Final Technical Report

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Alumina-Forming Austenitics: A New Approach to Thermal and Degradation Resistant Stainless Steels for Industrial Use

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List of Acronyms

AFA	alumina forming austenitic
YS	yield strength
UTS	ultimate tensile strength
%El	percent elongation
RA	reduction of area
AFA ^{LN}	low nickel (12wt%) alumina forming austenitic
MECS	Manufacturing Energy Consumption Survey
EIA	Energy Information Agency
EPRI	Electric Power Research Institute
DG	distributed generation
API	American Petroleum Institute
FCC	fluid catalytic cracking

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Executive Summary

A series of developmental AFA alloys was selected for study based on: 25 Ni wt.% (alloys A-F), 20 wt% Ni (alloys G-H), and 12 Ni wt.% (alloys I-L). An emphasis in this work was placed on the lower alloy content direction for AFA alloys to reduce alloy raw material cost, rather than more highly alloyed and costly AFA alloys for higher temperature performance. Alloys A-D explored the effects of Al (3-4 wt.%) and C (0.05-0.2 wt.%) in the Fe-25Ni-14Cr-2Mn-2Mo-1W-1Nb wt.% base range; alloys E and F explored the effects of removing costly Mo and W additions in a Fe-25Ni-14Cr-4Al-2.5Nb-2Mn-0.2C base, alloys G and H examined Nb (1-2.5wt.%) and removal of Mo, W in a Fe-20Ni-14Cr-3Al-2Mn-0.2 C wt.% base; and alloys I-L examined effects of C (0.1-0.2 wt.%) and Mn (5-10 wt.%) on a low cost Fe-14Cr-12Ni-3Cu-2.5Al wt.% base (no Mo, W additions). Creep testing resulted in elemental trends that included the beneficial effect of higher carbon and lower niobium in 20-25%Ni AFA alloys and, the beneficial of lower Mn in 12%Ni AFA alloys. Corrosion tests in steam and sulfidation-oxidation environments showed, in general, these alloys were capable of a ten-fold improvement in performance when compared to conventional austenitic stainless steels. Also, corrosion test results in metal-dusting environments were promising and, warrant further investigation.

Our engineering and market analysis suggested the initial interest in AFA will be in the 500-800°C range, rather than 800-900°C⁺ range. Key industries examined were: coal-fired power plants, microturbines, and petrochemical refineries.

Introduction

The alumina-forming austenitic (AFA) stainless steels are a new class of high-temperature ($\sim 600\text{--}900^\circ\text{C}$; $1112\text{--}1652^\circ\text{F}$) structural stainless steel alloy family with the potential for widespread applicability in the chemical/petrochemical process and energy production industries [1]. These steels combine the relatively low cost, excellent formability, weldability, and good high-temperature creep strength of state-of-the-art advanced austenitic stainless steels with fundamentally superior high-temperature corrosion resistance due to their ability to form protective aluminum oxide (alumina, Al_2O_3) surface layers.

Conventional high-temperature stainless steels rely on chromium-oxide (chromia, Cr_2O_3) surface layers for protection from high-temperature corrosion. However, compromised corrosion resistance of chromia in the presence of aggressive species such as water vapor, carbon, sulfur, etc., typically encountered in process and energy production environments necessitates a reduction in operating temperature to achieve component durability targets. This temperature reduction reduces process efficiency and increases environmental emissions. (Energy savings and reduction in greenhouse gas emission considerations are addressed in detail in the section “Potential Energy, Economic, Environmental, and Market Benefits”).

This project had two primary objectives:

- 1) Assess the potential for AFA stainless steel alloys to deliver a 10 fold improvement in high-temperature corrosion resistance over that of conventional stainless steels in a range of representative carburization, sulfidation, and steam environments relevant to chemical and petrochemical processing and industrial steam boilers. This corrosion data would permit identification of the type of industrial processes most likely to benefit from the deployment of AFA stainless steels. Potential industrial processes that may be significantly impacted by AFA stainless steels include hydrogen reforming and production, petroleum refining equipment in crude distilling, hydrotreating, syngas production, heat exchanger tubes, biomass gasification and combustion, steam boilers, etc. A successful alloy will allow higher service temperature of an increase of up to (150°C) which, according to estimates at ORNL, has the potential of increasing efficiency by 20-30% over current systems using stainless steels. While there are nickel-based alloys that could achieve the same performance, the AFA stainless steels alloys offer a potentially low-cost solution over the nickel-based alloys that are intrinsically more expensive and difficult to fabricate.

- 2) Complete the initial baseline economic, marketing, and manufacturing analysis needed to provide the basis for follow-on commercialization and deployment efforts for the AFA alloy family for the industrial processes identified in goal 1 above.

The anticipated outcome of this one year, stage 2 concept definition effort was to identify in which general classes of industrial environments (carburization, sulfidation, steam, etc) AFA stainless steels offer the greatest potential for 10 fold lifetime improvement. When combined with energy saving/greenhouse gas reduction considerations and the economic, marketing, and manufacturing analysis findings, the basis would be established to pursue stage 3 concept development activities. The baseline corrosion data generated would also be used to attract industrial end users for field testing of coupons and/or prototype components under any follow-on stage 3 work.

