

High Temperature Oxidation Behavior of Fe- and Ni-Based Alloy Foils in Water Vapor at 850 °C

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ABSTRACT

Operating temperatures above 700°C are desired to improve the efficiency of power generation systems such as microturbines. Therefore, the use of creep-resistant Ni-based or Fe-based alloys, which can form protective Cr₂O₃ and Al₂O₃ scales, is required. In this paper, Fe- and Ni-based alloy foils were oxidized in air + 10 % H₂O for up to 3,000 h at 850°C to identify the most promising alloys. The thickness and chemical composition of the spinel oxide formed on top of the Cr₂O₃ scale varied between S3100, N08120 and N06230 alloy foils. In addition, the rate of Cr and Mn loss (spinel and Cr₂O₃ oxidation and volatilization) or Al loss (oxidation) and the dissolution of strengthening precipitates, were found to be a function of the nature of the formed oxide (Fe or Ni-rich spinel, Cr₂O₃, Al₂O₃). Alloys N06230 and alumina-forming austenitic (AFA) steels were found to be well-suited for the applications as microturbine recuperator foil materials up to 850°C.

Keywords: Foil, Oxidation, Water vapor, Metal loss

INTRODUCTION

Decreased cost and enhanced electrical efficiency (currently < 35 %) of recuperated microturbines are essential for their widespread use as power generation systems [1, 2]. To further increase efficiency, research has been conducted towards increasing the microturbine's turbine inlet

temperature such that the outlet temperature to the recuperator would be above 750°C [1] (currently ~650°C) and optimizing the design of compact microturbine recuperators [3]. Recuperator temperatures over 600°C have been shown to challenge the oxidation lifetime of S34700 stainless steel foils used in primary surface recuperators [4-6]. Therefore, microturbine manufacturers have used Ni-based alloys such as N08120 and N06625 and advanced austenitics (S31025) to achieve ~650°C operation [7]. A key issue is that microturbine exhaust gas contains water vapor which could decrease the oxidation lifetime of Cr₂O₃-forming alloys such as S30400 or N06625 due to the formation of volatile CrO₂(OH)₂ [8, 9].

Greater Cr depletion was reported for the S30403 steel coupon after 679 h of exposure in flowing O₂ + 10 % H₂O (100 mL.min⁻¹ / 2.5 cm.s⁻¹) at 600°C in comparison to dry air [8]. The cyclic oxidation behaviors of austenitic and ferritic Fe-(10-30)Ni-(10-20)Cr model alloys were studied between 650 and 800°C in air + 10 % H₂O (1h cycle) [10]. The presence of higher Ni and Cr contents was reported to delay the transition time from protective oxidation behavior, characterized by Cr₂O₃ formation, to accelerated attack with the formation of Fe and Cr-rich oxides [10]. The effect of water vapor on the oxidation behavior on commercial Ni-based materials was studied by several authors [11-14]. The extent of Cr depletion in N06625 coupon exposed for 1,000 h in flowing air + 6 % H₂O at 900 °C was reported to increase with increasing gas flow rate from 0.5 to 600 cm.s⁻¹ [11]. The presence of water vapor led to the formation of large Fe-rich nodules on the surface of Fe-25Ni-20Cr foils oxidized in air + 10 % H₂O at 650, 700 and 800°C and increased Cr depletion within the foils [12,13]. The oxidation resistance of Cr₂O₃ and Al₂O₃ forming foils was compared after exposure in flowing air + 10 % H₂O (500 cm³.min⁻¹) studied between 760 and 871°C up to 8,640 h (360 days) [14]. At 760°C, the S34700 stainless steel foil underwent breakaway oxidation after about 720 h. The N08120, N06002, N06625 and N06230 specimens presented similar mass change (less than 0.5 mg.cm⁻² after 8,640 h) and comparable oxidation attack parameter (defined by the authors as the product of original foil thickness and average metal depth affected by oxidation and internal oxidation) were observed between for N08120, N06002 and N06625 alloys [14]. After 8,640 h exposure at 871°C, attack parameters were the highest for 347 stainless steel, alloy N08120 and alloy N07208, the lowest being for the alloys N06230, N06625 and N06002 [14]. In the study, the alumina forming alloy N07214 exhibited the lowest oxidation attack parameters at all temperatures due to the formation of an external Al₂O₃ scale [14].

