STEAM TURBINE MATERIALS AND CORROSION

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ABSTRACT

Ultra supercritical (USC) power plants offer the promise of higher efficiencies and lower emissions. Current goals of the U.S. Department of Energy's Advanced Power Systems Initiatives include coal generation at 60% efficiency, which would require steam temperatures of up to 760°C. This research examines the steamside oxidation of alloys for use in USC systems, with emphasis placed on applications in high- and intermediate-pressure turbines.

The list of alloys being examined is discussed, including the addition of new alloys to the study. These include alloy 625, selected because of its use as one of the two alloys used for turbine rotors, valves, casings, blading and bolts in the European AD700 full-scale demonstration plant (Scholven Unit F). The other alloy, alloy 617, is already one of the alloys currently being examined by this project. Other new alloys to the study are the three round robin alloys in the UK-US collaboration: alloys 740, TP347HFG, and T92.

Progress on the project is presented on cyclic oxidation in 50% air – 50% water vapor, furnace exposures in moist air, and thermogravimetric analysis in argon with oxygen saturated steam. An update on the progress towards obtaining an apparatus for high pressure exposures is given.

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 in the United States, the overall trend of increasing temperatures and pressures has stopped and stabilized 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 typical 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 re-examination 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]

OBJECTIVES

The research aims to bridge the gap in information between various steam conditions to study the resistance of target alloys and the role of pressure in the corrosion mechanisms. The objectives of this project are to:

- Determine the steam oxidation behavior of target alloys to identify viable materials for use in ultra-supercritical steam (USC) turbines.
- Determine the role of pressure on oxidation mechanisms.
- Examine curvature effects on spallation.

TECHNICAL PROGRESS

ALLOYS

Six alloys were investigated at the start of this research effort: Save12 (9.5Cr and 10.5Cr versions), HR6W, Haynes 230, Inconel 617 and Inconel 740. The compositions of these alloys are shown in Table 1. All are high strength alloys that were part of the Advanced Power System Initiative on USC boilers.[6] Then two superalloys identified[7-8] by EPRI as candidates for blade materials for USC conditions were added: Nimonic 90 and Inconel 718. Two NETL developed alloys, J1 and J5, were produced for alloy development into low coefficient of thermal expansion (CTE) alloys.[9] J1 has an equivalent composition to Mitsubishi alloy LTES700, a low CTE nickel-base alloy developed for use as fasteners and blades in both current and USC steam turbines.[10] Alloy J5 is a modified version of J1 for solid oxide fuel cell applications (Al was removed to prevent insulating alumina formation and was Mn added to promote Cr-Mn spinel formation for reduced Cr-oxide evaporation).

Table 1

Alloy compositions. Analysis types: XRF is x-ray fluorescence, Cert is a manufacturer's certificate for the specific heat, and Nom is a nominal composition.

Alloy	Analysis	Fe	Cr	Ni	Co	Mo	Nb	Mn	Si	Ti	Al	Other
SAVE12-9.5Cr	XRF	83.0	9.5	0.4	2.6	0.04	0.05	0.5	0.4	0.02		2.9 W 0.3 V
SAVE12-10.5Cr	XRF	82.9	10.3	0.2	3.0		0.06	0.5	0.8	0.01		2.9 W 0.3 V
HR6W	XRF	24.2	23.6	43.4	0.4	0.2	0.2	1.0	0.3	0.2	0.04	6.1 W 0.1 Cu
Inconel 230	XRF	1.3	22.6	58.8	<0.05	1.3		0.5	0.3		0.4	14.3 W
Inconel 617	XRF	0.6	21.9	54.0	11.8	9.5		0.7	0.1	0.5	1.0	0.01 V
Inconel 740	Cert	0.5	24.4	Bal	20.0	0.5	2.0	0.3	0.5	1.8	1.0	
Nimonic 90	XRF	1.5	19.2	59.7	15.6	0.12	0.04	0.02	0.3	2.3	1.2	0.06 Cu
Haynes 718	Cert	18.1	18.0	53.8	0.2	3.0	5.3	0.2	0.08	1.0	1.6	0.04 Cu
J1	Nom		12.1	Bal		18				1	0.8	
J5	Nom		12.5	Bal		22		0.5		1		0.04 Y
Inconel 625	Nom	<5	21.5	Bal	<1	9	*	<0.5	<0.5	<0.4	<0.4	Nb+Ta = 3.6
T92	Nom		9	<0.4		0.5		0.5	<0.5		<0.04	1.75 W 0.2 V 0.07 Cb
TP347HFG	Nom	Bal	18	11			*	2.0	1.0			Nb+Ta≥10xC

