OXIDATION OF ALLOYS FOR ADVANCED STEAM TURBINES

G. R. Holcomb, B. S. Covino, Jr., S. J. Bullard, S. D. Cramer, and M. Ziomek-Moroz
U. S. Department of Energy
Albany Research Center
1450 Queen Avenue SW
Albany, OR 97321

EXECUTIVE SUMMARY

Ultra supercritical (USC) power plants offer the promise of higher efficiencies and lower emissions. 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).[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 had stopped and stabilized at about 538°C and 24.1 MPa.[1] 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.[3] It has a net plant efficiency of 43.5%, compared to 37% for a typical subcritical 16.5 MPa/538°C/ 538°C plant.[3] Today there is again interest in the United States for advanced supercritical power plants. Table 1 shows four new advanced supercritical power stations at three sites in the United States.[4] Steam conditions of the Council Bluffs plant is to be 25.4 MPa/566°C/593°C using a Babcock-Hitachi supercritical sliding pressure Benson boiler.[5]

TABLE 1
New Advanced Supercritical Power Plant Starts in the United States.[4]

Location	Size	Status	In Service	Cost	Fuel
Council Bluffs Iowa	790 MW	Construction started 8/2004	2007	1.2 B$	Coal
Trimble County Kentucky	750 MW	Proposed 11/2004	2010	1.2 B$	Illinois Basin Coal
Oak Creek Wisconsin	600 MW (2)	In Development 12/2004	2009-2010	2.5 B$	Powder River Basin Sub-Bituminous

The purpose here is to report on research that examines the steamside oxidation of advanced alloys for use in USC turbine systems. Emphasis is placed on alloys for high- and intermediate-pressure turbine sections. To be examined are the effects from steam temperature, steam pressure, and, to a limited extent, the effect of sample curvature. 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 importance of steam chemistry is also recognized, and will be controlled during supercritical steam exposures.

The results include research in progress from cyclic oxidation in moist air, thermogravimetric analysis in steam, and furnace exposures in moist air. Experimental plans for supercritical exposures are described.

Alloys examined are of interest for use in USC turbine applications. A subset of the alloys examined by the Advanced Power System Initiative on USC boilers, selected for examination for USC turbines, include the ferritic alloy SAVE12, the austenitic alloy SUPER 304H, the high Cr and high Ni alloy HR6W, and three nickel-base superalloys Alloy 617, Alloy 230, and Alloy 740. Also of interest are four superalloys identified[6] as candidates for blade materials for USC conditions: Alloy M-252, Refractory 26, Nimonic 90, and Alloy 718. Two nickel-base alloys, J1 and J5, were produced with low coefficient of thermal expansion for use in solid oxide fuel cells.[7]

Cyclic oxidation experiments were conducted in air in the presence of steam at atmospheric pressure. This was to examine the adhesion and spallation behavior of protective oxides. The tests consisted of 1-hour cycles of heating and cooling in an atmosphere of 50% water vapor-50% air, by volume.

- Cyclic oxidation of nickel-base superalloys indicated a relatively steady rate of oxide scale loss after an initial mass gain. The Ni-base alloy HR6W did not show a decrease.
- Cyclic oxidation of the ferritic SAVE12 alloys resulted in high oxidation rates with linear kinetics after an initially higher oxidation rate. With a proprietary surface treatment to one side of each sample, the linear oxidation rates were modestly better.

Thermogravimetric Analysis (TGA) experiments were conducted at atmospheric pressure. This was designed to obtain information on oxidation kinetics using relatively short (300 hr) test durations in flowing Argon plus 40% steam at a constant elevated temperature (650-800°C).

- TGA tests resulted in measured parabolic rate constants on the order of 10^{-3} $mg^2cm^{-4}s^{-1}$ for the SAVE12 alloys and 10^{-7} to 10^{-8} $mg^2cm^{-4}s^{-1}$ for the nickel-base alloys.

Furnace Exposures have samples in moist air (3% water) at atmospheric pressure at 700°C and 800°C.

- Furnace exposures gave quite high oxidation rates for the ferritic steel SAVE12 at 800°C, with 10.5Cr having slightly higher rates than 9.5Cr. At 700°C, the oxidation rates of SAVE12 were much lower; with 10.5Cr showing much less mass increase than 9.5Cr.
- Nickel-base alloys all showed good oxidation resistance at both temperatures.

REFERENCES

1. R. Viswanathan, A.F. Armor, and G. Booras, “Supercritical Steam Power Plants—An Overview,” Best *Practices and Future Technologies*, October 2003, Proceedings (New Delhi, India), National Thermal Power Corporation's Center for Power Efficiency and Environmental Protection and the US Agency for International Development, 2003.
2. *Steam*, 40th ed., Eds. S.C. Stultz and J.B. Kitto, Babcock & Wilcox, 1992, p. 9.
3. R. Swanekamp, *Power*, 146 (4), 2002, pp. 32-40.
4. S. Klara and E. Shuster, “Tracking New Coal-Fired Power Plants—Coal’s Resurgence in Electric Power Generation,” 12/22/2004, www.netl.doe.gov/coal/.
5. M. Richardson, Y. Kidera, and Y. Shimogori, “Supercritical Boiler Technology Matures,” www.hitachi.us/supportingdocs/ forbus/powerindustrial/CG2004.pdf.
6. Y. Tamada, A.M. Beltran, and G.P. Wozney, EPRI Report TR-100979, Electric Power Research Institute, Palo Alto, CA, 1992.
7. D.E. Alman and P.D. Jablonski, Proceedings of the 10th International Symposium on Superalloys, Champion, PA (September 2004) TMS, in press.