

NPL REPORT MAT 45

**Advanced Materials for Low
Emission Power Plant**

Phase 2

First Annual Report

**A T Fry, M J Lodeiro, K
Mingard and J Nunn**

MAY 2010

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Materials Division

ABSTRACT

The following report describes the work performed as part of NPLs contribution to phase 2 of the UK US collaboration on Advanced Materials for Low Emission Power Plant. NPL is involved in three task concentration on steam oxidation, boiler corrosion and gas turbines. Test work has begun on all three task and this report describes the progress made.

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Approved by Dr Markys Cain, Knowledge Leader, Materials Team

CONTENTS

1 Objectives of the Project.....7

2 Technical Progress.....8

 2.1 Steam Oxidation 8

 2.2 Boiler Corrosion 10

 2.3 Gas Turbines 13

3 Objectives for Next Period 28

5 Exploitation / Publication of Results 29

6 Acknowledgements.....29

7 References.....29

1 Objectives of the Project

During the formulation of the collaboration the overall objectives for NPL within the phase 2 tasks were agreed as:

Task 1 Steam Oxidation

- To establish what the effect of pressure on the steam oxidation of alloys relevant to fossil-fuelled USC steam power plants was.
- To examine the effect of heat flux on steam oxidation and scale exfoliation of alloys relevant to fossil-fuelled USC steam power plants.
- To investigate the effect of specimen geometry on the oxidation kinetics, oxide scale morphology and spallation properties.
- To develop an agreed-upon standard laboratory test method for steam oxidation testing, and to confirm its validity.
- To create a compendium of oxide microstructures which would provide useful information with respect to predicting component lifetimes and recognizing corrosion mechanisms.

Task 2 Boiler Corrosion

- Improved understanding of fireside corrosion for low alloy materials
- Develop test methods for measuring the mechanical and corrosion properties of materials under boiler conditions.
- Generate data for the corrosion of materials under novel combustion atmospheres.

Task 3 Gas Turbines

- To examine the use of thermal imaging as a method for the non destructive evaluation of thermal barrier coatings.
- To assess the use of ultrasonic and Eddy Current probes for the life assessment of coatings.

In addition NPL is acting as technical task leader for task 1 within the phase 2 collaboration.

2 Technical Progress

2.1 Steam Oxidation

2.1.1 Effect of pressure

To examine the effect of pressure on the oxidation kinetics and oxide scale morphology a series of elevated pressure exposure tests have been planned. The materials to be used in these exposures are detailed in Table I along with the proposed test conditions.

Table 1 Materials to be tested at elevated pressure

Material	Temperature, °C	Pressure, bar	Time, h
P92	650	25, 50, 75	100, 300, 1000
Fe-10Cr	650	25, 50, 75	100, 300, 1000
Ni-10Cr	650, 750	25, 50, 75	100, 300, 1000
IN740	750	25, 50, 75	100, 300, 1000
VM12	650	25, 50, 75	100, 300, 1000
S304H	700	25, 50, 75	100, 300, 1000
TP347H	700	25, 50, 75	100, 300, 1000
TP347HFG	700	25, 50, 75	100, 300, 1000

Exposures will also be performed at ambient pressure to compare with the results from the elevated pressure tests. Tests are currently running at atmospheric pressure on the materials and temperatures listed in Table I, in addition a high-pressure test at 25 bar and 650 °C is currently running. The test is planned to finish after 1000 hours, exposure time at the time of writing is 700 hours. Ambient pressure tests to 100 hours have been completed and metallography is proceeding.

2.1.2 Effect of heat flux

Previous work has shown there to be a marked effect on the oxidation kinetics and scale morphology for 15Mo3 material, as shown in Figure 1.

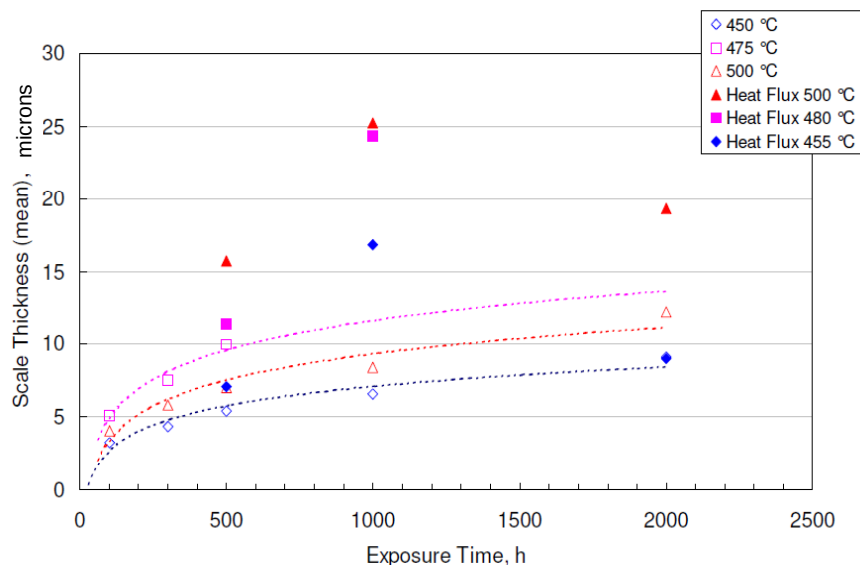


Figure 1 Scale thickness vs. time plot for 15Mo3 material exposed to isothermal and heat flux tests

Plant exposed 2.25Cr material has been obtained from industrial partners and is being prepared for Electron Back Scattered Diffraction (EBSD) examination. In addition 3 tubes of T23 (75 cm long) have been prepared for heat flux testing. These tests are currently being prepared.

2.1.3 Effect of specimen geometry

Conventional testing is conducted using flat coupon type specimens, nominally 10x10x3 mm. An intercomparison in phase 1 of the collaboration indicated that there is likely to be a significant effect on the spallation characteristics of alloys. To investigate this further four materials have been selected and specimens which are flat and/or curved have been machined from the same stock material. Table II shows the materials being used and the exposure conditions. The 100 hour exposure is complete and the 3000 and 5000 hour tests are currently running.

Table 2 Materials and conditions used to evaluate the effect of specimen geometry

Materials	Specimen Geometry		Temperature, °C	Time, h
Super 304H	Flat	Curved	700, 750	100, 300, 1000, 3000, 5000
TP347H	Flat	Curved	700, 750	100, 300, 1000, 3000, 5000
TP347HFG	Flat	Curved	700, 750	100, 300, 1000, 3000, 5000
T23	Flat	Curved	650	100, 300, 1000, 3000, 5000

2.1.4 Standard test procedure

A discussion was held with the other participants to establish the test procedures used within the different laboratories, but to date no standard test protocol has been put forward. The key points of the discussion are summarised in Table III.

Table 3 Steam oxidation test methods

Parameter	Laboratory				
	Cranfield	NPL	NETL	DBEL	Birmingham
Sample Preparation	Ground surface with 600 grit paper			Polished finish	1800 grit paper on flat as received tubes
Specimen Dimensions	Tube section	Flat 10x10x3 mm	Flat	Flat Thickness within $\pm 10 \mu\text{m}$	Flat
Heating up procedure	• Samples in • N₂ purge • Furnace on • When flange over 100 °C water added	• Heat up • Ar purge • Once at temperature steam on • Samples in	• Samples in • Ar purge • Heat up • Once at temperature add flowing steam	• Sample in • Heat up • Once at 200 °C steam is turned on	• Samples in • Ar purge • Heat up • Once at temperature steam on
Sample Extraction	• Furnace cooled • Samples see thermal cycle	• Gradually withdrawn from the furnace	• Furnace cooled • Samples see thermal cycle	• Furnace cooled • Sample see thermal cycle	• Uninterrupted test

A round robin has been planned once this has been done, with Doosan Babcock kindly agreeing to supply machined specimens to the partners. The round robin will consist of a 1000h test at 600, 650 and 700 °C on a 9Cr material. DBEL have agreed to supply duplicate specimens to the participants. Each participant performs specimen metrology prior to exposure. No further specimen preparation will be conducted. After exposure the participant will retain 1 specimen for characterisation and the other will be returned to DBEL for characterisation.

2.2 Boiler Corrosion

The aim of the boiler corrosion task is to generate improved understanding of the fireside performance of low alloy materials assessing the effect exposure conditions on the corrosion rate. In addition facilities are being developed to perform mechanical tests under corrosive atmospheres and boiler corrosion tests under novel atmospheres associated with oxy fuel combustion.

2.2.1 Low alloy fireside corrosion

A database of rig exposures has been collated and is currently being examined to identify the effect of different parameters on the corrosion rate of low alloy materials. In addition this data is being used to develop a neural network based model for the prediction of metal wastage. An example of the results from the neural network model is shown in Figure 2. This shows the ordered experimental data plotted with the predicted corrosion rate for a range of low alloy materials exposed to different conditions.

