The Development of Weak, De-alloyed Zones during Oxidation of High Temperature Alloys

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October 1999
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SUMMARY

The depletion of active elements in the near-surface zone during oxidation has been reviewed for a wide range of materials. Depleted zones have been observed in many classes of commercial alloys, including martensitic and austenitic steels, Ni-base superalloys and intermetallics. However there are only a limited number of cases where this de-alloyed zone is significantly weaker than the substrate material viz austenitic steels strengthened by chromium carbides and Ni-base superalloys that form chromia or alumina scales. In other cases the de-alloying of the sub-surface zone either has no effect on the strength of the material (austenitic steels strengthened by niobium carbides) or even enhances the strength of this zone (martensitic steels).
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1 INTRODUCTION

During high temperature oxidation, scale formation requires the supply of active elements from the alloy. If the active element is not the main constituent of the alloy then the supply of that element to the scale/alloy interface may become a rate-limiting factor. The rate at which the active element is consumed by oxide formation is countered by the diffusion rate, towards the interface, of that element in the substrate. Under these circumstances it is possible for a zone of material, depleted in the active element, to form under the scale. If the active element is depleted to a sufficient degree then the concentration may fall below that required to maintain the protective oxide and increased metal loss rates or even breakaway oxidation may be observed.

This detrimental effect of depleted zones may be balanced by a tendency of the depleted zone to improve the spallation resistance of oxide scales. The mechanism of oxide scale spallation is well understood and quantitative models have been developed to predict the onset of spallation during a temperature drop [1]. If any depleted zone is weaker than the bulk of the substrate, the spallation resistance of the scale will be enhanced by allowing the stresses that are developed by mismatch of the thermal expansion coefficients of scale and substrate, to relax through creep in this de-alloyed zone. An example of the influence of a weak de-alloyed zone on spallation behaviour has been demonstrated for Incoloy 800 [2]. This influence is shown in Figure 1 for the growth kinetics of an interfacial wedge crack with and without the presence of a weak de-alloyed zone.

This report presents the results of a survey of high temperature materials to determine the extent to which the development of weak de-alloyed zones may occur during oxidation. Oxidation atmospheres have been limited to air and steam. It is accepted that the data and conclusions may not be applicable to other atmospheres of interest but it may be possible to draw limited conclusions for the formation of weak de-alloyed zones in a range of industrially-relevant environments.

The survey is supported by a limited amount of experimental work to illustrate the main conclusions for each material class.

2 ASSESSMENT PROCEDURES

The methodology applied during this work has been to monitor the variation of alloy composition with distance from the oxide/alloy interface and from this to infer a measure of the alloy strength. The composition variations were either collated from published results or were measured in the scanning electron microscope (SEM) both qualitatively, though generation of ‘digimaps’, and quantitatively, using energy dispersive X-ray (EDX) analysis with ZAF correction.

Alloy strength has been inferred from thermodynamic calculations, supported by metallographic observation, to determine the influence of element depletion on the substrate microstructure. The influence of the modified microstructures on creep
strength has been assessed by the application of well-established metallurgical principles, eg the influence of the volume fraction of precipitates on alloy strength.

3 LOW ALLOY STEELS

Steels containing 1-2.5 wt% Cr together with Mo, V, W and/or Nb are in common use in high temperature plant in tube and plate form. The nominal compositions of some common alloys are given in Table I. Strengthening is primarily through carbide precipitates, which may be Mo₃C, Cr₇C₃, (Cr,Mo)₃C₆, (Cr,Mo)₆C or VC depending upon material, heat treatment and thermal exposure during service [3]. The size of the precipitates evolves during service exposure, increasing from <0.1 μm in new material to >1.5 μm after prolonged exposure [4]. Any decrease in chromium content of the substrate will lead to less carbide being formed and hence will result in a weakening of the substrate.

