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CRADA Final Report
For
CRADA Number
NFE-10-02715

Assessment of AFA Stainless Steels for Tube Products

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CRADA CRADA No. NFE-10-02715 Assessment of AFA Stainless Steels for Tube Products in Chemical Processing and Energy Production Applications

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CRADA No. NFE-10-02715 Assessment of AFA Stainless Steels for Tube Products in Chemical Processing and Energy Production Applications

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Work performed July 2008-Jan 2009

Abstract

Oak Ridge National Laboratory (ORNL) and Carpenter Technology Corporation (Carpenter) 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 assess material properties of several potential AFA family grades and explore the feasibility of producing alumina-forming austenitic (AFA) stainless steels in tubular form needed for many power generation and chemical process applications. Carpenter's Research Laboratory successfully vacuum melted 30lb heats of seven candidate AFA alloy compositions representing a wide range of alloy content and intended application temperatures. These compositions were evaluated by ORNL and Carpenter R&D for microstructure, tensile properties, creep properties, and oxidation resistance. In parallel, additional work was directed toward an initial tube manufacture demonstration of a baseline AFA alloy. Carpenter successfully manufactured a 10,000lb production heat and delivered appropriate billets to a partner for extrusion evaluation. Tube product was successfully manufactured from the baseline AFA alloy, indicating good potential for commercially produced AFA tubular form material.

Statement of Objectives

AFA alloy development efforts to date have been focused on plate, sheet, and foil product forms. However, the largest potential market and greatest potential energy savings impact for AFA alloys is likely as a material of construction for tubing in chemical and process industry, power generation, etc. applications. The goal of this ORNL-Carpenter CRADA was to 1) assess materials properties for several potential AFA alloy family grades of interest for tubing applications and 2) establish the viability for manufacturing AFA alloys in tubular product form.

Benefits to the Funding DOE Office's Mission

The ORNL AFA stainless steels are a new class of high-temperature alloys with a ≥ 50-200°C (~100-400°F) increase in 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. Thus, they are highly relevant to the DOE EERE program mission.

Technical Discussion of Work Performed by All Parties

Seven ~ 30 lb. vacuum induction melted (VIM) AFA alloy heats were cast and processed to plate form by Carpenter R&D following procedures developed under CRADA NFE-08-01374 Manufacture of Alumina-Forming Austenitic Stainless Steel Alloys by Conventional Casting and Hot-Working Methods with Carpenter Technology Corporation. The final solution anneal temperature was 1200°C, followed by water quenching, unless otherwise specified. Alloy chemistries are shown in Table 1. Alloys OC-5, 6, and 7 are variations of the baseline AFA grade OC-4 alloy, alloy OC-10 is a low Ni AFA grade, and alloy OC-11 is a rare earth modified (Y) AFA grades. Alloys OC-8 and OC-9 are developmental high alloy content modified AFA grade, compositions for these alloy are currently considered proprietary.

Table 1- Heat Analyses of experimental AFA Alloys OC5 – OC-11 (composition details for alloys OC-8 and OC-9 are considered proprietary at this time). Composition data is also presented for baseline AFA alloy OC-4.

Heat No	001597 OC-4*	001918 OC-5	001919 OC-6	001920 OC-7	001923 OC-10	001924 OC-11
C	.101	.106	.114	.112	.114	.115
Mn	1.97	1.99	1.99	1.92	6.96	2.04
Si	.14	.13	.13	.13	.13	.13
P	.013	.018	.022	.020	.010	.026
S	.0009	.0008	.0009	.0009	.0022	.0006
Cr	13.96	13.84	13.84	13.80	13.85	14.85
Ni	25.03	25.02	25.04	25.08	12.18	25.06
Mo	1.98	2.00	.18	1.98	.15	2.00
Cu	.51	.51	.51	.52	3.10	.12
W	.95	.96	.16	.96	.15	.14
V	.04	.05	.05	.05	.05	.05
Ti	.05	.05	.05	.05	.05	.05
Al	3.55	3.06	3.56	3.59	2.54	4.16
Nb	2.53	1.02	2.51	2.50	1.02	2.50
B	.0008	.0078	.0080	.0085	.0086	.0078
N	< .00010	<.001	.0010	.0010	.0017	.0010
Zr	-----	-----	-----	.16	-----	----
Hf	-----	-----	-----	-----	-----	.21
Y	-----	-----	-----	-----	-----	.0120
Fe	Bal	Bal	Bal	Bal	Bal	Bal

*OC-4 alloy from CRADA NFE-08-01374 Manufacture of Alumina-Forming Austenitic Stainless Steel Alloys by Conventional Casting and Hot-Working Methods with Carpenter Technology Corporation

