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# Oxidation behaviors of wrought nickel-based superalloys in various high temperature environments

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**Abstract:** Oxidation characteristics of Alloy 617 and Haynes 230 at 900 °C in simulated helium environment, hot steam environment containing  $H_2$  as well as in air and pure helium conditions were investigated. Compared to air condition, the oxidation rate of Alloy 617 was not significantly affected in helium and hot steam environments, while Haynes 230 showed lower oxidation rate in helium environment. On the other hand, the oxide morphology and structure of Alloy 617 were strongly affected by the environments, but those of Haynes 230 were less dependent on the environments. For Haynes 230, a  $Cr_2O_3$  inner layer and a protective MnCr<sub>2</sub>O<sub>4</sub> outer layer were formed in all environments, which contributed to the better oxidation resistance. As the mechanical properties, such as creep and tensile properties, were significantly affected by the oxidation behaviors, surface treatment methods to enhance oxidation resistance of these alloys should be developed.

Key words: oxidation; nickel-based superalloys; very high temperature reactor (VHTR); impure helium; hot steam

# **1** Introduction

Among the generation-IV reactor types which had been selected by international forum [1], the very high temperature reactor (VHTR) is the most promising near-term deployable reactor type along with a sodium-cooled fast reactor (SFR). VHTR has very attractive characteristics of passive safety features, higher thermal efficiency and high operating temperature. Because of high operating temperature, in addition to electricity generation, the heat can be used for various industries such as chemical process, and steel making [2]. Especially, if the VHTR is combined with either high temperature steam electrolysis (HTSE) or sulfur-iodine (S-I) process, massive production of hydrogen could be achieved economically and clean. Though both processes require high temperature up to 900 °C to achieve better efficiency, HTSE is less dependent on temperature than S-I process. The rapid development of solid oxide fuel cell (SOFC) technologies will certainly be applied to HTSE system for near-term application [3].

Among the variety of materials reviewed, several Ni-based superalloys are seriously considered the

materials for high temperature structural components [4]. Currently, wrought Ni-based superalloys, Alloy 617 and Havnes 230, are considered for intermediate heat exchanger (IHX) and hot gas duct (HGD) due to excellent high temperature corrosion resistance against various environments such as oxidation, carburization, and decarburization conditions. In these materials, the protective external Cr oxide prevents the direct interaction between metal and environments. However, despite the excellent oxidation resistance, when the materials are exposed to high temperature for prolonged period of nuclear power plant operation, oxidation at the surface would be significant. Then, oxidation would contribute to the mechanical property degradation of Ni-based superalloys by metal loss, internal oxide, carburization, decarburization, and so on.

In primary system of VHTR, the pressurized helium gas with impurities such as CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> will be used as a reactor coolant. In HTSE system, high temperature steam or steam and hydrogen mixture gases will be used to produce hydrogen [5]. Therefore, the oxidation resistance and their performance of oxide layer in impure helium and hydrogen added steam environments at high temperatures are the most important

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factors to consider in assessing materials damage and integrity. Therefore, in this study, high temperature oxidation behaviors of Alloy 617 and Haynes 230 are evaluated in air, pure helium, impure helium, steam, and steam with hydrogen environments.

# 2 Experimental

# 2.1 Materials

Commercial wrought Ni-based superalloys, such as Alloy 617 and Haynes 230, were used in this study. The chemical compositions of both the superalloys were analyzed by inductively coupled plasma mass spectroscope (ICP-MS) and summarized in Table 1. Alloy 617 was solid-solution hardened by Mo and Co, and Haynes 230 was hardened by W. Final solution annealing was performed at 1 175 °C, and water quenching or rapid air cooling was carried out. This heat treatment condition provides a coarse grain structure for the best creep-rupture strength. The typical microstructures are shown in Fig. 1. As shown in Fig. 1, Cr-rich or W-rich carbides are spread along the grain boundary.

