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ABSTRACT

Two non-destructive techniques have been used to measure the oxide thickness of steam grown oxides on external and internal surfaces. These two techniques used two different fundamental physical properties, namely the generation of eddy currents and the speed of sound in different materials. Calibration curves for each technique have been created. In addition ultrasonic measurements have been made on oxides grown between two contacting surfaces. Improvements on the measurement resolution have been demonstrated with oxides of 50 μm thickness being measured.

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1 Introduction

The two key driving forces in the development of the global power generation industry are the increasing demand for electricity and widespread concerns about the effects of emissions of greenhouse gases on the global environment. There are many predictions for the worldwide growths in energy and electricity demands, with a range of different assumptions; for example, the latest International Energy Authority (IEA) predictions indicate there being approximately a 40% rise in primary energy demand by 2030 [1]. Concerns about the emissions of CO_2, and other greenhouse gases (GHGs), into the atmosphere have been growing during the last two decades; as a result there have been increasing efforts to limit the amount of CO_2 emitted into the atmosphere. The Kyoto Protocol committed many countries in the world to reduce their GHG emissions by 2008-2012 compared to 1990 levels, with the EU committed to an 8% reduction by 2008-2012 [2]. It is anticipated that follow-on treaties will agree higher levels of reductions. National governments are also continuing to develop policies to limit greenhouse gas emissions; for example, the latest UK government target is for a 60% reduction in CO_2 emissions by 2050 [3]. There are many sources of GHG emissions, but in the UK (and other developed countries) where a centralised power generation system has developed over a long period, large power stations represent major, easily identifiable point sources for CO_2 emissions. These therefore provide a focus for efforts in reducing CO_2 emissions.

One route available to the industry is to increase the efficiency of the power plant; carbon capture is also possible but will still require improved efficiency to make such endeavours viable. Attempts to improve plant efficiency will lead to increases in temperatures and pressures in plant and thereby place higher demands on materials. Higher temperatures, pressures and working lifetime means improved non-destructive evaluation methods must be used to better understand the degradation of materials in service. One such measurement is the non-destructive measurement of internal oxide scale thickness, which is of great importance, since this can provide valuable information to help predict the remaining life of plant equipment.

The following report details work conducted to investigate two non-destructive methods for measuring the oxide scale thickness on pipe work.

2 Non-destructive Techniques

2.1 Ultrasonic

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 [1-5]:

- 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.

2.1.1 Equipment

The ultrasonic system is shown schematically in Figure 1. 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.

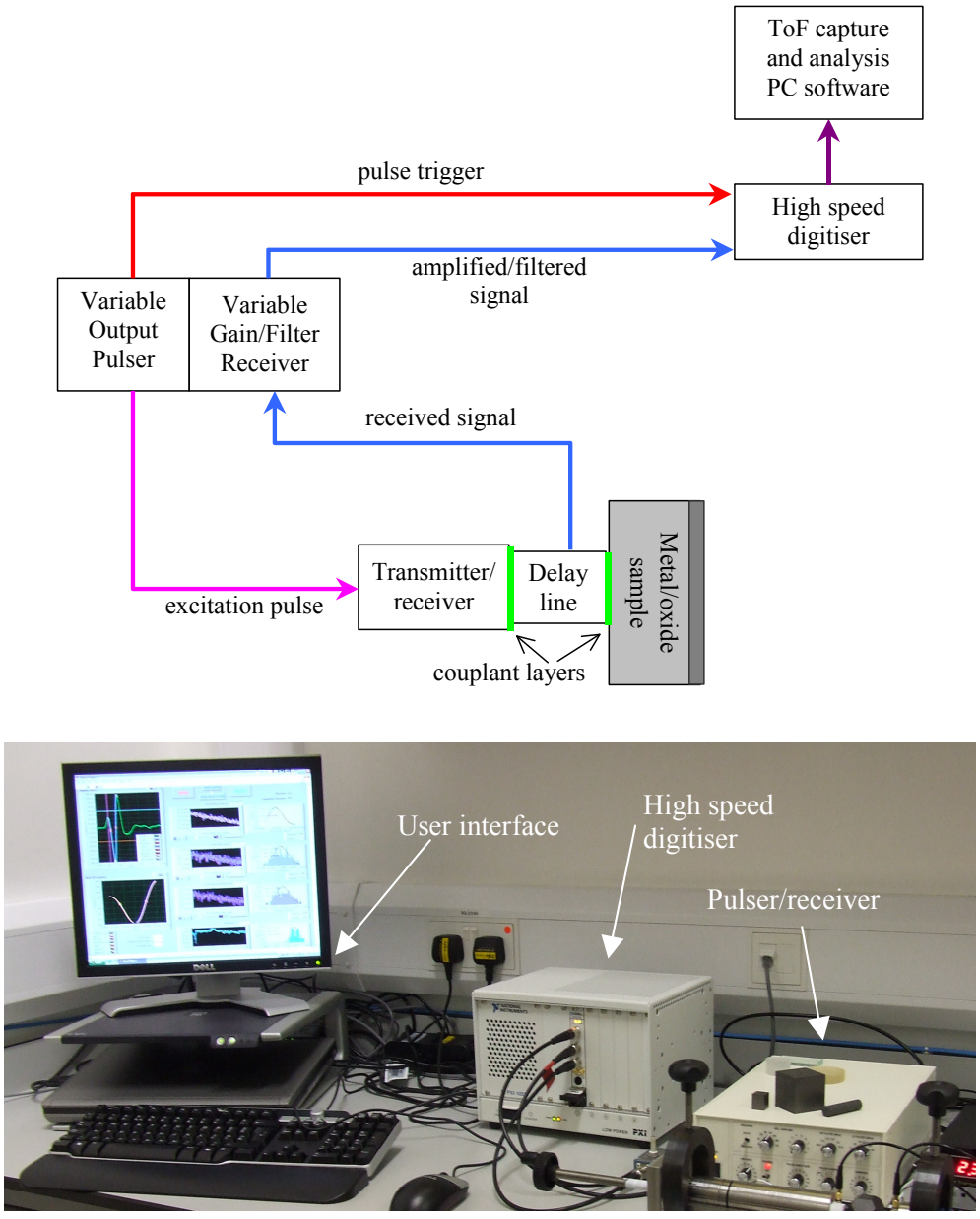

Figure 1 Ultrasonic thickness gauging equipment: schematic (above) and actual system (below).

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.

2.2 Eddy current

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.

2.2.1 Equipment

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.

3 Calibration of equipment

3.1 Specimen manufacture

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 2.

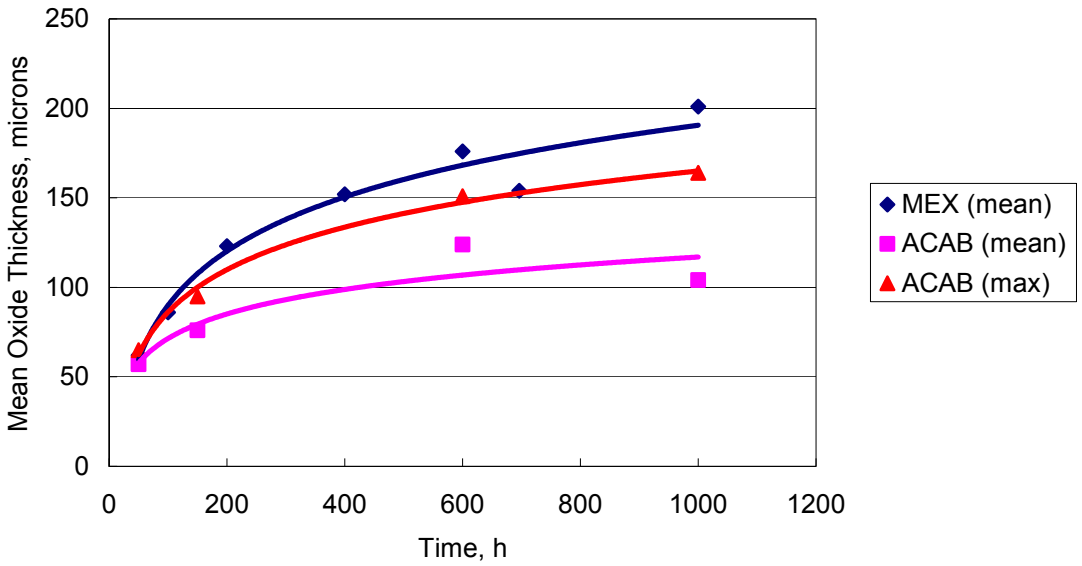

Figure 2 Oxide thickness measurements for the MEX and ACAB series of specimens, the maximum and mean values for the ACAB series and the mean value for the MEX series have been presented.

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.

3.2 Ultrasonic calibration

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 3. In all cases, a water-based gel couplant was used to improve the acoustic coupling between the transducer and sample.

Figure 3 30MHz transducers: polystyrene delay line (left) and silica delay line (right).

Figure 4 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.

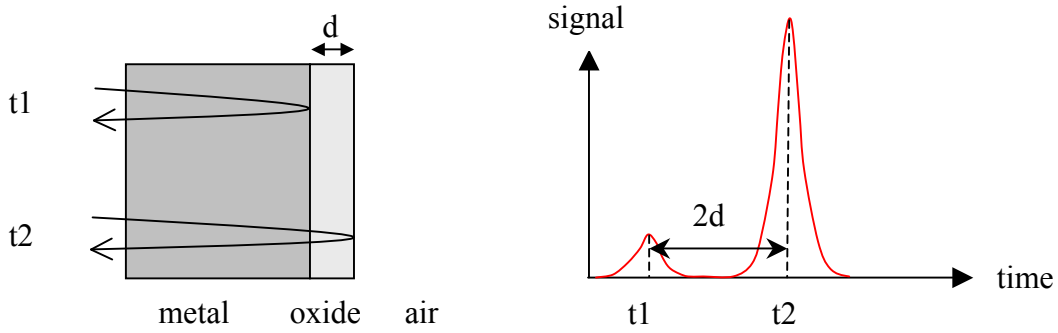

Figure 4 Schematic of basic principles of thickness measurement technique.

Figure 5 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).