Tensile properties for the OC-4 – OC-11 alloys are shown in Table 2. Room-temperature tensile properties for the alloys (except for OC-10) were comparable, with yield strengths (YS) in the ~250-300MPa range, ultimate tensile strengths (UTS) in the ~650-700MPa range, elongations (EL) on the order of ~50%, and reduction in area (RA) of ~50-70%. The low Ni content OC-10 alloy exhibited moderately lower YS and UTS, although with comparable EL and RA to the other alloys. At 760°C, alloys OC-4, 5, 6, 7, 10, and 11 exhibited comparable YS values, only moderately lower than observed at room temperature. However, UTS values at 760°C were reduced to about ½ the room temperature values. Good ductility, as measured by EL and RA, were observed at 760°C. In contrast, the YS and UTS of alloys OC-8 and OC-9 were significantly greater than that observed at room temperature, due to strengthening phase precipitation. The increased strength at 760°C for OC-8 and OC-9 was, however, accompanied by reduced levels of EL and RA.

Table 2- Tensile properties. OC-4 comparison data from 400 lb VIM/VAR heat pursued under a DOE EERE ITP project, not the present CRADA.

	Alloy	OC-4	OC-5	OC-6	OC-8	OC-9	OC-10	OC-11
Test Temp	Tensile Properties	Test Results						
Room	0.2%YS(MPa)	265	248	269	276	273	232	290
760°C		245	225	225	443	435	214	256
Room	UTS (MPa)	655	637	663	683	658	596	674
760°C		332	323	316	536	543	294	352
Room	%El	50.3	49.6	48.7	50.5	50.7	46.6	48.7
760°C		*	87.8	81.7	25.4	18.6	42.6	51.0
Room	%RA	56.4	64.6	61.7	61.5	50.8	68.8	55.8
760°C		73.4	82.9	80.8	29.6	20.3	45.1	51.8

*broke in fillet of test sample

Creep rupture properties for select OC-4 - OC-10 alloys are shown in Table 3. Alloy OC-5 exhibited superior creep rupture life at 750°C and 100MPa, consistent with composition-creep property studies in the AFA alloys system, which have shown that optimum creep resistance occurs with Nb levels in the 1 wt.% range, although higher levels of Nb (typically in the 2-3 wt.% range are needed for optimum oxidation resistance [1,2]. At 700°C/170MPa and 650°C/250MPa, alloy OC-5 also exhibited good creep resistance. Alloy OC-6, which is essentially OC-4 without costly Mo and W additions, showed degraded creep resistance above 700°C compared with OC-4, but better creep resistance at 650°C. The source of this behavior trend is under investigation, but for applications < 700°C it may be advantageous to use lower Mo, W alloy content AFA compositions (Mo and W are costly additions). The low Ni content OC-10 alloy, which also does not contain Mo and W additions, exhibited adequate creep resistance at 650-700°C, suggesting this grade, which is anticipated to be less significantly less costly than the other AFA grades, may be of interest for lower temperature applications. Interestingly, alloys OC-8 and OC-9 exhibited ½ the creep rupture life of OC-5 at 750°C and 100MPa, but significantly (> 3x) improved creep rupture life over OC-5 at 650 and 700°C. The source of this increased creep strength by OC-8 and OC-9 is under investigation.

Table 3- Creep rupture test results. Comparison data for OC-4 from sub-sized screening test samples studied under a DOE EERE ITP program project, not the present CRADA.

	Alloy	OC-4	OC-5	OC-6	OC-8	OC-9	OC-10
Temp °C	Stress MPa	Results (Rupture Time and Ductility)					
750	100	614 h	1581 h 41.7%El 86.7%RA	329 h 60.3%El 87.4%RA	867 h 31.2%El 53.2%RA	694 h 17.0%El 21.9%RA	522 h 3.2%El 7.0%RA
700	170	254 h	611 h 40%El 83%RA	384 h 47.6%El 83.4%RA	2513 h* 10.4%El 17% RA	1492 h 4.9%El 7.0%RA	264 h 8.5%El 14.8%RA
650	250	690 h	1314 h 43.5%El 77.1%RA	1108 h 50.0%El 56.2%RA	**3300+h	**3300+h	499 h 11.7%El 17.0%RA

* Broke in fillet of test sample
** test ongoing

High temperature oxidation testing was conducted for selected OC AFA alloys under a range of conditions, including sulfidation-oxidation at 550 and 650°C (Fig. 1), metal dusting at 550 and 650°C (Fig. 2), steam at 17bar and 900°C (Fig. 3), and air with 10 volume % water vapor at 650 and 800°C (Fig. 4). Comparison data for select commercial heat-resistant Fe- and Ni- base alloys are also shown. These exposures leveraged existing efforts and limited test furnace openings under other DOE funded programs at ORNL (details in figure captions).

