High Temperature Isothermal Oxidation of Heat-treated HR-120 Ni-based Alloys

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Abstract. The effect of heat treatment of HR-120 Ni-based alloys on the isothermal oxidation at high temperature was studied. HR-120 Ni-based alloys underwent a heat treatment process at two different temperatures, namely 1000 °C and 1200 °C for 3 h soaking time, followed by water quench. The heat-treated samples were then undergoing an isothermal oxidation test at 500 °C for 500 h exposure time in air. Oxidized samples have been characterized in terms of the kinetics of oxidation, phase analysis using x-ray diffraction (XRD) and oxide surface morphology using scanning electron microscope (SEM) and field emission scanning electron microscope (FESEM) equipped with energy dispersive x-ray (EDX) spectrometer. The heat treatment process exhibits an increasing of average grain size alloy as the temperature increases. Whereas, the oxidation kinetics of oxidized samples exhibits a parabolic rate law, representing a diffusion-controlled oxide growth rate. The oxidized of heat-treated sample at 1000 °C recorded low oxidation rate with low parabolic rate constant values. The oxide surface morphology of oxidized samples indicates the formation of continuous oxide scales with overgrown Nb-rich oxide particles after exposure for 300 h. At 500 h exposure time, the formation of Nb-rich oxide particles was growing with evidence of crack occurred around the overgrown oxide particles.

1. Introduction

Ni-based alloys are widely used in high temperature applications in nuclear, chemical and power industries due to their superior high temperature mechanical properties and excellent oxidation resistance [1]. Fe-Ni-Cr alloys is a family of Ni-based alloys, used in high temperature service with oxidizing environment. HR-120 alloys is a Fe-Ni-Cr alloys designed to provide a good resistance to oxidizing, carburizing and sulfidizing environments [2-3]. HR-120 alloys is used as a standard materials of construction for various types of thermal processing equipment such as industrial heating applications, industrial furnace and heat-treating operations. In heat-treating operations, the alloys is used for bar frame heat treating baskets and heat treating fixtures. In aforementioned applications, the components are often subjected to the repeated thermal stresses, which develop as a results of temperatures gradients on heating and cooling [4]. Therefore, excellent oxidation resistance was required to develop a protective oxide scales on the alloy surface.

HR-120 alloys contain a main elements of Ni, Fe and Cr with addition of numerous alloying elements to enhance the performance of the alloys. HR-120 alloys containing a high Cr content (24 wt.%) is a chromia forming alloy which can be used up to 1100 °C [3]. Cr in the alloys will form a protective chromia scale of Cr₂O₃ at elevated temperatures, characterized by a slow growth rate. Chromia is a
barrier against further oxidation owing to its very low diffusion coefficients for oxygen and metals, and then offer a high oxidation resistance [5]. Other researchers reported that the formation of oxide scale on alloys containing Cr elements composed of inner Cr$_2$O$_3$ layer and a continuous MnCr$_2$O$_4$ spinel layer [2, 5, 6]. An outer layer of MnCr$_2$O$_4$ located above a Cr$_2$O$_3$ layer is generally formed on the surface of the alloy in oxidizing environment due to the fast outward diffusion of manganese through Cr$_2$O$_3$ [2, 6]. In HR-120 alloys, Nb was added to provides solid solution strengthening and form carbides. Mn, Ti, Al and Si are necessary to improves surface stability through the formation of external oxide layer of MnCr$_2$O$_4$ and/or (CrTi)$_2$O$_4$ and internal oxide layer of Al$_2$O$_3$ and SiO$_2$, respectively, hence have excellent oxidation resistance [2, 7, 8]. Mn is found to be diffused into the scale, developing an outer layer of Cr-Mn spinel which can reduced the creation of volatile Cr species [8-9]. Ti also identified as an element containing in the oxide scale contribute in the protection layer. Al and Si are commonly form precipitates as internal oxides beneath the chromia scale.