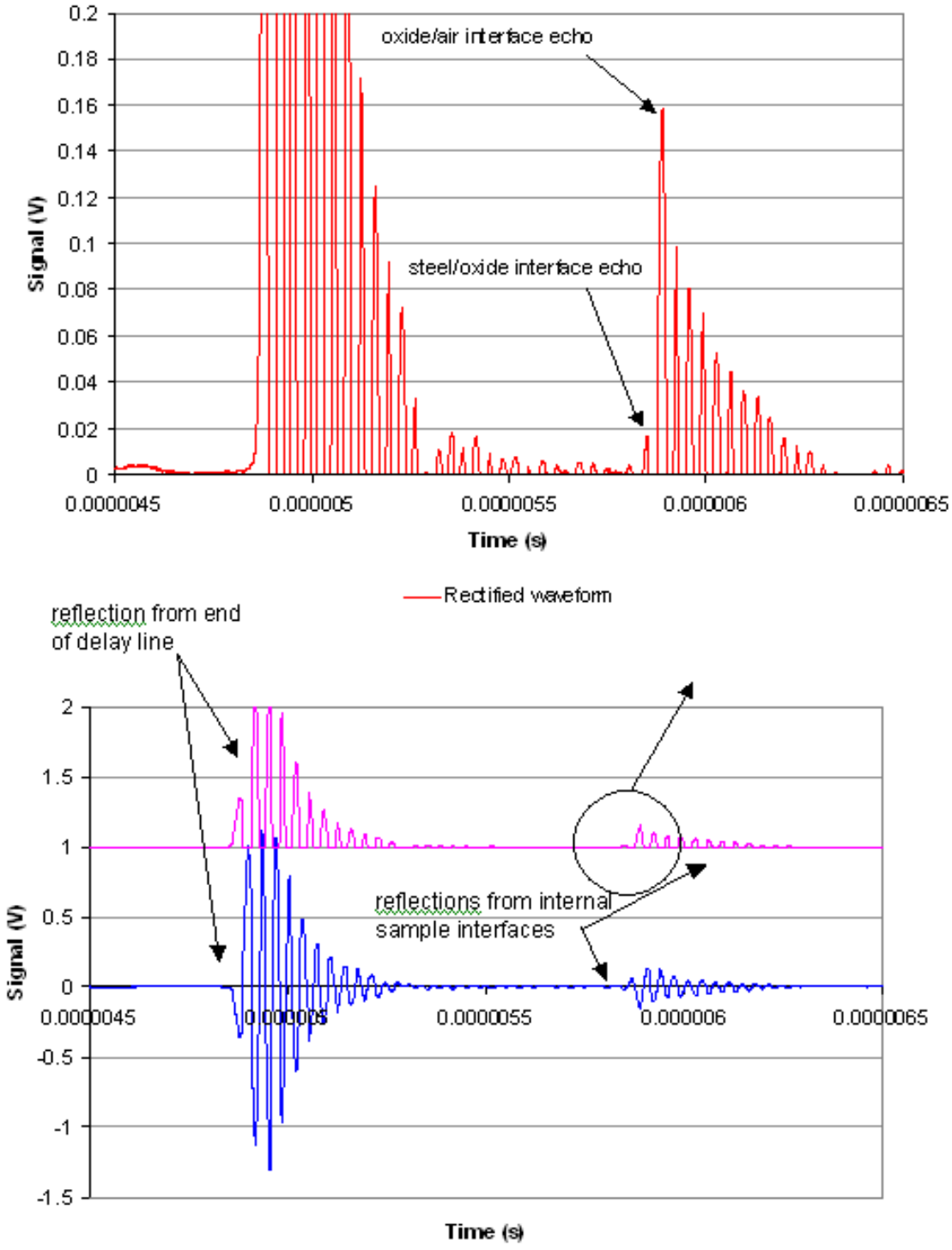

Figure 5 Typical results from measurements on flat plate calibration samples: original waveform (below) and close-up of signals of interest (above).

Figure 6 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.

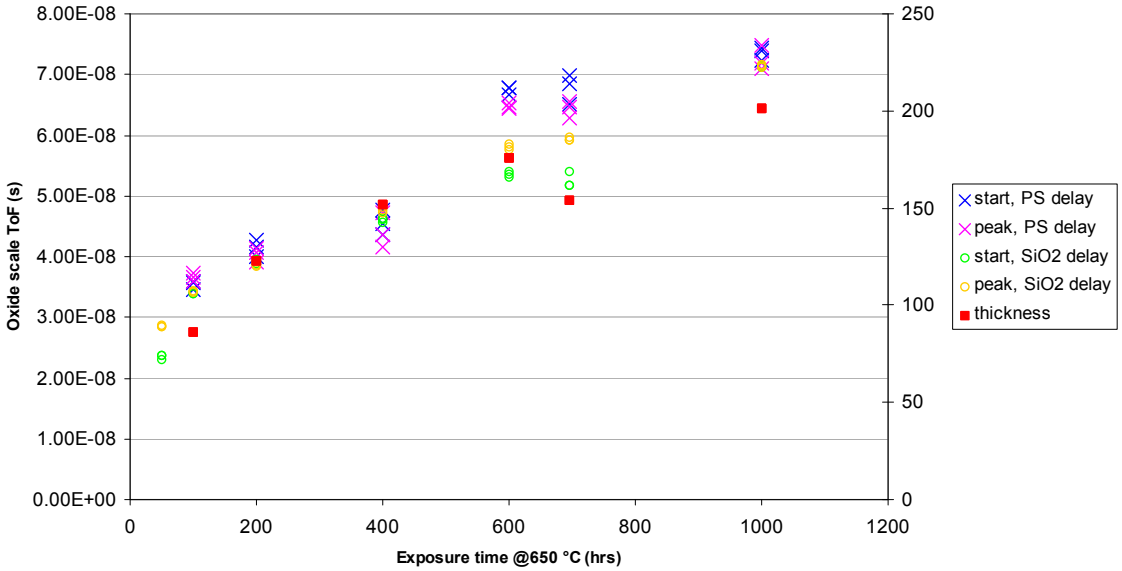

Figure 6 Plot of signal arrival and peak times for P92 samples using both transducer types.

Typical signal analyses are shown for P92 and T92 samples in Figures 7 and 8. 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.

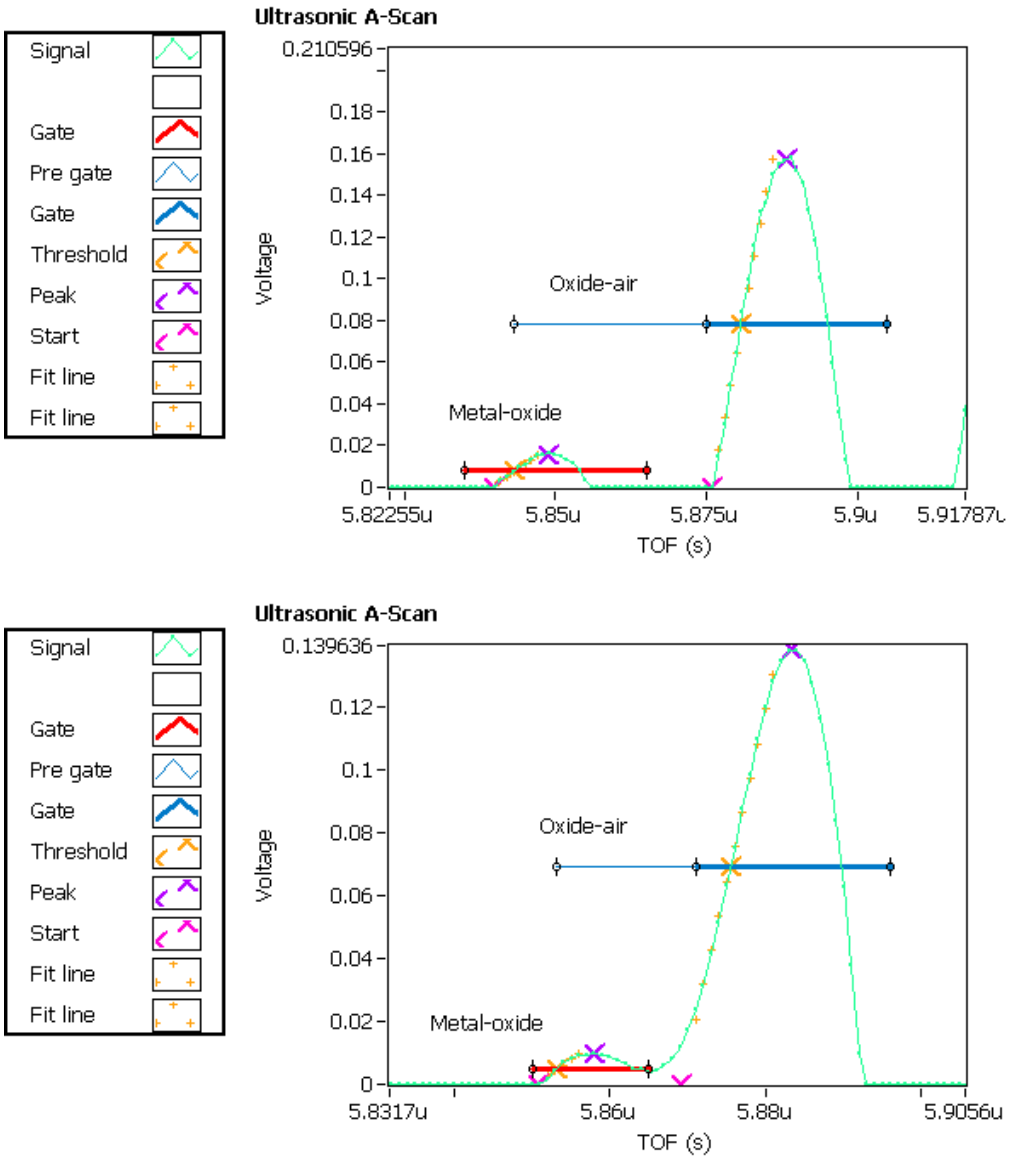

Figure 7 T92 large samples peak and start positions marked with crosses: long exposure time and thicker oxide (upper) and short exposure time and thinner oxide (lower).