The sulfidation-oxidation conditions (Fig. 1) are relevant to petrochemical crude refining and hydro-treating and were quite aggressive, as evidenced by the extensive materials loss incurred by many of the alloys. For these tests, resistance was assessed by measurement of intact metal remaining after exposure, normalized to one sample face thickness loss in microns. Compared to the commercial alloys, OC-5 and OC-6 exhibited promising levels of resistance in this screening sulfidation-oxidation test. Also shown for comparison purposes is the proprietary OC alloy OC-E, which showed the best sulfidation-oxidation resistance among the AFA alloy family (evaluated under DOE EERE ITP program). It is interesting to note that a greater advantage over the commercial alloys by AFA alloys was observed at 650°C than 550°C, suggesting the possibility of sluggish Al-based protective oxide formation at lower temperatures.

In contrast, metal dusting conditions studied for 500 h at 550 and 650°C did not produce extensive attack of the samples, with the exception of 347H, OC-10 (650°C only), and OC-8 (550°C only) (Fig. 2). In general, although the OC AFA alloys exhibited better resistance to the metal dusting conditions than 347H, the resistance was inferior to that of the high-Ni commercial alloys HR6W, 601, and 693 in this screening test. The variation in AFA OC alloy resistance with composition does suggest the potential to optimize the AFA alloy family for this application. Longer term exposures of a range of AFA and commercial alloys under these conditions will be needed to better assess the degree to which AFA alloys are of interest for metal dusting conditions.

Three-thousand hour exposures at 900°C (17 bar) steam (a highly aggressive condition) generally showed good oxidation resistance for the OC AFA alloys (Fig. 3). The commercial Ni-base alloy 625 exhibited mass loss on the order of -0.5 to -1 mg/cm^2, while the commercial Ni-base alloys 602CA and 617 showed mass gains in the 1-1.5 mg/cm^2 range, indicating susceptibility to attack. The high-Ni alloy HR6W and 310 stainless steel exhibited moderately lower mass gain after 3000 h of exposure (~0.8 mg/cm^2). The best OC alloys, OC-6, OC-7, and OC-9, exhibited mass gains of ~0.5 mg/cm^2, suggestive of good behavior and comparable to the alumina-forming powder-metallurgical Fe-base alloys APMT. This behavior was superior to that observed for the baseline OC-4 alloy. The OC-5 alloy also exhibited good oxidation resistance under this aggressive test condition, despite it's lower Nb level which was optimized for creep resistance [1,2].

Figure 4 shows oxidation data for select OC AFA alloys in a simulated exhaust environment of air with 10% water vapor at 650 and 800°C. At 650°C, commercial super 304H stainless steel shows high mass gains indicative of susceptibility to attack. The low Ni alloy OC-10 showed good oxidation resistance with mass gains of only 0.1 mg/cm^2 after ~2000 h of exposure. Alloys OC-5 and OC-9 exhibited mass gains < 0.03 mg/cm^2 after ~2000 h of exposure, indicating excellent oxidation resistance. Promising oxidation resistance was also observed at 800°C in air with 10% water vapor for alloys OC-5,6,7,8,9, and 11. This temperature/water vapor condition is too high for the low Ni alloy OC-10 (data not shown) and conventional commercial stainless steels such as 347 or super 304H (data not sown) stainless steel.

The baseline alloy OC-4 was selected for the initial tube manufacture trial. Carpenter successfully manufactured a 10,000lb production heat and delivered appropriate billets from this material to a partner for extrusion evaluation. Gleeble hot working studies conducted by Carpenter R&D (Fig. 5) determined peak ductility occurred at 2000°F (1093°C) with marginal ductility starting at 2100F (1149C). The findings of the hot working study were used to guide the trial tube extrusion. Fig. 6 shows examples of successful AFA OC-4 tube produced under this manufacture trial. In general, it was concluded that the AFA OC-4 material is amenable to commercial tube manufacture. Further details of the hot working studies and tube trial are considered proprietary.

The optimum hot working temperature of ~1100°C for OC-4 is below the optimum solution annealing temperature of 1200°C. Fig. 7 shows results of a creep rupture life screening study of 1100 and 1200°C solutionized AFA OC alloys (all material initially solutionized at 1200°C, 1100°C treatment conducted for 30 minutes followed by air cooling). Creep resistance was significantly reduced under some conditions, particularly OC-5 and OC-10 at 750°C and OC-4 and OC-10 at 650°C. This finding suggests that some AFA OC alloy/application conditions may require a final anneal above 1100°C to obtain optimum creep properties if processed at lower temperatures. However, it should be noted that the data in Fig. 7 were obtained from laboratory scale plate samples and annealing protocols, and not under extrusion conditions encountered in tube manufacture. Creep and microstructure study of the OC-4 tube trial material is planned to further study this issue.