Recently, additional alloys were added to the research program. Inconel 625 is one of two alloys used for turbine rotors, valves, casings, blading and bolts in the European AD700 full-scale demonstration plant (Scholven Unit F).[11] (The other alloy, Inconel 617, was already one of the alloys currently being examined by this project). The US/UK

Collaboration on Energy R&D: Clean Coal Technology Advanced Materials Program has led to the inclusion of three round-robin testing alloys: Inconel 740, T92, and TP347HFG. Thus there are two versions of Inconel 740 in the study. At this time there are no results for Inconel 625 or the US/UK alloys.

All surfaces on each sample (except where noted) were polished to 600 grit. Curvature effects were examined on Save12 (10.5Cr) and HR6W by machining samples from thick walled pipe. Each of the curvature samples had one curved surface, representing either the inside (concave) or outside (convex) surface of a pipe, Fig. 1. The curved surfaces were machined from as-received pipe (to remove mill-scale) and not subsequently polished to 600 grit.

Fig. 1. Section of Save12 10.5Cr pipe (2-in O.D.) and curvature samples cut from pipe. All but one side of the curvature samples are flat. Samples: concave (left) and convex (right).

SUPERCRITICAL STEAM

A test loop in supercritical steam with temperatures and pressures up to 760°C (1400°F) and 37.9 MPa (5500 psi) was designed. The material of construction for the autoclave was to be Rene 41. The autoclave was due for delivery on 12/31/2004. After much delay, the contract for the autoclave was cancelled. After consultation with autoclave manufactures, a new solicitation (DE-RQ26-06NT00425) was posted on 5/4/2006 for a system with temperatures and pressures up to 746°C (1375°F) and 34.5 MPa (5000 psi), Fig. 2. The new material of construction is to be Haynes 230. The feed water system, shown in Fig. 3, will allow for measurement and some control of water chemistry (pH, dissolved oxygen (DO), and conductivity). Tests would be done to represent an oxygenated system with 150-200 ppb DO and a pH of 9.2 to 9.6.

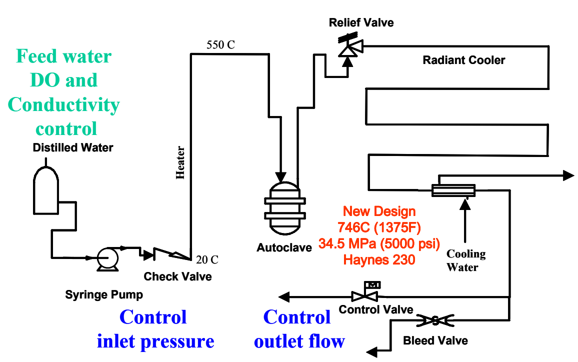

Fig. 2. Supercritical test loop for exposures in supercritical steam with temperatures and pressures up to 746°C (1375°F) and 34.5 MPa (5000 psi). Autoclave size of 1 liter.

