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Ultra Supercritical Steamside Oxidation

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Ultra supercritical (USC) power plants offer the promise of higher efficiencies and lower emissions, which are part of the U.S. Department of Energy's Vision 21 goals. Most current coal power plants in the U.S. operate at a maximum steam temperature of 538°C. However, new supercritical plants worldwide are being brought into service with steam temperatures of up to 620°C. Vision 21 goals include steam temperatures of up to 760°C. This research examines the steamside oxidation of advanced alloys for use in USC systems. Emphasis is placed on alloys for high- and intermediate-pressure turbine sections. Initial results of this research are presented.

INTRODUCTION

For many years the temperatures and pressures of steam boilers and turbines were intentionally increased. These increases allowed for greater efficiencies in steam and power production, and were enabled by improvements in materials properties such as high temperature strength, creep resistance, and oxidation resistance. From 1910 to 1960, there was an average increase in steam temperature of 10°C per year, with a corresponding increase in plant thermal efficiency from less than 10% to 40%.[1] The first commercial boiler with a steam pressure above the critical value of 22.1 MPa (3208 psi) was the 125 MW Babcock & Wilcox (B&W) Universal Pressure (UP) steam generator in 1957—located at the Ohio Power Company's Philo 6 plant.[2] A UP boiler can operate at both subcritical and supercritical conditions. It delivered steam at 34.1 MPa and 621°C with two reheats of 566°C and 538°C. The pressure and temperatures of the primary, first reheat (if present), and second reheat (if present) are designated by a nomenclature such as 34.1 MPa/621°C/566°C/538°C for the Philo 6 plant. In 1960, Eddystone 1 reached a world record in efficiency of 40% operating at 34.5 MPa/649°C/565°C/565°C.[1,3] The Eddystone 1 plant, and others of its generation, soon reduced operating temperatures and pressures primarily because of thermal fatigue issues within the boiler.[1] Eddystone 1 continues to operate at 32.4 MPa/610°C.[3] It still uses the highest steam pressures and temperatures in the world. Since 1960, the overall trend of increasing temperatures and pressures has stopped and stabilized at about 538°C and 24.1 MPa.[3]

In the past thirty years, advances in the high temperature strength of ferritic steels have allowed for the increase of operating temperatures and pressures, but without the thermal fatigue issues of the austenitic steels that had to be used to obtain the required high temperature strengths in the early 1960s. Ferritic steels, as used here, refers to the equilibrium structure. In practice, a martensitic or partially martensitic structure is obtained from heat-treating. Currently, the most efficient fossil power plants now operate at 24 MPa/600°C, deemed "State of the Art". Operations at 28 MPa/630°C are expected in the near term.[3] Current research programs are aimed at increasing the operating conditions even further, to as high as 760°C and 37.9 MPa. In general terms, plants operating above 24 MPa/593°C are regarded as ultra supercritical (USC), those operating below 24 MPa as subcritical, and those at or above 24 MPa as supercritical (SC).[3]

The purpose of this paper is to report on research that examines the steamside oxidation of advanced alloys for use in supercritical systems. Emphasis is placed on alloys for high- and intermediate-pressure turbine sections. Initial results are presented.

Benefits

The driving force for increased operating temperatures and pressures has been increased efficiency in power generation. Recently, an additional recognized benefit has been decreased CO_2 emissions. Estimates of the cost effectiveness of various ways to improve the efficiency of power plants are shown in Table 1. Table 1 shows that increasing the steam temperature is one of the more cost effective ways of increasing efficiency, while increasing the steam pressure is less effective. Improvements in efficiency for the newer generation of SC and USC power plants are shown in Table 2, as compared to a subcritical, 16.5 MPa/538°C/538°C, plant with an efficiency of 37% (HHV).[4]

TABLE 1. Cost Effectiveness of Methods to Improve Fossil Fuel Power Plant Efficiency.[3] Cost is in terms of millions of U.S. Dollars per net percent increase in LHV efficiency.

Rank	Method	Cost
1	Reducing condenser back pressure	3.1
2	Increase to 8th extraction point feed water heater, raising feed water temperature	3.8
3	Raising live steam and reheat temperatures	8.3
4	Raising live steam temperature	8.6
5	Using separate boiler feed pump turbine (BFPT) instead of main turbine driven pump	9.6
6	Raising live steam pressure	25.1
7	Change from single to double reheat	38.2
8	Using separate BFPT condenser	41

For reduced CO_2 emissions, calculations by Booras *et al.*[5] indicate that a subcritical 37% efficient plant 500 MW plant burning Pittsburgh #8 coal would produce about 850 tons of CO per kWh. Ultra supercritical plants at 43% and 48% efficiency would respectively produce about 750 and 650 tons of CO per kWh.