Table I Nominal Composition of Some Low Alloy Steels for High Temperature Service (weight %)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>W</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>13CrMo 4 4</td>
<td>0.08-0.18</td>
<td>1.0</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14MoV 6 3</td>
<td>0.08</td>
<td>0.5</td>
<td>0.5</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T22 (10CrMo 9 10)</td>
<td>0.15 max</td>
<td>1.9-2.6</td>
<td>0.87-1.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T23</td>
<td>0.04-0.10</td>
<td>1.9-2.6</td>
<td>0.05-0.30</td>
<td>0.2-0.3</td>
<td>1.45-1.75</td>
<td>0.02-0.08</td>
</tr>
<tr>
<td>T24</td>
<td>0.05-0.10</td>
<td>2.2-2.6</td>
<td>0.90-1.10</td>
<td>0.20-0.30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HCM2S</td>
<td>0.04-0.10</td>
<td>1.9-2.6</td>
<td>&lt;0.3</td>
<td>0.2-0.3</td>
<td>1.45-1.75</td>
<td>0.02-0.08</td>
</tr>
</tbody>
</table>

The oxides formed on these alloys during exposure to air or steam environments at service temperatures are primarily iron oxides, haematite and magnetite, with the possibility of chromium dissolved in the scale to form M₃O₅ spinel. The relative thickness of haematite and magnetite is temperature dependent as the substitution of chromium in the magnetite lattice increases the activation energy for magnetite growth [5]. During oxidation chromium and molybdenum are incorporated in the spinel although no evidence of their depletion in the substrate has been observed [6]. The measured element profile across a scale grown on a 2½Cr1Mo steel in flowing oxygen for 100 h at 600 °C is shown in Figure 2 - some slight enrichment of chromium is observed in the spinel scale but this does not lead to depletion in the substrate. The explanation of this observation was given by Cox et al [7] who postulated that chromium was able to diffuse only very slowly in the magnetite crystal structure. Hence chromium does not concentrate in the scale so does not deplete the alloy substrate.
Further investigation of elemental distribution after oxidation has been carried out on 1Cr material that had been withdrawn after service at ~550 °C for 140000 h. A thick two-layer scale has formed, Figure 3a. Elemental distribution maps are shown in Figure 3b where it can be seen that chromium concentrates in the inner spinel scale. There is no evidence from the digimap that a chromium-depleted zone forms beneath the oxide scale. The hardness profile, Figure 3c, for this specimen supports this view as no softening is observed in the sub-scale region of the substrate.

*Depleted zones are not expected to form in this class of material.*

4 **9- AND 12-Cr MARTENSITIC STEELS**

Modern 9- and 12-Cr steels have been developed for use at temperatures up to 600 °C with target service temperatures of 650 °C in the near future. Current thinking is that the properties can be improved significantly by the deliberate addition on interstitial elements such as nitrogen. Typical compositions of some steels in this class are given in Table II.

The strengthening mechanisms for these steels are complex and have been summarised [8] as follows

1. transformation hardening
2. precipitation of fine carbonitrides of V and Nb
3. precipitation of coarse M₂₃C₆ particles (where M is predominantly Cr and Mo)
4. solid solution strengthening by Cr, Mo and/or W
5. precipitation of Laves Phase, Fe₅(Mo,W)

| Table II Nominal Composition of Some Industrial 9-12Cr Steels |
|-------------------|---|---|---|---|---|---|---|
| P91 (X10 CrMoVNb 9 1) | 0.1 | 9.0 | 1.0 | 0.2 | 0.049 | 0.08 | 0.45Mn |
| P92/T92 (N616) | 0.07-0.13 | 9.0 | 0.45 | 0.2 | 0.045 | 0.07 | 1.75W, 0.45Mn |
| E911 | 0.1 | 9.2 | 1.0 | 0.2 | 0.07 | 0.07 | 0.35Mn, 1.0W, 0.2Ni |
| X19 CrMoVNbN 11 1 | 0.19 | 0.10 | 0.7 | 0.1 | 0.18 | 0.45 | 0.45Ni, 0.3Mn |
| X21CrMoV 12 1 | 0.23 | 12 | 1.0 | 0.3 | 0.05 | 0.06 | 0.55Ni, 0.5Mn |
| X12CrMoVNbN 10 1 | 0.12 | 10 | 1.5 | 0.2 | 0.05 | 0.06 | 1.0W, |
| X12CrMoWVNbN10 1 | 0.12 | 10 | 1.0 | 0.2 | 0.05 | 0.06 | 1.0W, |
| X18CrMoVNbB 9 1 | 0.18 | 9.3 | 1.5 | 0.2 | 0.06 | 0.01B |

