

Oxidation Reactivity of Heat-Resistant Ni-Cr Alloys Exposed in Wet Air at 900 °C

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ABSTRACT

The relative wet oxidation reactivity of two centrifugally-cast, heat-resistant Ni-Cr alloys is presented for an isothermal (900 °C) in wet (10% H₂O) air up to 500 h. Both 48Ni-45Cr and 41Ni-32Cr exhibit a similar weight loss after 500 h, which suggests a similar relative reactivity. However, there are three aspects that suggest there is a difference in the relative wet oxidation reactivity. These include: (i) a different kinetic rate law (cubic for 41Ni-35Cr and parabolic for 48Ni-45Cr), (ii) a different susceptibility to internal oxidation (deeper in 48Ni-45Cr) and (iii) a difference in the degree of oxide spallation observed upon cooling to room temperature (significantly higher for 41Ni-35Cr). These relative differences are discussed by establishing links to the oxide scale morphology for (i) above and the underlying microstructure for (ii) and (iii) above.

Key words: High temperature oxidation, ethylene cracking, Ni-Cr superalloys, water vapor, alloying elements.

INTRODUCTION

In the petrochemical industry, cracking furnaces that produces ethylene and other by-products operate at high temperatures (> 850 °C). As the production of ethylene progresses, carbon-rich solids (i.e. coke) form at the inner surface of the reactor tube coils, resulting in flow constriction and reduction of heat transfer. Steam and/or air is/are introduced to burn out the carbon-rich solids (decoking). This practice can increase the internal coil surface temperature to ~1200 °C, which increases the susceptibility to oxidation.¹⁻²

There are key characteristics a heat-resistant Ni-Cr alloy should possess for use in cracking furnaces. These include resistance to creep, coil sagging and oxidation, while exhibiting suitable mechanical strength at high temperatures. For oxidation resistance, heat-resistant Ni-Cr alloys should form a protective external oxide scale. This scale should effectively impede further oxidation, be adherent to avoid spallation^{3,4} and be compact with a low density of micro-pores, voids or any other defect that promotes internal oxidation, carburization or nitridation.³ For this reason, rare earth (e.g. Y), Mn and Si alloying elements are added to heat-resistant Ni-Cr alloys. Mn alloys promotes the formation of a Mn-rich spinel oxide layer on top of a Cr-rich oxide, which reduces the volatilization of the latter⁵. Si alloy promotes the formation of SiO₂ underneath the Cr-rich oxide layer, which reduces diffusion of Cr cations and, thus the overall oxidation rate.⁴

The effect of Nb during the oxidation of chromia-forming Ni-Cr alloys is not clear, since the oxidation kinetics of Nb-containing phase is the most unpredictable of all the phases present in Ni-Cr superalloys.¹ Weng *et al.*⁶ found that Nb improved the oxidation resistance of Ni-Cr alloys by promoting the formation of a denser scale, complete with a Nb-rich oxide layer beneath a Cr-rich oxide layer, which impedes O diffusion into the alloy. However, other experiments have shown that Nb-rich oxides that form below Cr-rich oxides are non-protective and unstable, transforming into other oxides, resulting in a more complex oxidation process over prolonged exposure times.¹ Regarding Fe alloying, Xu *et al.*⁷ found that increasing the Fe content from 5 wt.% to 15 wt.% increases the oxidation rate. However, with additional Nb alloying, the oxidation rate decreases at prolonged exposure times.

As different alloying elements are added in heat-resistant Ni-Cr alloys to achieve suitable oxidation and creep resistance, the oxidation process becomes more complex and difficult to predict based on thermodynamics alone. Moreover, predicting the degradation and service life of a component by using oxidation kinetics, such as the parabolic oxidation constant k_p , might not be sufficient given the complexity of the oxide scales formed coupled with the possibility of internal oxidation or water vapor effects. Therefore, the aim of this study is to determine the relative wet air (10% H₂O) oxidation reactivity two as-cast, heat-resistant Ni-Cr alloys at high temperature (900 °C) to help better understand performance of these alloys as reactor tube coils.

EXPERIMENTAL PROCEDURE

Two heat-resistant Ni-Cr alloys (41Ni-32Cr and 48Ni-45Cr), were centrifugally cast into radiant tubes. The composition of each, as determined by X-ray fluorescence (XRF), as listed in Table 1. Rectangular specimens, with dimensions 9 mm x 15 mm x 1.5 mm, were machined from the tube walls and ground to a 600 grit surface finish using SiC abrasive paper and water as a lubricant. Prior to oxidation testing, the specimens were ultrasonically cleaned in ethanol for 5 min., rinsed with acetone, dried with a warm air stream and weighed using a digital mass balance with a precision of 0.0001 g. Isothermal oxidation tests were carried out at 900 °C, in a tube furnace apparatus, as previously described⁵, for 24 h, 120 h and 500 h. Compressed air was passed through stirred DI water contained in a jacketed glass cell with the temperature controlled at 46 °C to create the wet air (10% H₂O) environment. The gas mixture was passed through the furnace with a flow rate of 4 cm/s. The quartz tube used for these tests had an inner diameter of 0.96 cm and sample cross-section area of 0.14 cm², which yields a volumetric flow rate of 145 ml/min.