Since the volatilization of the Cr₂O₃ scale was shown to decrease the lifetime of some Cr₂O₃ forming alloys, extensive research has been conducted towards the development of creep resistant alumina forming austenitic (AFA) steels which are also less expensive than Ni-based alloys [15,16]. Previous studies included laboratory exposures at 650° - 800°C where commercial AFA foils, 80-150 µm thick, demonstrated protective oxidation behaviors up to 10,000 h at 800°C [17,18] and longer exposures in engine tests [18].

The objective of this study was to identify potential oxidation and creep resistant materials to be employed as microturbine recuperator foils at even higher temperatures (T > 800°C). Therefore, the oxidation and volatilization behaviors of several Fe and Ni-based chromia forming foils and Fe-based alumina forming foils were compared in flowing air + 10 % H₂O at 850 °C. The oxidation induced Cr or Al depletion, sound metal loss, and dissolution of strengthening precipitates were characterized.

EXPERIMENTAL PROCEDURE

Materials

Several chromia-forming alloy foils (compositions shown in Table 1) were oxidized in dry air in a resistively heated box furnace up to 7,000 h at 800 °C and up to 500 h at 850°C using 100-h cycles. The specimens were also exposed in a resistively heated alumina tube furnace (diameter of 5.9 cm) with flowing (850 cm³.min⁻¹, velocity of 1.95 cm.s⁻¹) air + 10 % H₂O (g) (referred to as wet air) in

100 h-cycles up to 7,000 h at 800°C and up to 3,000 h at 850°C. A detailed description of the experimental procedure is available in [12]. The Fe-based and Ni-based foils presented a bright surface finish and were cut into ~20mmx10mm size (thickness shown in

Table 3), and then ultrasonically cleaned in acetone and ethanol prior to oxidation exposure.

Table 1: Composition of Fe and Ni based alloys (in wt.%) analyzed by inductively coupled plasma–optical emission spectrometry (ICP–OES) and combustion analysis.

Alloy/ wt.%	Ni	Cr	Fe	Mo	Nb	Co	Mn	Si	W	Al	Ti	La	C
Fe-based alloy													
S31000	19.5	24.1	54.0	0.07	0.01	0.05	1.66	0.33	-	0.01	0.01	-	0.05
Ni-based alloys													
N08120	39.5	25.8	32.2	0.45	0.42	0.09	0.52	0.33	0.1	0.04	0.01	-	0.05
N06230	58.2	22.3	1.03	1.17	0.02	1.07	0.67	0.42	14.5	0.37	0.01	0.02- 0.05	0.09
N06625	61.6	21.4	4.31	8.39	3.43	0.09	0.08	0.09	0.01	0.11	0.19	-	0.06

Fe-based commercial AFA (AFA1) and laboratory made AFA (AFA2) were also investigated (compositions in Table 2). Native oxides were present on the surface of the AFAs which were homogenized (2h), hot-forged, hot-rolled, cold-rolled and annealed for 1h at 1100 °C and cut into 20mmx10mm foils (thicknesses shown in Table 3).

Table 2: Composition of Fe based alumina former alloys (in wt.%) analyzed by inductively coupled plasma–optical emission spectrometry (ICP–OES) and combustion analysis.

Fe based alloys												
Alloy/ wt.%	Ni	Cr	Fe	Mo	Nb	Co	Mn	Si	W	Al	Ti	C Zr Y Hf
AFA1	25.1	14.9	base	2.01	2.50		1.93	0.15	-	3.98	-	0.09 - 0.009 0.14
AFA2	25.0	14.0	49.66	1.99	2.53	-	2.0	0.16	0.97	3.57	0.05	0.10 - - -

Table 3: Thickness of the studied foils

Alloy	Foil thickness (µm)
S31000	51 ± 5
N08120	85 ± 15
N06230	200 ± 10

N06625	100 ± 20
AFA1 (commercial)	80 ± 5
AFA2 (laboratory made)	120 ± 10

Characterizations

After the oxidation exposure, specimens were Cu plated and mounted in conductive epoxy for cross sectional characterization including Scanning Electron, Back-scattered Electron Microscopy (BSE) (TESCAN MIRA3 SEM), energy dispersive X-ray spectroscopy (EDAX Octane Elect Super Silicon Drift Detector) and electron probe microanalysis (EPMA JEOL 8200/8500).