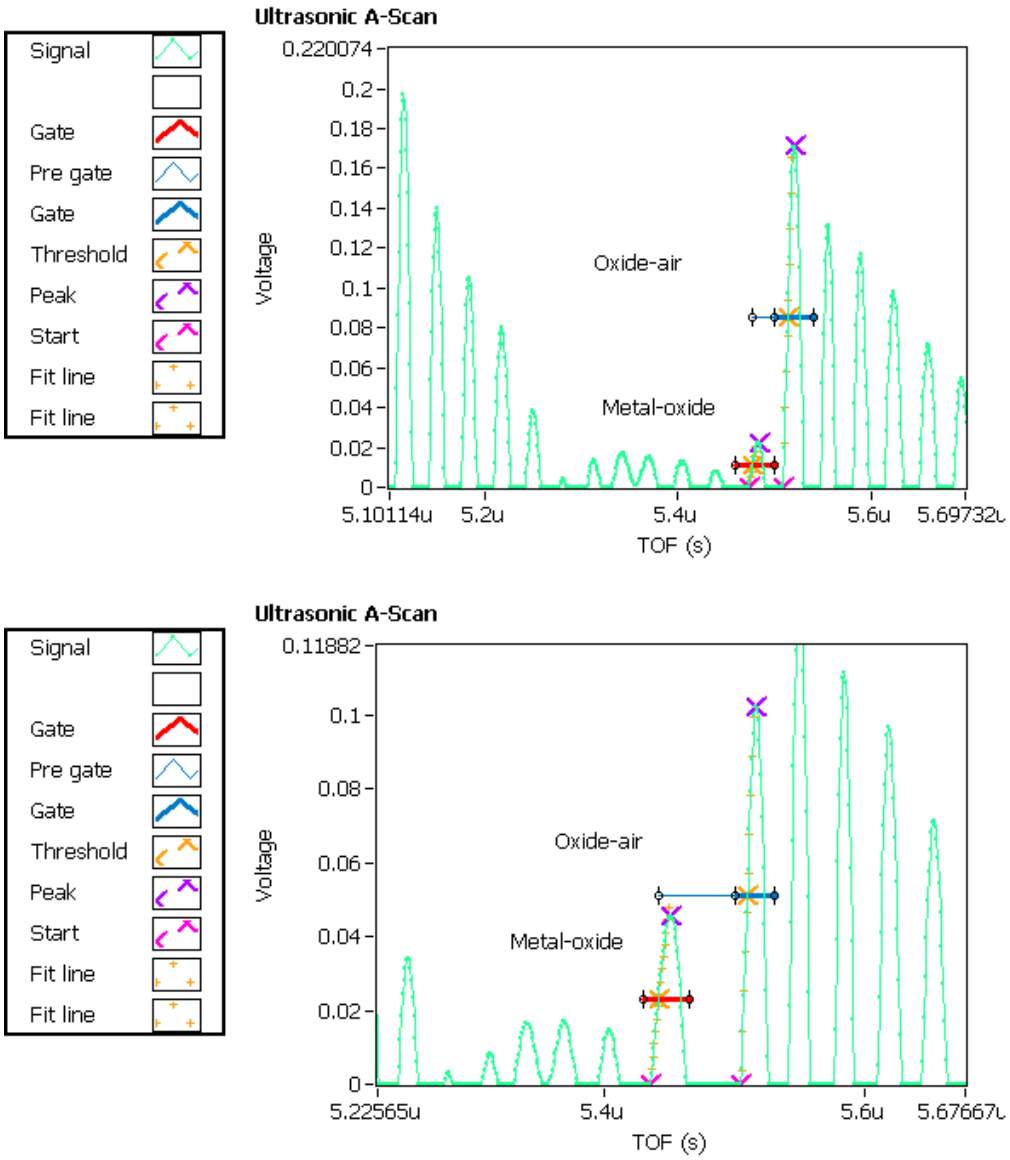

Figure 8 P92 large samples peak and start positions marked with crosses: long exposure time and thicker oxide (upper) and short exposure time and thinner oxide (lower).

Figure 9 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.

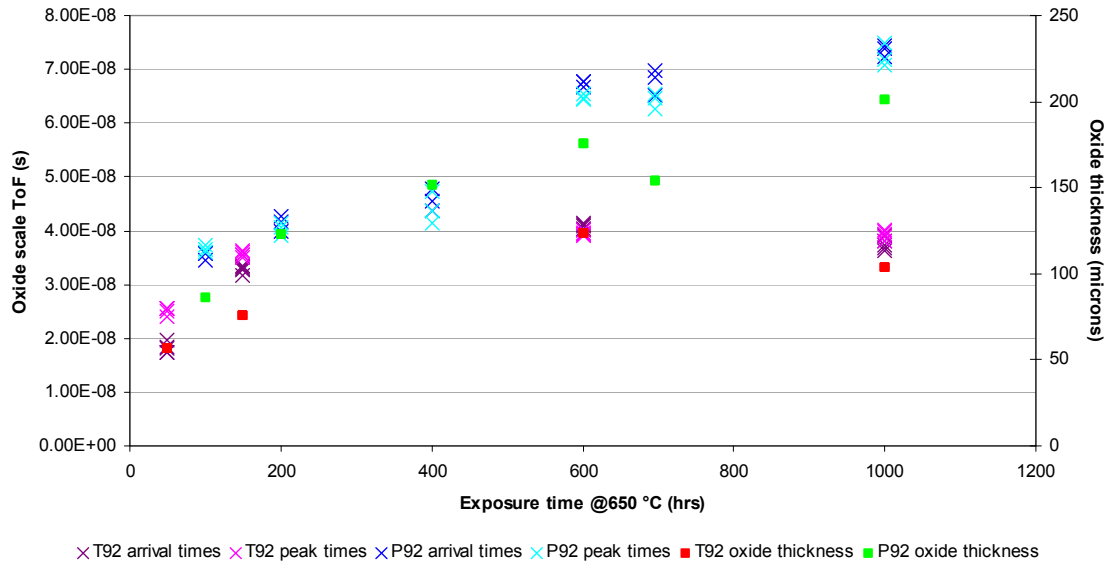

Figure 9 Plots of peak and arrival times and optically measured oxide thickness for P92 and T92 samples against exposure time.

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 10). The slope of this provides a calibration value for the oxide velocity of 5472 ms^{-1} (typically ~6000 ms^{-1} is quoted for oxide scales [3]). 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.

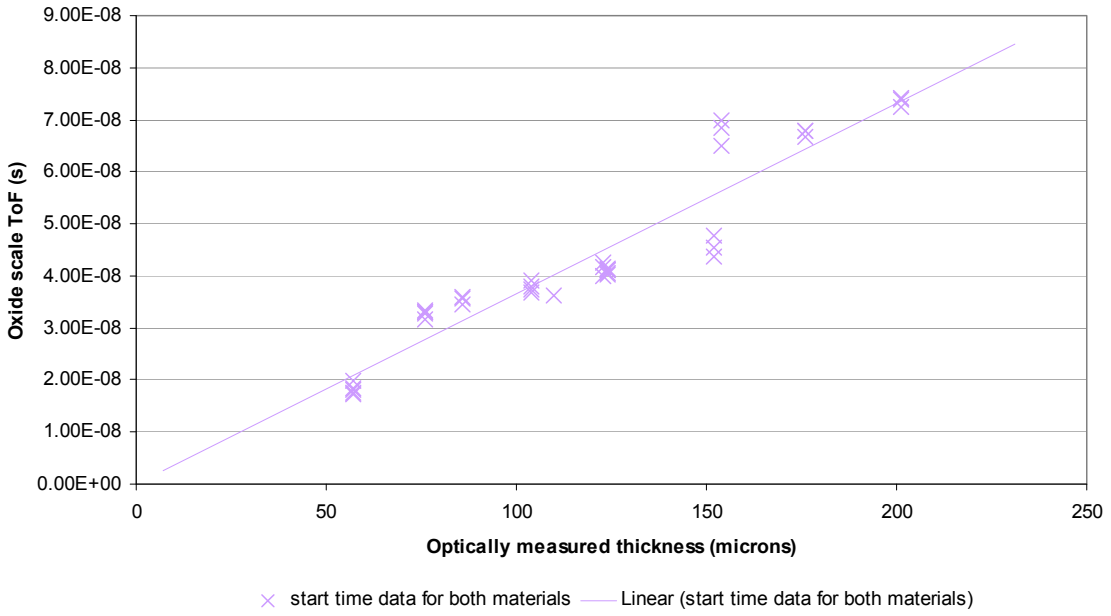

Figure 10 Experimentally observed linear relationship between ultrasonic transit time through the oxide layer and measured thickness.

3.3 Eddy current calibration

Three specimens were measured using the eddy current probe, 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 11.

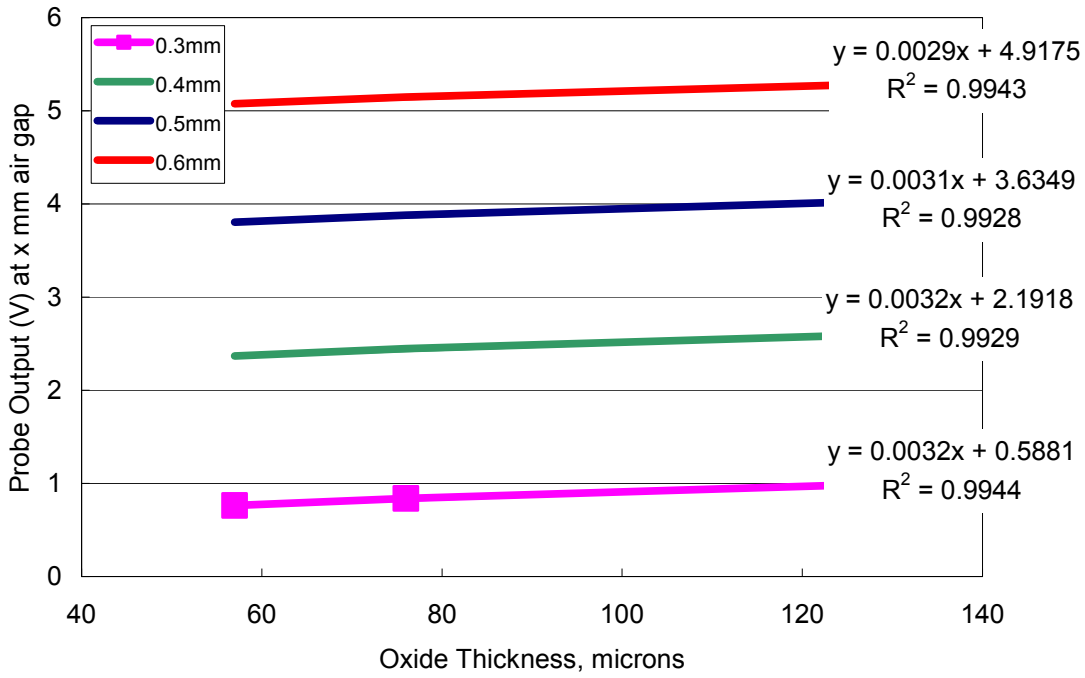

Figure 11 Eddy current probe output plotted as a function of oxide thickness and separation gap.