Calculations reported by Viswanathan *et al.*[3] indicate that factoring in the cost of CO_2 emissions is necessary for making SC and USC power generation cost effective, as shown in Table 3. In these calculations, the increased efficiencies are factored into the fuel savings, but the increased capital costs are more than the fuel savings. Factoring in the cost of CO_2 emissions, either by a carbon or CO_2 tax, or by regulation, could shift the cost benefits toward the use of SC and USC systems. This helps to explain why Europe and Japan (with CO_2 or energy taxes) have more ongoing construction of USC plants than does the U.S.

Worldwide Materials Research

International materials research during the last twenty years has led to numerous new alloys for steam boilers and turbines and an increase in steam temperatures. Much of the efforts for temperatures up to 650°C are aimed at improving on the ferritic steel 12Cr-1MoV. Major industrial research and development efforts in Japan, the USA, and Europe are briefly outlined below in Table 4.

TABLE 2. Net Plant Efficiency Improvement over a Subcritical 16.5 MPa/538°C/538°C Plant with an Efficiency of 37% (HHV).[4]

Steam Conditions	Recent Power Plant Examples	Net Percentage Point Increase in Efficiency	Net Plant Efficiency, %
28.4 MPa/538°C/538°C		2.5	39.5
28.4 MPa/538°C/566°C	Schwarze Pump – 1998	2.9	39.9
28.4 MPa/566°C/566°C		3.6	40.6
28.4 MPa/566°C/593°C	Nanaoota 1 – 1995 Noshiro 2 – 1995 Haramachi 1 – 1997 Millmerra – 2002	4.0	41.0
28.4 MPa/593°C/593°C	Matsuura 2 – 1997 Misumi 1 – 1998 Haramachi 2 – 1998 Tchibana Bay – 2000 Bexback – 2002	4.5	41.5
31.0 MPa/593°C/593°C	Lubeck – 1995 Alvedore 1 – 2000	4.9	41.9
31.0 MPa/593°C/621°C	Westfalen – 2004	5.2	42.2
31.0 MPa/593°C/593°C/593°C	Nordjylland - 1998	6.5	43.5

TABLE 3. Cost Calculations Comparing Subcritical and Supercritical Plants at 80% Capacity. Total Cost is on a 20-yr, constant dollar basis.[3]

Cost Categories	Subcritical	Supercritical 566°C	Supercritical 593°C
Capital, $/MWh	25.03	26.3	26.8
Operation & Maintenance, $/MWh	6.2	6.3	6.3
Fuel, $/MWh	13.9	13.1	12.9
Total cost of Electricity $/MWh	45.1	45.7	46.0

Materials Requirements

The components exposed to supercritical water in SC and USC power plants include high-pressure steam piping and headers, superheater and reheater tubing, and water wall tubing in the boiler,[6] and high and intermediate pressure-rotors (HP and IP), rotating blades, and bolts in the turbine section.[7] A brief synopsis of the materials requirements for each of these is presented below.

Steam Piping and Headers. Require high-temperature creep strength. These are heavy section components and are particularly subject to fatigue from thermal stresses. Ferritic steels have lower thermal expansion coefficients than austenitic steels, and so are preferred with respect to thermal fatigue. Current ferritic steels are limited to 620°C—the theoretical limit is thought to be about 650°C.[6]

TABLE 4. Major International Research and Development Efforts.[8-9]

Research Effort	Time Span	Targets	Notes
EPDC, Japan Electrical Power Development Company	1981-2000	30.0 MPa 630°C/630°C	Materials development and component manufacture with 50 MW pilot plant operations.
NIMS, Japan National Institute for Materials Science	1997-2007	650°C	Ferritic steel development.
EPRI, USA Electric Power Research Institute	1978-2003		Boiler and turbine thick-walled components, standardization and trial components in service. Validated NF616 (ASME P92) and HCM12A (ASME P122).
DOE Vision 21, USA Department of Energy	2002-2007	35.0 MPa 760°C	Materials development and qualification as part of the larger Vision 21 efforts.
COST 501, Europe Co-Operation in the Field of Science and Technology	1986-1997	530°C/565°C	Turbine and boiler materials development for all major components.
COST 522, Europe	1998-2003	30.0 MPa 620°C/650°C	Turbine and boiler materials development for all major components.
THERMIE AD700, Europe	1998-2013	35.0 MPa 700°C/720°C	Materials development and qualification, component design, and demonstration plant.

