

Measurement Note

DEPC-MN043

Measuring Heat Transfer Through Steam Grown Oxide Scales.

Summary

Heat transfer can be a controlling factor in many industrial processes. In the case of heat exchangers, and particularly in those exposed to steam environments, their efficiency is greatly effected by the growth of an insulating oxide scale which may cause overheating of the components, which in turn will lead to potential failure through creep mechanism. Understanding of the thermal conductivity of the scale and the characterisation of the evolution of this property with the growth of the scale will allow for a more precise prediction of component lifetime.

This measurement note will illustrate how the thermal diffusivity and therefore conductivity of a single layer system can be measured using the Laser Flash technique. Multilayered systems are evaluated using a combination of the Laser Flash technique and through modelling using the NPL developed TherMOL model. This model was initially developed in an earlier programme, but here it has been modified to allow for the evaluation of more complex systems. Recent developments of this model are outlined.

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Single Layered System

The Laser Flash technique is often used to measure the thermal diffusivity or rate of heat transfer within a homogeneous material, which can be considered as a single layer. This involves using an unfocused laser beam that impinges onto the flat surface of a specimen. The heat generated by the laser is absorbed in a thin layer at the surface of the sample and the subsequent thermal distribution and heat flux within the material is then dependant only on the thermal diffusivity of the material. Thus by measuring the rate of heat transfer through the material, the thermal diffusivity can be derived. The thermal diffusivity in a homogeneous material is given by:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial^2 x} \quad (1)$$

where T is the temperature, t is the time, x is the thickness of the layer and α is the thermal diffusivity. The thermal diffusivity is given in by:

$$\alpha = \frac{\lambda}{\rho C_p} \quad (2)$$

where λ is thermal conductivity, C_p is specific heat capacity and ρ is the density of the material.

Thermal conductivity can be defined as the quantity of heat transmitted, due to a unit temperature gradient, in a unit time under steady conditions in a direction normal to a surface of a unit area, when the heat transfer is dependent only on the temperature gradient. We can calculate the thermal conductivity for single layer homogeneous materials simply by using the laser flash data. The laser flash equipment is schematically shown in Figure 1.

Measurement Procedure

The pulse energy of the laser is set at a suitable value to produce a temperature rise of approximately 3 to 5 °C at the rear face of the

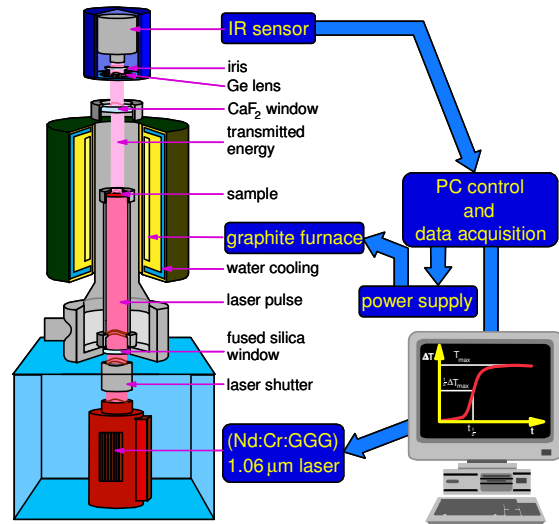


Figure 1 Schematic representation of the Laser Flash apparatus.

sample. This is achieved by comparing the pulse width, which has an allowable range of 0.2 ms to 1.2 ms, to the time to reach half the value of the maximum temperature rise as shown in Figure 2. The operator aims to obtain a ratio of pulse width to half max time of 1:10 as a minimum but ideally 1:40.

Although a rise of around 4 °C is the minimum rise capable of giving a useful detector signal to noise ratio at ambient temperature, a low value is desirable both to reduce heat losses and to minimise the possibility of damage to the front face arising from the much larger temperature rise at that face.

