Effect of Surface Preparation on the Isothermal Oxidation of Fe-33Ni-19Cr Alloy

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Abstract. The effect of surface preparation on the isothermal oxidation behavior of Fe-33Ni-19Cr alloy was study in this paper. The surface preparation of the test samples was obtained by grinding process using different grit of silicon carbide abrasive paper, namely P600, P800 and P1000. The surface area and weight of the sample were measured before the oxidation test, by using Vernier caliper and analytical balance. The ground sample of Fe-33Ni-19Cr alloys were isothermally oxidized at 1000℃ for 150 hours in laboratory air. The weight of oxidized samples was recorded after the isothermal oxidation test at every 25 hours exposure duration in order to determine the oxidation kinetic of all samples. The oxide surface morphology of Fe-33Ni-19Cr alloy was characterized by scanning electron microscope. The oxidation kinetic of all samples displayed a weight gain pattern as the exposure duration increase, followed a parabolic rate law. While the result of surface morphology shows that the lowest grit of surface finish, P600, display less oxide exfoliation occurred.

1 Introduction

The Ni-based alloys used for high strength and high temperature applications which also called superalloy was developed to use in turbine engine and high performance at high or raise temperature application for mechanical properties [1]. Even they are expose in long term at temperature above 650°C, they are specially appropriate choice for these demanding applications because of their ability to retain most of their strength. Combination of great low temperature ductility, high strength and high surface stability, make these alloys becomes more versatile [1]. Ni-based superalloy was generally used for a number of applications which include turbine discs of jet engines, as well as pipe lines in oil and gas fields due to the excellent high temperature oxidation resistance, corrosion resistance and mechanical accomplishment [2]. Oxidation resistance of this superalloy and bond covering materials in high temperature situations is a great extent directed by their capacity to specially shape an adherent oxide scale on the metal surface. These alloys are also suitable to work under unstable environmental conditions. Furthermore, the Ni, Cr and Co, are element which represent the base of these systems. Carbide and other compounds are formed because of the existing of the minor addition of the elements like B, C, Ti, Nb, Al and Fe [3]. Unfortunately,

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at the temperature above 900℃, the damaging of the microstructure components may occur from formation of nitrides, carbides and other phases.

Fe-Ni-Cr alloy is a Ni-based alloy, has excellent mechanical properties with high temperature oxidation resistance, used in the power plants application [4]. Generally, for this alloy, the development of protective chromia scales that form on the surfaces by the oxidation of Cr during elevated temperature exposure can act as protective oxides layer [5]. The existence of a critical Cr content to form a continuous chromia scale has been investigated. At high temperature exposure, the formation of a protective Cr$_2$O$_3$ scale is required to avoid degradation by severe oxidation processes for alloys. A number of investigations have been carried out to improve the understanding of the growth mechanism of Cr$_2$O$_3$ scales.

However, the oxide will exfoliate at elevated temperature exposure if the protective oxide layer did not well adhere to the alloy surface. The initial oxide layer formation was determined by good surface preparation. The optimum groove mark induced by surface preparation will enhance the formation of protective oxide layer. The grinding effect during surface preparation results the cold working effect on the subsurface regions of the alloy, which assist diffusion. Additionally, the subsurface region will form fine grain structure which increase the grain boundary area. This would affect the higher short circuit diffusion of ion species through grain boundary area. As a result, rapid initial oxide layer was form on the alloy surface which act as a barrier and protect the alloy [6-7]. On the other hand, the ground surface sample was developing a micro scratch that provides a base structure for oxide nucleation. Primarily, another researcher would also grind the sample surface to enhance the suitable surface roughness [6-11]. Therefore, this study will be focused on the investigation of the oxidation behaviour of Fe-33Ni-19Cr alloy with different surface preparation.

2 Experimental

The material used in this study was as-received Fe-33Ni-19Cr alloy with measured chemical composition using optical emission spectrometer in weight percent (wt%) as follow: 32.51 Ni, 18.90 Cr, 0.078 C, 0.053 Al, 0.489 Ti, 0.001 S, 0.315 Si, 0.556 Mn, 0.007 P, 0.082 Cu and balance Fe. The test samples were cut to a rectangular shape with nominal dimensions of 10mm x 10mm x 3mm. The test sample was undergoing a series of grinding process at different grit size of silicon carbide abrasive paper, namely P600, P800 and P1000. The surface area and weight of all samples were measured before the oxidation test. The test samples were arranged in a quartz boat for the oxidation test. The isothermal oxidation test was run at 1000℃ for 150 hours in laboratory air using LT furnace. The oxidation test was run discontinuously at 25, 50, 75, 100, 125 and 150 hours. The oxidized samples weight was measured after each interval duration to determine the oxidation kinetic. The surface morphology of the oxidized samples were investigate using scanning electron microscope (SEM).

3 Results and Discussion

3.1 Oxidation Kinetics

The graph for total weight change per surface area as a function of time is shown in Fig. 1. The results show that increasing oxidation time was increase the weight gain value. P600 sample shows lowest weight gain pattern, followed by P800 and P1000 samples. P600 samples recorded a lowest weight gain value at 25 hours exposure which is 0.3242 mgcm$^{-2}$, compared with P800 and P1000 samples which are 0.3620 mgcm$^{-2}$ and 0.4045 mgcm$^{-2}$, respectively. The highest weight gain value noted at 150 hours exposure showing an
increasing weight gain recorded for all samples which are 0.7996 mg cm\(^{-2}\), 0.8986 mg cm\(^{-2}\) and 0.9873 mg cm\(^{-2}\) for P600, P800 and P1000 samples, respectively.

