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CRADA FINAL REPORT

CRADA NFE-08-01392 Evaluation of Alumina-Forming Austenitic Stainless Steel Alloys in Microturbines

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CRADA NFE-08-01392 Evaluation of Alumina-Forming Austenitic Stainless Steel Alloys in Microturbines

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Abstract

Oak Ridge National Laboratory (ORNL) and Capstone Turbine Corporation (CTC) participated in an in-kind cost share cooperative research and development agreement (CRADA) effort under the auspices of the Energy Efficiency and Renewable Energy (EERE) Technology Maturation Program to explore the feasibility for use of developmental ORNL alumina-forming austenitic (AFA) stainless steels as a material of construction for microturbine recuperator components. ORNL delivered test coupons of three different AFA compositions to CTC. The coupons were exposed in steady-state elevated turbine exit temperature (TET) engine testing, with coupons removed for analysis after accumulating ~1,500, 3,000, 4,500, and 6,000 hours of operation. Companion test coupons were also exposed in oxidation testing at ORNL at 700-800°C in air with 10% H₂O. Post test assessment of the coupons was performed at ORNL by light microscopy and electron probe microanalysis. The higher Al and Nb containing AFA alloys exhibited excellent resistance to oxidation/corrosion, and thus show good promise for recuperator applications.

Statement of Objectives

Capstone Turbine Corporation has developed a 200 kW microturbine that is more efficient, cleaner, and less expensive than currently available technology. One of the major technical challenges to achieve economic viability and market penetration is the recuperator or heat exchanger, which enables the high efficiency and low NO_x emissions. Durability requirements with the higher operating temperatures cannot be met by conventional chromia-forming stainless steels such as type 347 due to formation of volatile Cr oxy-hydroxides, which result in accelerated oxidation and unacceptable loss of metal thickness. This necessitates the use of expensive high-Ni austenitic and Ni-base alloys, which can compromise the economic viability and potential for market penetration of these high-efficiency turbines. The ORNL AFA alloys have shown promise for far greater oxidation/corrosion resistance than conventional stainless steels, are not susceptible to volatilization effects, and are potentially significantly less expensive than the high-Ni/Ni-base alloys. The goal of this CRADA was to assess the ORNL AFA alloy high-temperature oxidation and corrosion resistance in an operating turbine engine environment

Benefits to the Funding DOE Office's Mission

The ORNL AFA stainless steels are a new class of high-temperature alloy family with ≥ 50 -200°C (~100-400°F) increased upper-temperature oxidation (corrosion) limit over that of conventional stainless steels. AFA steels deliver these uniquely superior properties without sacrificing the typical lower cost, formability and weldability of conventional stainless steels. Due to their outstanding oxidation resistance, which results from the formation of a protective aluminum oxide (alumina, Al_2O_3) surface layer, AFA stainless steels can be used at higher temperatures and for longer times than conventional chromium-oxide (chromia, Cr_2O_3)-forming stainless steels in highly-corrosive operating environments. These unique attributes of AFA steels make them highly desirable in a wide range of energy production and chemical industry applications, where implementation of more durable, higher-temperature capable materials can result in significant savings in cost and energy, and reductions in environmental emissions. This CRADA effort is devoted to evaluation of AFA alloys for recuperator components in high efficiency, low emission miniturbines, an application that is highly relevant to the DOE EERE program mission.

Technical Discussion of Work Performed by All Parties

Trial scale heats of AFA alloys were manufactured into plate and sheet form using commercially viable processes as part of a companion CRADA with Carpenter Technology Corporation, CRADA NFE-08-01374 Manufacture of Alumina-Forming Austenitic Stainless Steel Alloys by Conventional Casting and Hot-Working Methods. Three alloys from that effort were selected for study in the present CRADA, alloys OC-1, OC-2, and OC-4 (Table 1).

Table 1- Composition analyses of as-cast AFA alloy heats provided Carpenter Technology Corporation (weight percent, wt.%).

