

Oxide Growth Behaviour of 800H and HR-120 Series Ni-based Alloys on Isothermal Oxidation

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ABSTRACT

The isothermal oxidation of two types of Ni-based alloy, alloys 800H and HR-120 was investigated in this study. The alloy underwent an isothermal oxidation test at 950 °C for 150 hours of exposure. Oxidised alloys were tested using oxidation kinetics methods, phase analysis using X-ray diffraction (XRD) and oxide morphology using scanning electron microscopy (SEM) techniques. Oxidation kinetics were determined based on the weight change per surface area of the oxidised alloy over a 30-hour interval. As a result, both alloys displayed a pattern of weight gain as the exposure period increased. Both alloys have followed a parabolic rate law, indicating a controlled kinetics of oxide scale diffusion. XRD analysis showed that the main Cr-containing oxide has formed on the surface of the alloy with the addition of Ti oxide for the 800H alloy and Nb oxide for the HR-120 alloy due to the different alloying element content of the two alloys. Oxide surface morphology records the uniform oxide scale that forms on the surface of the alloy.

Keywords: Ni-based alloy, 800H alloy, HR-120 alloy, isothermal oxidation

1. INTRODUCTION

The group of heat-resistant alloys known as superalloys consists of alloys of cobalt (Co), iron (Fe), and nickel (Ni). This alloy has unique qualities that make it suitable for a wide variety of industrial applications. On the other hand, even though it is a heavier element than Co, Ni has a higher specific modulus and is more resistant to the effects of harsh environmental conditions. This explains why Ni-based alloys are commonly used as high-temperature structural materials in various applications [1-3]. Due to its excellent high-temperature oxidation resistance, corrosion resistance, and mechanical performance, Ni-based alloys are one of the types of superalloys that have been widely used for hot-stage components in aircraft engine manufacturing, gas turbine materials, and the chemical industries [1-2].

The ability of Ni-based alloys to resist oxidation in high-temperature environments is largely determined by their ability to form a specific protective layer and oxide scale adhere to the metal surface [4]. The addition of chromium (Cr), manganese (Mn), titanium (Ti), silicon (Si) and aluminium (Al) in the alloy system acts as an oxide-forming element to form an oxide layer on the surface of the alloy [5-7]. Maintaining a high adhesiveness of the oxide scale on the surface of heat-resistance materials is important for long-range oxidation resistance. It is well known that Ni-based alloys, when subjected to high temperatures and harsh conditions, produce an oxide scale on the surface of the material. Some of these oxides are titanium dioxide (TiO₂), dichromium trioxide (Cr₂O₃), and dialuminium trioxide

(Al₂O₃) [1,3-5]. In contrast, the presence of these oxides has the potential to slow the rate of oxidation and stop any further oxidation of the base material. Additionally, oxide exfoliation was found to be a potentially hazardous process under prolonged service conditions, potentially causing significant structural damage.

Fe-Ni-Cr alloys are a family of Ni-based alloys developed for heat resistance, high-temperature applications and oxidising atmospheric conditions. The Cr content in the alloy system ranges from 14 to 30 wt.% which contributes to high temperature oxidation and corrosion resistance. The formation of Cr₂O₃ will increase the stability of the surface, thus providing excellent corrosion and oxidation resistance along with good strength. Promising heat-resistant materials that provide excellent oxidation resistance include alloy 800H and alloy HR-120 which contain 19 wt.% and 24 wt.% Cr acting as an oxide-forming element. 15 to 25 wt.% Cr will form a Cr₂O₃ surface oxide scale that grows slowly during high-temperature services [6]. Other alloying elements such as Mn, Ti, Si and Al can significantly affect the oxidation behaviour of the materials [5-7]. Furthermore, the addition of niobium (Nb) into the alloy system will increase the formation of Nb-containing precipitates such as Nb carbides [8-10]. The addition of Nb elements in small amounts to the alloy system also increases the high-temperature oxidation resistance and thermal stability [11].

Alloy 800H is a heat-resistance alloy with excellent oxidation resistance and good strength in high-temperature conditions [3,7]. This alloy is commonly used in steam generators, industrial furnaces and heat-treating

equipment. Meanwhile, HR-120 alloy is a heat-resistance alloy that has exceptional strength at high temperatures and good oxidation resistance [10]. It is utilized for waste incinerators, heat treatment apparatus, radiant tubes and furnace parts. Alloy 800H and alloy HR-120 were chosen as applicant materials for high-temperature oxidation studies with potential applications and similar material composition.

