High Temperature Cyclic Oxidation of Ni-based 800H Superalloy at 700°C in Air

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Abstract. The high temperature cyclic oxidation has been investigated on 800H superalloy, composed of Fe-33Ni-19Cr alloy at 700°C for 150 cycles in laboratory air. Two types of samples has been used, where the Fe-33Ni-19Cr alloy has been experienced a different heat treatment temperatures, which are 1000°C and 1100°C, which has differ grain size. The alloy was subjected to a short oxidation period at 700°C for one hours, followed by cooling for 20 minutes for each cycle. The oxide phase analysis has been analyzed using x-ray diffraction (XRD) technique. The cross sectional line scan analysis has been examined using field emission scanning electron microscope (FESEM) equipped with energy dispersive x-ray (EDX) spectrometer. The phase analysis recorded four types of structure has formed on the oxidized sample, composes of austenite phase represent the base metal, corundum oxides, spinel oxides and fluorite oxides structure. The cross sectional analysis indicate that the oxidized samples were formed a several oxide layer, mainly compose of Cr-Mn and Cr-Ti rich oxide with detection of internal oxide precipitates compose of Al-oxide and Si-oxide precipitates.

1 Introduction

Ni-based superalloy are commonly used in high temperature application due to the excellent performance such as high temperature strength, toughness, oxidation resistance, creep resistance and corrosion resistance [1-4]. Ni-based superalloy are commonly used in aircraft engine, turbine blade, turbine disks, power plants and other application [1-2]. In these aforementioned applications, this superalloy were encounter a repeated thermal cycling which can affect material degradation. Ni-based 800H superalloy consists of Fe-33Ni-19Cr alloy has been considered as a suitable materials used at high temperature condition because of their ability to maintain their mechanical properties at increased temperature coupled with their superior oxidation resistance [4-6].

The superalloy have been developed to achieve oxidation resistance by utilizing the selective oxidation concept [2, 7]. These concepts are affected by many factors such as alloy composition, surface conditions, oxidizing environment, and oxide scale behaviour [2]. When a metal is exposed at high temperature conditions to an oxygen rich environment, oxide nuclei will formed and start to impinge on each other, to developed a

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thermodynamically stable and slow growing oxide scales, hence encapsulate the alloy surface to form a protective thin oxide layer. At the initial stage, the rate of oxidation is rapid and all elements in the alloy are oxidized to form various oxide phases. The high amount of Cr as the oxide forming element will form a slow growing surface oxide scale of Cr$_2$O$_3$ [7-9]. In addition, the amount of various oxides is approximately dependent on the alloying element in the alloy such as Mn, Ti, Al and Si, to form external oxide scale and internal oxide precipitates. Mn and Ti may incorporate into the scale, forming a stable outer oxide layer [1, 3, 6-7, 9-11]. Whereas, Al and Si will precipitate as internal oxides [1, 7, 10, 12-13].

Since the physical properties of oxides are different from alloy, it will cause a stress generation and relief in oxide or metal during cooling and heating subjected to cyclic condition. Two stress sources are growth stress and thermal stress. Most superalloys undergo thermal cycling during service. The temperature during cyclic condition will cause loss of protective scale by spallation effect. Normally, spallation and crack formation are driven by oxide growth stress and thermal stress. Oxide stress occurs during oxide thickening, whereas thermal stress is formed through heating and cooling, developed a coefficient of thermal expansion mismatch at metal-scale interface [6]. In order to avoid spallation, it is important to improve metal-scale adherence. There are several methods that have been used to improve scale adherence such as surface treatment, aging treatment, thermomechanical treatment and heat treatment that focused on the alteration of alloy grain structure [3, 14-15].

Therefore, in this study, the effect of different grain size of alloy obtained from different heat treatment temperature exposure will be investigated in high temperature cyclic oxidation condition, to examine the effect of grain size alteration on the oxide scale growth of Ni-based 800H superalloy.

2 Methodology

Ni-based 800H superalloy was used in this study, which is Fe-33Ni-19Cr alloy (ASTM-B-409: ASME-SB-409, UNS N08810). The chemical composition of this alloy has been analyzed using optical emission spectrometer (OES), presented in Table 1.

