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REPORT

Mechanical Properties of High Temperature Corrosion Scales on Materials for High Temperature Heat Exchangers

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SUMMARY

In order to develop reliable life prediction methodologies there is a requirement for appropriate data to support any predictive model. This paper presents a set of data for scales grown on the ODS alloy, PM2000, during oxidation in air at 1100 and 1150 °C. The data represent the parameters required during development of models for quantitative assessment of scale breakdown in this alloy. The data are broadly consistent with previously published values for this material.

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1 INTRODUCTION

This work formed the NPL contribution (Project UK5) to the COST 501 programme under WP13, Clean Combustion Technologies. The project was targeted at the specific subprogram, high temperature heat exchangers, within WP13.

Materials based upon the ODS series of alloys, with compositions based upon Fe-20Cr-5Al-0.5Ti-0.5Y_2O_3, are strong candidates for use in high temperature heat exchangers [1]. These components are crucial to the operation of high temperature plant for many applications including gasification, gas re-heating etc. The service conditions experienced by these components are temperatures in excess of 1100 °C in atmospheres ranging from simple mixtures of nitrogen and oxygen [2] to more complex environments containing active sulphur and chlorine species. Several candidate alloys are available but final selection depends upon several factors including cost, ease of fabrication, strength and corrosion resistance. The latter factor is critically dependent upon the ability of the alloy to maintain an intact, protective oxide scale during service.

Data on the spallation resistance of these alloys under service conditions are sparse. Data generation projects are time-consuming and expensive, hence there is a need for a model to predict spallation during service for example spallation maps such as those developed by Evans [3]. These models require reliable input data for the properties of the protective scale, which in turn requires validated measurement methods for the generation of these properties. Typical property requirements for these models are thermal expansion coefficients and elastic moduli for scale and substrate, creep properties of the substrate and a measure for the strength of the interface between scale and substrate. This paper summarises the measurement of a series of relevant properties of oxide scales grown on a typical ODS alloy, PM2000.

2 DATA GENERATION

2.1 GROWTH KINETICS AND SCALE CHARACTERISATION

Scales were grown in still air at temperatures of 1000, 1100 and 1150 °C for times up to 264 h. Scale thickness was measured on polished cross-sections and was also calculated from mass gain measurements using a conversion factor, 1 mg cm^{-2} ≡ 5.35 μm. The results are presented in Figure 1 together with predicted values of scale thickness from a model of scale growth derived from a British Gas/AEA collaboration [1]. The equation used for the scale thickness predictions is:-

$$w = 0.504\, T^{1.5}\, t^{0.427} \exp\left(\frac{-18283}{T}\right) \qquad (1)$$

where w is the mass gain in units of mg cm^{-2}
t is the oxidation time in hours, and
T is the absolute temperature

It can be seen that agreement between data and predictions is poor when the coefficients in Equation (1) are used; however it must be remembered that these coefficients have an uncertainty [1]. If these uncertainties are taken to their limit to yield the maximum predicted oxidation rate, then equation (1) becomes:

$$w = 0.767T^{1.5}t^{0.447}\exp\left(\frac{-17339}{T}\right) \quad (2)$$

Predicted values from equation (2) are also plotted in Figure (1) and it can be seen that the data generated within this project falls within the expected scatter band.

The scales grown were analysed by EDX in the SEM to determine the chemical constitution of the scale. All the scales formed after oxidation at 1100 and 1150 °C were uniform and consisted exclusively of alumina. Typical results are shown as a 'digimap' in Figure 2.

2.2 GROWTH STRESS

Growth stresses have been measured as a function of time for oxidation at 1000 and 1100 °C. Two techniques were used - high temperature X-ray diffraction and specimen extension tests. Data from specimen extension tests were found to be unreliable for this material, as the extensions measured were very low (<1 μm) and the analysis requires data on creep rate as a function of stress: available data show excessive scatter for this material ie creep rates vary by up to 2 orders of magnitude for some stress and temperature conditions. Growth stresses measured at 1100 °C after ~1.5 h using the X-ray diffraction technique were low (~ -390MPa) indicating that either the generation of growth stresses was inhibited or that any stresses that were generated were relaxed by either creep deformation in the substrate or cracking of the oxide scale.

