U.S. DEPARTMENT OF ENERGY

UK-US Collaboration on Fossil Energy R&D

Department for Business, Energy & Industrial Strategy

Project duration
2010-2016

Project Partners
UK:
Cranfield University
National Physical Laboratory*
US:
National Energy Technology Laboratory*
University of Pittsburgh

Task leaders

Steam Side Oxidation

Background

In recent years, interest in increasing the efficiency of power plants based on steam generation 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. The overall focus of this international program is on using ferritic-martensitic steels to the maximum possible temperature, before switching to austenitic steels and/or Ni-based alloys. The relatively low Cr content of these alloys raises concerns regarding their resistance to steam oxidation at these higher temperatures. Earlier work in this collaboration addressed the reliability of data from atmospheric pressure, laboratory-based steam oxidation tests. This raised issues regarding how representative the laboratory-grown oxides were compared to those formed on service-exposed material and how the tests could be made more reliable by introducing added complexity.

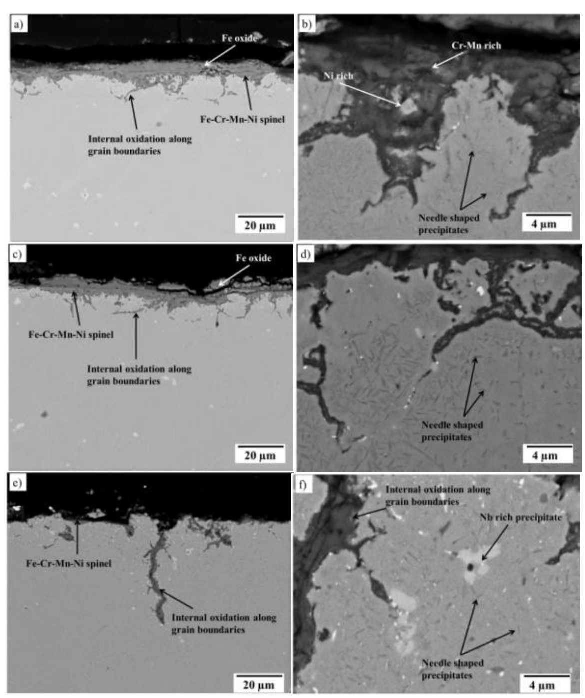

Figure 1. SEM of cross-sections of heat flux tubes after test exposures of (a,b) 100, (c,d) 300, and (e,f), 1000 hours.

In general laboratory-scale exposures are conducted under isothermal conditions at ambient or slightly elevated pressure, using a relatively low flow rate of steam. The coupons used in these tests are normally flat cuboids which have been ground to homogenise the surface and remove any pre-existing features. However, there is a concern that these samples and exposures are not representative of service conditions, and so it is necessary to quantify the influence of transient conditions, such as heat flux, pressure and sample geometry/surface conditions. To address such concerns a new collaborative program of work was initiated to determine the influence of these added features on oxidation kinetics and oxide scale morphology. The overall aim was to improve the understanding of alloy performance in ultra-supercritical (USC) steam conditions and qualify suitable test procedures.

Objectives

- To improve understanding of the effect of pressure on the steam oxidation of alloys relevant to fossil-fuelled USC steam power plants.
- To examine the effect of heat flux on the steam oxidation and scale exfoliation of alloys relevant to fossil-fuelled steam power plants.
- To investigate the effect of specimen geometry and surface finish on the oxidation kinetics, oxide scale morphology and spallation properties.
- To investigate what happens to hydrogen after it is formed as a reaction product during steam oxidation.

Work Program

High-temperature, high pressure oxidation tests in steam were performed on a range of alloys, from low alloy ferritic-martensitic steels to fine-grain austenitic stainless steels and Ni-based superalloys, in steam conditions at atmospheric to ultra-supercritical pressures. Tests were conducted over a temperature range of 650 to 800°C and pressure range of 1 bar up to 267 bar to investigate the influence of pressure on oxidation kinetics and scale morphology for this range of alloys.

Hydrogen permeability during oxidation in steam was measured on iron and nickel foils to determine the ratio of hydrogen that permeates through the alloy to the hydrogen that is transported back into the steam phase.

Steam oxidation tests were also conducted at ambient pressure under the influence of a heat flux. Tests were conducted on a low alloy steel (15Mo3) and on the austenitic alloy Sanicro 25.

The effect of specimen geometry was examined using a range of specimen shapes to replicate the curvature of boiler components. These were also used to evaluate the influence of steam flow rate during the test exposures. In addition, the surface finish of the samples was varied to include different levels of grinding, compared to testing in the as-received condition, to determine whether critical differences are being introduced during the specimen preparation procedures.