**Table 1** Chemical compositions of Alloy 617 and Haynes 230

Allov	w(Ni)/	w(Cr)/	w(Co)/	w(Mo)/	w(W)/	w(Fe)/
	%	%	%	%	%	%
Alloy 617	Bal.	21.6	11.8	8.92	-	1.14
Haynes 230	Bal.	21.5	0.36	1.09	13.8	2.94
Allow	w(Al)/	w(Mn)/	w(Si)/	w(Ti)/	w(C)/	
Alloy	w(Al)/ %	w(Mn)/ %	w(Si)/ %	w(Ti)/ %	w(C)/ %	
Alloy Alloy 617	w(Al)/ % 1.5	w(Mn)/ % 0.05	w(Si)/ % 0.5	w(Ti)/ % 0.35	w(C)/ % 0.1	

#### **2.2 Experimental procedures**

Coupon type specimens with 12 mm in diameter and 1 mm in thickness were used for oxidation tests. The specimens were oxidized in air, pure helium (contains  $(2-3)\times 10^{-6}$  H<sub>2</sub>O and O<sub>2</sub>), controlled helium and steam environments at 900 °C. The controlled helium conditions were selected to simulate various oxidation/carburization conditions expected in VHTR and listed in Table 2. The controlled helium gases, He-K1 and He-K2, were maintained using impurity controlled, once through helium loop with a flow rate of 500 mL/min [6]. Steam oxidation tests were conducted in pure steam and steam 20% (volume fraction) H<sub>2</sub> mixture environments at 900 °C. The flow rates of steam and steam 20% H<sub>2</sub> mixture were 20 mL/min at room temperature. The details of experimental set-up and procedures were described previously [6-7].

After the specimens were exposed to various conditions, oxide evolution as function of time and gas



**Fig. 1** Typical microstructures of as-received Ni-based superalloys: (a) Alloy 617; (b) Haynes 230

Table 2 Compositions of helium gases with impurities

Gas	Не	<i>p</i> (H <sub>2</sub> )/ Ра	<i>p</i> (H <sub>2</sub> O)/ Ра	<i>p</i> (CO)/ Pa	<i>p</i> (CO <sub>2</sub> )/ Pa	<i>p</i> (CH <sub>4</sub> )/ Ра
He-K1	Bal.	4	7	5	1	2
He-K2	Bal.	-	7	5	1	-

conditions was characterized using X-ray diffraction (XRD) analysis. Oxide morphology and cross section microstructure were analyzed to understand the microstructure changes and oxidation mechanism. Scanning electron microscope (SEM) and energy dispersive spectroscope (EDS) were used to observe microstructure and to measure the chemical compositions of each precipitate.

# **3 Results and discussion**

# 3.1 Oxidation in air and pure helium

Figure 2 shows the mass gain per unit area versus time plots of both Ni-based superalloys after the isothermal oxidation at 900 °C for up to 1 000 h in air and pure helium. As shown in the figure, the oxidation rate generally follows the well-known parabolic rate law. The parabolic rate constant of Alloy 617 is considerably higher than that of Haynes 230 in both conditions. Though both alloys are known chromia forming alloys with similar chromium content, the difference in rate constant indicates that other elements influence the oxidation behaviors of the alloys.

In air, as the oxygen activity is high enough, the oxygen molecules are rather evenly adsorbed on entire surface and form oxides. As a result, the oxide grains on



**Fig. 2** Oxidation kinetics of Alloy 617 and Haynes 230 at 900°C in air and pure helium [8]

the surface have a nodular-type structure for both alloys (Fig. 3). From SEM observation (Fig. 4) and XRD analysis (not shown here), the mixture of triple oxide layers and double layers was formed on the surface of Alloy 617 in air condition (Fig. 4(a')), consisting of inner Cr<sub>2</sub>O<sub>3</sub> layer covered by outer Ni-rich oxides such as NiO and NiCr<sub>2</sub>O<sub>4</sub> [8]. Below the surface oxide layers, internal and inter-granular Al<sub>2</sub>O<sub>3</sub> is well developed due to the preferential oxidation of Al in Alloy 617. The extensive development of internal oxide could be the proof of the poor protectiveness of surface oxide layers for Alloy 617. On the other hand, the surface oxide layers are mainly comprised of MnCr<sub>2</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> for Havnes 230, as shown in Fig. 4(b'). The existence of outermost  $MnCr_2O_4$ layer was considered an effective barrier to oxygen diffusion into metal surface and consequently enhanced the oxidation resistance of the alloy [8]. The change of slope for Haynes 230 observed in Fig. 2 is the direct

result of that. The parabolic rate constants were calculated and shown in Table 3.