Superheater and Reheater Tubing. Require high-temperature creep strength, thermal fatigue strength, weldability, fireside corrosion resistance, and steamside corrosion resistance. Ferritic steels are preferred due to their thermal fatigue resistance. However, high temperature creep strength limits these alloys to 620°C (current alloys) and 650°C (theoretical limit). Fireside corrosion resistance further limits ferritic steels to about 593°C, which corresponds to a steam temperature of about 565°C.[6]

Waterwall Tubing. Similar issues to superheater and reheater tubing, but at lower temperatures so that lower alloyed materials are typically used.

High-and Intermediate Pressure Rotors. The HP and IP rotors are large forgings that carry the rotating blades. They are subject to centrifugal loads during operation and to thermal stresses during startups and shutdowns. The key materials properties are creep strength, low-cycle fatigue strength and fracture toughness.[7]

Rotating Blades. Require high-temperature strength, creep resistance, and a coefficient of thermal expansion similar to the rotor.[7] In addition, the alloys used need to be able to be peened. In each row of blades, a circular cover is used to couple the blades together and to act as a seal. The tenon part of the blades protrudes from the cover and is peened into heads, which attaches the blades to the cover.[7]

Bolts. Require high-temperature strength, creep resistance, notch sensitivity resistance, and a coefficient of thermal expansion similar to the rotor. The bolts must remain tight between scheduled shutdowns (20,000 to 50,000 hours).[7]

Corrosion in Supercritical Water

Steamside corrosion in supercritical power plants is of importance because of three factors.[10] The first is that section loss combined with high pressures can lead to component failures. The second is loss of heat transfer in water walls, superheaters and reheaters due to the buildup of low conductivity oxides. This leads to an increase in metal temperature that increases corrosion and creep. The third factor is the buildup of thick oxides, which are much more prone to spallation. Spallation increases the chance for tube blockages and for steam turbine erosion.

RESEARCH APPROACH

The research presented here aims to bridge the gap in information between the various steam conditions to study the resistance of target alloys. To be examined are the effects from steam temperature, steam pressure, and, to a limited extent, the effect of sample curvature. The importance of steam chemistry is also recognized, and will be controlled during the experiments.

The primary alloys to be tested are the ferritic alloy SAVE12, the austenitic alloy SUPER 304H, the high Cr and high Ni alloy HR6W, and three nickel-base superalloys Inconel 617, Haynes 230, and Inconel 740. All represent the highest high-temperature strength alloys in their respective alloy classes. The nominal compositions of these target alloys are given in Table 5. There are two versions of the SAVE12 alloy (nominally 11Cr) that will be examined: a more corrosion resistant version (10.5Cr), and a higher strength version (9.5Cr).

TABLE 5. Nominal compositions of target alloys for USC applications.[6,10,11]

	Fe	Cr	Ni	Co	Mo	W	V	Nb	C	Si	Mn	Other
SAVE12[6]	Bal	11		3		3	0.2	0.07	0.10	0.3	0.2	0.04 Nd 0.04 N
Super 304H[6]	Bal	18	9					0.40	0.10	0.2	0.8	3 Cu 0.1 N
HR6W[6]		23	43			6		0.18	0.08	0.4	1.2	0.08 Ti 0.003 B
Inconel 617[11]		22.0	55.0	12.5	9.0				0.07			1.0 Al
Haynes 230[11]	<3.0	22.0	55.0	<5.0	2.0	14.0			0.10			0.35 Al <0.015B 0.02 La
Inconel 740[10]		24	Bal	20			V	2				2 Ti Al

Curvature effects will be examined on HR6W and on the two SAVE12 alloys by machining samples from thick walled pipe. Each of these curvature samples will have one curved surface, representing either the inside (concave) or outside (convex) of the pipe. The curvature can modify the spallation behavior of oxides by changing the stress fields that are the driving force to detach part or all of the scale.