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 12.

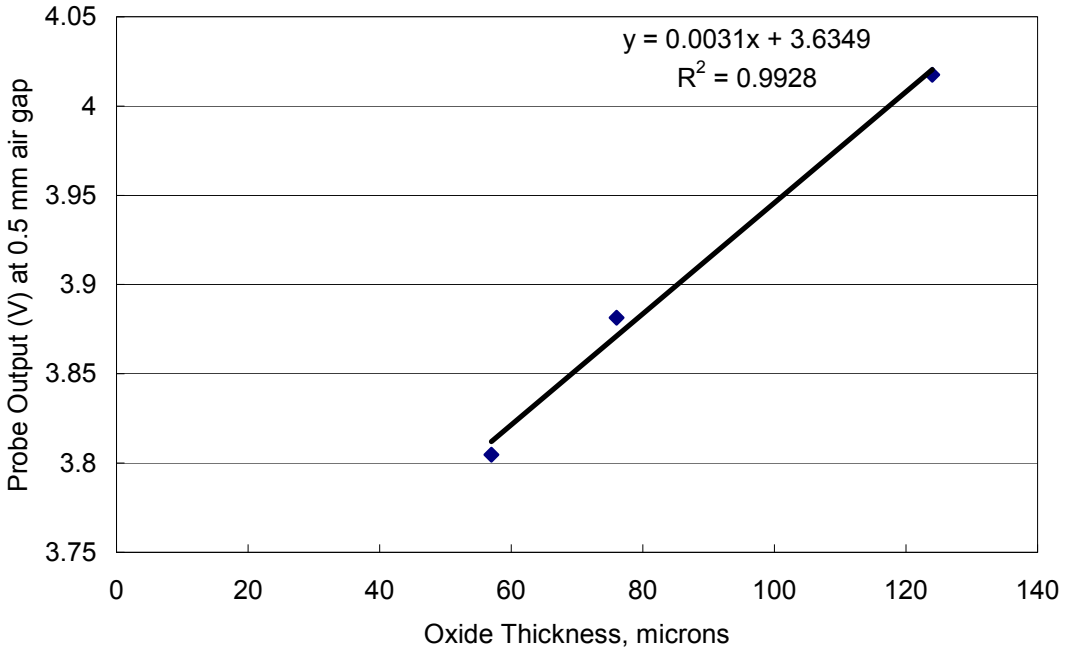

Figure 12 Eddy current probe output as a function of oxide thickness for a separation gap of 0.5 mm between the oxide surface and the probe.

Whilst the eddy current measurements appeared to be able to provide oxide thickness measurements, the technique requires the probe to be placed close to the oxide layer, otherwise the signal suffers from too much attenuation. The specimen design as detailed in [6] prevents this method being used for the pin and collar specimens, hence further measurements on additional specimens was only conducted using the ultrasonic method.

4 Pin in collar samples

Once the calibration measurements had been performed, the ultrasonic time of flight thickness gauging technique was used on the pin-in-collar samples AARF-AARL 500, 1000 and 3000 hour exposures, prior to mechanical testing. These specimens and the mechanical testing are fully reported in [6]. Figure 13 shows a schematic of the specimen design. A full list of the specimen materials is presented in Table I.

Initially ultrasonic signal measurement was attempted from the top of the pin and the bottom of the collar in order to monitor the oxide on one of the flat surfaces, but this proved too problematic due to the increased attenuation through these thicker regions. This restricted measurements to the curved collar surface which was ground with a flat region to improve transducer contact. The smaller transducer was subsequently used for all measurements to reduce the amount of material removal required. Measurements were made as before but with signal gain increased to 45 dB due to the smaller signals received from the curved internal surface.

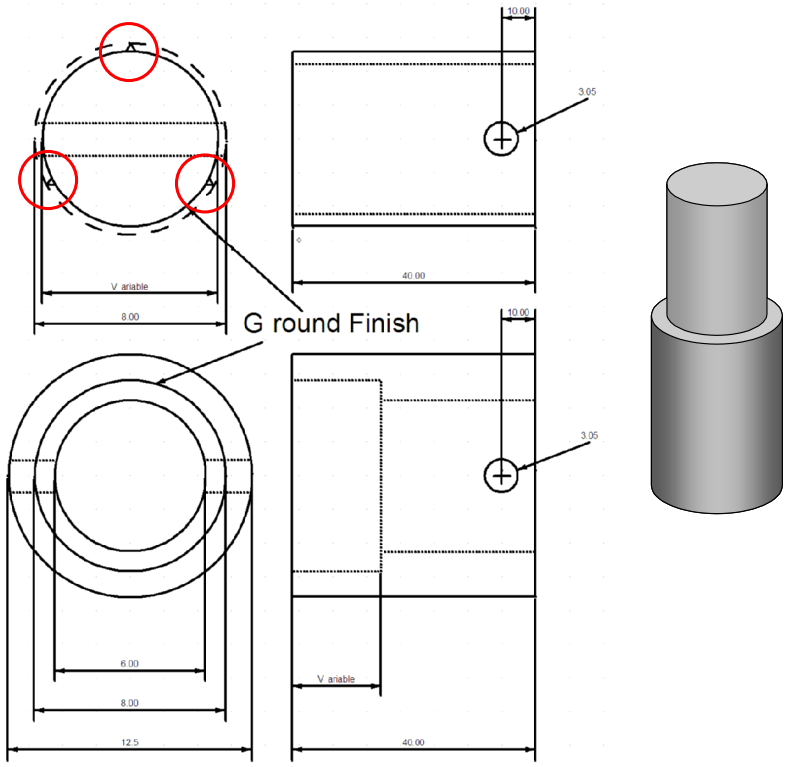

Figure 13 Schematic of the pin and collar design showing the location of the spacing pips on the pin.

Tightly curved geometries, as used in this case, and shown in Figure 14, are more complex due to the effects of diffuse scattering of the signal away from the transducer (particularly higher frequency components) resulting in even smaller signals and poorer resolution; broadening of the pulse resulting in lower resolution and the superposition of many return signals from different points along the curved surface, slightly shifted in time, resulting in masking of the characteristic waveform. There is also the possibility of there being no air interface within the oxide growth gap between pin and collar. This in itself would most likely produce a non-characteristic waveform with two very small signals of similar size or the second being smaller due to signal attenuation from the increased path length. Figure 15 shows a typical response from the pin-in collar specimens.

Figure 14 Examples of the variety of geometries tested and the flattened test area.

Table I Material combinations, exposure time and temperature.

Specimen ID		Materials		Temperature, °C	Time, h
		Pin	Collar		
AARB	001	IN617	IN617	750	500
	002				1000
	003				2000
	004				3000
AARC	001	IN740	IN617	750	500
	002				1000
	003				2000
	004				3000
AARD	001	IN939	IN617	750	500
	002				1000
	003				2000
	004				3000
AARE	001	P92	IN617	650	500
	002				1000
	003				2000
	004				3000
AARF	001	IN617	IN738	750	500
	002				1000
	003				2000
	004				3000
AARG	001	IN740	IN738	750	500
	002				1000
	003				2000
	004				3000
AARH	001	IN939	IN738	700	500
	002				1000
	003				2000
	008				3000
	007			750	500
	005				1000
	006				2000
	004				3000
AARI	001	P92	IN738	650	500
	002				1000
	003				2000
	004				3000
AARJ	001	IN738	P92	650	500
	002				1000
	003				2000
	004				3000
AARK	001	IN740	P92	650	500
	002				1000
	003				2000
	004				3000
AARL	001	P92	P92	650	500
	002				1000
	003				2000
	004				3000