Background

Alumina grows at a rate ~ 1 to 2 orders of magnitude lower than chromia and was also significantly more thermodynamically stable in oxygen (Fig. 1), which contributes to its fundamentally superior high-temperature corrosion resistance [1]. Therefore, AFA stainless steels readily meet the DOE/ITP Program objective of seeking new thermal and degradation resistant materials with the potential to increase component lifetime by a factor of ten. Alumina scales have proven to be particularly beneficial in laboratory test environments containing aggressive carbon- or sulfur- species such as those typically encountered in chemical and petrochemical process industry applications [2,3]. A further key advantage of alumina over chromia is its greater stability in the presence of water vapor [4]. Water vapor is encountered as a component in many high-temperature industrial environments (e.g. chemical/petrochemical processing, steam boilers, combustion and gasification-particularly biomass). With both oxygen and water vapor present, volatile chromium oxy-hydroxide species can form and significantly reduce component lifetime.

Despite the many advantages of protective alumina layer formation, all cast/wrought Fe-base high-temperature structural alloys available today for use above $\sim 600^{\circ}\text{C}$ (1112°F) use chromia surface layers for protection. This is due to the extensive solid solubility and excellent metallurgical compatibility of chromium (Cr) in iron/iron-nickel Fe/Fe(Ni), which permits ready formation of protective chromia with ample alloy design flexibility to co-optimize corrosion resistance with other needed properties such as creep resistance, weldability, etc. The uniqueness of the AFA stainless steels is that they offer a superior barrier to oxidation/corrosion resistance while at the same time providing superior creep resistance over the conventional Fe-based structural alloys.

Results and Discussion

AFA Alloys (Gold)

A series of development AFA alloys were laboratory melted and processed into 0.5” annealed plate for evaluation. The 13 alloy compositions are listed in Table 1 (standard 25% Nickel series) and Table 2 (10% Ni series and AFA^{LN} series).

Tensile Testing

Tensile tests were performed on all 13 alloys at room and two elevated temperatures, 1200°F (650°C) and 1400°F (750°C). Data can be found in Tables 3 and 4 and comparative Type 347 data is shown below.

Test Temp (F)	0.2% YS (ksi)	UTS (ksi)	% El	% RA
70	37	90	50	65
1200	20	40	36	70
1400	19	31	37	70

Source: Carpenter datasheet (Type 347)

An overall comparison with Type 347 shows all 13 AFA alloys have similar-to-slightly higher room temperature strengths (YS and UTS) with similar-to-slightly lower ductility (% El and RA). At the elevated temperatures, the AFA alloys have much higher strengths with corresponding lower ductility. These data demonstrate the significant strength benefit of AFA alloys at elevated (1200-1400°F) temperatures.

Some key data trends for the 13 AFA alloys were: yield strength showed a slight decrease (5-10ksi), room vs. elevated temperatures, while ultimate tensile strength dramatically dropped (>25ksi), 1200 vs. 1400°F test temperature. Ductility varied with individual alloys with some alloys breaking outside the gage length. Relatively low ductility (% El and % Reduction of Area <30) was determined for five alloys at the 1200°F test temperature. They were: OC-C, OC-D, OC-E, OC-F and OC-L. The first four alloys were from the 25% Ni series and had the highest Al content (4%) evaluated in the study. The last alloy was from the 12% Ni series and had 0.2%C with high Mn (10%). Typically, the 1400°F test temperature resulted in higher ductility than test results from 1200°F temperature. Only OC-K (low C and high Mn) from the 12% Nickel series had low ductility.

Creep Testing (750°C)

Creep testing was performed for 12 alloys at 750°C using a stress of 100MPa. Off analysis heat (001963, OC-I*) was not evaluated. Results can be found in Tables 5 and 6. Data shows that for the 25%Ni series, low carbon (.05%) was detrimental to creep life. This can be seen by comparing OC-A&B (528 vs. 1457hrs) and OC-C&D (698 vs.

1665hrs). High Nb (2.5%) heats OC-E,F&H had lower creep life times than the alloys with 1%Nb. Heat OC-G, which has 20% Ni and 1% Nb, had comparable creep life to alloys with 25% Ni and 1% Nb.

For the 12% Ni alloys, creep life times were typically lower than the higher nickel content alloys. The best alloy had a creep life of 817hrs and had the lowest Mn content.

The % creep at rupture data showed all 8 alloys in the 20 and 25% Nickel series had similar elongation behavior, ~29% creep. For the lower nickel (12%) AFA^{LN} series, % creep at rupture were significantly lower, 5-14% creep. Increasing Mn and lower carbon (.1% vs. .2%) were detrimental to both creep life and % creep at rupture.

Creep Testing at 650°C

Creep testing was performed for 12 alloys at 650°C using a stress level of 250MPa. Off analysis heat (001963, OC-I*) was not evaluated. Results are listed in Tables 5 and 6. Data shows that for the 25% nickel series, low carbon was not detrimental to creep life as was observed at 750°C test temperature. In fact OC-A had a longer creep life than the higher carbon OC-B. This result is thought to be related to formation of metastable gamma prime Ni₃Al at 650°C, which is favored by lower C and higher Nb content. Like the 750°C creep data, the high Nb (2.5%) heats OC-E,F and H had lower creep life times than the alloys with 1%Nb. Heat OC-G, which has 20% Ni and 1% Nb, had comparable creep life to alloys with 25% Ni and 1%Nb. For the 12% Ni alloys, creep life times were typically lower than the higher Ni content alloys. The best alloy had the lowest Mn content. These trends were similar to the results from the 750°C creep tests.

The % creep at rupture data showed 6 of 8 alloys in the 20 and 25% Ni series had similar results, ~29% creep. OC-A and G were lower, 19.6% and 21.2%, respectively. For the lower Ni (12%) series, % creep at rupture was significantly lower, 6-16%. Like at 750°C test temperature, the lower carbon alloy, OC-K, had the lowest % creep at rupture.

