

High Temperature Oxidation Resistance of a Newly Developed Ni-Based Alumina-Forming NiCoCrMoAl Alloy

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ABSTRACT

A new Ni-based alumina-forming alloy, NiCoCrMoAl, has been invented with the high creep strength and excellent high temperature oxidation and corrosion resistance for high temperature applications. The static oxidation tests of the alloy, along with the other commonly used Ni-based high temperature alloys, such as UNS N07214, N06230, N06002, N06625 and N06617, were conducted at the temperatures of 871 °C (1600 °F), 982 °C (1800 °F), and 1149 °C (2100 °F). The oxidation kinetics and cross-sections of the alloys were analyzed to understand their oxidation mechanism and behaviors. At the test temperatures, the alumina-forming alloys, NiCoCrMoAl and N07214, showed excellent oxidation resistance as a result of the formation of a continuous and adherent alumina scale. In addition, the NiCoCrMoAl alloy exhibited similar or superior oxidation resistance when compared to the N07214 alloy, which was attributed to a consistent alumina scale formed on NiCoCrMoAl with less internal oxidation attack. The chromia-forming alloys showed good oxidation resistance, without observed spallation, due to the formation of a protective chromia scale at 871 and 982 °C. At 1149 °C, the chromia-forming alloys showed inferior oxidation resistance, in which N06625 experienced breakaway oxidation after two cycles (336h). Amongst the chromia forming alloys, the N06230 alloy showed the best oxidation resistant performance at the test temperatures.

Keywords: High temperature, Oxidation, Ni-Base alloy, Alumina-former, Chromia-former

INTRODUCTION

The development of superalloys in extremely high temperature environments, such as turbine engine applications, has been driven to meet the demand for better performance and higher efficiency of high temperature components. These superalloys require key properties, such as excellent mechanical strength, good thermal stability, good fabricability, and resistance to high temperature oxidation and corrosion.^{1,2}

Based on their chemistry, microstructure, and properties, fabricable high temperature superalloys could be categorized into solid-solution strengthened alloys, gamma-prime forming alloys, and alumina-forming alloys, etc.³ Solid solution strengthening is a mechanism in which atoms of one element are added to the base metal to form a solid solution.⁴ Solid solution strengthening alloys also utilize carbide formation to increase their high temperature strength. The most popular solid-solution strengthening alloys include HAYNES[®] (1) 230[®] (UNS⁽²⁾ N06230), HASTELLOY[®] X (UNS N06002), HAYNES 617 (UNS N06617), and HAYNES 625 (UNS N06625) etc. Gamma-prime alloys utilize strengthening mechanism through the precipitates of gamma prime phase, and include HAYNES 282[®] (UNS N07208), HAYNES 263 (UNS N07263), HAYNES Waspaloy (UNS N07001), and HAYNES X-750 (UNS N07750) etc. The gamma prime alloys are generally used below 871 °C (1600 °F) due to the limitation of the dissolution of gamma prime phase at temperatures above their solvus. Alumina forming alloys have excellent oxidation resistant behavior at temperatures as high as 1149 °C (2100 °F) or greater due to the formation of a protective alumina scale. Alumina forming alloys include HAYNES 214[®] (UNS N07214) and HAYNES HR-224[®] (a NiFeCrAl alloy).

Metallic materials primarily rely on the formation of a chromium oxide (chromia – Cr₂O₃) or aluminum oxide (alumina – Al₂O₃) scale to resist high temperature oxidation and corrosion attack. Most commercial alloys are designed to form a chromia scale to achieve oxidation and corrosion protection from elevated to high temperature. These alloys include the solid solution strengthening alloys N06230, N06002, N06617 and N06625 as mentioned above. Although the chromia scale has good high temperature oxidation protection over a large range of temperatures, its performance can be reduced by scale thinning with CrO₃ evaporation and scale buckling due to development of compressive stresses.⁵⁻⁸ At high temperatures, ~1000 °C (1830 °F) and above, Cr₂O₃ can react with oxygen to form volatile CrO₃. Hence, the chromia scale can lose its protective feature due to the volatility of chromium oxide when exposed to high temperatures. Because of its high affinity to oxygen, aluminum is added to certain alloys to form highly stable and protective alumina scale against high temperature oxidation and corrosion.⁹ Addition of aluminum in alumina forming alloys is carefully controlled to design the alloys with good

(1) HAYNES, HASTELLOY, 230, 282, 214, and HR-224 are registered trademarks of Haynes International Inc.