The work will consist of three types of tests:

- **Supercritical Steam Tests:** Long-term tests at the supercritical steam temperatures and pressures. The test duration of 3000 hours will consist of three 1000 hr segments.

- **Cyclic Oxidation:** Experiments using cyclic oxidation tests in air in the presence of steam. This will test the adhesion and spallation behavior of the protective oxides that form on the test alloys.

- **TGA in Steam:** Experiments using thermogravimetric analysis (TGA) with steam at atmospheric pressure. This will test alloys for susceptibility to steam oxidation using relatively short test durations.

Supercritical Steam Tests: Experiments will be carried out using a commercially procured René 41 autoclave (rated at 760°C and 5500 psig) and an Albany Research Center (ARC) built steam generator. These experiments will allow data to be gathered in a flowing supercritical steam environment. The present design of the system is shown in Fig. 1. The test apparatus system is currently in the process of being assembled.

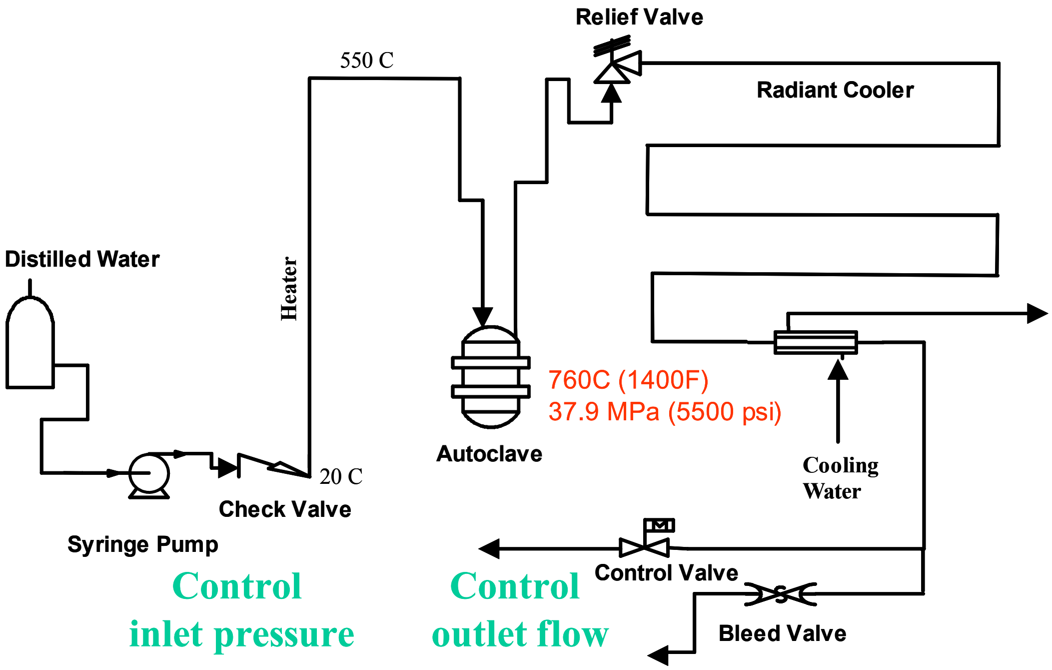

Fig. 1: Supercritical steam loop with inlet pressure control and outlet flow control.

Typical experiments will be 3000-hour exposures run in the autoclave at 760°C with steam pressures of 3300, 4000, and 5000 psi. Tests will be interrupted every 1000 hours for sample examinations and the swapping in and out of some of the samples. Deaerated water (with measured dissolved oxygen (DO) levels and conductivity values) will be used to generate steam at a flow rate of 2 mm/sec and a target DO of 200 ppb. Steam will be delivered to the pressure vessel from a high-pressure steam generator and the flow rate through the sample region will be controlled.

Cyclic Oxidation: Tests with cyclic heating and cooling (1 hour cycles) will be done in a tube furnace equipped with a programmable slide to raise and lower the samples, Fig. 2. Water will be metered into heated tubing and fed into the tube furnace. The exposures will be in steam/air mixtures at up to 800°C. Both flat and curvature samples will be examined.

