

**Lifetime Prediction of High Temperature Components:
Breakdown of the Protective Oxide Scale**

S Osgerby, S R J Saunders, H E Evans, D D Gohil and J P Banks
Centre for Materials Measurement and Technology
National Physical Laboratory

Summary

Guidelines are provided on some aspects of material behaviour and plant operation, which allow designers and operators of high temperature plant to estimate lifetimes of components where the useful service lifetime is determined by the integrity of protective oxide scale. The methodology follows a simple checklist with guidance on where more detailed investigation may be necessary. The methodology is supported by detailed case studies that illustrate several different failure mechanisms. The main case study addresses the issue of scale spallation during a single cooling cycle for two alloys - one forming a chromia scale and the other forming an alumina scale.

© Crown copyright 1998
Reproduced by permission of the Controller of HMSO

ISSN 1361-4061

National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

Extracts from this report may be reproduced provided the source is
acknowledged and the extract is not taken out of context.

Approved on behalf of Managing Director, NPL, by Dr C Lea,
Head, Centre for Materials Measurement and Technology

1 INTRODUCTION 1

2 SCOPE OF CODE OF PRACTICE

3 PROCEDURE FOR LIFETIME PREDICTION 1

4 BASIS OF PREDICTIVE MODELS 2

4.1 Two-bar modelling of stress redistribution 2

4.2 Spallation maps 2

4.2.1 The finite-element model 3

5 DATA REQUIREMENTS 3

6 UNCERTAINTIES OF MEASUREMENT/PREDICTION 4

7 ILLUSTRATIVE EXAMPLES 5

7.1 Through-thickness cracking of chromia scale on creep resistant austenitic steel 5

7.2 3-D spallation maps for alumina and chromia formers 6

7.2.1 Incoloy 800HT 6

7.2.1.1 Creep and Elastic Properties 6

7.2.1.2 Oxidation Kinetics 7

7.2.1.3 FE Scoping Runs 8

7.2.1.4 3-D Spallation Map 8

7.2.2 Haynes 214 9

7.2.2.1 Creep and Elastic Properties 9

7.2.2.2 Oxidation Kinetics 10

7.2.2.3 3-D Spallation Map for Haynes 214 10

7.3 Sulphur/chlorine - limit maps 11

7.4 Downtime/dewpoint corrosion 12

8 INFLUENCE OF SUBSTRATE GEOMETRY 12

9 PRACTICAL MEASURES FOR LIFETIME EXTENSION 13

9.1 Material Selection 13

9.2 Operating Parameters 13

10 ACKNOWLEDGEMENTS 13

REFERENCES 14

Appendix A: Relevant Material Properties for Oxide Scale Failure Mechanisms 26

1 INTRODUCTION

Components that operate at high temperature are invariably subjected to environmental attack as well as to mechanical and thermal stresses. Lifetime prediction for components limited by mechanical failures is well developed but the parallel situation for environment-limited lifetime has been somewhat neglected.

The ideal service situation is when the protective scale that forms remains intact. In this case the rate of environmental attack can be predicted and allowances made during design of components for these applications. Procedures for prediction of chemical stability from thermochemical data are well established, as are kinetic data in simple oxidising atmospheres where diffusion processes are rate-determining. Problems occur when the protective oxide scale is disturbed by either mechanical or chemical action resulting in increased rates of environmental attack.

The purpose of this Code of Practice is to provide guidance on addressing certain aspects of scale breakdown due to mechanical or chemical means. It is accepted by the authors that not all of the possible mechanisms have been addressed.

2 SCOPE OF CODE OF PRACTICE

This Code of Practice addresses scale breakdown due to particular mechanical and chemical influences which include spallation during a single thermal cycle; the influence of accelerators, eg sulphur- and chlorine-containing compounds, in the service atmosphere; and downtime/dewpoint corrosion.

The Code of Practice is supported by the development of a database of mechanical properties of oxide scale. This database, which will shortly be available commercially from NPL, contains over 200 datasets of mechanical properties of oxide scales which can be used in calculation of component lifetime.

3 PROCEDURE FOR LIFETIME PREDICTION

The proposed methodology for lifetime prediction in situations where the end of the useful lifetime is defined as failure of the protective oxide scale, is summarised thus:

- (1) Define the envelope of operating conditions for the plant in terms of materials used, service environments and stress systems. Care should be taken to consider all aspects of the running cycle including heat-up, base load, overload, cool down and downtime.
- (2) Identify the possible failure mechanisms for individual components within the plant, eg spallation during cooling, through-thickness scale cracking due to imposed mechanical stress etc.
- (3) For each potential failure situation identify the data requirements for lifetime prediction. A list of data required for several failure modes is given in Appendix A.
- (4) Collate any available data. Ideally, essential data that are not available should be generated but may also be inferred by inspection of data from similar materials/systems.
- (5) Calculate the limiting lifetime for each failure mechanism using any of the predictive models that are available.
- (6) Consider any possible synergistic effects eg influence of substrate geometry, increased corrosion rate due to action of superimposed mechanical stress as a result of system strain etc.

4 BASIS OF PREDICTIVE MODELS

4.1 Two-bar modelling of stress redistribution

Stress redistribution between substrate and scale is modelled using the well-established two-bar approach. This approach considers the oxide/substrate system as two separate, load-bearing elements constrained at their extremities to ensure that the strain in both elements is the same. The strength and fracture characteristics of each element are then assigned separately. The basis of the model and the subsequent equations describing stress redistribution are shown in Figure 1. This modelling approach has the implicit assumption that the interface between scale and substrate is ideal, ie shear movement does not occur.

This approach can be used to model stress redistribution between scale and substrate under the influence of external (system) mechanical stresses and during the development of growth and residual strains in the scale. The model can be used to predict the onset of cracking in scales but is not suitable for prediction of crack growth or spallation where finite element techniques are more appropriate.

4.2 Spallation maps

Oxide spallation from flat surfaces occurs, principally, by a wedging process [1] for oxide thicknesses of industrial relevance formed on oxidation-resistant alloys. This process is illustrated schematically in Figure 2a. Finite-element computations [1,2] for both chromia- and alumina-forming alloys show that the initiation of spallation during cooling can be described by a critical strain energy criterion [3]. This considers fracture of the oxide/metal interface, and hence spallation, to occur at a critical value of the strain energy in the oxide layer developed during cooling as a result of thermal mismatch strains between oxide and alloy. This criterion leads [4] to the following expression for the critical temperature drop, ΔT_c , to initiate spallation:

$$\Delta T_c = \left[\frac{\gamma_F}{\xi E_{ox} (\alpha_{sub} - \alpha_{ox})^2 (1 - \nu_{ox})} \right]^{0.5} \quad (1)$$

Where ξ is the oxide thickness
 E is Young's Modulus
 ν is Poisson's Ratio
 α is the linear thermal expansion coefficient
 γ_F is the interfacial fracture energy
the subscripts _{ox} and _{sub} refer to oxide and substrate respectively.

As a first approximation, all the parameters are taken to be independent of temperature.

γ_F cannot be readily measured and will, generally, be much higher than true fracture values due to the dissipation of energy during cooling by creep relaxation in the alloy. The rate of this relaxation will be highest in the vicinity of the tip of the wedge crack at the oxide/metal interface.

In order to obtain a meaningful method of prediction, it is necessary to use finite-element (FE) methods to model the creep relaxation process within the alloy, the rate of which will be strongly dependent on both temperature and local stress. For refractory oxides such as alumina and chromia, creep in the oxide layer during cooling from typical service temperatures is negligible. The approach is to use the FE model to obtain a value of ΔT_c for a particular combination of oxidation temperature, cooling rate and alloy creep properties for a given value of oxide thickness (usually 5 μm). The computed value of ΔT_c is then used in equation (1) to obtain a value of the fracture energy, γ_F . This, according to the strain-energy model and computations [1], is independent of oxide thickness for a given combination of temperature, cooling rate and creep properties. For this combination, equation (1) can then be used to predict ΔT_c for other oxide thicknesses. In this study, the FE computations were undertaken for at least three oxidation temperatures

for each alloy so that, by knowing the kinetics and temperature dependence of oxide growth, a 3-dimensional, spallation map could be produced. This defines a surface in ΔT_c /time/temperature space beneath which the alloy would not suffer from oxide spallation.

4.2.1 The finite-element model

The model considers spallation to occur over a circular zone of 8 μm radius within a spall cell of 80 μm radius overlying the substrate alloy of 190 μm half thickness. Axisymmetric, cylindrical geometry is used throughout and the finite-element mesh in the vicinity of the spall zone is shown in Figure 2b.

The wedging process is initiated by through-thickness shear cracking of the oxide layer as a result of the compressive stresses developed during cooling. This shear-crack plane is shown in Figure 2b and lies at an angle of 45° to the oxide/metal interface. It is composed of interfacial elements, 0.1 μm thick, having the same physical properties of the surrounding oxide but with zero shear modulus. This ensures that compressive normal stresses are transmitted across the crack but that no shear stresses can be sustained in the crack plane, ie it is free to slide. The computations, reported here, assume that a shear crack exists within the oxide at the start of cooling and that this penetrates to within 0.1 μm of the alloy surface. This is not inconsistent with observations on alumina layers [5] where thin grain boundary defects, a few microns long, have been reported. The present approach incorporates a degree of conservatism into the predictions of the critical temperature drop to initiate spallation.

Similar interfacial elements are used to model the actual oxide/metal interface. In practice, this interface is treated as a zone (Figure 2b) of 0.1 μm thickness which, again, can be given distinct material properties. In particular, any element can be permitted to "fail", ie to become non load-bearing, at a critical value of the tensile normal stress acting across the interface. Such failure of the crack-tip element permits the wedge crack to propagate along the interfacial zone in length increments of 1 μm (the length of each interfacial element). In some cases, this interfacial zone may represent an actual separate phase, eg alumina underlying chromia in the case of Alloy 800 to be considered later, whereas in others (eg Haynes 214) it is simply taken to be a thin inner layer of the main oxide scale.

5 DATA REQUIREMENTS

The data that are required for prediction of scale breakdown vary according to the specific mechanism of failure. A summary of the requirements for several failure mechanisms is given in Appendix A. For example, in the case of scale cracking and/or spallation due to imposition of mechanical or thermal stress, the data that may be required are:

- Young's modulus and Poisson's ratio of oxide and substrate
- Thermal expansion coefficients for oxide and substrate
- Creep properties of substrate
- Strength of the interface between oxide and substrate
- Oxide fracture strain in tension and compression or fracture toughness and void distribution.

