000	1	1.302E+0
4	800	2	1.14E+00

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 Figures 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 HT8002hrs. This optimum condition gave a protection efficiency of 55.29%.

Two factors and level of factorial design experiment were used to study the influences of heat treatment temperature and time on the corrosion behaviour of the materials. Table 3b, shows the upper and lower level s of each variable with their response values..Figure 4, shows the estimated response surface for the samples. It is observed that the corrosion rate increases with increase in heat treatment temperature and time. For example as the temperature increases from 800 to 1000°C and the time from 1 to 2 hours the corrosion rate increased rapidly (see figure 4). Equation 1 shows the dependence of corrosion rate on temperature and time.

$$\text{Corrosion rate} = 1.97125 + 0.47475 * \text{Temperature} + 0.39375 * \text{Time} \quad (1)$$

Figure 4a: Interaction curve for the corrosion behavior

Figure 4b: 3-D plot for the corrosion behavior of the 718 alloy

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 0.47475. Also as the time increases from 1 to 2 hours the corrosion rate rises by 0.39375. 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 (significant level of $\alpha=0.05$). The last column of table 3c shows the contribution (p) of each parameter to the response, indicating the degree of influence on the results.

The "Model F-value" of 0.34 implies the model is not significant relative to the noise. There is a 77.25 % 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, A (Temperature) and B (time) are not significant model terms

Table 3c: ANOVA for selected factorial model

Source	Sum of squares	DF	Mean square	F value	P value
Model	1.52	2	0.76	0.34	0.7725
A	0.90	1	0.90	0.40	0.6408
B	0.62	1	0.62	0.28	0.6923
Residual	2.25	1	2.25		
Cor Total	3.77	3			

4.0 CONCLUSIONS

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

1. The heat treated alloy shows better corrosion resistance than the untreated alloy.
2. Heat treatment temperature and time have great influence on the corrosion behaviour and morphology of the alloy.
3. The sample heat treated at 800°C for 2 hours gave a high protection efficiency of 55.29%
4. It has been established that heat treatment can be used in improving the corrosion resistance of the alloy.

REFERENCES

1. G.B. Viswanathan, P.M. Sarosi, M.F. Henry, D.D. Whitis, W.W. Milligan, M.J. Mills "Investigation of Creep Deformation Mechanisms at Intermediate Temperatures in Rene 88 DT." *Acta Mater*, 53, pp. 3041-3057, 2005.
2. D. Locq, A. Walder, M. Marty, P. Caron "Development of New PM Superalloys for High Temperature Application" *EUROMAT, Intermetallics and Superalloys Vol. 10*, WILEY-VCH Verlag GmbH, Weinheim, Germany (D.G. Morris et al.,eds) ,pp. 52-57, 2000.
3. S.T. Wlodek, M. Kelly, D. Alden "The Structure of N18 Superalloys 1992" *TMS, Warrendale, PA, U.S.A (S.D. Antolovich et al.,eds)* ,pp. 467-476, 1992.
4. M. Soucail, M. Marty, H. Octor "Development of Coarse Grain Structures in a Powder Metallurgy Nickel Base Superalloy N18. *Scripta Mater*, 34, 4, pp.519-525, 1996.
5. Khadijah M. Emran, "Effects of concentration and temperature on the corrosion properties of the Fe-Ni-Mn alloy in HCL solutions." *Res Chem Intermed* (2015) 41: 3583-3596
6. W.A. Wesley and H.R. Copson, "Effect of Non-Condensable Gases on Corrosion of Nickel in Steam Condensate," *TRANS. ELECTROCHEM. SOC.*, May, 1949.
7. Li, L.; Gong, X.; Ye, X.; Teng, J.; Nie, Y.; Li, Y.; Lei, Q. Influence of Building Direction on the Oxidation Behavior of Inconel 718 Alloy Fabricated by Additive Manufacture of Electron Beam Melting. *Materials* **2018**, 11, 2549.
8. Moussaoui, K.; Rubio, W.; Mousseigne, M.; Sultan, T.; Rezai, F. Effects of Selective Laser Melting additive manufacturing parameters of Inconel 718 on porosity, microstructure and mechanical properties. *Mater. Sci. Eng. A* **2018**, 735, 182–190.
9. Hua, Y.; Liu, Z. Experimental Investigation of Principal Residual Stress and Fatigue Performance for Turned Nickel-Based Superalloy Inconel 718. *Materials* **2018**, 11, 879.
10. Calandri, M.; Manfredi, D.; Calignano, F.; Ambrosio, E.P.; Biamino, S.; Lupoi, R.; Ugues, D. Solution Treatment Study of Inconel 718 Produced by SLM Additive Technique in View of the Oxidation Resistance. *Adv. Eng. Mater.* **2018**, 20, 1800351.
11. Zhang, H.; Li, C.; Guo, Q.; Li, H.; Liu, Y. Deformation Mechanism of L12-0 Phase in Bimodal γ -0 Precipitation Hardened Inconel 718 Superalloy. *Adv. Eng. Mater.* **2018**, 20, 1800652.
12. Ma, W.; Xie, Y.; Chen, C.; Fukunuma, H.; Wang, J.; Ren, Z.; Huang, R. Microstructural and mechanical properties of high-performance Inconel 718 alloy by cold spraying. *J. Alloys Compd.* **2019**, 792, 456–467.
13. Lin, Y.C.; Yin, L.-X.; Luo, S.-C.; He, D.-G.; Peng, X.-B. Effects of Initial γ Phase on Creep Behaviors and Fracture Characteristics of a Nickel-Based Superalloy. *Adv. Eng. Mater.* **2018**, 20, 1700820.
14. Zhang, H.; Li, C.; Liu, Y.; Guo, Q.; Huang, Y.; Li, H.; Yu, J. Effect of hot deformation on γ and γ' phase precipitation of Inconel 718 alloy during deformation and isothermal treatment. *J. Alloys Compd.* **2017**, 716, 65–72.
15. Sano, K.; Oono, N.; Ukai, S.; Hayashi, S.; Inoue, T.; Yamashita, S.; Yoshitake, T. γ' -Ni₃Nb precipitate in Fe–Ni base alloy. *J. Nucl. Mater.* **2013**, 442, 389–393.
16. Lyu, F.; Liu, F.; Hu, X.; Yang, X.; Huang, C.; Shi, D. The delta Phase Precipitation of an Inconel 718 Superalloy Fabricated by Electromagnetic Stirring Assisted Laser Solid Forming. *Materials* **2019**, 12, 2604.
17. Nunes, R.M.; Pereira, D.; Clarke, T.; Hirsch, T.K. Delta Phase Characterization in Inconel 718 Alloys Through X-ray Diffraction. *ISIJ Int.* **2015**, 55, 2450–2454.

18. Deng, D.; Moverare, J.; Peng, R.L.; Söderberg, H. Microstructure and anisotropic mechanical properties of EBM manufactured Inconel 718 and effects of post heat treatments. *Mater. Sci. Eng. A* **2017**, 693, 151–163.
19. Paula Rojas, Rosa Vera, Carola Martinez, Maria Villaroel, 'Effect of the Powder Metallurgy manufacture Process on the Electrochemical Behaviour of Copper, Nickel and Copper Nickel Alloys in Hydrochloric Acid', *Int. J. Electrochem. Sci.*, 11 (2016) 4701-4711