Calibration of the flow rate was performed before each test to ensure consistency in all the tests. A thermocouple was used to ensure the “hot zone” temperature was within in the desired range (896 °C to 905 °C). A set of three or four specimens of one of the alloys was positioned one by one within the isothermal zone from the outlet end of the quartz tube using an alumina push rod that also served as a ruler to ensure positioning in the isothermal zone. The space between specimens was about 2 mm. Once the oxidation exposure time was attained, the outlet tubing was disconnected, the tube furnace was switched off and within 30 min the quartz tube was pulled out of the furnace with care. The samples were cooled off and taken out by pushing with the alumina rod one by one into designated vials. The weight after oxidation, and also after descaling, was recorded for each specimen using the

same digital mass balance. Descaling was achieved by sequentially immersing the specimens in two heated solutions. The first solution (solution #1) contained 2 vol.% citric acid, 5 vol.% dibasic ammonium citrate and 0.5 vol.% disodium EDTA in deionized water. This solution was held at 90 °C and each specimen was immersed for 1 h, followed by an ultrasonic rinse in methanol and drying with a warm air stream. The second solution (solution #2) contained 10 wt.% of potassium permanganate and 4 wt.% of caustic soda in deionized water. Similarly, this solution was held at 90 °C and involved a 1 h immersion, followed by an ultrasonic rinse in methanol and drying with a warm air stream. Immersion in solution #1 was repeated until no further weight loss was observed (i.e. after the second immersion).

Table 1
Chemical Composition (wt.%)

Alloy	C	Si	Ti	Cr	Mn	Fe	Ni	Cu	Nb	Al	W	V	P	S
41Ni-32Cr	0.46	1.6	0.06	33.5	1.1	17.44	44.8	0.02	0.87	<0.001	<0.001	0.05	0.01	0.006
48Ni-45Cr	0.28	2.32	0.15	40.6	0.81	7.05	48.2	0.02	0.04	<0.001	0.65	0.04	0.01	0.005

The surface morphology of oxidized specimens was examined and analyzed using a scanning electron microscope (SEM) equipped with an X-ray energy dispersive spectroscopy (EDS), in both plan and cross-sectional views. Cross-sections were prepared using standard metallographic procedures. However, the surface was pre-treated to preserve the oxide scale. This treatment involved first sputtering a thin gold layer onto the surface and then electroless plating a Ni layer (formula 1 from [8]). The thicknesses of the oxide, scale, Cr-depleted zone and depth of internal oxidation were measured using ImageJ[†] software on at least three SEM images of randomly selected regions. Spalled oxide scales, observed after 500 h, were removed from the quartz tubes and subsequently analyzed using X-ray diffraction (XRD). A Bruker D8-Discover with DAVINCI.DESIGN diffractometer, equipped with a Co sealed tube source was used for this purpose. The scan type was a coupled $\theta/2\theta$ with ± 4 mm X and Y sample oscillation. The following PDF cards were used to identify the oxide phases: PDFs 04-021-0178 and 00-038-1479 for Cr₂O₃, PDF 04-002-1876 for Cr₂MnO₄, PDF 00-021-1276 for TiO₂ and PDF 04-015-9607 for TiMnO₃.

RESULTS AND DISCUSSION

Initial Microstructure of the Alloys

Figure shows backscattered electron (BSE) images and an associated set of EDS element maps of the 48Ni-45Cr and 41Ni-32Cr microstructures. A granular microstructure is evident in both alloys: one which exhibits a (dark) bone-like intergranular network phase. The EDS maps indicate that this dark intergranular network phase is a Cr-rich carbide phase. The 41Ni-32Cr microstructure also shows an additional bright intergranular phase (Figure 1.b), which the associated EDS maps reveals as a Nb-rich carbide phase. Table 2 lists the elemental composition of each of the phases numbered in the BSE images shown in Figure 1. The presence of MnS (phase #5) in 41Ni-32Cr is noted, since impurities, such as S, can segregate to the alloy/scale interface during oxidation, serving to promote oxide scale spallation by weakening the interfacial bond.³

[†] Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, <https://imagej.nih.gov/ij/>, 1997-2018.

