Oxide scale growth on Fe-40Ni-24Cr alloy at high temperature oxidation

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Abstract. Fe-40Ni-24Cr alloy is a Ni-based alloy used at high temperature application. In this study, Fe-40Ni-24Cr alloy had undergone a solution treatment at two different temperatures, namely 1050℃ and 1150℃, for 3 hours soaking times followed by water quench. A solution-treated Fe-40Ni-24Cr alloy was experienced a high temperature isothermal oxidation test at 500℃ for 500 hours exposures duration. The growth of oxide scale was characterized in terms of oxidation kinetics and surface morphology using field emission scanning electron microscope equipped with energy dispersive x-ray spectroscopy. The oxidation kinetics of all samples shows an increasing weight gain pattern as the exposure durations increases. The oxidation kinetics was obeyed a parabolic rate law, indicating the oxide growth rate was followed diffusion-controlled mechanism. The surface morphology of oxidized solution-treated Fe-40Ni-24Cr alloy displayed a formation of continuous oxide scale with evidence of overgrown Nb-rich oxide particles distributed along the oxidized samples surface. Oxidized Fe-40Ni-24Cr alloy which undergo solution treatment at 1150℃ exhibited the formation of oxide spallation. The spallation has a tendency to occur around the area of overgrown Nb-rich oxide particles.

1 Introduction

Ni-based alloy is a family of superalloy which is used at high temperature oxidation due to the excellent high temperature strength, oxidation resistance and creep resistance [1-3]. Fe-40Ni-24Cr alloy is a type of Ni-based alloy with good oxidation resistance and excellent strength at elevated temperature. It is used for heat treating equipment, waste incinerators, radiant tubes, muffles, retorts and furnace component which involved in the exposure of the component at high temperature condition and longer service duration. Therefore, oxidation behaviour has become one of the most important factors to assess the properties of this alloy. It is important to evaluate them through oxidation kinetics and the nature of oxide scale formed by high temperature oxidation.

Ni-based alloy is characterized by the high phase stability of the face centre cubic austenite matrix. The Fe-Ni-Cr alloy form a protective surface of Cr2O3, which have excellent oxidation resistance in many severe environments [4]. The high Ni content maintains an austenitic structure. The Fe content provides resistance to internal oxidation. The high Cr

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content in this alloy has a capability to form a protective \( \text{Cr}_2\text{O}_3 \) oxide which developed a protective layer on the component. Oxidation resistance is provided by the formation of a protective oxide layer which is formed when the metal is exposed to oxygen at high temperature and encapsulates the materials, and thus protecting the rest of the component. Many Ni-based alloy contains a combined of several alloying element, including Nb. Nb as alloying element has been extensively used in superalloy for many purposes for improvement of both mechanical properties and oxidation resistance [3-6]. In order to control oxidation, the favourable of Nb have been studied. The effect of Nb in Ni-based alloy is of great importance. Therefore, it needs further and deeper investigations for the high temperature application of Ni-base alloy.

Generally, the oxidation resistance of alloys depends on the protective properties of oxide layer formed on the surfaces in the oxidizing atmospheres. However, the formation of the oxide layer significantly varies with the chemical composition, microstructure and surface condition of the alloy. Therefore, various methods have been proposed to enhance the oxidation resistance of alloys either through altering the chemical composition of the materials or changing the structure of the alloys. Among these methods, grain refinement has been reported as an efficient way to enhance oxidation resistance of the alloys [7-9]. In this study, the effect of grain alteration by solution treatment has been investigated on the oxidation behaviour of Fe-40Ni-24Cr alloy which focused on the oxidation kinetics and oxide scale formation on the alloy surface.

2 Experimental

Fe-40Ni-24Cr alloy used in this study was commercial HAYNES® HR-120® alloy supplied by Haynes International, Inc. The chemical composition 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 samples were cut using wire electrical discharge machine to dimension of approximately 10 mm x 10 mm x 3 mm. The cut samples were undergoing a solution treatment process at 1050℃ and 1150℃ for 3 hours soaking time, with 10℃/minute heating rate, followed by water quench. These samples were denoted as ST1050 and ST1150 for samples solution-treated at 1050℃ and 1150℃, respectively. The solution-treated samples were ground using silicon carbide grinding paper up to P600 grit finished. The samples dimension was measured prior the high temperature isothermal oxidation test. The samples weight was measured before and after the oxidation test. The solution-treated samples were then experienced a discontinuous isothermal oxidation test at 500℃ for 500 hours. The oxidized solution-treated samples were characterized in terms of oxidation kinetics and surface morphology using field emission scanning electron microscope (FESEM) equipped with energy dispersive x-ray (EDX).