RESULTS

Mass change

Short-term oxidation

The mass change of the studied materials after exposure in dry air at 850°C is reported in Figure 1a. No spallation of the oxide scale formed on the specimens was observed in dry and wet air exposures. The S31000 specimen exhibited higher mass gains than the N08120, N06625 and N06230. The alloys N06625 and N06230 showed the lowest mass gain up to 500 h.

No significant differences in the mass change were observed for the S31000, N06230 and N08120 specimens in wet air compared to the dry air exposure (Figure 1b). For the N06625 foil, a mass loss of -0.1 mg.cm^{-2} was measured in wet air after 500 h (Figure 1b), but a mass gain of 0.1 mg.cm^{-2} was observed in dry air (Figure 1a). The AFA foil specimens were not tested in dry air and exhibited low mass change in wet air (Figure 1b).

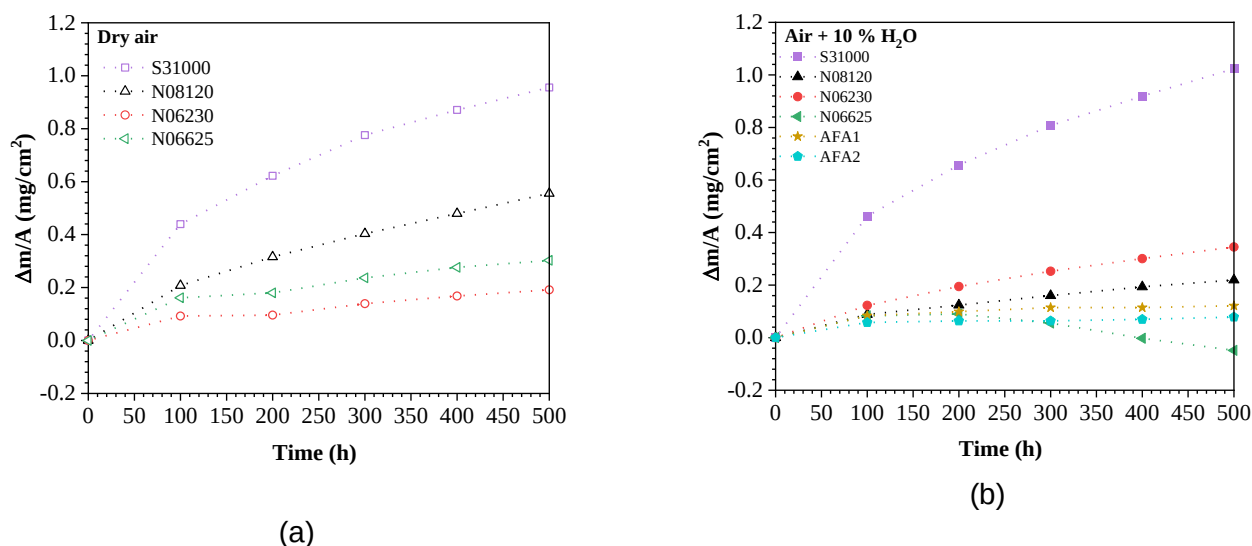


Figure 1: Specimens mass change after 100 h cyclic exposure in (a) dry air and (b) in flowing air + 10% H₂O at 850°C.

Long-term oxidation behavior

Similar trends in the mass change behavior were observed between the short-term and long-term oxidation tests. The S31000 foil continued to exhibit a large mass gain to reach about 5 mg.cm^{-2} after 3,000 h (Figure 2). For the N08120, N06230, AFA1 and AFA2 mass gains were observed up to

3,000 h. The lowest mass gains were 0.2 mg.cm^{-2} after 3,200 h for the AFA1 specimens and 0.1 mg.cm^{-2} after 3,000 h for the AFA2 specimens. For the alloy N06625, after an initial mass gain for 300-400 h, a linear mass loss was measured.