Accurate measurement of these properties is not a trivial matter and recent work at NPL [6,7] has developed techniques that define procedures to measure failure strain and adhesion of the oxide scale.

Thermal expansion may be measured by dilatometry or by X-ray techniques. Direct measurement on composite (scale plus substrate) samples is not recommended as stress redistribution may occur leading to erroneous results. Thermal expansion coefficients for ceramics are usually measured on bulk samples rather than on scales and the data are readily available [8]. Thermal expansion coefficients for substrates can normally be obtained from the material manufacturer.

Creep properties of the substrate may be difficult to obtain from published literature. The commonest form of creep data, stress rupture time, is of no use within this modelling approach where creep rate values are

utilised. Data may be available from the material manufacturer, from data compilations or may be collated from the scientific literature. If there is still insufficient data available to produce an analytical expression then the data should be generated using procedures that conform to a recognised test standard [9].

A database of mechanical properties of oxide scales, containing many of the necessary data, has been compiled and is commercially available from NPL.

6 UNCERTAINTIES OF MEASUREMENT/PREDICTION

To estimate the uncertainty of measurement for any one scale or substrate property it is necessary to have an understanding of the measurements involved in deriving that property, the uncertainties associated with each individual measurement and the mechanism by which those measurements contribute to the final property value. It is sometimes necessary to know other materials properties in order to calculate the uncertainty in the measurement of the specific property of interest, leading to a circularity in the derivation of uncertainties. Guidance of the calculation of uncertainties is given in the ISO TAG4 document 'Guide to the expression of the uncertainty of measurement' [10], and a useful worked example for the case of creep properties is given by Loveday [11].

Within the finite element computations the principal sources of error arise from uncertainties in the creep properties of the alloy and in the fracture stress of the oxide/metal interface.

Of the two alloys considered here, the creep behaviour of Incoloy 800 is the more difficult to define because the alloy may experience strengthening from precipitates of Cr-rich carbides and γ' phase ($\text{Ni}_3(\text{Al,Ti})$). The creep strength of the alloy depends critically on the carbon available to precipitate and also on the total (Al + Ti) content since this will determine the quantity of γ' out of solution. The intrinsic variability of creep strength arises largely because the relatively low (Al + Ti) content can straddle the γ' phase boundary [12] so that the quantity of the precipitated phase can vary considerably (from zero upwards) for relatively small changes in the total (Al + Ti) content. An algorithm to describe creep rate in the relatively weak version of Incoloy 800 used in this study is given later in this document.

An added complication in modelling the behaviour of Incoloy 800 is that a surface zone depleted in aluminium and chromium develops during oxidation. Within this zone there is likely to be a region of alloy, adjacent to the oxide layer, denuded of precipitates and, thus, having particularly low creep strength. No direct measurements of creep properties are available for such a zone and a simple multiplication factor of 10^3 on bulk steady-state creep rate is used in the FE modelling. The uncertainty in creep properties obviously leads to potential errors in the computed values of ΔT_c . These may be as large as 30% on the value of ΔT_c but quantification of these is itself uncertain.

By contrast, the creep properties of Haynes 214, also used in this study, are well established and are unlikely to vary much within the alloy composition range. This lack of sensitivity arises because the alloy is designed to be strengthened by γ' particles and the (Al + Ti) content is always sufficient to achieve this. The formation of the alumina surface layer will reduce the aluminium content of the alloy but the rapid rate of aluminium diffusion within the specimen cross-section means that particle-denuded zones are unlikely to form.

The second major uncertainty in the finite element computations is in the fracture stress, σ_o , of the oxide/metal interface. For both the alloys considered, fracture is taken to occur within an alumina region of 0.1 μm thickness at the interface. No direct measurements of the fracture stress have been made for such a thin interlayer but an assumed value of 1700 MPa is used in the computations. This corresponds to an elastic fracture strain of about 0.45%. This high value implies that no interfacial voids are present.

The sensitivity of the predictions to the assumed value of interface fracture stress has been assessed for Alloy 800 and shown in Figure 3. These computations were performed using creep properties appropriate

to a weak version of the alloy (details given later), a weaker denuded zone of 32 μm depth and a 5 μm chromia layer. The oxidation temperature was 800 $^{\circ}\text{C}$ and cooling occurred at 100 $^{\circ}\text{C h}^{-1}$. The computed value of ΔT_c increases with interfacial fracture stress but not linearly. The line shown in the figure indicates that ΔT_c is proportional approximately to $\sigma_o^{0.6}$ which means that an uncertainty of a factor 2 on the fracture stress leads to an uncertainty of some 50% in the predicted value of the critical temperature drop. Similar values are likely to apply also to the computations on the Haynes 214 alloy.

7 ILLUSTRATIVE EXAMPLES

7.1 Through-thickness cracking of chromia scale on creep resistant austenitic steel

Consider the example of a chromia scale growing at constant temperature on an austenitic steel which is subjected to a constant imposed mechanical stress, σ . The steel deforms at a strain rate, $\dot{\epsilon}$, determined by its creep resistance according to the expression (in its simplest form):

$$\dot{\epsilon} = A \sigma^n \quad (2)$$

where A and n are material constants

However, at the service temperature the chromia scale does not creep but only deforms elastically, thus

$$\dot{\epsilon} = \frac{\dot{\sigma}_{\alpha}}{E_{\alpha}} \quad (3)$$

where a dot above any symbol denotes the first derivative with respect to time.

In order to maintain continuity across the interface, the strain rates in oxide and substrate must remain equal. Stress redistribution occurs and in order to accommodate the change in stress, equation (2) becomes

$$\dot{\epsilon} = \frac{\dot{\sigma}_{\text{sub}}}{E_{\text{sub}}} + A \sigma_{\text{sub}}^n \quad (4)$$

The total force on the system remains constant; therefore, the stress redistribution can be described by:

$$\sigma = \sigma_{\alpha} \phi + \sigma_{\text{sub}} (1 - \phi) \quad (5)$$

where ϕ is the area fraction of oxide in the cross section of the component.

Differentiation of equation (5) with respect to time gives:

$$\dot{\sigma} = \phi \dot{\sigma}_{\alpha} + \sigma_{\alpha} \dot{\phi} + (1 - \phi) \dot{\sigma}_{\text{sub}} - \sigma_{\text{sub}} \dot{\phi} \quad (6)$$

Realising that $\dot{\sigma} = 0$ and substituting equations (3), (4) and (5) gives the expression for the evolution of the stress on the substrate

$$\dot{\sigma}_{\text{sub}} = \frac{\dot{\phi} \left(\sigma_{\text{sub}} \left(1 + \frac{1-\phi}{\phi} \right) - \frac{\sigma}{\phi} \right) - E_{\alpha} \phi A \sigma_{\text{sub}}^n}{1 - \phi \left(1 + \frac{E_{\alpha}}{E_{\text{sub}}} \right)} \quad (7)$$

The only remaining kinetics to be defined is the evolution of ϕ with time, which for a cylindrical component and parabolic scale growth becomes:

$$\dot{\phi} = \frac{2 k_p}{R^2 \phi} \quad (8)$$

where k_p is the parabolic rate constant for oxidation
 R is the radius of the component

Equations (4), (7) and (8) are integrated numerically as an interdependent set to generate the strain/time trajectory for the component. The influence of stress redistribution on creep of the component and lifetime is demonstrated in Figure 4 where lifetime has been determined by using failure strain of the oxide as the end point of the calculation.

Parallel calculations can be carried out using similar equation sets, eg the stress in the oxide scale can be used as the failure criterion or the description of creep behaviour may be refined by incorporating a description of primary creep.

7.2 3-D spallation maps for alumina and chromia formers

The following section describes the process of data collation and calculations necessary to produce a three-dimensional spallation map for chromia on Incoloy 800HT and for alumina on Hayes 214.

7.2.1 Incoloy 800HT

7.2.1.1 Creep and Elastic Properties

As has been discussed in the section on uncertainties, there is a large intrinsic variation in creep rate within the alloy's composition range depending on the absence or presence of γ' precipitates. The composition, determined at NPL, of the batch in the present study is given in Table I. The material was received in the annealed condition.

Table I: Composition (wt%) of the Current Batch of Alloy 800

Cr	Ni	Al	Ti	Si	C	Fe
21.3	29.7	0.7	0.24	0.60	0.07	Bal

At this composition, extensive γ' will not be expected [12] and the alloy will have relatively low creep strength. Appropriate creep data for an alloy in this condition were obtained from La Malfa and Quaranta [13] for temperatures of 700° and 650 °C. Their results yield the following algorithm for creep rate, $\dot{\epsilon}$:

$$\dot{\epsilon} = 1.39 \times 10^7 \sigma^6 \exp\left(\frac{-53800}{T}\right), \quad s^{-1} \quad (9)$$

where stress, σ , is in MPa and temperature, T , in K.

As discussed earlier in the section on uncertainties, the formation of the chromia layer during exposure will produce a Cr-depleted zone under the oxide layer. EPMA measurements of chromium concentration have been made after 408 h exposure at 900 °C. The depletion profile is shown in Figure 5 together with the best-fit of the solid symbols to a simple error function; extrapolation of this yields an interface concentration of chromium of 8.82 wt%. This type of depletion profile is entirely consistent with

measurements [14] on the similar 20Cr25Ni steel. Thermodynamic calculations by Hurst [15] indicate that at 800 °C, $M_{23}C_6$ precipitates will not form at local chromium concentrations less than about 14 wt%. This implies from Figure 5 that there will be a particle-free zone, ie a denuded zone, of some 6 μm depth underlying the oxide layer. Since the $M_{23}C_6$ particles are responsible for the strength of this batch of alloy, it is anticipated that this zone will also have low creep strength. No direct measurements of the creep properties of this zone are available and, for present purposes, it is assumed to have a creep rate 10^3 of that given by equation (9), ie

$$\epsilon = 1.39 \times 10^{10} \sigma^6 \exp\left(\frac{-53800}{T}\right) \text{ s}^{-1} \tag{10}$$

This ratio (10^3) of creep strengths between solid-solution- and particle-strengthened alloys is not unusual although the stress exponent of creep rate is usually less in the particle-free material. This difference is neglected in the present exercise.

An additional point to note is that the error function fit to the chromium depletion profile (Figure 5) implies that the chromia layer grows with parabolic kinetics and that the depth of the particle-free zone will also penetrate the alloy parabolically [15]. It is expected, therefore, that after 10,000 h exposure at 800 °C, the depth of the particle-free zone will have increased to about 30 μm . The finite element computations examine the sensitivity of the predictions to zone depth over this range (actually, 8 to 32 μm).

