Compatibility of Ferritic/Martensitic Steels with Flowing Lead-Bismuth Eutectic at 450–550°C and $10^{-6}$ mass% Dissolved Oxygen

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Ferritic/martensitic (FM) steels for nuclear power plants

- Maximum temperature for 100,000 h stress rupture strength
  \[ \sigma_{RS/100,000\,h} = 100\,\text{MPa} \] according to Ennis and Czyrska-Filemonowicz (Sadhana 28[3-4], 2003, 709-730)

- **T91/P91:** ~590°C
- **E911:** ~610°C
- **T92/P92:** ~615°C

Other favourable properties in comparison to austenitic materials:
- High thermal conductivity
- Moderate thermal expansion
- Higher allowable irradiation dose
- Likely to be less prone to dissolution or embrittlement in liquid metal (important for SFR, LFR, ADS)

- Sufficient long-term resistance against degradation needs to be demonstrated for
  - Thermal ageing
  - Irradiation
  - Corrosion, i.e., coolant/steel interactions in nuclear reactors
Impact of oxygen addition to Pb alloys on steel corrosion

- Stimulation of the oxidation of steel constituents
- Formation of an oxide scale on the steel surface
- Spatial separation of the steel from liquid metal
- Reduced dissolution rate or risk of embrittlement

Steel constituents must be less noble than the constituents of the liquid metal
- Applicable to Pb, lead-bismuth
- Not applicable to lead-lithium (Pb17Li) or Na

However, thick oxide scales impair heat-transfer across the steel surface
- Practical limit of oxygen addition

Relevant to
- Lead-cooled fast reactor (LFR)
- Accelerator driven system ("Actinide Burner")

Example: T91/LBE/550°C
Activities at KIT/IAM-WPT related to ADS and LFR

- Long-term corrosion in oxygen-containing lead-bismuth eutectic (LBE)
  - At a flow velocity of 2 m/s
  - $T = 450–550^\circ C$
  - $c_O = 10^{-7}–10^{-6}$ mass%

- Creep-to-rupture in oxygen-containing Pb alloys
  - Static Pb or LBE
  - $T = 450–650^\circ C$
  - $c_O = 10^{-7}–10^{-6}$ mass%

- Instruments and methods of oxygen control in Pb alloys
  - Via oxygen-containing gas (gas/liquid oxygen transfer)
  - Oxygen sensors
# FM steels tested in the CORRIDA loop

## Concentration (in mass%) of alloying elements other than Fe

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>V</th>
<th>Nb</th>
<th>Ta</th>
<th>Y</th>
<th>Mn</th>
<th>Ni</th>
<th>Si</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91-A</td>
<td>9.44</td>
<td>0.850</td>
<td>&lt;0.003</td>
<td>0.196</td>
<td>0.072</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.588</td>
<td>0.100</td>
<td>0.272</td>
<td>0.075</td>
</tr>
<tr>
<td>T91-B</td>
<td>8.99</td>
<td>0.89</td>
<td>0.01</td>
<td>0.21</td>
<td>0.06</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.38</td>
<td>0.11</td>
<td>0.22</td>
<td>0.1025</td>
</tr>
<tr>
<td>E911*</td>
<td>8.50–9.50</td>
<td>0.90–1.10</td>
<td>0.90–1.10</td>
<td>0.18–0.25</td>
<td>0.060–0.100</td>
<td>–</td>
<td>–</td>
<td>0.30–0.60</td>
<td>0.10–0.40</td>
<td>0.10–0.50</td>
<td>0.09–0.13</td>
</tr>
<tr>
<td>EUROFER</td>
<td>8.82</td>
<td>&lt;0.0010</td>
<td>1.09</td>
<td>0.20</td>
<td>n.a.</td>
<td>0.13</td>
<td>n.a.</td>
<td>0.47</td>
<td>0.020</td>
<td>0.040</td>
<td>0.11</td>
</tr>
<tr>
<td>EF-ODS-A</td>
<td>9.40</td>
<td>0.0040</td>
<td>1.10</td>
<td>0.185</td>
<td>n.a.</td>
<td>0.08</td>
<td>0.297†</td>
<td>0.418</td>
<td>0.0670</td>
<td>0.115</td>
<td>0.072</td>
</tr>
<tr>
<td>EF-ODS-B</td>
<td>8.92</td>
<td>0.0037</td>
<td>1.11</td>
<td>0.185</td>
<td>n.a.</td>
<td>0.078</td>
<td>0.192†</td>
<td>0.408</td>
<td>0.0544</td>
<td>0.111</td>
<td>0.067</td>
</tr>
</tbody>
</table>

* Nominal composition
† In the form of yttria (Y₂O₃)

## Microstructure

- **Fully martensitic:** E911, T91-A, T91-B
- **Mainly ferritic:** ODS-A, ODS-B

Nominally 9 mass% Cr

Elements besides Cr that are likely to improve oxidation performance

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*Corrosion Department*

**Institute for Applied Materials – Material Process Technology (IAM-WPT)**

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Exposure to flowing LBE (1)

T91-A, T91-B, E911, EF-ODS-A, EF-ODS-B

- T = 450(+5)°C, 
  $c_O = 1.1 \times 10^{-6}$ mass%, 
  $v = 2(+/–0.2)$ m/s, 
  $t \leq 8000$ h

- T = 550(+5)°C, 
  $c_O = 1.4 \times 10^{-6}$ mass%, 
  $v = 2(+/–0.2)$ m/s, 
  $t \leq 20,000$ h, 
  except for T91-B