Creep Comparison

A creep comparison is shown in Figure 1. The best creep resistant alloy from the 20-25% nickel series (AFA) and the 12% nickel series (AFA^{LN}) were plotted on a curve which contains Type 347, 347HFG, Super 304H, NF709, and Alloy 617. These alloys were selected for comparison since they are designed to be used at elevated temperature where creep strength is a key property. The first three alloys are conventional stainless steels with low nickel content (10-12%). NF709 is an advanced-creep resistant stainless steel with 25% nickel and Alloy 617 is a high-cost, nickel-base alloy containing 10%Co and 8%Mo. Figure 1 shows both AFA and AFA^{LN} alloy had superior creep properties compared to the conventional stainless steels, equivalent creep properties to the advanced austenitic alloy, 709, and slightly inferior creep properties to Alloy 617, the high-cost, nickel-base alloy.

From a creep perspective, alloys OC-B and D stand out among the 25% Ni alloys, alloy OC-G in the 20% Ni range, and alloys OC-I and J in the 12% Ni range with promising combinations of creep resistance at both 1200°F and 1400°F.

Figure 1: Creep comparison of best alloys

Source: Comparison data from Oak Ridge National Labs

Figure 1: Creep comparison of best alloys

Table 1: Alloy compositions
Program AFA Standard 25% Nickel Series (OC-A to F)

AFA- Standard 25% Nickel Series						
Heat No	001955 OC-A	001956 OC-B	001957 OC-C	001958 OC-D	001959 OC-E	001960 OC-F
C	.047	.204	.049	.209	.209	.201
Mn	2.00	2.00	2.00	2.00	2.00	1.99
Si	.14	.15	.14	.14	.14	.14
P	.022	.022	.023	.022	.025	.024
S	.0011	.0008	.0011	.0009	.0007	.0007
Cr	14.06	13.99	14.03	13.97	14.01	13.98
Ni	25.02	25.05	25.05	25.03	25.02	25.05
Mo	2.00	2.00	2.00	1.99	.15	1.98
Cu	.52	.51	.52	.52	.52	.52
W	.96	.96	.96	.96	.14	.97
V	.05	.05	.05	.05	.05	.05
Ti	.05	.05	.05	.05	.05	.05
Al	3.06	3.03	4.13	4.11	4.12	4.17
Nb	1.02	1.00	.99	1.01	2.52	2.53
B	.0096	.0104	.0100	.0104	.0098	.0092
N	.0029	.0027	.0026	.0037	.0035	.0041
Fe	Bal	Bal	Bal	Bal	Bal	Bal

Table 2: Alloy compositions (continued)

AFA 20% Ni Series (OC- G&H) and AFALN Series (OC-I to L)

	20% Ni Series		AFA ^{LN} Series				
Heat No	001961 OC-G	001962 OC-H	001963 OC-I*	001969 OC-I	001964 OC-J	001965 OC-K	001966 OC-L
C	.200	.200	.130	.171	.200	.100	.200
Mn	2.00	2.00	4.79	4.99	6.79	9.93	9.96
Si	.13	.15	.14	.13	.13	.14	.14
P	.022	.024	.010	.021	.0023	.021	.024
S	.0009	.0009	.0005	.001	.0010	.0012	.0010
Cr	13.84	13.84	14.00	13.84	13.84	13.92	13.89
Ni	20.05	20.01	12.08	12.08	12.05	12.04	12.09
Mo	1.99	.15	.15	.15	.15	.15	.15
Cu	.52	.52	2.44	3.04	3.06	3.04	3.06
W	.97	.14	.15	.15	.15	.14	.15
V	.05	.05	.05	.05	.05	.05	.05
Ti	.05	.05	.05	.05	.05	.05	.05
Al	3.07	3.08	2.56	2.52	2.56	2.52	2.54
Nb	1.01	2.53	1.03	1.03	1.01	1.01	1.01
B	.008	.008	.003	.011	.009	.009	.009
N	.0026	.0040	.0037	.0032	.0047	.0040	.0044
Fe	Bal	Bal	Bal	Bal	Bal	Bal	Bal

OC-I* - Off chemistry (Boron ,Carbon and Copper were lower than minimum elemental aimed ranges. OC-I is remelted alloy.)

Table 3: Tensile test matrix

AFA Standard 25% Ni Series (OC-A to F)

Alloy		OC-A	OC-B	OC-C	OC-D	OC-E	OC-F
Test Temp	Tensile Properties	Test Results					
70F	0.2%YS(ksi)	33.2	45.2	36.8	43.7	37.8	40.3
1200F		39.7	47.4	51.0	59.7	59.9	65.1
1400F		30.8	33.5	36.1	34.4	35.0	37.5
70F	UTS (ksi)	87.4	103.3	90.4	103.9	99.1	102.0
1200F		76.9	89.8	91.8	100.1	96.3	108.4
1400F		46.7	48.7	48.2	48.2	47.1	50.6
70F	%El	55.0	44.6	58.4	43.2	42.9	44.5
1200F		58.6	29.1	24.3	14.8	23.5	26.7
1400F		48.0	66.3	41.9	79.2	90.3	*
70F	%RA	70.2	59.3	71.0	59.2	58.6	52.2
1200F		62.8	34.3	28.6	21.4	19.9	21.3
1400F		79.4	78.3	52.1	87.6	82.8	79.7

* Invalid elongation, broke outside gage section.