References

1. M.P. Brady, Y. Yamamoto, M.L. Santella, P.J. Maziasz, B.A. Pint, C.T. Liu, "The Development of Alumina-Forming Austenitic Stainless Steels for High-Temperature Structural Use, JOM, 60 (7), pp. 12-18 (2008).
2. Y. Yamamoto, M.P. Brady, M.L. Santella, H. Bei, P.J. Maziasz, B.A. Pint, "Overview of Strategies for High-Temperature Creep and Oxidation Resistance of Alumina-Forming Austenitic Stainless Steels," Metallurgical and Materials Transaction A, Volume 42, Number 4, pp. 922-931(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 good potential to commercialize the AFA stainless steels in tube product form. The AFA alloy family was licensed to Carpenter Technology Corporation in April 2011.

Plans for Future Collaboration

ORNL will continue to assist Carpenter Technology Corporation in AFA alloy scale-up activities.

Conclusions

1) AFA stainless steels are amenable to manufacture in tube product forms by industrially established processes.

2) A basis was established for selection of several candidate AFA composition ranges/grades for future scale up activities targeted to specific high temperature oxidation and creep conditions in a range of industrial applications.

Acknowledgements

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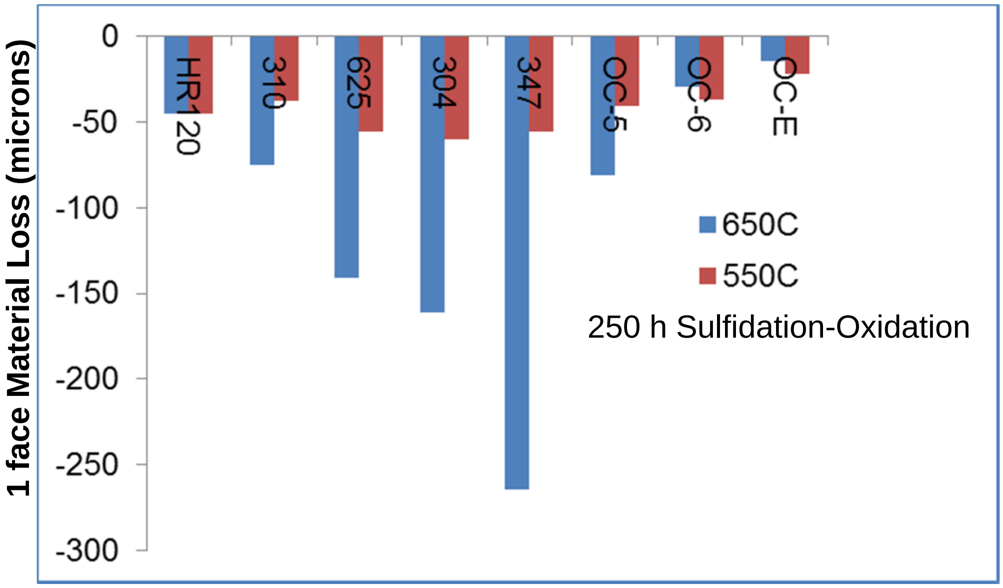


Fig. 1- Cross-section analysis of 1 face material loss for samples exposed for 250 h at 550°C and 650°C sulfidation-oxidation conditions of Ar-20% H_2-5%-H_2S-20% H_2O. Comparison commercial alloy data from DOE EERE ITP project, not the present CRADA.

