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CRADA Final Report
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Evaluation of Alumina-Forming Austenitic Stainless Steel Alloys in Industrial Gas Turbine

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Abstract

Oak Ridge National Laboratory (ORNL) and Solar Turbines Incorporated (Solar) 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 industrial gas turbine recuperator components. ORNL manufactured lab scale foil of three different AFA alloy compositions and delivered them to Solar for creep properties evaluation. One AFA composition was selected for a commercial trial foil batch. Both lab scale and the commercial trial scale foils were evaluated for oxidation and creep behavior. The AFA foil exhibited a promising combination of properties and is of interest for future scale up activities for turbine recuperators. Some issues were identified in the processing parameters used for the first trial commercial batch. This understanding will be used to guide process optimization of future AFA foil material production.

Statement of Objectives

Recuperated gas turbines are able to achieve higher efficiencies than simple cycle engines operating at similar firing temperatures because they utilize the waste heat exiting the turbine exhaust to contribute to preheating the air from the compressor, thereby conserving fuel for the combustion process. An additional benefit is that these turbines can be run using opportunity fuels such as landfill gas, which would eliminate a significant source of greenhouse gas emission. 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 NOx emissions. Durability requirements for the higher operating temperatures (~650°C) of state-of-the-art recuperated engines have necessitated a change of material from inexpensive type 347 Fe-base austenitic stainless steels, typically used in previous generations of recuperated gas turbines, to alloys containing a higher Ni content, such as Ni-base Inconel 625 to achieve the desired recuperator life goals. The rising cost of Ni, which was only $2-3/lb in the year 2000 but is now $9-20/lb, has rendered alloys with higher Ni content less attractive. This situation is challenging the economic viability and potential for market penetration of these high-efficiency recuperated gas 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. They also show potential for the good creep resistance needed for industrial gas turbine recuperator designs (recuperators made from thin alloy foils in the 3-4 mil thick range, 0.08 to 0.1 mm). The goal of this CRADA was to manufacture and assess foil form of ORNL AFA alloys under high-temperature oxidation and creep resistance conditions relevant to industrial gas turbines.

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, creep resistance, 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. They also utilize nanoscale NbC precipitates to achieve a high degree of creep resistance. 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, as well as reductions in environmental emissions. This CRADA effort is devoted to evaluation of AFA alloys for recuperator components in high efficiency, low emission industrial turbines, an application that is highly relevant to the DOE Energy Efficiency and Renewable Energy **(**EERE) goals of reduction of greenhouse gas emissions and improved energy efficiencies.

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

This material was further processed at ORNL by cold rolling and solution treating at 1200°C to manufacture laboratory scale 4 mil (~0.1mm) thick foil for property evaluation (Fig. 1a). Based on properties obtained (oxidation and creep details to be presented), alloy OC-4 was downselected for a commercial foil trial batch (Fig. 1b). At this exploratory stage, 5-20 lb quantities of OC-4 were manufactured by a commercial foil vendor to thicknesses of 3.2 mil (~0.8mm) and 4.2 mil (~0.1mm) in 6-7" widths. This width is not sufficient for trial recuperator component manufacture, but can be used for oxidation and creep evaluation.

The commercial trial OC-4 foil had a dull surface finish. Scanning electron microscopy (SEM) cross-section characterization (Fig. 2) indicated Al-oxide and Al-nitride were present at the surface. This was likely the result of inadequate surface cleanup at intermediate annealing stages, and the inadvertent use of nitrogen cover gas at the inlet/outlet areas of the hydrogen annealing line. AFA alloys can be very reactive to nitrogen, with formation of AlN detrimental to both oxidation and creep resistance, and require well controlled bright annealing conditions with argon cover gas used at hydrogen annealing inlet/outlet areas. Based on these observations, process parameters and intermediate annealing stage surface cleaning operations for future AFA foil batches will be modified. Despite this surface contamination, the commercial trial OC-4 foil still exhibited yield strengths of 40-44 ksi, ultimate tensile strengths of 97-100 ksi, and elongation in the 26-32% range. The grain size number was 7.5, which equates to a grain diameter of ~27 microns. (For comparison, grain diameters of the lab scale foils were: OC-1: 31 microns, OC-2: 92 microns, and OC-4: 45 microns).