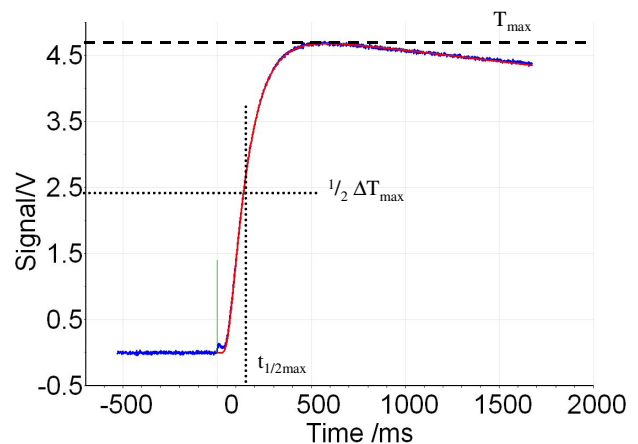


Figure 2 Heat rise in volts, detected from the rear face by the IR detector.

Specimen Preparation

In this study specimens were machined such that they had a diameter of 12.5 mm $\pm$ 0.05 mm, and a thickness between 1 and 3 mm. This was dependant on the amount of oxide scale grown. Ideally the thickness should not vary by more than 1% across the specimen. It has been estimated that a 1% error in the thickness will lead to an error of 2% in the final diffusivity. The unoxidised material was carbon coated prior to testing in the Laser Flash to aid heat absorption.

Thermal Diffusivity Calculation

The relationship between the thermal diffusivity and the transient temperature rise can be derived by considering an idealised adiabatic model, and then applying corrections to allow for departures from this idealised situation.

The adiabatic model assumes that when the laser is fired, an instantaneous uniform pulse of energy is absorbed uniformly in a very thin surface layer of the sample. This energy then passes axially through the sample, and eventually raises the temperature of the rear surface. No heat is lost by the sample, and there is no radial heat flow. Under these conditions the thermal diffusivity α , is given by:

$$\alpha = 0.138785 \frac{L^2}{t_{0.5}} \quad (3)$$

where L is the thickness of the sample, and $t_{0.5}$ is the time taken for the temperature of the

rear face to reach half its maximum value [1].

Corrections are then made to the raw data to allow for errors introduced by the finite length of the laser pulse [2] or radiant heat losses [3,4]. The method used in this case is that of Dusza [5], which simultaneously corrects for both finite pulse and radial heat losses.

The adiabatic model also assumes a one-dimensional heat flow and that there is no heat loss from the test piece. To maintain these boundary conditions radial heat flow is minimised by reducing the area of contact between the sample and its support, and by ensuring that the ratio of the flat area of the disc to the curved area is large (i.e., that the sample is thin). Further information and details regarding the uncertainty of this technique have been reported by Chapman *et al* [6].

Laser Flash Results

Laser Flash measurement have been performed on unoxidised samples of P92, Esshete 1250 and IN740, the compositions of which are presented in Table I. In conjunction the specific heat capacity and coefficients of thermal expansion for these materials was also measured. The thermal diffusivity and conductivity for the three materials are shown in Figures 3-5. Interestingly there is an obvious difference between the three materials. The results show that P92 exhibits a fall in thermal diffusivity as the temperature of the material increases, this is a normal response for steels with similar compositions [7], whilst the Esshete 1250 and IN740 both show increasing thermal diffusivity with

Table I Elemental composition of the test materials

Alloy	Composition, wt% (Fe balance)															
	C	Si	Mn	P	S	Al	Cr	Mo	Ni	V	W	Nb	N	Ti	Cu	B
P92	0.12	0.1	0.61				9.37	0.45		0.23	1.98		0.04			
Esshete 1250	0.09	0.56	6.23	0.024	0.26		15.3	1.09	9.9	0.25		1	0.03		0.14	0.038
IN740	0.03	0.45	0.27	0.003	0.002	0.75	24.3	0.52	49.4		0.003	1.83		1.58		

