

## Corrosion Issues at High Temperature

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### Corrosion measurements

During service at elevated temperatures components react with the external atmosphere and form corrosion products. Classical wisdom is to select materials such that the scale formed during service is protective. If this remains the case then the high temperature corrosion behaviour follows approximately parabolic kinetics, however, if this protective scale is disrupted for whatever reason, then the rate of metal wastage can accelerate significantly. This behaviour is shown schematically in Figure 1.

The measurement issues arising from this behaviour relate to the accuracy required in measuring metal loss and to the detection of any deviation from this behaviour.

The simplest measure of environmental attack is mass change. As the component interacts with the environment, gaseous species e.g. oxygen, water vapour, sulphides and chlorides react to form corrosion products. If these corrosion products are solid and remain attached to the component then the overall mass increases, if, however, the corrosion products are gaseous or are removed from the component in some way then a mass reduction is observed. Alternatively, reaction to form liquid phases is also possible, and again non-protective behaviour is observed.

Mass change measurements can be made continuously or discontinuously. Continuous measurements require the use of a recording microbalance of the type shown in Figure 2. A less sophisticated (and less expensive) route is to remove specimens from the exposure environment periodically and record the mass at room temperature. Both these techniques are in common use and have been studied extensively to develop best practice [1,2].

Mass change measurements are normalised to the exposed surface area of the component. Thus they are normally expressed in units of  $\mu\text{g mm}^{-2}$ . If the scale formed is homogeneous and a simple composition then it is also possible to convert the mass gain to a scale thickness. Examples of the conversion factors for some simple scales are given in Table I.

**Table I Conversion Of Mass Gain To Scale Thickness For Some Simple Oxide Scales**

Scale	1 $\mu\text{g mm}^{-2}$ mass gain is equivalent to 'x' $\mu\text{m}$ scale thickness
$\text{Al}_2\text{O}_3$	0.53
$\text{Cr}_2\text{O}_3$	0.60
$\text{Fe}_2\text{O}_3$	0.64

Where the corrosion product forms a complex or multi-layered scale simple mass gain cannot easily be converted into scale thickness or metal wastage. In this case it is necessary to section the exposed material and measure the extent of environmental attack directly. This procedure is not as straightforward as first appears and has been the topic of a recent European project to develop an accepted best practice [2]. The measurements required to characterise metal wastage are shown in Figure 3. Potentially four layers relating to

corrosive attack may be present relating to deposits, external scale, internal corrosion and grain boundary penetration. In order to obtain a statistically valid distribution of corrosion product around the sample of interest, ideally at least 24 measurements, at random, i.e equally spaced, positions should be made. This data will then allow probability plots to be obtained as well as calculation of some extreme value parameters [3].

### **Mechanical properties**

The initiation of scale breakdown invariably begins with cracking of the scale. This occurs through the generation of stresses in the scale: These stresses are introduced either (i) intrinsically during scale growth, (ii) due to differences in thermal expansion properties between scale and substrate during heating or cooling, or (iii) by the application of external stresses to the component. Stresses in the scales may be either tensile or compressive in nature – both result in cracking but the morphology of the cracks is different in each case. Figure 4 shows examples of both types of cracking. Cracks developing under tension, Figure 4a, are perpendicular to the surface, whereas those that develop under compression, Figure 4b, are inclined at an angle of 45° to the surface.

Detection of scale cracking can be carried out using acoustic emission (AE). Initiation and growth of a crack is accompanied by the generation of a sound wave. In order to detect these signals a waveguide is required to enable the acoustic transducer to remain at ambient temperature whilst the material under investigation remains at elevated temperature. A schematic representation of the experimental set up requires and some typical results are shown in Figure 5. Various AE parameters are recorded during the tests, HITS, COUNTS, ENERGY etc, and each indicates an acoustic event. For the oxide systems of interest use of the first high ENERGY signal has been taken to be the most sensitive method on detecting the first crack in the oxide when measuring fracture strain. It is also important to be able to distinguish oxide cracking from other acoustic signals that may arise from movement of the sample during straining, dislocation generation or noise generated in the loading train. Some of the “extraneous” signals can be eliminated by using two waveguides, spaced equally about the area of interest, and appropriate software that collects only signals arriving at the detectors simultaneously. Typical values of fracture strain for oxides are from very close to zero to about 1.5% [4] depending on oxide thickness and applied strain. Thicker oxides have lower fracture strains as do oxide layers stressed in tension..