**Fig. 3** Surface oxide morphologies after ageing for 1 000 h in air: (a) Alloy 617; (b) Haynes 230

**Table 3** Parabolic rate constants of Alloy 617 and Haynes 230 at 900  $^{\circ}$ C

Environment	$k/(10^{-13}\text{g}^2\cdot\text{cm}^{-4}\cdot\text{s}^{-1})$					
Environment	Alloy 617	Haynes 230				
Air	8.8	3.8 ( <i>t</i> <160 h), 0.43 ( <i>t</i> >160 h)				
Не	8.1	2.8				

#### 3.2 Oxidation in controlled helium

As shown in Fig. 5, the parabolic rate constants in impure helium gases are almost the same as those in air



Fig. 4 Evolution of oxide layers at 900 °C in air for 1 000 h: (a), (a') Alloy 617; (b), (b') Haynes 230

for Alloy 617. From the SEM/EDS analysis, the oxidized surface of Alloy 617 is covered with the isolated nodular structure of  $MnCr_2O_4$  on the top of  $Cr_2O_3$  (Fig. 6). As mentioned in the previous section,  $Cr_2O_3$  alone was not enough to provide effective diffusion barrier. Consequently, the oxidation kinetics in the controlled helium gases, He-K1 and He-K2, are the same as those in air for Alloy 617. On the other hand, the oxidation resistance is considerably increased for Haynes 230 in controlled helium gases as shown in Fig. 5. As shown in Fig. 7, continuous  $MnCr_2O_4$  layer covers the chromia layer in both conditions for Haynes 230. It is the dense  $MnCr_2O_4$  oxide layer compared to static air that makes the oxidation resistance better in impure helium gases [6].

In the controlled helium environments, it has been



**Fig. 5** Oxidation kinetics of Alloy 617 and Haynes 230 after being oxidized at 900 °C for 500 h in impure helium gases



**Fig. 6** Surface oxide morphologies of Alloy 617 (a) and Haynes 230 (b) after ageing at 900 °C for 500 h in He-K1 [6]



**Fig. 7** Evolution of oxide layers of Alloy 617 (a) and Haynes 230 (b) after ageing at 900 °C for 500 h in He-K1

known that  $H_2O$  and  $CO_2$  molecules are rapidly dissociated because of low oxygen partial pressure, and the formation of cellular oxides for Alloy 617 and platelets for Haynes 230 is enhanced. The formation of platelet oxides is more evident for Haynes 230 containing Mn than for Alloy 617. The whiskers are known to be the main source of cellular or platelet-type oxide morphology, and frequently appeared in H<sub>2</sub>O- and CO<sub>2</sub>-containing environment [9–12].

#### 3.3 Oxidation in hot steam

Figure 8 shows the mass gain curves of the alloys during isothermal oxidation at 900 °C in steam with and without hydrogen. The mass gain curves followed a parabolic rate law under all conditions with distinctive slope changes for Haynes 230 in 100–200 h. The oxidation rate of alloy 617 was faster than that of Haynes 230 under all conditions. For both alloys, the oxidation rate was not significantly different in both air and steam conditions. On the other hand, the oxidation rate sclearly increased with the addition of hydrogen to hot steam for both alloys. The difference of oxidation rate would be inferred from the oxide microstructures in different environments.

Alloy 617 oxidized in steam and steam + 20%  $H_2$ were made up of oxide structures consisting of external layer, sub-layer, and internal oxides. Again, the external layers consisted of polygonal MnTiO<sub>3</sub> oxide particles and an underlying continuous  $Cr_2O_3$  oxide layer identified through XRD and EDS analyses. Below the outer  $Cr_2O_3$  layer,  $Cr_2O_3$  sub-layer and  $Al_2O_3$  internal oxide were formed along the grain boundaries (Fig. 9). Unlike the oxides formed in air, Ni oxides were not formed because of low oxygen partial pressure. Also, sub-layer  $Cr_2O_3$  was formed because oxygen inward diffusion occurred in low oxygen partial pressure conditions such as steam environments [13–14]. In the case of Haynes 230, the oxide layer consisting of outer MnCr<sub>2</sub>O<sub>4</sub> and inner  $Cr_2O_3$  oxide layer and  $Cr_2O_3$  sub-layer was formed (Fig. 9). In the case of air condition, MnCr<sub>2</sub>O<sub>4</sub> oxide layer formed on the surface of Haynes 230 effectively lowered the oxidation rate. Also MnCr<sub>2</sub>O<sub>4</sub> grain formed in steam was denser than that formed in air, which explains the lower oxidation rate in steam condition.