Oxidation data at 700-800°C in air with 10% H_2O (100 h cycles) for lab scale OC-1, OC-2, and OC-4 foils and the trial commercial 3.2 and 4.2 mil OC-4 batches are shown in Fig. 3. Anticipated turbine operating temperatures are in the range of ~650-700°C, so 700-800°C lab scale evaluation in air with 10% H_2O is considered an aggressive screening test. At 800°C in air with 10% H_2O, the OC-1 foil showed rapid mass gains and Fe-base oxide formation (Fig. 3a). Similar poor oxidation behavior was observed for the OC-2 foil within the first 1000 h of exposure under this condition. In contrast, the OC-4 lab scale foil exhibited low mass gains and excellent oxidation resistance out to 10,000 h of total exposure (Fig. 3b). At 700°C in air with 10% H_2O, the OC-1 lab scale foil exhibited good oxidation resistance out to 5000 h of exposure, at which point a transition to nonprotective Fe-base oxide nodule formation was observed. Both the OC-2 and OC-4 lab scale foil exhibited low mass gains and excellent oxidation resistance at 700°C in air with 10% H_2O. These trends are consistent with previously observed composition-oxidation trends in the AFA alloy family, where increased levels of among Al, Cr, Nb, and Ni were linked with improved oxidation resistance (in this case, the lower level of Ni in OC-1 was likely the cause for its reduced oxidation resistance compared to OC-2 and OC-4) [1-2]. The excellent long-term oxidation resistance of the OC-4 lab scale foil at 800°C in air with 10% H_2O

is superior to not only 347 alloy foils, but also advanced austenitic variations of commercial 20-Ni foil (Fe-25Ni-20Cr+Nb wt.% base alloy 709 type material) and alloy 120 alloys (Fe-27Ni-25Cr wt.% base) foils [3].

Oxidation data at 700-800°C in air with 10% H_2O (100 h cycles) for the trial foil batches of OC-4 are shown in Fig. 3c. Although the mass gains for the initial transient oxidation stages for the 3.2 and 4.2 mil OC-4 trial commercial foil were higher than for the lab scale OC-4 foil, stable and excellent oxidation resistance was still observed. The increased initial transient mass gain was attributed to the near-surface region of Al-nitride/Al-oxide contamination in the commercial foils (Fig. 2).

Screening creep data (conditions proprietary) for the OC-1, OC-2, and OC-4 lab scale foils are shown in Fig. 4. The creep resistance of the lab scale foils was comparable, but with a somewhat higher primary creep regime for alloy OC-4. For comparative purposes, data is also shown for some developmental alloy 709 (20Cr-25Ni + Nb) foils. Under these accelerated test conditions, all of the AFA OC lab scale foils showed superior creep resistance. Additional creep data for the lab scale OC-1, OC-2, and OC-4 and trial commercial batch of OC-4 foil are shown in Fig. 5 (data from references 3 and 4; data obtained from a DOE EERE ITP project and not under the present CRADA effort). At 677°C and 117 MPa, the OC-4 lab scale foil exhibited superior creep resistance to the OC-1 and OC-2 foils. Similar trends were observed at the very aggressive screening condition of 750°C and 100MPa.

The 3.2 and 4.2 mil trial commercial OC-4 foil exhibited a similar creep rupture lifetime to the OC-4 lab scale foil (Fig. 5). However, the secondary creep rate was higher in the commercial batch than the lab scale foil. The reasons for this behavior difference are under investigation, but may be related to differences in solutionizing temperature and/or residual cold work between the lab scale and commercial batches. Further comparisons with commercial alloy 709 and 120 foils [3,4] suggest that at high temperature/high load conditions such as 750°C and 100MPa, the AFA OC-4 foil exhibits moderately inferior creep resistance. At 700°C and below, preliminary findings suggest OC-4 may exhibit superior, lower secondary creep rates. The improved behavior of OC-4 at temperatures below 700°C is under investigation and may be related to metastable γ'phase precipitate formation increasing creep resistance at the lower temperatures. Further study of this behavior pattern is needed, and minor modification of OC-4 composition may be beneficial to optimize creep behavior. Overall, the combination of oxidation and creep resistance of the OC-4 foil shows good promise for use in turbine recuperators.

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2. M.P. Brady, K.A.Unocic, M.J. Lance, M.L. Santella, Y. Yamamoto, and L.R. Walker, "Increasing the Upper Temperature Oxidation Limit of Alumina Forming Austenitic Stainless

Steels in Air with Water Vapor," Oxidation of Metals, Volume 75, Numbers 5-6, 337-357 (2011).

