Investigation of Isothermal Oxidation on Heat-treated Fe-40Ni-24Cr Alloy at 950°C

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Abstract. In this research, Ni-based superalloy which is Fe-40Ni-24Cr alloy was experienced a heat treatment process to alter the grain size of the sample to observe its influence on the oxidation properties. The alloys were heat-treated at temperatures of 950°C, 1050°C, and 1150°C for 2 hours followed by water quench. The heat-treated alloys were undergoing an isothermal oxidation test at 950°C for 150 hours in laboratory air. The weight gain of oxidized heat-treated alloy was recorded in order to determine the oxidation kinetic of the test samples. Scanning electron microscopy (SEM) technique was employed in this study to analyze the oxidation behaviour of heat-treated samples. Grain size measurement shows that the grain size increases as the heat treatment temperature increases. The oxidation rate of heat-treated Fe-40Ni-24Cr alloy obeys the parabolic rate law indicating the diffusion-controlled oxide growth mechanism. The fine grain size of alloy heat-treated at 950°C possess a better oxidation resistance and has a lower oxidation rate compared to coarse grain samples. The surface morphology indicate that the fine grain heat-treated alloy at 950°C shows uniform oxide layer formed on the surface, while alloy heat-treated at 1050°C and 1150°C shows the uneven oxide growth, oxide flaking and oxide spallation.

1 Introduction

In this modern world, high performance aircraft jet engine could not function without the discoveries and advances in superalloys. Some superalloys are used at cryogenic or room temperatures despite it is developed for high temperature use. Superior heat and oxidation resistance are necessary during its applications and the material must alongside retain its mechanical reliability and microstructure [1]. Nickel (Ni)-based superalloys are used for elevated temperature components of gas turbines in industrial and aerospace applications due to their excellent thermal and surface stability at elevated temperatures [2-3]. Over time, several changes have been made in the manufacturing of Ni-based superalloys to improve the processing methods and to optimize the chemical composition and microstructure [4]. Nickel-chromium (Ni-Cr) and iron-nickel-chromium (Fe-Ni-Cr) alloys are the distinctive heat resistance Ni-based alloys. Fe-Ni-Cr alloys are resistant to oxidation and heat that was developed for high temperature oxidizing environments. The Fe-Ni-Cr alloys have excellent oxidation resistant in many severe environments as it forms a protective film of chromium

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oxide, Cr$_2$O$_3$ [5]. They also have good resistance to oxidation and sulfidation and have good strength at high temperatures. They have a maximum operating temperature of 1205°C. Microstructures and the mechanical properties of Ni-based superalloys can be modified by heat treatment. The mechanical properties such as strength, fatigue and creep resistance could be improved with suitable heat treatment process. Heat treatment is normally used to obtain the optimal combination of size, morphology and distribution of γ' precipitates that leads to an enhanced mechanical performance. This is because the strengthening of Ni-based superalloys is strongly influenced by coherent precipitation of γ' phase in the γ matrix [6].

Therefore, the aim of this study is to investigate on the oxidation behaviour of heat-treated Fe-40Ni-24Cr alloy at 950°C. The grain size of the heat-treated alloys at different heat treatment temperatures have a significant impact on the oxidation kinetic and oxide scale formation of the alloy.

2 Methodology

Fe-40Ni-24Cr alloy was used as the material in this study. The chemical composition in weight percent was measured using optical emission spectrometer (OES), which are: 40.45 Ni, 24.11 Cr, 0.05 C, 0.08 Al, 0.03 Ti, 0.44 Si, 0.7 Mn, 0.01 P, 0.11 Cu, 0.25 Mo, 0.17 Co, 0.44 Nb, 0.05 W and balance Fe. The Fe-40Ni-24Cr alloy was experienced a series of heat treatment process at different temperature, namely 950°C, 1050°C, and 1150°C for 2 hours soaking time, followed by water quench. These samples are denoted as HT950, HT1050 and HT1150 for alloy heat-treated at 950°C, 1050°C, and 1150°C, respectively. The grain size of the heat-treated alloy was measured using linear intercept methods ASTM E112. The heat-treated alloys were then undergoing a series of grinding process. The grinding process was carried out so that the samples have a good surface finish and accurate dimensions required so that the oxidation layer can be formed evenly on the sample. The heat-treated Fe-40Ni-24Cr alloy were grind until P600 grit surface finished. The dimension and weight of the heat-treated samples was measure before the oxidation test. The weight of oxidized heat-treated sample was measure after the oxidation test to determine the kinetic of oxidation. The ground samples are then arranged in a quartz boat for the oxidation test. The heat-treated alloy was undergo the isothermal oxidation test at 950°C for 150 hours. The oxidation test was run discontinuously for every 25 hours interval durations until 150 hours to record the kinetics of oxidation of all samples. The oxidized heat-treated samples were characterized in terms of oxidation kinetics and surface morphology using scanning electron microscope (SEM) technique.