(2) UNS Unified Numbering System for Metals and Alloys (UNS). UNS numbers are listed in Metals & Alloys in this Unified Number System, 10th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2004)

fabricability, such as good welding and hot working characteristics.¹⁰ One concern of some alumina forming alloys, such as N07214, is often about their poor creep strength at high temperatures.

A new Ni-based NiCoCrMoAl alloy, HAYNES 233^{TM (3)} alloy, has been recently developed to have high creep strength and excellent oxidation resistance at temperatures up to at least 1149 °C (2100 °F), along with good fabricability. The high creep strength of the NiCoCrMoAl alloy comes from its unique alloy chemistry design, and the Mo addition is the major creep strength contributor as a solid-solution strengthener. The creep strength of the new NiCoCrMoAl alloy is comparable to N06230 and N06617 and much higher than N06002 and N07214 at 982 °C (1800 °F).³ Due to its Al content, additional strengthening (*i.e.* age-hardening) from gamma-prime precipitations can be achieved when the alloy is exposed to an intermediate temperature range. After an age-hardening treatment, the alloy was stronger than N06230 at 649-927°C (1200-1700°F). The newly developed NiCoCrMoAl alloy is an alumina forming alloy, which offers excellent oxidation and corrosion resistance.

This paper studies the oxidation behaviors of the newly developed NiCoCrMoAl alloy tested at 871-1149 °C (1600-2100 °F), and the oxidation tests also included an alumina forming commercial alloy, N07214, and four chromia forming alloys, N06230, N06002, N06625 and N06617. The oxidation kinetics of the alloys tested were analyzed, and their oxidation performance was ranked by using criteria which include the measurement results of metal loss and internal oxidation. The oxide scale and internal oxidation penetration formed in the alloys were characterized to understand their oxidation mechanism and behavior in this study.

EXPERIMENTAL

The nominal chemical compositions of the alloys studied are listed in Table 1. Among these Ni-based alloys, two are alumina formers, NiCoCrMoAl (3.3 wt.% Al) and N07214 (4.5 wt.% Al), and the others are chromia formers having Cr content of about 21-22 wt.%. It is noted that the N06617 alloy contains approximately 1.2 wt.% Al, which could result in the formation of internal aluminum oxides, improving its high temperature oxidation resistance. Because of the beneficial effects of reactive elements on high temperature oxidation resistance, some alloys studied contain Y, Zr, and/or La additions, such as small amounts of Zr and Y in the NiCoCrMoAl and N07214 alloys and 0.02 wt.% La in the N06230 alloy.

⁽³⁾ 233 a trademark of Haynes International Inc.

Table 1
Nominal chemical composition of the alloys studied (wt.%)

Alloy	Ni	Co	Cr	Al	Si	Ti	Fe	Mo	W	C	others
NiCoCrMoAl	Bal.	19	19	3.3	0.2 ^a	0.5	1.5 ^a	7.5	0.3 ^a	0.1	0.03Zr 0.5Ta 0.025Y ^a
N07214	Bal	2	16	4.5	0.2 ^a	0.5 ^a	3	0.5 ^a	0.5 ^a	0.04	0.01Y 0.1Zr ^a
N06230	Bal.	5	22	0.3	0.4	0.1 ^a	3	2	14	0.1	0.02La
N06002	Bal.	1.5	22	0.5 ^a	1 ^a	0.15 ^a	18	9	0.6	0.1	
N06625	Bal.	1 ^a	21	0.4 ^a	0.5 ^a	0.4 ^a	5 ^a	9	-	0.1	3.7Nb
N06617	Bal.	12.5	22	1.2	0.2 ^a	0.3	3 ^a	9	-	0.1	

^a maximum value

The alloys were received in a mill-annealed condition, and the test coupons were cut to an approximate size of 2.5cm x 2.5cm x 0.3cm for the static oxidation tests. Silicon carbide paper was used to polish the test coupons to a 120-grit finish, and then the coupons were cleaned with acetone and weighed before they were inserted into a tube furnace for the static oxidation tests. The static oxidation tests were performed in a tube furnace in a lab flowing air environment, and each static oxidation test consisted of six thermal cycles at a constant testing temperature, such as 871°C(1600°F), 982°C(1800°F), or 1149°C(2100°F). Each oxidation cycle involved a given 7-day exposure to the temperature and subsequent coupon removal from the furnace for weight measurement. The total test duration of the static oxidation test was 1,008 hours (42 days). After the completion of the static oxidation tests, the test coupons were cross-sectioned using standard metallographic techniques. Optical metallographic techniques were used to evaluate internal oxidation penetration, and the oxide scales and internal oxides were analyzed using Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS).