Table 1. Chemical composition of Fe-33Ni-19Cr alloy in weight percent (wt. %) with balance Fe.

| Alloy / Element | Ni  | Cr  | C   | Al  | Ti  | Si  | Mn  | P   | Cu  | N   |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Fe-33Ni-19Cr    | 33  | 19  | 0.078 | 0.534 | 0.489 | 0.315 | 0.556 | 0.007 | 0.082 | 0.02 |

The Fe-33Ni-19Cr alloy has experienced a heat treatment process at two different temperature in order to varies the grain size of the alloy. The heat treatment process were done at 1000°C and 1100°C for 3 hours soaking time, followed by water quench. These samples are denoted as H10 and H11 for samples heat-treated at 1000°C and 1100°C, respectively. H10 produced an average grain size of 56.72µm, which is fine grain size, while H11 produced an average grain size of 64.77µm, which is coarse grain size. Both heat-treated samples were undergo a cyclic oxidation test at 700°C for 150 cycles in laboratory air using CARBOLITE tube furnace type 3HA 12/300 system. Both samples were subjected to a short oxidation period at 700°C for one hour, followed by cooling process near a room temperature for 20 minutes for each cycle. This process was repeated until 150 cycles. The oxide phase analysis was examined using x-ray diffraction (XRD) technique model SIEMENS machined coupled with BRUKER D5000 XRD instrument.
software. The phase analysis was accomplished with the aid of DiffracPlus Evaluation Software and PDF-2 search/match applications to identify the phases of the oxide scales. The oxidized alloy was examined in cross sectional view using field emission scanning electron microscope (FESEM) attached with energy dispersive x-ray (EDX) analyzer model CARL ZEISS 35 VP.

3 Results and Discussion

3.1 Phase Analysis

The XRD spectrum of both oxidized Fe-33Ni-19Cr alloy of H10 and H11 samples after cyclic oxidation exposure for 150 cycles was depicted in Fig. 1. The four major phases was identified, with corresponding the crystal structure, which are austenite, corundum, fluorite and spinel structure. The austenite peaks corresponding to the based alloy were recorded at five different diffraction angle 20.

![XRD pattern of oxidized Fe-33Ni-19Cr alloy after 150 cycles: (a) H10 and (b) H11.](image-url)
The oxide phases with corundum structure was detected which are Cr-rich oxides composed of Cr$_2$O$_3$ and (Cr$_{0.88}$Ti$_{0.12}$)$_2$O$_3$ and also hematite Fe$_2$O$_3$ phase. The Cr-rich oxide and hematite peaks were overlaps on each other due to similar crystal structure of the oxide. The formation of Cr-Ti rich oxide was said to mitigate the Cr evaporation effect due to the lower Cr vapour pressure of (Cr,Ti)$_2$O$_3$ compared to Cr$_2$O$_3$ [6]. In addition, the flourite oxide structure of Ti-rich oxides were detected consists of TiO$_2$ and (Ti$_{0.97}$Cr$_{0.03}$)O$_2$. The presence of Ti-rich oxides was confirmed by the peak at 20 27.5 (110). The formation of Ti-rich oxides in Fe-Ni-Cr alloy system was also reported by other researchers [1, 10]. On the other hand, the spincel oxide structure compose of MnCr$_2$O$_4$, NiCr$_2$O$_4$, NiFe$_2$O$_4$, FeCr$_2$O$_4$ and magnetite Fe$_3$O$_4$ phases were detected. The overlap of spincel phases was also reported by other researcher [11], hence cannot be clearly distinguish in between each other. Other researcher also reported the formation of NiCr$_2$O$_4$ oxide [1-2, 14] NiFe$_2$O$_4$ oxide [13] and FeCr$_2$O$_4$ oxide [16, 18] on oxidized of Ni-basad alloy [19-23].

The formation of chromia oxides composes of Cr$_2$O$_3$ and MnCr$_2$O$_4$ has been reported by several researcher [3, 9, 11]. These oxide act as a barrier against further oxidation due to its very low diffusion coefficient for oxygen and metal, and then offer a high oxidation resistance. According to [11], the addition of a small amount of manganese will reduced the oxidation rate at high temperature exposure by forming a continuous MnCr$_2$O$_4$ spinel layer. Mn is found to be diffuse into the scale, developing an outer layer of Cr-Mn spinel, which can reduces the creation of volatile Cr-species [7, 10]. Mn may diffuse into the outer oxide layer with Cr due to its large solubility in Cr.