2.3 RESIDUAL STRESS

Measurements of residual stress in the oxide were carried out using the well-established $\sin^2\varphi$ method [4]. The data are presented in Table I. Also presented are values calculated using the assumption that no relaxation due to creep of the substrate occurs thus:

$$\sigma_R = \frac{-E_{ox}\Delta T(\alpha_{sub} - \alpha_{ox})}{(1-\nu)} \quad (3)$$

where σ_R is the residual stress
E is the Young's modulus
α is the thermal expansion coefficient
ν is Poisson's ratio
$_{ox}$ and $_{sub}$ refer to oxide and substrate respectively

Table I Residual Stress Data

Oxidation Temperature °C	Oxidation Time h	Oxide Thickness μm	Residual Stress (measured) GPa	Residual Stress (predicted) GPa
1100	24	2	-4.09	-4.41
	96	3	-4.20	
	264	6	-3.97	
1150	24	2.5	-3.74	-4.62
	96	5	-4.15	
	264	7	-4.32	

It can be seen that the residual stresses measured are lower than those predicted, implying that relaxation of the stresses had occurred due to creep in the substrate. The mean values for the data at the two temperatures, -4.09 GPa at 1100 °C and -4.07 GPa at 1150 °C are effectively the same value. This result implies that creep is rapid in the temperature range 1100 - 1150 °C such that all stresses are relaxed during the temperature drop in this range.

2.4 HARDNESS AND MODULUS

Hardness and modulus of the scale were measured using nanoindentation - a high precision, low load, depth-sensing indentation technique. This technique generates a load / displacement curve during the indent from which the hardness and modulus of the indented material can be derived [5]. The data are presented in Figure 3, together with data for the alloy substrate and previously published data for alumina scales [6] and PM2000 [7]. It can readily be seen that the measured values are consistent with those published previously and are independent of oxidation time.

2.5 FAILURE STRAIN

Test methods are available to measure failure strain of the oxide under flexural loading [8]. In the case of room temperature measurements, specimens in the form of rectangular beams are oxidised and the majority of the oxide is then removed by grinding to leave an oxide 'island'. A 4-point loading system is used to attempt to maximise the region of homogeneous strain - unfortunately the material proved unsuitable for this test method with excessive local deformation at the contact points. Therefore little strain was applied between the inner rollers and the oxide remained intact. Methods to strain material under uniaxial loading in tension and compression are under development and it is anticipated that data will be generated in future work.

2.6 ADHESION

Scale adhesion is a property that is extremely difficult to measure. Several test methods are available but all of them generate a different parameter to define scale adhesion. Three methods have been attempted during this work:

- Scratch testing provides a qualitative route to rank materials in terms of a critical load to initiate specific scale failure mechanisms along the scratch path. A quantitative analysis treatment for these data has been proposed by Bull [9] and a simplification of the approach developed by Osgerby et al [10]. This approach gives an interfacial stain energy term for scale adhesion.

- Indentation techniques can also give a quantitative measure of scale adhesion. Indentation generates an area of delaminated scale around the indent. The extent of this delamination is related to an interface toughness using the analysis developed by Drory and Hutchinson [11] and subsequently simplified by Osgerby et al [10].

- Tensile strain applied to an oxidised specimen ultimately results in spallation of the scale. Measurements of the strain to generate spallation; the crack spacing at this strain; oxide thickness; and tensile stress can be used to determine the maximum shear stress that the

scale can support. Several models have been developed based upon this approach and these have been critically reviewed by Damerell [12].

Scratch testing of scales grown on PM2000 produced tracks with very little damage outside of the scratch path. A typical scratch track is shown in Figure 4 where it can be seen that the oxide scale is intact right up to the edge of the scratch path and debris from the scratch has been deposited on the specimen surface. It is not therefore possible in this case to determine critical loads for failure mechanisms in the scratch test that allow quantitative analysis of scale adhesion. This result implies that the scale adhesion is qualitatively very good in comparison with measurements made on other oxide/substrate systems (10).

