Evaluation of Commercial Alumina-Forming Austenitic Foil for Advanced Recuperators

Bruce A. Pint, Michael P. Brady, Yukinori Yamamoto Kinga A. Unocic and Wendy J. Matthews*

Oak Ridge National Laboratory, Materials Science and Technology Division Oak Ridge, TN 37831-6156 Phone: (865) 576-2897, E-mail: pintba@ornl.gov *Capstone Turbine Corp., Chatsworth, CA 91311

ABSTRACT

A corrosion- and creep-resistant austenitic stainless steel has been developed for advanced recuperator applications. This fully austenitic alloy is optimized for creep strength while allowing the formation of a chemically-stable external alumina scale at temperatures up to 900°C. An alumina scale eliminates long-term problems with the formation of volatile Cr oxyhydroxides in the presence of water vapor in exhaust gas. The first batch of commercially fabricated foil was produced with a composition selected from prior laboratory creep and oxidation results. The results for ~ 80 and $\sim 105 \mu$ m thick foil are compared to the prior laboratory-fabricated foils and other commercial candidates. Results from initial creep testing at 750°C show comparable creep strength to other commercial Fe-base foil candidates. Laboratory exposures in humid air at 650°-800°C have shown excellent oxidation resistance for this composition. Similar oxidation resistance was observed for sheet specimens of the first set of alloys exposed in a modified 65kW microturbine for up to 6,000h.

INTRODUCTION

A current focus of the U.S. Dept. of Energy's Combined Heat and Power (CHP) program is to increase the efficiency and performance of gas turbines while decreasing the cost per kW. Turbines are especially well-suited for CHP systems where system efficiency can exceed 80% by using the waste heat from the turbine for process heat, steam generation and/or heating and cooling [1-4]. For small gas turbines (<5 MW) and especially microturbines (25-300 kW) [5,6], one method of improving efficiency is to use the turbine exhaust gas to preheat the compressed air before it enters the combustor [7-9]. Beyond recuperation, there are relatively few options available to increase the efficiency of electricity generation using gas turbines (<30% for microturbines, <40% for small gas turbines) except by improving the efficiency of the recuperator or by increasing the turbine inlet temperature. Increasing the inlet temperature increases the temperature throughout the hot section including the recuperator. Higher recuperator inlet temperatures raise concerns about durability and materials selection.

There are numerous recuperator designs, but most turbine systems rely on thin-walled metallic systems in order to maximize heat transfer [7-9]. In the past decade, a traditional recuperator material, type 347 stainless steel foil (80-100 μ m thick, composition in Table 1), has been replaced in many commercial turbine recuperators. It has become clear that the corrosion resistance of 347 foil in this environment is limited to <600°C and rapid degradation can occur at higher temperatures [10-14]. (In ambient air environments, the corrosion resistance of 347 foil is adequate at >600°C.) The presence of water vapor in the exhaust gas has been identified

Table	1.	Alloy	chemical	composition	(weight	%)	and
averag	je gr	ain siz	e (<i>µ</i> m) of tl	he candidate n	naterials.		

Alloy	Cr	Ni	Al	Si	Nb	Other	Grain Size (µm)	
Type 347	17.8	9.9	0.01	0.5	0.5	1.6Mn	5	
709	20.3	24.7	0.05	0.4	0.2	1.5Mo,1.0Mn	16	
120	24.7	37.6	0.1	0.2	0.6	0.3Mo,0.7Mn	23-28	
625	23.1	63.8	0.2	0.2	0.2	8.9Mo,3Fe	12	
AFA:								
F1 (lab.)	14.2	20.0	3.0	0.1	2.5	2Mn,1W,2Mo,0.1	1C 31	
F2 (lab.)	14.3	25.0	3.0	0.1	1.0	2Mn,1W,2Mo,0.0	05C 92	
F4 (lab.)	14.0	25.0	3.6	0.1	2.5	2Mn,1W,2Mo,0.1	IOC 45	
F4 (commercial)								

as a major factor in degrading the oxidation resistance of all chromia-forming steels. The surface oxide can react to form a volatile oxy-hydroxide [15,16]:

$$1/2 \operatorname{Cr}_2 O_3(s) + 3/4 O_2(g) + H_2 O(g) = \operatorname{Cr}O_2(OH)_2(g)$$
 (1)