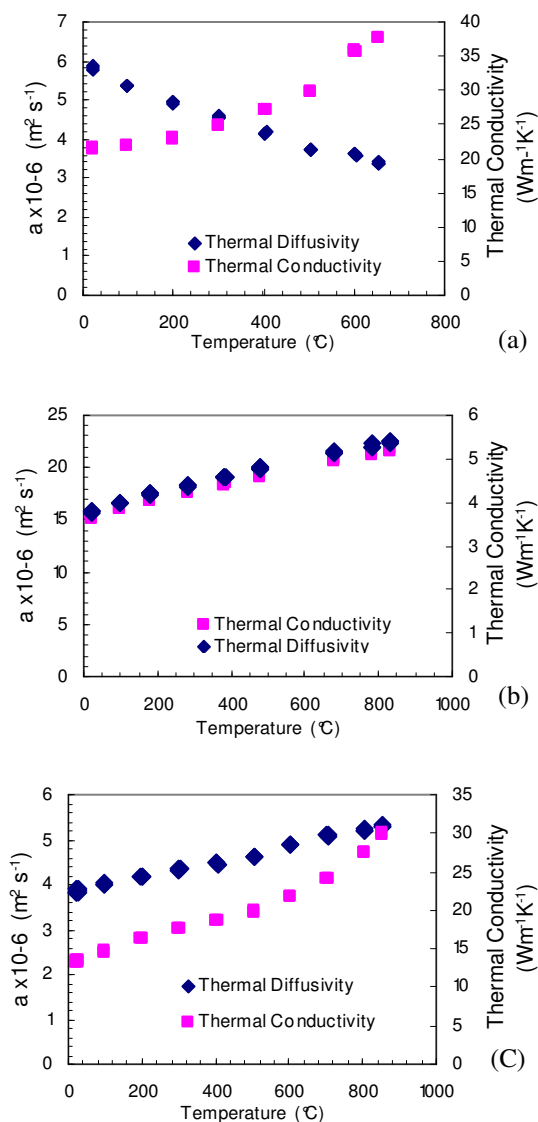


Figure 3 Thermal diffusivity and conductivity for unoxidised (a) P92, (b) Eshete 1250 and (c) IN740 as measured using the Laser Flash technique.

increasing temperature. This is not replicated in the thermal conductivity values due to the increasing values of specific heat capacity for all three materials.

Multilayered Systems

For multilayered systems the laser flash technique is used to obtain the raw heat transfer data. This data is then used within an NPL developed heat transfer model “TherMOL”. The model developed as part of the Lifetime Performance of Materials

programme originated as a 2D model used to calculate the transient heat or mass transfer through multi-layered and multi-material systems. As part of the work conducted with the Performance of Materials programme this model has been modified as outlined below.

TherMOL 3D

The latest version of the NPL heat transfer software (TherMOL 3D) solves the heat diffusion equation using the more popular finite volume (FV) approach [8, 9]. This is based on the physical concept of using macroscopic control volumes to numerically solve the conservation laws of heat transfer. After introducing necessary simplifications and assumptions, the discretisation equations are obtained by integrating over the control volumes surrounding the nodes. This often leads to the same discretisation equations as the Taylor series method used by finite differences, however the FV method is much more flexible and has much in common with the Galerkin finite element method [10] but is easier to implement. In the FV method used by the new TherMOL software, the integration domain is covered by control volumes where each volume engulfs one node that lies on a variable grid. Adopting a variable grid with the FV method has improved the stability of the new software from the previous version, in particular when applied to modelling very thin layers.

This new approach has also enabled the inclusion of air gaps to the system, and a number of simulations have been completed to assess as to whether air gaps should be considered when modelling the heat transfer through steam grown oxide scales.