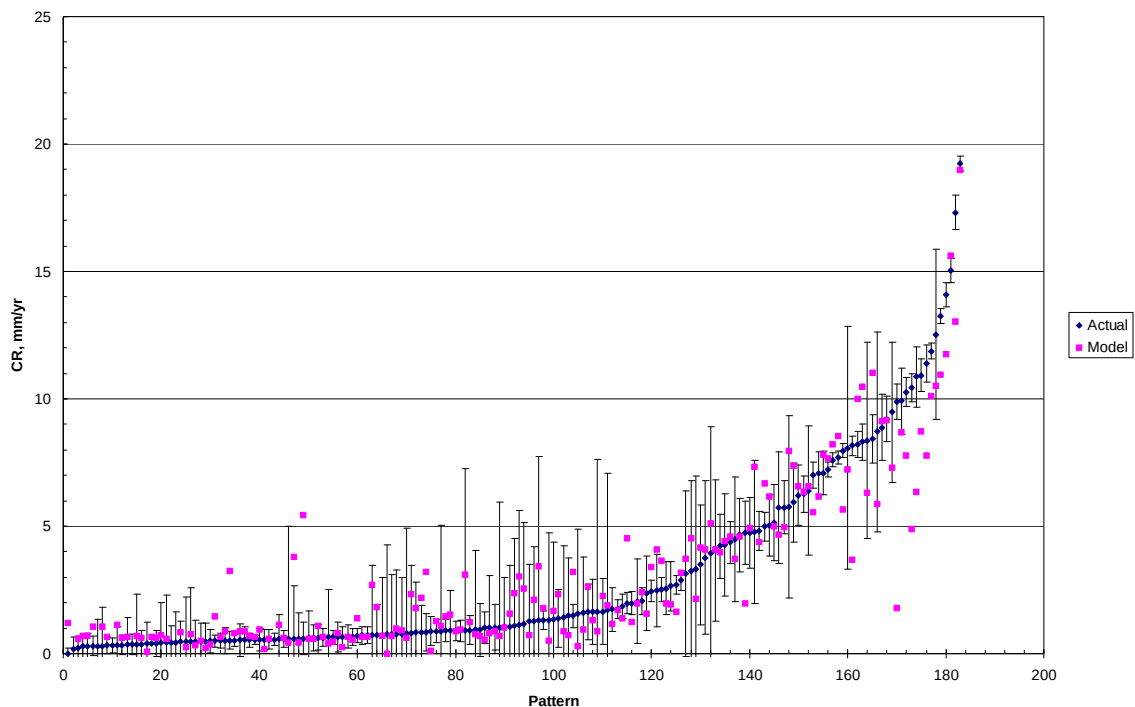


Figure 2 Measured corrosion rate compared with predicted corrosion rate for a range of low alloy materials

2.2.2 Mechanical tests in controlled atmospheres

NPL has been developing two mechanical test rigs for testing miniaturised test specimens under controlled atmospheres. The first of these rigs is designed to perform small punch indentation creep tests (SP), under controlled atmospheres whilst measuring the deformation of the SP specimen. The rationale behind this work is to better understand the deformation in an SP test and to relate this to a full-scale creep test. Not only will this help in comparing the results between the two tests but will also aid model development and validation. Figure 3 shows some results of so FEA modelling performed on SP tests of single crystal materials. The FE contour plots clearly show how strain develops in key regions of the SP specimen.

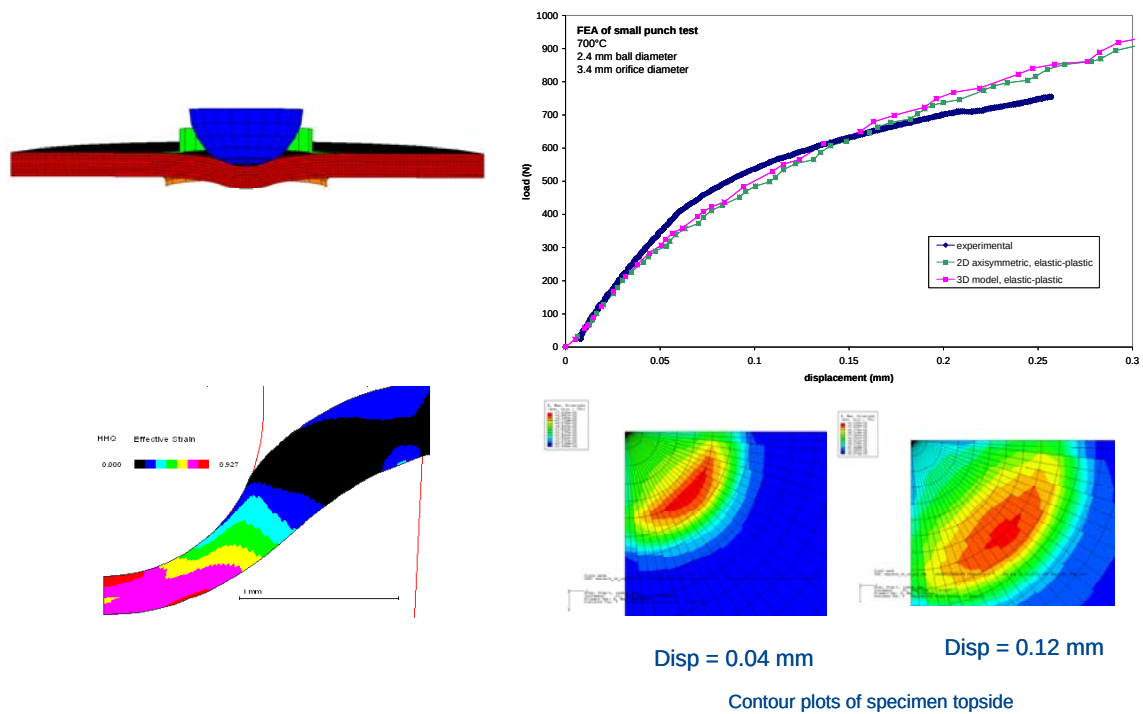


Figure 3 FE results modelling the strain accumulation during a small punch test on a single crystal alloy

Tests have been performed on specimens of P92 material at room temperature for a range of fixed displacements to examine the punch shape, as shown in Figure 4.

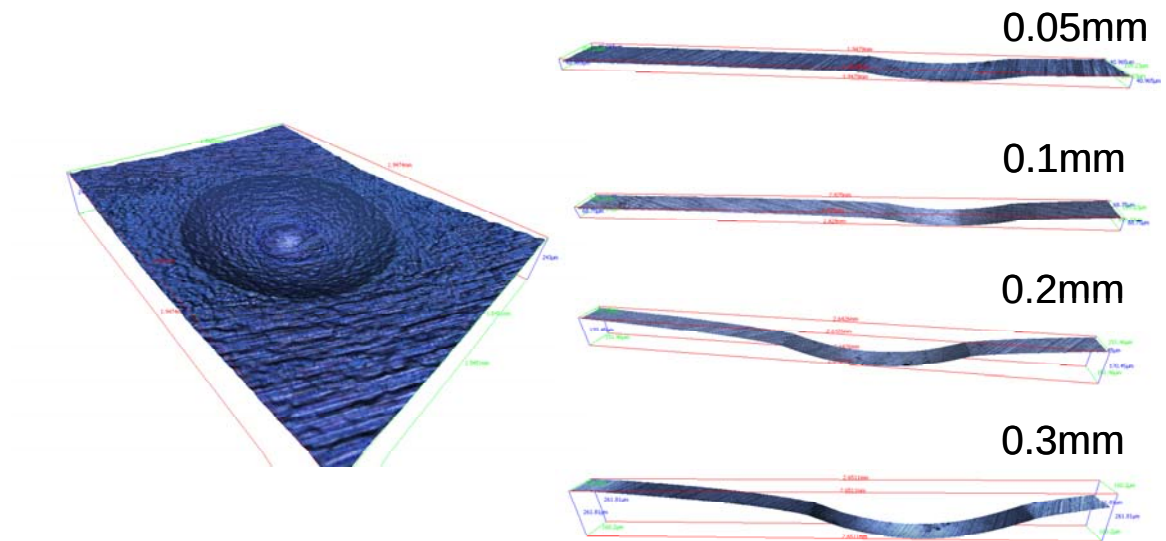


Figure 4 Cross sections from interrupted SP tests to examine the punch shape on P92 material at room temperature

To accurately measure the punch shape and hence infer the strain in the specimen a probe has been designed. The probe had to have low frictional forces, apply a minimum amount of force to the specimen, have a small contact point, be resistant to high temperature and corrosive environments and be able to translate in the XYZ planes. A design prototype has been constructed and tested on a ball bearing, the results of these tests show that the probe will function as required and should produce the necessary measurement data, as shown in Figure 5.