Indentation using a Rockwell indenter generated the damage feature shown in Figure 5. The original analysis implied that the scale should be completely delaminated therefore using this analysis for the partial delamination exhibited in this alloy implies that a lower bound value for adhesion is obtained. The mean radii of the indent and partially delaminated area were measured from calibrated images and most of the other input parameters for the Drory and Hutchinson analysis have been measured during this work or obtained from the literature [7]. One parameter, the work hardening coefficient required an estimated value and this was attributed as 0.1 ie the value used for the model material in the original analysis [11]. The analysis gives a value for the interface toughness, Γ_c, of the oxides as 170 J m^{-2} < Γ_c < 960 J m^{-2}. The interfacial toughness measured tended to increase with scale thickness contrary to the behaviour normally expected from consideration of scale failure, where thicker scales are expected to fail at lower strains. The interfacial toughness data relate to values for fracture of the interface in the range 8 - 20 MN $m^{-1.5}$. These values are high compared to previously published data for alumina scales [13] where a value of 2.5 MN $m^{-1.5}$ was reported. The values generated in this work are however consistent with the qualitative information from the scratch test which implied excellent adhesion of the alumina scale in this alloy.

Attempts to measure scale adhesion using flexural straining techniques were unsuccessful for the reasons given in section 2.5.

3 DISCUSSION AND CONCLUSIONS

The data presented above represent the parameters, measured on the oxide scale, that are required for input into models that predict scale failure and spallation. Frequently these data are not readily available or only one particular parameter has been measured. It is the intention of this work to create a set of data that can be used in modelling activities and is readily available as a single source.

The collation of data in this work is complemented by a parallel activity to develop a database of mechanical properties of oxide scales for a wide range of engineering material systems. A database, containing over 200 datasets on alumina, chromia and iron-oxide scales, has been established using Microsoft Access © and is available as a commercial package from the authors' establishment.

Further work is required to improve the test methods available for scale adhesion such that they generate parameters that can be used directly in modelling scale failure. Further work to improve test methods for determination of oxide failure strain is also required.

4 ACKNOWLEDGEMENTS

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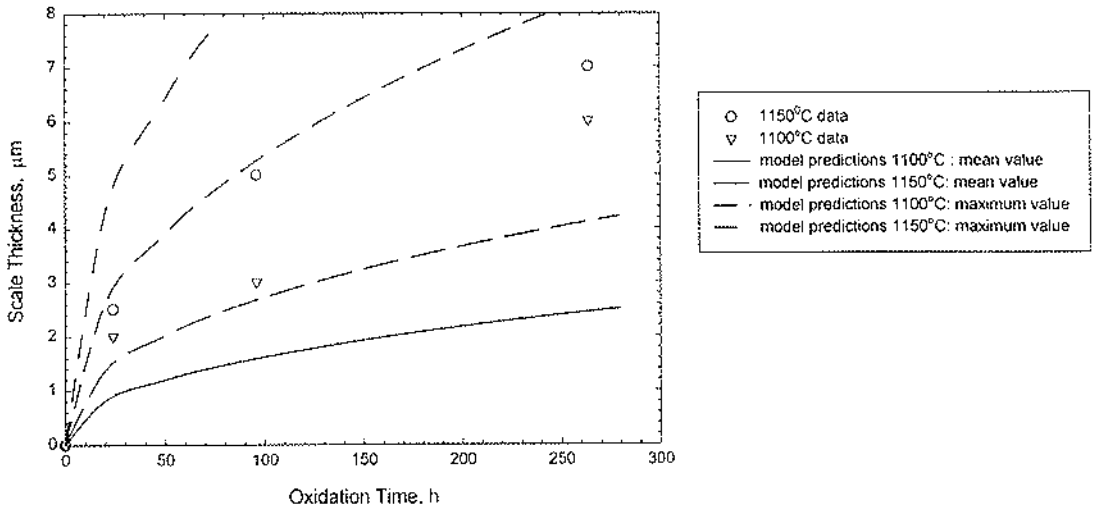