Alloys 800H and HR-120 are standard materials for heat processing-related applications such as heat-treating equipment. These applications often involve repeated thermal cycling of the components, which results in temperature gradients during heating and cooling. This heat production affects the degradation of the materials. As a result, the oxidation resistance of materials and microstructural stability have gained significant importance [7,10]. For the protection of alloys in high-temperature applications, a continuous layer of a slowly growing and thermodynamically stable oxide layer is essential for superior oxidation resistance [12-13]. Therefore, to understand the development of oxide scale on the alloy surface, the effect of exposure to high-temperature oxidation on both alloys was studied.

2. MATERIALS AND METHODS

2.1. Materials

Two types of Ni-based alloys were used in this study, namely 800H alloy and HR-120 alloy. The chemical composition was measured using optical emission spectroscopy as shown in Table 1. The dimensions of the alloy were 10 mm x 10 mm x 3 mm.

Table 1. Materials composition

Element / Alloy	800H	HR-120
Ni	32.51	40.45
Cr	18.90	24.11
C	0.078	0.048
Mn	0.556	0.702
Al	0.534	0.080
Si	0.315	0.441
Ti	0.489	0.029
Nb	-	0.441
Cu	0.082	0.114
Fe	Balance	Balance

2.2. Methods

Alloy 800H and alloy HR-120 underwent a heat treatment process at 1100 °C for 3 hours of soaking time, followed by quenching in water. A heat treatment process is performed to homogenize the grain structure before the isothermal oxidation test. The heat treatment resulted in a grain size of 64.7 µm for the 800H alloy and 36.3 µm for the HR-120 alloy. The isothermal oxidation test was performed at 950 °C for 150 hours with 30-hour exposure intervals. Before the oxidation test, all samples were ground to P600 grit. The dimensions and weight of each sample were measured before the oxidation test. In addition, after each exposure interval of 30 hours, weight changes were

recorded for the determination of oxidation kinetics. Isothermal oxidation then proceeds in a high-temperature LT furnace using laboratory air.

Oxidised alloys were characterised in terms of oxidation kinetics, phase analysis using X-ray diffraction (XRD) techniques and oxide morphology using a scanning electron microscope (SEM). Oxidation kinetics are measured from weight change per surface area. Further analysis of the oxidation kinetics has been done to determine the oxidation rate law and the oxidation rate constant. Equation (1) is used to determine the oxidation rate law and Equation (2) is used to determine the parabolic rate constant [7]. In these equations, x is the change in weight per surface area, t is time and c is a constant. The value of m represents the oxidation rate law, where m equal to 1 is the linear rate law and m equal to 2 is the parabolic rate law. The parabolic rate constant is designated as K_p .

$$\log x = \left(\frac{1}{m}\right) \log t + c \quad (1)$$

$$x^2 = K_p t + c \quad (2)$$

3. RESULTS AND DISCUSSION

Oxidised alloys were analysed in terms of oxidation kinetics, phase analysis and oxide morphology.

3.1. Oxidation Kinetic

The oxidation kinetic curves for alloys 800H and HR-120 are shown in Figure 1. Both alloys 800H and HR-120 exhibit a pattern of weight gain during isothermal oxidation as the exposure period increases. Similar observations have been recorded by other researchers, showing mass gains during high-temperature oxidation of Ni-based alloys at different temperatures and grain structures [1,4]. A significant difference between these two alloys is that the amount of weight gain for the 800H alloy is higher than for the HR-120 alloy. Alloy 800H recorded a steady increase in weight gain from the start of oxidation up to 150 hours of exposure. On the other hand, the HR-120 alloy recorded a lower weight gain with a steady increase from the beginning to the 90-hour exposure period. Only a slight increase in weight was recorded at 120 hours of exposure from 0.1036 mgcm⁻² at 90 hours to only 0.1050 mgcm⁻² at 120 hours. This condition indicates that only a small amount of oxide scale is formed. Apart from that, there is a possibility of an oxide exfoliation event that exfoliates some of the oxide scale which reduces the total weight recorded. After 120 hours of exposure, the weight change begins to increase, possibly to form a new oxide layer to overcome the exfoliation oxide that occurred before.

