Characterization of Oxide Scales on Super-Alloy HR120 at 1000 °C in Air and Steam Environments

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Abstract. Oxidation resistance of super-alloy HR120 in air and steam environments at 1000 °C was investigated. Scanning electric microscopy and X-ray diffraction analysis were used to characterize the corrosion products. The results show that weight gain in steam was much higher than that in air. Oxide scales formed in air were MnCr₂O₄ and Cr₂O₃, whereas oxides developed in steam were NiFe₂O₄, (Cr, Fe)₂O₃ and little internal Cr-Si oxides. Steam can increase the corrosion rate and fine the oxides formed on the sample's surface. Moreover, enhanced oxidation of HR120 in steam was mainly attributed to the evaporation of chromium oxyhydroxides.

1. Introduction
Super-alloy HR120 containing 25% Cr exhibits excellent corrosion resistance and high strength at elevated temperature. This new alloy has been used in carburizing and sulfidizing environments. HR120 is a potential heat-resistance alloy for super-heater in advanced power plants [1]. However, from the published literature its oxidation behaviour in a steam environment is not fully understood [2-5]. Ledouxet.al [3] investigated the oxidation kinetics using thermo-gravimetry under the air condition. A non-protective transient stage was found during test at 1050 °C. A multi-layered oxide scale (SiO₂–Cr₂O₃–XCr₂O₄ with X = Mn and/or Fe, Ni) formed on the surface. Sarver and Tanzosh [5] found that in steam the oxide scale was Cr oxide above a thin Si containing layer at 800°C. There is no clear understanding on the effect of water vapour on the oxidation behaviour of HR 120, though most of the service conditions of super-alloy HR120 contain water vapour at high temperatures.

Therefore, the aim of this article is to investigate the influence of water vapor on the oxidation behaviour of super-alloy HR120 at high temperature.

2. Materials and Method
The oxidation tests were conducted in a horizontal furnace at 1000 °C for up to 120 h, as shown in a previous article [6]. The flow rates of air and steam were 90 mL/min and 134.4 mL/min, respectively. The nominal composition of super-alloy HR120 is listed in Table 1. Before oxidation tests, specimens with a size of 15 mm×15 mm×3.1 mm were ground up to 1000# SiC papers and then were ultrasonically cleaned in ethanol. The weight gain was measured using an electronic balance with an accuracy of 10-5 g. After tests, X-ray diffraction (XRD, X’pert PRO, Panalytical, Holland) and scanning electron microscope (SEM, SU3500, HITACHI, Japan) equipped with energy-dispersive X-ray spectroscopy were employed to characterize the oxidation products formed on the surface.
Table 1. Compositions of super-alloy HR120

|   | Ni | Fe | Cr | Co | W | Mo | Nb | Mn | Si | N | Al | C | B |
|---|----|----|----|----|---|----|----|----|----|---|----|---|---|
|   | 37 | 33 | 25 | 3  | 2.5| 2.5| 0.7| 0.7| 0.6| 0.2| 0.1 | 0.05| 0.004 |

3. Results and Discussion

Figure 1 shows the weight gain of HR120 at 1000 °C under air and steam conditions. Both oxidation kinetics curves obeyed the power oxidation law. After 25 h test, the weight gain in steam was much higher than that in air, while weight gain under the two tested conditions was similar for the first 25 h. As chromium is the main beneficial element for oxidation resistance in super-alloy HR120, at the initial stage (<25 h) of exposure the uniform chromia film is formed at the samples’ surface in both air and steam environments. However, for a relatively longer exposure time, the structure of uniform chromia layer was altered, which accounted for the higher weight gain in the presence of steam.