3. B.A. Pint, M.P. Brady, Y. Yamamoto, M.L. Santella, P.J. Maziasz, W.J. Matthews, "Evaluation of Alumina-Forming Austenitic Foil for Advanced Recuperators," Journal Of Engineering For Gas Turbines And Power-Transactions of the ASME, Volume: 133 Issue: 10 Article Number: 102302 (Oct 2011).

4. B.A. Pint, M.P. Brady, Y. Yamamoto, K.A. Unocic, W. Matthews, "Evaluation of Commercial Alumina-Forming Austenitic Foil for Advanced Recuperators", Proceedings of GT2011 ASME Turbo Expo 2011: Power for Land, Sea, and Air, June 6-10, 2011, Vancouver, Canada (2011).

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. The AFA alloy family has been licensed to a commercial alloy producer, Carpenter Technology Corporation.

Plans for Future Collaboration

ORNL is currently pursuing trial scale-up of OC-4 with commercial foil vendors to manufacture material in appropriate widths and volumes suitable for manufacture of test recuperator components.

Conclusions

1) AFA stainless steels show good promise for use in gas turbine recuperators.

2) Commercial scale processing of AFA foil is possible, but requires better control of annealing atmospheres than conventional stainless steel foils.

3) Alloy OC-4 shows an attractive combination of oxidation and creep resistance. However, this composition may need further modification to optimize microstructure stability for creep resistance.

Acknowledgements

This work was funded under the DOE EERE Commercialization and Deployment program. ORNL is managed by UT-Battelle, LLC for the US DOE under contract DE-AC05-00OR22725.

a)

b)