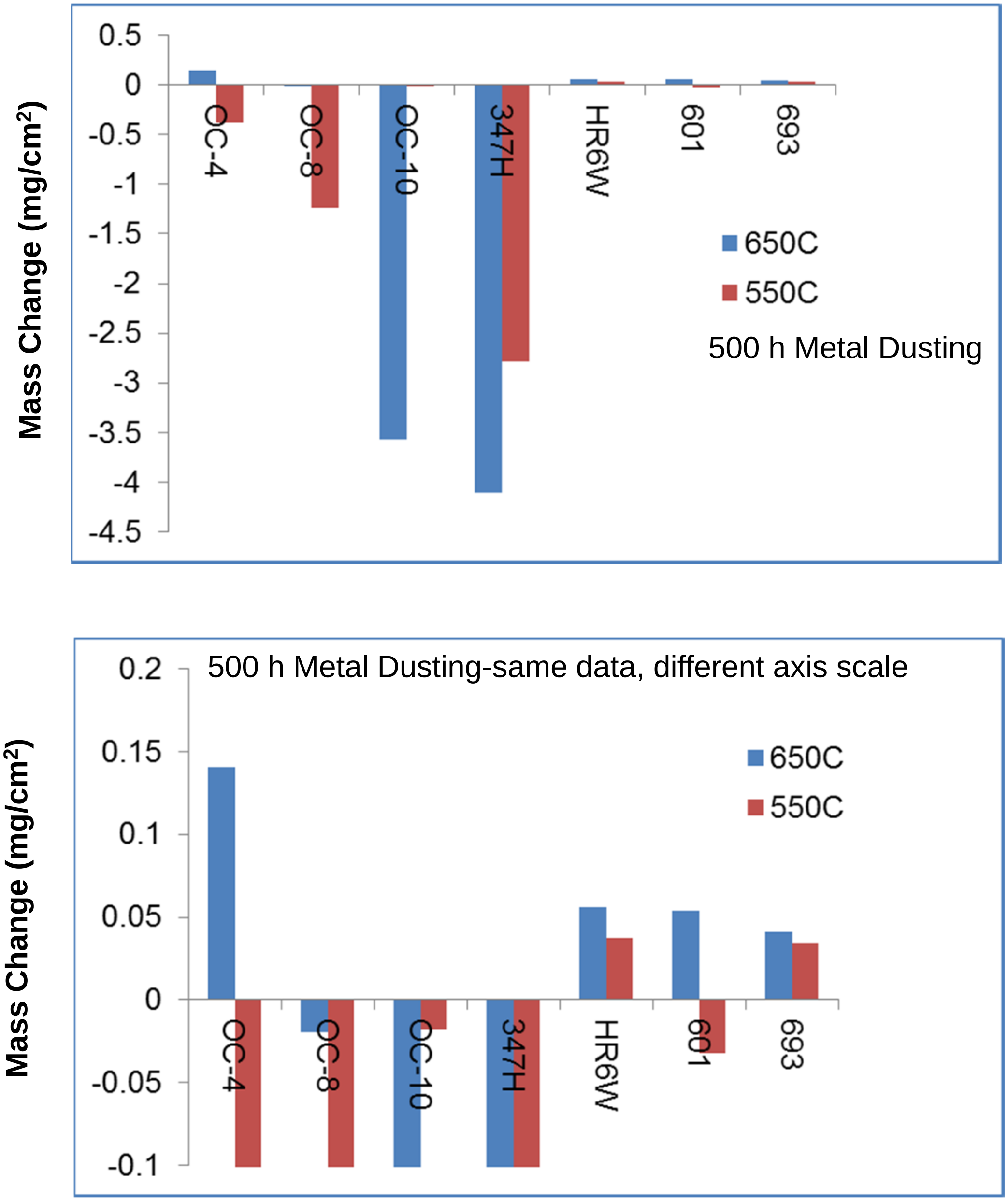


Fig. 2- Specific mass change of samples exposed for 500 h at 550°C (carbon activity of 69.4) and 650°C (carbon activity of 8.1) in a metal dusting environment of $59\%H_2$-$35\%CO$-$4\%H_2O$-$2\%CO_2$. Comparison commercial alloy data from DOE EERE ITP project, not the present CRADA.

