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Ultra Supercritical Turbines—Steam Oxidation

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ABSTRACT

Ultra supercritical (USC) power plants offer the promise of higher efficiencies and lower emissions, which are goals of the U.S. Department of Energy's Advanced Power Systems Initiatives. 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. Current Advanced Power Systems goals include coal generation at 60% efficiency, which would require steam temperatures of up to 760°C. This research examines the steamside oxidation of advanced alloys for use in USC systems, with emphasis 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 steam generator in 1957—located at the Ohio Power Company's Philo 6 plant.[2] Since 1960, the overall trend of increasing temperatures and pressures has stopped and stabilized in the United States at about 538°C and 24.1 MPa.[3] In Europe and Japan, where fuel costs are a higher fraction of the cost of electricity, temperatures and pressures continued to rise. An example of a state of the art power plant in Europe is the Westfalen (2004) plant, with steam conditions of 31.0 MPa/593°C/621°C.[4] It has a net plant efficiency of 43.5%, compared to 37% for a subcritical 16.5 MPa/538°C/ 538°C plant.[4] Today there is again interest in the United States for advanced supercritical power plants. Large increases in the cost of natural gas have led to the reexamination of coal power plants, and advanced supercritical plants offer advantages in lower fuel costs and lower emissions of SO_X, NO_X, and CO_2.[5] Current U.S. Department of Energy research programs are aimed at 60% efficiency from coal generation, which would require increasing the operating conditions 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]

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. The temperature limit for use of ferritic steels appears to be limited to about 620 to 630°C. For temperatures above 630°C, the most promising candidate alloys are nickel-base superalloys.

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.

For reduced CO_2 emissions, calculations by Booras *et al.*[6] indicate that a subcritical 37% efficient plant 500 MW plant burning Pittsburgh #8 coal would produce about 850 tons of CO_2 per kWh. Ultra supercritical plants at 43% and 48% efficiency would respectively produce about 750 and 650 tons of CO_2 per kWh.

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

RESEARCH APPROACH

The research presented here aims to bridge the gap in information between the various steam conditions to study the steamside oxidation 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 2.

TABLE 2. Nominal compositions of target alloys for USC applications.[7-9]

	Fe	Cr	Ni	Co	Mo	W	V	Nb	C	Si	Mn	Other
SAVE12[7]	Bal	11		3		3	0.2	0.07	0.10	0.3	0.2	0.04 Nd 0.04 N
Super 304H[7]	Bal	18	9					0.40	0.10	0.2	0.8	3 Cu 0.1 N
HR6W[7]		23	43			6		0.18	0.08	0.4	1.2	0.08 Ti 0.003 B
Inconel 617[8]		22.0	55.0	12.5	9.0				0.07			1.0 Al
Haynes 230[8]	<3.0	22.0	55.0	<5.0	2.0	14.0			0.10			0.35 Al <0.015B 0.02 La
Inconel 740[9]		24	Bal	20				2				2 Ti Al

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). A limited number of tests will be done on SAVE12 samples that have been surface treated on one side to increase oxidation resistance.

Curvature effects will be examined on HR6W and on the two SAVE12 alloys (without surface treatment) 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 research approach consists of three types of tests:

- **Supercritical Steam Tests:** Long-term tests at the supercritical steam temperatures and pressures. The test durations of 1000 and 3000 hours.

- **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 (300 hr) 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.

Typical experiments will be 1000-hour and 3000-hour exposures run in the autoclave at temperatures up to 760°C with steam pressures of 3300, 4000, and 5000 psi. 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, a target DO of 150-200 ppb, and a target pH of 9.2-9.6. 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.