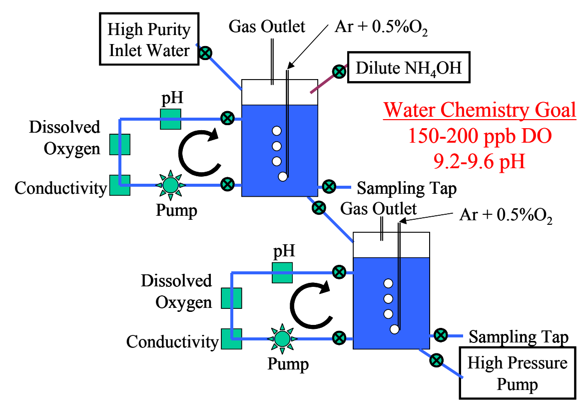

Fig. 3. Feed water system for supercritical steam exposures.

CYCLIC OXIDATION

Cyclic oxidation experiments were conducted in air in the presence of steam at atmospheric pressure. This was designed to examine the adhesion and spallation behavior of the protective oxides that form. The tests consisted of 1-hour cycles of heating and cooling (55 minutes in the furnace and 5 minutes out of the furnace) in a tube furnace equipped with a programmable slide to raise and lower the samples. Water was metered into the bottom of the furnace along with compressed air (50% water vapor-50% air, by volume). The exposure temperature for these initial tests was 760°C. Both flat and curvature samples were examined.

Results are shown in Figs. 4-9. Overall, all of the nickel-base alloys have relatively thin oxide scales and also have internal oxidation. Of these, Inconel 740 and Haynes 230 have scales with the least amount of metal damage. Both of these also have slowly declining masses with test duration, which is probably due to Cr-oxide evaporation. No spalling was observed in the collection cups used to hold the samples during removal from the apparatus for mass measurement. While not definitive (spalling could have occurred within the furnace), other alloy systems examined with this apparatus have shown spalling in the collection cups.

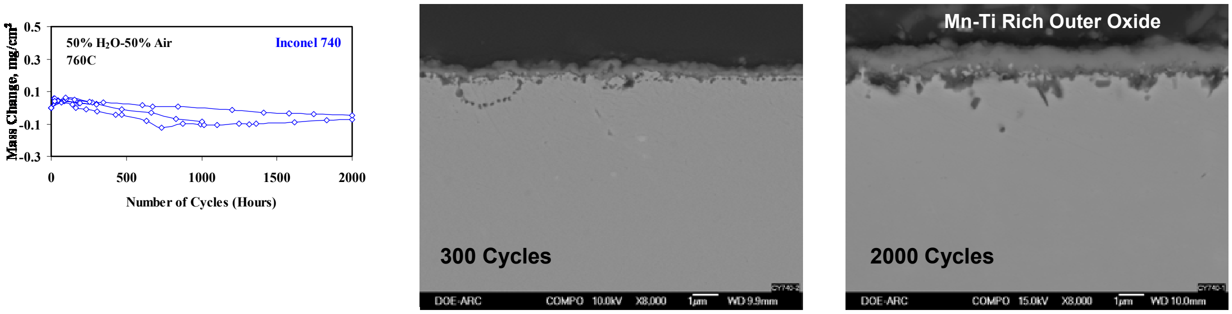

Fig. 4. Cyclic test results for Inconel 740 in 50%H_2O-50% air at 760°C.