There is considerable interest in measurement of adhesion of oxide scales, and a variety of different methods have been attempted [5,6,7,8,9,10]. Many of the simpler methods, such as tensile tests, indentation and scratch tests, require complex models to interpret the observed results, and often there is little agreement as to which is the most appropriate model. The most direct method is to use the pull test in which a dolly is glued to the oxide layer of interest. Unfortunately, most oxide systems of technical interest have interfacial strengths greater than that of the glue (about 60 –80 MPa), so frequently failure occurs in the glue. The position is further complicated by the fact that each of the simpler adhesion test methods yields a different interfacial strength property; tensile tests (interfacial shear strength), indentation (interfacial fracture toughness) and for scratch tests often exhibit multi-mode failure paths that make interpretation difficult. A modification of the scratch test is to make a scratch on a polished cross-section; in which case a suitable numerical model can be used to obtain equivalent values to the pull test.

### **Additional information**

This work was part of the Degradation of Materials in Aggressive Environments (DME) research programme supported by the Department of Trade and Industry (DTI). The programme aimed to stimulate innovation in the use of materials through improved understanding of their performance. With the main focus on measurement, the research carried out is relevant to a wide range of industrial sectors and their supply chains: these include power generation, construction, aerospace, automotive and electronics.

A new DTI supported research programme entitled 'Life Performance of Materials' (LPM) has recently begun. Following on from the DME programme, LPM will address industrial problems relating to in-service performance, degradation modelling, and failure and lifetime prediction. The main aims of the programme are to measure and predict life performance of materials and coatings through development of new knowledge based products and obtain evidence for enhanced maintenance strategies for products, process plants and structures and improved design of components, finished products and process plant design. The work also aims to reduce the risk of failure due to degradation of materials.

The scope of both the DME and LPM programmes is extensive and covers much more than high temperature degradation. Projects within the LPM programme that will take place at NPL are in the aqueous corrosion and high temperature degradation areas. These include:

*Environment assisted cracking of aerospace materials*

*Environment assisted cracking of steam turbine steels*

*Evaluation of test methods for weldable martensitic stainless steels*

*Principles of steam oxidation*

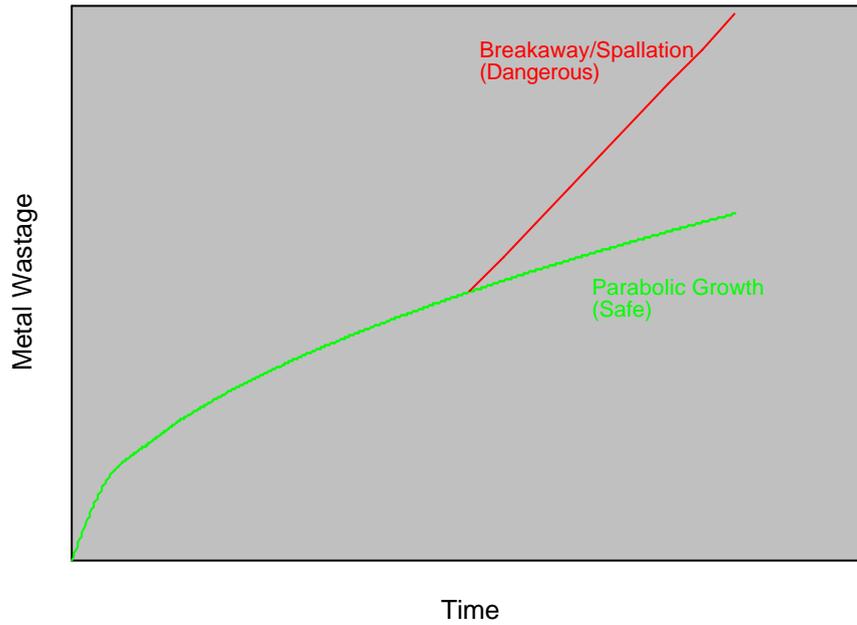
*Life prediction of thermal barrier and corrosion resistant coatings for gas turbine operations*