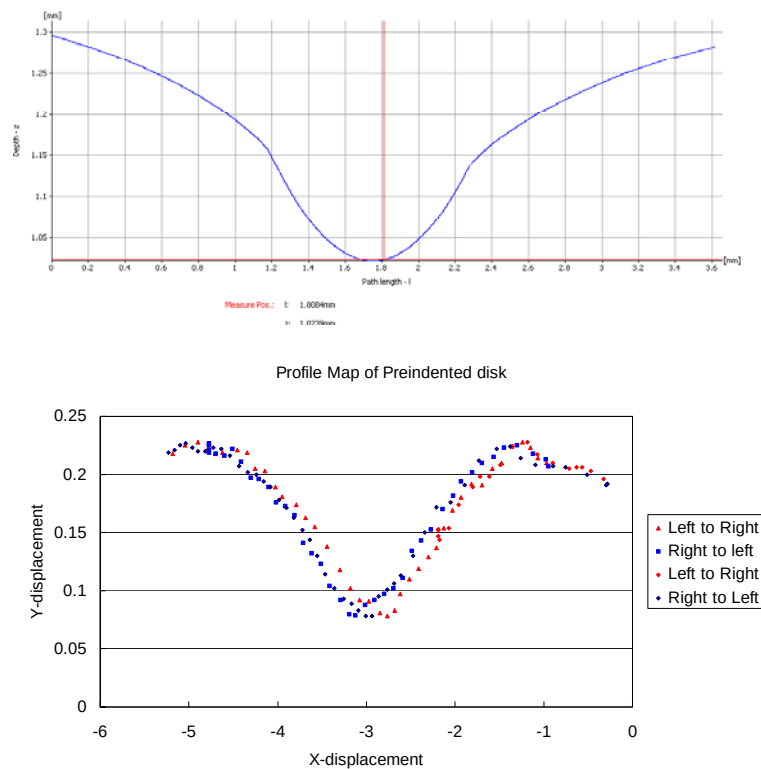


Figure 5 Probe output as it traverses the small punch specimen compared to optical profilometry values (top) obtained with a confocal microscope

2.2.3 Corrosion under novel conditions

NPL has received confirmation that funding has been obtained for the NMS project on oxy fuel combustion. This work aims to examine the corrosion performance of alloys under oxy fuel conditions.

2.3 Gas Turbines

Within this task NPL will be focussing on the development of thermography for use in the non-destructive evaluation of thermal barrier coatings (TBCs). In addition the use of ultrasonic and eddy current probes will also be assessed.

2.3.1 Non-destructive evaluation of coatings

NPL is investigating two methods for evaluation of damage in TBCs. Piezospectroscopy and infra-red (IR) Thermography.

2.3.2 Piezospectroscopy

In this method the TBC specimen is excited by laser light and the resulting luminescence, arising from Cr ions in the TGO is analysed [1]. The frequency of the emitted light is a function of the local stress in the TGO. However it is often difficult to determine the stress unambiguously from the light spectra and a suite of analysis routines have been developed to clarify the signals. Two approaches are currently in use; the first produces a fit, constrained by physical laws, of two stress levels whilst the second, less precise fit, simply looks for the single peak value. The first approach provides reliable quantified data but the fit may fail due to noisy input data or nonuniform background signals; the latter approach is more qualitative but reproduces the trend of TGO stresses observed using the more precise method. This is illustrated in Figure 6.

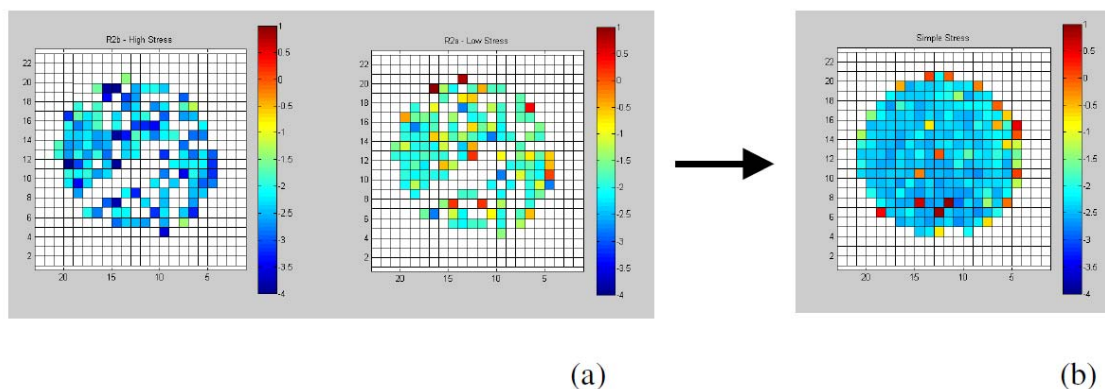


Figure 6 Residual stress maps in TGO from spectra analysed using (a) precise two peak method (b) single peak value method

2.3.2 IR Thermography

Specimens have been examined using a scanning IR camera in both transmittance and reflective mode. These two modes of operation give complimentary contrast from defects (delaminations) within the TBC system as shown in Figure 7.

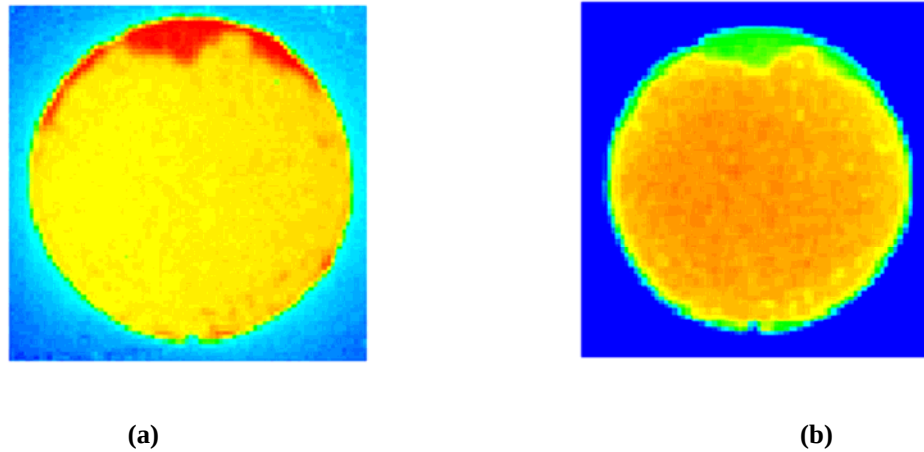


Figure 7 Appearance of delaminated area (top) in TBC system using IR thermography reflective mode (b) transmission mode

2.3.3 Investigation of Amdry 997 System

Amdry 997 bondcoats were produced on IN738 substrates using 3 different production routes, High Velocity Oxy-Flame (HVOF), Vacuum Plasma Spray (VPS) and electroplating. Subsequently a ceramic topcoat was applied to each system using either Air Plasma Spray (APS) or EB-PVD. The six coated systems were subjected to thermal cycling (100 h at 1000 °C) and examined periodically using the two techniques described above.

- Piezospectroscopy detects changes during ageing of EB-PVD systems and can provide advance warning of failure (Figure 8)
- Piezospectroscopy is not effective in monitoring APS systems due to poor signal generation (Figure 9)
- IR Thermography appears to give early warning of failure (Figure 10)

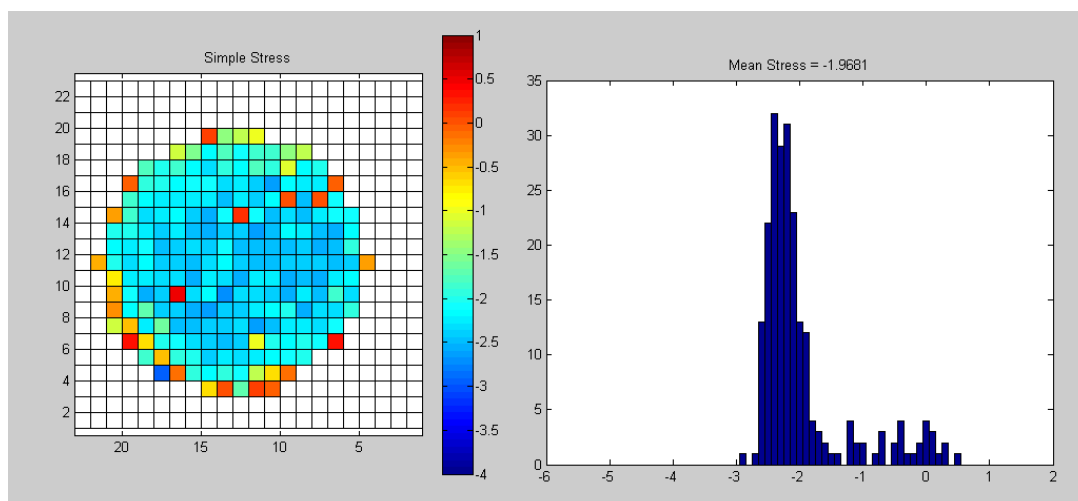


Figure 8 Residual stress map of IN738/Amdry 997 HVOF/ EB-PVD system after 2300 h exposure, showing delamination around edge of specimen