Table 4: Tensile test matrix (continued)

AFA 20%Ni Series (OC-G&H) and AFA^{LN} Series (OC-I to L)

Alloy		OC-G	OC-H	OC-I*	OC-I	OC-J	OC-K	OC-L
Test Temp	Tensile Properties	Test Results						
70F	0.2%YS(ksi)	41.4	38.4	33.7	39.6	39.6	34.6	38.5
1200F		38.0	43.6	29.7	37.6	36.6	31.9	36.3
1400F		33.5	32.5	28.5	29.3	29.7	30.9	29.4
70F	UTS (ksi)	97.9	96.2	85.0	91.8	92.7	87.2	91.6
1200F		83.9	82.8	66.1	72.8	72.4	68.5	70.4
1400F		48.9	45.3	39.4	41.8	42.8	42.7	42.2
70F	% El	43.8	42.1	44.0	45.1	44.0	46.1	45.3
1200F		46.2	36.2	38.2	34.5	25.9	36.9	21.3
1400F		40.9	81.3	57.9	*	46.3	23.6	*
70F	% RA	60.9	61.5	68.1	66.4	68.1	66.4	62.6
1200F		55.9	38.0	55.4	41.2	31.7	39.5	19.3
1400F		75.3	83.9	71.6	60.1	54.8	23.1	42.3

* Elongation invalid, broke outside gage section.

Table 5: Creep test matrix

AFA Standard 25% Ni Series (OC-A to F)

Alloy		OC-A	OC-B	OC-C	OC-D	OC-E	OC-F
Test Temp(C)	Stress Mpa	Results (Creep Rupture Time and Ductility)					
750	100	528h 29.27% creep	1457h 29.15% creep	698h 29.1% creep	1665h 27.0% creep	567h 29.4% creep	568h 28.95% creep
650	250	1406h 19.6% creep	905h 28.7% creep	854h 29.4% creep	1152h 28.4% creep	549h 29.1% creep	606h 39% creep

Table 6: Creep test matrix (continued)

AFA 20%Ni Series (OC-G&H) and AFA^{LN} Series (OC-I to L)

Alloy		OC-G	OC-H	OC-I	OC-J	OC-K	OC-L
Test Temp(C)	Stress Mpa	Results (Creep Rupture Time and Ductility)					
750	100	1490h 29.0% creep	393h 29.3% creep	817h 14.4% creep	677h 8.1% creep	223h 5.2% creep	305h 11.1% creep
650	250	1063h 21.2% creep	679h 28.4% creep	702h 11.4% creep	640h 16.3% creep	290h 5.9% creep	379h 12.2% creep

High Temperature Corrosion Evaluation

Two primary test environments were selected for corrosion evaluation of AFA alloys under the present program: 1) 1 atm. steam at 650°C, which is relevant to industrial boilers, and, 2) an aggressive simulated sulfidation-oxidation environment of Ar-20% H_2 -20% H_2O -5% H_2S at 650°C relevant to petrochemical crude refining and hydrotreating. The primary benchmark commercial control alloys studied included: higher-Ni austenitics (> 20 Ni wt.%) 310, 709, HR120, and the Ni base alloy 625; and lower Ni-austenitics (< 12wt.% %) super 304H, 304, and 347. In addition to these environments, select AFA alloy samples were exposed in other ongoing testing at ORNL (as furnace space permitted) in: 550 and 650°C simulated metal dusting conditions (furnace runs funded under DOE ITP AFA Steels Deployment Project); 17 bar steam at 550°C and 17 bar steam at 900°C (furnace runs funded under DOE Advanced Ultrasupercritical Steam Project); and 650, 700, 750, 800°C air + 10% H_2O .

The sulfidation-oxidation conditions were quite aggressive, as evidenced by the extensive materials loss suffered by many of the alloys after only 250 h of exposure at 650 and 550°C (Fig. 2). Materials loss measurements from cross-section assessment, rather than specific mass change, were used to assess sulfidation-oxidation exposures due to extensive scale spallation by many alloy samples with specific mass loss exceeding 100 mg/cm² in some cases. At 650°C, the commercial control alloys 304, 347, HR120, 310, and 625 all suffered from extensive attack. The best of the commercial alloys, 310, still showed material loss in excess of 75 microns (defined as loss of intact metal from one exposed face). In contrast, the best AFA alloy OC-E only lost 15 microns of metal, 5.5x better than 310. Other AFA alloys, OC-B, D, F, G, and K also showed good resistance, with losses less than 30 microns. The data generally suggest improved sulfidation-oxidation resistance in AFA alloys with increasing C level from 0.1 to 0.2 wt.%.

Figure 2: Materials loss assessed by sectioning from 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 .

At 550°C, the extent of advantage for the AFA alloys in the sulfidation-oxidation conditions was less than that at 650°C, even though the overall extent of attack was generally less at the lower temperature. This advantage extent loss may result from sluggishness of slow-growing alumina surfaces at the lower 550°C exposure temperature in the presence of aggressive species such as H₂S and H₂O, compared to 650°C. It suggests that the greatest advantages of AFA alloys may occur at temperatures > ~550-600°C (depending on environment). The best commercial alloys at 550°C were 310 and super 304H, which exhibited metal loss on the order of 35 microns. The best AFA, OC-B, exhibited loss of 19 microns, roughly a 1.8x improvement over the 310 and super 304H. The AFA 12 Ni alloys I, J, K, and L also showed generally good resistance at this temperature. Collectively, the aggressive, short-term screening conducted indicate that AFA alloys show good promise for significantly improved sulfidation-oxidation resistance (conditions relevant to petrochemical crude refining and hydro-treating).