During steam oxidation of these materials a duplex oxide scale develops. This scale is usually composed of an outer layer of magnetite and an inner iron-chromium spinel. Under conditions of high oxygen partial pressure haematite may also form at the scale
surface. The boundary between the magnetite and spinel corresponds to the original metal surface [9].

Chromium depletion has been observed after isothermal oxidation of these alloys in dry air at 650 °C [10]. The chromium content of the substrate immediately beneath the oxide scale is shown in Figure 4 as a function of oxidation time for two typical alloys. This behaviour is also observed in service-exposed material: Figure 5 shows the Cr profile of a 12CrMoV turbine blade which had been in service in a steam atmosphere at 560 °C for 45000 h.

It has been shown above that under some oxidation conditions a zone depleted in chromium will form. The next question to be answered is whether the presence of this zone affects the local creep properties of the material. Amongst the five possible strengthening mechanisms mentioned above there are two (viz. 3 and 4) which rely directly upon chromium to strengthen the material. In addition the chromium content may affect two of the other mechanisms (viz. 2 and 5) by influencing the solubility of the hardening phase in the matrix [11]. The influence of chromium on the atomic fraction of secondary phase in a material based upon alloy E911 has been calculated using the thermodynamic software package, MTDATA™ and the results are shown in Figure 6. It can be seen that chromium depletion has no influence on the amount of vanadium nitride and M_{23}C_{6} present and that the amount of Laves phase at equilibrium actually increases. The result of chromium depletion in this alloy is therefore expected to be a slight strengthening of the alloy. This hypothesis is partially confirmed by the results of a hardness traverse, shown in Figure 7, across a specimen that had been oxidised in steam at 600 °C for 500 h - no significant change in hardness near the interface is observed.

*Sub-surface zones, depleted in chromium, form during the oxidation of this class of material. However these zones are not weaker than the substrate alloy and hence do not improve spallation resistance.*

5 AUSTENITIC STEELS

This class of material contains typically 15-25% chromium for oxidation resistance and 8-30% nickel to maintain an austenitic structure. The compositions of some common materials are given in Table III. Strengthening mechanisms for these materials include:-

1. Solid solution strengthening
2. Carbide precipitation
3. Precipitation of intermetallic phases eg Ni₃Al in some batches of Incoloy 800

Alloys that rely upon chromium carbides for strength have suffered from sensitisation due to removal of chromium from the matrix by formation of these carbides. This can be avoided by the addition of either interstitial elements (carbon, nitrogen or boron) or carbide-forming elements (titanium or niobium).
During high temperature oxidation the formation of a chromia scale results in a depletion of this element beneath the scale. An example of this behaviour is shown in Figure 8 for Incoloy 800HT after oxidation at 900 °C for 500 h. This behaviour is widespread among austenitic stainless steels and has been observed in 18Cr/11Ni, 19Cr/25Ni, 19Cr/35Ni, 20Cr/35Ni (12) and 20Cr/25Ni/Nb (13) alloys after oxidation at temperatures ranging from 600 to 900 °C.