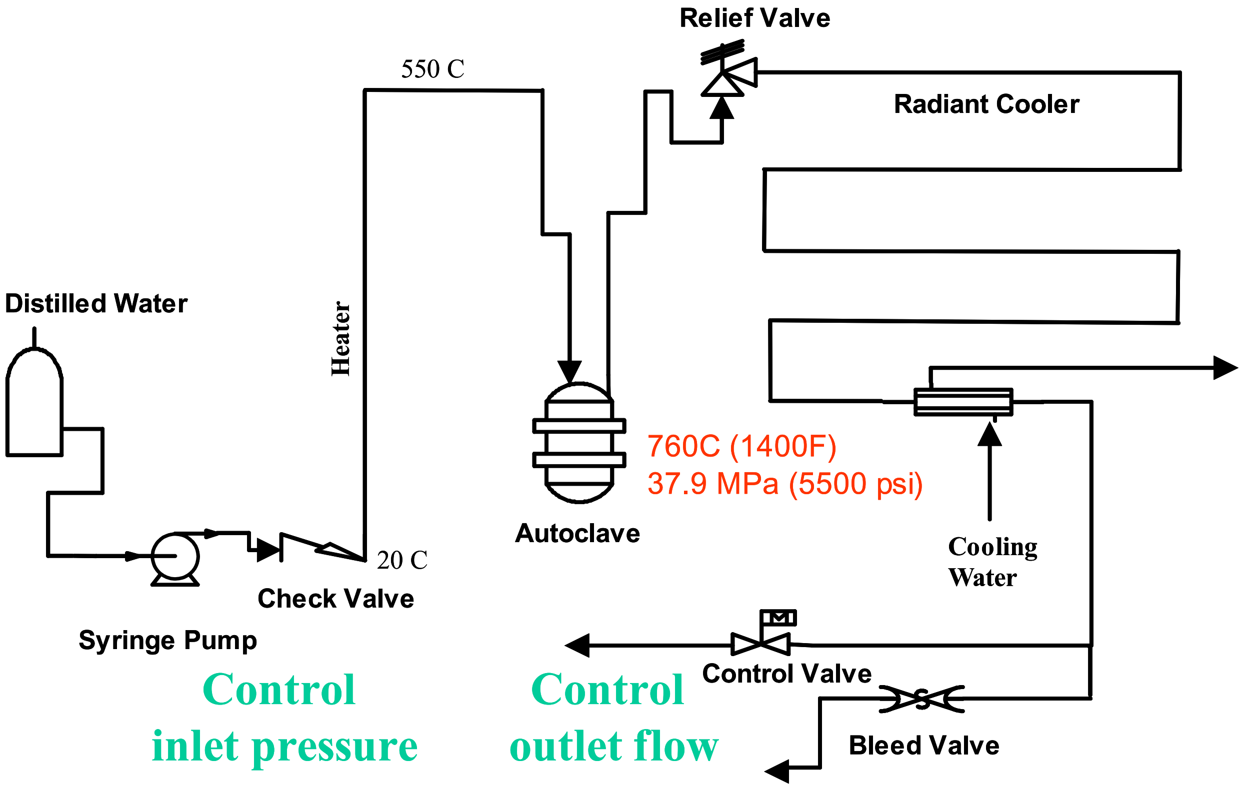

Fig. 1: Supercritical steam loop with inlet pressure control and outlet flow control.

Cyclic Oxidation: Tests with cyclic heating and cooling (1 hour cycles) have been initiated in a tube furnace equipped with a programmable slide to raise and lower the samples, Fig. 2. Water is metered into heated tubing and fed into the tube furnace. The exposures are 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. Current tests 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[9] 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.

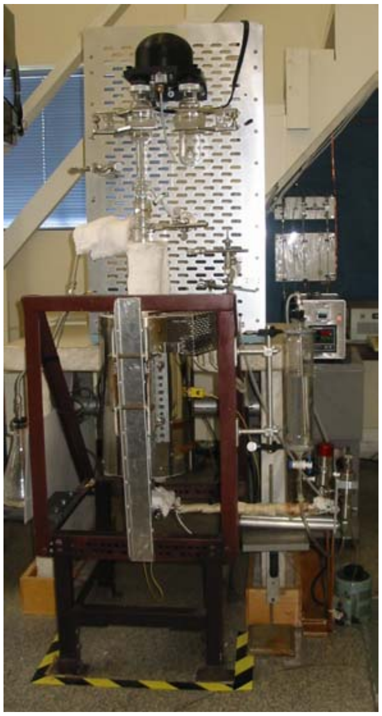

Fig. 3: TGA apparatus for testing in atmospheric pressure steam at up to 800°C.