The analysis of the oxidation rate law of each sample was done by plotting a double log plot of weight change per surface area (w/A) data as a function of time, based on equation (1), where \(x\) is weight change per surface area, \(t\) is time and \(m\) is constant. The \(m\) values of 1, 2 and 3 represent linear, parabolic and cubic oxidation, respectively. The \(m\) value for all samples recorded at 2.07, 2.02 and 2.09 for P600, P800 and P1000, respectively, denoted that all samples approximately follows parabolic rate law \((m = 2)\). This identification indicates that the oxide growth rate for all samples was followed diffusion-controlled mechanism.

The parabolic rate constant was identified from equation (2) where \(x\) is weight change per surface area, \(t\) is time in seconds, \(K_p\) represent parabolic rate constant and \(C\) is a constant. The parabolic rate constant has been interpreted from square of weight change over time. From the calculated value, the highest \(K_p\) value was determined from P1000 sample, which is \(2 \times 10^{-6}\) mg\(^2\) cm\(^{-4}\) s\(^{-1}\) indicating the highest oxidation rate take place on that sample. While the lowest oxidation rate occurred on P600 sample with the parabolic rate constant of \(1 \times 10^{-6}\) mg\(^2\) cm\(^{-4}\) s\(^{-1}\). P600 sample denoted the best oxidation resistance compared to P800 and P1000 samples.

\[
\log x = \frac{1}{m} \log t + c \tag{1}
\]

\[
x^2 = K_p t + c \tag{2}
\]

3.2 Surface Morphology

Fig. 2 shows the SEM image of oxidized Fe-33Ni-19Cr alloy after exposure for 100 hours. The images display the continuous and uniform oxide scale formed on the alloy surface with visible of oxide exfoliation and overgrown porous oxide structure. Numerous oxide exfoliation area was recorded on the P1000 sample compared to P600 sample.

Fig. 3 show the SEM images of oxidized Fe-33Ni-19Cr alloy after 150 hours exposure. SEM image of P600 sample in Fig. 3 (a) exhibited the small oxide exfoliation area surrounded by porous oxide structure. This porous oxide has a wobbly structure which is has a tendency to exfoliate during further exposure duration. Whereas, SEM image of P1000 sample in Fig. 3 (b) exhibited a large oxide exfoliation area compared to P600 sample. The formation of porous oxide structure also visible on the alloy surface. On the other hand, it was seen in the SEM image, the flaky oxide structure near the oxide exfoliation area with evidence of crack formation on the structure. This flaky oxide also has a tendency to exfoliate causing the exposure of the protection oxide layer of the alloy. When the oxide exfoliates, it will expose the based metal and reduce the protective barrier. This will cause a fresh oxide will continue
to grow to seal the unprotected area, hence further increase the weight of the sample. This will lead to increase in the weight gain pattern as recorded on the P1000 sample as displayed in Fig 1.

![Fig. 2. SEM images of oxidized Fe-33Ni-19Cr alloy after 100 hours: (a) P600, (b) P1000.](image)

On the other hand, the effect of surface preparation has affected the formation of oxide scale on the surface. Oxidized samples that has been grind using P600 grit encounter less oxide exfoliation compared to P1000 sample. This phenomenon was proved that the surface preparation prior the isothermal oxidation test has been success due to the good adhesion of oxide scale on the alloy surface. This finding was supported by [6], which stated that the rougher surface develops a more resistant to scale spallation. Their research finding shows that thermal cycling would result in repetitive spallation of the oxide scales which initiated the reduction of chromium content in the metal surface. In addition, the temperature and surface treatment play an important factor in the high temperature condition.

![Fig. 3. SEM images of oxidized Fe-33Ni-19Cr alloy after 150 hours: (a) P600, (b) P1000.](image)

During surface preparation, the grinding process will introduce the cold working effect on the subsurface regions of the alloy, contain a large number of dislocations which promote diffusion of metal ion species. It also causes the alloy regions to recrystallize, hence refine the grain at the subsurface regions. As the grain refined, it will increase the volume of grain boundary, which provides rapid diffusion routes for chromium, which allows the metal ion to diffuse to the alloy surface and form a continuous and protective oxide layer. This phenomenon may be eliminating the internal precipitation due to scale formation that prevents the access of gas to the metal. Even though the scale exfoliate, it forms rapidly by the relatively rapid diffusion of chromium across the grain boundaries to the surface [6]. This mechanism cannot be achieved in the alloys which had been chemically etched, because of
the removal of the surface regions which had been mechanically damaged. This fact was
generating the idea to grind the alloy surface prior the oxidation test, without etching [7]. On
the other hand, the ground surface sample was developing a micro scratch that provides a
base structure for oxide nucleation. Principally, the sample surface of the oxidation test was
ground to an optimum surface finish to enhance the suitable surface roughness to promotes
the oxide scale growth.

4 Conclusion
The effect of surface preparation at three different grit size of silicon carbide abrasive paper
on the oxidation behaviour of Fe-33Ni-19Cr alloy has been study. All samples were obeyed
a parabolic rate law, indicating a diffusion-controlled oxide growth rate. P600 sample
exhibited the lowest weight gain pattern and parabolic rate constant value compared with
P800 and P1000 samples, consequently presented good oxidation resistance. The surface
morphology of P600 sample recorded a continuous oxide scale formed on the alloy surface
with visible of oxide exfoliation and porous oxide structure. Similar observation was
recorded for P1000 oxidized sample surface, except that the area and number of oxide
exfoliation is larger compared with P600 sample.

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