Figure 1 Scale Growth Kinetics for PM2000 in air at 1100 and 1150 °C

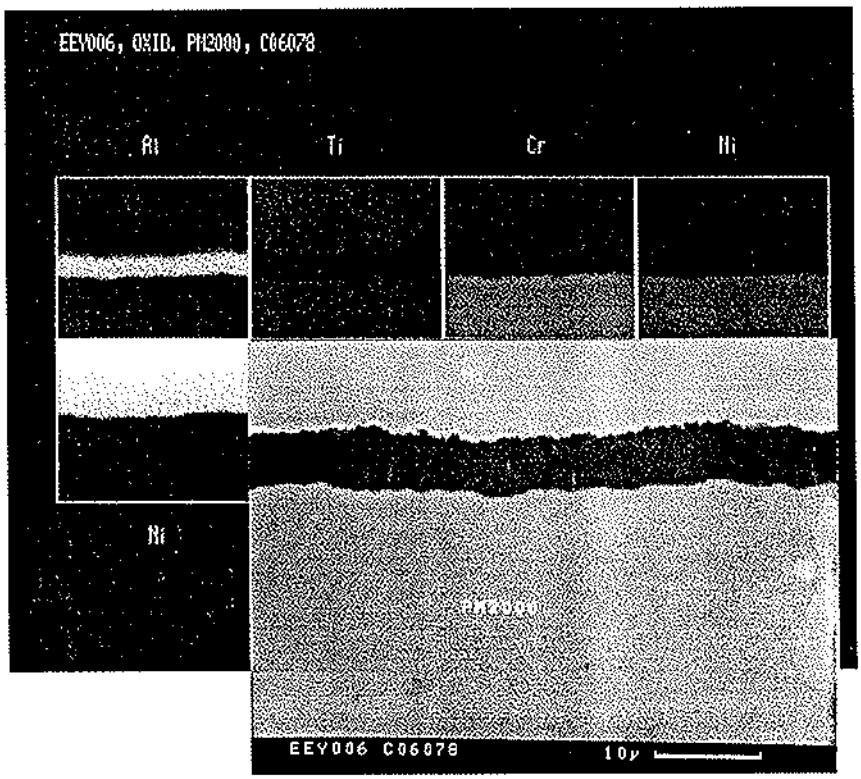

Figure 2 SEM micrograph and digimap of scale formed on PM2000 after oxidation in air at 1150 °C for 96 h

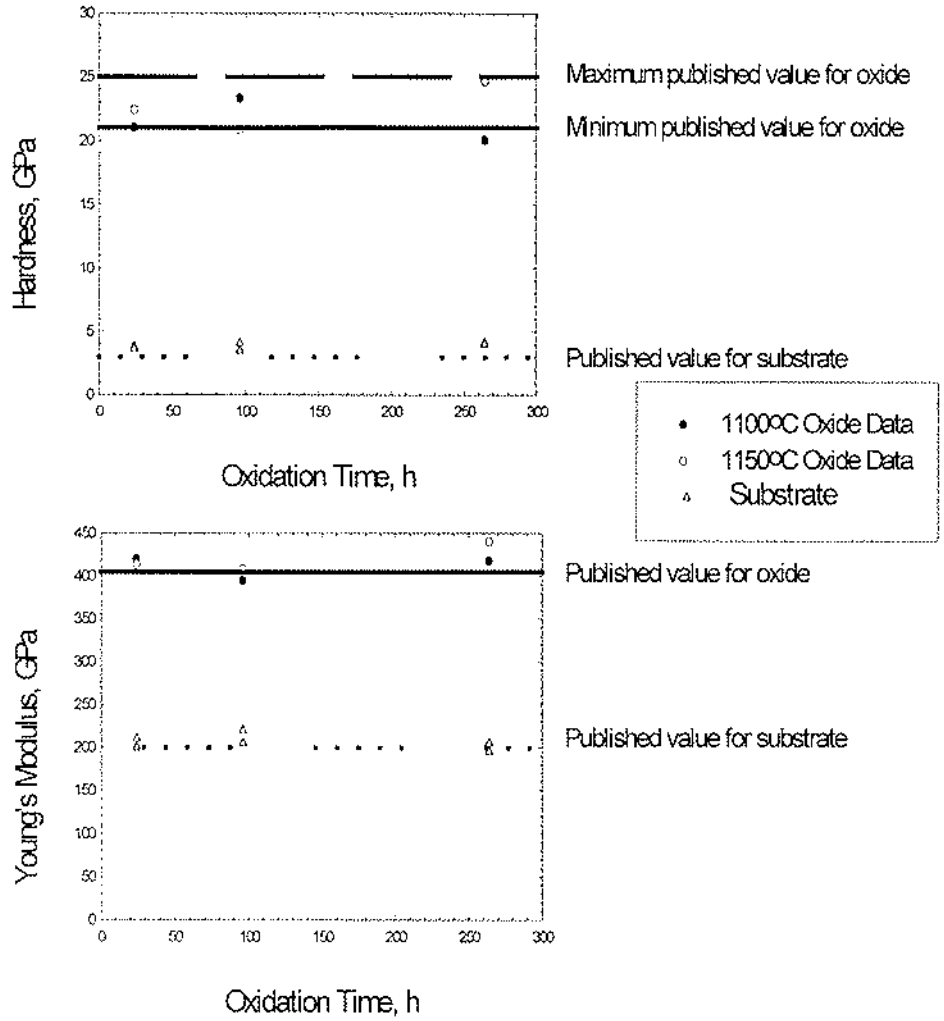

Figure 3 Hardness and Young's Modulus of Scale and Substrate after Oxidation at 1100 and 1150 °C