Generally, the oxidation resistance of alloys depends on the protective properties of the oxide layers formed on their surface in the oxidizing atmospheres. However, the formation of oxide layer significantly varies with the microstructure, chemical composition and surface condition of the alloy matrix [10]. Therefore, various methods have been proposed to enhance oxidation resistance of alloys such as altering the chemical compositions or changing the structure of alloys [10-12]. Among these methods, grain refinement has been reported as an efficient way to enhance the oxidation resistance of alloys. Consequently, the effects of grain sizes through heat treatment process on the high temperature oxidation behaviour of alloys was investigated in this study. It was reported that the oxidation rate decreased with the decreasing of grain size for Ni-based alloys. In contrast, study on the oxidation rate of Fe-based alloys shows that the oxidation rate increase with the decreasing of grain size. Hence, the grain refinement process might have different effects on the alloys with different of chemical content. Therefore, the objective of the present study is to investigate the effects of different grain sizes alloys on the oxidation behaviour of HR-120 alloys in terms of the oxidation kinetics and oxide scales formation.

2. Methodology

HR-120 Ni-based alloys was used in this studies (ASTM-B-409; ASME-SB-409, UNS N08120). The compositions of this alloys was analyzed using optical emission spectrometer which are 40.45 wt.% Ni, 24.11 wt.% Cr, 0.05 wt.% C, 0.08 wt.% Al, 0.03 wt.% Ti, 0.44 wt.% Si, 0.70 wt.% Mn, 0.01 wt.% P, 0.11 wt.% Cu, 0.25 wt.% Mo, 0.17 wt.% Co, 0.44 wt.% Nb, 0.05 wt.% W and balance Fe. HR-120 Ni-based alloys was cut to a dimension of 10 mm x 10 mm x 3 mm for heat treatment process. The alloys were undergo a heat treatment process at 1000 $^\circ$C and 1200 $^\circ$C for 3 h followed by water quench. These samples denoted as HT1000 and HT1200 for sample undergo a heat treatment process at 1000 $^\circ$C and 1200 $^\circ$C, respectively. The average of alloy grain size after each heat treatment was measured based on ASTM E112. The heat-treated alloys were undergo an isothermal oxidation test at 500 $^\circ$C for 500 h exposure time in air. The weight of the samples was recorded before and after the oxidation test to measured the kinetics of oxidation. The oxide phases present was characterized using x-ray diffraction (XRD) technique model SIEMENS coupled with BRUKER D5000 XRD instrument software. The surface morphology of oxidized alloys has been characterized using scanning electron microscope (SEM) model JOEL JSM-6460 LA and field emission scanning electron microscope (FESEM) model CARL ZEISS 35 VP. Both machines were equipped with energy dispersive x-ray (EDX) spectrometer.

3. Results and Discussions

3.1. Heat Treatment

The heat treatment process of HR-120 Ni-based alloys in this studies was done to vary the grain size of the alloy. The fine grain size was desired due to the higher grain boundary area which favour the metal ion diffusion during high temperature exposure. As a results, the heat treatment process at 1000 $^\circ$C
exhibit a fine grain size which is 29.46 μm. Whereas, the heat treatment process at 1200 °C exhibit a coarse grain size which is 40.86 μm.

3.2. Oxidation Kinetics

Figure 1 shows the oxidation kinetics of oxidized HR-120 Ni-based alloy at 500 °C for 500 h exposure time. The graph was plotted based on weight change per surface area as a function of time. Overall, both oxidized samples exhibit the increasing of weight change trend as the exposure time increase. HT1000 indicate lower weight gain compared to HT1200 sample. Similar observation of increasing weight gain trend as the exposure duration increase were recorded by other researchers [1, 10, 13]. To further identify the oxidation rate law, the analysis of the data in Fig. 1 has been done based on equation (1), where \( x \) is a weight change per surface area, \( t \) is a time and \( m \) is a constant. The value of \( m \) equal to 1, 2 and 3 represent a linear, parabolic and cubic oxidation rate law, respectively. The double log plots of weight change per surface area as a function of time has been recorded as shown in Figure 2(a). As a result, the \( m \) value for HT1000 and HT1200 samples are 2.30 and 2.38, respectively, which obeyed a parabolic rate law. The fitting parameter R² value for both curve are 0.893 for HT1000 sample and 0.957 for HT1200 sample. The R² value approaching one denotes the increasing of consistency of the data with the fitting. The parabolic rate law is desirable in this study due to the excellent oxide growth rate effect of the alloy. In the parabolic rate law, the oxide growth rate is related to the weight gain of the samples. The weight gain was rise sharply at the beginning of the exposure due to the rapid initial oxide scales formation to encapsulate the surface, hence protecting the alloys. Then, the weight gain start to slowing down as the exposure time increase due to the increasing in the oxide scale thickness, hence decreasing the oxide growth rate. This phenomena indicating the diffusion-controlled oxide growth rate.