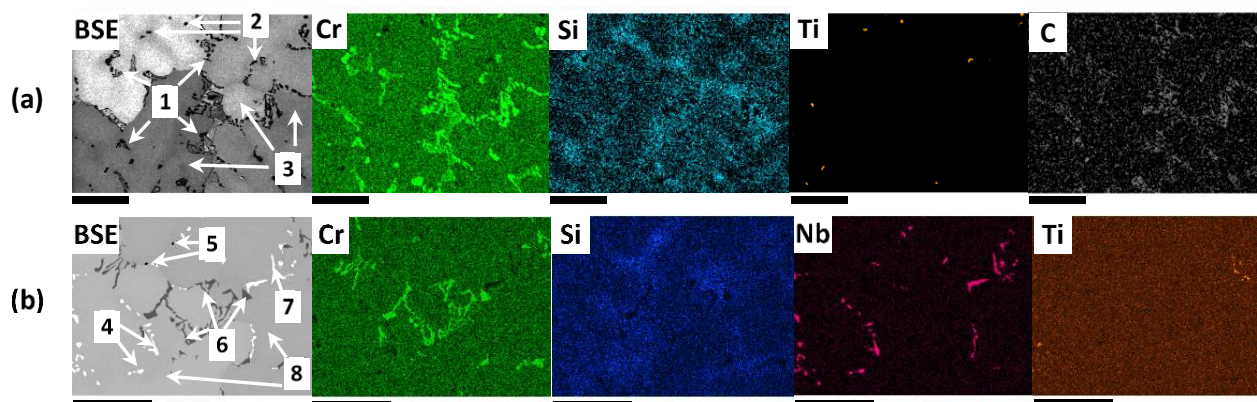


Figure 1: Cross-sectional BSE images and associated EDS element maps showing the as-cast microstructure of (a) 48Ni-45Cr and (b) 41Ni-32Cr. All scale bars are 50 μm .

Table 2
Elemental composition (wt.%) of phases identified in Figure 1, as measured by EDS

Phase #	Cr	Ni	Fe	Mn	Si	Ti	Nb	Other
1 (dark irregular segregations)	88.9 – 85.5	5.6 – 6.9	2.3 – 3.0	0.2 – 0.6	0.0 – 0.2	0.1 – 0.4	-	W = 1.4 – 3.6
2 (dark roundish segregations)	15.0 – 27.1	8.7 – 24.1	0.1 – 0.2	0.0 – 17.2	-	34.2 – 36.6	-	N = 6.9 – 29.9
3 48Ni-45Cr matrix	37.8 – 38.1	49.0 – 49.7	7.6 – 8.2	0.7 – 0.9	1.9 – 2.7	0.1	-	W = 0.8 – 1.2
4 (white segregations)	3.7 – 7.1	1.4 – 5.4	0.4 – 2.4	0.1 – 0.2	0.1 – 0.4	2.1 – 3.2	81.0 – 89.8	V = 0.2
5 (black particles)	16.0 – 16.3	10.8 – 12.3	3.5 – 3.6	38.9 – 41.1	1.3	-	0.0 – 0.9	S = 23.8 – 24.7
6 (dark irregular segregations)	89.8 – 91.5	1.5 – 1.8	3.6 – 4.6	0.3 – 0.4	-	-	0.3 – 0.4	V = 0.2 – 0.3
7 (whitish segregation)	3.8	1.7	1.7	0.1	0.2	28.5	60.6	N = 2.0
8 41Ni-32Cr matrix	30.6 – 30.8	45.8 – 46.1	20.4 – 20.5	0.8 – 1.0	1.3	0.1	0.2 – 0.3	-

Isothermal Oxidation Kinetics, Morphology and Mechanism of Formation

Figure 2.a shows the oxidation kinetics of both alloys based on the gravimetric measurements made after descaling. Pieces (flakes) of spalled oxide were found in the quartz tube upon removing the specimens from the tube furnace, which was expected based on relevant literature.⁹ Qualitatively speaking, the thicker oxides ($> 2 \mu\text{m}$) formed after 500 h spalled more easily during the cooldown to room temperature. It is very likely that thermal shock and stresses, caused by the incompatibility of thermal expansion of different oxides in composition within the scale, for example between SiO_2 and Cr_2O_3 layers ($\alpha = 0.5 \times 10^{-6} \text{ K}^{-1}$ vs. $8.5 \times 10^{-6} \text{ K}^{-1}$ respectively),³ promoted spallation. Interestingly, observations of the spalled areas, as shown in Figure 3 for example, reveal consistently less oxide spallation for 48Ni-45Cr. The size of the spalled oxide scale flakes differed depending on the duration of the test. For example, the flakes were similar in size for both alloys, about $140 \mu\text{m}$ to $230 \mu\text{m}$ and