The other (elastic) material properties used in the computations are given in Table II and reflect typical values.

Table II - Elastic Material Properties used in the FE Computations

Material	Young's Modulus, GPa	Poisson's Ratio	Thermal Expansion Coefficient $\times 10^6$	Fracture Stress, MPa
Chromia	260	0.3	8.5	NR
Oxide/metal interface (alumina)	387	0.3	7.9	1700
Particle-free zone	157	0.3	17.8	NR
Bulk alloy	157	0.3	17.8	NR

NR - Not required for FE calculations

7.2.1.2 Oxidation Kinetics

$$k_p = \frac{\xi^2}{t} = 2.07 \times 10^{-6} \exp\left(\frac{-31020}{T}\right) \text{ , } \text{m}^2 \text{s}^{-1} \tag{11}$$

where t is the exposure period.

This equation is also consistent with the growth of adherent chromia layers on chromium [17-19] and with limited metallographic measurements [20] on Incoloy 800 at 1000 °C.

7.2. 3 FE Scoping Runs

The influence of the strength of the oxide/metal interface zone on the critical temperature for spallation has been shown in Figure 3 and discussed in the section on uncertainties. The computations necessary for construction of the spallation map have used a fracture stress of 1700 MPa and a chromia thickness of 5 μm .

The influence of alloy creep strength on the kinetics of growth of the interfacial wedge crack during cooling from 900 °C at 100 °C h⁻¹ is shown in Figure 6. The solid symbols represent the behaviour where the entire alloy cross-section has uniform creep properties given by equation (9) whereas the open symbols show the effect of a layered substrate, ie with a 32 μm particle-free denuded zone underlying the oxide layer creeping according to equation (10). In both cases, the interfacial wedge crack was nucleated after a temperature drop of about 100 °C, independent of the creep strength of the immediate substrate, but its subsequent growth was then delayed as a result of stress relaxation at the crack tip. This behaviour is consistent with computations reported elsewhere [1,2]. The denuded alloy permitted more rapid stress relaxation because of the lower creep strength within the particle-free surface zone and significant relaxation occurred to lower temperatures. This can be appreciated from Figure 7 which shows the variation with temperature drop of the normal stress acting across the element ahead of the crack tip. It can be seen that, with the weak zone, the interfacial stress can actually reduce initially with continued cooling. The effect of this is to increase the temperature drop significantly at which further crack growth occurs and, as shown in Figure 6, to improve the spallation resistance of the alloy.

The computational results shown in Figures 6 and 7 used a 32 μm denuded zone which extended under the entire oxide/metal interface in the FE model. To demonstrate how localised is the volume of substrate which experiences stress relaxation, a repeat run was made where the 32 μm zone was confined to the area of interface underlying the spall zone (ie of only 8 μm radius compared with 80 μm , previously). This structure was then cooled from 900 °C at 100 °C h⁻¹ to give crack growth kinetics virtually identical to those shown in Figure 6. Subsequent results were obtained using this constrained weak zone in order to facilitate the computational process. An additional important result was that the depth of the denuded zone had little influence on the computed value of the critical temperature drop, ΔT_c . Thus for the above conditions of oxidation temperature and cooling rate, an 8 μm zone depth produced a value of 682 °C, whereas for a 32 μm zone depth, ΔT_c was obtained as 688 °C. This second-order difference has been ignored in the construction of the spallation map where the approximation is made that ΔT_c is independent of the depth of the particle-free denuded zone for values of practical interest.

7.2.1.4 3-D Spallation Map

The purpose of the map is to provide a surface in ΔT_c /exposure time/oxidation temperature space which defines the limit to an operating regime within which oxide spallation can be avoided. The finite-element computations which underpin this construct are, as outlined earlier, obtained at a chromia-layer thickness of 5 μm but the critical spallation temperature at other oxide thicknesses are then obtained from equation (1). Oxide thickness is then converted, through equation (4), to exposure time and temperature within the range 700-900 °C.

A comparison of the crack growth kinetics obtained during cooling from each of 700, 800 and 900 °C is given in Figure 8. As expected, the lower the oxidation temperature the less stress relaxation is possible and the sooner does crack growth continue. The effect is to reduce the critical temperature drop for spallation as given in Table III. These values of ΔT_c are then used in equation (1) to obtain values of the effective fracture energy, γ_F , also given in Table III.

Table III: The Dependence on Oxidation Temperature of the Critical Temperature Drop for Spallation, ΔT_c , and the Effective Fracture Energy, γ_F .

Oxidation Temperature °C	Temperature drop ΔT_c , °C	Effective Fracture Energy γ_F , Jm ⁻²
900	688	37.3
800	511	20.6
700	296	6.9

These values of the effective fracture energy are substantially greater than elastic values (of order, 1 J m⁻²) but are consistent with the dissipation of energy associated with creep relaxation. It should also be noted that the effective fracture energy will vary with cooling rate but this has not been examined in this project. It is expected that higher cooling rates will reduce γ_F since the amount of time available for creep relaxation will become less.

The 3-D spallation map for the conditions examined (in particular, a cooling rate of 100 °C h⁻¹) is shown in Figure 9 for exposure times to 40,000 h. For the temperature range considered (750-900 °C), the critical temperature drop decreases with increasing oxidation temperature even though the intrinsic spallation properties are worse at lower temperatures. This arises because the increased propensity to spall, for any given oxide thickness, is countered by the longer exposure time required to reach that thickness at lower temperatures. The spallation behaviour is also sensitive to exposure time itself, at least in the early stages of oxidation where the rate of change of oxide thickness is highest. Thus, in the temperature range considered, negligible spallation would be expected until exposure times of between 1000 and 2000 h. This is consistent with the NPL experiments at 900 °C where no spallation was detected after 408 h oxidation.

7.2.2 Haynes 214

Material was received in the form of cold rolled and annealed sheet with nominal composition as given in Table IV.

Table IV: Nominal Composition (wt%) of the Haynes 214

Ni	Cr	Al	Fe	Mn	Si	Zr	C	B	Y
Bal	16	4.5	3	0.5 max	0.2 max	0.1 max	0.05	0.01 max	0.01

7.2.2.1 Creep and Elastic Properties

The algorithm for creep rate used in the finite-element modelling was obtained from data given in the Haynes 214 properties manual supplied by the manufacturer as:

$$\dot{\epsilon} = 25.0 \sigma^{5.24} \exp\left(\frac{-48450}{T}\right) + 4.54 \times 10^{22} \sigma^{6.24} \exp\left(\frac{-106030}{T}\right), \tag{12}$$

where stress, σ , is in MPa and temperature, T, in K. This 2-term relationship is shown graphically in Figure 10 as a function of temperature for three different stress levels. It is likely that the predicted

increase in rate at temperatures around 800 °C is due to the start of re-resolution of particles which, in this alloy, are the main source of creep strength. For the oxidation range considered in this present example (900° to 1100 °C), it is reasonable to suppose that most of the aluminium content of the alloy will be in solution and, having a high diffusion coefficient, will be mobile. This means that, even though aluminium is removed during oxidation, appreciable depletion zones will not develop in an analogous manner to chromium in Incoloy 800; weak de-alloyed zones will not then develop under the oxide layer. This assumption is likely to be less good at the lower range of oxidation temperatures and some caution is advised in any use of the modelling predictions for such conditions.

The finite-element computations were, therefore, undertaken on the basis that the creep properties of the entire alloy cross section could be described according to equation (12). The elastic properties of the alumina oxide layer were again as given in Table II and the interfacial zone was also taken to be alumina with a fracture stress of 1700 MPa. Young's modulus for the alloy was 177.0 GPa, its Poisson's ratio was 0.3 and the thermal expansion coefficient, $20.0 \times 10^{-6} \text{ K}^{-1}$. These values were taken to be temperature invariant - the incorporation of temperature dependencies for these parameters yields second order effects which affect the model predictions less than the uncertainties in the creep behaviour of the material.

7.2.2.2 Oxidation Kinetics

As was the case for Incoloy 800, construction of the 3-D spallation map requires an algorithm for the growth kinetics of the alumina layer. Based on NPL measurements and those obtained on other alloy systems [21-23], the following algorithm for the parabolic rate constant was used:

$$k_p = 6.6 \times 10^{-7} \exp \left(\frac{-286400}{8.314 T} \right), \quad \text{m}^2 \text{ s}^{-1} \quad (13)$$

7.2.2.3 3-D Spallation Map for Haynes 214

The method of map construction was identical to that used for Incoloy 800, described earlier, except that the finite-element computations were undertaken for oxidation temperatures of 900°, 1000° and 1100°C but, again, with an associated cooling rate of 100°C h⁻¹. In each case, the thickness of the oxide layer was 5 µm and the interfacial zone, 0.1 µm.

A comparison of the crack-growth kinetics obtained during cooling from each of these three temperatures is given in Figure 11. This shows broadly similar trends to those found for Incoloy 800 (Figure 6) in that initial development of the interfacial crack was delayed by substrate creep until the temperature had dropped sufficiently to inhibit creep, at which stage crack growth could occur rapidly. A somewhat different response was found during cooling from 900 °C where interfacial cracking tended to occur progressively with reducing temperature. It is likely that this is a consequence of the relatively high creep strength of the alloy at such low temperatures (Figure 8) which limited the extent of crack-tip stress relaxation and associated crack blunting. If near-surface, weak de-alloyed zones were to form in this alloy at this low oxidation temperature, stress relaxation rates would increase and it is expected that the crack-growth kinetics would revert to those characteristic of higher temperatures.

For the temperature range examined in this example, ΔT_c decreased with decreasing oxidation temperature (Table V). This table also gives the corresponding values of the effective fracture energy calculated from equation (1).

As was the case with Incoloy 800, these values of the effective fracture energy are considerably larger than would be expected if elastic conditions obtained. Their decrease with decreasing oxidation temperature is consistent with the reduction in rates of creep relaxation at lower temperatures.

The 3-D spallation map for the conditions examined (in particular, a cooling rate of 100°C h⁻¹) is shown in Figure 12 for exposure times to 40000 h. As was the case for Incoloy 800 (Figure 9), ΔT_c decreases with increasing oxidation temperature but there is a less strong dependency. This decrease with increasing

Table V: The Dependence on Oxidation Temperature of the Critical Temperature Drop, ΔT_c, for Spallation and the Effective Fracture Energy, γ_F.