When hydrogen was added to steam, the surface oxide morphology changed into platelet shape (Fig. 10). It has been known that hydrogen is easily absorbed and



**Fig. 8** Oxidation kinetics of Alloy 617 and Haynes 230 after being oxidized at 900 °C for 1 000 h in steam conditions

ionized to proton, and effectively increases the Cr cation defect in oxide [15]. Increased Cr defects in turn promote cation diffusion to surface through screw dislocation tunnel in oxide. As a result, platelet oxides were formed and the oxidation rate in steam +20% H<sub>2</sub> was enhanced.

The oxidation characteristics, such as parabolic rate constant, transitional and steady-state oxide phases, and surface morphology of Alloy 617 and Haynes 230 in various high temperature environments are summarized in Tables 4 and 5.

#### 3.4 Impact of oxidation on mechanical properties

When superalloys are exposed to high temperature conditions expected in VHTR, diffusion and subsequent oxidation within a hundred micrometers from the surface practically control the materials-environment interactions. To maintain long-term integrity of components made of wrought nickel-based superalloys, the development of protective oxide layer on the outermost surface is of uttermost importance. Though Alloy 617 has been known to have excellent oxidation resistance by forming Cr<sub>2</sub>O<sub>3</sub>, the oxide layer did not provide sufficient protection in several VHTR relevant environments such as impure helium and steam conditions as we discussed above. Consequently, Alloy 617 was subjected to internal oxidation, decarburization and carburization depending on environments. When Al<sub>2</sub>O<sub>3</sub> internal oxides were formed below the surface layer in Alloy 617, the tensile stress in perpendicular direction would easily break them, as shown in Fig. 11, resulting in reduced creep resistance. Moreover, through the interactions with elements diffusing through the not-so-protective surface oxide, Cr-rich M<sub>23</sub>C<sub>6</sub> type carbides are decomposed into



**Fig. 9** Evolution of oxide layers of Alloy 617 in  $H_2O$  (a), Alloy 617 in  $H_2O+20\%$   $H_2$  (b), Haynes 230 in  $H_2O$  (c), and Haynes 230 in steam+20%  $H_2$  (d) for 1 000 h



Fig. 10 Surface oxide morphologies of Alloy 617 (a) and Haynes 230 (b) oxidized for 24 h in steam +20%  $H_2$ 

Environment (θ= 900 °C)	Rate constant/ $(10^{-13}g^2 \cdot cm^{-4} \cdot s^{-1})$	Transitional-state oxide	Steady-state oxide	Surface morphology
Air	8.8	NiCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	NiO/NiCr <sub>2</sub> O <sub>4</sub>	Polygonal
Не	8.1			
He-K1	8.5		TiO <sub>2</sub> , MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Platelet
He-K2	9.0		TiO <sub>2</sub> , MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Platelet
H <sub>2</sub> O (steam)	9.7	Cr <sub>2</sub> O <sub>3</sub>	MnTiO <sub>3</sub> /Cr <sub>2</sub> O <sub>3</sub>	Platelet
Steam+20%H <sub>2</sub>	14.3	Cr <sub>2</sub> O <sub>3</sub>	MnTiO <sub>3</sub> /Cr <sub>2</sub> O <sub>3</sub>	Platelet

Table 4 Summary of oxidation characteristics of Alloy 617 in various environments

Table 5	Summary	of	oxidation	cha	racteristics	of F	Tavnes	230	in	various	envir	ronments
	~											