Moreover, the formation of protective oxide layer of Cr$_2$O$_3$ oxide, offer a resistance to high temperature oxidation due to the continuous and slow growing scale behaviour. The formation of protective Cr$_2$O$_3$ oxide on oxidized Ni-based alloy was also reported by numerous researchers [1-2, 4-5, 8, 16-17]. On the other hand, internal oxidation is a common phenomenon observed in metal alloys at high temperatures, usually greater than 600℃ [18]. The formation of Al-rich and Si-rich oxide precipitates on oxidized Ni-based alloy has been reported by several rechearchers [1, 7, 10, 12-13]. However, in this study, the detection of Al and Si precipitates through XRD cannot be seen due to thick oxide layer formed on the sample surface. However, further analysis using FESEM-EDX technique has identify the formation of these internal oxide. Al$_2$O$_3$ and SiO$_2$ oxide precipitates usually formed beneath the surface oxides, which both oxides contribute to the protective consequence at temperature condition. Similar finding has been reported [7, 10].

### 3.2 Cross Sectional Analysis

Fig. 2 (a) shows a FESEM image with EDX line scan analysis of cross sectional fine grain H10 sample after cyclic oxidation for 150 cycles. Four oxide layers was produced on the oxide scale, compose of top outer layer (area 1) enriches in elements O, Cr, Mn and Ti, proposing the formation of Cr-rich oxide containing Mn and Ti, such as Cr$_2$O$_3$, MnCr$_2$O$_4$, (Cr$_{0.88}$Ti$_{0.12}$)$_2$O$_3$ and/or (Ti$_{0.97}$Cr$_{0.03}$)O$_2$. According to other researchers [6-7, 10], Mn and Ti may incorporate into the scale, forming a stable outer oxide layer, thus reduces the Cr volatility of Cr containing oxides. The inner oxide layer of area 2 revealed the enrichment of elements Fe and Ni with trace amount of Cr suggesting the formation of spinel oxides phases, which are FeCr$_2$O$_4$, NiCr$_2$O$_4$ and/or NiFe$_2$O$_4$. Layer 3 which is close to the scale-metal interface revealed the high amount of element Si, while, layer 4 indicated the presence of Al as the internal oxide. Similar observation was reported by other researcher, which is Al and Si normally formed an internal oxides on Fe-Ni-Cr alloy system [7, 10]. In addition, the EDX line scan analysis also revealed a slightly high amount of Al at area 5, suggesting the formation of internal precipitate Al oxide.
Fig. 2 (b) shows a FESEM image with EDX line scan analysis of cross sectional coarse grain H11 sample after cyclic oxidation for 150 cycles which formed three oxide layers. The outer oxide layer (area 1) consist of elements O, Cr and Ti, while, layer 2 which close to scale-metal interface enriched in elements O and Si. The internal oxide layer (area 3) consists of elements O and Al. These results suggesting that outer oxide layer composed of Cr-rich containing Ti oxide, while Si oxide and Al oxide precipitates as internal oxide. No evidence of element Mn detected on the oxide layer, indicating that the outer oxide layer of H11 sample did not formed a Cr-Mn rich oxide. The probability of oxide formed on the outer layer are Cr-Ti rich oxide and Cr-rich oxide. This observation shows that the coarse grain H11 sample only formed Cr-rich and Cr-Ti rich oxides, where these oxide has a beneficial effect to lessen the Cr evaporation effect.

Whereas, H10 sample was developed a Cr-rich, Cr-Ti rich and Cr-Mn rich oxides. The formation of Cr-Ti and Cr-Mn rich can reduces the creation of volatile Cr-species, hence producing good protective oxide layer on the alloy surface. The chromia oxides consists of Cr$_2$O$_3$ and MnCr$_2$O$_4$ offering a high oxidation resistance. The results indicate that fine grain H10 sample favour the outward ion diffusion of Mn element to incorporated with Cr in the outer oxide layer by the rapid diffusion through grain boundary area. Fine grain sample has higher grain boundary area compared to coarse grain sample. Even though the XRD analysis of H11 sample has detected the formation of corundum and spinel oxide structure, but the oxide peaks was overlap, hence reducing the availability to recognized each of oxide phases formed on the alloy surface.

![Fig. 2: Cross sectional FESEM image with corresponding EDX line scan analysis of oxidized Fe-33Ni-19Cr alloy after 150 cycles: (a) H10 and (b) H11.](image)
Summary

The cyclic oxidation behaviour of Ni-based 800H superalloy, which is Fe-33Ni-19Cr alloy was studied in air at 700°C up to 150 cycles. Based on the oxidation test, the formation of oxide phases compose of corundum, fluorite and spinel oxide structure is responsible for imparting resistance against high temperature oxidation of the studied alloy. The formation of protective Cr-rich oxide scales composed of Cr-Mn and Cr-Ti rich oxides were formed on the outer oxide layer. Whereas, Al-rich and Si-rich oxide precipitates formed as internal oxide beneath the scale-metal interface. Both oxide precipitates contribute to the protective consequence at temperature conditions.

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