3 Results and Discussion

3.1 Heat Treatment of Fe-40Ni-24Cr Alloys

The heat treatment process on Fe-40Ni-24Cr alloy indicate that the higher the heat treatment temperature, the larger the grain size of the sample. HT950 sample which has been heat-treated at 950°C indicates the average grain size of 71.4 µm, recorded a fine grain size. Meanwhile, the average grain size of the HT1050 sample which has been heat-treated at 1050°C is 91.3 µm. HT1150 sample which has been heat-treated at 1150°C obtained an average grain size of 105.1 µm, indicating the coarse grain structure. The results show an increasing trend of the average grain size of the alloy’s microstructures as the heat treatment temperature increases.
3.2 Oxidation Kinetic of Oxidized Fe-40Ni-24Cr Alloys

Fig. 1 shows the graph of weight change per surface area versus time that was oxidized at 950°C for 150 hours. The graph shows an increasing trend of the sample weight as the oxidation time increases. The oxidation kinetic curve for HT950 sample shows the lowest weight gain, followed by HT1050 sample. Whereas, the oxidation kinetics curve of HT1150 sample shows the highest weight gain pattern.

Fig. 1. Oxidation kinetic of heat-treated Fe-40Ni-24Cr alloy at 950°C for 150 hours.

HT950 sample which has the fine grain structure exhibit lowest weight gain and thus has a high oxidation resistance. Hence, this fine grain sample shows a lower oxidation rate. This is because, fine grain size has higher grain boundary area which act as a diffusion path of outward metal ion migration from based metal to metal-gas interface. The higher ion diffusion rate on fine grain sample was developed a rapid initial oxide layer that formed on the alloy surface that protects the alloys’ surface from further hostile oxide formation. When the whole alloy surface was covered with the thin oxide layer, the formation of oxides was slowly decrease as the oxide layer itself act as a barrier for further reaction with the oxidizing environment. This mechanism was explained about the weight gain pattern of fine grain HT950 sample as shown in Fig. 1, which exhibited the steadily and lowest weight gain.

The oxidation kinetic curve of HT1050 sample displays a moderate weight gain. Similar observation was noticed for this sample, as it developed a low weight gain value comparable with HT950 sample. On the other hand, the HT1150 sample which has coarse grain structure, indicates the highest weight gain per surface area value. The weight gain for coarse grain structure increases due to the continuous oxide growth during the exposure to the working temperature. The higher weight gain of this coarse grain sample due to the possibility of continuous oxide growth that forms a protective oxide layer at the alloys surface. From the weight gain data, it can be note that thick oxide layer was formed on the alloy surface of HT1150 sample as it recorded a high weight gain value compare with HT950 and HT1050 samples.

The double log plot of graph in Fig. 1 has been done to determine the oxidation rate law of all samples. Equation (1) was use to analyze the data where \( x \) is weight change per surface area, \( t \) is time and \( m \) is constant. The \( m \) value with 1, 2 and 3 represent linear, parabolic and cubic oxidation rate laws, which can be determined from the double log plots. From the analysis that has been done, it was confirmed that all samples follow the parabolic rate law. The parabolic rate constant was determined from parabolic rate law of equation (2), where \( K_p \) denote parabolic rate constant. The parabolic rate constant value was calculated from the square of weight change per surface area as a function of time. The analysis recorded a parabolic rate constant for HT950, HT1050 and HT1150 are \( 5.336 \times 10^{-7} \text{ mg}^2\text{cm}^{-4}\text{s}^{-1} \).
5.933 \times 10^{-7} \text{ mg}^2\text{cm}^{-4}\text{s}^{-1} and 1.943 \times 10^{-6} \text{ mg}^2\text{cm}^{-4}\text{s}^{-1}, respectively. The higher value of parabolic rate constant indicates a higher oxidation rate of the samples. Therefore, from the values obtained, HT1150 sample has the highest oxidation rate while HT950 sample has the lowest oxidation rate that served its high oxidation resistance.

\[ \log x = \frac{1}{m} \log t + C \]  
\[ x^2 = K_p t + C \]  