Effect of Air Gaps

To develop the model, P92 was chosen as the substrate material onto which an oxide scale, consisting of an outward growing magnetite layer and an inward growing Fe-Cr spinel, has formed during steam oxidation exposures. The air gap has formed between these two layers, which is consistent with the majority of our experimental observations

for this material. The air gap has been grown (6 to 48 μm) to simulate the spallation process, and the thermal conductivity of the

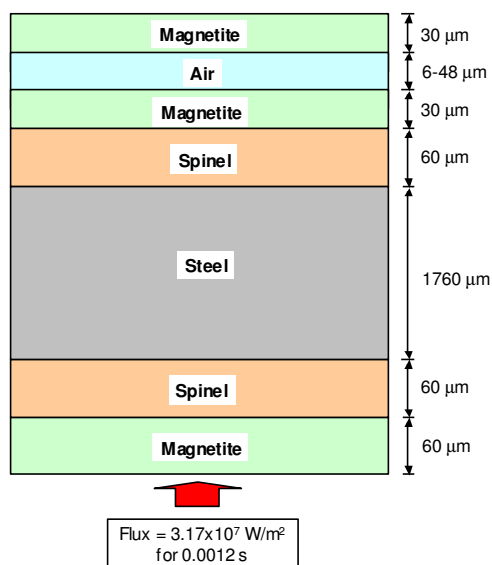


Figure 4 Schematic showing the geometry of the test specimen used to evaluate the effect of air gaps/voids on the thermal conductivity

The material properties of the constituent layers as shown in Figure 4 are presented in Table II. The properties of the oxide scales have been averaged and these values used in the modelling. This approach has been adopted because at this stage discrete measurement on the different oxide scales have not been performed. The results showing the effect of an increasing air gap on the heat transfer are shown in Figure 5. Additionally the effect of increasing the thickness (20 to 200 μm) of the oxide scale has been evaluated to examine the effect on thermal conductivity of increasing amounts

Table II Thermal material properties

Material	Conduction (W/m.K)	Density (kg/m ³)	Specific Heat (J/kg.K)
Air	0.025	1.29	1010
P92	27.77	7770	498
Magnetite	0.93	5010	750
Spinel	0.93	5010	750

of oxide, Figure 6. Once again the material properties shown in Table II have been used.

Figure 5 and 6 clearly illustrate that both the presence of an air gap or void and the presence of an oxide scale effect the heat transfer, and are worthy of inclusion in future modelling exercises. The effect of an increasing void or air gap within the structure of the oxide scale can be shown to dramatically effect the thermal properties of the component, as shown in Figure 7. This Figure compares the thermal diffusivity obtained from the plots in Figure 5 with data book values for a range of common materials. In this case the effective thermal diffusivity of the oxidised P92 sample deteriorates from a value typical for a stainless steel to a value typical for cork after

