CORROSION OF STRUCTURAL MATERIALS BY LIQUID METALS USED IN FUSION, FISSION AND SPALLATION

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Corrosion issues in liquid metals

- **Liquid metal embrittlement**
  Process resulting in a loss of toughness or/and ductility

- Solid metal/liquid metal reactions
  No intermetallic compounds between Li, Na, Pb, Bi and Fe, Cr or Ni

- Reaction with liquid metal impurities
  - **Oxidation**
  - Carburation, nitruration, …

- **Dissolution**

- Corrosion-erosion

- Transfer processes
  (non-isothermal systems)

Liquid metal embrittlement of martensitic T91 steel by lead and lead-bismuth
From A. Legris & al., JMN 301 (2002) 70-76
Corrosion of structural materials by liquid metals used in fusion, fission and spallation

- Background
- Liquid metal embrittlement
- Oxidation
- Dissolution
A ductile metal experiences a drastic loss in tensile elongation and/or becomes brittle when exposed to liquid metal.

Embrittlement is specific to a pair (solid/liquid metals).

Mechanisms: based on intergranular sensitization (liquid metal, oxygen...)

Main factors:
- Wetting
- Temperature
- Irradiation
- Solid metal microstructure
- Liquid metal impurities (oxygen)

Lead-bismuth embrittlement on T91 steel between 150°C and 500°C
From B. Long & al., JMN 377 (2008) 219-224
- A ductile metal experiences a drastic loss in tensile elongation and/or becomes brittle when exposed to liquid metal
- Embrittlement is specific to a pair (solid/liquid metals)
- Mechanisms: based on intergranular diffusion of the liquid metal
- Main factors
  - Wetting
  - Temperature
  - Irradiation
  - Solid metal microstructure
  - Liquid metal impurities

Lead-bismuth embrittlement on irradiatedT91 steel, From B. Long& al., JMN 431 (2012) 85-90
In liquid sodium

- **Austenitic steels**

Creep strength of 304 austenitic steel in air and in pure sodium (O<10 ppm)
From E. Yoshida & T. Furukawa in Nuclear corrosion science and engineering, 2012 (chap. 21)

- **Ferritic steels**

Stress strain curves of low chromium ferritic steel in air and in liquid sodium
From C. Richet & D. Féron in corrosion and alteration of nuclear materials, Den monography, 2010

*Fig. 4. Comparison of the force versus cross-head displacement of tensile tests of T91 steel at 573 K and 2.5 × 10^{-7} m s^{-1} in sodium. “T91 Na” stands for test in low saturated sodium, and “T91 Ar” stands for test in argon of vacuum aged specimen (48 h at 723 K).*
In liquid lithium

- Austenitic steels

Stress strain curves in air and in liquid lithium at 200°C including pre-exposed specimens in liquid lithium (1000h, 550°C) *

* From Borgsted & Grundmann, Nuclear engineering & design, 1986, 273-286

After pre-exposure in liquid lithium (550°C), austenitic and ferritic steels exhibit some susceptibility at 200-250°C in liquid lithium
Liquid metal embrittlement

- Ferritic/martensitic steels, including ODS,
  - are susceptible in lead and its alloys (PbLi and PbBi)
  - some susceptibility observed in sodium and in lithium at low temperatures

- Austenitic stainless steels
  - Some susceptibility observed at low temperature in liquid lithium
  - Low (negligible?) susceptible in lead and its alloys (PbLi and PbBi)
  - No susceptibility in “pure” liquid sodium

- Comments
  - LME Susceptibility ?
  - LME mitigation ?
  - Safety issues
Corrosion of structural materials by liquid metals used in fusion, fission and spallation

- Background
- Liquid metal embrittlement
- Oxidation
- Dissolution
Structural materials: mainly steels and nickel based alloys

Ellingham diagram

Lead and its alloys: function of the oxygen content

Sodium: reducing env., only aluminum & chromium oxides

Lithium: very reducing env.
Corrosion modeling
- Spinel interface
- Magnetite interface

Porosities in magnetite: lead penetrations 20 µm

Localised corrosions

Fe$_3$O$_4$

Fe$_{3-x}$Cr$_x$O$_4$
Where does the growth occur?
- interface oxide/liquid: cationic growth
- interface metal/oxide: anionic growth
Steel / lead-bismuth system
Localisation of the interfaces where oxide growth occurs

1- Oxidation in Pb-Bi saturated with $^{16}$O-$^{18}$O at 470°C
2- Oxidation in Pb-Bi saturated with $^{16}$O at 470°C
Corrosion of T-91 (ferritic steel) in liquid lead or liquid lead-bismuth