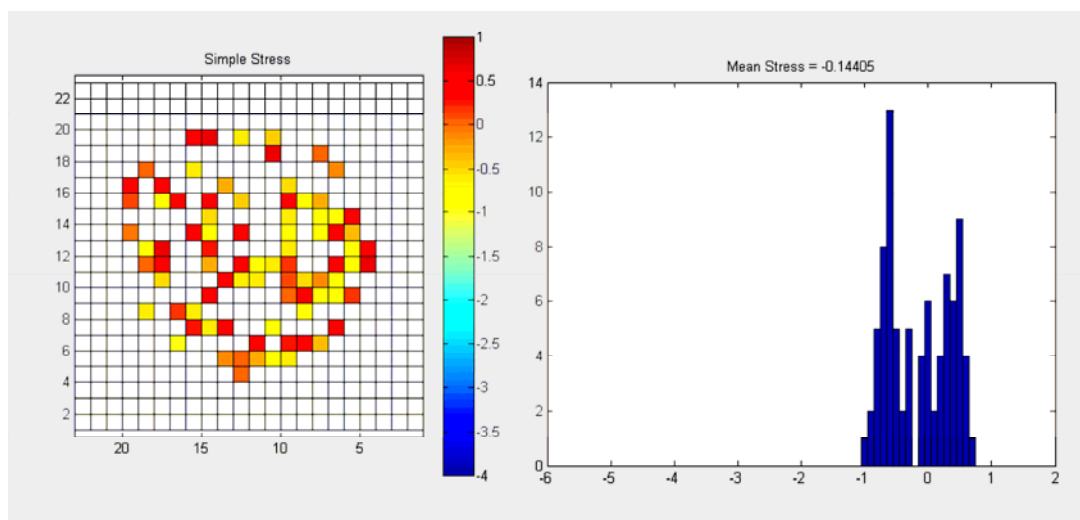


Figure 9 Residual stress map of IN738/Amdry 997 VPS/ APS system after 1400 h exposure showing lack of data from piezospectroscopy measurements

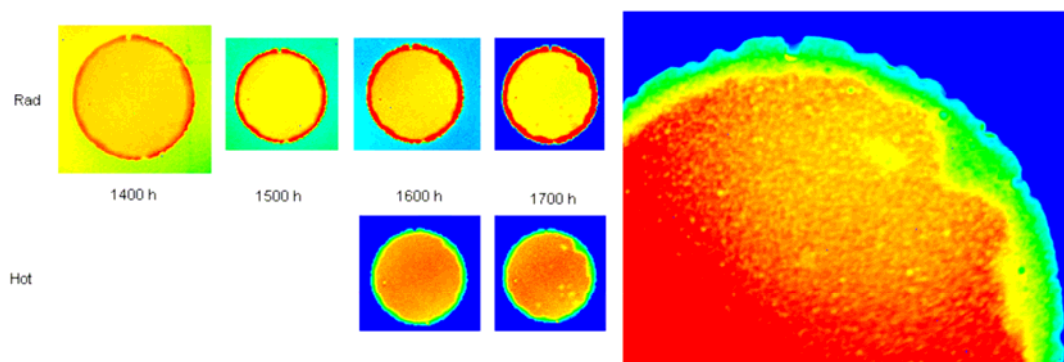


Figure 10 IR Maps showing detection of failure at edge of IN738/Amdry 997 Electroplate/ APS system 300 h before final failure

Modified systems using a high-powered flash are being examined in order to assess the limitations posed by surface emissivity variations in TBC specimens that have been subjected to combustion gases. The main difference in the systems is the use of a pulsed light/heat source and faster frame acquisition.

Thermograms have revealed areas of TBC that have become detached; these correspond well with the stress results from the piezospectroscopy.

2.3.4 Ultrasonic and Eddy Current probes

2.3.4.1 Ultrasonic equipment

Ultrasonic thickness gauging techniques have commonly been used to measure oxide scale thickness for many years. Several conclusions can be drawn from previous work on these measurements [2-6]:

- Broadband, single element transducers are preferable to dual elements (frequently used for remnant metal wall thickness), as they have better axial resolution required to determine thicknesses as small as those associated with oxide scale.
- Improvements in resolution are achieved by either increasing the transducer frequency or reducing the wave velocity e.g. from using normal incidence shear waves.
- The thickness resolution obtained for longitudinal waves at 20 MHz is typically ~0.25 mm, reducing to ~0.1 mm at 50 MHz.
- Delay lines can be useful to enable separation of return signals from ringing associated with the initial excitation pulse.
- Highly damped transducers are also beneficial, shortening return signals which would otherwise interfere with each other and make identification and measurement of the relevant echoes more difficult.
- Transducers must be coupled to a relatively smooth surface; hence surface preparation is often essential.
- The oxide layer thickness can only be measured where it remains bonded to the substrate, where exfoliation has occurred there is no acoustic coupling and no signal transmission.
- Differences in the relative acoustic impedance mismatches for the two interfaces of interest results in the steel/oxide echo being very much smaller in amplitude than the oxide/air echo.
- The thickness of the oxide layer is calculated by measuring the time difference between the signals reflected from the steel/oxide interface and the steel/air interface.

- The size disparity often makes it difficult to identify and/or separate the two relevant signals in order to make the time measurement between them.
- Software is required to detect appropriate echoes and measure the very short time interval between the two interface echoes, knowing the sound velocity for the oxide material then enables thickness determination.

The ultrasonic system is shown schematically in Figure 11. The pulser unit, supplied by JSR Ultrasonics, has an adjustable pulse amplitude (100 - 900 V) with a series of pulse energy levels of high or low impedance output and variable damping with resistances of 30 – 300 Ω . These excitation pulses can be produced at pulse repetition frequencies (PRF) from 100 Hz to 1600 Hz. Similarly, the integrated receiver unit has adjustable gain from –13 to 76 dB, and variable low and high pass filters for the received signal. The bandwidth of the system is 50 MHz. The trigger output from the pulser/receiver is used to trigger data capture by the high-speed digitiser, resetting the time to zero with every excitation pulse.

The high-speed digitiser, supplied by National Instruments, has a maximum real-time capture rate of 100 MHz; this can be increased to 2.5 GHz using random interleaved sampling for regularly repeated signals. Averaging is performed on multiple consecutive signals to minimise noise and the effect of sporadic signals (usually averaged over 100 complete waveforms). The waveforms are captured, analysed and displayed on software written in LabView.

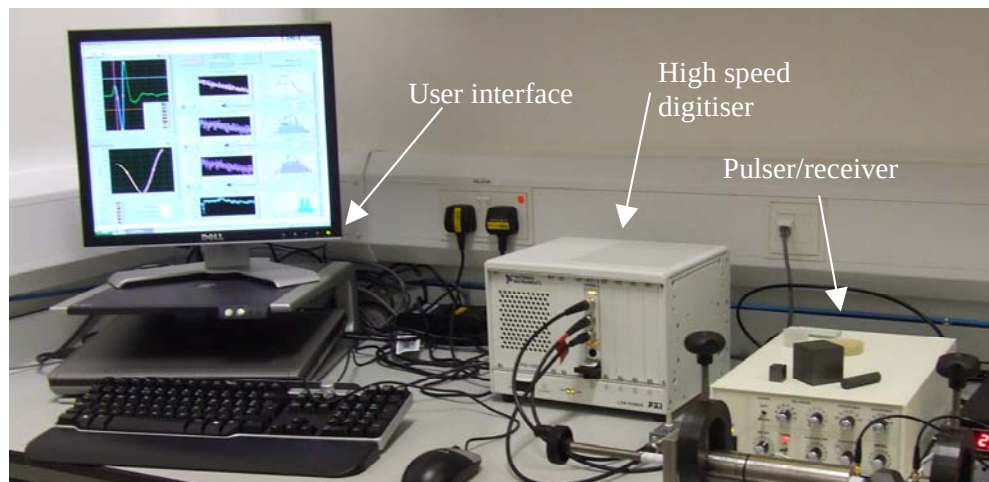
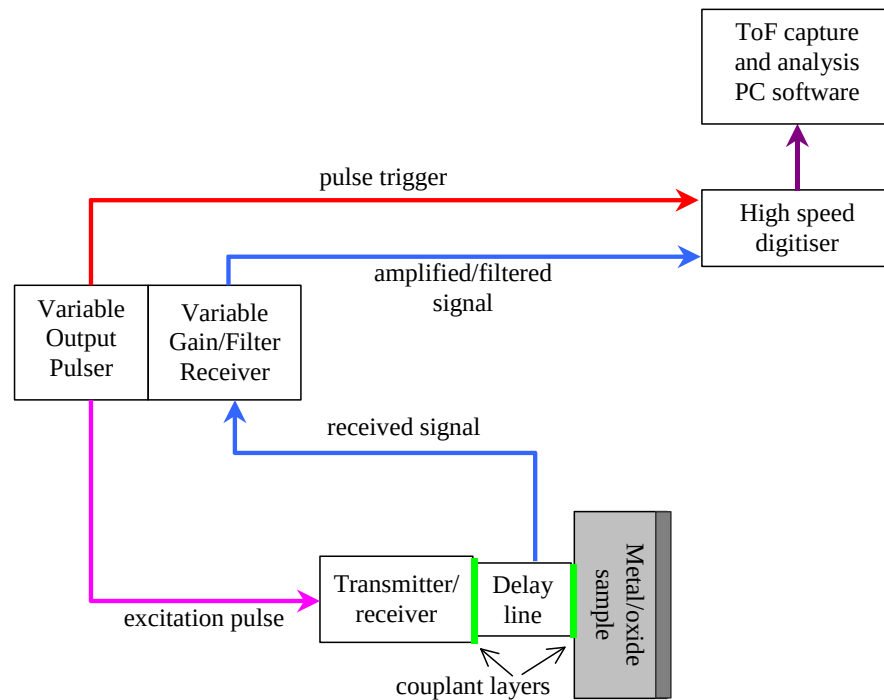