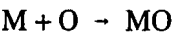
Oxidation Temperature, °C	Temperature Drop, ΔT _c , °C	Effective Fracture Energy, γ _F , J.m ⁻²
1100	542	58.3
1000	373	27.6
900	322	20.6

temperature arises, even though the intrinsic spallation characteristics are worse on cooling from lower oxidation temperatures (Figure 11), because the oxide thickness increases more rapidly at the higher temperatures. It is also clear that ΔT_c for the Haynes alloy decreases more rapidly with exposure time than it does for Incoloy 800. This is a consequence of the higher temperature range considered for the former and the consequent more rapid rate of oxidation. For an oxidation temperature of 1100°C, spallation is expected on cooling to room temperature after only 50 h exposure; after oxidation for between 500 to 1000 h, ΔT_c values between 620° and 520 °C are predicted, in broad agreement with NPL measurements.

7.3 Sulphur/chlorine - limit maps

In addition to mechanical stresses, protective oxides are also subject to "chemical" loads. These result from the presence of aggressive gases in the high temperature environment and can result in disruption of the protective oxide scale leading to increased rates of metal loss. Guidance is required to identify potentially dangerous acceleration of metal loss rates in the service environment.

The principle chemical reaction promoting formation of a protective layer is a simple oxidation:



While oxygen is not always the major constituent of the service atmosphere, the effective partial presence is normally such that a protective layer of alumina or chromia can form by reaction with Al or Cr additions to the alloy particularly when temperatures are greater than about 600 °C. At lower temperatures the base alloy component can itself form the protective oxide if the oxide formation rates are sufficiently low as is the case mild steel and low alloy steels where protection is conferred by the presence of magnetite and/or haematite layers.

The situation becomes more complex when other scale forming components are present in the atmosphere, and the two most commonly found during combustion or gasification processes of fossil fuels are sulphur- and chlorine-containing compounds where, respectively, SO₂ and H₂S can form from reaction with the sulphur-compounds, and HCl forms in both cases from the chlorine-compounds. The presence of these compounds allows additional reactions with the alloy to form metal sulphides on chlorides, which, if solid, allow higher rates of cation diffusion (mostly sulphides), or if liquid or gaseous (mostly chlorides) either flux or mechanically disrupt the protective oxide scale. A further complication, considered in section §7.4, is the formation of deposits where again scale fluxing can occur.

While a qualitative understanding of the affects of S- and Cl-additions to the atmosphere is known [24] it is not possible to quantitatively predict these effects. Consequently, an experimental approach has to be adopted. The work discussed here attempts to construct sulphur/chlorine/temperature diagrams for two systems based on extrapolations of measured metal loss rates to estimate annual metal loss rates. Examples

of these diagrams for a combustion and a gasification environment with respectively carbon steel and Incoloy 800 over relevant temperature ranges were chosen to illustrate the methodology. Sulphur and chlorine levels were chosen to induce accelerated metal loss rates.

Generally tests were for a maximum of 500 h so that an approximately 18 fold extrapolation is required to predict an annual rate for metal loss. The kinetics of metal loss were either linear or parabolic dependent upon exposure conditions and the appropriate law was chosen for the extrapolation ie within a single map both linear and parabolic rate laws were used for different levels of sulphur- and chlorine-containing species. A metal loss rate of 100 μm per year is generally considered to be industrially acceptable, but this has been exceeded in nearly all of the test conditions considered. Data can be presented either as a 3-dimensional surface or in the form of contour plots where the contours are determined by linear interpolation between the experimentally determined values. Figure 13 shows an example of these plots for Incoloy 800 in a gasification environment at 600 °C. The metal loss rate increases with both sulphur and chlorine content of the environment and shows a potentially catastrophic metal loss when both additions were added at their highest concentrations. The data is presented in three different ways - a 3-D surface; contours in oxidation temperature/oxidation time space; and contours in oxidation temperature/scale thickness space. The contour maps are probably the easiest plots to interpret where the plant engineer can locate the operating conditions in terms of oxidation temperature and either time or scale thickness and interpolate the contours to derive the critical temperature drop for spallation in his component.

7.4 Downtime/dewpoint corrosion

The effect of downtime or dewpoint corrosion can be simulated in the laboratory using either the procedure recommended by EPRI [25] or that developed at NPL [26]. The two test procedures have been compared for Incoloy 800H and AISI 310 stainless steel, exposed to a simulated coal gasification atmosphere followed by the dewpoint corrosion cycle [26]. The materials were tested in two conditions, coated with char and coated with a char plus salt mixture.

The chemistry and morphology of the corrosion product has been investigated and compared to that observed during service [25]. One important result is that the NPL test reproduced the chlorine-rich layer that was observed in service, whereas the EPRI test did not generate this layer.

The cycle sequence during the simulation can be adjusted either to represent service behaviour or to accelerate the effect of the downtime/dewpoint attack.

8 INFLUENCE OF SUBSTRATE GEOMETRY

For thin oxides, the important difference in the stress systems between flat and curved substrates is the presence, in the latter case, of a radial normal stress across the oxide/metal interface. This stress may be tensile or compressive and can originate from both the oxidation process and during temperature changes. Under circumstances where the in-plane oxide stress, σ_θ , is compressive, eg during cooling of convex geometry with $\sigma_{\text{metal}} > \sigma_{\text{oxide}}$, the oxide spallation mode may well be by wedging.

It can be appreciated that a tensile stress across the interface in addition to that developed at the tip of the wedge crack due to the wedging action will increase the crack's growth rate and, thus, produce a lower ΔT_c than that for a flat substrate. For thin oxides on concave substrates, the greater contraction of the substrate during cooling will produce compressive normal stresses across the oxide/metal interface and these will tend to retard the cracking process. The nett effect will be an improvement in spallation resistance.

In the case that growth stresses can be neglected, ΔT_c is given as:

$$\Delta T_c = \frac{K_{Ic} R (1 - \nu_{\alpha})}{2 E_{\alpha} (\pi a)^{1/2} (\alpha_{sub} - \alpha_{\alpha}) \xi} \quad (14)$$

where K_{Ic} is the fracture toughness of the scale
 R is the local radius of curvature
 E is the Young's modulus of the oxide
 ν is Poisson's ratio
 a is the composite defect size of the oxide
 ξ is the oxide thickness

An attempt was made during this work to validate equation (14) using a series of surface preparation techniques on the ODS alloy, PM2000. However it has not proved possible to initiate spallation on the batch of the alloy used in this work, probably due to variations in the creep strength of the substrate.

At this stage of understanding, however, no quantitative (numerical) modelling, that allows for creep relaxation, has been undertaken for curved substrates and no estimate can be made of the magnitude of these changes in ΔT_c . It is anticipated that, as in the case for flat specimens, the influence of substrate creep will dominate the crack-growth kinetics and will determine whether the critical strain-energy criterion is an acceptable description of the spallation process.

A more detailed review of the influence of substrate geometry on scale integrity has been published separately [27].

9 PRACTICAL MEASURES FOR LIFETIME EXTENSION

Material Selection

Many problems can be avoided by correct specification of materials at the design stage. An important feature of materials, that has only been recently identified, is that the development of a weak surface zone (by de-alloying during scale growth) produces significant benefits in spallation resistance. This beneficial feature does not develop in all alloys and may be present in one material but not in a closely-related alloy eg the feature develops in Incoloy 800 because one element, chromium, is a major constituent of both the oxide and the strengthening phase. In addition, the diffusion rate of chromium in the alloy is sufficiently low that surface depletion zones develop. A similar 20Cr25Ni steel shows appreciably poorer spallation resistance than Incoloy 800 because the chromium-depleted zone developed in this alloy is not weak as the strengthening mechanism in this case is through NbC particles.

The novel concept of developing weak surface zones as a method of improving spallation resistance is unlikely to be relevant to existing plant structures but offers a development strategy for new high temperature alloys.

9.2 Operating Parameters

The spallation behaviour depends critically on the extent of creep relaxation of crack-tip stresses during cooling. This process is aided by low cooling rates or by the insertion of a dwell period at an intermediate temperature during cooling. Although neither of these factors has been studied in this project, previous computations [2] on an MCrAlY coating alloy have shown that ΔT_c can reduce by a factor 2 by increasing cooling rates from 100°C h^{-1} to $10^5^\circ\text{C h}^{-1}$. There is an obvious incentive to maintain cooling rates as low as possible.

10 ACKNOWLEDGEMENTS

The work described in this paper was carried out under the 'Materials Degradation in Aggressive Environments Programme': a programme of underpinning research financed by the UK Department of Trade and Industry.