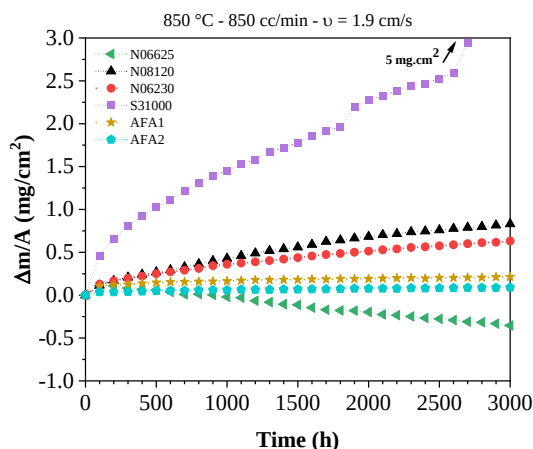


Figure 2: Mass change of specimens after 3,000 h after 100 h cycle exposure in air + 10 % H₂O at 850 °C.

Oxide scale characterization

BSE images of the cross-sections of the specimens after 1,000 h exposures in wet air at 850 °C are reported in Figure 3. For the S31000, N08120 and N06230 specimens, spinel oxides formed on top of a Cr-rich scale (likely Cr₂O₃). The thickness of the oxide scale formed on the S31000 specimen was greater ($9 \pm 1 \text{ } \mu\text{m}$) than that on the alloys N08120 ($4 \pm 1 \text{ } \mu\text{m}$) and N06230 ($2.5 \pm 0.5 \text{ } \mu\text{m}$). The spinel-type oxide scale formed on the surface of the Cr₂O₃ scale of S31000 and N08120 specimens were Mn, Cr and Fe-rich (Figure 4a,b). On the N06230 foil, a Mn, Cr, Fe and Ni-rich spinel was found (Figure 4c).

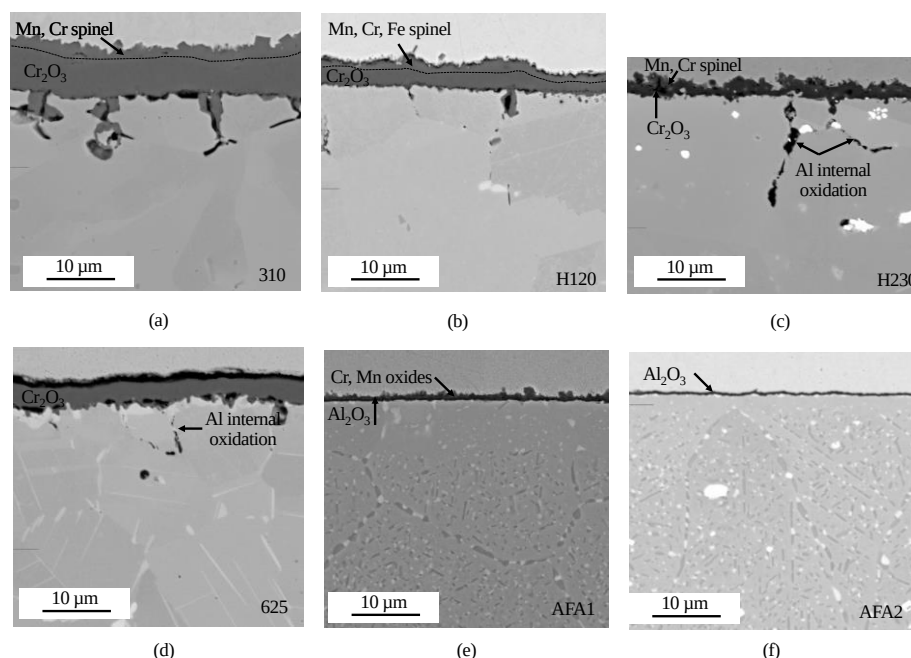


Figure 3: BSE images of (a) S31000, (b) N08120, (c) N06230, (d) N06625, (e) AFA1 and (f) AFA2 after 1,000 h of exposure in 100 h cycle flowing air + 10 % H₂O at 850 °C.