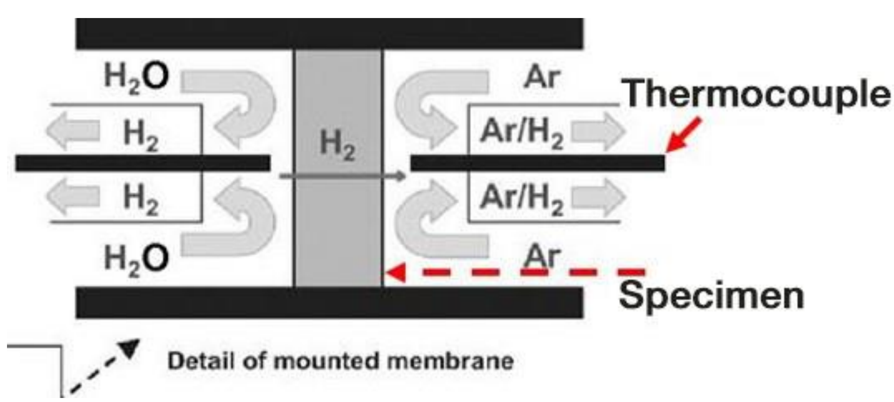

Figure 2. Hydrogen permeability during oxidation testing.

Key Results

- Increasing pressure was shown to increase the oxidation rate of low alloy ferritic-martensitic alloys and of Ni-base superalloys.
- No significant increase in oxidation rate was found for coarse-grained austenitic stainless steels. However, fine-grained austenitic stainless steels produced scales which varied from protective chromia to less protective, iron-based oxide scales similar to the coarse-grained alloys. This effect was attributed to the oxidation reaction kinetics being too rapid for diffusion of Cr from the bulk alloy to the surface to maintain a chromia scale.
- A neural network model was produced to predict the oxide thickness of alloys as a function of composition, pressure, temperature and time.
- A method to test tubular samples was developed and used to illustrate the deleterious effect that heat flux has on the internal oxidation of an austenitic alloy.
- No significant effect of specimen geometry was observed. However, specimen surface preparation was observed to influence the oxidation rate.
- Hydrogen was found to permeate significantly through iron foils, but less so through nickel foils, during oxidation testing in Ar-H_2O.
- Machining the surfaces of austenitic steels was found to encourage formation of slow-growing protective chromia scales compared to the less protective iron-based oxides formed on as-received surfaces; but this behaviour was transient.

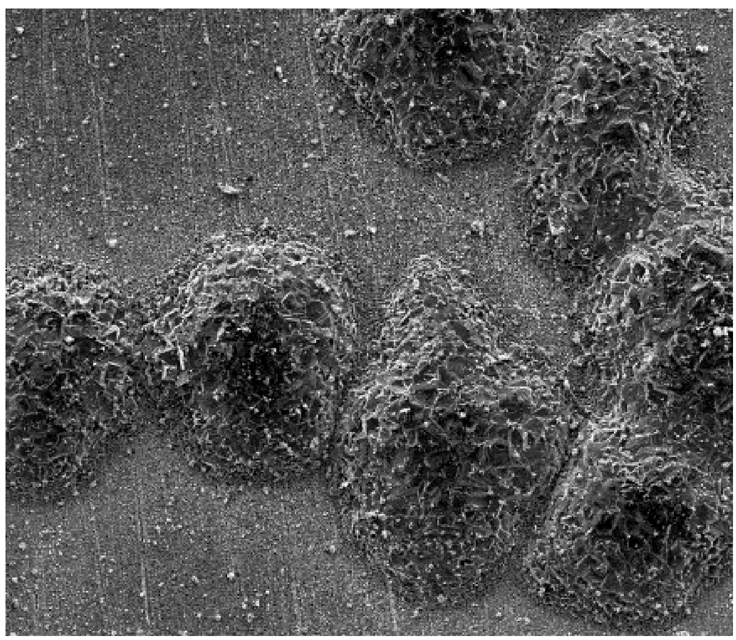

Figure 3. Surface of fine-grain austenitic stainless steel 347H after exposure in 209 bar steam at 685°C. Iron-oxide nodules spread and break down the thin protective chromia scale.

Potential Future Activities

- Investigation of oxidation in supercritical CO_2 for advanced indirect- and direct-power cycles that use CO_2 as the working fluid instead of steam.
- Investigation of the effect of microstructural variation on oxidation to determine the mechanisms introduced through surface preparation.
- Investigation of the transport of species through the oxide scales, e.g. using doped steam or CO_2.

For further information on the UK-US Collaboration on Energy Research and Development please visit – https://fossil.energy.gov/usuk/