Environment (θ= 900 °C)	Rate constant/ $(10^{-13}g^2 \cdot cm^{-4} \cdot s^{-1})$	Transitional-state oxide	Steady-state oxide	Surface morphology
Air	3.8 ( <i>t</i> <160 h) 0.43 ( <i>t</i> >160 h)	MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Polygonal
He	2.8			
He-K1	1.1		MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Platelet
He-K2	0.9		MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Platelet
H <sub>2</sub> O (steam)	2.0 ( <i>t</i> <100 h) 0.8 ( <i>t</i> >100 h)	MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Platelet
Steam+20%H <sub>2</sub>	7.2 ( <i>t</i> <100 h) 2.0 ( <i>t</i> >100 h)	MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	MnCr <sub>2</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Platelet

Cr and C, which results in loss of grain boundary carbides [16–17]. Once the decarburization happens, carbides in the materials matrix disappear and the creep or creep-fatigue property decreases [18–19]. On the other hand, carburization conditions could cause significant low temperature embrittlement [20]. Recently, it was reported that a long-term exposure to decarburizing/ oxidizing and carburizing conditions caused loss of ductility for both Alloy 617 and Haynes 230, as shown in Fig. 12, though the main contributing factors to the embrittlement are different [17]. Therefore, more protective oxide layers on the surface of alloys are needed to maintain the adequate mechanical properties for the lifetime of the reactor, or up to 60 years in VHTR environments.

## 3.5 Surface treatments for oxidation resistance

It has been known that  $Al_2O_3$  would provide excellent protection against most environments. In addition to its stability at higher temperature,  $Al_2O_3$  has higher band gap energy, thus the diffusion rate of the cations through alumina is much smaller than through chromia [21]. However, the minimum Al concentrations to form external  $Al_2O_3$  oxide layer are rather high in Ni-Cr-Al ternary system. In addition, adding more Al would have detrimental effects on mechanical properties. For example, Haynes 214 containing about 4% Al was not as strong and creep-resistant as Alloy 617. Alternatively, surface could be coated with  $Al_2O_3$  by various methods like chemical vapor deposition (CVD), thermal spray, and pack cementation. However, once





**Fig. 12** Change in tensile properties after ageing at 900 °C in simulated VHTR environments for 500 h

such oxide coating breaks down by external loading during plant operation, localized oxidation would cause more severe damage to the components. Therefore, advanced surface treatment methods have to be developed to provide not just oxidation resistance but the self-healing capability when it was damaged during the operation.

**4** Conclusions

helium at 900 °C under 70 MPa

1) The oxidation kinetics of Alloy 617 was almost the same in air, pure helium, and controlled environments. In steam condition, the addition of hydrogen increased the oxidation rate of Alloy 617. On the other hand, the oxidation kinetics of Haynes 230 strongly depended on the environments. The addition of hydrogen in steam environment increased the oxidation rate of Haynes 230.

2) The oxide morphology and structure of Alloy 617 were strongly affected by the environments, while those of Haynes 230 were less dependent on the environments.

3) The oxidation resistance of Haynes 230 was consistently better than that of Alloy 617. The formation of  $MnCr_2O_4$  outer layer on top of  $Cr_2O_3$  inner layer was considered the main contribution factor to such improved oxidation resistance of Haynes 230.

4) As the oxidation behaviors and the protectiveness of surface oxide layer affect the mechanical properties of wrought nickel-based superalloys, advanced surface treatment methods have to be developed to maintain the adequate mechanical properties during the long-term operation.

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# 镍基变形高温合金在高温环境下的氧化行为

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摘 要:研究了 617 和 Haynes 230 高温合金在含 H<sub>2</sub>O 和 O<sub>2</sub> 的不纯氦气、含氢的热蒸汽、空气以及纯氦气中的 900 ℃ 氧化行为。与空气相比,氦气、含氢的热蒸汽对 617 合金的氧化速率没有明显影响,而 Haynes 230 合金在 氦气中表现出较慢的氧化速率。617 合金的氧化层形貌和结构受环境的影响明显,而 Haynes 230 受环境的影响不 明显。在所有的氧化环境中,Haynes 230 合金的氧化层都包含有中间层 Cr<sub>2</sub>O<sub>3</sub> 和外保护层 MnCr<sub>2</sub>O<sub>4</sub>,这使其具有较 好的抗氧化性能。合金的表面抗氧化性能明显影响其力学性能,如蠕变和拉伸性能。因此,有必要采取表面处理 来增强合金的抗氧化性能。

关键词:氧化;镍基高温合金;超高温反应堆(VHTR);非纯氦气;热蒸汽