Heat No/Alloy	OC-1	OC-2	OC-4
C	.109	.051	.101
Mn	1.98	1.98	1.97
Si	.14	.14	.14
P	.016	.013	.013
S	.0012	.0010	.0009
Cr	14.24	14.26	13.96
Ni	20.03	24.98	25.03
Mo	1.99	1.98	1.98
Cu	.51	.51	.51
W	.97	.96	.95
V	.04	.04	.04
Ti	.05	.05	.05
Al	3.02	3.04	3.55
Nb	2.53	1.03	2.53
B	.0068	.0069	.0008
N	.0005	.0005	<.0010
Fe	Bal	Bal	Bal

As-cold rolled OC-1, OC-2, and OC-4 sheet material ~2.5 mm thick was annealed, cold rolled to 0.8 mm thick and given a final solution anneal at ORNL. Four samples each of OC-1, OC-2, and OC-4 were prepped to a 600 grit surface finish and delivered to CTC for steady-state elevated TET engine testing. The engine used for testing was assembled with a recuperator and a removable aft dome, as shown in Fig. 1 [1]. It was operated at an elevated TET set-point ~55C° (~100°F) above normal operating temperature with minimal shutdowns to avoid cyclic effects on the oxidation behavior. Test samples were tack welded at the hot inlet side of the core (Fig. 2) and were removed after accumulating ~1,500, 3,000, 4,500, and 6,000 hours and delivered to ORNL for evaluation.

Light microscopy cross-sections of select, representative OC-1, OC-2, and OC-4 coupons after engine testing are shown in Fig. 3. Alloys OC-2 and OC-4 formed continuous, protective alumina surface layers and exhibited excellent oxidation/corrosion resistance over the course of 6000 h of engine testing (Fig. 3). In contrast, alloy OC-1 was susceptible to internal oxidation and nitridation of Al, which resulted in Fe-rich oxide nodules and poor oxidation resistance. This attack was evident after only 1500 h of engine testing (Fig. 3), with more extensive attack accompanying the longer engine exposures (6000 h sample shown in Fig. 3).

Fig. 4 shows electron probe microanalysis (EPMA) measurements of Al concentration at the oxide-alloy interface inward for engine tested OC-1, OC-2, and OC-4 coupons. For alloy OC-1, analysis was conducted in regions of continuous alumina away from areas where internal attack of Al/Fe-rich oxide nodules were evident. This was possible for the 3000 h exposed sample; however, some internal attack of Al was evident in the region analyzed from the 4500 h sample. All three OC alloys showed depletion of Al at the alloy-oxide interface, generally increasing with engine test time. This is due to consumption of Al from the alloy to form alumina. The depth of Al depletion was shallow, on the order of only ~2-3 microns. Composition profiles were also obtained for other base alloy constituents, Cr, Ni, etc., with essentially no depletion evident (data not shown in Fig. 4).

It is not clear if Al depletion was the trigger for the internal attack of Al observed in alloy OC-1. Little Al depletion was evident in the 3000 h engine test data (Fig. 4a), for which regions of internal attack were observed. Significant depletion of Al was evident in the 4500 h OC-1 sample; however, the data was obtained in a region where internal attack of Al had occurred and the depletion evident may be a consequence of the internal attack rather than the trigger. For alloys OC-2 and OC-4 the concentration of Al at the oxide-alloy interface was clearly depleted, but the depth of depletion was so shallow even after ~6000 h that this may not be an issue for long-term durability in this application, especially given that the engine tests were conducted at elevated TET.

Fig. 5 shows oxidation data for alloys OC-1, OC-2, and OC-4 conducted in laboratory testing at ORNL at 700-800°C in air with 10% H₂O. These results mirror the trends observed in the engine testing. At 700°C in air with 10% H₂O, alloy OC-1 exhibited a transition to Fe-oxide nodule formation and scall spallation/mass loss after ~2500 h of exposure. In contrast, both OC-2 and OC-4 showed low mass gains and excellent oxidation resistance out to 7000 h of exposure conducted. Increasing the temperature to 800°C increased the susceptibility to attack, with alloy OC-1 exhibiting a transition to mass loss after < ~500 h of exposure and alloy OC-2 after ~1500

h. The alloy OC-4 sheet sample showed low mass gains and excellent oxidation resistance out to ~7500 h of exposure conducted. (It should be noted that in testing under other programs, OC-4 has exhibited mixed results at 800°C in air with 10% H₂O, with some samples showing excellent oxidation resistance but one plate sample showing attack after ~2500 h of exposure).