The oxidation kinetics were further analysed to determine the oxidation rate law according to Equation (1), as shown in Figure 2. From the analysis, it was found that both alloys recorded m values equal to 1.85 and 1.83 for 800H and HR-120 alloys, respectively. These results show that both alloys follow the parabolic rate law with a value of m in the range of 1.51 to 2.55 which represents m equal to 2. The parabolic rate law is intended in this study because the kinetic of the

oxide growth rate is controlled by diffusion. The optimal growth rate can be identified from the value of the rate constant.

The analysis of the parabolic rate constant is performed according to Equation (2), as shown in Figure 3. From the analysis of the linear trends of both alloys, it can be seen that the 800H and HR-120 alloys recorded a parabolic rate constant value of $4.75 \times 10^{-8} \text{ mg}^2\text{cm}^{-4}\text{s}^{-1}$ and $3.54 \times 10^{-8} \text{ mg}^2\text{cm}^{-4}\text{s}^{-1}$, respectively. These results show that the HR-120 alloy recorded a lower parabolic rate constant, indicating a low oxidation rate, thus having good oxidation resistance. This result is in agreement with the oxidation kinetic curve for this alloy, which recorded a lower weight gain. In addition, it was found that this alloy has a smaller grain size compared to the 800H alloy. As mentioned in Section 2.2, the heat treatment process for both alloys produced a grain size of $64.7 \mu\text{m}$ for the 800H alloy and $36.3 \mu\text{m}$ for the HR-120 alloy, indicating the smaller grain size possessed by the HR-120 alloy. The success of fine grain size alloys resulting in lower parabolic rate constants and low weight gain has been recorded in our previous research [3,7].

In addition, studies also show that fine-grain size alloys produce uniform oxide scales without oxide exfoliation. Other researchers who studied the effect of high-temperature oxidation on different grain sizes also found that the fine grain size of Ni-based alloys has a significant effect on weight change [4]. The findings of their study are that coarse-grained and fine-grained alloys are quickly oxidized at an early stage where the mass of the sample increases rapidly. The fine-grained sample recorded a lower mass increase during the first 100 hours, which was almost five times less than the coarse-grained sample [4]. The lower mass gain indicates that the grain refining process increases the oxidation resistance of the alloy. On the other hand, the mass of fine particles increases slowly, indicating that the oxidation process changes to a steady state. A slow increase in mass indicates that a protective oxide layer is forming over the fine grains. Therefore, this observation indicates that the adhesion of the oxide layer formed in the fine grains is also improved.

The findings in this research show that the HR-120 alloy that has a fine grain structure shows a lower weight gain with a lower parabolic rate constant related to the increased oxidation resistance of the alloy. The lower parabolic rate constant indicates that the kinetic oxide growth rate is diffusion-controlled. Initially, an intense oxide scale was formed on the surface of the alloy to form a continuous oxide layer to provide initial surface protection of the alloy. As the exposure time increases, the thickness of the oxide scale increases to improve the protective properties. When optimum protection is achieved, oxide scale formation reaches a steady state, which slows down the further diffusion process. The increase in optimum oxide scale thickness as a function of exposure time is indicated by the lower parabolic rate constant values for this HR-120 alloy.

On the other hand, the 800H alloy recorded a high parabolic rate constant value, indicating a high oxidation rate. This

result is consistent with the oxidation kinetic curve of this alloy in Figure 1, which records a high weight gain.