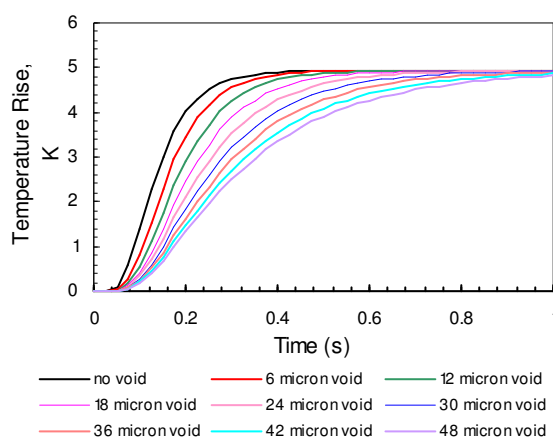


Figure 5 Effect of an increasing air gap/void on the heat transfer of P92

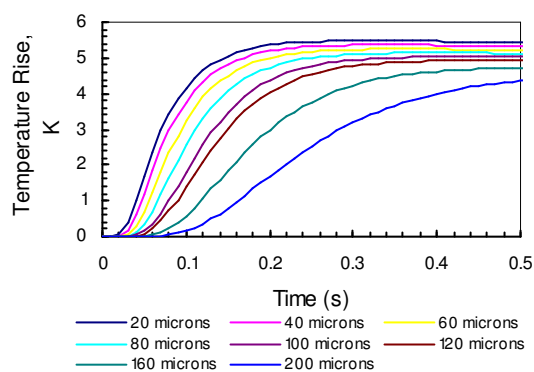


Figure 6 Effect of an increasing oxide scale on the heat transfer of P92

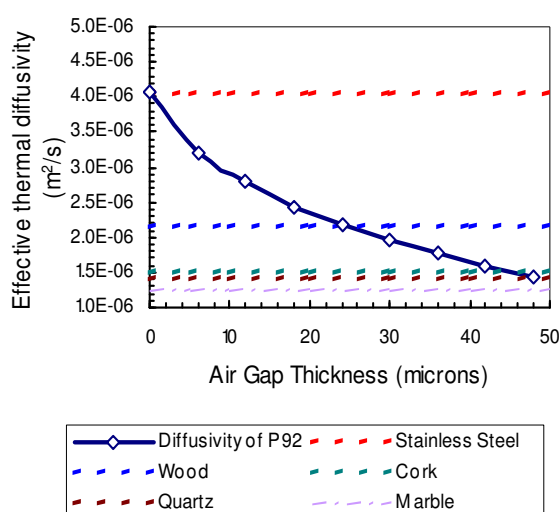


Figure 7 The effect of a growing air gap on the effective diffusivity of an oxidised P92 sample.

a void of approximately 50 microns is formed. This over simplified example, whilst using approximate values for the thermal properties of the constituent layers does give a clear illustration of the effect of an insulating layer on the heat transfer through typical heat exchanger materials.

Thermal Properties of Steam Grown Oxide Scales

Samples of P92, Esshete 1250 and IN740 were exposed to steam atmospheres at 650, 700 and 750 °C respectively. The steam was produced from double distilled water and deoxygenated, down to between 10 and 15 ppb of dissolved oxygen. It was then introduced into a tube furnace at atmospheric pressure. The samples were exposed to this atmosphere for a range of times to produce oxide scales of varying thicknesses. The Laser Flash apparatus was then used to produce heat transfer data which could be used in the TherMOL software to evaluate the thermal properties of the oxide scales. Figure 8 shows the temperature rise with time plots for the unoxidised P92 substrate plotted with the results from an oxidised sample, which had been oxidised in steam at 650°C for 1000h, to produce an oxide scale 150 µm thick. The Figure clearly shows how the presence of an oxide scale reduces the thermal conductivity of the system. On

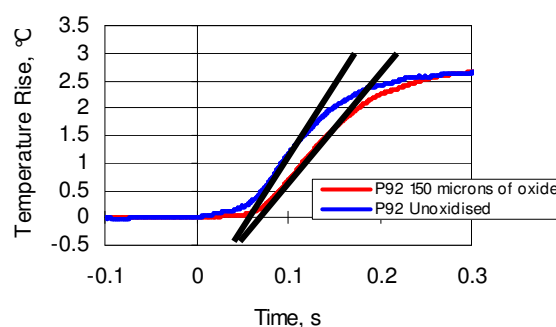


Figure 8 Temperature rise charts for unoxidised P92 and P92 with 150µm of oxide.

analysing the laser flash data for the oxidised system it is possible to calculate the thermal conductivity of the oxide scale, by having fully characterised the behaviour of the substrate, as shown in Figure 9, and removing this contribution from the laser flash data for the oxidised system. This modelling exercise has been performed for all of the materials listed in Table I with varying degrees of success.

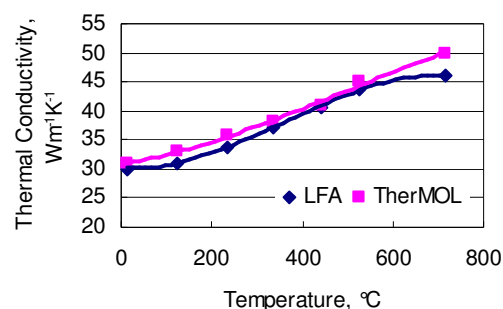


Figure 9 Thermal conductivity of the P92 substrate at various temperatures obtained using the Laser Flash technique and TherMOL models.

In the case of P92 the thermal conductivity of the oxide scale has been evaluated successfully. By considering the magnetite and the Fe-Cr Spinel as a single system, using mean values for the thermal properties and combining the thickness of the oxides on the top and bottom face, the laser flash

data illustrated in Figure 8 was analysed using the TherMOL model. The resultant values for the thermal conductivity of the combined oxide scale are presented in Figure 10. This shows the thermal conductivity varying between 2 and 2.9 $\text{W m}^{-1} \text{K}^{-1}$ over a 600°C temperature range.