Uniform corrosion rates increase with the oxygen content (no protective effect of the oxide), with the temperature and with the flow rate in liquid sodium.
Steel behavior in liquid metals with dissolved oxygen (oxidizing conditions)

- In lead and its alloys (Pb and PbBi)
  - Formation of oxides which may have protective properties
  - High chromium steels improved the corrosion resistance
  - Strict range of oxygen concentration
  - Stability of the oxide layers is needed (flowrate)
  - Mitigation: coatings (typically Al₂O₃) or steels with aluminum to form a self-healing protective layer

- In liquid sodium
  - Formation of non-protective oxide
  - Full understanding of the effect of oxygen still to be completed
  - Increase of the corrosion rates with temperature, oxygen & flow

*(no oxidation in lithium and lead-lithium alloy)*
## Solubility of the main alloying elements at 500°C

<table>
<thead>
<tr>
<th>Liquid metal</th>
<th>Fe ppm</th>
<th>Cr ppm</th>
<th>Ni ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>4</td>
<td>4</td>
<td>200</td>
</tr>
<tr>
<td>Na(^{(1)})</td>
<td>0.25</td>
<td>0.005</td>
<td>1.1</td>
</tr>
<tr>
<td>Pb</td>
<td>0.77</td>
<td>0.10</td>
<td>31 000</td>
</tr>
<tr>
<td>Pb-17Li</td>
<td>1.1</td>
<td>0.1-10</td>
<td>3600</td>
</tr>
<tr>
<td>Pb-Bi</td>
<td>30</td>
<td>150</td>
<td>25 000</td>
</tr>
</tbody>
</table>

From F. Balbaud-Célérier & al., Techniques de l’ingénieur, COR640 V1, 2013

### High solubility of Ni => Nickel based alloys not suitable

Steels (ferritic/martensitic/austenitic): main structural alloys
Austenitic stainless steel in liquid sodium (low oxygen content) formation of a ferrite film at the surface (ferrite/ferrite and austenite /Sound austenite)
Corrosion in liquid metals dissolution

Same observations on austenitic stainless steel in reducing liquid metal conditions: preferential dissolution of nickel

**Fig. 23** Corrosion of type 316 stainless steel exposed to thermally convective lithium for 7400 h at the maximum loop temperature of 600 °C (1112 °F). (a) Light micrograph of polished and etched cross section. (b) SEM showing the top view of the porous surface. Source: Ref 6

Immersion de 316L ds Pb-Bi
T = 500 °C – t = 3045h
COLIIMESTA – test statique
Faible teneur en O

Immersion de 316 ds Pb-17Li en circulation
T = 455 °C – t = 1400h
Chopra, Tortorilli, JNM 122-123 (1984) 1201

304 ds Na T = 550 °C – t = 60000h T = 600 °C – t = 20000h CREVONA loop (KIT) Ganesan et al., JNM 312 (2003) 174
Steels behavior in liquid metals in reducing conditions

- Preferential dissolution of nickel
- Large influences of flow, temperature and chemistry
- In lead and its alloys (PbLi and PbBi)
  - Dissolution rates generally quite high (ferritic and austenitic steels)
  - Mitigation: coatings (typically \( \text{Al}_2\text{O}_3 \))
- In liquid sodium
  - Acceptable dissolution rates (ferritic and austenitic steels)
  - Investigations for modelling & simulation
- In liquid lithium
  - Other alloys under consideration (vanadium/niobium)

*(transfer process –dissolution/precipitation- in non-isothermal circuits)*
Application
Fusion, fission and spallation

Limits of Use
Steels (nickel alloys not suitable).
The influence of impurities in the liquid metals needs more consideration.

Main Radiation Effects
Irradiation effects are not discussed

Research Details
Mainly based on experiments

Major Issues and Challenges
Long term issues (prediction of corrosion performances over 40-60 years)

Coolant Processing and Handling
Experimental difficulties linked to the experimental conditions (high temperature, chemical hazards, toxicity...).
Modelling and simulation under development.

Others

In liquid sodium, corrosion phenomena, including liquid metal embrittlement are considered under control (austenitic SS).

In liquid lead and its alloys, corrosion issues may need mitigation strategies (steels).

More investigations in liquid lithium (embrittlement & dissolution)

Achievement
Corrosion phenomena & mechanisms

R&D Needs
– Experimental (parameters)
– Modeling & simulation
– Mitigation
Thank you

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