Figure 11 Ultrasonic thickness gauging equipment: schematic (above) and actual system (below).

For these tests, the pulse amplitude used was around 300 V negative spike excitation with a 12.5 MHz high pass filter, a 50 MHz low pass filter and a signal gain of 30 dB. The digitisation rate was maintained at 1 GHz throughout. The system was operated in pulse echo mode with the same transducer acting as both transmitter and receiver. The waveforms were recorded as both RF signals and with negative rectification to enable identification of the relevant signals for subsequent analysis.

2.3.4.2 Eddy Current Equipment

The induction and measurement of eddy currents in a material by use of a probe held close to the surface is a common method for detection of flaws and thickness measurements of surface layers. A flaw or a change in the probe – specimen separation can alter the flow of eddy currents induced in the surface of a specimen which in turn induces a change in the total inductance of the probe coil. This change in inductance can be measured and hence used to determine a change in probe-specimen separation, in this case caused by the growth of an insulating oxide layer between the probe and a steel substrate.

In this preliminary work, a 2 mm diameter coil with associated electronics to generate a 2 MHz current has been used to compare oxide films grown on samples of P92, a 9wt% Cr martensitic alloy.

The system used was made by Micro-epsilon. This is used conventionally for measurement of probe-sample separation, with the change in inductance of the coil represented by a single voltage output that can be calibrated in terms of the separation. For the oxide thickness measurements conducted as part of this work the change in voltage output was recorded as a function of the separation between probe and oxide surface, to determine differences in the specimens relative to each other and not to give an absolute or calibrated value. With a coil diameter of 2 mm, the area sampled was about 4 mm in diameter.

Each specimen was mounted on a table that could be driven in the x-y plane, with the probe mounted above the table with a vertically mounted stepper motor to move it in the z direction. Probe-specimen separation was measured by a mechanical displacement gauge (Sony DK812 contact displacement probe with <0.5 µm resolution) mounted next to the eddy current probe, and the separation changed between approximately 0.3 and 0.6 mm.

2.3.4.3 Calibration

Specimens of steam oxidised grade 92 material were produced for calibration measurements. These were flat coupons with dimension of 15x15x3 (ACAB series) and 7x10x2 mm (MEX series). Varying oxide thicknesses were produced by exposing the specimen for different times in an atmosphere of 100% flowing steam at 650 °C. For each exposure time two specimens were produced, one for NDE and the other for destructive optical thickness measurements.

The specimens for optical measurement were nickel plated, sectioned and mounted prior to polishing and optical measurement. The results of the optical thickness measurement are presented in Figure 12.

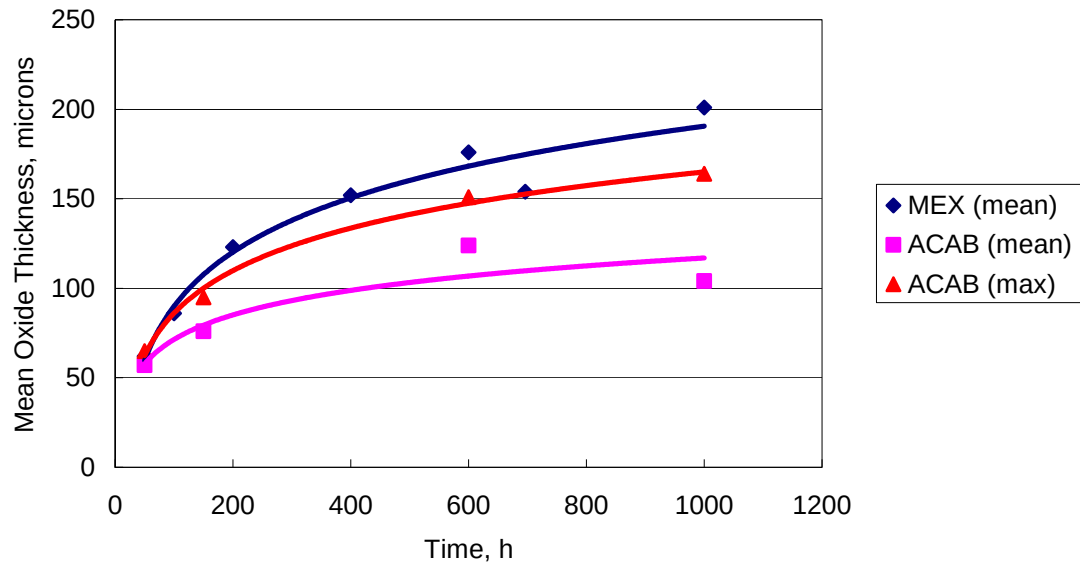


Figure 12 Oxide thickness measurements for the MEX and ACAB series of specimens, the maximum and mean values for the ACAB series and the mean value for the MEX series have been presented

For the ultrasonic NDE specimens, each specimen was ground on one face after exposure to remove the oxide scale and enable good acoustic contact with the transducer. The eddy current samples were measured in the as exposed condition. Ultrasonic waveforms were captured at three locations on each sample, whilst single point measurements were performed with the eddy probe.

Two different 30 MHz longitudinal wave contact transducers were used to measure the oxide thicknesses produced: one with a 10 mm diameter fixed silica delay line and another with a 5 mm diameter removable polystyrene delay line, shown in Figure 13. In all cases, a water-based gel couplant was used to improve the acoustic coupling between the transducer and sample.



Figure 13 30MHz transducers: polystyrene delay line (left) and silica delay line (right)

Figure 14 shows the basic methodology of the technique. The time difference between the initial return from the metal/oxide interface and the larger return from the oxide/air interface equates to the time taken to travel across the oxide and back, i.e. double the path length. Using samples of known thickness, this process can determine the oxide velocity, or conversely, once the velocity is known the time difference can be used to ascertain the thickness of the oxide layer.

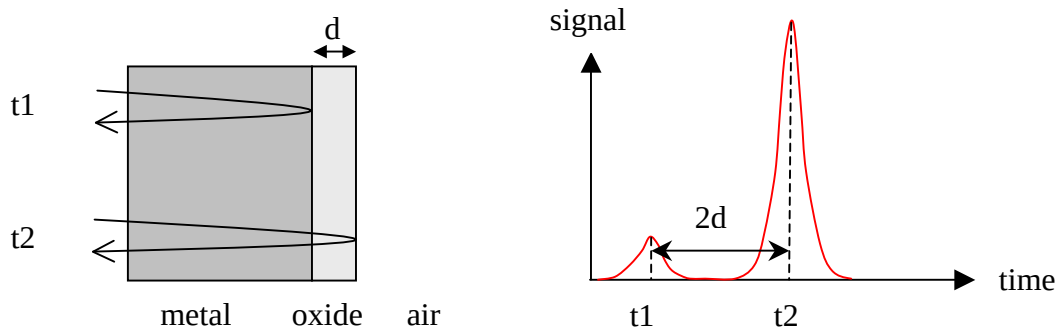


Figure 14 Schematic of basic principles of thickness measurement technique

Figure 15 shows a typical trace from the transducer with the polystyrene delay line. The initial signal is produced by the interface between the delay line and sample surface, the subsequent signals are produced by the oxide/steel and oxide/air boundaries, as indicated on the trace. The analysis is performed initially by identifying the arrival time of each of the signals of interest. The arrival time is taken as either the start time of the signal (where a straight line fit through the initial slope of the waveform crosses the zero axis) or the time to peak (using a quadratic fit).