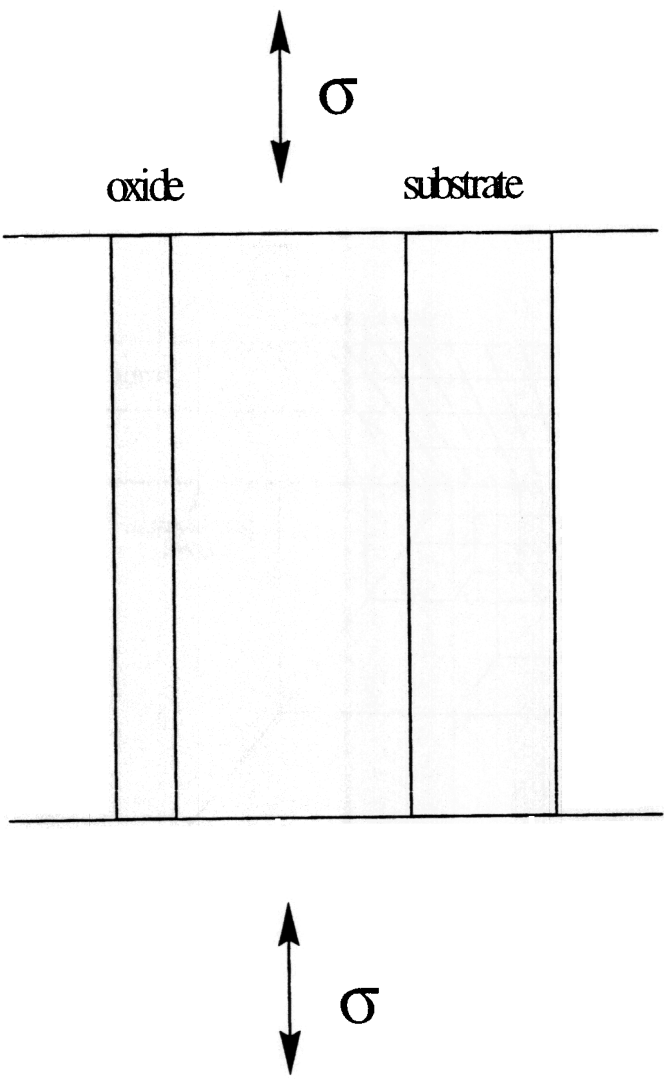
REFERENCES

- 1 H E Evans, G P Mitchell, R C Lobb and D R J Owen; Proc. Roy. Soc., 1993, A440, 1.
- 2 H E Evans, A Strawbridge, R A Carolan and C B Ponton, Mater. Sci. Eng., 1997, A225, 1.
- 3 U R Evans, *An Introduction to Metallic Corrosion*, Edward Arnold, London, 1948, p 195.
- 4 H E Evans and R C Lobb, Corros. Sci., 1984, 24, 209.
- 5 J P Banks, D D Gohil, H E Evans, D J Hall and S R J Saunders, in *Materials for Advanced Power Generation*, Eds. D Coutouradis et al, Part II, Kluwer Academic, The Netherlands, 1994, p 1543.
- 6 S Osgerby, S R J Saunders and J P Banks, Measurement of Failure Strain in Oxide Scales, NPL Measurement Note CMMT(MN)031, August 1998.
- 7 S Osgerby, S R J Saunders and J P Banks, Scale and Coating Adhesion: A Procedure for Laboratory Tests. NPL Measurement Note CMMT(M N)026, June 1998.
- 8 Thermophysical Properties of Matter, The TPRC Data Series vol 13 Thermal Expansion: Nonmetallic Solids, eds Y S Touloukian, R K Kirby, R E Taylor and T Y R Lee, IFI/Plenum, New York 1977.
- 9 BS 3500 pt 3:1969 (1987) Methods for Creep and Rupture Testing of Metals, 'Part 3' Tensile Creep Testing.
- 10 ISO TAG4 'Guide to the expression of the uncertainty of measurement', 1993.
- 11 M S Loveday, Creep Testing: Reference Materials and Uncertainty of Measurement, in Proc. The Donald McLean Symposium: Structural Materials, Engineering Applications through Scientific Insight. Eds. E D Hondros and M McLean, Inst. of Materials, London, 1996, pp 277-293.
- 12 D I Roberts, in *Alloy 800*, Eds. W Betteridge et al, North-Holland Publishing Co., Amsterdam, 1978, p 403.
- 13 U La Malfa and S Quaranta, as Ref 6, p 71.
- 14 H E Evans, D A Hilton and R A Holm, Oxid. Met., 1976, 10, 149.
- 15 P Hurst, as Ref 12, p 271.
- 16 H E Evans, D A Hilton, R A Holm and S J Webster, Oxid. Met., 1978, 12, 473.
- 17 D Caplan, A Harvey and M Cohen, Corros. Sci., 1963, 3, 161.

- 18 D Caplan and G I Sproule, *Oxid. Met.*, 1975, **9**, 459.
- 19 E A Gulbransen and K F Andrew, *J. Electrochem. Soc.*, 1954, **104**, 334
- 20 C L Angerman, *Oxid. Met.*, 1972, **5**, 149.
- 21 H Hindam and D P Whittle, *Oxid. Met.*, 1983, **18**, 245.
- 22 M J Bennett, H Romary and J B Price, in "Heat-Resistant Materials", Eds. K Natesan and D J Tillack, ASM International, 1991, pp.95-106.
- 23 M Turker and T A Hughes, *Oxid. Met.*, 1995, **44**, 505.
- 24 S I Ali and A Moccari, *British Corrosion Journal*, 1979 **14** 142-148
- 25 R A Perkins, D L Marsh and A M Sarosiek, *Downtime Corrosion in Syngas Coolers of Entrained Slagging Gasifiers*, EPRI Report AP-5996, 1988.
- 26 S Osgerby, D D Gohil and S R J Saunders, *Cyclic High Temperature Corrosion in Coal Gasification Plant and Downtime Corrosion: A Procedure for Laboratory Tests to Simulate Industrial Experience*. NPL Measurement Note NPL MN (025) 1997.
- 27 H E Evans, *Methods of Predicting Oxide Spallation and the Influence of Substrate Geometry*, NPL Report CMMT(A)22, National Physical Laboratory, April 1996.

Figure Captions

- Figure 1 Two-bar model for stress redistribution.
- Figure 2 Finite element mesh for oxide spallation simulation.
- Figure 3 Influence of interfacial fracture stress on predicted critical temperature drop for spallation.
- Figure 4 The influence of stress redistribution between oxide and substrate on creep deformation
- Figure 5 Chromium depletion profile in Incoloy 800HT after oxidation at 900 °C for 264 h.
- Figure 6 The influence of alloy creep strength on growth kinetics of interfacial wedge cracks.
- Figure 7 Normal stress at crack tip as a function of temperature drop for Incoloy 800.
- Figure 8 Crack growth kinetics in Incoloy 800 during cooling from 700, 800 and 900 °C.
- Figure 9 Three-dimensional spallation map for Incoloy 800.
- Figure 10 Stress and temperature dependency of the creep behaviour of Haynes 214
- Figure 11 Crack growth kinetics for Haynes 214
- Figure 12 Three-dimensional spallation map for Haynes 214
- Figure 13 Metal wastage in Incoloy 800 at 600 °C as a function of sulphur and chlorine level in the atmosphere



Basic Equation Set:

Equivalent strain in both elements

$$\epsilon_{ox} = \epsilon_{sub}$$

Deformation of substrate

$$\dot{\epsilon} = \frac{\dot{\sigma}_{sub}}{E_{sub}} + A \sigma_{sub}^n$$

Deformation of oxide

$$\dot{\epsilon} = \frac{\dot{\sigma}_{ox}}{E_{ox}}$$

Stress distribution between phases

$$\sigma = \sigma_{ox} \phi + \sigma_{sub} (1 - \phi)$$

Symbols	
ϵ , strain	$\dot{\epsilon}$, strain rate
σ , stress	$\dot{\sigma}$, stress rate
E , Young's modulus	A , creep constant
n , stress exponent for creep	ϕ , volume fraction of oxide

Figure 1 Two-bar model for stress redistribution.

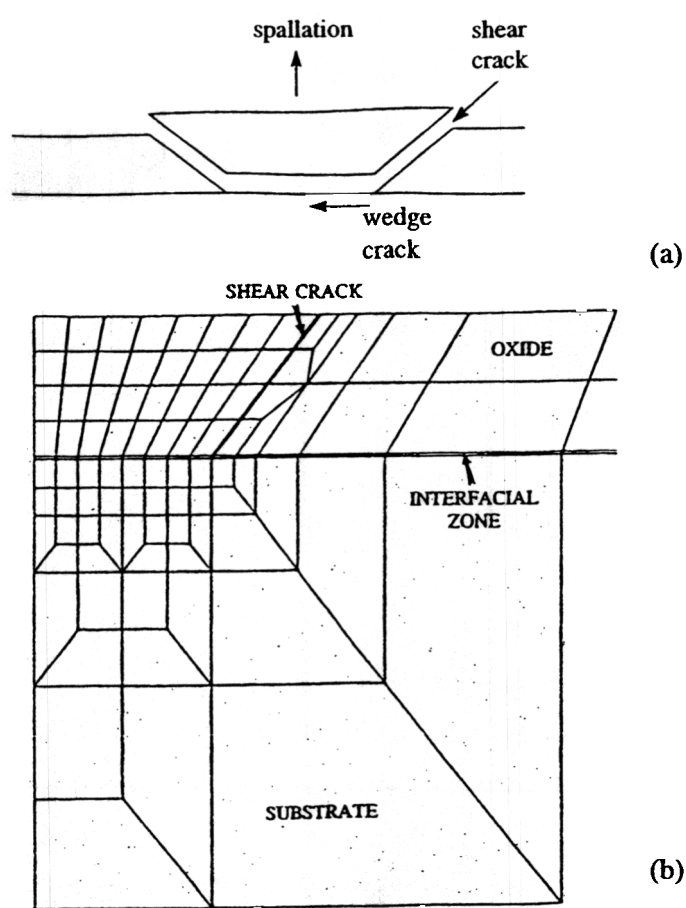


Figure 2 Simulation of oxide spallation, (a) schematic representation of mechanism (b) Finite Element Mesh

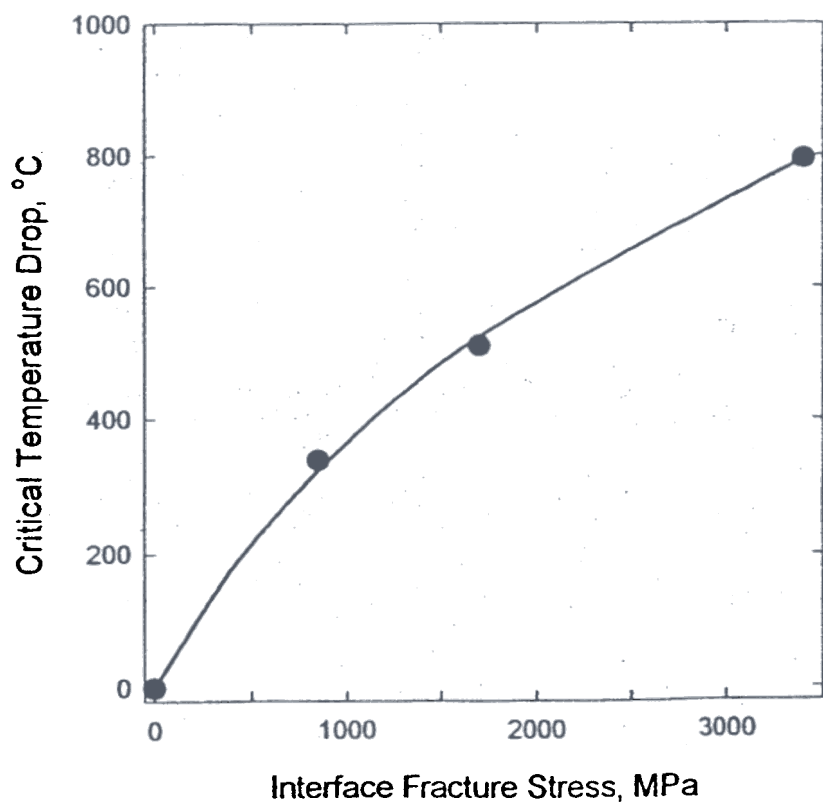


Figure 3 Influence of interfacial fracture stress on predicted critical temperature drop for spallation