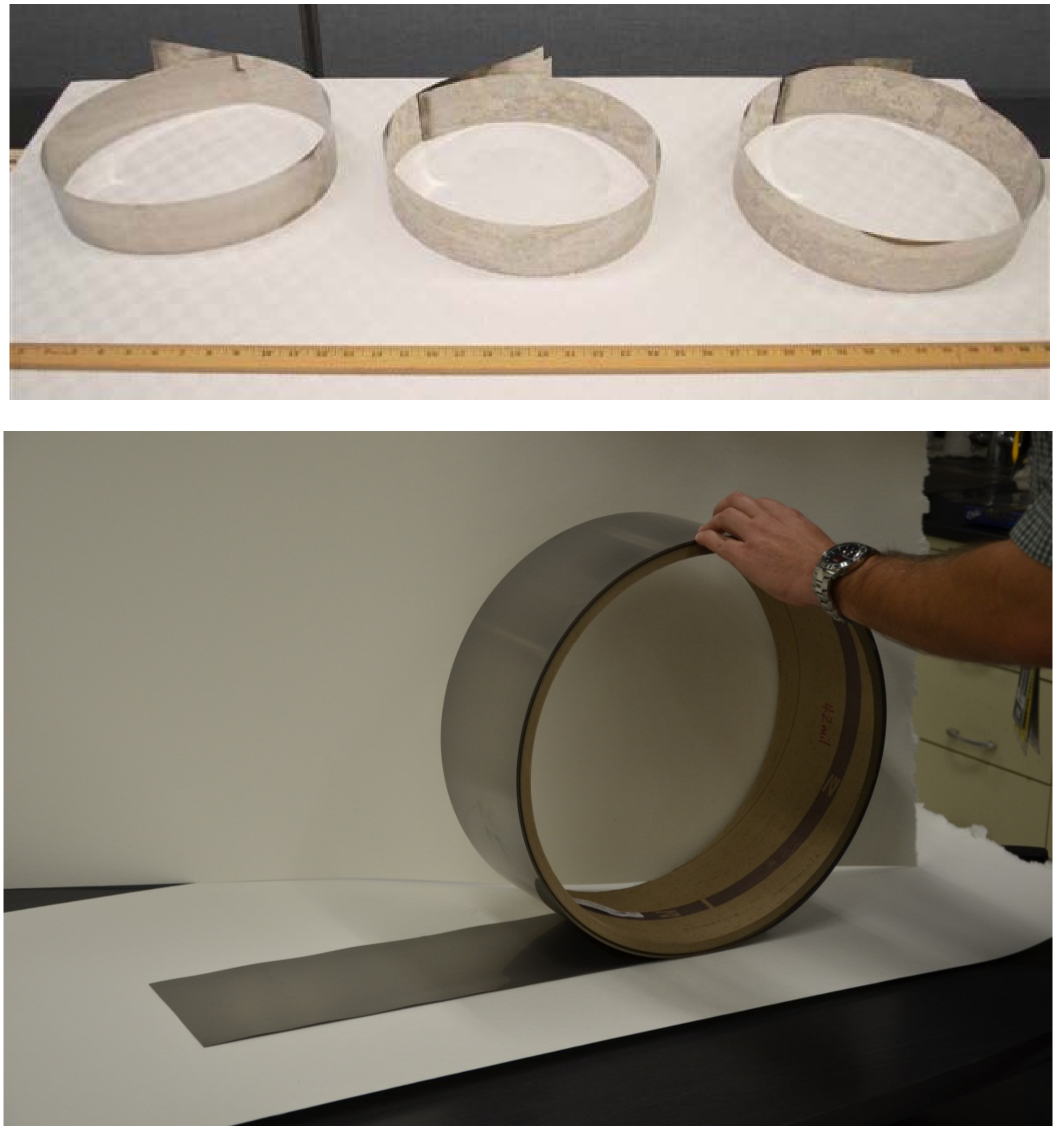

Fig. 1- Lab scale foil (a) for OC-1, OC-2, and OC-4 and (b) trial commercial vendor foil of OC-4. Lab scale foil from companion CRADA with Carpenter Technology Corporation, CRADA NFE-08-01374 Manufacture of Alumina-Forming Austenitic Stainless Steel Alloys by Conventional Casting and Hot-Working Methods.

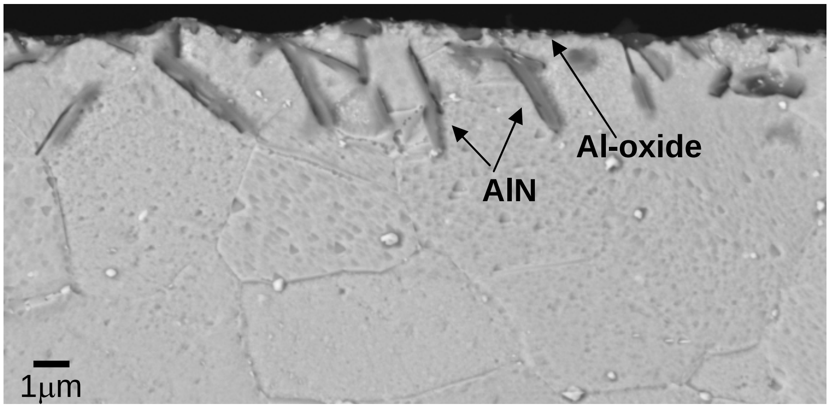

Fig. 2- Cross-section scanning electron microscopy backscatter electron image of as-received trial commercial 4.2 mil OC-4 foil showing local surface O/N contamination.