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 of interest that were tested were AISI 304, AISI 347, René 41 (the high pressure autoclave material with a nominal composition[8] of Ni-19Cr-11Co-10Mo-3.1Ti-1.5Al-<0.3Fe-0.09C-0.01B), and ARC research alloys[10-12] X3, X8, J1, and J5 (compositions of Fe-16Cr-16Ni-2Mn-1Mo-2Si, Fe-16Cr-16Ni-2Mn-1Mo-2Si-1Al, Ni-12.1Cr-18Mo-1Ti-0.8Al and Ni-12.5Cr-22Mo-1Ti-0.5Mn-0.04Y respectively). Alloy J1 is an equivalent composition to Mitsubishi alloy LTES700, a low coefficient of thermal expansion nickel-base alloy developed for use as fasteners and blades in both current and USC steam turbines.[13]

Figure 4 shows the TGA results from the longest running test on AISI 347 at 760°C in O_2 saturated steam. Figure 4A shows a relatively large mass increase with time, with little noise in the data. In Fig. 4B, the slope is the parabolic rate constant, and is relatively constant after 25 hr.

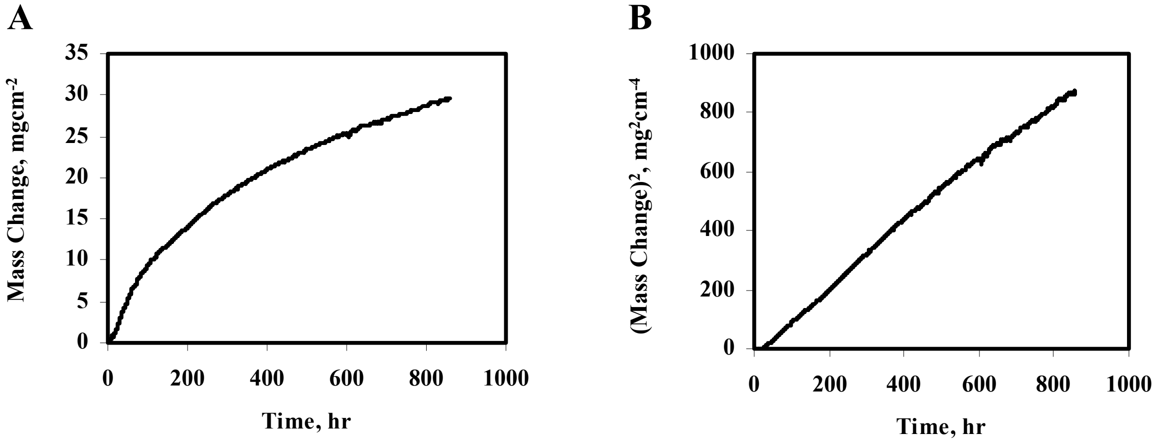

Fig. 4: TGA results from AISI 347 at 760°C with O_2 saturated feed water. The slope in B is the parabolic rate constant (with conversion from $mg^2cm^{-4}hr^{-1}$ to $mg^2cm^{-4}sec^{-1}$).

Table 3 summarizes the conditions and results to date. The parabolic rate constant has varied from fast kinetics for AISI 347 (2.1×10^{-4} $mg^2cm^{-4}sec^{-1}$) to very slow kinetics for Haynes 230 (4.9×10^{-9} $mg^2cm^{-4}sec^{-1}$). The columns "Log-Log Slope" and "Parabolic R^2" are measures of how well parabolic kinetics describes the results. The "Log-Log Slope" is the slope of the log(mass change) versus log(time), and should be 0.5 for parabolic kinetics. The parabolic R^2 values are how well the data correlate with parabolic behavior using the calculated k_p (with 1 being exact correlation and 0 being no correlation).

TABLE 3. Results from TGA experiments.

Alloy	Temp, °C	Feed Water Saturated with	60% Ar Carrier Gas?	Log-Log Slope	Parabolic Rate Constant, $mg^2cm^{-4}sec^{-1}$	Parabolic R^2
AISI 304	700	N_2	No	0.50	1.2×10^{-8}	0.882
AISI 347	760	O_2	No	0.88	2.1×10^{-4}	0.988
AISI 347	760	O_2	No	0.72	2.9×10^{-4}	0.997
X3	760	O_2	No	0.56	3.5×10^{-8}	0.863
X8	760	O_2	No	0.45	3.2×10^{-8}	0.773
Haynes 230	760	O_2	No	0.31	4.9×10^{-9}	0.451
Haynes 230	800	O_2	Yes	0.56	6.9×10^{-8}	0.878
René 41	800	O_2	No	0.58	7.2×10^{-7}	0.983
Inconel 617	800	O_2	Yes	0.29	1.9×10^{-8}	0.330
J1	800	O_2	Yes	0.58	3.8×10^{-7}	0.990
J5	800	O_2	Yes	0.52	1.7×10^{-7}	0.990

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 scale on the AISI 347 consisted of two layers—a wide inner layer of Cr-Fe oxide (Cr:Fe of 1:1) and a thin outer layer of iron oxide. The scale on the Haynes 230 was a Cr-Ni oxide (Cr:Ni of 3:1).