3 Results and Discussion

3.1 Solution Treatment

The results of solution treatment on Fe-40Ni-24Cr alloys displayed an increasing grain size of alloy as the solution treatment temperature increases. Solution treatment at 1050℃ recorded a fine grain size which is 32.85 μm. Whereas, solution treatment at 1150℃ recorded a coarse grain size which is 37.13 μm.
3.2 Oxidation Kinetics

The weight change per surface area (w/A) as a function of time (t) of Fe-40Ni-24Cr alloy oxidized at 500°C is presented in Fig. 1. The oxidation rate law was identified using a double log plots as plotted in Fig. 2 (a). The equation (1) was use to fit 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. Overall, all samples produced a good fitting results with \( m \) ranging from 1.83 to 2.37, representing the parabolic rate law \((m = 2)\). The parabolic rate constant was determined from parabolic rate law equation (2), where \( K_p \) denote parabolic rate constant. The square of weight change as a function of time was plotted, and the \( K_p \) value is calculated as shown in Fig. 2 (b), and all data shows a good fitting result.

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

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

![Fig. 1. Oxidation kinetics of solution-treated Fe-40Ni-24Cr alloy at 500°C.](image)

The oxidation kinetics for fine grain ST1050 sample shows low oxidation rate. Whereas, ST1150 sample shows a slightly high oxidation rate compared to ST1050 sample. The weight gain of both samples shows a sharp increasing at the beginning up to 100 hours, then constantly gaining weight until 500 hours. The significant different in between these samples is, ST1150 recorded more weight gain compared to ST1050 which indicating the thick oxide layer was formed on the sample surface. The high oxidation rate was recorded for coarse grain ST1150 sample. The \( K_p \) value for ST1050 was smaller than ST1150 sample, which are 5.49 x 10\(^{-9}\) and 10.46 x 10\(^{-9}\) mg\(^2\)cm\(^{-4}\)s\(^{-1}\), respectively, indicating that ST1050 sample has a low parabolic rate compared to ST1150. In parabolic rate law, the growth of oxide occurs with a continuing declining rate of oxidation. The reaction rate is inversely proportional to the weight of oxide formed or the scale thickness.

The low oxidation rate was determined from rapid initial oxide formation for fine grain sample, generates a rapid protective oxide scale. As the oxide scales thicken, the diffusion rate decrease, recorded a small weight gain. The mechanism of initial oxide formation for fine grain sample was begin with the formation of oxide nuclei when this alloy was exposed at high temperature condition. Oxygen ion from the atmosphere was absorb into the alloy surface, react at the metal-gas interface forming an oxide nuclei. As the exposure time increase, the oxide nuclei were growth laterally and the size was increase as the reaction rate increase. The oxide nuclei then start to impinge on each other to form a continuous oxide layer and will covered the alloy surface. This mechanism has decreased the reaction rate. When the continuous oxide layer completely formed on the alloy surface, the oxide scale will continue to growth vertically to further increase the oxide scale thickness. This phenomenon
has developed a protective oxide scale on the alloy surface and governed by diffusion-controlled growth rate, which is, as the oxide scale thickness increase, the diffusion rate was decreases.

The formation of initial oxide scale on the coarse grain size was slightly comparable with fine grain size except for the impingement process of oxide nuclei. The oxide nuclei were initiate by the rapid outward metal ion diffusion through grain boundary area. The fine grain size has higher grain boundary area compared to coarse grain size. Therefore, the impingement process of fine grain size was occur faster compared to coarse grain size.

The quick impingement of fine grain size due to close area of adjacent oxide nuclei. The delay of the impingement process of coarse grain size due to the faraway location of adjacent oxide nuclei to impinge on each other during lateral oxide growth. Consequently, the growth of the oxide nuclei will continue until all nuclei was impinge. On the other hand, the oxide formation also governs by the vertical oxide growth. As the exposure time increase, the oxide thickens vertically. The limited ion diffusion in coarse grain sample is most probably due to the lesser grain boundary area which provides a rapid diffusion path for outward ion movement toward metal-gas interface.