![Figure 1. Weight gain versus oxidation time in the air and steam environments](image)

Figure 2 displays that surface and cross sectional morphology of specimens exposing to air and steam for 120 h at 1000 °C. The spinel with smaller oxides crystal formed in steam were more porous than that formed in air, indicating the different morphologies of the oxides. The size of oxides also decreased in a steam environment, as showed in Figure 2(a) and Figure 2(b). In Figure 2(c-d), the average thickness of oxide scale due to the lattice diffusion was higher in steam than that in air at 1000 °C. What’s more, the maximum penetration depth in steam due to grain boundary diffusion was found to be much larger than that in air. The thick oxide scale in the presence of steam is consistent with the weight gain data shown in Figure 1.
The element distribution of oxide scale gives a deeper understanding of oxidation behaviour of HR120, so EDS mapping analysis was done on the cross section of exposed samples, as showed in Figure 3 and Figure 4. From Figure 3, it is found that the oxide scale formed in air was mainly composed of Cr, O and Mn. However, in steam environment the oxide scale showed multi-layered structure including the outer layer of Fe-Ni-O, a middle layer with Cr-O and an internal oxidation layer with Cr-Si-O, as showed in Figure 4. In addition, some Nb-rich precipitates were observed underneath the oxide scale. From the results, it is concluded that the oxidation behaviour and metallic diffusion were greatly affected by the water vapour.

The oxide scale was also characterized with XRD, as showed in Figure 5. XRD analysis shows that the oxides formed in the air consisted of $\text{MnCr}_2\text{O}_4$ and $\text{Cr}_2\text{O}_3$, while in steam the oxides were $\text{NiFe}_2\text{O}_4$. 

**Figure 2.** Surface and cross sectional morphology of specimens for 120 h. (a) Air, surface (b) steam, surface (c) cross section, air (d) cross section, steam

**Figure 3.** EDS mapping results of HR120 in air after 120 h at 1000 °C
and (Cr, Fe)2O3. Moreover, intensity of alloy’s peaks in steam was much lower than that in air, indicating a thicker oxide scale formed in the steam environment.

It is well known that at elevated temperatures alloys containing 25% or higher chromium content can develop a uniform protective chromia layer at the surface in a dry or wet environment [7-8]. However, it is not the case for super-alloy HR120 containing 25%Cr in the presence of steam. From the EDS and XRD results, it is confirmed that the oxide scales in steam were composed of NiFe2O4, (Cr, Fe)2O3 and internal Cr-Si-O oxides.

![Figure 4. XRD results of specimens exposing to air and steam at 1000 °C](image)

From the viewpoint of internal oxidation, the partial pressure of oxygen required for SiO2 formation is lower than that for Cr2O3[10], so the partial pressure of oxygen at metal/oxide interface in steam is higher than the oxygen pressure at the same position in air. That is to say, the inward diffusion of oxygen in steam is faster than that in air. To further figure out the effect of water vapor, attention should be focused on the Cr2O3 layer in air and steam. From Figure 4, it is clear that the Cr2O3 layer was much thinner than that formed in air. This may potentially be due to the evaporation of volatile chromium oxyhydroxides, such as CrO2(OH)2.

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2\text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + 3\text{O}_2 = 4\text{CrO}_2(\text{OH})_2
\]

The above reaction indeed occurred even at lower temperature, which had been observed by Asteman et.al. Evaporation of volatile chromium oxyhydroxides changed the chemistry of formed oxides. As a result, the diffusion rates of Fe and Ni ions were significantly improved with the evaporation of chromium oxyhydroxides for providing more transportation paths. In addition, the partial pressure of oxygen in steam is sufficient for the development of NiO and Fe2O3 at 1000 °C. Therefore, NiFe2O4 and Fe2O3 formed above the Cr2O3 layer. Therefore, oxidation of super-alloy HR120 in steam was more serious than that in air gas at 1000 °C.

4. Conclusions

1. The oxide scale formed on super-alloy HR120 in steam at 1000 °C was composed of NiFe2O4, (Cr, Fe)2O3 and small amount of internal Si-Cr-O oxides.

2. The weight gain in steam is much higher, whereas the Cr2O3 layer is thinner than that formed in air at 1000 °C.

3. Accelerated oxidation of super-alloy HR120 was mainly explained by the evaporation of chromium oxyhydroxides.
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