| Table III Nominal Composition of Some Austenitic Steels |
|-----------------|----------------|----------------|----------------|----------------|----------------|
| Alloy           | C   | Cr     | Ni     | Mn   | Si   | Other           |
| AISI 304        | 0.08| 18.0-20.0 | 8.0-10.5 | 2.0 | 1.0 |
| AISI 304L       | 0.03| 18.0-20.0 | 8.0-10.5 | 2.0 | 1.0 |
| AISI 310        | 0.25| 24.0-26.0 | 19.0-22.0 | 2.0 | 1.5 |
| AISI 316        | 0.08| 16.0-18.0 | 10.0-14.0 | 2.0 | 1.0 | Mo 2.0-3.0 |
| AISI 321        | 0.08| 17.0-19.0 | 9.0-12.0 | 2.0 | 1.0 | Ti 5xC min |
| 353MA           | 0.05| 25     | 35     | 1.3 | N, Ce |
| Esshete 800     | 0.10| 19.0-23.0 | 30.0-35.0 | 1.5 | 1.0 max | Ti 0.15-0.60, Al 0.15-0.60 |
| Esshete 1250    | 0.08-0.09| 15   | 10     | 6    | 0.5 | Mo 1.0, V 0.2, Nb 1.0, 0.06 Ti |
| NF709           | 0.15| 20     | 25     | 1.5 | Mo 1.5, Nb 0.25 0.1Ti |
| Incoloy 800     | 0.07| 21     | 30     | 0.6 | Al 0.7, Ti 0.25 |
| NAR-AH-4        | 0.05-0.10| 22.0-24.0 | 10.0-12.0 | 1.0 max | 1.0 max | N 0.18-0.25, La+Ce 0.03-0.07 |
| SUPER304H       | 0.07-0.13| 17.0-19.0 | 7.5-10.5 | 1.0 max | 0.3 max | Cu 2.5-3.5, Nb 0.3-0.6, N 0.05-0.12 |

The extent to which the formation of this de-alloyed layer affects the local creep properties is best illustrated by comparison of two specific materials Incoloy 800 and NF709. The influence of local chromium depletion on equilibrium phase concentration is shown in Figure 9. It can be seen that at the specified chromium level NF709 has approximately twice as much $M_{31}C_6$ as Incoloy 800 and also that the γ is present to a higher temperature in NF709 than Incoloy 800. As the chromium level is reduced the influence on the solubility of the strengthening phases in Incoloy 800 is greater than in NF709 with $M_{31}C_6$ going into solution at 850 °C at the 10% Cr level in Incoloy 800 but remaining as precipitates until 1000 °C in NF709. These microstructural changes imply that the degree of softening in the sub-surface zone in Incoloy 800 is likely to be greater than in NF709. This view is strengthened by a cursory examination of the spallation behaviour of the two alloys - a 5 μm thick chromia layer grown on NF709 at 850 °C spills on cooling whilst an equivalent oxide scale grown on Incoloy 800 at 900 °C remains intact during cooling. Previous finite element modelling of spallation of oxide scale grown on Incoloy 800 predicted that
without the development of a weak sub-surface zone that spallation would occur on cooling from 900 °C.

The influence of chromium depletion on an alloy that forms niobium carbide is illustrated in Figure 10 for the case of Esshete 1250. It can be seen that the chromium content of the alloy has a minimal influence on the amount of strengthening phase present at equilibrium. The mass fraction of NbC formed is actually slightly increased at temperatures in the range 600-700 °C and slightly reduced at higher temperatures (900-1000 °C).

**Sub-surface zones, depleted in chromium, form during oxidation of these materials. If the main strengthening phase in the alloy is chromium carbide then these zones are weaker than the substrate. However if the strengthening phase is niobium carbide then chromium depletion has no influence on local strength in the alloy.**

6 **NI-BASE SUPERALLOYS**

The main strengthening phase for this class of alloys is the \( \gamma' \) (Ni\(_3\)(Al,Ti)) precipitate. The creep strength of the alloys depends critically upon the volume fraction and solvus temperature of this phase. Any local reduction in the volume fraction of \( \gamma' \) causes the material in that area to be weaker than the bulk material.