From these results, the alloys rank in order of oxidation resistance from least to most as OC-1, OC-2, and OC-4. The primary differences are an increase in Ni content from 20 wt.% in alloy OC-1 to 25 wt.% in alloys OC-2 and OC-4. Relative to alloy OC-2, alloy OC-4 has a higher Nb level, 2.5 wt.% Nb vs 1 wt.%, and a higher Al level, 3.5 wt.% Al vs 3 wt.%. These findings follow composition-oxidation trends observed in other AFA alloys [2].

References

1. W.J. Mathews, "Long-Term Microturbine Exposure of an Advanced Alloy for Microturbine Primary Surface Recuperators", Proceedings of ASME Turbo Expo 2008, June 9-13, 2008, Berlin, Germany, GT2008-50037.
2. M. P. Brady, Y. Yamamoto, M. L. Santella and L. R. Walker, "Composition, Microstructure, and Water Vapor Effects on Internal/External Oxidation of Alumina-Forming Austenitic Stainless Steels, Oxidation of Metals, Volume: 72 Issue: 5-6 Pages: 311-333 DEC 2009

Subject Inventions (As defined in the CRADA)

No new intellectual property (IP) was generated under this CRADA.

Commercialization Possibilities

The results obtained under this CRADA indicate promising potential for use of AFA alloys as a gas turbine recuperator material. Negotiations are in progress for licensing of the AFA alloys with a commercial alloy producer, which would make the material available to turbine manufacturers such as CTC.

Plans for Future Collaboration

ORNL is currently pursuing trial scale-up of OC-4 in foil form suitable for manufacture of test recuperator components. Follow-on projects will be pursued with CTC for engine evaluation of this OC-4 foil when available.

Conclusions

- 1) AFA stainless steels show good promise for use in gas turbine recuperators.
- 2) Alloy OC-4 shows the greatest level of oxidation resistance in air with 10% H₂O and good resistance over 6000 h of elevated temperature TET engine testing.

3) Further study of local Al depletion in the AFA alloys resulting from oxidation is needed to better delineate what extent and depth of Al depletion is an issue for long term ($>> 10,000$ h) durability in turbine recuperator applications.

Acknowledgements

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Fig. 1- Recuperator with Removable Aft Dome [1].

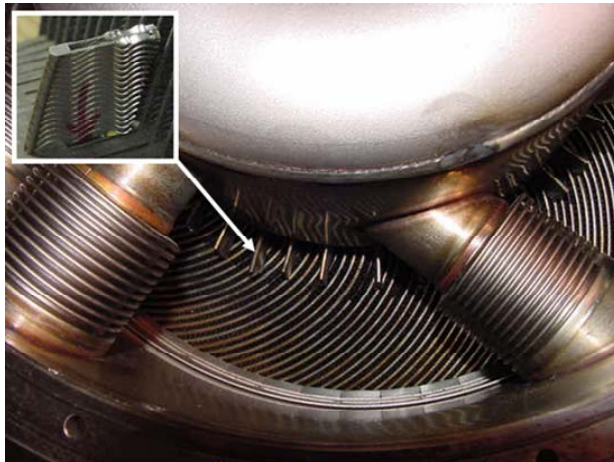


Fig 2- Steady-state elevated TET engine testing - Tack-welded sample shown inset [1].

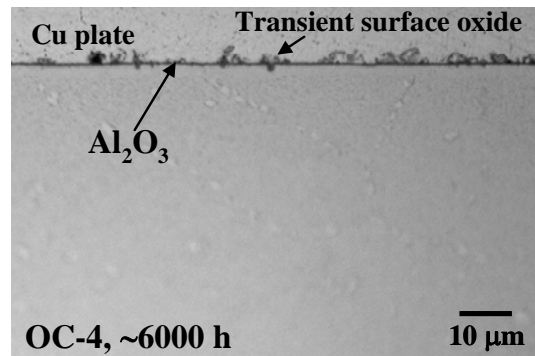
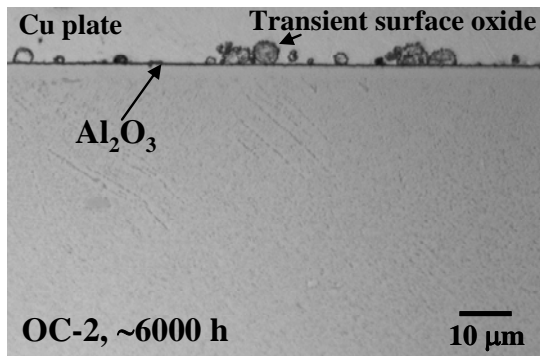
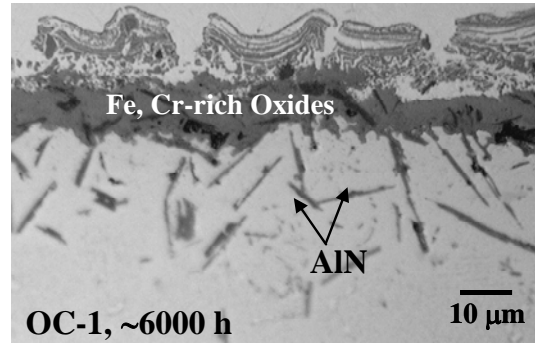
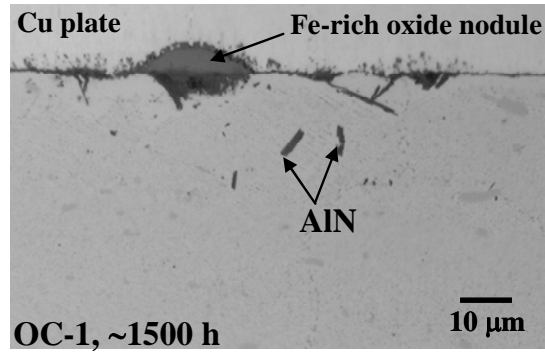