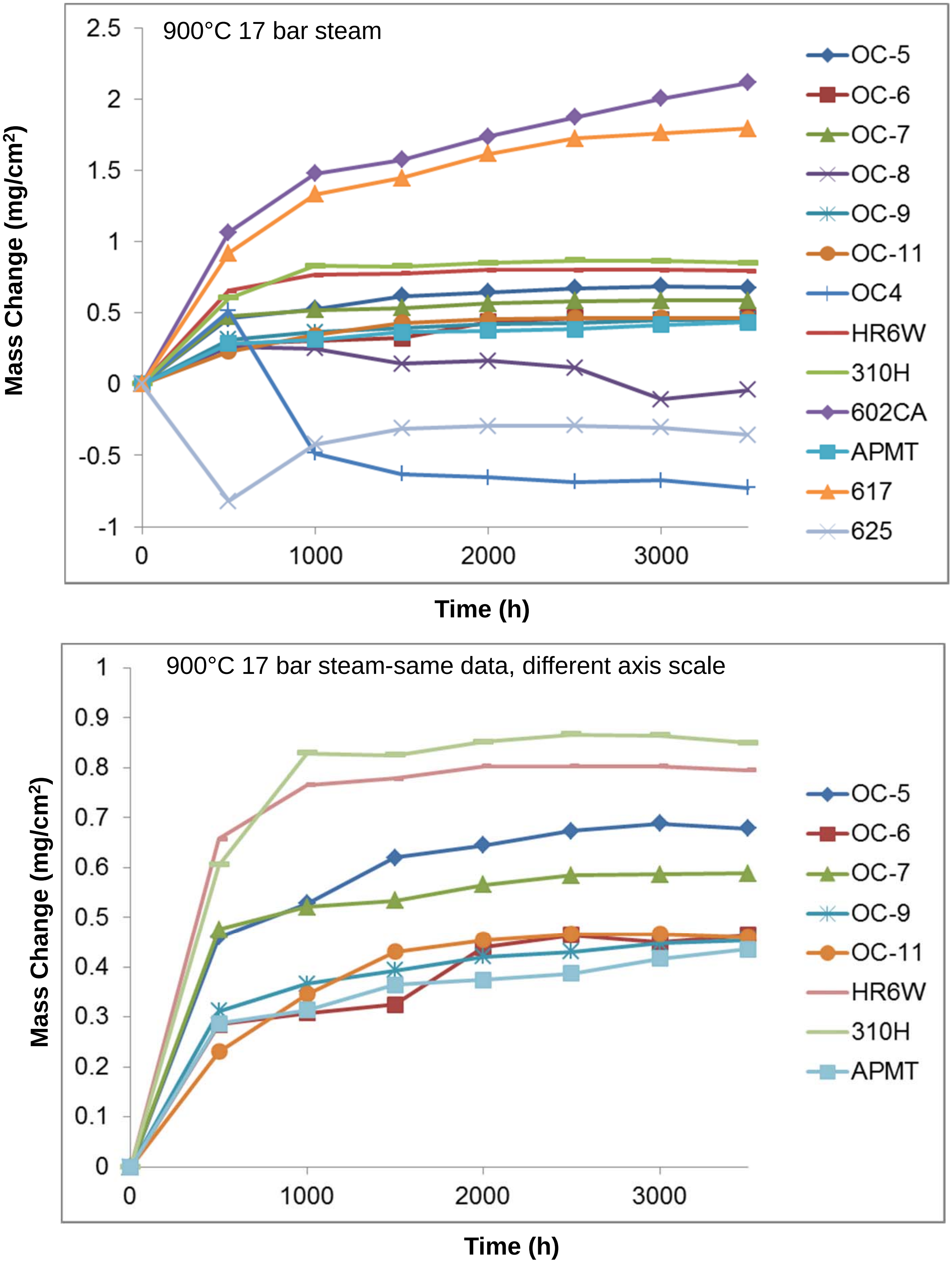
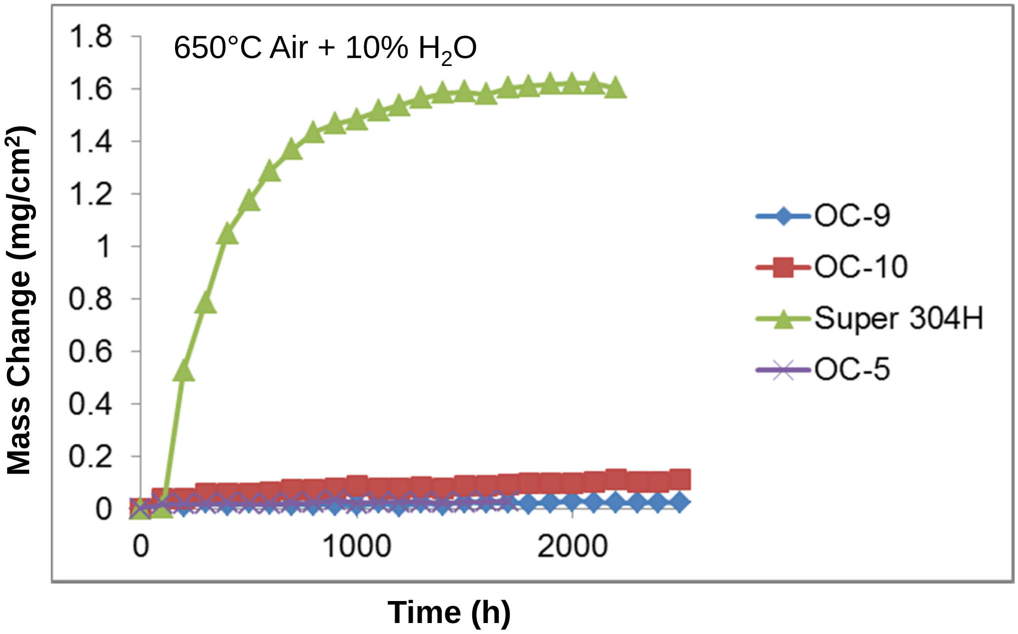


Fig.3- Specific mass change of samples exposed at 900°C in 17 bar steam. Comparison commercial alloy data from DOE Advanced Ultrasupercritical Steam Project, not the present CRADA.