TGA in Steam: Experiments with thermogravimetric analysis (TGA) have been initiated to examine alloys for susceptibility to steam oxidation using relatively short test durations, Fig. 3. The TGA tests consist of suspending a sample from a Cahn D-101 microbalance in flowing steam for 300 hours at a constant elevated temperature (650-800°C). Steam is generated by injecting a metered amount of water into heated tubing to supply a minimum flow rate of 2 mm/sec of steam in the reaction chamber. Initial experiments have used either N_2- or O_2-saturated water as inputs. Future tests may also use a carrier gas of 50% Ar along with the steam. Even though the presence of Ar is further removed from the actual steam conditions of a power plant, it has been reported[10] that the resulting scale morphologies more closely match industrial conditions than with pure steam alone (for tests conducted at atmospheric pressure).

Fig. 2: Cyclic oxidation apparatus for testing in atmospheric pressure steam/air mixtures at up to 800°C.

Fig. 3: TGA apparatus for testing in atmospheric pressure steam at up to 800°C.

Post experiment analyses consist of determining the parabolic rate constant (if present), noting the susceptibility to spalling in these isothermal tests, and using metallographic cross sections to determine scale morphology and composition.

INITIAL RESULTS

Samples of five of the six target alloys have been obtained for study. The remaining alloy to be obtained is the austenitic alloy Super 304H. While obtaining the target alloys, most of the tests using the TGA apparatus have principally been done on alloys other than the target alloys. The other alloys that were tested were AISI 304, AISI 347, René 41 (the autoclave material and so is of interest, the nominal composition[11] is Ni-19Cr-11Co-10Mo-3.1Ti-1.5Al-<0.3Fe-0.09C-0.01B), and ARC research alloys[12-13] X3 and X8 (nominal compositions of Fe-16Cr-16Ni-2Mn-1Mo-2Si and Fe-16Cr-16Ni-2Mn-1Mo-2Si-1Al, respectively).

Figure 4 shows the TGA results from the longest running test on AISI 347 at 760°C in O_2 saturated steam. The results are shown three different ways. Figure 4A shows a relatively large mass increase with time, with little noise in the data. For other alloys with much lower corrosion rates, the corresponding plots are much noisier. Sources of the noise include water condensation on the hang-down wire and noise associated with reaching a steady state of steam production. Adjustments in the upward flow of steam and the downward flow of nitrogen from the balance mechanism, coupled with insulation around the containment tube have been able to reduce and eliminate condensation on the hang-down wire. Adding a carrier gas of 50% Ar may reduce noise related to reaching a steady state of steam production at the beginning of each run. In Fig. 4B, the slope is the parabolic rate constant, and is relatively constant after 25 hr.

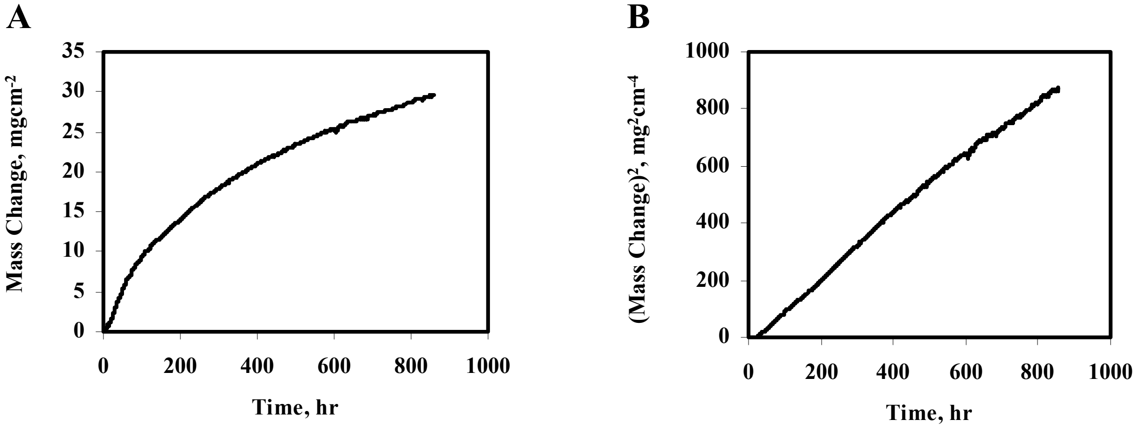

Fig. 4: TGA results from AISI 347 at 760°C with O_2 saturated feed water. The slope in B is the parabolic rate constant (with conversion from mg^{2}cm^{-4}hr^{-1} to mg^{2}cm^{-4}sec^{-1}).