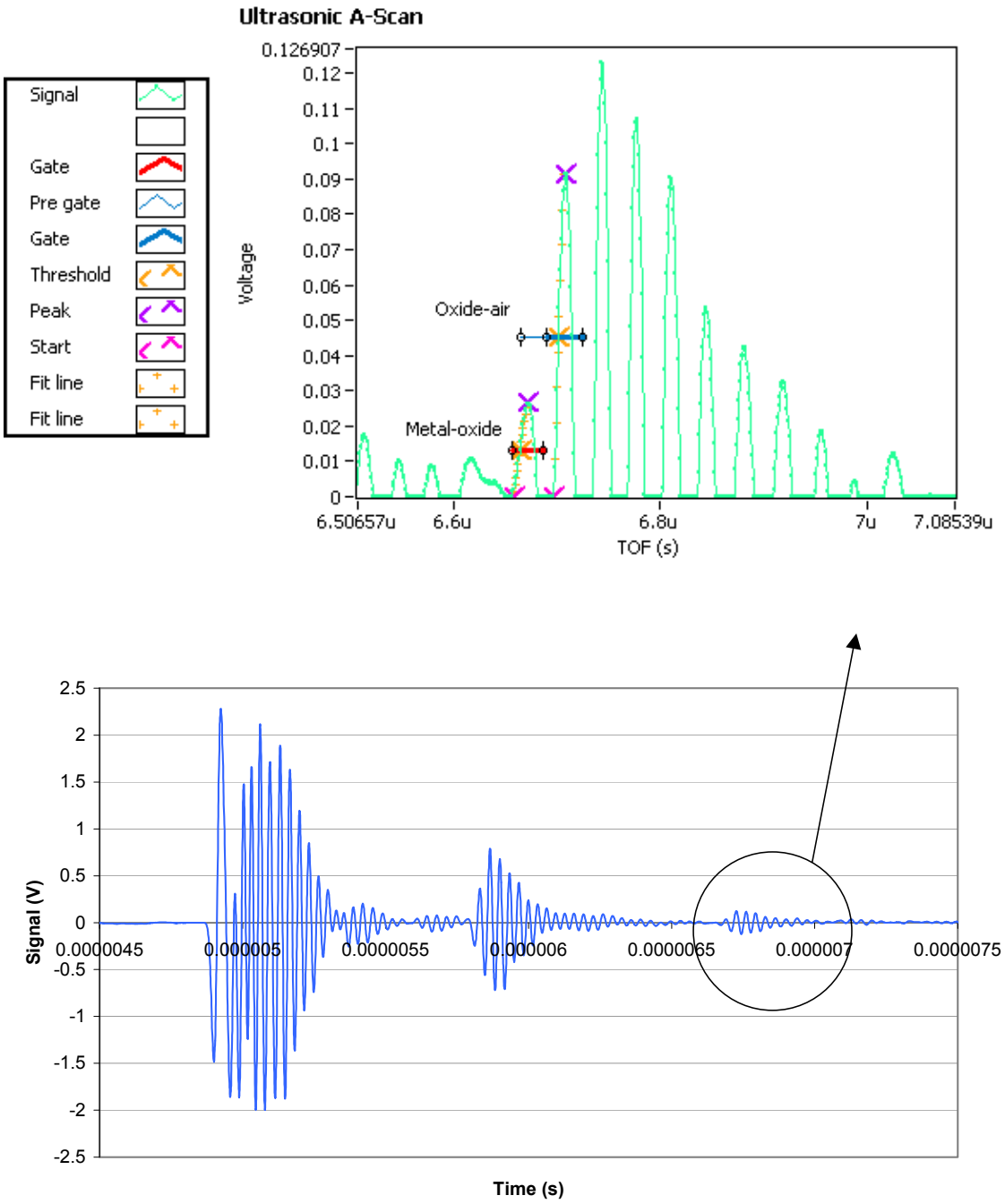

Figure 15 Typical pin-in collar sample measurement (AARK004).

In many cases there was no detectable characteristic oxide layer signal, this may have been due to the increased signal attenuation in the Inconel alloys or the thickness may have been below the minimum measurable thickness. Measurable signals were only available for AARJ, AARK and AARL (all P92 collar samples). Optical thickness measurement data is shown in Figures 16 – 20.

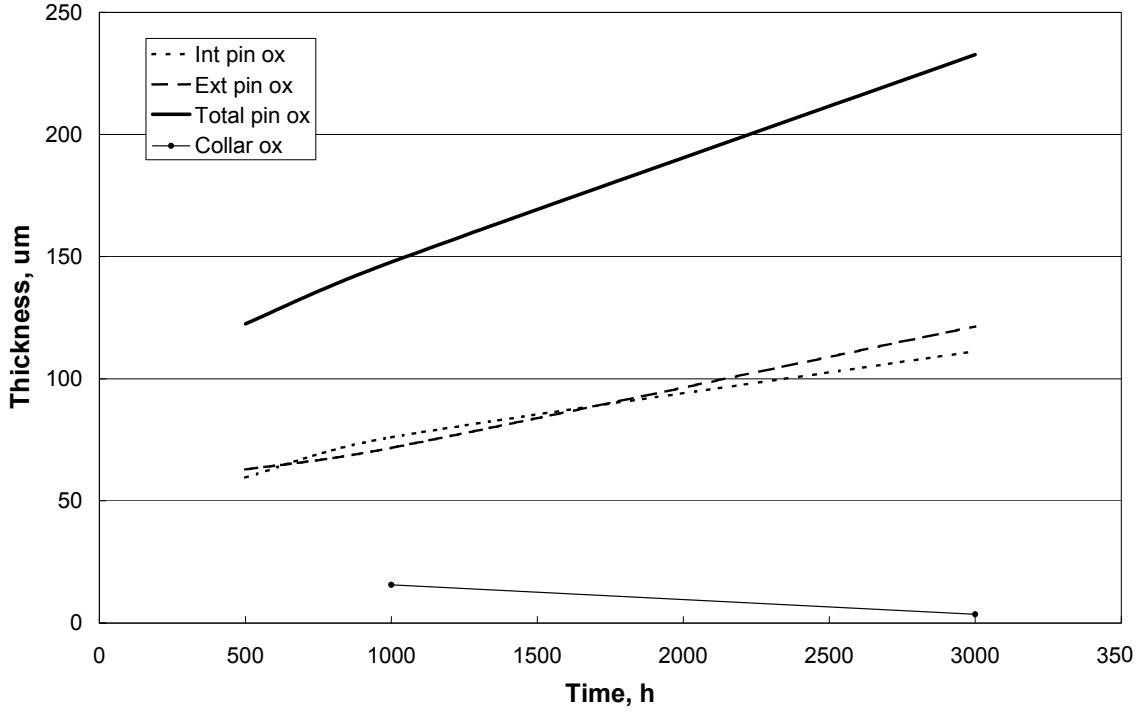

Figure 16 Oxide thickness as a function of time for a P92 pin in an IN738 collar (AARI).

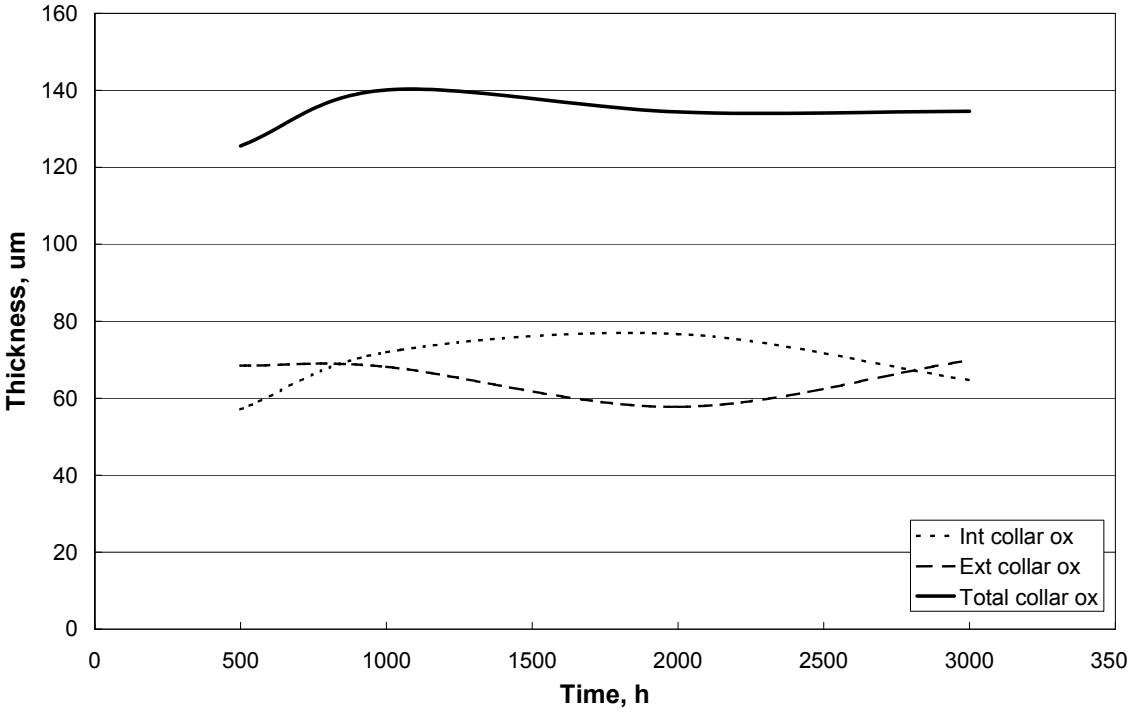

Figure 17 Oxide thickness as a function of time for an IN738 pin in a P92 collar (AARJ).

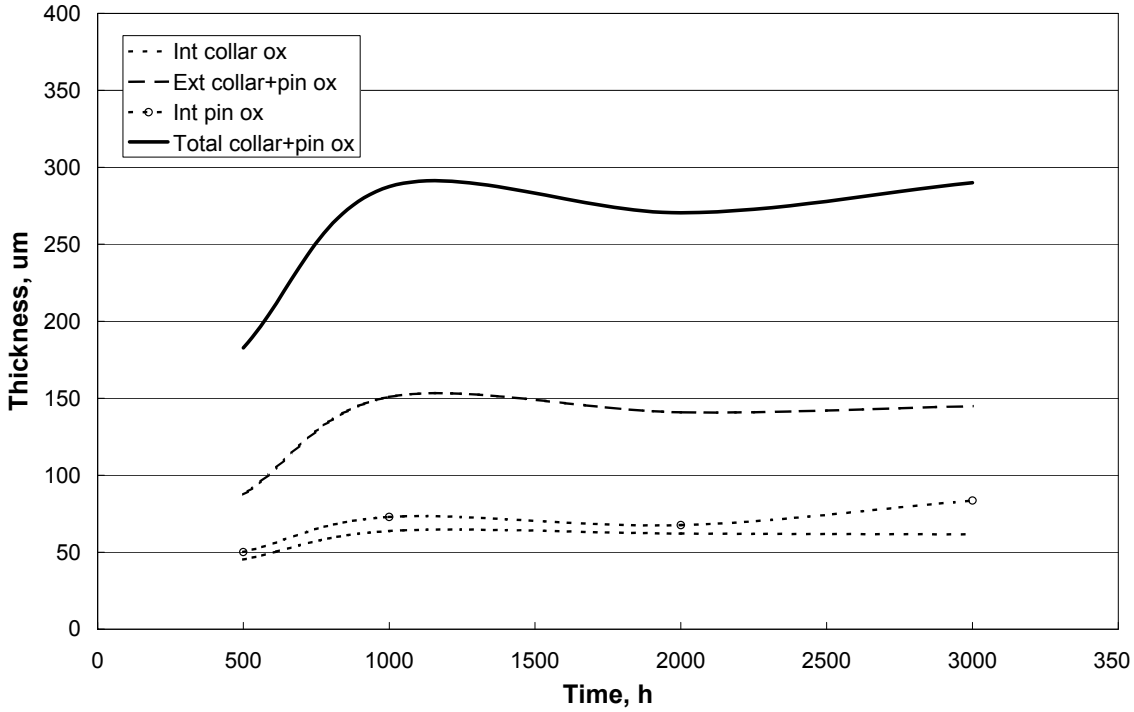

Figure 18 Oxide thickness as a function of time for a P92 pin in a P92 collar (AARL).