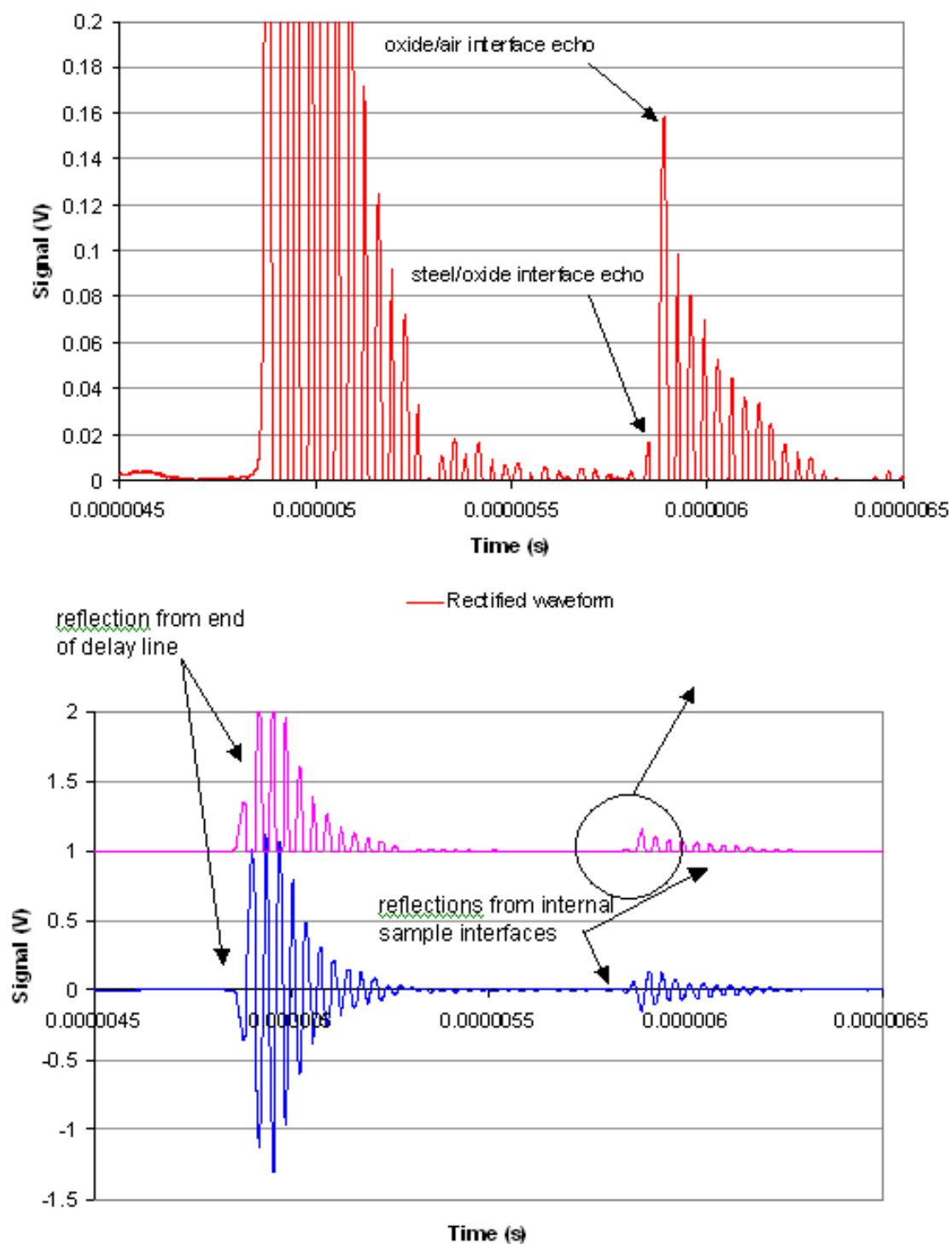


Figure 15 Typical results from measurements on flat plate calibration samples: original waveform (below) and close-up of signals of interest (above)

Figure 16 shows good correlation between measurements made with the two transducers for P92 and the excellent correlation with the measured oxide thickness for several exposure times. On this basis subsequent measurements were performed with the polystyrene delay line transducer because of its smaller diameter producing a smaller area averaging effect of the oxide thickness.

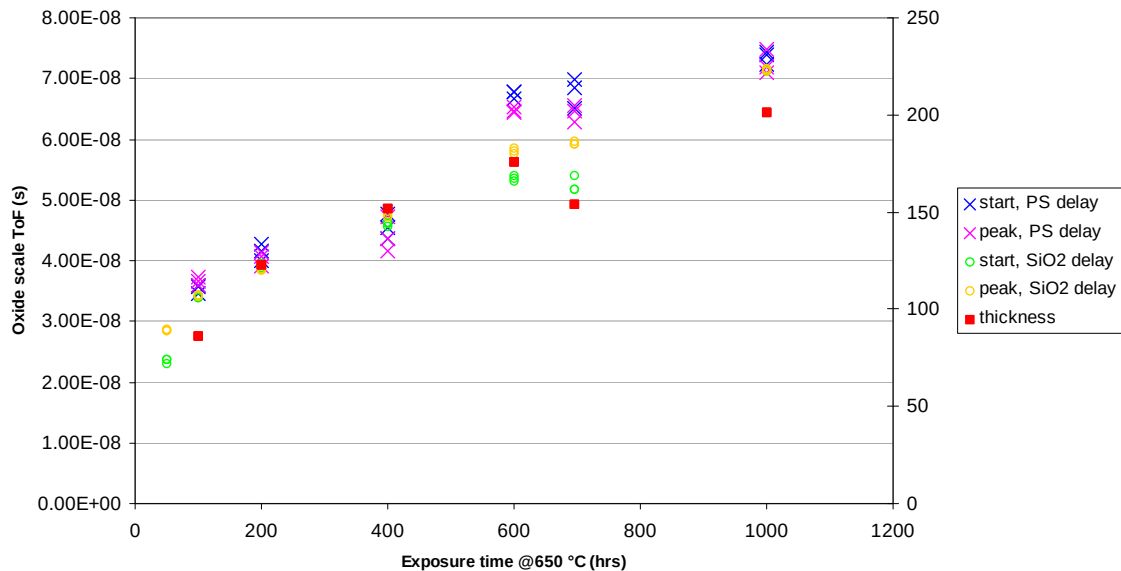


Figure 16 Plot of signal arrival and peak times for P92 samples using both transducer types

Typical signal analyses are shown for P92 and T92 samples in Figures 17 and 18. These show the metal/oxide and oxide/air signals, as determined from the user-positioned gates in the analysis package, the arrival/peak times of which are calculated from the signal within the gate. Using this technique, oxides with a thickness of less than 60 microns were distinguishable and possibly could be resolved down to 40-50 microns under ideal conditions.