Consumption of the limited Cr reservoir present in an 80-100 μ m thick foil is greatly accelerated by the combination of oxidation (parabolic kinetics) and volatilization (linear kinetics). At the long exposure times required in service (minimum 30-40kh recuperator lifetime), the Cr loss rate is dominated by the linear volatilization kinetics[17-20]. More details about the parameters, such as gas velocity, that effect the kinetics can be found elsewhere[16,19].

For recuperators operating at >600°C, replacement alloys in use include Nb-modified Fe-20Cr-25Ni (composition similar to alloy 709), alloy 120 and, for larger turbines, Ni-base alloy 625 [21-22]. All of these alloys have higher Cr and Ni contents than Type 347 stainless steel, Table I, which results in better oxidation resistance. However, all of these alloys rely on the formation of a Cr-rich oxide, and thus are degraded by the oxyhydroxide volatilization described above. Significant Cr losses have been observed in foils exposed in laboratory testing for 10-20kh [18,23]. From these results it appears clear that, for the next generation of advanced recuperators operating at 700°C or higher requires more oxidation resistant alloys.

It is well known that alloys that form protective Al-rich oxides are more resistant to water vapor because of the higher stability of α -Al₂O₃[16]. Alumina-forming alloys and coatings are standard in the hot section of gas turbines [24]. An early recuperator material study evaluated the creep and oxidation resistance of commercial alumina-forming alloys [25]. Those results showed that no wrought Fe-base alumina-forming alloy had sufficient strength for the application. Aluminum additions to austenitic steels tend to stabilize the weaker ferritic phase resulting in very high creep rates [26,27]. To address this material capability gap, a new class of Fe-base creep-resistant alumina-forming austenitic (AFA) alloys has been developed based on careful control of the composition on: (1) a macrolevel to maintain a fully-austenitic alloy and (2) a micro-level to nucleate stable precipitates that provide creep strength without inhibiting the formation of a protective alumina scale [27-30]. The AFA alloy properties are particularly well-suited for thinwalled recuperators for both microturbines and small gas turbines. As progress continues on the development of this class of alloy, current results are presented on the creep and oxidation behavior of commercially-made 80 and 105μ m (3.2 and 4.2 mil) AFA foils. The composition was selected based on prior laboratory creep and oxidation results as well as field exposures in a modified 65 kW microturbine.

EXPERIMENTAL PROCEDURE

Three ~13 kg vacuum induction melted (VIM) heats of AFA (F1-F4) were cast by Carpenter Technology Corp. as tapered 10 cm x 10 cm x 22 cm long ingots. A ~180 kg VIM heat of F4 was subsequently cast for commercial processing to foil. Alloy compositions are shown in Table 1. Further details of the laboratory-scale processing were provided previously [23]. Commercial pieces of ~18 cm wide foil were fabricated with thicknesses of ~380, 105, 80μ m (15, 4.2, 3.2mil) were produced. An example cross-section is shown in Figure 1. Typical grain sizes for foils are given in Table 1. The average grain size of the specimens was calculated using the mean lineal intercept length, counting between 150-600 grains.

Creep specimens were machined by electro-discharge machining. The creep specimens were 114 mm (4.5 in.) long with a gage length of 25.4 mm (1 in.) and 6.35 mm (0.25 in) wide. The shoulders were approximately 16mm wide. Pads of the same thickness as the foil were spot-welded on the shoulders for re-enforcement and 3.17 mm (0.125 in.) diameter pin holes were cut in the shoulders for gripping. The extensioneter was a rod-in-tube type that transmitted extension out of the hot zone of the furnace to averaging LVDT sensors. Because of the small section areas, specimens were dead loaded. Creep testing was performed in laboratory air at 677°C with 117 MPa load and at 750°C with 100 MPa load to induce rupture in a reasonably short time.