3.3 Surface Morphology of Oxidized Fe-40Ni-24Cr Alloys

Scanning electron microscope technique was used to analyzed the surface morphology of oxidized surface. Two samples from 25 hours of oxidation and three samples from 150 hours of oxidation were analyzed. Fig. 2 (a) shows the surface morphology of HT950 sample oxidized for 25 hours. The SEM image shows the continuous oxide layer was formed on the sample surface with evidence of small area of oxide spallation. Fig. 2 (b) shows the surface morphology of HT1150 sample oxidized for 25 hours. The SEM image displays the formation of oxide spallation at numerous parts with formation of void on the spallation area. The void tends to formed underneath the oxide scale which is exposed when the oxide exfoliates from the sample surface. On the other hand, the image also display the formation of overgrown oxide scale which has the permeable structure. This overgrown oxide scale has a tendency to spall during prolong exposure to high temperature oxidation due to the wobbly structure. Oxide spallation occurs in this coarse grain sample due to the weak adhesion of oxide scale on the alloy.

![SEM image of oxidized Fe-40Ni-24Cr alloy after 25 hours](image1)

![SEM image of oxidized Fe-40Ni-24Cr alloy after 25 hours](image2)

Fig. 2. SEM image of oxidized Fe-40Ni-24Cr alloy after 25 hours; (a) HT950; (b) HT1150.

Fig. 3 shows the surface morphology of heat-treated Fe-40Ni-24Cr alloy oxidized for 150 hours. Fig. 3 (a), (b) and (c) shows the SEM images for HT950, HT1050 and HT1150 samples, respectively. All samples indicated the formation of continuous oxide layer on the alloy surface. On the other hand, evidence of oxide spallation, overgrown oxide scale and voids also formed on the alloy surface. The main different is that the area of oxide spallation for HT950 sample was smaller compared to HT1050 and HT1150 samples. The formation of oxide spallation on HT1150 samples was occurred on a large area indicating that this sample was formed a loose oxide scale that tend to spall after prolong exposure at high temperature condition. The number of voids also increase as the area of oxide spallation increase. The void was formed underneath the spall oxide which was exposed due to spallation mechanism. This indicates that the oxide scale forms on the oxide structure contains pores below it. The pores was occurred due to rapid metal ion diffusion that develops an open passage towards the oxide surface. The outward metal ion diffusion was enhanced by the grain boundary area.
on the alloy. When the diffusion rate is high to developed an oxide layer, it will generate the voids along the grain boundary area. This void was unstable, which is, as the oxidation test duration increase, it will act as a break point of oxide spallation. When the oxide spall, it will expose the surface of the alloy and disturb the protection behaviour. This phenomenon will generate a fresh oxide scale to reformed on the exposing area which tend to thicken the oxide scale. This will lead to increase in the weight gain of the sample as indicate in the Fig. 1. The formation of numerous and large area of oxide spallation represented the low protection behaviour of oxide scale developed on the alloy surface.

![SEM images of oxidized Fe-40Ni-24Cr alloy after 150 hours](image)

**Fig. 3.** SEM image of oxidized Fe-40Ni-24Cr alloy after 150 hours; (a) HT950; (b) HT1050 and (c) HT1150.

### 4 Conclusion

Based on this study, it can be concluded that the increase in the heat treatment temperature of the alloys leads to increase the grain size. Fe-40Ni-24Cr alloy which is heat-treated at 1150°C (HT1150) indicate the coarse grain size of 105.1 µm, whereas the alloy heat-treated at 950°C (HT950) indicate the fine grain size of 71.4µm. The oxidation kinetics of all heat-treated oxidized samples recorded an increasing weight gain pattern as the exposure time increase, with followed a parabolic rate law. HT950 sample exhibited the lowest weight gain pattern and lowest oxidation rate compared to HT1050 and HT1150 samples, hence presented a superior oxidation resistance. The surface morphology analysis from scanning electron microscope shows a continuous oxide scale formed on the samples surface after 25 hours and 150 hours exposure with evidence of oxide spallation, overgrown oxide scale and voids. HT1150 samples recorded a numerous voids formation with larger oxide spallation area.

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References

1. M. H. Thammaiah, *Isothermal Oxidation Comparison of Three Ni-Based Superalloy* (2016)
2. J. Jiang, G. Xiao, Y. Wang, Y. Liu, J. Alloys & Comp. 784, (2019)
3. C. N. Athreya, K. Deepak, D. Kim, B. de Boer, S. Mandal, J. Alloys & Comp., 778 (2019)
4. M. Konter, M. Thumann, J. Mat. Pro. Tech. 117 (3), (2001)
5. A. Col, V. Parry, C. Pascal, Cor. Sci. 114, (2017)
6. C. Li, Z. Yuan, Y. Fan, S. He, W. Xuan, X. Li, Y. Zhong, Z. Ren, J. Mat. Pro. Tech. 246, (2017)