After confirming that these samples were obeyed a parabolic rate law, the determination of the parabolic rate constant value was done. The parabolic rate constant value of each samples was identified based on equation (2), where \( x \) is a weight change per surface area, \( t \) is a time in seconds, \( K_p \) is a parabolic rate constant and \( C \) is a constant. The square of weight change per surface area as a function of time was plotted as shown in figure 2 (b). All data shows a good fitting parameter results which are 0.945 for HT1000 sample and 0.964 for HT1200 sample. The value of parabolic rate constant, \( K_p \) of HT1000 and HT1200 samples are \( 2.61 \times 10^{-9} \) and \( 11.60 \times 10^{-9} \) mg cm⁻² s⁻¹, respectively. HT1000 sample exhibits lower \( K_p \) value compared to HT1200 sample, indicating a low oxidation rate, hence good oxidation resistance. Good oxidation resistance was come from the rapid initial oxide scale formation of fine grain alloy due to the higher grain boundary area which act as a diffusion path for upward metal ion diffusion toward the metal surface. This phenomenon was formed a rapid initial protective oxide layer which preventing the metal alloy form further extensive oxides scale formation.

\[
\log x = \frac{1}{m} \log t + C \quad (1)
\]

\[
x^2 = K_p t + C \quad (2)
\]
3.3. Phase Analysis

A phase analysis of HT1000 and HT1200 samples after isothermal oxidation for 500 h exposure time is shown in figure 3. Both HT1200 and HT1200 samples recorded similar results as displayed in figure 3 (a) and (b), respectively. Overall, 4 peaks were identified composed of austenite, Cr-rich oxide, spinel oxide and Nb-rich oxide phases. Five austenite peaks were detected, corresponding to the base metal. The Cr-rich oxide consists of Cr2O3 and (Cr0.88Ti0.12)O3 were detected. The formation of Cr-Ti oxide of (Cr0.88Ti0.12)O3 are believed to give beneficial effect due to the low Cr vapour pressure of this oxide [14]. The spinel oxide phase was also detected, which are MnCr2O4, MnFe2O4, FeCr2O4, NiCr2O4 and NiFe2O4. Interestingly, the formation of MnCr2O4 oxide would reduce the Cr activity of Cr2O3 oxide, hence lowering the Cr volatilization effect [8-9]. The formation of less intense of Nb-rich oxide compose of NbO2 was also detected.

![Figure 2](image1.png)

**Figure 2.** (a) Double log plots indicating parabolic rate law; (b) Square of weight change indicating parabolic rate constants value.

![Figure 3](image2.png)

**Figure 3.** XRD results of oxidized samples after 500 h exposure time: (a) HT1000; (b) HT1200
3.4. Oxide surface morphology

Figure 4 shows SEM images of HT1000 and HT1200 samples after 300 h exposure time. Fig. 4 (a) shows a formation of uniform oxide scales on the alloys surface with evidence of isolated overgrown oxide particles at area A of HT1000 sample. The EDX analysis at point A (figure 4 (b)) indicate the enrichment of element Nb and O, representing the formation of Nb-rich oxide. In addition, the EDX analysis also detected a minor content of other elements which are Cr, Mn, Fe and Ni which corresponding to other oxide phases. Fig. 4 (c-d) shows SEM image corresponding with EDX results of HT1200 sample. Similar observation was acquired for HT1000 and HT1200 samples. This HT1200 sample displayed a formation of uniform oxide scale with evidence of overgrown oxide particle. The main difference is the size of the particles. This sample indicate a bigger size of Nb-rich oxide particle as identified using EDX analysis at point B. On the other hand, the EDX analysis also detected several minor content of elements Cr, Mn, Fe, Ni and Ti, which corresponding to other oxide phases.