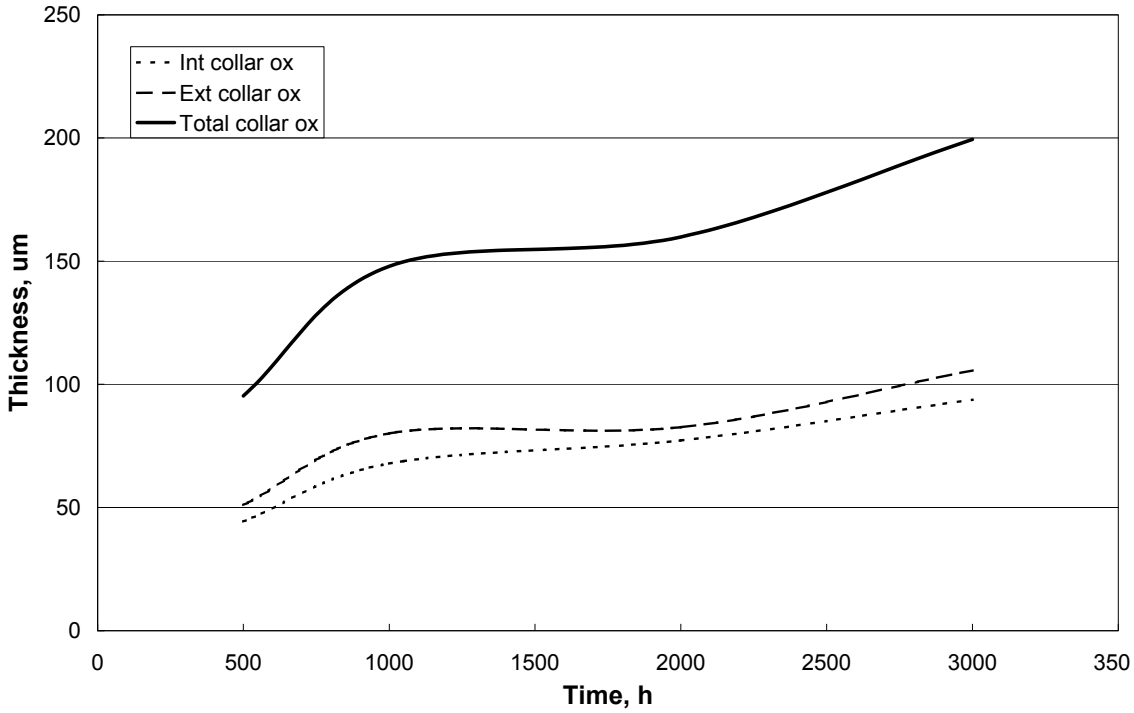

Figure 19 Oxide thickness as a function of time for an IN740 pin in a P92 collar (AARK).

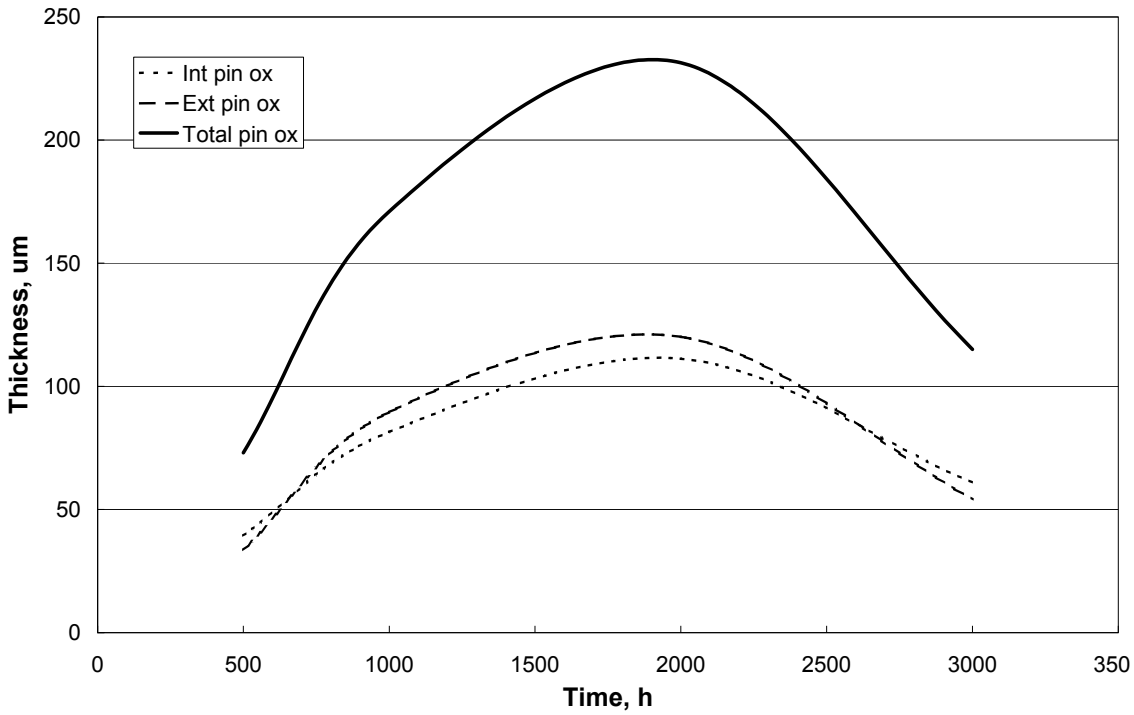

Figure 20 Oxide thickness as a function of time for a P92 pin in an IN617 collar (AARE).

As the optical thickness measurements were carried out at multiple points in a single plane centred in the region of ultrasonic measurement, the data have been re-plotted as probability graphs with the ultrasonic thicknesses placed at the 50 % probability position for comparison, presented in Figures 21 and 22. Figure 21 shows the data for specimen series AARJ, which consisted of an IN738 pin and a P92 collar. The results show good agreement for the measured total oxide thickness for the specimens exposed for 500 and 2000 hours, but do not agree with the total oxide thickness of the 1000 hour specimen. In this case good agreement was found for half the thickness. Examination of micrographs taken of the cross section of the specimen show that there is a discontinuity between the inward growing Fe-Cr spinel and the outward growing magnetite layer, as shown in Figure 23. The presence of this gap would result in only half the thickness being measured, as is shown in Figure 21.

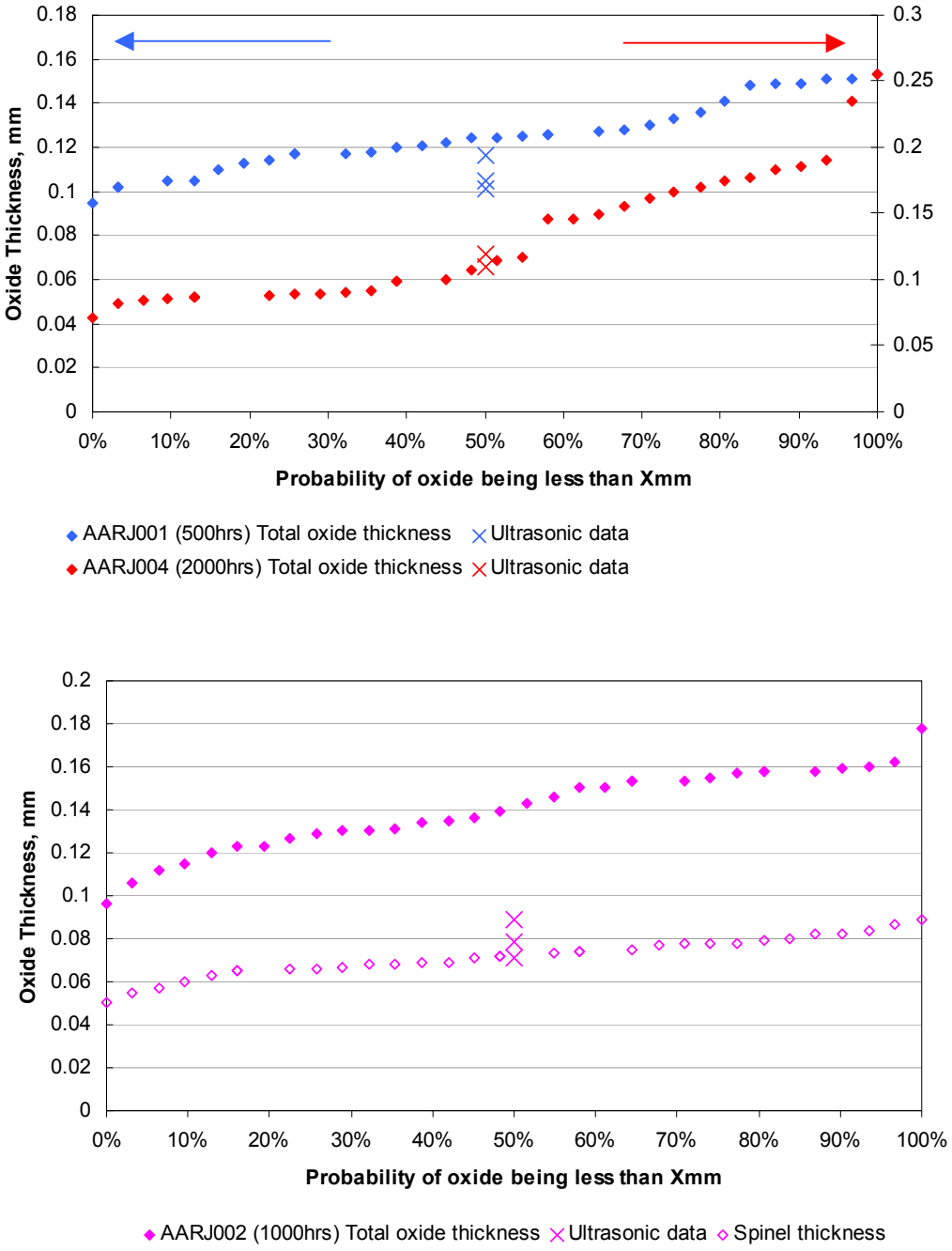

Figure 21 Optically measured thickness and ultrasonic results for P92 collars and IN 738 pins: ultrasonic results within measurement range for total oxide thickness (above) and matching spinel thickness only due to discontinuity (below).