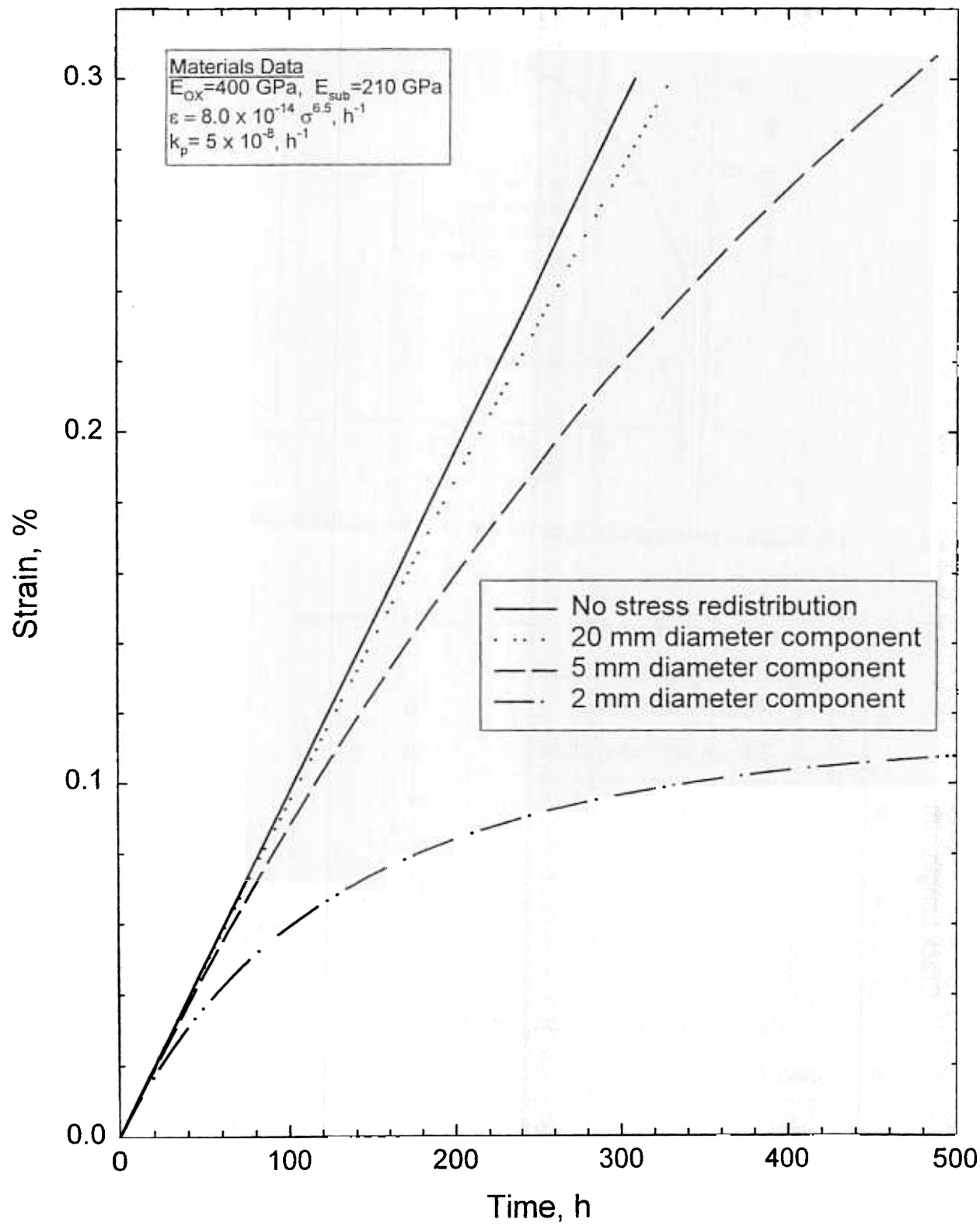


Figure 4 The influence of stress redistribution between oxide and substrate on creep deformation

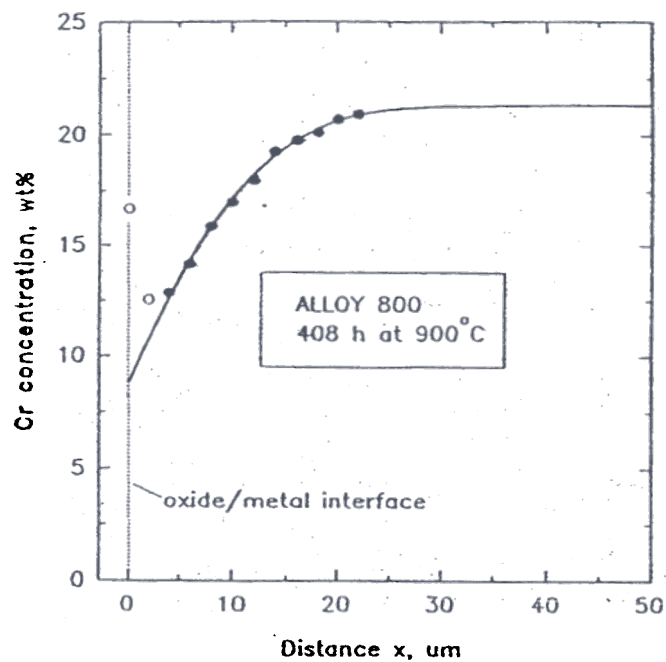


Figure 5 Chromium depletion profile in Incoloy 800HT after oxidation at 900 °C for 264 h

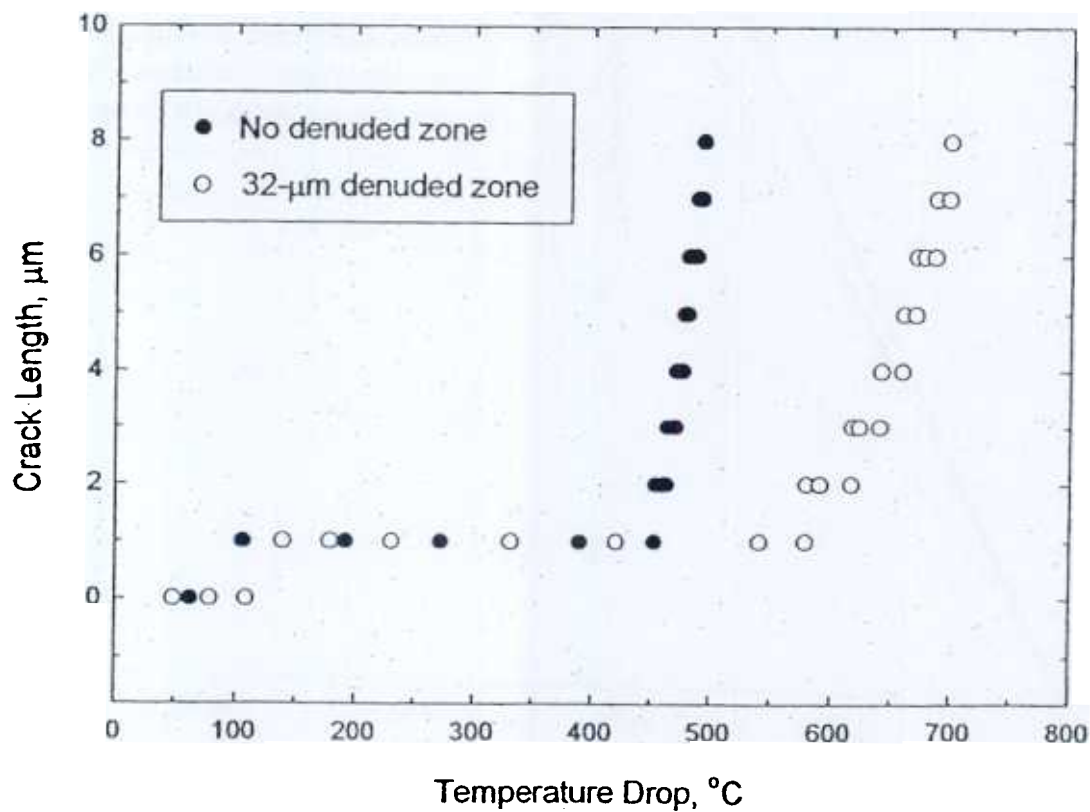


Figure 6 The influence of alloy creep strength on growth kinetics of interfacial wedge cracks

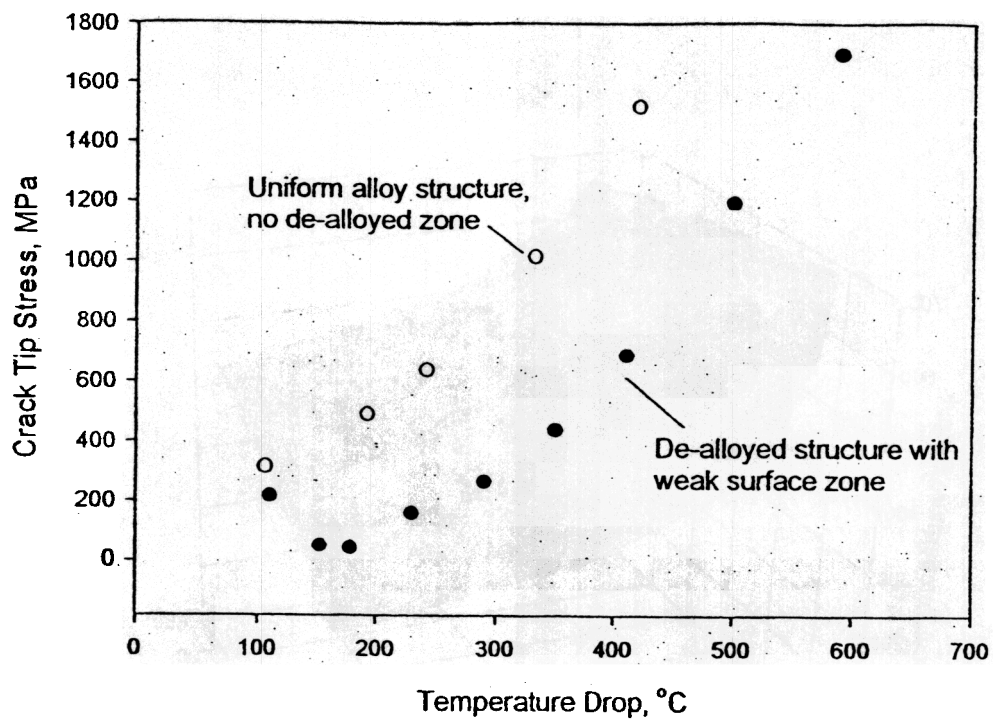


Figure 7 Normal stress at crack tip as a function of temperature drop for Incoloy 800HT