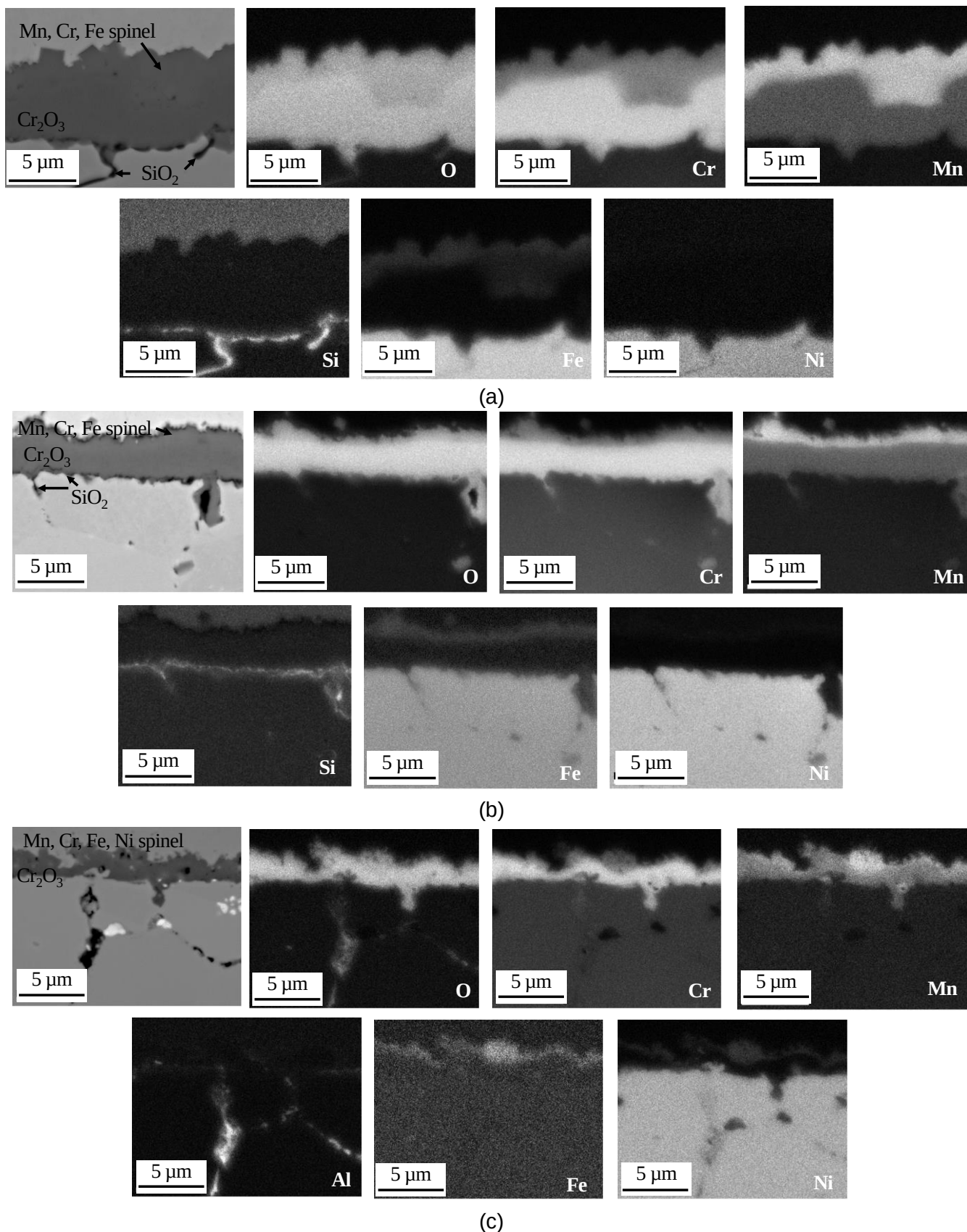


Figure 4: EDS elements maps of the oxide scale on the surface of (a) S31000, (b) N08120 and (c) N06230 specimens after 1,000 h of exposure in 100 h cycle air + 10 % H₂O at 850°C.