| Table IV Typical compositions of some Ni-base superalloys |
|---|---|---|---|---|---|---|---|---|
| Alloy | C | Ni | Co | Cr | Mo | Al | Ti | B | Other |
| IN713C | 0.12 | Bal | 0.53 | 13.64 | 4.1 | 8 | 6.0 | 0.87 | 0.00 | Zr 0.1, Ta+Nb 2.1, Fe 0.39, Si 0.17 |
| IN738LC | 0.09 | Bal | 8.0 | 16.0 | 1.5 | 3.2 | 3.3 | 0.01 | Ta 1.5, W 2.4, Nb 0.6, Zr 0.03 |
| IN939 | 0.15 | Bal | 19 | 22.5 | - | 1.9 | 3.7 | 0.00 | W 2, Ta 1.4, Nb 1, Zr 0.09 |
| Nimonic 90 | 0.13 | Bal | 17 | 19.5 | - | 1.4 | 2.4 | - |
| Nimonic 101 | 0.01 | Bal | 19.5 | 24.2 | 1.5 | 1.5 | 2.9 | - | Nb 1 |
| Nimonic 105 | 0.20 max | Bal | 18.0-22.0 | 13.5-15.75 | 4.5-5.5 | 4.5 | 0.9-1.5 | - |
| Haynes 214 | | Bal | 16 | 4.5 | - | - | Fe 2.5, Y 0.01, |
| Mar M002 | 0.14 | Bal | 10.0 | 9.0 | 5.5 | 1.5 | - | Ta 2.5, W 10, Hf 1.5, Zr 0.05, B 0.015 |
| CMSX-4 | - | Bal | 9.0 | 6.5 | - | 5.6 | 1.0 | - | W 6.0, Re 3.0, Ta 6.5, Hf 0.1 |
| CMSX-6 | - | Bal | 5.0 | 10.0 | 3.0 | 4.8 | 4.7 | - | Ta 2.0, Hf 0.1 |
| SRR99 | - | Bal | 5.0 | 8.5 | - | 5.5 | 2.2 | - | Ta 2.8 |
The oxidation characteristics of Ni-base superalloys are traditionally classified in a simplistic manner as alumina- or chromia-forming. The early attempts to use this classification were based upon the ‘oxide-map’ formulation developed by Wallwork and Hed [14] and by Giggins and Pettit [15]. An example of this classification is shown in Figure 11. This classification is undoubtedly simplistic and in both classes of alloys more complex scales are formed however for the purposes of this review the alloys will be classified in the simple manner.

6.1 CHROMIA-FORMERS

Chromium depletion has been observed directly in a wrought Ni-base superalloy, Nimonic 90, after oxidation at 750 °C. The composition profiles observed after various times are shown in Figure 12.

Indirect evidence is also available from observation of the development of precipitate-free zones at the surface of oxidised specimens. The presence of precipitate-free zones in alloys containing low volume fractions of γ' was first observed by Betteridge and Franklin [16] and subsequently explained by Fleetwood [17] in terms of chromium depletion around chromium carbides, leading to a continuously varying γ' solvus and hence a gradation of γ' volume fraction which shows as a clear zone after chemical etching. This behaviour is confirmed in Figure 13 for a material based upon Nimonic 101 where the denuded zone can be readily observed in a specimen oxidised for 1044 h at 800 °C (Figure 13a) and the volume fraction of γ' can be seen to decrease near the specimen surface (Figure 13b); the expected volume fraction of γ' in the bulk alloys is ~24% [18].

The reduction in the volume fraction of γ' in the chromium depleted zone leads to a local decrease in strength. The weakening effect may be extensive as the influence of γ' volume fraction, f, on the stress, σ, to give a specified creep rate has been variously given [18] as:

\[ \sigma \propto A f^{1/2} - f, \quad \sigma \propto f^{1/3} \quad \text{and} \quad \sigma \propto \left( \frac{f^{1/2} - 1}{1} \right)^{1/2} \]

where A is a material constant.