![Fig. 2. Weight change as a function of exposure time of solution-treated Fe-40Ni-24Cr alloy at 500℃; (a) double log plots indicating a parabolic rate law and (b) square of weight change indicating parabolic rate constant, \( K_p \) value. The fitting parameter \( R^2 \) with a value approaching one denotes the increasing consistence of the data with the fitting.](image)

### 3.3 Surface Morphology

Fig. 3 shows FESEM images of ST1050 sample at different magnifications. Low magnification image in Fig. 3 (a) displayed a continuous oxide layer was formed on the sample surface with formation of overgrown oxide particles. The close-up image of the overgrown oxide particle in Fig. 3 (b) demonstrated a protruding structure with some fine crack formation around the oxide particle. An elemental EDX analysis at the upmost area (A) on the oxide particle detected the presence of O and Nb, indicating the formation of NbO_2 oxide phase. This oxide phase was identified using XRD analysis which is not discussed in this paper. Fig. 3 (c) shows high magnification image (25,000 x) on the continuous oxide layer, demonstrated a uniform oxide structure formed at the alloy surface.

Nb alloying element was added to the Fe-40Ni-24Cr alloy system to enhance their properties, but significantly added to the development of Nb rich precipitates which are NbC and (Nb,Ti)C that will strengthen the alloy [10-12]. However, the exposure of this material to high temperature and longer time will increase the tendency to formed Nb-rich oxide precipitate which tend to grow faster with protruding structure that will served as a preferred site for crack formation and further deteriorate the materials into the certain extend. The main
feature of oxidized Fe-40Ni-24Cr alloy in this study is the formation of Nb-rich oxide particle which tend to form an overgrown large particle on the surface. Besides, this alloy formed a Cr-rich oxide which serve as a protective barrier between metal and environment. This was characterized by EDX analysis on the sample surface at Fig. 3 (c), recorded the enrichment of element Cr and O, which indicating the formation of Cr-rich oxide. Other researches have also revealed the similar results, that the Nb-rich precipitates encourages the occurrence of pitting [13]. In addition, the pitting is due to the massive compositional differences between the matrix and precipitate. The extensive growth of oxide scale tend to create a small difference in volume thermal expansion coefficients between the oxides and metals [14].

Fig. 3. FESEM images of ST1050 sample at 500℃ at different magnification: (a) 1000x, (b) 5,000x and (c) 25,000x.

Fig. 4 (a) shows FESEM image of ST1150 sample exposed for 500 hours, displayed the formation of continuous oxide layer with occurrence of overgrown oxide particle distributed along the alloy surface. Fig. 4 (b) indicating the evidence of oxide spallation at the isolated oxide particle area. An elemental EDX analysis at this spallation area (B) recorded the presence of major element of O, Nb, Cr, Ti and C. This analysis indicates that the former oxide formed at this region composes of Nb-rich, Cr-Ti oxide, Cr-rich and/or Ti-rich oxide. Carbon element was detected from the carbides of NbC, (Nb,Ti)C and/or TiC. The formation of Nb-rich and Ti-rich oxide precipitates was formed on the alloy surface due to the presence of Nb-based and Ti-based precipitates in the alloy namely NbC, (Nb,Ti)C and/or TiC.

Fig. 4. FESEM images of ST1150 sample at 500℃ at different magnification: (a) 1000x, (b) 5,000x and (c) 25,000x.

During isothermal oxidation test, the oxide nuclei start to develop at the alloy surface due to the absorption of the oxygen gas at the metal surface, interact with metal ion on the surface. The outward metal diffusion was induced by the outward metal ion diffusion to the metal-gas interface. The readily existence of Nb-based and/or Ti-based precipitates also contributed to the outward diffusion of Nb ion and/or Ti ion to the surface which developed a Nb and/or Ti containing oxide particle at the alloy surface. Since Nb and/or Ti precipitates are present at the isolated area in the alloy, the formation of Nb-rich and/or Ti-rich oxide was also developed at the isolated area which is distributed along the alloy surface. Fig. 4 (c)
shows close-up image of the oxidized sample on the continuous oxide area exhibited the uniform and protective oxide scale was formed. The dense oxide scale was formed indicating a good protection layer.

4 Conclusion

Isothermal oxidation kinetics of Fe-40Ni-24Cr alloy obeyed parabolic rate law. Fine grained of solution-treated sample ST1050 exhibited low weight gain and low parabolic rate constant value, hence low oxidation rate compared to coarse-grained solution-treated sample ST1150. The surface morphology of both samples exhibited the formation of uniform oxide scale with overgrown Nb-rich oxide particles formed on the alloy surface. The main difference of these oxidized alloys is the formation of Nb-rich oxide particle on the ST1150 sample, tend to exfoliate due the faster growth rate of this overgrow oxide particles on the surface.

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