The metal dusting conditions studied for 500 h at 550 and 650°C generally resulted in far less corrosion than that observed for the sulfidation-oxidation conditions (Fig. 3). One difference was that there was far more attack for 500 h at 550°C in metal dusting than that observed at 650°C (Fig. 3). This is attributed to the much higher carbon activity of the gas at 550°C, 69.4, vs. 8.1 at 650°C. The high Mn 12Ni AFA OC alloys J, K, and L showed surprisingly low mass changes at both temperatures, suggesting the potential for resistance in metal dusting, superior to both 347 and 800H and almost in the range of that of the high Ni alloys HR6W and 693. However, alloys OC J, K, and L still showed evidence of possible local pitting attack and longer term exposures are needed to confirm their potential resistance to metal dusting. Such work is beyond the scope of this exploratory effort, but worth pursuing in future development and scale up efforts given the promise shown thus far.

One-thousand hour exposures at 550°C (17 bar) steam, 2000 h exposure at 650°C (1 bar) steam, and 2500 h exposure at 900°C (17 bar) steam is shown in Figs. 4-6. At 550°C (Fig. 4), specific mass gains for OC and commercial alloys were less than 0.05 mg/cm², indicative of outstanding oxidation resistance. This result is important as it demonstrates protective behavior of OC AFA alloys at low temperatures where formation of protective Al-oxide based surfaces could potentially be sluggish, as was the postulated trend in the sulfidation-oxidation environments (Fig. 2). At 650°C in 1 bar steam (Fig. 5), the 25/20 Ni OC AFA alloys and commercial HR120, 625, and 310 controls all showed relatively low mass gains below ~0.2 mg/cm² after 2000 h of exposure, indicative of a high level of oxidation resistance. The NF 709 sample surprisingly showed a transition to more rapid mass gain between 1000 and 2000 h of exposure, although it is considered likely that this may be an artifact of this particular sample and not reflective of poor steam oxidation resistance for this commercial alloy. The lower-Ni 300 series stainless steels super 304H, 304, and 347 alloys showed significant attack, spallation, and mass loss > -5 mg/cm², indicating that they are not suitable for use in steam at these temperatures. In contrast, the 12 Ni OC AFA alloys J, K, and L showed promising resistance (compared to 304H, 304, and 347) with mass gains remaining below 0.5 mg/cm² range. Visual examination of the alloy J, K, and L coupons did show evidence of some non-uniform attack, and longer

exposures are needed to determine if these areas are healed or will result in transition to breakaway kinetics.

Fig. 6 shows 2500 h exposures for select OC and commercial alloys at 900°C in 17 bar steam, a highly aggressive condition. (This temperature is too high for the developmental 20 and 12Ni OC alloys series, which suffered from extensive attack after only 500 h of exposure under this condition.) The commercial Ni-base alloy 625 exhibited mass loss on the order of 0.5 to 1 mg/cm², while the commercial Ni-base alloys 602CA and 617 showed mass gains in the 1-1.5 mg/cm² range, indicating susceptibility to attack. The high-Ni alloy HR6W and 310 stainless steel exhibited moderately lower mass gain after 2500 h of exposure (~0.8 mg/cm²). However, it should be noted that mass changes for these commercial alloys between 1000 and 2500 h of exposure were relatively stable and suggest a degree of steady-state protection may have been reached. The best OC alloys were C and F₂, which have high levels of Al, and exhibited total mass gains on the order of 0.3 mg/cm² after 2500h, comparable to the costly, powder metallurgy alumina-forming APMT alloy. The AFA OC alloys D and E showed a transition to accelerated attack. Longer-term exposures and cross-section analysis will be needed to fully assess the relative behavior of the AFA and commercial alloys at this aggressive screening condition (that work is outside the scope of the current exploratory program). The results obtained for these 2500 h exposures at 900°C in steam do, however, indicate potential for AFA to exhibit superior steam oxidation resistance.

Figures 7-9 show oxidation data for select OC AFA alloys in a simulated exhaust environment of air with 10% water vapor at 650, 700, 750, and 800°C. At 650°C, super 304H shows high mass gains indicative of susceptibility to attack (Fig. 7). The 12Ni OC alloy K also showed relatively high mass gains, whereas the 12Ni OC alloys I, J, and L show good oxidation resistance with mass gains less than 0.2 mg/cm² over 2000 h of exposure. With the exception of the 20Ni alloy OCH, the 25/20Ni OC alloys exhibited small mass gains (≤ 0.1 mg/cm²), indicative of excellent oxidation resistance under this condition over 2000 h of exposure. It is interesting to note that specific mass gains at 650°C in air with 10% H₂O were generally lower for the 12Ni OC alloys, OC-I, J, K, and L than that observed in 650°C 1 bar steam (Fig. 5).

At and 700 and 750°C in air with 10% H₂O (Figs. 8, 9), the relative oxidation resistance among the 12Ni AFA OC alloys have differentiated, with the best resistance observed for the lower Mn content OC-I alloy (it is noted that all 12Ni AFA OC alloys showed mass loss at 750°C and are not suitable for use at this temperature, but still superior to that exhibited by super 304H). The other AFA OC alloys all continued to show good oxidation resistance at 750°C in air with 10% H₂O, with mass gains < 0.2 mg/cm² (Fig. 15). At 800°C in air with 10% H₂O, the 25Ni series alloy D and the 20 Ni series alloys G and H showed good oxidation resistance out to 3000-4000 h of exposure.