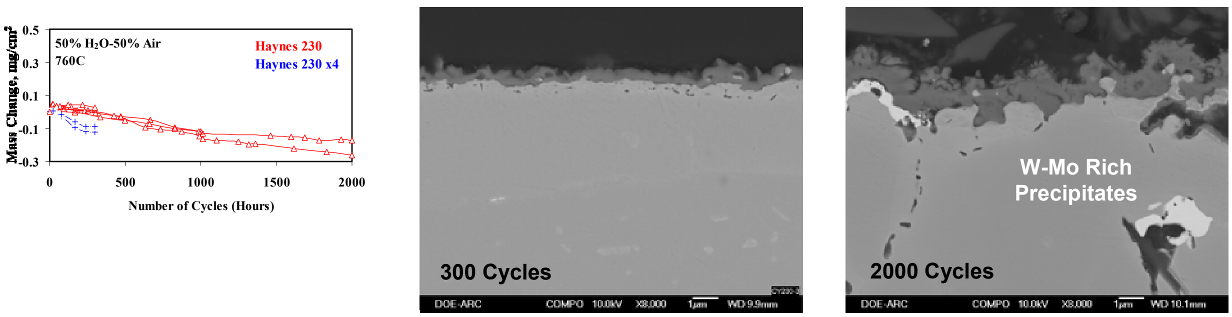

Fig. 5. Cyclic test results for Haynes 230 in 50%H_2O-50% air at 760°C.

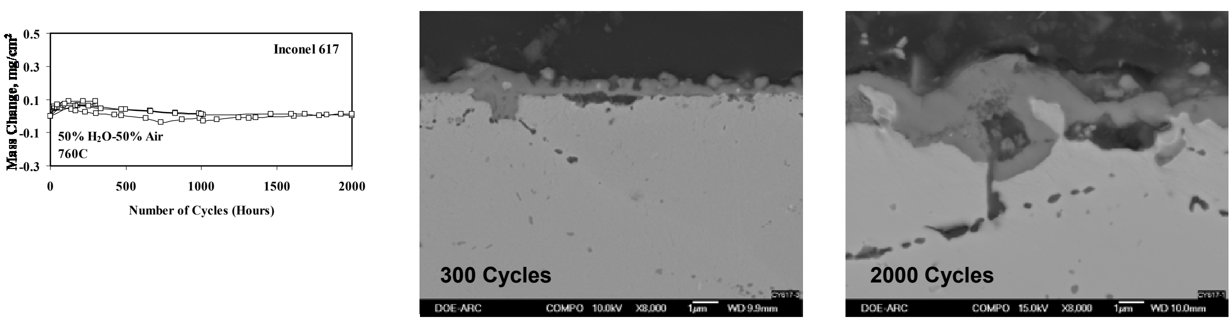

Fig. 6. Cyclic test results for Inconel 617 in 50%H_2O-50% air at 760°C.

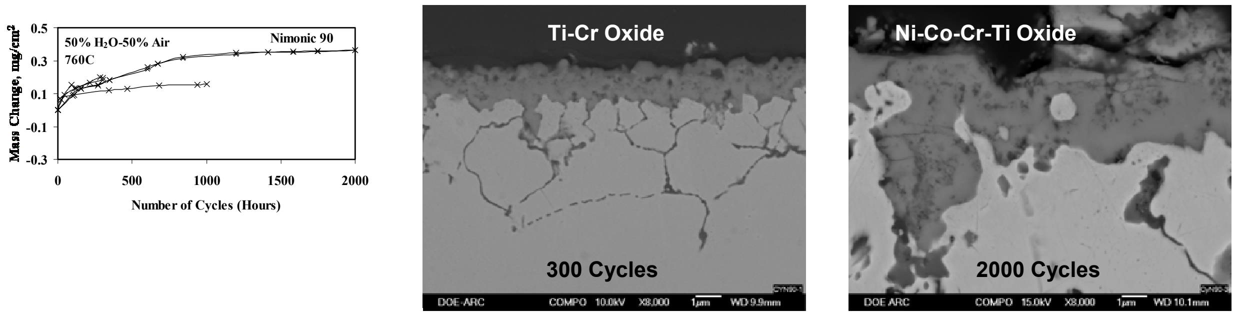

Fig. 7. Cyclic test results for Nimonic 90 in 50%H_2O-50% air at 760°C.