Foil oxidation coupons (~12 mm x 18 mm x ~100 μ m) were tested in the as-annealed surface condition and (~25 x 25 x 0.9mm) sheet specimens were polished to a 600 SiC grit finish for exposure in a 65 kW microturbine at Capstone Turbine Corp.. This turbine has been modified to produce exhaust temperatures of ~720°C and has been detailed elsewhere [22]. For laboratory exposures, all of the specimens were cleaned in acetone and methanol prior to oxidation. Exposures were 100 h cycles at 650°, 700° or 800°C and mass changes were measured after every cycle using a Mettler-Toledo model XP205 balance, with an accuracy of ±0.01 mg/cm². The amount of water injected was used to calibrate the water content at 10±1 vol.% for these experiments. Up to 40 specimens were positioned in alumina boats in the furnace hot zone so as to expose the



Figure 1. Light microscopy of polished cross-sections of commercial AFA F4

specimen faces parallel to the flowing gas. As a further evaluation of the oxidation resistance, sheet coupons of the F1-F4 compositions were placed in the hot gas path of a modified 65 kW microturbine at \sim 720°C [22]. After exposure, specimens were Cu-plated and sectioned for metallographic analysis.

RESULTS Selection of F4 Composition

Figure 2 shows the polished cross-sections of sheet specimens of the three initial AFA alloys exposed in the 65kW microturbine at ~720°C for 6,004h. The F1 composition with only 20%Ni showed relatively poor oxidation resistance compared to F2 and F4.

Figure 3 shows the tensile creep behavior of the three compositions. The shorter lifetime for AFA F2 can be attributed to the lower C content (0.05%) in this alloy, Table 1. The Nb:C ratio was too low, likely resulting in a low fraction of the NbC strengthening precipitates [31]. A slightly higher creep rate was observed for AFA F1 compared to F4. However, one problem with this comparison is that the grain sizes of the three foils were not the same, Table 1. Nevertheless, the F4 composition appeared to have the best combination of creep and oxidation resistance and was selected for a larger heat.



Figure 2. Light microscopy of polished cross-sections of sheet specimens after 6,004h at 720°C in microturbine exhaust. (a) AFA F1, (b) AFA F2 and (c) AFA F4.



Figure 3. Tensile creep behavior of laboratory-made AFA foils with strain % plotted versus exposure time at 677°C (1250°F) in air with a load of 117MPa (17ksi).

Laboratory Oxidation Testing

Figures 4-6 compare the performance of specimens of the AFA foils at 650°, 700° and 800°C in humid air to specimens of one of the advanced recuperator materials, commercial alloy 120 foil. One difference was that the commercial alloy 120 foil had a bright annealed (oxide-free) finish. In contrast, the



Figure 4. Specimen mass change for commercial 347 and 120 foil (80-100μm thick) compared to AFA foils during 100h cycles in humid air at 650°C.



Figure 5. Specimen mass change for commercial alloy 120 foil (80μ m thick) compared to AFA foils during 100 h cycles in humid air at 700°C.

laboratory-made and commercial AFA foils had a residual oxide layer (tarnish) from the final anneal that likely resulted in lower initial mass gains. At 650°C, the specimen of commercial type 347 foil exhibited a high mass gain after ~1 kh of exposure due to the formation of thick, Fe-rich oxide nodules on the surface,



Figure 6. Specimen mass change for commercial alloy 120 foil (80μ m thick) compared to AFA foils during 100 h cycles in humid air at 800°C.

Figure 4. The higher-alloyed 120 foil specimens have shown protective behavior for >30kh at this temperature. However, the alloy 120 foil specimens began to show a linear mass loss after ~4kh of exposure, Figure 4. The measured specimen mass change reported in Figures 4-6 is the summation of oxide scale growth, oxy-hydroxide volatilization and spallation of the scale:

$$\Delta M_{\text{specimen}} = \Delta M_{\text{oxide growth}} - \Delta M_{\text{volatile}} - \Delta M_{\text{spall}}$$
(2)

There was no evidence of scale spallation from these specimens, so that oxide growth and oxy-hydroxide volatilization were summed in the mass gain data. The net mass loss thus can be attributed to the loss of Cr due to volatilization of $CrO_2(OH)_2$. being greater than the mass gain due to oxide growth.