The high-temperature corrosion data obtained provide a basis to assess composition/corrosion resistance trends in the AFA alloy family. Among the 25Ni OC alloys, the 1Nb and 0.2C alloy OC-B and OC-D, the 20Ni alloy OC-G, and the 12Ni alloy OC-I show good promise. Compellingly, these alloys also showed good promise

from creep evaluation. The 2.5Nb, 25Ni OC alloys E and F generally showed the best overall oxidation/corrosion resistance in the environments examined. Of interest is the similar resistance of OC-E to OC-F, despite no Mo and W additions (which should permit lower alloy cost). However, creep resistance feedback for these alloys indicates only modest creep rupture resistance, comparable to previous 2.5Nb alloys which generally exhibit inferior creep resistance but superior corrosion resistance to 1Nb alloys. Overall, the data obtained in the present project provide a strong basis to downselect and optimize OC AFA compositions for 25/20 Ni and 12Ni base AFA OC alloys for future scale up activities.

Figure 3: 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

Figure 4: Specific mass change of samples exposed at 550°C in 17 bar steam

Figure 5: Specific mass change of samples exposed at 650°C in 1 bar steam

Figure 6: Specific mass change of samples exposed at 900°C in 17 bar steam.

Figure 7: Specific mass change of samples exposed at 650°C in air with 10% H₂O

Figure 8: Specific mass change of samples exposed at 700°C in air with 10% H₂O

Figure 9: Specific mass change of samples exposed at 750°C in air with 10% H₂O

Benefits Assessment

GPRA analysis for potential impacts of AFA stainless steels were conducted at the initial proposal stage in 2009. The original estimates are presented in Table 8.

Table 7: 2009 Estimate GPRA analysis for potential impacts of AFA stainless steels

		Impact in 2020	Cumulative Impact Through 2025
Energy Metrics			
Total Primary Energy Displaced (trillion Btu)	Chemical Processing	36	100
	Petroleum Refining	10	24
	Steam Boilers-Other	<u>11</u>	<u>32</u>
	Total	57	156
Financial Metrics			
Net Economic Benefit (\$ million/year)	Chemical Processing	410	1150
	Petroleum Refining	65	182
	Steam Boilers-Other	<u>51</u>	<u>142</u>
	Total	526	1474
Environmental Benefits			
CO ₂ Emissions Displaced (million TCE)	Chemical Processing	0.5	1.5
	Petroleum Refining	0.2	0.5
	Steam Boilers-Other	<u>0.2</u>	<u>0.5</u>
	Total	0.9	2.5

These estimates considered impacts of AFA in the Chemical Processing, Petroleum Refining, and Steam Boilers Industry. AFA alloys were assumed applicable to 15% of processes and that AFA alloys will yield a 30% improvement in process efficiency through higher temperature operation and reductions in shutdown enabled by longer-lived materials. For petroleum refining applications, a 20% improvement in processing efficiency was assumed to be possible through raising operating temperatures and by eliminating shutdowns for maintenance and repair. AFA alloys were assumed to be ultimately used in 20% of the available market; however, in higher temperature applications such as steam methane reforming of hydrogen, it was noted that the ultimate adoption rate could be much higher. For steam boilers, the 2006 Manufacturing Energy Consumption Survey (MECS) data from the Energy Information Agency (EIA) indicated consumption of 5.5 quads annually for industrial steam generation in the pulp & paper, plastics & rubber, non-metal mineral (glass and cement) and primary metals industries. If 45% of this energy is used to raise steam, and 10% of this market is captured, ultimately 5% of this total can be affected. Assumed process improvements of 25% due to raising operating temperatures and by eliminating shutdowns for maintenance and repair were anticipated. In all cases, initial commercialization of AFA alloy material in operating plants was assumed to occur in 5 years, and full market penetration at 15% of potential sites was assumed to occur by 2020.

Based on the findings of the present project, the AFA alloys still show excellent potential for significantly improved durability in these applications. However, the findings also suggest a narrower window of applicability than initially estimated. This is due to the lessening of the AFA alloy advantage over commercial austenitic and Ni-base alloys observed at the lower temperature range of interest ($\sim < 550\text{-}600^{\circ}\text{C}$). Further, a definitive advantage for AFA in metal dusting screening conditions was not observed. Therefore, the revised calculations shown in Table 18 assume applicability to only 5% of processes. Market penetration of 10% was assumed by 2020, and 50% in 2025. As can be seen, although the impact is lessened relative to the 2009 estimate, it still indicates significant potential energy savings, environmental benefits, and net economic benefit of commercialization of the AFA alloy class.

Table 8: Revised GPRA analysis for potential impacts of AFA stainless steels

		Impact in 2020	Cumulative Impact Through 2025
Energy Metrics			
Total Primary Energy Displaced (trillion Btu)	Chemical Processing	8	145
	Petroleum Refining	8	146
	Steam Boilers-Other	<u>7</u>	<u>128</u>
	Total	23/yr.	419
Financial Metrics			
Net Economic Benefit (\$ million/year)	Chemical Processing	94	1794
	Petroleum Refining	58	1126
	Steam Boilers-Other	<u>31</u>	<u>594</u>
	Total	183/yr.	3514
Environmental Benefits			
CO ₂ Emissions Displaced (million TCE)	Chemical Processing	0.1	2.3
	Petroleum Refining	0.1	2.6
	Steam Boilers-Other	<u>0.1</u>	<u>1.8</u>
	Total	0.3/yr	6.7

Commercialization

Coal-Fired Power Plants

In its 2010 World Energy Outlook, the International Energy Agency projects that coal-powered electricity generation will remain the largest source of electricity generation through 2035. Coal's resilience as a source of electrical power generation is due to its abundance, low cost and proven reliability in baseload operations.

Coal-fired power generation is expected to become increasingly efficient as new installations migrate from subcritical to ultra-supercritical technologies. Drivers for advanced coal technologies include lower emissions and improved efficiency.

