Oxidation of Alumina-forming ODS Alloys

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Outline of the Presentation

• Introduction – factors affecting the oxidation of ferritic stainless steels
• Scale growth
• Scale adhesion
• Breakaway effects
• Improvements that can be made to mitigate degradation due to oxidation
## Major constituents of some commercial FeCrAl alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Wt%</th>
<th>Ppm</th>
<th>balance Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Cr</td>
<td>Y</td>
</tr>
<tr>
<td>Aluchrom YHf</td>
<td>5.5</td>
<td>20.0</td>
<td>480</td>
</tr>
<tr>
<td>Kanthal AF</td>
<td>5.2</td>
<td>21.0</td>
<td>340</td>
</tr>
<tr>
<td>Kanthal APM</td>
<td>5.9</td>
<td>21.0</td>
<td>200</td>
</tr>
<tr>
<td>MA956 (ODS)</td>
<td>4.6</td>
<td>20.0</td>
<td>0</td>
</tr>
<tr>
<td>PM2000 (ODS)</td>
<td>5.9</td>
<td>21.0</td>
<td>0</td>
</tr>
</tbody>
</table>
Scale Growth

• Want to form protective, stable $\alpha$- alumina scale as soon as possible

• Subsequent oxide growth should be as slow as possible to conserve aluminium supply
  - Pre treatment of alloy to ensure formation of $\alpha$-alumina scale
  - Use reactive element additions to control scale growth rate
  - Add a non-ODS layer to minimize lack of compliance between oxide and substrate
  - Start with more aluminium in base alloy
Scale cross-section

50µm foil Aluchrom YHf 3000h at 900°C
A – initially formed outward growing transient alumina
B – inward growing α-alumina
Columnar growth of alumina

Model FeCrAlY alloy oxidised for 500 h at 1200°C
Scale Growth

- Can preoxidise alloys at T > 1000°C to ensure that α-alumina results – but ‘waste’ aluminium
- Work by Quadakkers et al has shown that gas annealing at 1200°C in an Ar + 4%H₂ + 2%H₂O mixture quickly gives an excellent protective scale for many alloys
- Although alloys with more than 6% Al have low ductility, extra Al can be incorporated into the finished components by a gas phase reaction followed by a diffusion treatment.
- Can modify the surface layer of the alloy by mechanical treatment or add an overlayer
- Additions of a ‘soft’ FeCrAl layer to ODS alloys appears to have a beneficial effect.
Mass change data from PM2000 slow cycle / ‘isothermal’ exposures in combustion gas at 1200°C
PM2000 + sputtered FeCrAlY + EBPVD TBC

500 hours at 1200°C in combustion gas (N₂+14%O₂+3.2%CO₂+1%Ar+5%H₂O)
Scale Adhesion

- Presence of reactive elements such as yttrium, hafnium and titanium help scale adhesion.
- Reactive elements also act as scavengers for tramp elements such as sulphur, which otherwise segregate to metal - oxide interface and affect adhesion.
- Even carbon can form chromium carbides at the scale metal interface, although may be tied up with titanium, for example.
- The build up of oxide growth stresses or accumulation of point defects at the scale metal interface can also affect adhesion.
Fe-20Cr-5Al with S<5ppm, oxidised at 1060°C for 4.5h
Auger spectrum, Fe-20Cr-5Al with S<5ppm, oxidised at 1060°C for 4.5h (in-situ bending experiment)
Oxidation of an FeCrAlY alloy with 530ppm carbon at 1200°C

Carbide growth at different cooling rates: (a) furnace cooled, (b) air cooled, (c) liquid N₂ quenched

Distortion of parallel sided coupon of Fe-20Cr-5Al alloy after oxidation for 528 h at 1050°C.
Breakaway Effects

- Lack of aluminium in sufficient quantities to reheat protective alumina scale that has fractured can lead to growth of voluminous iron and chromium rich oxides.
- Iron/chromium scale then formed offers little protection and sample quickly goes into “breakaway” oxidation.
- Related to the amount of aluminium remaining in the sample and the size of the aluminium reservoir.
SEM image of breakaway oxidation in PM2000, oxidised at 1300°C for 140h containing critical remnant aluminium concentration
Taper section sample geometry
MA956 oxidised at 1350°C for 24h.
A schematic diagram showing the cut face from which elemental profiles were recorded during the microprobe analysis.
Al profiles along wedges of Kanthal APM alloy, oxidised at 1350°C for three different times.
Wedge-shaped sample of an FeCrAl model alloy oxidised at 1300°C for 96h in laboratory air.
Time

Al Level

Possible breakaway

Upper limit for breakaway

Spalling

Al$_{\text{crit}}$

Al$_{\text{break}}$

Cr$_2$O$_3$ Formation

Time

After H. E. Evans et al.
Remnant Al content at onset of breakaway (1200°C)

AI wt% vs. Sample Reference
Control of Oxidation of ODS Alloys

- Gas annealing at $1200^\circ$C in an Ar + 4%H$_2$ + 2%H$_2$O mixture quickly forms an excellent protective $\alpha$-alumina scale for some alloys.

- Incorporate more than 6% Al into the finished components by a gas phase reaction followed by a diffusion treatment may prolong lifetime.

- Addition of a ‘soft’ FeCrAl layer to ODS alloys may have a beneficial effect on the control of scale spallation.

- Sufficient quantities of reactive elements and titanium are needed to control any tramp elements and excess carbon which may be present.
Acknowledgements

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