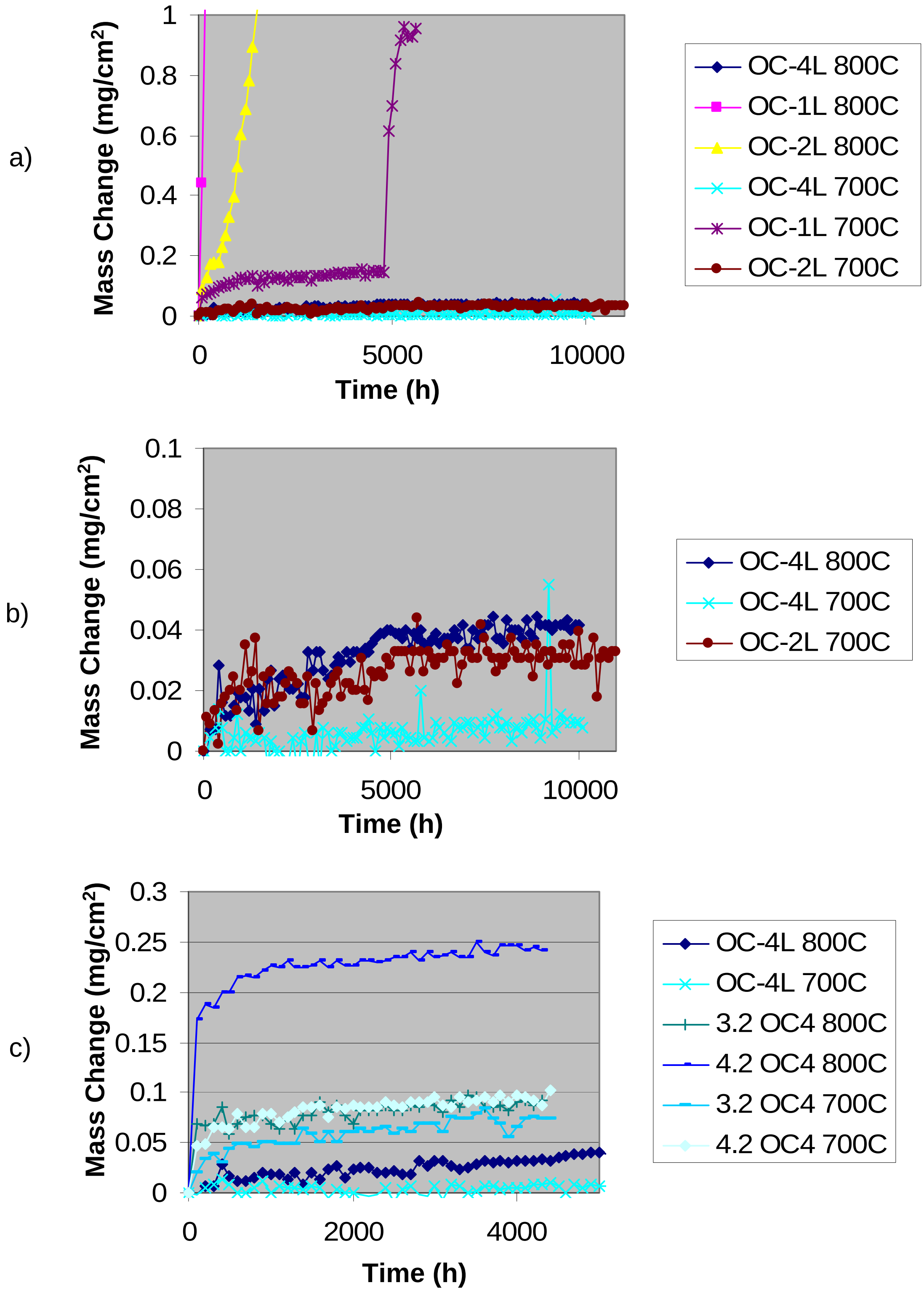

Fig. 3- Oxidation data for lab scale and trial scale foils at 700 or 800°C in air with 10% H_2O.
a) Lab scale foils (marked by L); b) same data as shown in (a) at different scale;
c) commercial Trial 3.2 and 4.2 mil OC-4 foil, OC-4 Lab foil from figures (a,b).