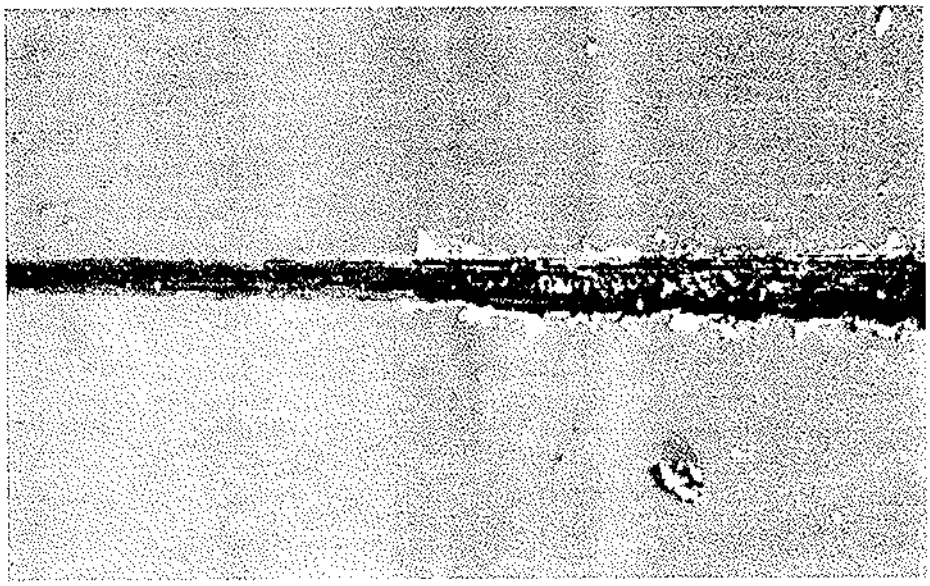

Figure 4 Scratch track in PM2000 oxidised at 1150 °C for 264 h

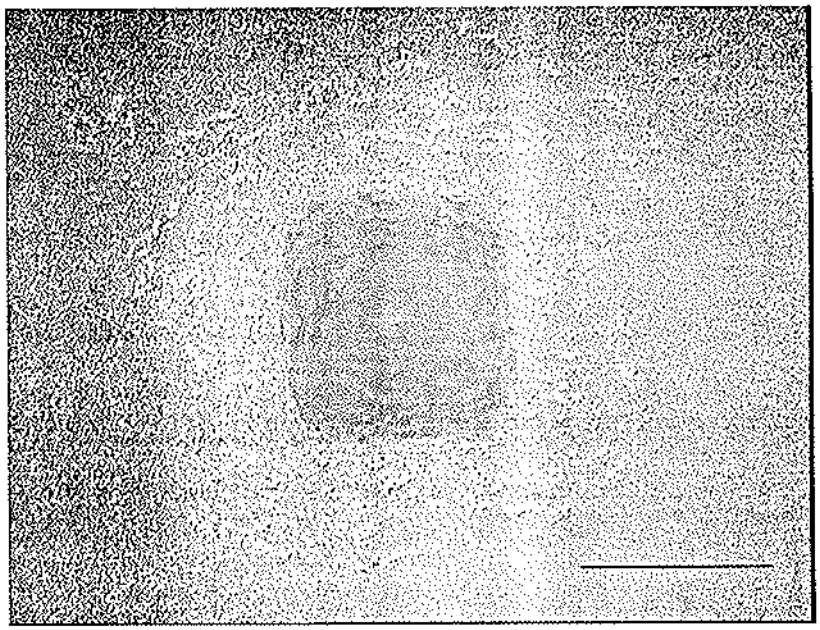

Figure 5 Indent and delamination in scale formed on PM2000 during oxidation at 1150 °C for 24 h