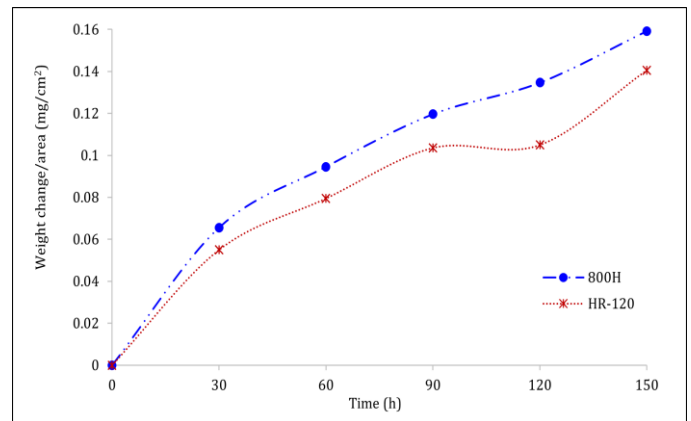


Figure 1. Oxidation kinetic

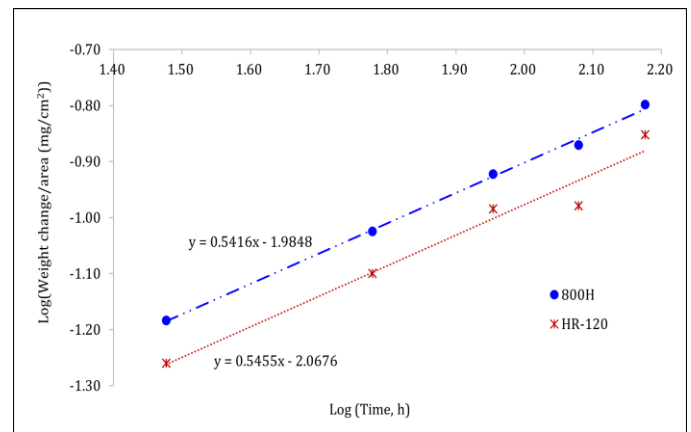


Figure 2. Oxidation rate law

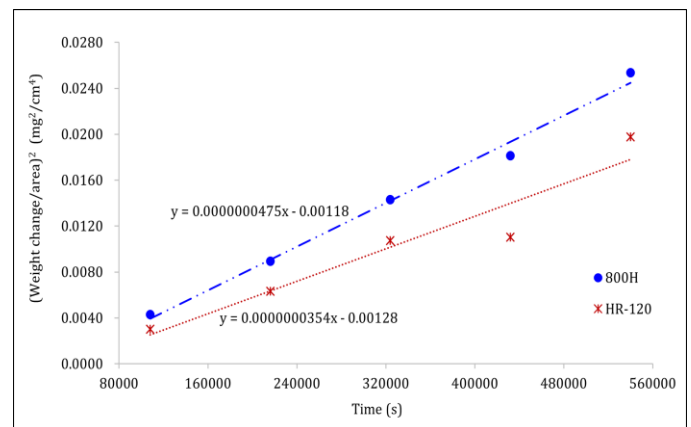


Figure 3. Parabolic rate constant

3.2. Phase Analysis

Phase analysis was performed using the XRD technique as illustrated in Figures 4 and 5. Analysis was performed on the oxidised alloy exposed for 150 hours. There are several findings recorded in this analysis namely the formation of Cr-containing oxide peaks, the detection of base alloy peaks and the formation of Cr-Ti-rich oxide peaks.

First, the formation of Cr-containing oxides consisting of two main protective oxides, MnCr_2O_4 and Cr_2O_3 , was

detected on both 800H and HR-120 alloys. These oxides are recorded to have protective behaviour [4-7,14]. The formation of Cr_2O_3 is intended because of its excellent oxidation protection and has good surface stability and good adhesion to metal surfaces. A sufficient amount of Cr in the range of 15 to 25 wt.% will form surface oxide, Cr_2O_3 , which grows slowly during high-temperature services [6]. The addition of Mn to the alloy system also increases the formation of a protective oxide scale consisting of MnCr_2O_4 . According to other researchers [6,14], the addition of Mn to the Fe-Ni-Cr alloy system promotes the formation of Cr-Mn spinel oxides, which can reduce the effect of Cr volatilization at high temperatures. The results of this analysis strongly suggest that the development of MnCr_2O_4 and Cr_2O_3 indicates that the oxide scales developed on the sample surface have good protective properties. On the other hand, an intense oxide peak was detected on alloy 800H compared to alloy HR-120 due to the thick oxide scale developed on the surface of alloy 800H, consistent with the high weight gain recorded on this sample.