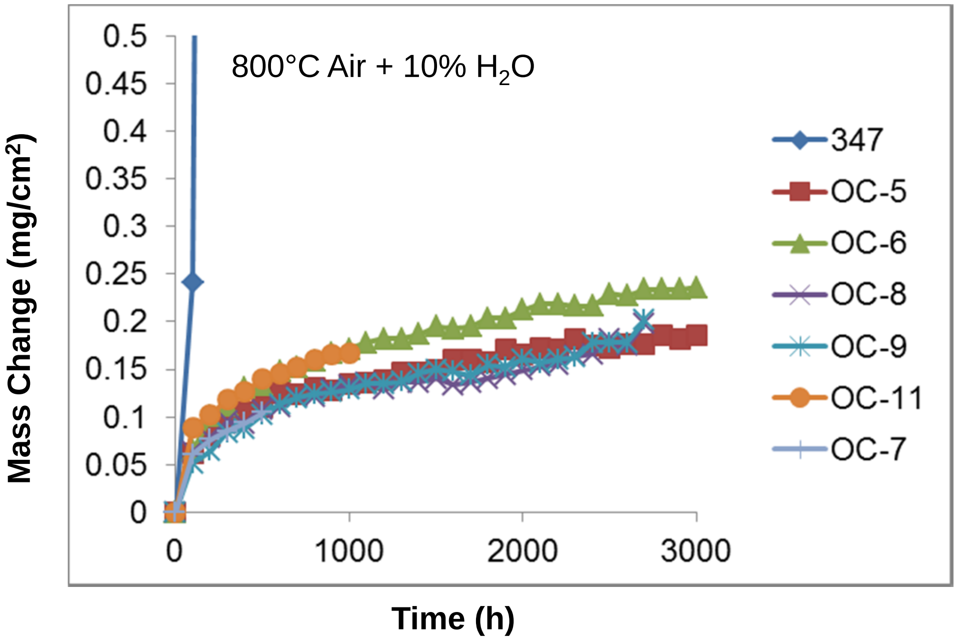


Fig. 4- Specific mass change of samples exposed at 650°C and 800°C in air with 10% H_2O.

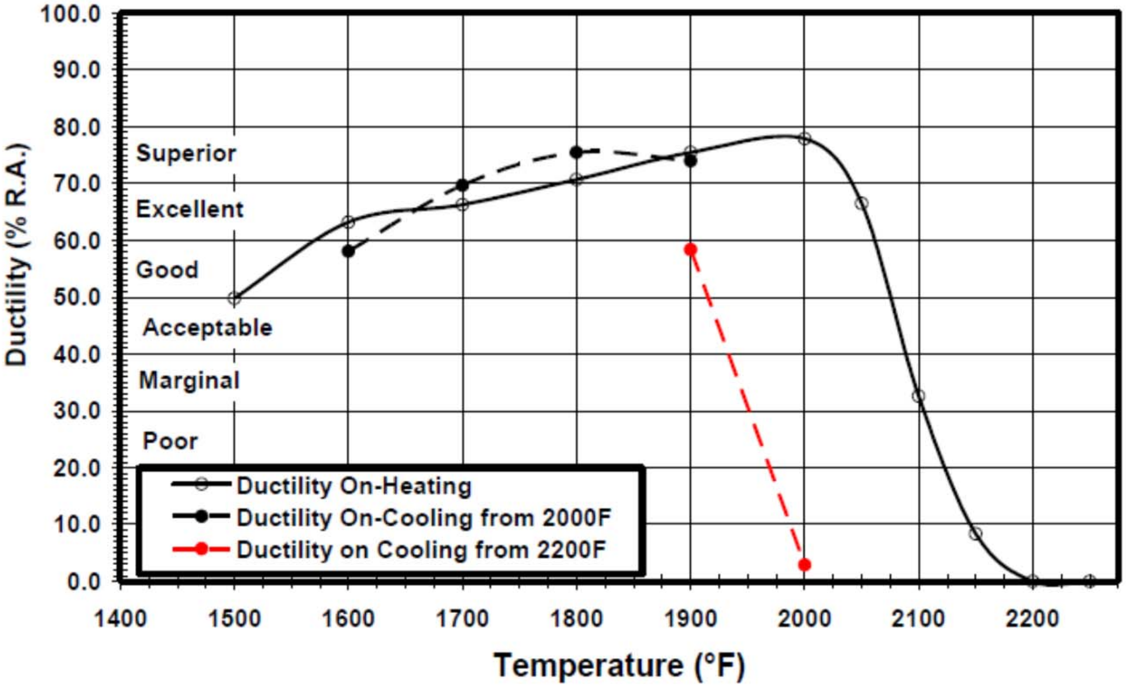


Fig. 5- Tensile ductility (reduction in area) as a function of temperature for on-heating and on-cooling tests of AFA OC-4 alloy at a strain rate of $5s^{-1}$.