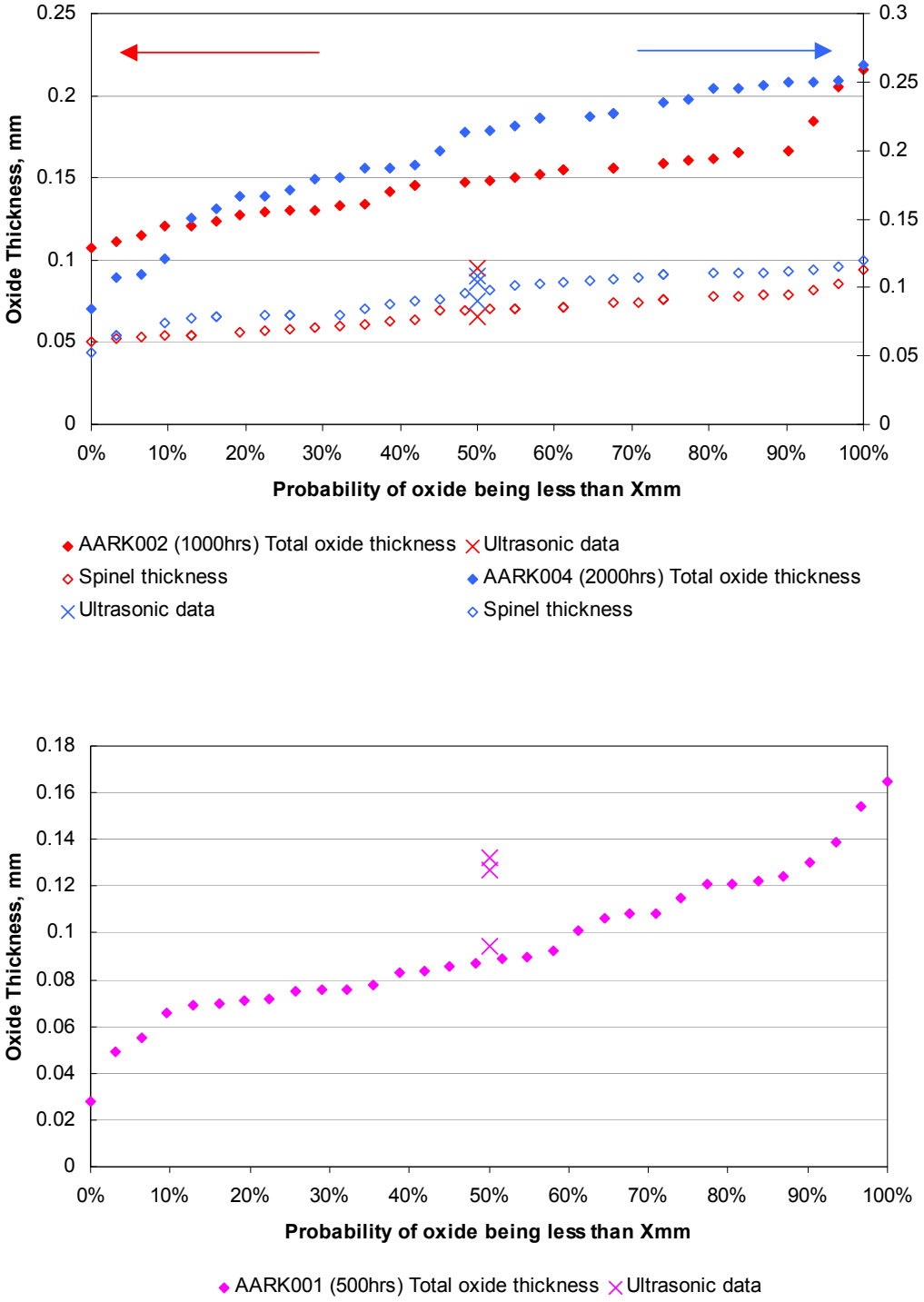

Figure 22 Optically measured thickness and ultrasonic results for P92 collars and IN 740 pins: ultrasonic results matching spinel thickness only due to discontinuity (above) and within measurement range for total oxide thickness (below).

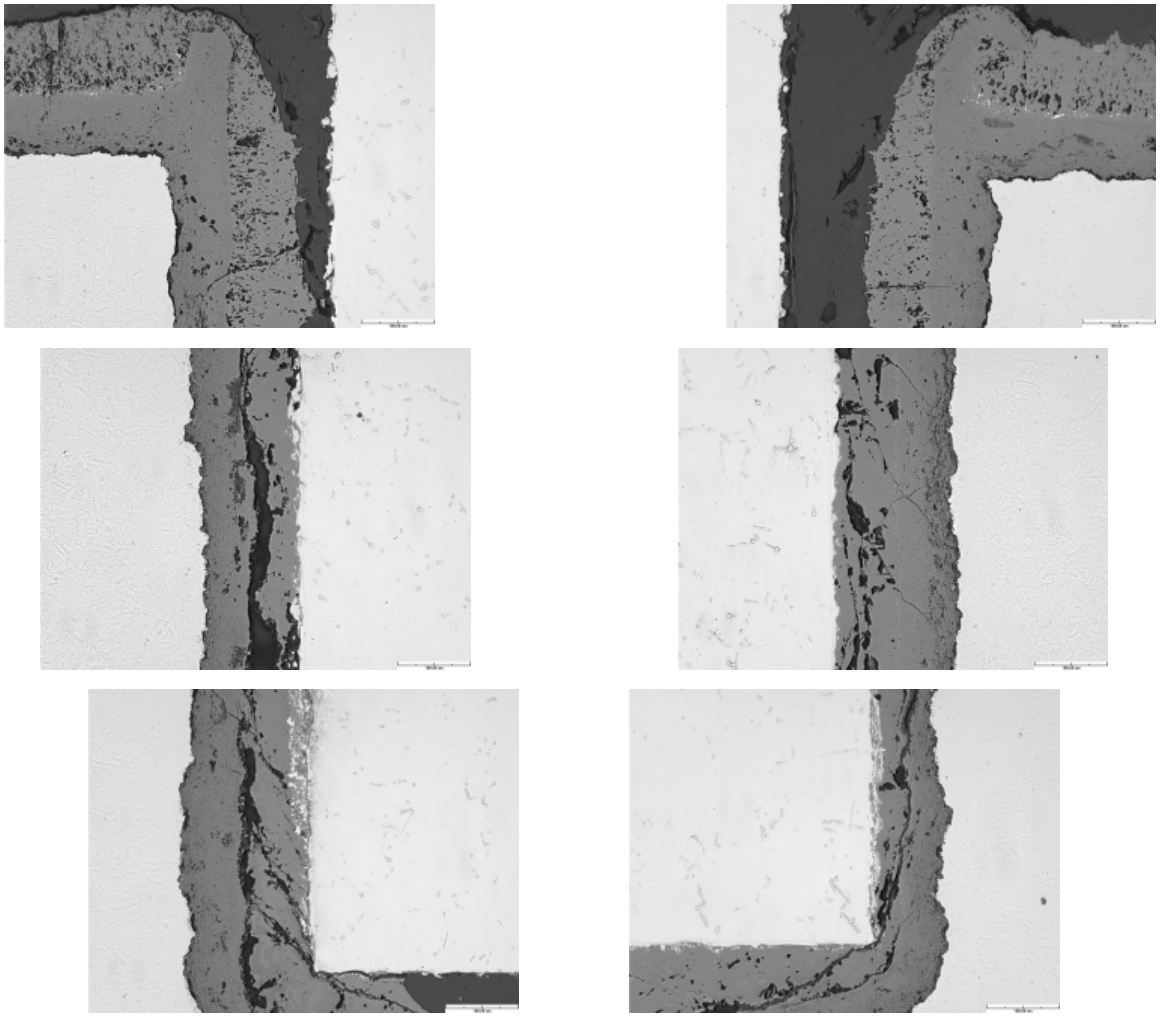

Figure 23 Cross section of specimen AARJ002, showing the discontinuity between the two oxide layers (left hand side of the image)

For the specimen series AARK, which consisted of an IN740 pin with a P92 collar, there was once again good agreement between the optically measured oxide thickness and the US data. A similar effect was seen between the different specimens. Where the oxide scale was complete the ultrasonic measurements were of the complete scale thickness, whilst where there was delamination between the two constituent oxides, only half the thickness was measured, as shown in Figure 22. Cross sectional micrographs of the specimens used are presented in Figures 24 – 26. In this case it would appear that all the specimens had delaminations, the ultrasonic results for AARK001 suggest that the full thickness was measured. It should also be noted that the cross sections were prepared after tensile testing was conducted, so the oxide may have been damaged during this process and the cracks seen in the optical micrographs may be due to this testing. Hence they may not have been present during the US measurements.