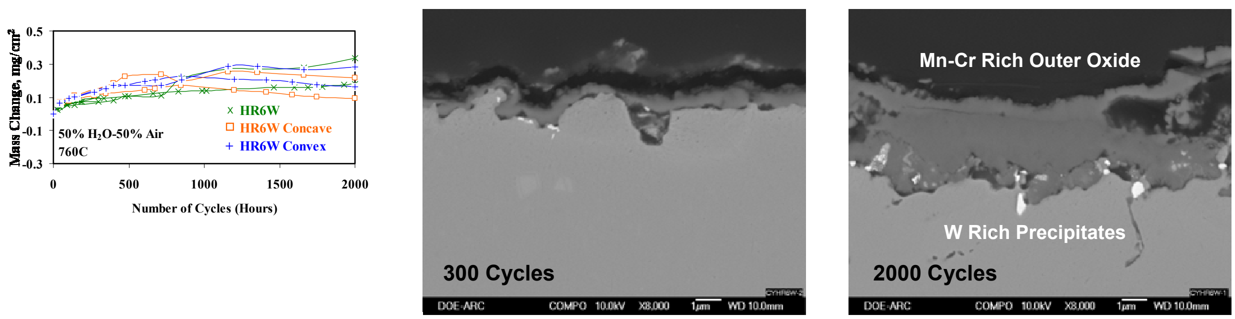

Fig. 8. Cyclic test results for HR6W in 50%H_2O-50% air at 760°C.

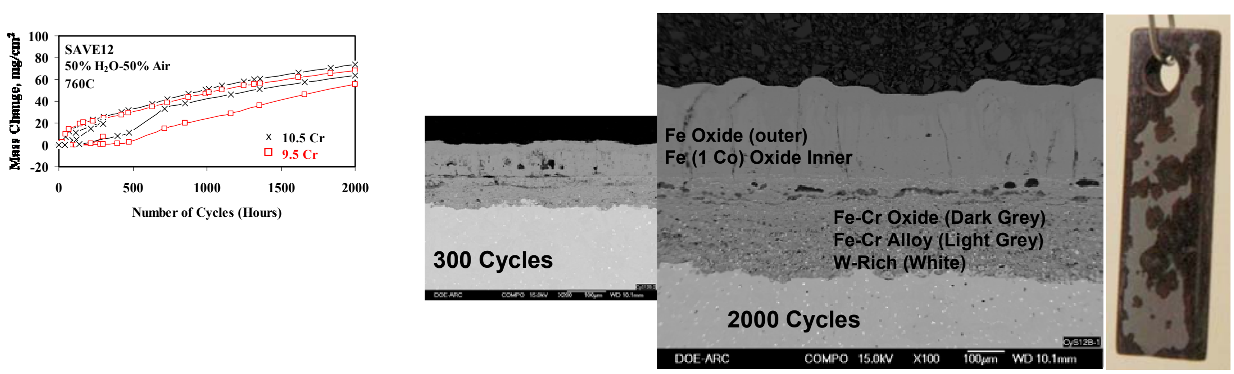

Fig. 9. Cyclic test results for Save12 in 50%H_2O-50% air at 760°C.

The figure for HR6W includes results for curvature samples. However, the curvature results closely match the results for the planar samples.

Save12 results in very thick oxides. Initial oxidation of Save12 also varies by quite a bit. A photo of an exposed sample (included in Fig. 9) shows a mottled surface with heavily oxidized regions next to relatively intact regions. So the variation in initial oxidation is attributed to relative percentages of each type of surface. As with the HR6W results, the Save12 curvature samples showed no significant difference from the planar samples.

THERMOGRAVIMETRIC ANALYSIS (TGA)

Experiments were conducted using thermogravimetric analysis (TGA) with steam at atmospheric pressure. This was designed to obtain information on oxidation kinetics using relatively short (300 hr) test durations. 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 O_2-saturated water into heated tubing to supply a minimum flow rate of 2 mm/s of steam in the reaction chamber. Initial experiments used pure steam. More recent tests used a carrier gas of 60% Ar along with the steam. Table 2 summarizes the results of the 300 hr TGA tests in O_2-saturated steam plus 60%Ar at 800°C.