Fig. 6- AFA OC-4 alloy tube product manufactured under this CRADA.

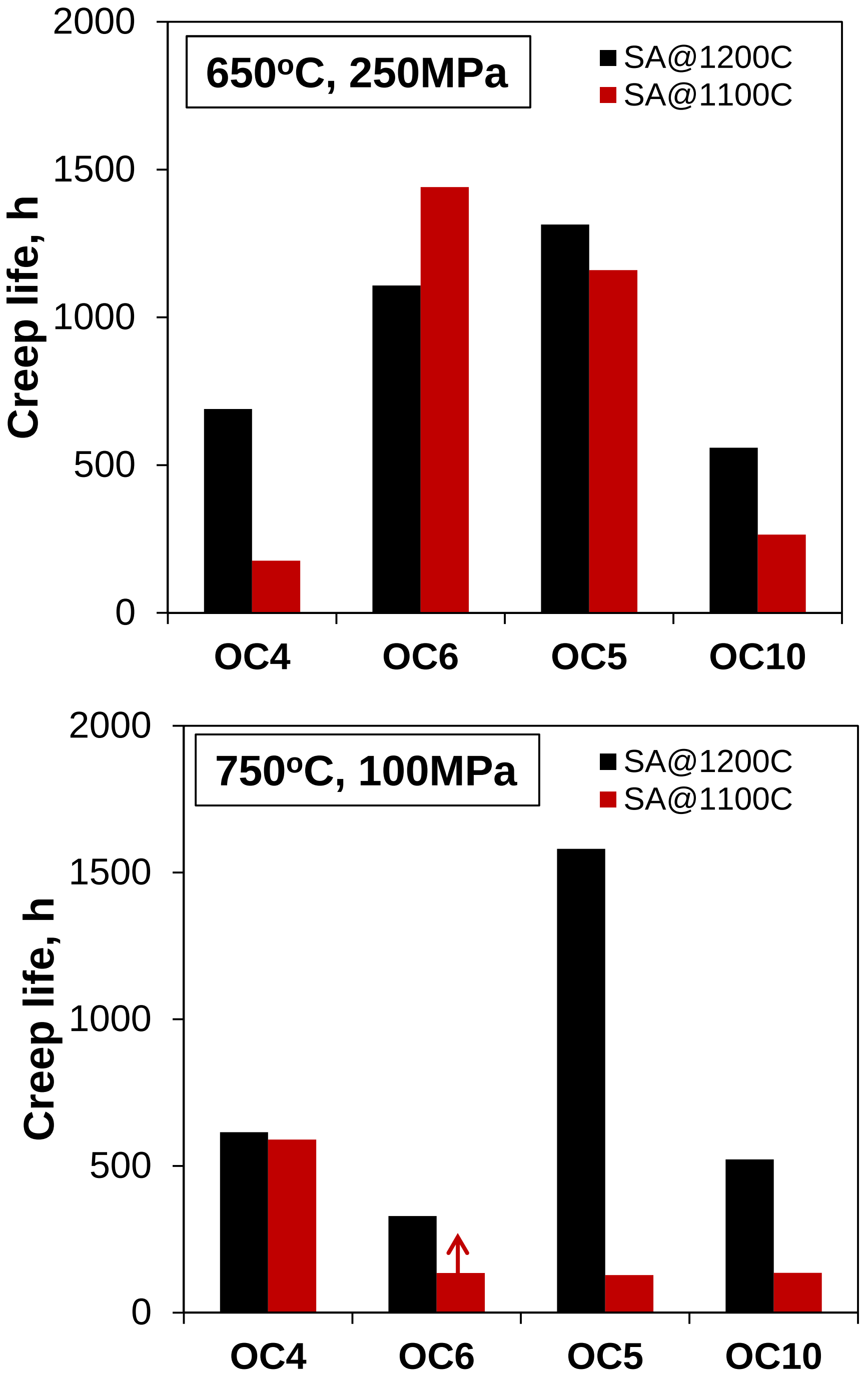


Fig. 7- Creep rupture life data as a function of solution annealing (SA) Temperature.