U.S. DEPARTMENT OF ENERGY

UK-US Collaboration on Fossil Energy R&D
Advanced Materials

DEPARTMENT OF ENERGY & CLIMATE CHANGE

project duration
April 2004 - April 2009

project partners

UK:
Cranfield University
Doosan-Babcock Energy
* National Physical Laboratory

US:
* Oak Ridge National Laboratory
National Energy Technology Laboratory

** Task Leaders*

Steam Oxidation

background

In recent years interest in the development of steam-generating power plants with increased efficiencies has led to the need to develop and qualify materials capable of operating at steam temperatures and pressures significantly higher than those employed in current power plants. On-going programs in Europe and Japan envisage steam conditions increasing in stages from 600°C to 700°C (1112 to 1292°F), and in the USA to 760°C (1400°F). The overall focus of these national programs is on using ferritic steels to the maximum possible temperature, before switching to austenitic steels or Ni-based alloys.

As a result, there has been considerable emphasis on improving the high-temperature creep properties of 9-12% Cr ferritic steels which currently appear to be capable of use up to approximately 620°C (1148°F) and 30 MPa (4500 psi). However, the relatively low Cr content of these alloys affects their resistance to steam oxidation at these higher temperatures. For the highest steam temperatures envisaged, only nickel-based alloys have the required strength, and for 760°C, a precipitation-strengthened Ni-based alloy is being considered, but with a severe cost penalty.

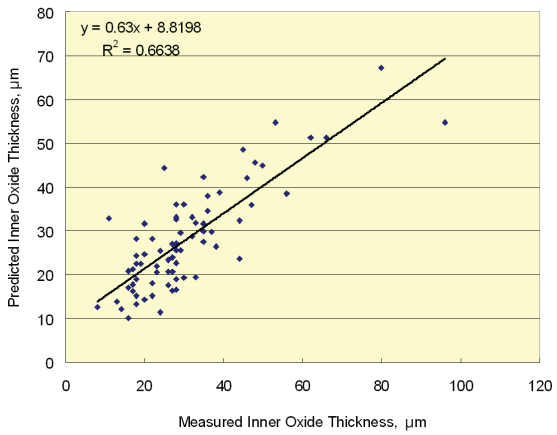

Figure 1.
The predicted inward growing oxide thickness compared with the experimental values for a range of 9-12% Cr steels.

Whilst there is extensive practical experience of the behavior of 'standard' alloys in conventional steam conditions, it is not clear if the established trends in oxidation and scale exfoliation behavior will extend into the advanced steam conditions, or whether the newer alloys will follow the trends established for the conventional ferritic and austenitic steels. Further, there are few data for the steam oxidation of the higher-strength austenitic steels, and data are very sparse for Ni-base alloys in steam.

The overall intent of this task was to leverage efforts in the UK and US to provide a better insight of the steam oxidation of these classes of alloys by collaborating on (a) the evaluation of available information, and (b) the generation of data still needed to provide the basis for confident use and prediction of steam oxidation behavior.

objectives

- To establish the current state of knowledge regarding steam oxidation of materials used in fossil-fuelled power plant
- To collate and analyze existing information to identify missing critical data
- To generate critical data as required which could be used in subsequent design and life prediction of components
- To develop mechanistic models for the exfoliation of oxides grown under steam environments

work programme

The project was split into three discrete areas; the first was focussed on reviewing the current state of knowledge of steam oxidation that was pertinent to ultra-supercritical (USC) steam cycles and collating relevant and reliable steam oxidation data that already existed internationally.

The second aspect of this project was concerned with identifying where critical data were missing and then undertaking a work programme to generate these data, whilst evaluating the effect of laboratory practices on the data generated.

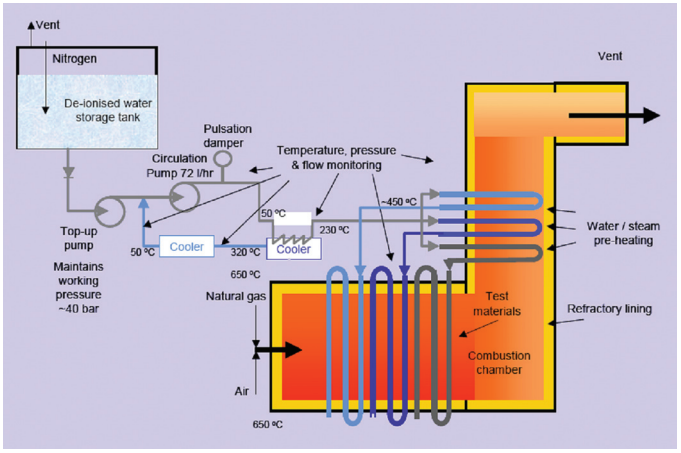

Figure 2.
Schematic of the high pressure flowing steam test facilities installed at Cranfield University.

The third part of this project focussed on developing models to simulate the oxide growth and exfoliation. Figure 1 shows results from the neural network model used to predict the oxide thickness of the inward growing (Fe, Cr) spinel.

key results

- Over 1 million hours of steam oxidation data have been generated in US and UK laboratories, covering 30 alloys and a range of temperatures
- The effects of water chemistry, pressure and steam delivery method used during laboratory campaigns have been studied with water chemistry and pressure being demonstrated to affect the oxidation kinetics. Improved test methods and a unified approach can now be formulated
- An inter-comparison exercise demonstrated the difficulties in comparing steam oxidation data from different laboratories. Differences in the measured oxidation rates where observed accompanied by varying exfoliation behavior, highlighting the necessity for a standardised testing approach
- A model for estimating the reactive evaporation of protective chromia scales in ultra supercritical conditions, 760 °C (1400 °F), was developed. It appears that alloy additions of Ti may aid in reducing this type of corrosion damage
- Models based on the mechanistic behavior of oxides during the initial growth and service have been developed. These models predict the oxide growth and exfoliation behavior of alloys and provide an important tool to plant designers and operators to enable improved use of materials through less conservative design and extended component lifetimes. Accurate predictive methods will also help to avoid conditions that would lead to tube failure
- Neural network algorithms have been developed from 'pedigree' laboratory data that predict the specific mass change and oxide growth for 9-12% Cr alloys in steam environments. The kinetics from these models are available to modelers for use as a 'standard' data set in model development, within set limits of temperature, time and alloy composition
- Two high-pressure steam facilities have been developed and commissioned; Figure 2 shows a schematic of the Cranfield facility; these are now available for future test programmes

future activities

- The effect of pressure on the oxidation kinetics and scale morphology will be investigated using high-pressure laboratory tests
- Deviations in alloy composition and their impact on oxidation resistance will be examined using one material with a range of compositions, all of which fall within the specification of that alloy; thus providing a measure of the scatter which could come from different alloy melts
- Critical data will be generated on the effect of specimen geometry and heat flux, and a unified test method developed with a view to future standardization
- Development and validation of models for (a) scale exfoliation and (b) oxidation kinetics when accompanied by chromia evaporation
- A compendium of oxidation kinetics and oxide microstructures will be created for specific materials. This will provide a valuable insight into the interdependency of oxide morphology and exfoliation behavior