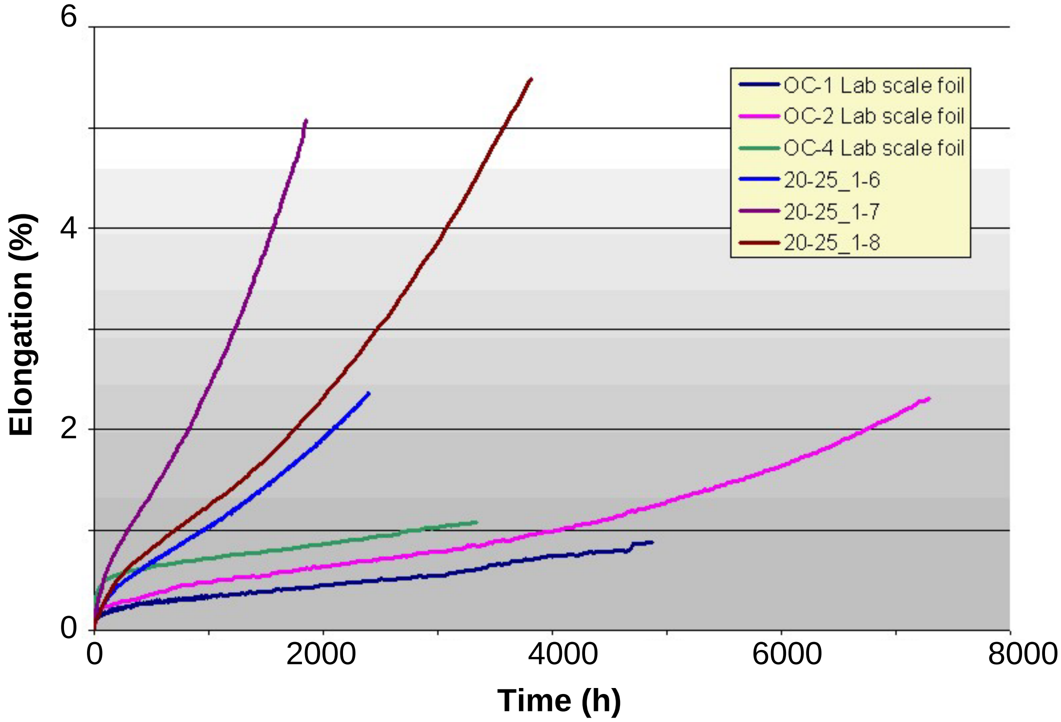

Fig. 4- Creep data for lab scale OC foil (conditions proprietary) compared to several variations of commercial 20-25 foil (Fe-25Ni-20Cr+Nb alloy 709 type material). Samples not tested to rupture.

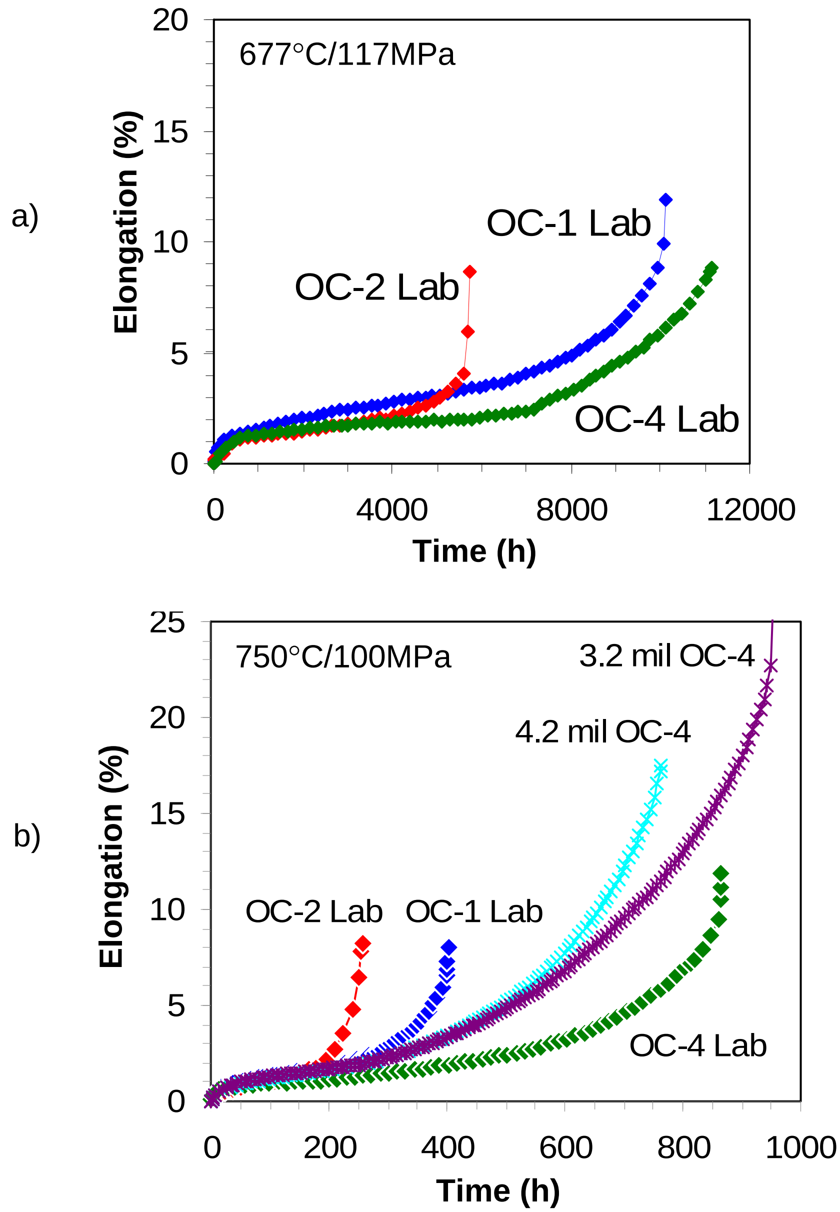

Fig. 5- Creep data [3,4] for lab scale foil at 677°C and 117 MPa (a) and at 750°C and 100 MPa (b) along with data for the trial commercial 3.2 or 4.2 mil OC-4. Note that this data was obtained under a DOE EERE ITP project, not the present CRADA. OC-4 data in (a) was stopped prior to rupture due to a power outage.