The reaction order and parabolic R^2 are measures of how well the data fit parabolic kinetics of:

$$\text{Mass change} = k_p t^{1/n} \qquad (1)$$

where k_p is the parabolic rate constant, t is time, and n is the reaction order (n = 1 for linear kinetics and n = 2 for parabolic kinetics). The parabolic R^2 measures how well the data correlate with parabolic behavior using the calculated k_p (with 1 being exact correlation and 0 being no correlation). The parabolic R^2 values for Save12, J1, J5, and one of the Alloy 617 tests were quite close to 1, showing excellent correlation with parabolic kinetics and with relatively little noise in the data. The oxidation rates of Alloy 230, HR6W, Alloy 740, and one of the Alloy 617 tests were lower, and with more noise in the mass change data, which resulted in lower parabolic R^2 values. As discussed last year, further TGA tests of the highly resistance nickel-base alloys has been curtailed.

Table 2

Thermogravimetric analysis (TGA) for 300 hr tests in O_2-saturated steam plus 60%Ar at 800°C

Alloy	%Cr	Reaction Order, n	Parabolic R^2	Parabolic Rate Constant, k_p $mg^2cm^{-4}s^{-1}$
12 (9.5Cr)	9.5	1.78	1.000	1.2×10^{-3}
12 (9.5Cr)	9.5	1.90	1.000	1.4×10^{-3}
12 (10.5Cr)	10.5	1.70	1.000	1.6×10^{-3}
12 (10.5Cr)	10.5	1.76	0.995	1.7×10^{-3}
J1	12.1	1.73	0.990	3.5×10^{-7}
J5	12.5	1.91	0.990	1.5×10^{-7}
617	22	1.62	0.960	1.4×10^{-7}
617	22	2.63	0.585	3.9×10^{-8}
230	22	1.78	0.878	6.9×10^{-8}
230	22	1.79	0.645	3.7×10^{-8}
6W	23	1.87	0.524	3.3×10^{-8}
740	24	2.20	0.527	7.2×10^{-7}

FURNACE EXPOSURES

Experiments were added that exposed samples to moist air at atmospheric pressure. These tests consisted of exposing the samples to air that was bubbled through water, resulting in up to 3% water vapor in the atmosphere. Samples were periodically removed from the furnace for mass measurements, and then replaced in the furnace for further exposure. More recent tests have attempted to improve the procedures by ensuring that the input air is water saturated and that the temperature cycles are more tightly controlled (100 hr cycles with 200 °C/hr ramp rates). The results for furnace exposures in moist (3% H_2O) air are shown in Fig. 10.

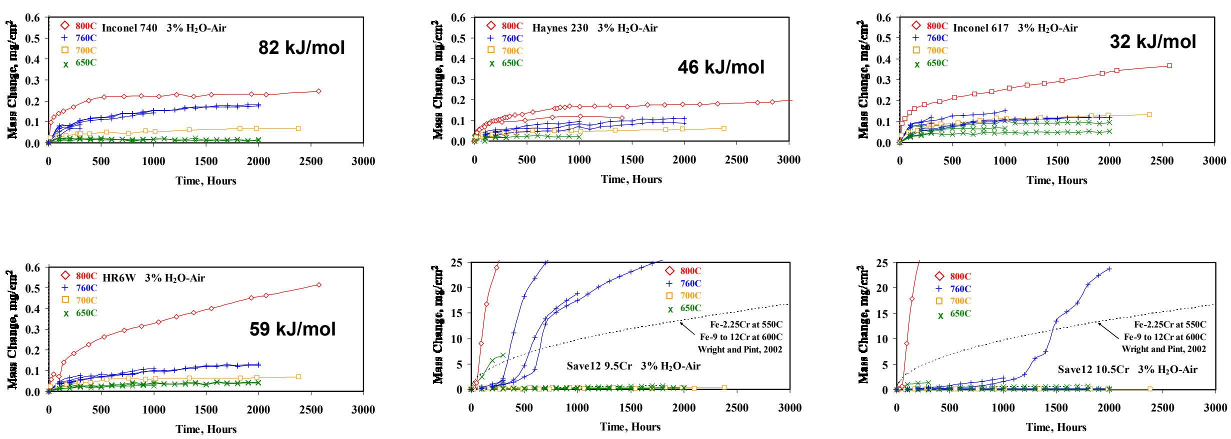

Fig. 10. Furnace exposure results for superalloys and Save12.