The influence of γ' volume fraction on the stress to achieve a given creep rate is illustrated for all three expressions in Figure 14 where the stress is normalised at a volume fraction of 25%. A reduction of γ' volume fraction from 25% to 15% results in a reduction in stress for an equivalent creep rate of ~20%. An alternative representation is that this reduction in γ' volume fraction results in an increase in creep rate of a factor of ~2.5, assuming a ‘n value’ of 4 in the Norton Creep Law. This difference in creep rates is similar to that observed by Gibbons and Hopkins [18] for alloys containing 24% and 14.3% volume fraction of γ' during creep testing at 800 °C.
6.2 ALUMINA-FORMERS

Direct observation of the formation of zones depleted in aluminium after simple oxidation exposures has not been reported in the published literature. However depleted zones have been observed after isothermal creep tests (Figure 15). Precipitate-free zones have also been observed after thermal cycling in the single crystal alloys, SRR99, CMSX-4 and CMSX-6[19], adjacent to surface cracks formed during thermal fatigue testing. These depleted zones also show lower microhardness than the bulk alloy, indicating that they have lower strength [19].

Any zones, depleted in aluminium, that form during oxidation of Ni-base superalloys would be expected to be much weaker than the bulk alloy as aluminium is a major constituent of the main strengthening phase, γ'. The influence of reducing the aluminium content of superalloys whilst maintaining other aspects of the composition constant was investigated by Gibbons and Hopkins [18] who observed a linear relationship between the total content of hardening elements (Al, Ti and Nb) and the volume fraction of γ in a series of alloys based upon Nimonic 101. This behaviour is illustrated in Figure 16.

*Depletion of either chromium and/or aluminium may occur during oxidation of Ni-base superalloys. In both cases this results in the formation of a weak sub-surface zone.*

7 ODS MATERIAL

These materials usually consist of an iron matrix containing chromium and aluminium for corrosion resistance and a dispersoid of yttria for strength. Typical compositions of these materials are given in Table V. The oxide scale formed is normally alumina.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Al</th>
<th>Fe</th>
<th>Ni</th>
<th>(Y_2O_3)</th>
<th>Mo</th>
<th>Ti</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA760</td>
<td>20</td>
<td>6</td>
<td>-</td>
<td>Bal</td>
<td>0.9</td>
<td>2</td>
<td>-</td>
<td>3.5 W, 0.15 Zr</td>
</tr>
<tr>
<td>MA956</td>
<td>20</td>
<td>4.5</td>
<td>Bal</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>MA6000</td>
<td>15</td>
<td>4.5</td>
<td>1</td>
<td>Bal</td>
<td>1.0</td>
<td>2</td>
<td>2.2</td>
<td>2 Ta, 4 W, 0.13 Zr,</td>
</tr>
<tr>
<td>ODM751</td>
<td>16.5</td>
<td>4.5</td>
<td>Bal</td>
<td>-</td>
<td>0.5</td>
<td>1.5</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>PM1000</td>
<td>20</td>
<td>0.3</td>
<td>2.0 max</td>
<td>Bal</td>
<td>0.6</td>
<td>-</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>PM2000</td>
<td>20</td>
<td>5.5</td>
<td>Bal</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

Quadakkers et al [20] have measured the aluminium profile in ODM751 after oxidation at 1200 °C for 10400 h. They observed a uniform distribution of the element throughout the specimen thickness, Figure 17. The lack of a depleted zone is a result of the relatively rapid diffusion of aluminium in these materials and the more severe problem during oxidation of these materials is the gradual depletion of the
overall level of aluminium in the specimens leading eventually to breakaway oxidation [20].

8 INTERMETALLICS

The main intermetallic materials considered for use in high temperature applications are based upon the Ni$_3$Al, NiAl, Ti$_3$Al and TiAl systems [21]. The Ni$_x$Al systems are designed for use at temperatures 800 °C to 1300 °C, however at present little success has been achieved to develop the properties of these materials to an acceptable level for use in gas turbines and they are not expected to enter service in the near future [21]. Conversely the development of γ-TiAl materials have progressed to the stage where their introduction into service is being actively considered [21].