The migration to advanced ultra-supercritical temperatures (AUSC) is expected to occur from 2020-2035. The slow adoption is due to ongoing concept and technology validation thru 2020, to include the validation of materials that will perform at the higher temperatures and pressures. The two main components of the coal-fired power plant are the boiler and the steam turbine. In the boiler, the coal is combusted and the bulk of the components (waterwalls, superheater, reheater, header) are made of tubing and pipe carrying the superheated steam and mixed liquids.

The expanding steam drives the steam turbine, which is the simplest and most efficient engine to convert heat energy to work. The key components of the turbine are very similar to those of an aerospace gas turbine engine (rotors/discs, blades/vanes, casings/cylinders, fasteners), but the materials must survive the more aggressive environment of superheated steam. The rotors and casings pose the most significant material challenges because of the extremely demanding requirements as well as the need for much larger section sizes compared to those used in aerospace turbines. The same challenges apply to the boiler tubing and pipe except that formability and weldability replaces section size concerns.

In order to operate in AUSC conditions, alloys must meet the following performance criteria:

1. Long-term creep strength – 100,000 hours at up to 1400°F
2. Hot corrosion – coal ash, erosion, corrosion fatigue, SCC
3. Oxidation – superheated steam up to 1400°F, steamside oxidation is a limiting factor
4. Long-term stability – 100,000 hours minimum, 30-year design life for plant
5. Formability – large forgings for rotors, tube manufacture and bending for boilers
6. Weldability – for welded rotors/casings and tube assemblies
7. Fatigue

Higher pressures and temperatures necessitate the use of higher-performance and higher-cost materials. For example, AUSC conditions could result in ~2M lbs of nickel-based tubes used in a generic boiler (Mike Santella, 25th Annual Conference on Fossil Energy Materials, Portland, OR, 04/28/11). EPRI reports that a plant operating at ~700°C will incur installation costs of high-nickel alloy piping 3x greater than for supercritical plants (John Wheeldon, Introduction to Advanced Ultra-Supercritical Workshop, 04/07/11).

Nickel-based materials will also be required in steam turbine components as temperatures increase. Components such as buckets, nozzles, rotors, casing, and bolting will utilize nickel-based materials instead of stainless and alloyed steels typically employed.

The AFA alloys should be considered for use in higher temperature coal applications, and could potentially represent a lower cost alternative to Ni base alloys in some AUSC components.

Microturbines

Turbines use recuperators in order to improve their overall efficiency. Recuperated gas turbine cycles are used predominantly in microturbines with generating output less than 1MW. Recuperated turbines are also used primarily for power generation industry applications. Exceptions include Rolls Royce's WR-21 (used for marine applications) and the Honeywell AGT1500 (M1 Abrams tank).

Growth in microturbines is expected to be fueled by a trend toward distributed generation. Distributed generation (DG) refers to the production of electricity at or near the place of consumption. Examples of DG include backup generators at hospitals, solar power systems on residential rooftops, and combined heat and power systems at university campuses.

Among the energy technologies frequently mentioned for distributed generation are fuel cells, solar photovoltaic cells, and wind-powered generators. As the chart below illustrates, the Energy Information Agency's 2011 outlook anticipates strong growth for distributed generation. The EIA singles out microturbines as the fastest-growing DG technology, with growth "averaging 16% per year."

Figure 10: Improved interconnection supports growth in distributed generation

The EIA chart shows approximately 2.5 million KW of additional microturbine capacity added to the US from 2009-2035. Therefore the US total market potential for AFA thru 2035 is about 5,000 tons, assuming an average turbine size of 65KW with 200 to 400 lbs of AFA required per unit. The Global market is likely a factor of two to three times larger:

Table 9: Market potential for AFA in microturbines

Market Potential for AFA in Microturbines		
KW added 2009-2035	2,500,000	
Avg KW per unit	65	
# Turbines 2009-2035	38,462	
of which small recuperator	30,769	use 200lbs @
of which large recuperator	7,692	use 400lbs @
Recuperator Alloy (tons)	4,615	Tons
Annualized (2009-2035)	171	TPY

Recuperators preheat the air used in the combustor in order to reduce fuel consumption in the combustor and increase efficiency. Most recuperators operate at a maximum temperature of 600 to 750°C; Recuperators are exposed to turbine exhaust, which is a complex mixture of combustion byproducts (particularly water vapor) and air, contributing to oxidation. Common materials used are HR-120, 625, and SS 347. The AFA alloys offer an attractive lower cost alternative to HR-120 and 625 when temperatures of operation exceed 600-650°C (347 no longer viable at these temperatures due to accelerated oxidation attack in water vapor)

Figure 11: Intrinsic raw material cost

(Source: Carpenter estimate of intrinsic raw materials costs, excluding processing costs and surcharges)

Petrochemical

There are more than 3,400 refining processing units installed globally addressing processes such as crude distillation, coking, visbreaking, fluid catalytic cracking, catalytic reforming, and hydro-processing (hydro-treating and hydro-cracking). Chemical and mechanical engineering advances are continually sought after to accommodate new

products and improve plant efficiency, reliability, and safety while decreasing emissions and pollutants.