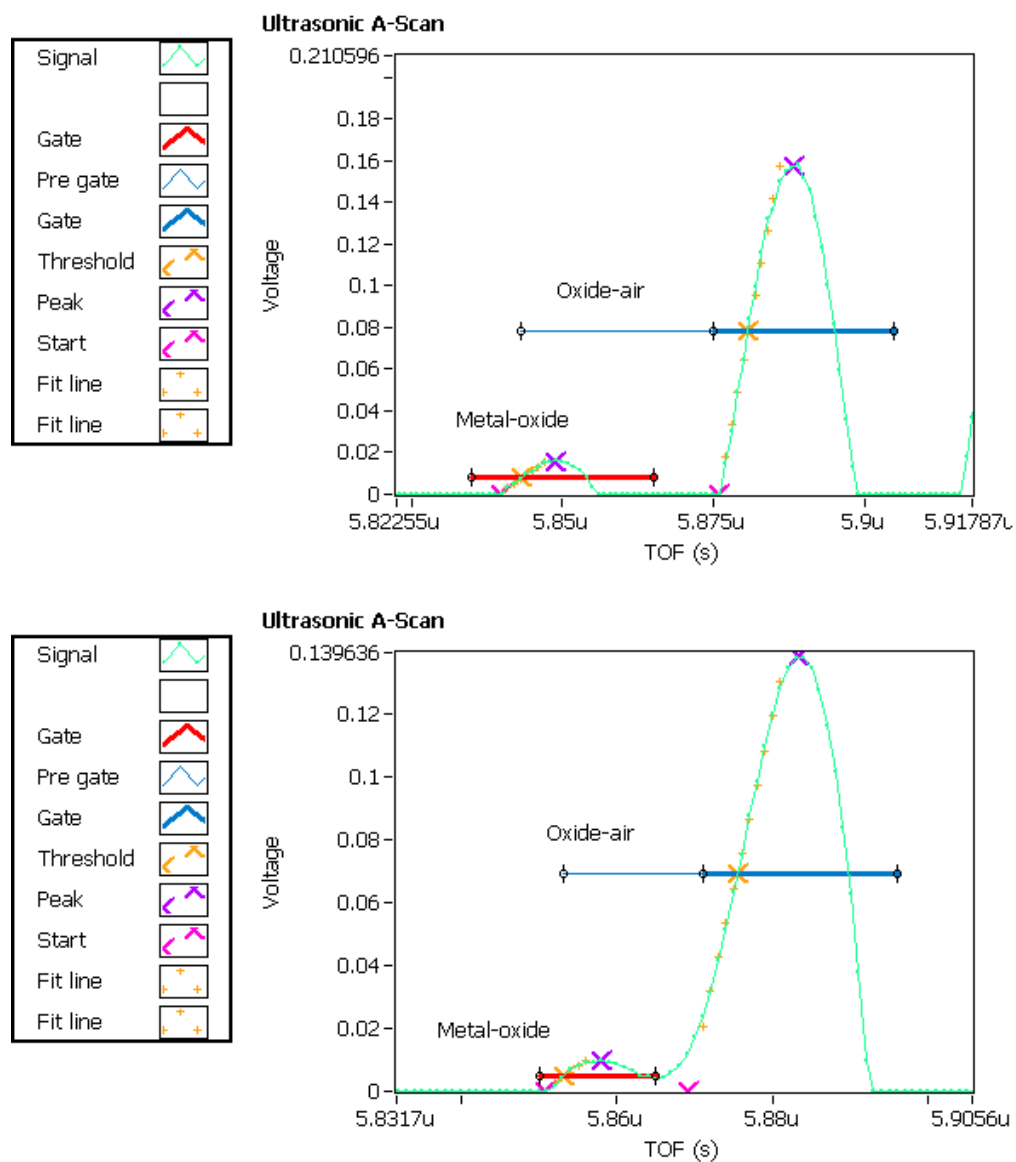


Figure 17 T92 large samples peak and start positions marked with crosses: long exposure time and thicker oxide (upper) and short exposure time and thinner oxide (lower)

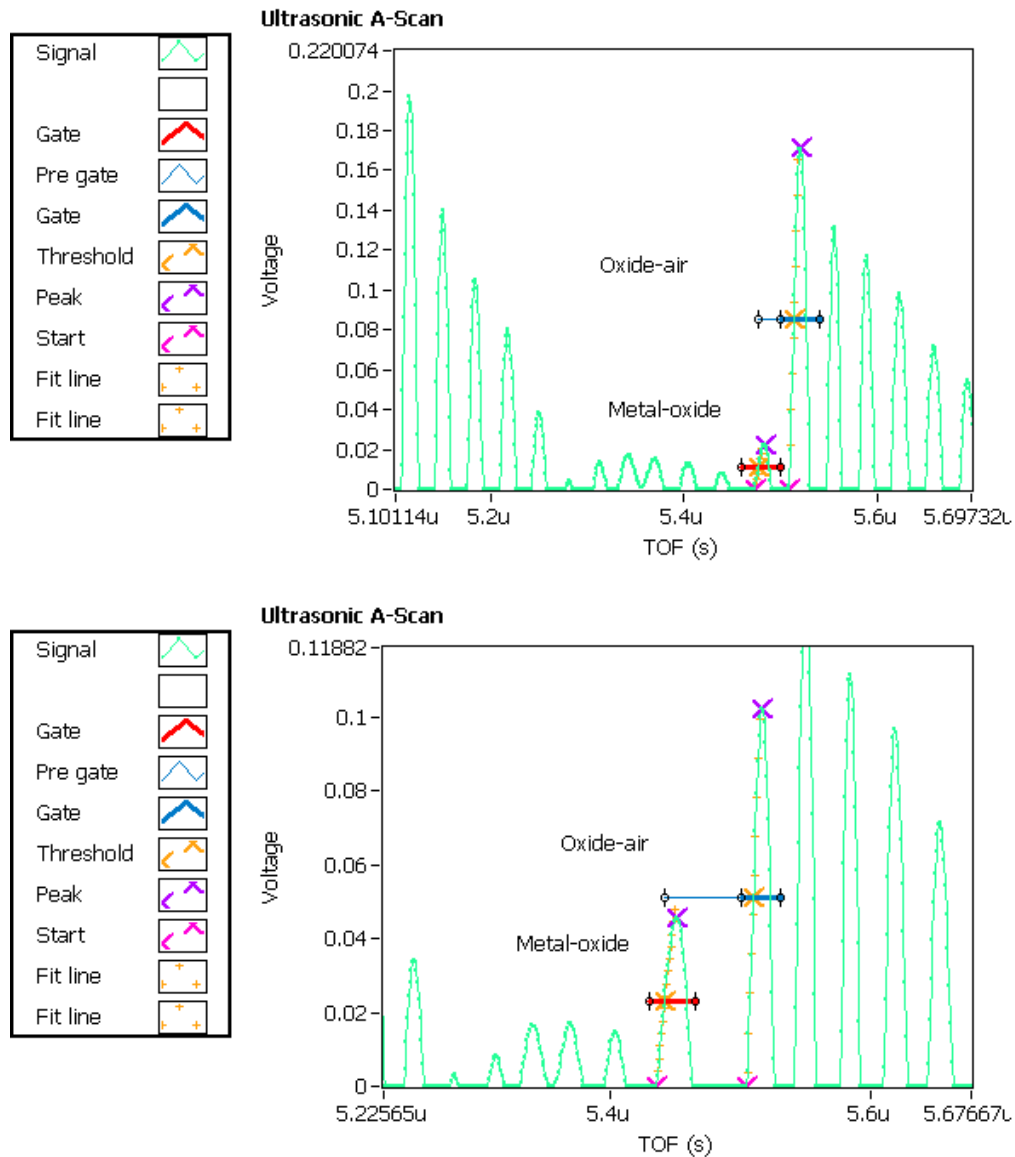


Figure 18 P92 large samples peak and start positions marked with crosses: long exposure time and thicker oxide (upper) and short exposure time and thinner oxide (lower).

Figure 19 shows the correlation between the optically measured thicknesses of grade 92 calibration samples and the oxide time difference determined using both start times and peak times using the polystyrene delay line transducer. These show good correlations in all cases with the thicknesses following the same trends as the time differences and the start and peak times matching closely.

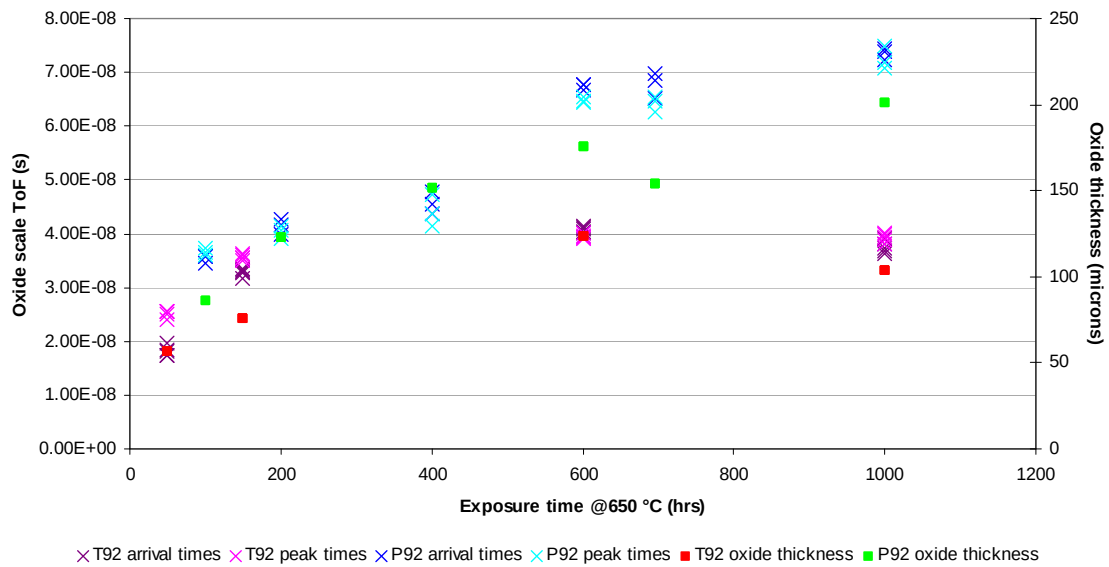


Figure 19 Plots of peak and arrival times and optically measured oxide thickness for P92 and T92 samples against exposure time

By looking at the start time data only for both sets of samples and plotting against the measured thickness, a very good straight-line correlation was obtained (Figure 20). The slope of this provides a calibration value for the oxide velocity of 5472 ms^{-1} (typically $\sim 6000 \text{ ms}^{-1}$ is quoted for oxide scales [4]). Some inconsistency can be expected due to spatial averaging effects and sample-to-sample or point-to-point variations between optical measurements and ultrasonic determinations of oxide thickness.