Fig. 3- Light microscopy cross-sections of OC-1, OC-2, and OC-4 after steady-state elevated TET engine testing. Occasional transient surface oxide particles were observed on OC-2 and OC-4. These tend to be Mn- and Nb- rich oxides, and, unlike the Fe-oxide nodules formed on OC-1, they are undercut by continuous alumina.

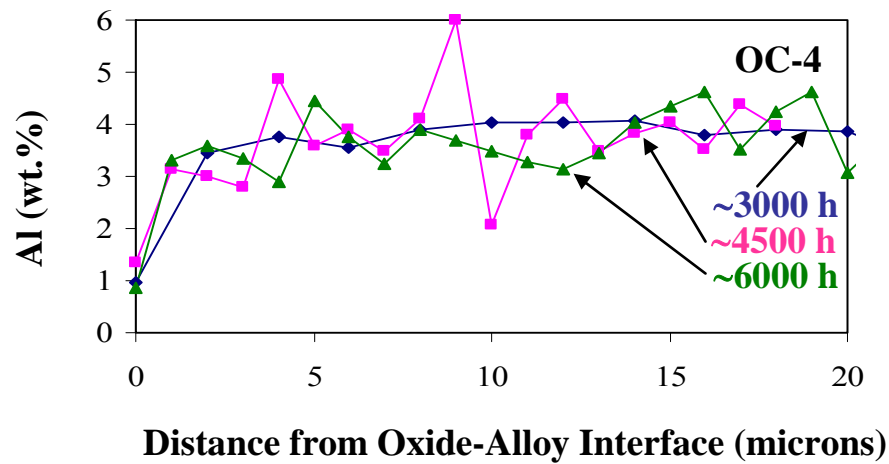
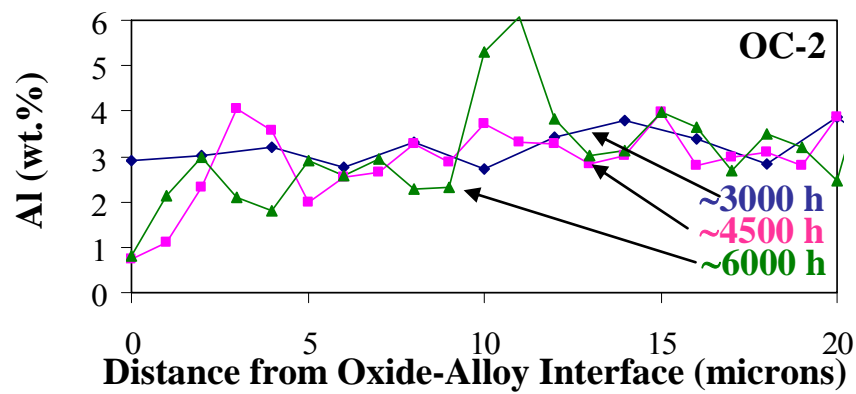
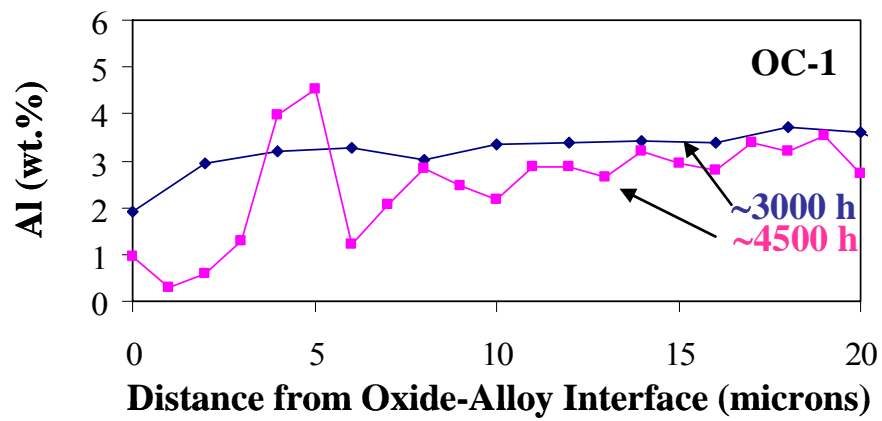