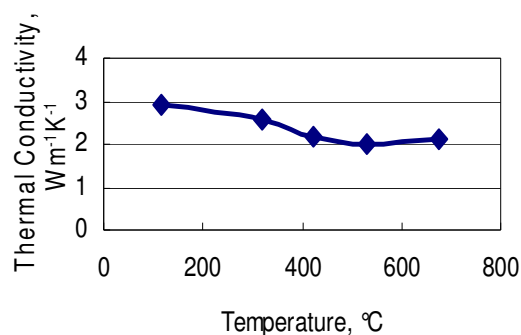


Figure 10 Thermal conductivity of the oxide scale grown on a P92 substrate exposed to steam for 1000h at 650°C.

In the case of the Esshete 1250 and IN740 materials the modelling highlighted some problems. In both cases the model accurately evaluated the unoxidised substrates. However, when it came to evaluating the oxide scales formed on the substrates it became difficult to obtain discrete values for the thermal conductivity. There are two main reasons for this and both relate to the oxide scale. For P92 a thick continuous oxide scale is formed during the oxidation process, in the case of IN740 the oxide forms a continuous layer but is extremely thin, even after 3000h at 750°C as shown in Figure 11. The contribution of the oxide to the rate of heat transfer through the system is minimal and so did not provide a large enough difference in the temperature rise with time to be able to be accurately evaluate a single value for the thermal conductivity of the oxide. Conversely, whilst the Esshete 1250 material produced a thick enough oxide scale, it was not a continuous layer, resulting in paths of least resistance for the heat to pass through, i.e. the regions between the islands of oxide. Consequently, once again a single value of the thermal conductivity of the oxide could not be obtained.

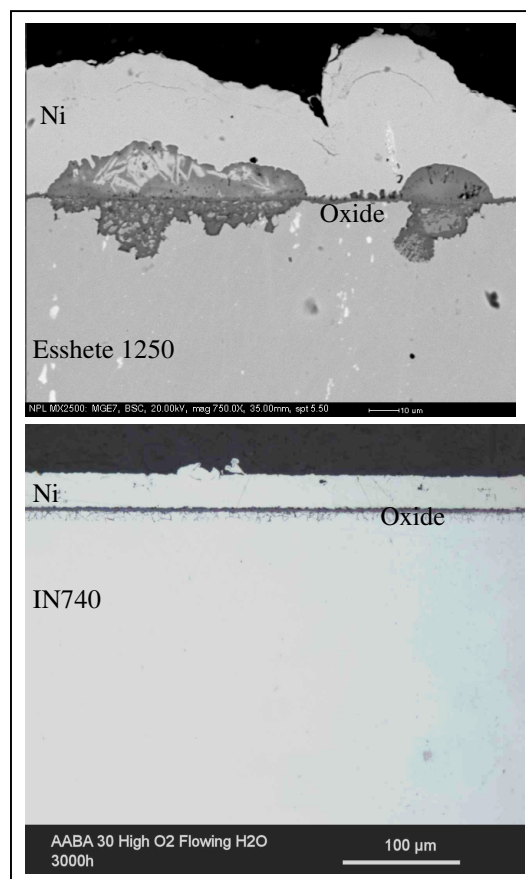


Figure 11 Micrographs of Esshete 1250 and IN740, showing the oxides grown after 300h at 700°C and 3000h at 750°C respectively.

Conclusion

- It has been shown that the thermal conductivity of steam grown oxide scales can be measured using a combination of the Laser Flash technique and numerical modelling.
- The applicability of this has been demonstrated, which has shown that a reasonably thick continuous oxide scale layer is required for accurate evaluation of the thermal conductivity of the oxide.
- The affect of voids in the scale and an increasingly thick oxide have been demonstrated to greatly influence the heat transfer through heat exchanger materials.

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