The exposures times for the commercial AFA foil coupons are relatively short at each temperature compared to the alloy 120 and laboratory-made AFA foil specimens. However, they show a similar trend as the laboratory-made F4 foil at each temperature. One commercial F4 coupon initially showed a higher mass gain at 650°C. This may be due to an imperfection or burr on the foil specimen and longer exposures will indicate if there is cause for concern about the oxidation resistance. The laboratory-made F4 foil has reached 5 kh and showed no indication of mass loss. In general, the mass changes are so low for the AFA specimens that the data reflect the sensitivity of the balance, $\pm 0.01 \text{ mg/cm}^2$.

At 700°C in humid air, the volatilization and oxidation processes are faster and the AFA foil specimens have clearly differentiated from the alloy 120 specimens, which showed a steady mass loss after ~1 kh, Figure 5. The laboratory made F4 foil specimen has passed 9kh without showing any mass loss. Figure 6 shows the mass change at 800°C. Foil specimens of F1 and F2 showed earlier failure at this temperature while the F4 specimen has been exposed for almost 10kh, without indication of rapid oxidation. In contrast, the alloy 120 foil specimens (dashed lines in Figure 6) experienced first a mass gain due to oxide growth, then a mass loss due to volatilization and finally a more rapid mass gain as thick Fe-rich oxide nodules formed between 6-8kh. Several of the alloy 120 specimens stopped before 10kh. Prior work reported almost 50% of the Cr reservoir had been consumed from the metal after 10kh at 800°C in wet air [23]. For the commercial AFA F4 foil specimens, one specimen was stopped after 1,000h at each temperature for characterization, while additional specimens are being exposed for longer times.

Laboratory Creep Testing

Figure 7 shows creep results for the commercial AFA foil materials in laboratory air compared to the laboratory-made AFA foils and several commercial foils. The 750°C/100MPa conditions have been used in prior studies to rapidly compare creep behavior of candidate alloy foils. The finer grain size $(27\mu m)$ in the commercial foil can likely explain the slightly higher creep rate observed for the commercial foils compared to



Figure 7. Creep behavior of two commercial foils compared to laboratory-made and commercially-made AFA foils with strain % plotted versus exposure time at 750°C (1382°F) in air with a load of 100MPa (14.5ksi).

the laboratory F4 foil. Two curves for alloy 120 are shown, indicating a range of creep behavior for this material. Exact processing information was not available for these different heats so it is not possible to address in this study the range in creep behavior observed. The AFA material is much stronger than type 347 foil and is initially comparable to the commercial 20-25Nb foil (based on alloy 709). However, the 20-25Nb foil has shown a longer rupture life and is currently in test, along with an alloy 120 foil specimen. Further heat treatment or composition modifications may be needed to improve the creep strength of AFA F4, if that is needed. Additional testing at 677°C (see Figure 3) will be conducted because that temperature is closer to the actual operating temperature.

Further AFA alloy development is still in progress. The F4 composition was selected for commercialization based on its superior oxidation resistance and adequate creep strength, relative to other AFA compositions. Further composition modifications are being explored, such as a higher C content in composition F2, that could produce a better combination of properties.

CONCLUSION

The development of creep- and oxidation-resistant alumina-forming austenitic steels for advanced recuperator applications has progressed to the evaluation of the properties of the first batch of commercial foil. This AFA composition was selected based on laboratory and engine exposures of three candidate compositions. Initial results on the commercial foil has shown promising oxidation and creep results at 650°-800°C. These evaluations will continue in order to compare the longterm behavior of the AFA foils to other commercial alloys that have been exposed for up to 30 kh. Larger castings of AFA F4 composition have been made, portions of a 4,500kg and a 900kg ingot are now being prepared to fabricate the next batches of commercial foil in the correct size and specification for recuperator air cell fabrication, so that foil folding and welding evaluations can be conducted.

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