Table 6 summarizes the conditions and results to date. For determination of the parabolic rate constant, only the linear portion of the TGA curves (similar to Fig. 4B) was used. The "Log-Log Slope" over the same linear portion is also reported. It is expected to be 0.5 for parabolic kinetics.

The results in Table 6 show that AISI 347 had much higher corrosion rates than the other alloys examined. The parabolic rate constant was the same for both tests with AISI 347. Haynes 230 had a very low corrosion rate. The morphologies of two of the corroded samples are shown in Figs. 5-6. Even taking into account the longer exposure time for the AISI 347, the scale is much thicker for the AISI 347 (~ 80 µm, Fig. 6) than for the Haynes 230 (~1.4 µm Fig. 5). The AISI 347 scale consists of two layers—a wide inner layer and a thin outer layer.

TABLE 6. Results from TGA experiments. The linear time range is the period from which the log-log slope and parabolic rate constants were determined.

Alloy	Temp, °C	Feed Water Saturated with	Nominal Test Duration, hr	Log-Log Slope	Parabolic Rate Constant, $mg^2cm^{-4}sec^{-1}$	Linear Time Range
AISI 304	700	N_2	170	0.50	1.2×10^{-8}	< 120 hr
AISI 347	760	O_2	300	0.86	2.2×10^{-4}	> 20 hr
AISI 347	760	O_2	850	0.59	2.9×10^{-4}	> 25 hr
X3	760	O_2	350	0.56	3.5×10^{-8}	all
X8	760	O_2	230	0.45	3.2×10^{-8}	< 180 hr
Haynes 230	760	O_2	150	0.31	4.9×10^{-9}	all
René 41	800	O_2	300	0.58	7.2×10^{-7}	all

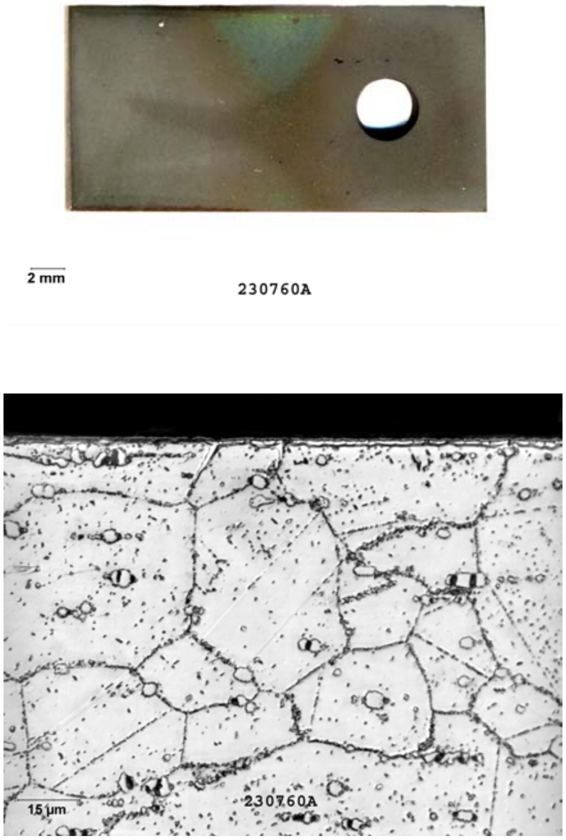

Fig. 5: Haynes 230 after exposure in O_2 saturated steam at 760°C for 150 hr. Above is the sample after exposure; below is a cross section using light microscopy. Note that the cross section scale is different than in Fig. 6.

Fig. 6: AISI 347 after exposure in O_2 saturated steam at 760°C for 850 hr. Above is the sample after exposure; below is a cross section using light microscopy. Note that the cross section scale is different than in Fig. 5.

SUMMARY

An outline for examining steamside corrosion in USC power generation plants was presented to aid in increasing operating temperatures of steam boilers and turbines for increased efficiencies and lower emissions. Three basic types of experimentation are planned: high temperature-high pressure exposures in steam, cyclic oxidation at atmospheric pressures in air plus steam, and shorter duration thermogravimetric analysis (TGA) in steam and steam plus argon.

Initial TGA results are presented for exposure of AISI 304, AISI 347, Haynes 230, René 41, Fe-16Cr-16Ni-2Mn-1Mo-2Si, and Fe-16Cr-16Ni-2Mn-1Mo-2Si-1Al. These results show a very low oxidation rate for one of the target alloys: Haynes 230.

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