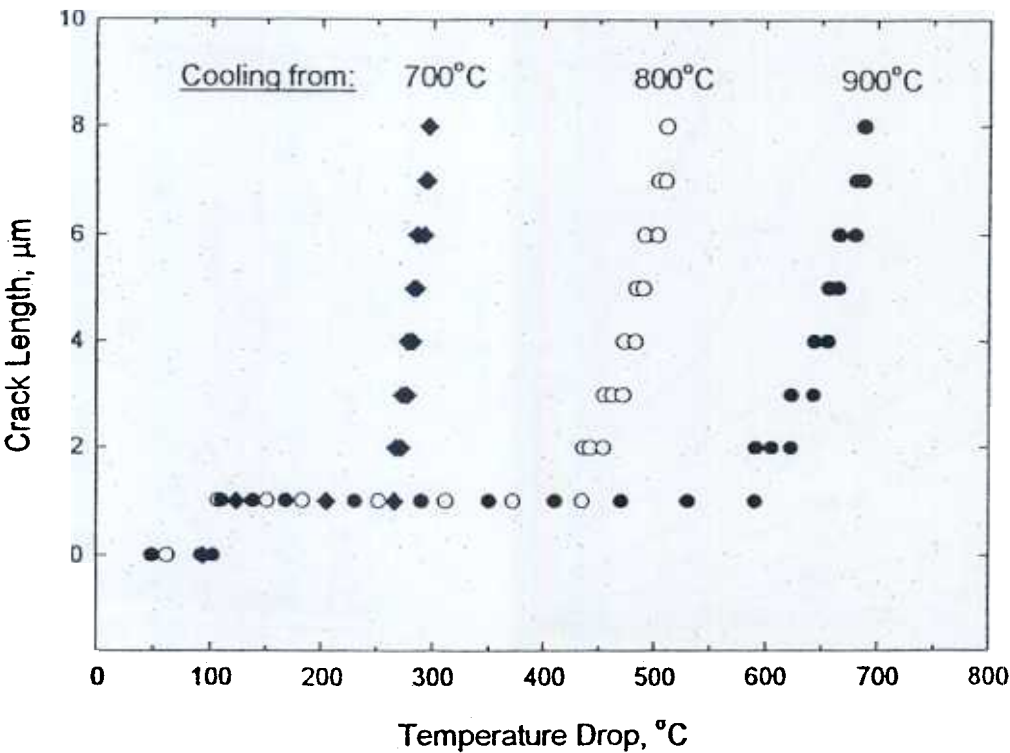


Figure 8 Crack growth kinetics in Incoloy 800 during cooling from 700, 800 and 900 °C