The oxidation of γ-TiAl is complex with both components forming stable oxides. Typical structures after oxidation >800 °C are an outer scale of TiO$_2$ and an inner scale comprising TiO$_2$ and Al$_2$O$_3$ [22]. The influence of compositional changes due to depletion of either element can be inferred by reference to the Ti-Al phase diagram [21] which is shown in Figure 18. Depletion of aluminium beneath the inner scale has been observed [23] in a TiAl material. This resulted in the formation of Ti$_2$Al in the depleted region: the kinetics of scale growth and depleted zone development are shown in Figure 19 for γ-TiAl oxidised at 900 °C. It has been observed [24] that the aluminium-depleted zones contain significant amounts of dissolved oxygen and exhibit poor mechanical properties.

9 CORROSION-RESISTANT COATINGS

These coatings are designed for corrosion-resistance rather than strength. In addition the structures are unlikely to be homogenous, particularly in the case of coatings produced by diffusion processes. The influence of oxidation on elemental depletion is likely to be complex. In addition, although depletion in chromium and/or aluminium may occur, the effect on strength is not likely to be great.

10 CONCLUSIONS

Depletion of active elements in the near-surface zone may occur during oxidation of a wide range of commercial alloys, including martensitic and austenitic steels, Ni-base superalloys and intermetallics. However there are only a limited number of cases where this de-allyed zone is significantly weaker than the substrate material viz austenitic steels strengthened by chromium carbides and in Ni-base superalloys. In other cases the de-allying of the sub-surface zone either has no effect on the strength of the material (austenitic steels strengthened by niobium carbides) or even enhances the strength of this zone (martensitic steels).
ACKNOWLEDGEMENTS

This work was carried out under the Degradation of Materials in Aggressive Environments Programme, a programme of underpinning research funded by the United Kingdom Department of Trade and Industry.

The author expresses his thanks to colleagues at NPL: Stuart Saunders for useful discussions throughout the collation of this work and to Uvais Sheriff, Diane Vincent and Gary Wright who provided experimental support.

The service-exposed materials were supplied by Len Pinder (Powergen) and Douglas Gass (Siemens Power Generation)

REFERENCES


Figure 1  The influence of alloy creep strength on growth kinetics of interfacial edge cracks in Incoloy 800, oxidised at 900 °C.

Figure 2  Elemental distribution of Cr and Mo in a 2.25Cr1Mo steel oxidised in flowing oxygen at 600 °C for 100 h (after Simms [8]).
Figure 3  Characterisation of 1Cr steel after service at ~550 °C for 100000 h
(a) SEM Secondary Electron Image (b) Elemental distribution (digimap),
(c) Hardness profile
Figure 4  Chromium depletion in 9-Cr steels after oxidation in dry air at 650 °C. (Data from Reference [10]).

Figure 5  Chromium depletion profile in a 12CrMoV turbine steel withdrawn from service after 45000 h in a steam atmosphere at 560 °C.
Figure 6  Thermodynamic calculation of the equilibrium amount of phase as a function of chromium content in E911 martensitic steel

Figure 7  Hardness Profile for E911 Specimens Oxidised in Steam at 600 °C for 500 h
Figure 8 Chromium depletion profile in Incoloy 800 after oxidation for 500 h at 900 °C
Figure 9  The influence of chromium depletion of phase equilibria in austenitic steels (a) Incoloy 800 (b) NF709
Figure 10  The influence of chromium depletion on phase equilibria in Esshete 1250

Figure 11  Oxide map/phase diagram for ternary Ni-Cr-Al system at 1000 °C
Figure 12  Chromium depletion in Nimonic 90 after oxidation for various times at 750 °C

Figure 13  Manifestation of chromium depletion in Ni-base superalloy after oxidation at 800 °C for 1044 h (a) optical micrograph (b) volume fraction of γ' as a function of distance from surface.
Figure 14 The Predicted Influence of $\gamma'$ Volume Fraction on the Stress to Achieve a given Creep Rate for Three Model Relationships

Figure 15 Optical micrographs of Ni-base superalloys after creep testing in air
(a) Nimonic 105 - 6047 h at 900 °C (b) Mar M002 - 510 h at 1040 °C