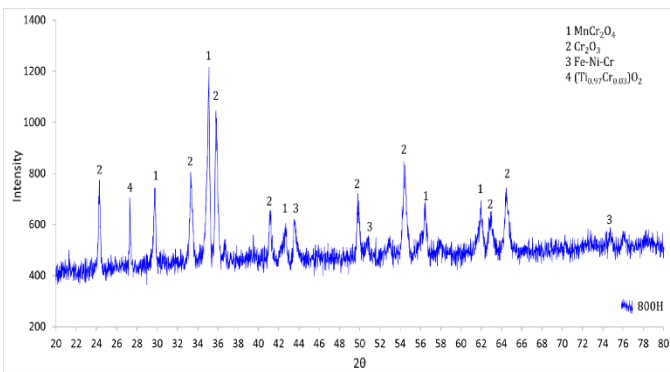


Figure 4. XRD pattern for 800H alloy

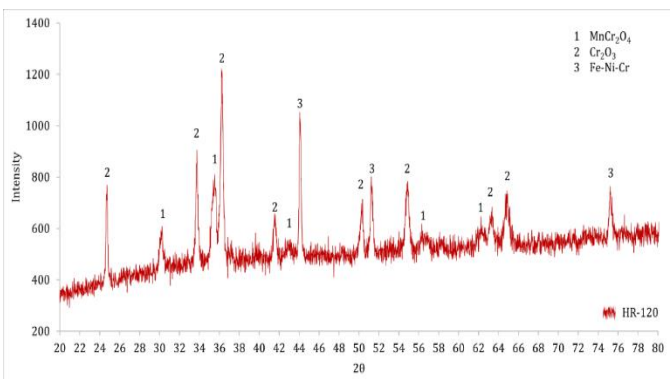


Figure 5. XRD pattern for HR-120 alloy

The second finding from this analysis is the detection of base metal peak labels as Fe-Ni-Cr in the figure. The peaks are indicated by diffraction angles 2θ equal to 43.5° (111), 50.7° (200), and 74.7° (220). An important finding is the peak intensity, of which a higher intensity was detected on the HR-120 alloy. This analysis shows that a thin oxide scale is developed on the surface of the HR-120 alloy, resulting in intense X-ray penetration into the base metal and high-intensity peaks. This finding is in line with the oxidation kinetic curve of the HR-120 alloy, recording a low weight gain compared to the 800H alloy.

The third finding is the detection of $(\text{Ti}_{0.97}\text{Cr}_{0.03})\text{O}_2$ oxide on alloy 800H as shown in Figure 4. The presence of Cr-Ti-rich oxide is said to reduce the effect of Cr evaporation, where the formation of Cr evaporation leads to the development of oxide exfoliation. This oxide has a lower vapor pressure of Cr, thus providing a protective behaviour [7]. Studies on Ni-based alloys have found that the formation of this oxide improves the protection behaviour of Ni-based alloys [1,7]. From the XRD analysis of 800H and HR-120 alloys, it can be seen that the formation of Cr-containing oxides contributes the most to the formation of the oxide scale.

3.3. Oxide Morphology

The oxide formation analysis was analysed using SEM and EDX techniques as illustrated in Figures 6 and 7. The oxide morphology analysis on the 800H alloy shown in low magnification in Figure 6(a) displays the formation of a continuous oxide layer with a spherical structure, protruding on the surface, then forming a thick oxide scale. Instead, there are spots of oxide exfoliation in the image as labels in the blue line of the oval-shaped structure. This area of oxide exfoliation was further analysed with high magnification and a close-up view in Figure 6 (b) shows that several oxide layers have formed. Beneath the exfoliation area, there are oxide particles, possibly new oxides that form to cover the exposed area. EDX analysis on the exfoliation area (blue line) shows the presence of the main elements Cr, and Mn, suggesting the main oxides, Cr_2O_3 and MnCr_2O_4 . In addition, there is the detection of Fe and Ni elements which indicate the base metal content. A minor element of Ti was also detected, originating from $(\text{Ti}_{0.97}\text{Cr}_{0.03})\text{O}_2$ as analysed in the XRD analysis in Figure 4. In addition, a minor content of Al and Si elements was also detected suggesting the formation of Al-based and Si-based oxides. Al and Si are the alloying elements added to this alloy system. According to previous studies, Al and Si will form an internal oxide layer underneath the chromium oxide [6]. However, Al-based and Si-based oxides may not be observed during analysis by XRD because Al and Si generally precipitate as internal oxides in the isolated area beneath the Cr oxide scale, thus it is quite difficult to detect those phases.