The oxidation kinetics of the alloys were plotted using the coupon weight change measured after each cycle of the static oxidation tests as a function of exposure time. The weight change (mg/cm²), ΔW , was calculated by

$$\Delta W = (W_t - W_0)/A_0 \quad (1)$$

where W_t is the weight (mg) of coupon after oxidation for a certain time t , W_0 is the initial coupon weight (mg), i.e. before oxidation testing, and A_0 is the coupon surface area (cm²) before oxidation testing.

To further evaluate the overall oxidation attack on the alloys studied, Metal Loss, Average Internal Penetration, Maximum Internal Penetration, Average Metal Affected and Maximum Metal Affect were used to quantify the oxide formation, scale spallation and internal oxidation attack, which are illustrated in Figure 1. After the static oxidation tests, the test coupons were descaled in an acid solution, and the metal loss (Metal Loss) was calculated from the difference of the initial coupon weight before the oxidation test and the weight after the descaling of the tested coupon. By combining the measurement of the internal oxidation penetration from the optical metallographic examination, the criteria of Average Metal Affected and Maximum Metal Affected were used to represent and rank

the alloy performance in this study. Average Metal Affected is the sum of Metal Loss $((A - B)/2$ in Fig. 1) and Average Internal Penetration (C in Fig. 1), and Maximum Metal Affected is the sum of Metal Loss and Maximum Internal Penetration (D in Fig. 1).

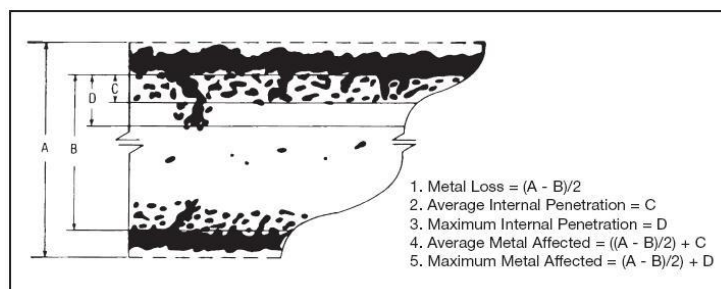


Figure 1: A methodology to evaluate alloy degradation after the static oxidation tests in the current study ¹¹

RESULTS AND DISCUSSION

Figures 2-4 show the static oxidation kinetics of the alloys tested at 871°C (1600°F), 982°C (1800°F) and 1149°C (2100°F), respectively, representing the weight change, ΔW (mg/cm²), over the test duration (hours). The weight change kinetics clearly revealed the oxidation resistance of the alumina forming alloys, NiCoCrMoAl and N07214, were superior to the chromia forming alloys as the alumina formers showed lower weight gains from 871 to 982°C. Moreover, no weight loss and scale spallation were observed for the two alumina formers in the tests. The NiCoCrMoAl alloy showed lower weight gain than the N07214 alloy at 871 °C, and the two alumina formers showed very close weight growth kinetics at 982 and 1149°C, which implies the comparable or slightly better oxidation resistant performance of NiCoCrMoAl than N07214 in the static oxidation tests.

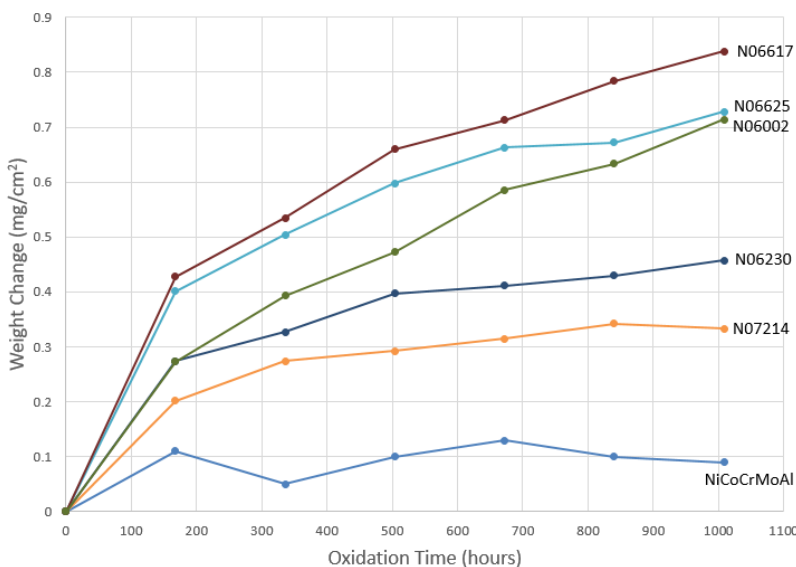


Figure 2: Static oxidation kinetics of the alloys tested at 871°C (1600°F).