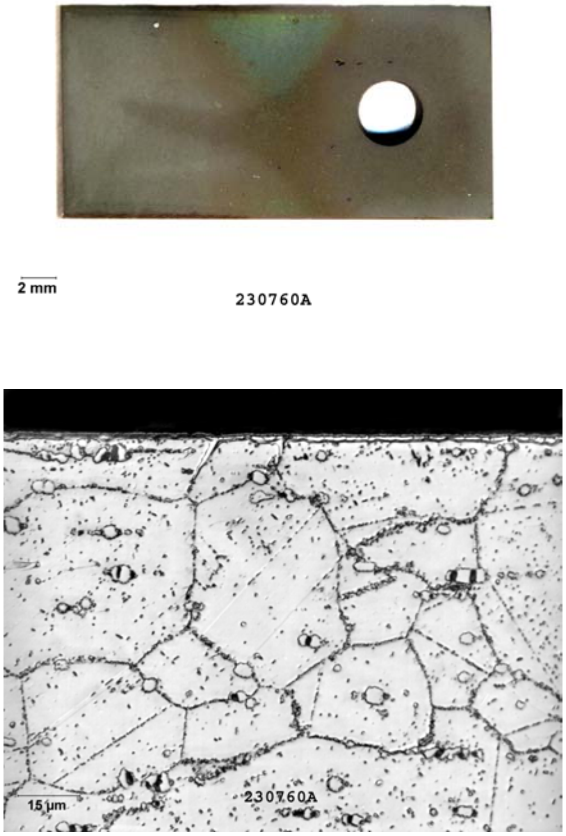

Fig. 5: Haynes 230 after exposure in O_2 saturated steam at 760°C for 150 hr. Above is the sample after exposure; below is a cross section using light microscopy.

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.

Initial results for cyclic oxidation testing at 760°C are shown in Figs. 7 and 8 for the three nickel-base superalloys and for the SAVE12 alloys, respectively. The nickel-base superalloys had an initial mass increase followed by a slow decrease in mass. The SAVE12 alloys are at higher temperatures then they were designed for and show large increases in mass with time. These tests are ongoing and so scale analyses have not been performed.

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 results for cyclic oxidation and TGA tests were presented.

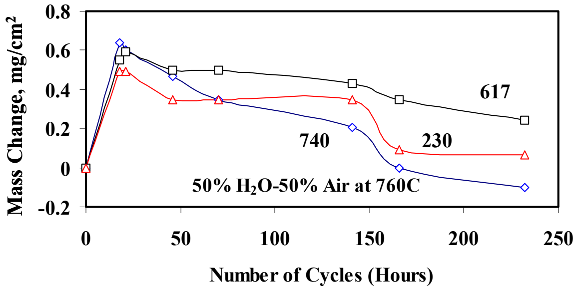

Fig. 7: Cyclic oxidation results for nickel-based superalloys at 760°C in 50% H_2O-50% air with hourly cycles.

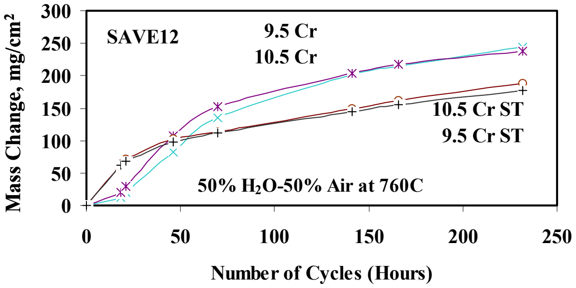

Fig. 8: Cyclic oxidation results for The 9.5Cr and 10.5Cr versions of SAVE12 at 760°C in 50% H_2O-50% air with hourly cycles. The curves marked as ST had a proprietary surface treatment on one side of each sample.

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