Figure 5 (a-c) shows FESEM images of HT1000 sample after 500 h exposure time. Figure 5 (a) display an oxide scale formation consists of large area of overgrown oxide which is further analysis by EDX at point C. The EDX analysis in figure 5 (c) detected the enrichment of element Nb and O, representing the formation of Nb-rich oxide. After prolong exposure for 500 h, the Nb-rich oxide particle continue to grow, compared to small area after 300 h exposure time. On the other hand, the observation at higher magnification on the oxide surface as indicate in figure 5 (b) reveals the formation of uniform and continuous oxide scale. Figure 5 (d-f) shows FESEM images of HT1200 sample after 500 h exposure time. Figure 5 (d) shows the formation of overgrown oxide particle on the continuous oxide layer with bigger in size compared to exposure for 300 h. The close-up image of continuous oxide layer was captured in figure 5 (e) reveals a good and uniform oxide scale formed on the alloy surface. The EDX analysis at point D recorded several elements consists of Nb, Cr, Al, Fe and O. The Nb-rich oxide composed of NbO$_2$ was previously detected on the overgrown oxide particle at 300 h. Whereas the detection of element Cr and Fe were representing the formation other oxide phases as analyzed by XRD techniques probably composed of Cr$_2$O$_3$ and/or FeCr$_2$O$_4$ oxides. On the other hand, the detection of Al element was detected from internal oxide precipitates due to the exposure of this area during overgrowth of oxides scale at area D. This finding was also reported by other researchers that Al and Si are commonly form precipitates as internal oxides underneath the chromia scale [7-8].

Figure 4. SEM images corresponding with EDX analysis of oxidized samples after 300 h exposure time: (a-b) HT1000; (c-d) HT1200.
Figure 5. FESEM images corresponding with EDX analysis of oxidized samples after 500 h exposure time: (a-c) HT1000; (d-f) HT1200.

4. Conclusions
The isothermal oxidation of HR-120 Ni-based alloys has been done on heat-treated HT1000 and HT1200 samples. The oxidation kinetic of both samples indicate the weight gain trend as the exposure time increase. Both samples were followed parabolic rate law indicating the diffusion-controlled oxide growth rate. HT1000 sample recorded a low parabolic rate constant, hence has a good oxidation resistance. The phase analysis reveals several oxide phases formed on the oxidized surface composed of Cr-rich, spinel oxides and Nb-rich oxide structures. The surface morphology of oxidized samples reveals the formation of uniform and continuous oxide scales with evidence of overgrown Nb-rich oxide particles.

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References
[1] Athreya C.N., Deepak K, Kim D.I., Boer B., Mandal S.and Sarma V.S. (2019) J. Alloys & Comp. 778 224-233
[2] Tillous K.E., Dulcy J. and Belmonte T. 2014 Oxid. Met. 82 163-179
[3] Ledoux X., Mathieu S., Vilasi M., Wouters Y., Del-Gallo P.and Wagner M. 2013 Oxid. Met. 80 25-35
[4] Chen L.J., Liaw P.K., Wang H., He Y.H., McDaniels R.L., Jiang L., Yang B. and Klarstrom D.L. 2004 Mech. of Mater. 36 85-98
[5] Col A. and Parry V. C. 2017 Pascal, Corros. Sci. 114 17-27
[6] Nguyen T.D., Zhang J., Young D.J. 2016 Corros. Sci. 112 110-127
[7] Cao G., Firouzdor V., Sridharan K., Anderson M. and Allen T.R., 2012 Corros. Sci. 60 246-255
[8] Zarek J., Young D.J., Essuman E., Hänsel M., Penkalla H.J., Niewolak L. and Quadakkers W.J., 2008 Mater. Sci. & Eng. A 477 259-270
[9] Holcomb G.R. and Alman D.E. 2006 Scripta Mater. 54 1821-1825
[10] Wang X. and Szpunar J.A. 2018 J. of Alloys and Comp. 752 40-52
[11] Munitz A., Salhov S., Guttmann G., Deromiw N. and Nahmany M. 2019 Mater. Sci. & Eng. A 742 1-14
[12] Munitz A., Meshi L. and Kaufman M.J., 2017 Mater. Sci. & Eng. A 689 384-394
[13] Xu Y.X., Lu J.T., W.Y. Li and Yang X.W. 2018 Corros. Sci. 140 252-259
[14] Tan L., Ren X., Sridharan K. and Allen T.R. 2008 Corros. Sci. 50 2040-2046