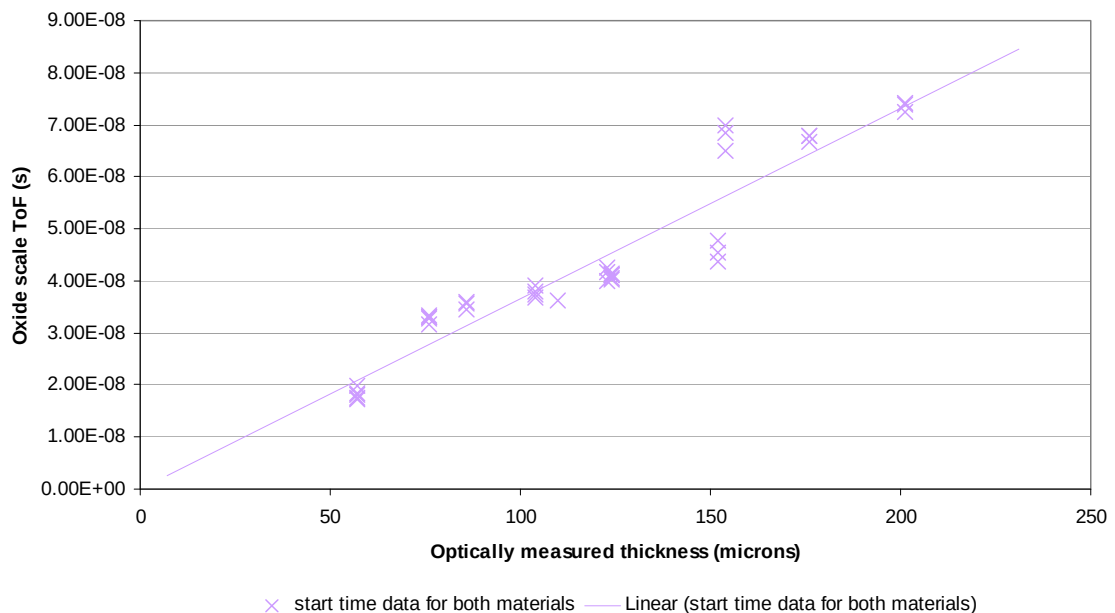


Figure 20 Experimentally observed linear relationship between ultrasonic transit time through the oxide layer and measured thickness

The eddy current probe was calibrated using three specimens (the 50, 150 and 600 hour specimens). Measurements were made by varying the air gap between the oxide layer and the probe; this generated a curve and thus meant that a precise setting of the gap thickness could be avoided, shown in Figure 21.

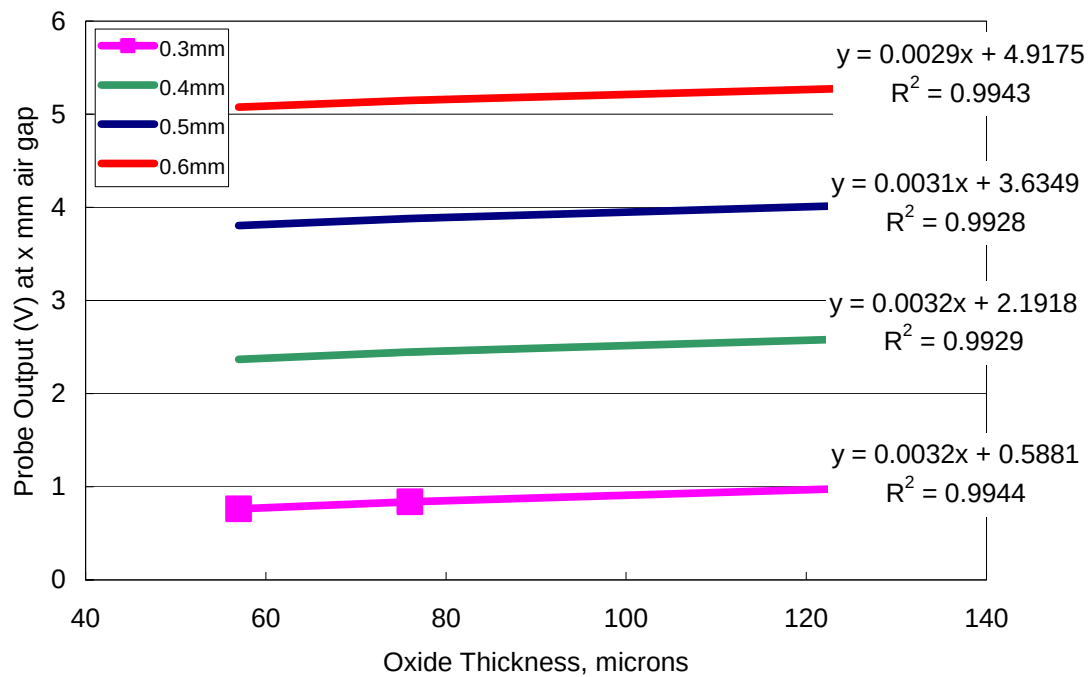


Figure 21 Eddy current probe output plotted as a function of oxide thickness and separation gap

By selecting a set separation gap and plotting the probe output against the oxide thickness a calibration curve can be created, which in this instance appears to show a linear correlation between the two parameters, as shown in Figure 22.

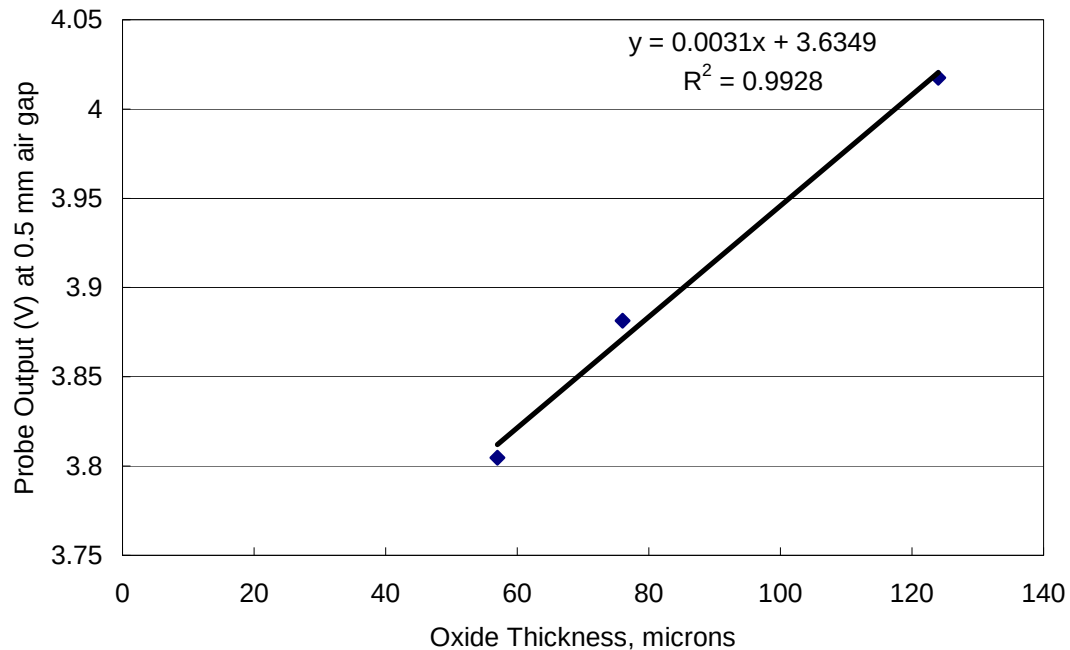


Figure 22 Eddy current probe output as a function of oxide thickness for a separation gap of 0.5 mm between the oxide surface and the probe

The eddy current measurements appeared to be able to provide oxide thickness measurements, although the technique requires the probe to be placed close to the oxide layer, otherwise the signal suffers from too much attenuation. Whether the technique is sensitive enough to measure changes in metal substrate thickness below a TBC is yet to be seen.

3 Objectives for Next Period

- Steam oxidation exposures at ambient and elevated pressure are continuing.
- Specimens that have been exposed will have metallographic measurements completed.
- Heat flux tests will be performed on T23 tubes and the specimens sectioned and examined.
- A proposed test procedure will be circulated for comment and the round robin initiated.
- Continue examining the relationship between exposure conditions and corrosion rate for low alloy waterwall materials.
- Continue development of mechanical test apparatus for conducting tests in controlled atmospheres.
- Perform full-scale creep tests to compare with miniaturised tests.
- Adapt existing equipment to perform oxy-fuel exposures.
- Test the applicability of ultrasonic and eddy current probes on TBCs.
- Apply thermography to curved and exposed surfaces.

5 Exploitation / Publication of Results

An abstract on the effects of heat flux has been accepted for the EPRI conference in Santa Fe.

6 Acknowledgements

This work was carried out under the UK/US Collaboration on Advanced Materials for Low Emission Power Plant a programme of research whose UK activities are funded by the United Kingdom Department of Business Innovation and Skills.

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