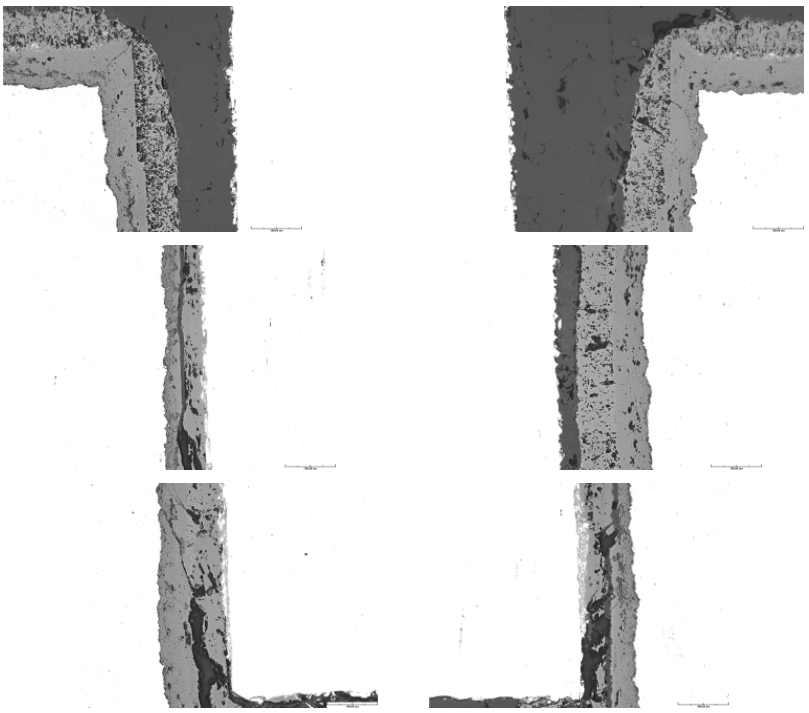

Figure 24 Cross section of specimen AARK001

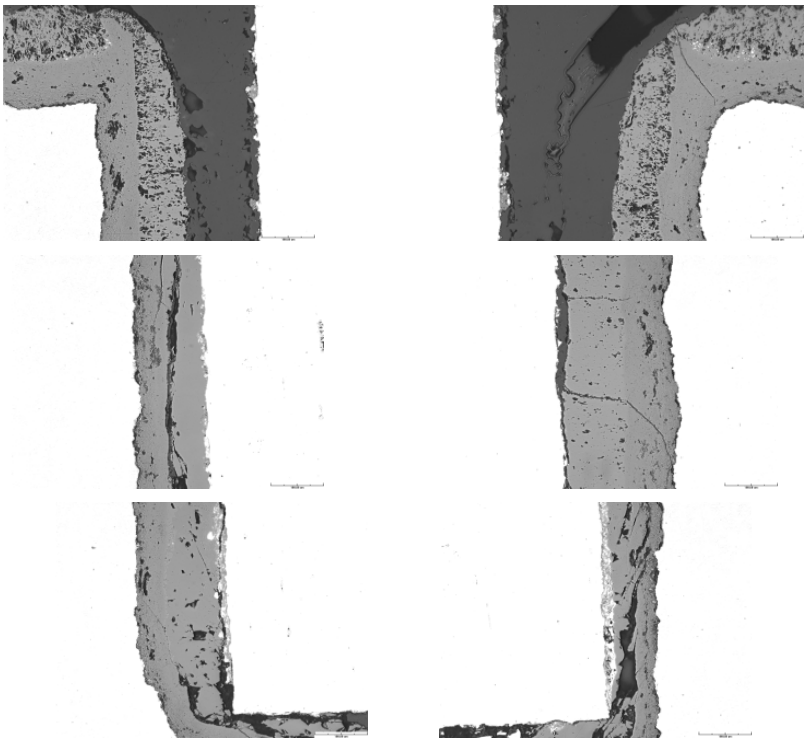

Figure 25 Cross section of specimen AARK002

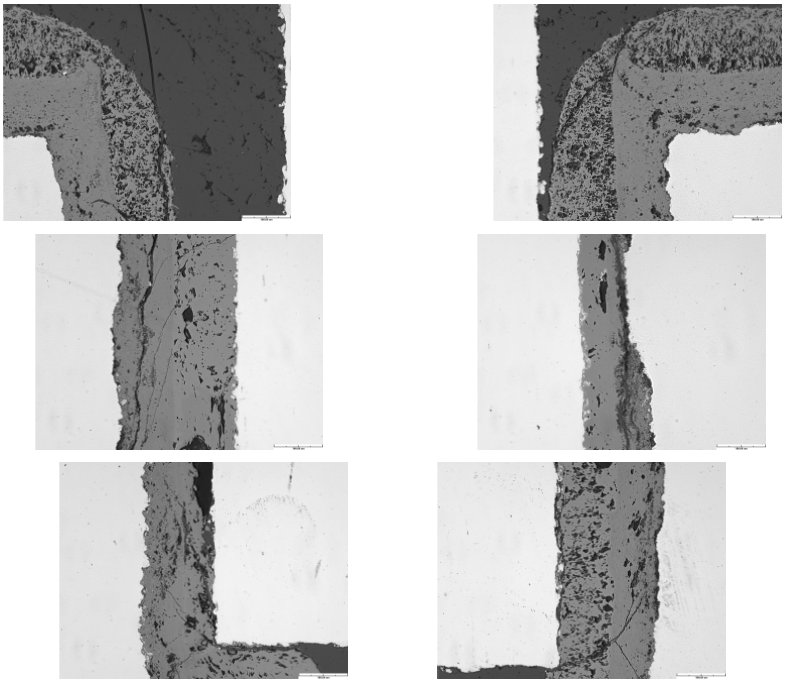

Figure 26 Cross section of specimen AARK003

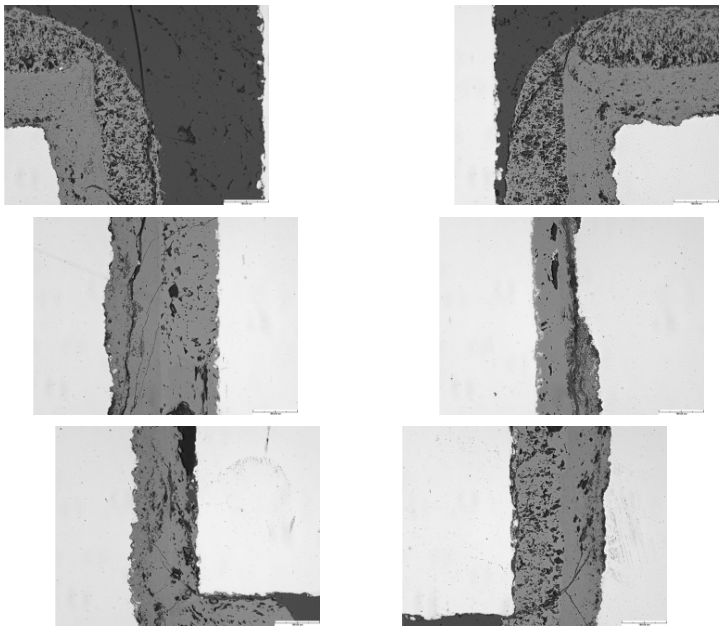

Figure 27 Cross section of specimen AARK004

The oxide formation in the P92-P92 samples (AARL) presented without any interface to mark the boundary between the oxide growing out from the pin and that growing out from the collar. In essence the oxide appeared as one layer with no air boundary between the pin or the collar. These measurements did not produce useful data, as the return signals did not show the characteristic appearance where an air interface is

present. This made detection of the two oxide/metal interface signals almost impossible to distinguish from background noise.

The other samples exhibited either large amounts of porosity in one of the oxide layers (acting as an air interface and producing a back reflection signal) or a discontinuity or crack between either the collar oxide and the pin oxide or at the interface between the spinel and magnetite layers of the collar oxide. Hence in some examples the measured ultrasonic thickness is more consistent with the spinel only thickness rather than the total oxide thickness. The cracks and discontinuities were thought to be present prior to tensile testing (most of the shear cracks produced by mechanical testing resulted in fine 45° angle cracks rather than large planar cracks running parallel to the collar surface).

5 Discussion and Conclusions

Two non-destructive techniques have been used to measure the oxide thickness of steam grown oxides on external and internal surfaces. These two techniques used two different fundamental physical properties, namely the generation of eddy currents and the speed of sound in different materials. The method which used eddy currents proved to show a linear response in the voltage measured at the probe as a function of oxide thickness. Using such a calibration curve as shown in Figure 12 it was possible to measure the thickness of similar oxides on P92 substrates as a function of probe-surface separation. However, for the specimens produced as part of an investigation of the oxidation properties of contacting surfaces, this technique was not able to measure the oxide thickness on the inside of specimens, i.e. through a substrate on the inside of a pipe. The ultrasonic method however was able to do this even given the extremely challenging specimen geometries of the pin-in-collar specimens illustrated in Figure 14.

Ultrasonic inspection is typically used in industry for inspection of metal thickness, whilst this is a very useful measurement and can give valuable information regarding the remaining life of pipework, it does not provide a measure of the thickness of oxides still adherent on the inside of tubing and pipework. One of the reasons that ultrasonic measurements are not normally used for oxide thickness measurements has been the limited resolution of the measurement for relatively thin layers. It has been demonstrated that by optimising transducers, measurement settings and analyses that improved resolution can be obtained with accurate measurements down to oxide thicknesses of 50 μm becoming possible. Previous limits of around 100 to 250 μm have been quoted depending on the transducer being used for the measurement. This work has shown that higher resolution is possible. Measurements of oxide thickness in the range that spallation normally occurs for martensitic 9-12%Cr alloys are obtainable, these tend to be in the order of 100 to 150 μm.

It has also been shown that the ultrasonic technique is susceptible to microstructural and morphological features in the oxide. This is a feature of the measurement method and cannot be overcome, so when examining an area it would be better to use a larger diameter transducer or to measure in several places in a localised area and use an average thickness value. The size and geometry of the specimens used in this work prevented such an approach. In terms of measuring the oxide grown between contacting surfaces, it was seen that where the oxides grow together in a homogenous and fully dense manner, as with the P92/P92 specimens there was no demarcation in the

scale to provide the ultrasound reflection, and hence no measurement could be made. This measurement limitation would not be applicable to pipe and tube inspection.

To summarise, it has been shown

- Eddy current measurement can be used to measure the oxide thickness on exterior surfaces, with the measured voltage showing a linear correlation to oxide thickness.
- A calibration curve for eddy current measurements on an oxide grown on a 9%Cr martensitic steel have been produced.
- Ultrasonic measurements can be used to measure the oxide thickness of interior surfaces.
- The speed of the ultrasound wave has been measured and calibrated for steam grown oxides on a 9%Cr martensitic alloy.
- It has been demonstrated that improved resolution is possible by using appropriate transducers, amplifiers and analyses.
- Ultrasonic measurements of oxide thickness agree well with optical measurements provided there is no discontinuity in the oxide scale, where this occurs the measurement correlates with the thickness of the Fe-Cr spinel layer, as it is at this interface with the magnetite layer where fracture was seen to occur.
- Considering the tight radius and difficult geometries used in this work the use of ultrasonic transducers to make higher resolution measurements of the oxide thickness has been demonstrated and should be easier to apply to large scale items such as pipe work and tubing in plant.

6 Acknowledgements

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7 References

1 Private Communication Paul Crowther, RWE International
2 Private Communication Colin Brett EON UK
3 S Labreck, D Kass, T Nelligan “Ultrasonic Thickness Measurement of Internal Oxide Scale in Steam Boiler Tubes”, ECNDT 2006
4 Oxide Scale Measurement, GE Inspection Technologies Website
5 Measuring Internal Oxide Scale in Boiler Tubes, Panametrics Product Application, Olympus IMS Website
6 A T Fry, L J Brown, M G Gee and E Piedra, “Procedures for Steam Oxidation Testing of Static and Dynamic Specimens, NPL Report MAT 41, March 2010