The International Energy Agency estimates that there will be \$1trillion of refining infrastructure investment from 2010-2035 (World Energy Outlook, 2010)

Table 10: Worldwide refining process units

Worldwide Refining Process Units (as of 01/04)						
	Crude Distillation	Coking + Visbreaking	FCC	Catalytic Reforming	Hydro-treating	Hydro-cracking
# of Units	>710	>330	360	550	1,316	168
Total World Capacity (million barrels/day)	82.0	8.0	14.3	11.3	40.3	4.6
Average Capacity (barrels/day)	114,000	45,700	39,700	20,500	30,600	27,400

(Chart source: Chapter 7, Practical Advances in Petroleum Processing, Volume 1, Edited by Chang S. Hsu, ExxonMobil Research and Engineering Company, Baton Rouge, Louisiana, USA, and, Paul R. Robinson PQ Optimization Services, Katy, Texas, USA)

Materials play a critical role in the safe and economical functioning of petrochemical facilities. The American Petroleum Institute (API) has developed simplified flow diagrams for several process units commonly found in refineries, mapping them to primary damage mechanisms. An example of the fluid catalytic cracking (FCC) process is provided below, followed by a table summarizing a limited number of damage mechanisms for the main refining processes. Note that this assessment focuses on a limited number of damage mechanisms that the AFA alloys are best suited to address.

Figure 12: Example of fluid catalytic cracking (FCC) process

Sulfidation, oxidation and creep are the common damage mechanisms across refining processes. Metal dusting and carburization are also significant, though less pervasive. (Source: API Recommended Practice 571, Damage Mechanisms Affecting Fixed Equipment in the Refining Industry, 2nd Ed., April 2011). The promising sulfidation-oxidation and creep resistance of AFA alloys therefor make them of strong interest for these applications.

Table 11: Damage mechanisms in refining processes

Damage Mechanisms in Refining Processes				
Refining Process	Sulfidation	Oxidation	Carburization	Metal Dusting
Crude Unit/Vacuum	x	x		
Coking	x	x	x	
Visbreaking	x	x	x	
Fluid Cat. Cracking (FCC)	x	x	x	
Hydro-processing	x			
Catalytic Reforming		x	x	x
Sulfur Recovery	x	x		
Hydrogen Reforming		x		x

Accomplishments

A series of developmental AFA alloys was selected for study based on 25 wt% Ni, 20 wt% Ni, and 12 wt% Ni wt.% . An emphasis in this work was placed on the lower Ni AFA alloys to reduce alloy raw material cost, rather than more highly alloyed and costly AFA alloys for higher temperature performance. Our engineering and market analysis suggested most of the initial interest in AFA will be in the ~500-800°C application range, rather than ~800-900°C application range. Additionally, the amount of Al, C, Mo, W, Mn, and Nb was varied in the experimental design to determine the effects. The series of alloys were successfully processed and thoroughly evaluated at Carpenter Technology Research and Development and at Oak Ridge National Laboratory. Key elemental trends in AFA and AFA^{LN} were defined relative to creep and oxidation resistance. Superior resistance of AFA alloys versus benchmarked alloys for both creep, elevated tensile strength, and oxidation resistance in several environment was proven as well as a ten-fold improvements in sulfidation resistance while steam and metal dusting showed positive results as well. Additionally, an economic, marketing, and manufacturing analysis was performed by both parties.

Conclusions

The high-temperature creep and corrosion data obtained provide a basis to assess composition/corrosion/creep resistance trends in the AFA alloy family. Among the 25Ni OC alloys, the 1Nb and 0.2C alloy OC-B and OC-D, the 20Ni alloy OC-G, and the 12Ni alloy OC-I show good promise. Compellingly, these alloys also showed good promise from creep evaluation. The 2.5Nb, 25Ni OC alloys E and F generally showed the best overall oxidation/corrosion resistance in the environments examined. Of interest is the similar resistance of OCE to OCF, despite no Mo and W additions (which should permit lower alloy cost). However, creep resistance feedback for these alloys indicates only modest creep rupture resistance, comparable to previous 2.5Nb alloys which generally exhibit inferior creep resistance but superior corrosion resistance to 1Nb alloys. Overall, the results obtained in the present project provide a strong basis to downselect and optimize OC AFA compositions for 25/20 Ni and 12Ni base AFA OC alloys for future scale up activities.

- For standard AFA, high Nb (2.5 vs. 1%) was detrimental to creep life @ 650 and 750°C test temperatures while low carbon (.05 vs. .2%) was detrimental to creep life @ 750°C.
- Lowering Mn (5% vs. 7 and 10%) was beneficial to creep life in AFA^{LN}.
- Standard AFA had better creep life than AFA^{LN}; however, both alloys had better creep resistance than benchmark alloys, T347 and 347HFG.
- Compare to Type 347, AFA alloys had slightly higher room temperature strengths (YS and UTS) with slightly lower ductility (%El and RA). At elevated temperature, these AFA alloys had much higher strengths with lower ductility.

Recommendations

- Further evaluate a low nickel, low Nb version of standard AFA alloy.
- Scale-up AFA^{LN} with 5%Mn.
- Investigate weldability and low-term exposure for these two alloys.
- Field test these alloys based on corrosion test results and market analysis.

References

1. M.P. Brady, Y. Yamamoto, M.L. Santella, P.J. Maziasz, B.A. Pint, C.T. Liu, JOM-Journal of Metals, Minerals, and Materials Society, 60 (7), pp. 12-18 (2008).
2. G.Y. Lai, "High Temperature Corrosion of Engineering Alloys", ASM International, Materials Park, OH USA 1990
3. B. Gleeson, in "Corrosion and Environmental Degradation", Volume II, M. Schutze, Ed., Materials Science and Technology Series, Wiley-VCH, Weinheim, Germany, chapter 5, pp. 173-228 (2000).
4. E. J. Opila, Mat. Sci. Forum, 461-464, p. 765-773 (2004).