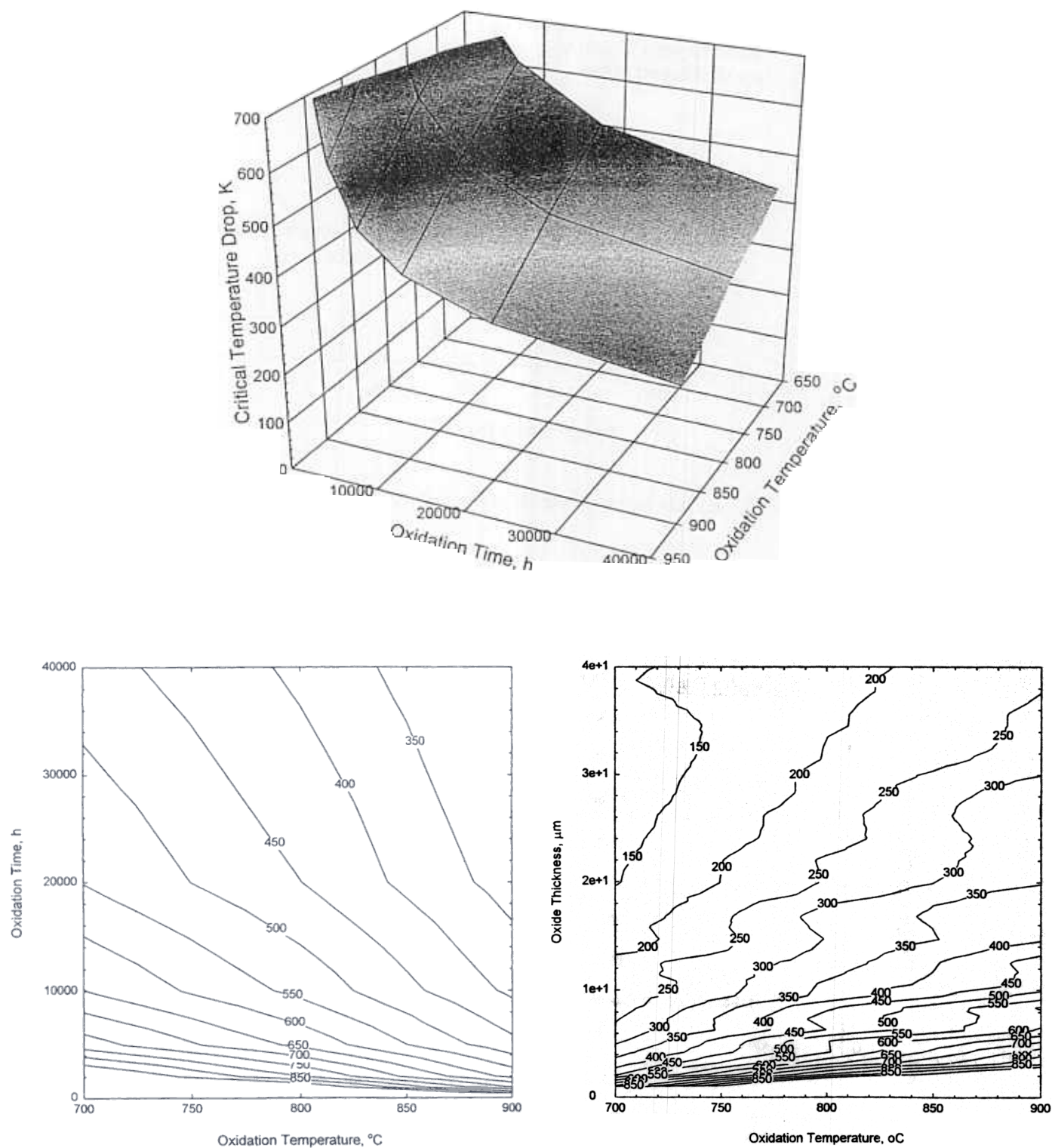


Figure 9 Three dimensional spallation map for Incoloy 800HT

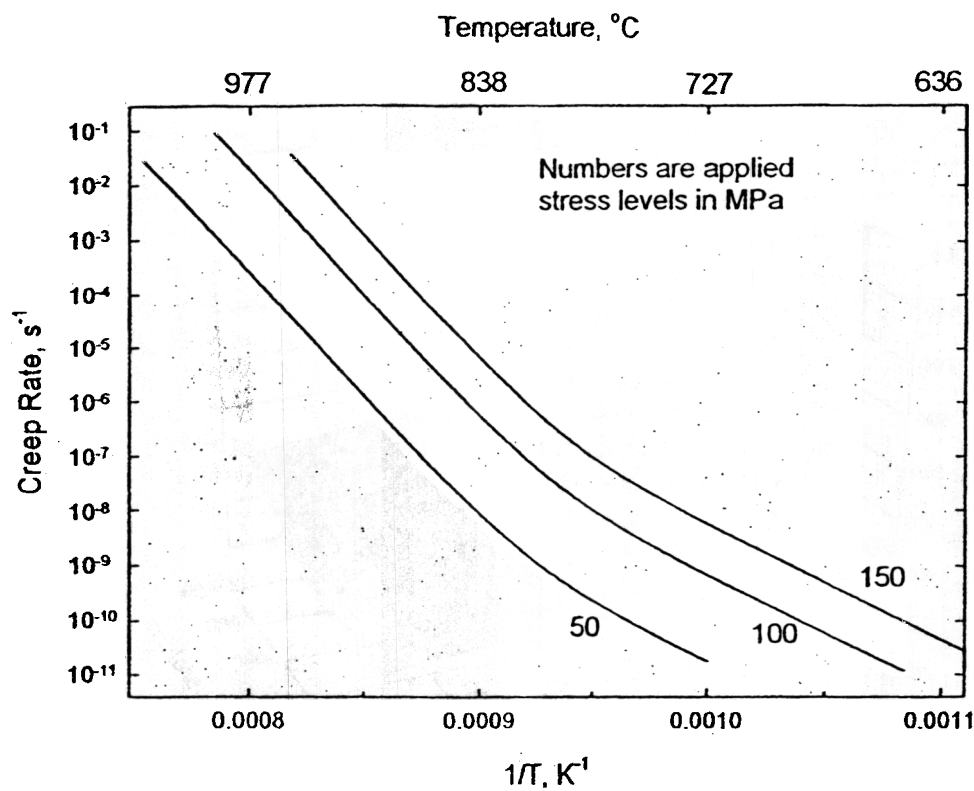


Figure 10 Stress and temperature dependency of the creep behaviour of Haynes 214

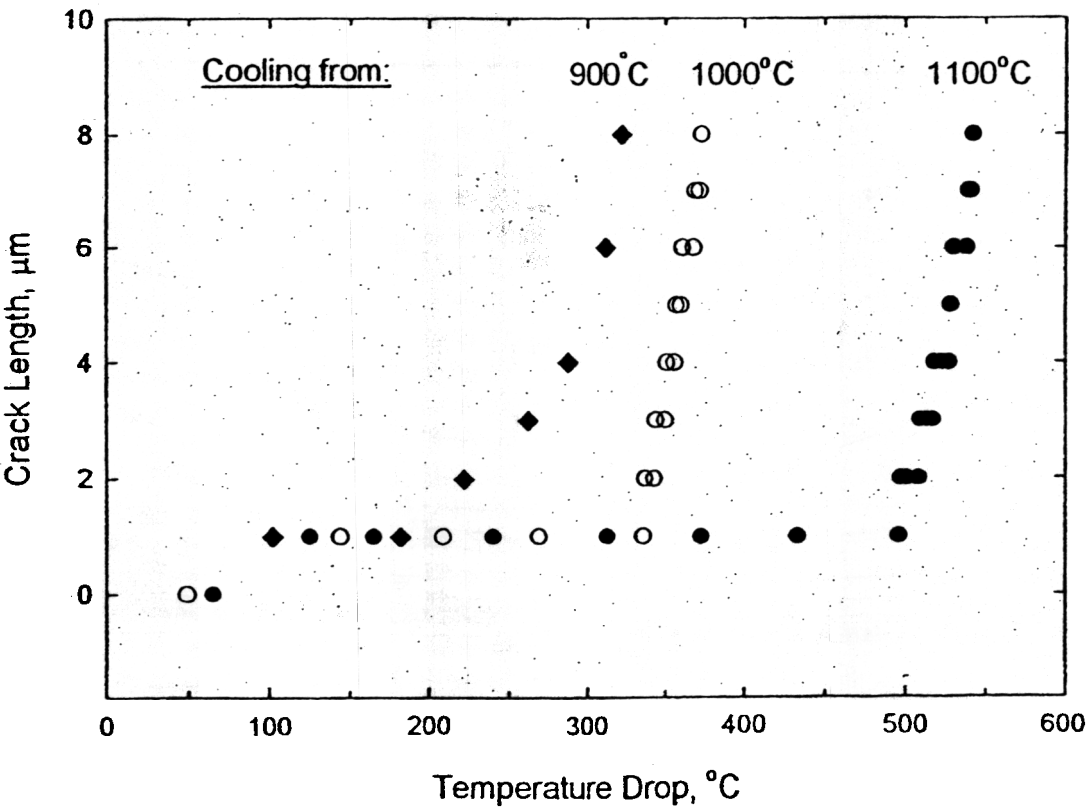


Figure 1 Crack growth kinetics for Haynes 214

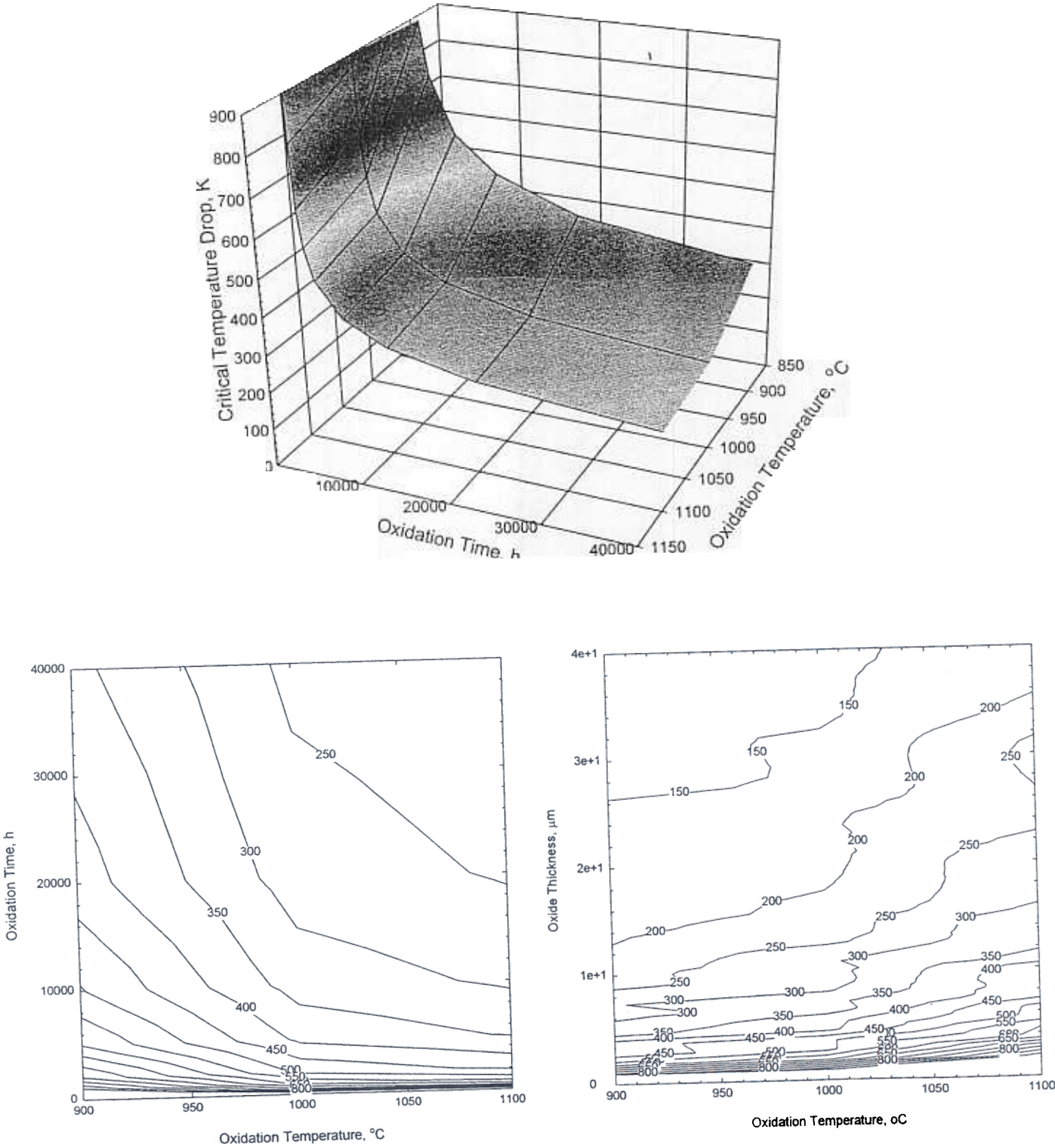
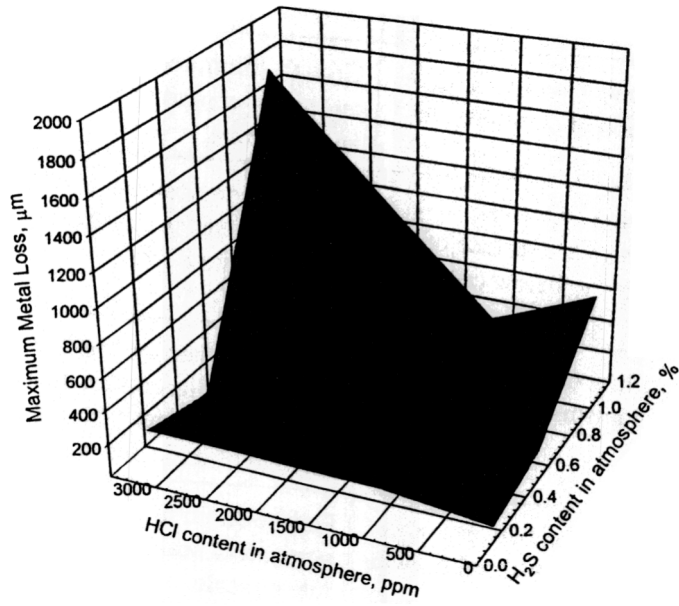


Figure 12 Three-dimensional spallation map for Haynes 214



Contour map

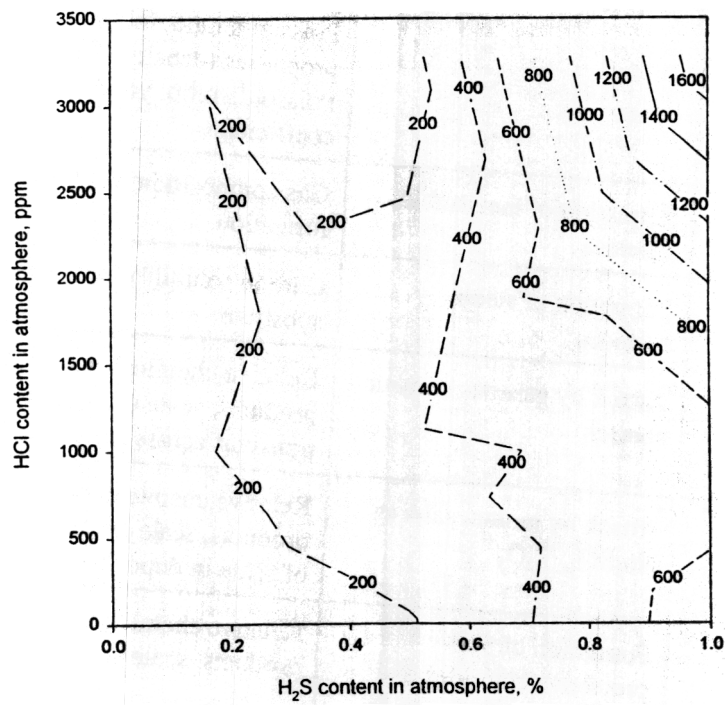


Figure 13 Metal wastage in Incoloy 800 at 600 °C as a function of sulphur and chlorine level in the atmosphere

Appendix A: Relevant Material Properties for Oxide Scale Failure Mechanisms

Observed Scale Failure Behaviour	Mechanism	Material Properties
Through Thickness Scale Cracking	Mechanical failure of scale in tension or compression	Growth strain, residual strain, failure strain in tension or compression, creep strength of scale and substrate,
Breakaway oxidation	Depletion of active elements near surface of substrate to below critical level	Original composition of substrate, elemental diffusion rates in substrate, growth rate of scale, substrate thickness
Spallation	Buckling or wedging mechanisms are possible	Thermal expansion coefficients for scale and substrate, failure strain of scale in compression, strength of interface, creep strength of scale and substrate
Oxide healing	Competition between scale cracking and lateral growth of oxide scale	Failure strain in tension or compression, creep strength of scale and substrate, lateral growth rate of scale
Erosion*	Oxide: substrate removal by particle impact	Erodent particle parameters (size, shape, velocity, density, angle of impact, Young's modulus, Poisson's ratio), Oxide properties (Ductile Brittle Transition Temperature, growth rate, density, Young's modulus, Poisson's ratio, failure strain), substrate properties (density, Young's modulus, Poisson's ratio, yield stress, work hardening coefficient)
Metal Dusting*	Formation of metastable carbides	Gas composition, kinetics of (chromia) scale formation
Carburisation*	Formation of stable carbides	Carbon solubility and diffusivity in scale and substrate
Sulphidation	Attack by gaseous sulphur species	Relative chemical stability of corrosion products, scale cracking parameters, sulphur transport across scale
Hot salt corrosion*	Attack by molten salts eg Na_2SO_4 , V_2O_5	Relative chemical stability of corrosion products, scale cracking parameters, solubility of scale in deposit
Chlorination	Formation of non-protective chlorides and oxychlorides (volatile or molten)	Relative chemical stability of corrosion products, scale cracking parameters

*These failure modes are outside the scope of this Code of Practice but have been included here for completeness