Fig. 4- Al concentration measured by EPMA at the oxide-alloy interface inward into the alloy for OC-1, OC-2, and OC-4 after steady-state elevated TET engine testing.

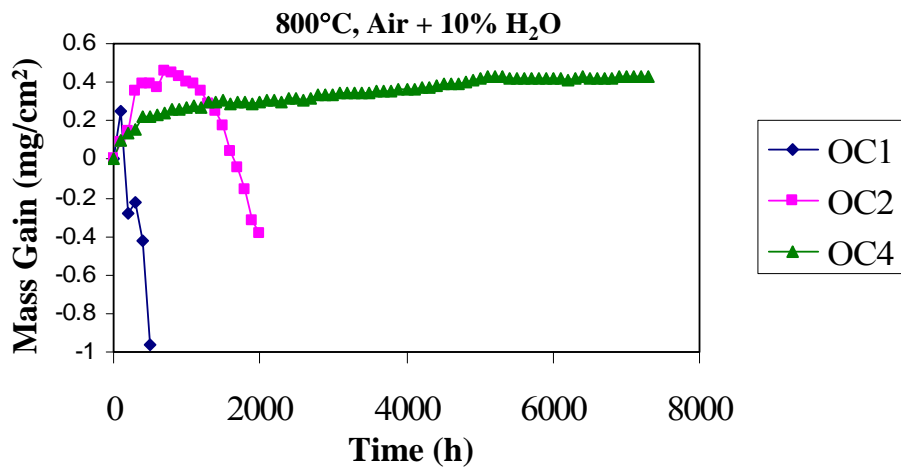
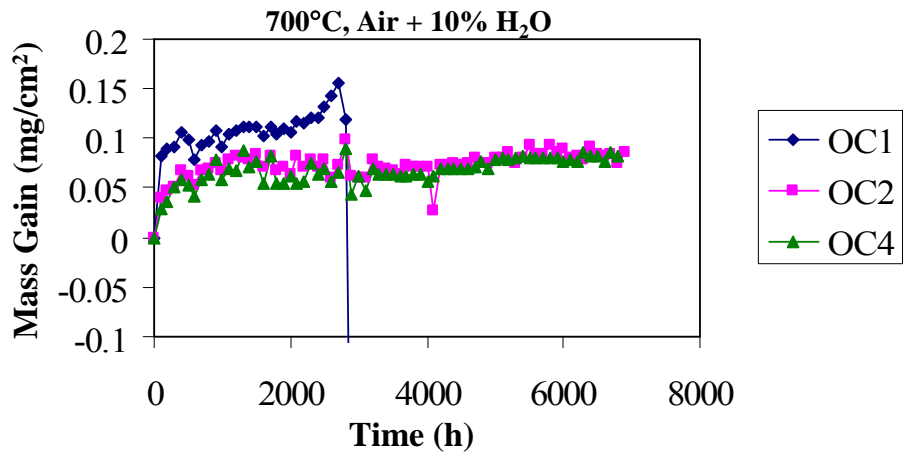


Fig. 5- Specific mass gain in at 700-800°C air with 10% H₂O for OC-1, OC-2, and OC-4 sheet samples from same material batch as was exposed in the steady-state elevated TET engine testing.