*Metal wastage under complex atmospheres or thermal cycling*

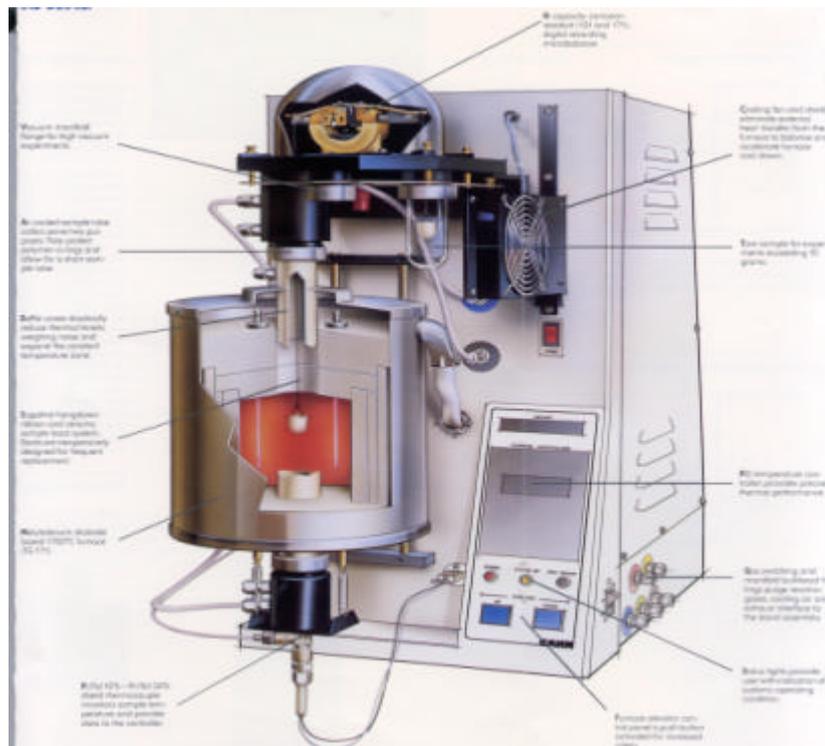
Further projects are being developed in other technical areas (degradation of polymers and polymer composites; performance of electronic materials; corrosion in concrete; lifetime and health studies of materials). These projects will be the subject of competitive tender by DTI.

## References

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**Figure 1 Schematic representation of protective and non-protective corrosion kinetics**