- T91-B: 
  T = 550(+5)°C, 
  $c_O = 1.6 \times 10^{-6}$ mass%, 
  $v = 2(+/–0.2)$ m/s, 
  $t \leq 15,000$ h
Exposure to flowing LBE (2)

**EUROFER**
- $T = 550(+5)\, ^\circ\text{C}$,
- $c_O = 1.3–2.3 \times 10^{-6}$ mass%,
- $v = 1.8(+/-0.5)\, \text{m/s}$,
- $t \leq 7500\, \text{h}$
Oxidation of F/M steels in flowing LBE at 450–550°C:
Protective scaling

- Formation of a thin Cr-rich oxide scale
  - Probably chromia (Cr$_2$O$_3$)
  - Negligible scale growth or metal recession
- Either a local or short-term phenomena at 9% Cr
  - Rarely observed for E911 at 450°C
  - Remnants found in considerably thicker oxide scale on T91 at 550°C
- Thin scale forms more frequently or is more persistent for EF-ODS at 450°C and especially at 550°C
- Protected domains present on EUROFER at 550°C after longest exposure time (7500 h)
- Fine-grained microstructure is likely to be decisive rather than slightly different Cr content
Oxidation of F/M steels in flowing LBE at 450–550°C: Accelerated oxidation

- The formed scale typically consists of three layers:
  - Magnetite (Fe₃O₄) at the interface with the LBE
  - Cr-deficient spinel, i.e., Fe(FeₓCr₁₋ₓ)₂O₄
  - Internal oxidation zone (IOZ)

- Magnetite is usually missing at 550°C/10⁻⁶ mass% O
- Fe dissolution instead of magnetite formation

- Internal oxidation is negligible at 450°C/10⁻⁶ mass% O, except for EF-ODS

- Likely to start where the thin protective scale did not form or lost integrity
  - Cr enrichment at Fe₃O₄ / Fe(FeₓCr₁₋ₓ)₂O₄ interface
  - Oxide filled pits or irregular scale thickness where growing pits abutted onto each other

Images show:
- Steel E911 after exposure for 5012 h at 550°C
- E911 after exposure for 8039 h at 450°C
- T91-A after exposure for 1200 h at 550°C and 10⁻⁵ < cₒ/mass% < 10⁻⁶
Oxidation of F/M steels in flowing LBE at 450–550°C: Direct liquid-metal attack

- After accumulation of LBE underneath the oxide scale
  - May occur for both the thin and thicker scale
  - Different outcome depending on oxide scale composition or structure
  - Observed only once at 450°C, for E911 after 8039 h
  - Occurred more frequently at 550°C than at 450°C
  - EUROFER seems to be especially prone to direct liquid-metal attack at 550°C (under certain conditions)

- Substantial local loss of material
  - E911: ~125 µm after 8000 h at 450°C
  - EUROFER: ~200 µm after 3000 h at 550°C
  - T91- A, -B: ~200 and 150–175 µm, respectively, after 15,000 h at 550°C
  - EF-ODS-B: ~60 µm after 15,000 h at 550°C
  - Depends not only on the corrosion rate but also on incubation time

- Potentially initiated by, e.g.,
  - Open porosity of the oxide scale
  - Local scale detachment
  - Cracking of the scale

  After exposure at 550°C for
  - (top) 15,028 h
  - (middle) 7518 h
  - (bottom) 3000 h
Quantification of accelerated oxidation in flowing LBE: At 450°C, 10^{-6} mass% O, 2 m/s

- Results from measurements in the microscope
- Comparatively large scatter in the data for metal recession
- Data indicates slower-than-parabolic oxidation kinetics for metal recession, magnetite and spinel growth
- Rate laws were derived on the basis of the general power law
  \[ \Delta x^n = k_n t + C_n \]
- Corrosion rate decreases with increasing Cr content for same type of steel
  - T91-A/T91-B
  - EF-ODS-A/EF-ODS-B
Quantification of accelerated oxidation in flowing LBE: At 550°C, 10^{-6} mass% O, 2 m/s

- Increase in corrosion rate by factor 2–3 in comparison to 450°C
- Absolute difference between materials increases
- Scatter in the data increases
- Data indicates slower-than-parabolic oxidation kinetics for metal recession and spinel growth
- Scatter and missing data for <5000 h aggravates the analysis of the kinetics
- EUROFER and especially EF-ODS perform slightly better than T91 or E911
- Mainly an effect of fine-grained microstructure
Summary

- F/M steels with 9%Cr show three stages of oxidation in flowing LBE at 450–550°C, 10⁻⁶ mass% dissolved oxygen, 2 m/s
  - Protective scaling – short term or local phenomenon
  - Accelerated oxidation – the general degradation mechanism
  - Direct liquid-metal attack – locally, after accumulation of liquid metal underneath the oxide scale
- Fine-grained microstructure rather than (slightly) higher Cr content promotes protective scaling
- Average rate of accelerated oxidation is lower
  - For higher Cr-content at 450°C
  - For fine-grained materials at 550°C
- Observed kinetics of accelerated oxidation is slower than parabolic
  - Corrosion rate increases by factor 2–3 for increase in temperature from 450 and 550°C
- Liquid metal attack shows
  - Different outcome depending on the actually formed oxide scale
  - High local material loss in comparison to accelerated oxidation, e.g., increase by factor 10 for EUROFER at 550°C and E911 at 450°C, by factor 3–5 for T91 and EF-ODS at 550°C
Acknowledgements

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