Included in the furnace exposure plots is a dotted line showing the average oxidation behavior of 2.25Cr steels at 550°C and 9-12Cr steels at 600°C. The parabolic rate constants used to generate these curves are from the compilation by Wright and Pint[12] for the corrosion of steels in water vapor and steam. This gives a comparison for the experimental results with acceptable oxidation rates of currently used alloys. Many of the Ni-base alloys have oxidation rates too low for the oxidation behavior of 2.25Cr steels at 550°C and 9-12Cr steels at 600°C to be visible in the same data range.

All of the nickel base alloys had modest mass gains at 650 and 700°C. Nimonic 90 (at 760°C) and HR6W (at 800°C) had higher mass gains than the other nickel alloys. To a lesser extent, Alloy 617 (at 800°C) also had higher mass gains and trends than Alloy 740 or Alloy 230. Overall, the best alloys in this test were Alloys 230 and 740. The oxidation rates for Save12 were quite high, and showed breakaway oxidation in some cases. The 10.5Cr version of Save12 looked acceptable at 650°C with low oxidation rates and no observed cases of breakaway oxidation.

PROGRESS COMPARED TO ORIGINAL PLAN

The original key milestones were as follows:

- Completion of facility for high-temperature and high-pressure steam exposures.
- Analysis of steam oxidation data of candidate USC turbine materials as a function of temperature and pressure, and in selected materials, sample curvature.
- Application of steam oxidation data to advance the knowledge of oxidation and spallation mechanisms in USC steam.

The first milestone has not been met. The delivery of the Rene 41 autoclave was postponed, delayed, and then finally cancelled. The original delivery date was 12/31/2004. A new solicitation for an autoclave made from Haynes 230 was posted in May of 2006.

The delay in the autoclave will postpone the pressure component on the second milestone listed above.

The cyclic, furnace exposure and TGA tests are proceeding as planned. Findings are listed below in Summary/Conclusions. A second and third cyclic rig may be added later this year.

The TGA tests have shown a limitation in the TGA system at low oxidation rates (that the nickel base alloys have even at 800°C). Future tests at lower temperatures will primarily be restricted to alloys that oxidize faster, such as the Save12 alloys.

Efforts to examine the effects of specimen geometry with simple curvature samples, Fig. 1, have not shown any conclusive differences.

OBJECTIVES FOR NEXT PERIOD

The objectives for the next year include:

- Obtain, setup, and operate a high temperature and pressure autoclave system.
- Continuing TGA, cyclic, and furnace tests.
- Examine other methods to quantify the effects of curvature and geometry on steam oxidation. These include selective oxidation studies on wire samples of various diameters, and possibly the use of hardness indents to show spallation and adhesion properties.

SUMMARY/CONCLUSIONS

The status of research to examine the steamside oxidation of advanced alloys for use in supercritical systems was presented. The alloys of interest were mainly nickel-base superalloys. The initial results from cyclic oxidation in moist air at 760°C, TGA in steam plus 60% Ar at 800°C, and furnace exposures in moist air at 700°C and 800°C were described:

- From a simplistic mass change standpoint, all of the Ni-base alloys look acceptable at up to 800°C.
- Save12 9.5-Cr shows breakaway oxidation ≥ 650°C.
- Save 12 10.5-Cr appears acceptable (from steam oxidation standpoint) at 650°C.
- All the Ni-base alloys show internal oxidation below the oxide scale. Of the alloys examined, Inconel 740 and Haynes 230 show the least damage from internal oxidation
- No evidence of curvature effects.

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