**Figure 2 Typical Continuous Microbalance Equipment**

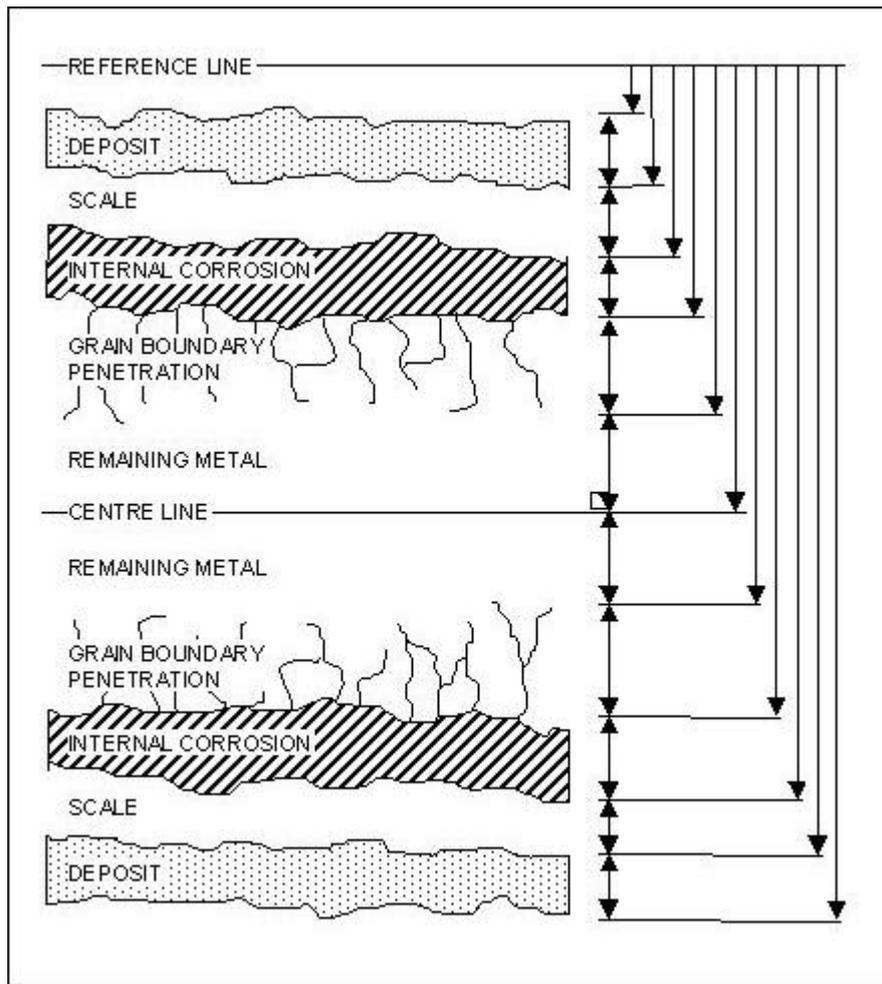
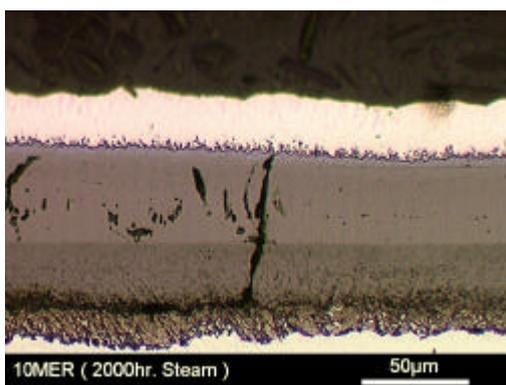
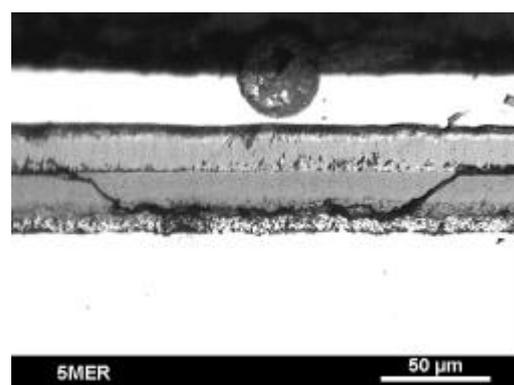


Figure 3 Definition of Different Layers during Measurement of Corrosive Attack (after Reference 2)



(a)



(b)

Figure 4 Examples of cracking in oxide scales grown in a steam atmosphere on 9-Cr martensitic steel at 600 °C after cooling to room temperature (a) tensile crack (b) compressive (shear) crack.

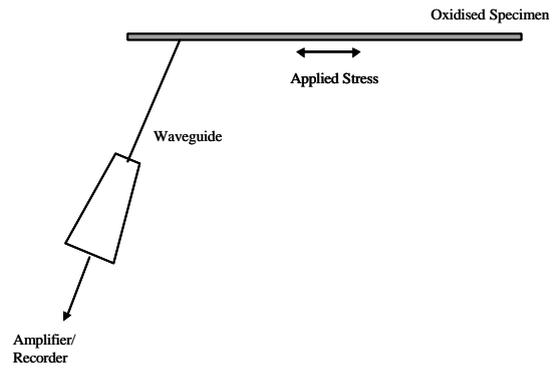


Figure 5 Schematic Representation of Measurement of Acoustic Emission Due to Scale Cracking