The analysis of the oxide morphology of the HR-120 alloy is shown in Figure 7(a), showing that a continuous oxide layer has formed on the surface of the alloy with evidence of oxide exfoliation as a label in the red line oval shape structure. A close-up view of the oxide exfoliation area shown in Figure 7(b) shows a network of voids, suggesting the passage of grain boundaries. Grain boundaries are one of the short circuit paths for ion diffusion that have a higher diffusion rate. On the other hand, new oxide precipitates were also detected around the oxide exfoliation area. This phenomenon shows that, when there is an exposed area effect from exfoliation, the presence of metal ions and oxygen ions will react to form new oxides. EDX analysis on the oxide exfoliation area (red line) detected the elements Cr, Mn, Fe, Ni, Si and Nb. Cr and Mn will form Cr-rich and Cr-Mn-rich oxide formations, as analysed by XRD. Fe and Ni elements are detected from the base alloy structure, while Si will probably form Si-based oxides beneath the outer oxide layer. In this analysis, there is the detection of a small

content of Nb, probably from Nb-rich oxides. This oxide cannot be detected by XRD analysis because of the limited precipitates formed. However, from our previous research, this oxide will form precipitates in isolated regions on the alloy surface [10]. This oxide will also increase the formation of pitting to a certain extent, which also contributes to the exfoliation effect of the oxide.

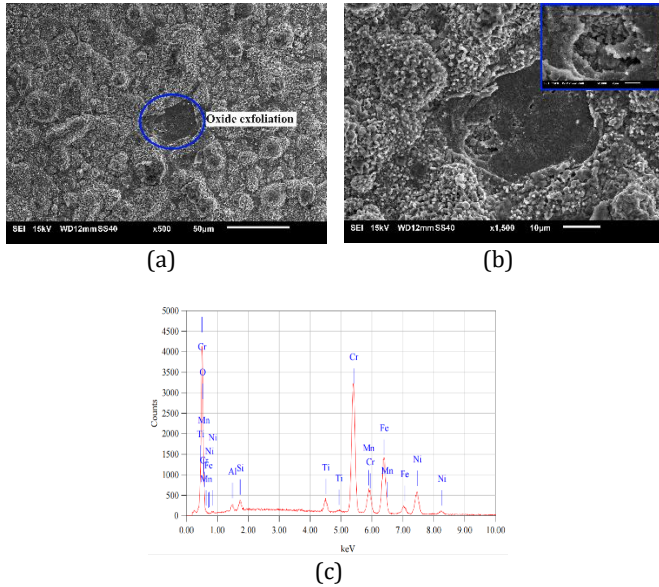


Figure 6. SEM images for 800H alloy

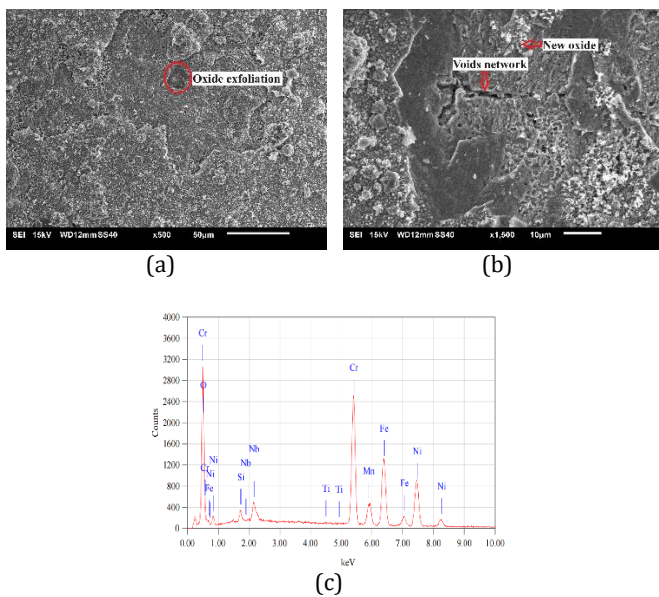


Figure 7. SEM images for HR-120 alloy

In general, both alloys show a continuous oxide scale with the formation of a protective oxide layer consisting of Cr-containing elements such as Cr_2O_3 , MnCr_2O_4 and $(\text{Ti}_{0.97}\text{Cr}_{0.03})\text{O}_2$ which is found to have a protective behaviour as a surface protector on Ni-based alloys [1,4-7,14].

4. CONCLUSION

In conclusion, isothermal oxidation tests were performed on 800H and HR-120 alloys, indicating a pattern of weight gain with the 800H alloy recording a higher weight. Both

alloys follow a parabolic rate constant indicating a diffusion-controlled oxide growth kinetic with the HR-120 alloy recording a lower parabolic rate constant, indicating a low oxidation rate, therefore having good oxidation resistance. MnCr_2O_4 and Cr_2O_3 were detected by XRD analysis, providing protection for the alloy. Finally, a uniform oxide scale has formed on the surface of the alloy.

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