

FROM RESEARCH TO INDUSTRY



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

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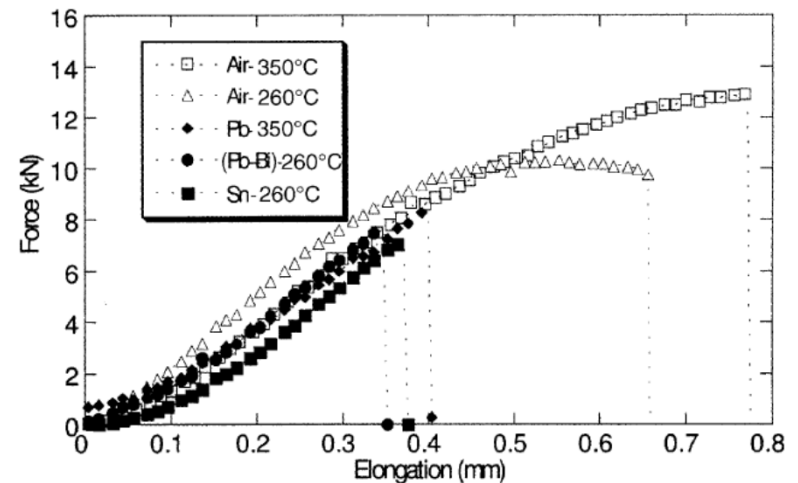
1st IAEA workshop on

« **Challenges for coolants in fast spectrum system: chemistry and
materials** »

Vienna, 5th-7th July, 2017 |

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, nitration, ...
- **Dissolution**
- Corrosion-erosion
- Transfer processes
(non-isothermal systems)



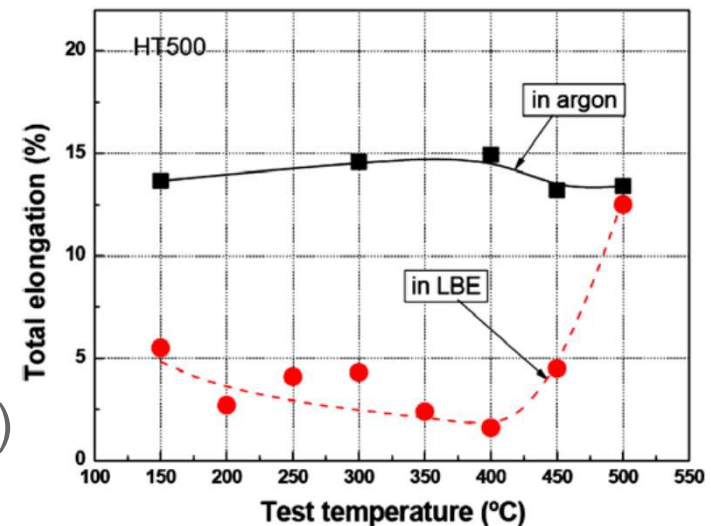
Liquid metal embrittlement of martensitic T91 steel by lead and lead-bismuth

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

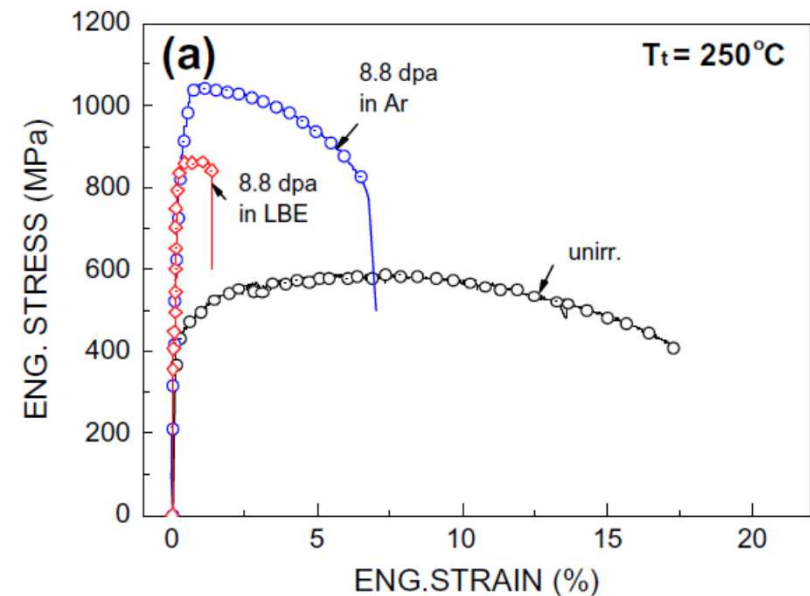
- A ductile metal experiences a drastic loss in tensile elongation and/or becomes brittle when exposed to liquid metal
- Embrittlement is specific to a pair (solid/liquid metals)
- Mechanisms: based on intergranular sensitization (liquid metal, oxygen...)
- Main factors
 - Wetting
 - **Temperature**
 - 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



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

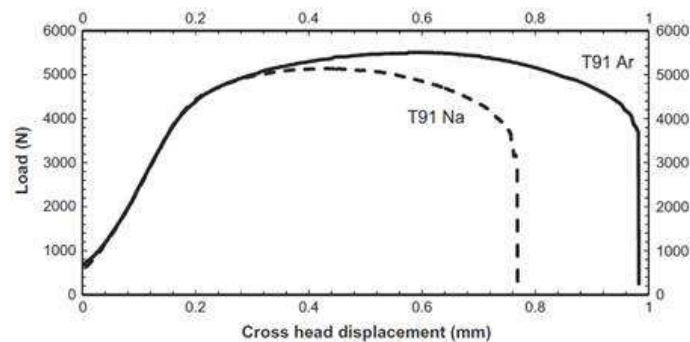
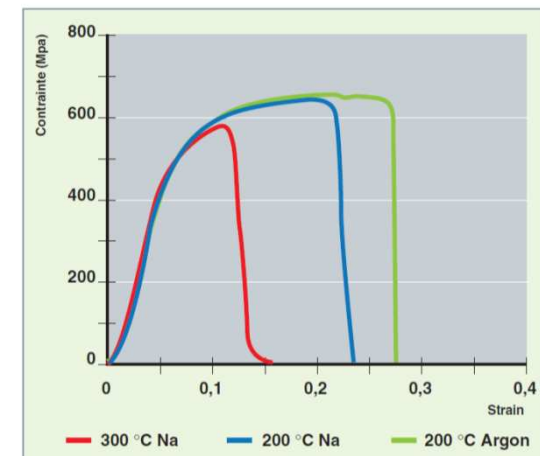
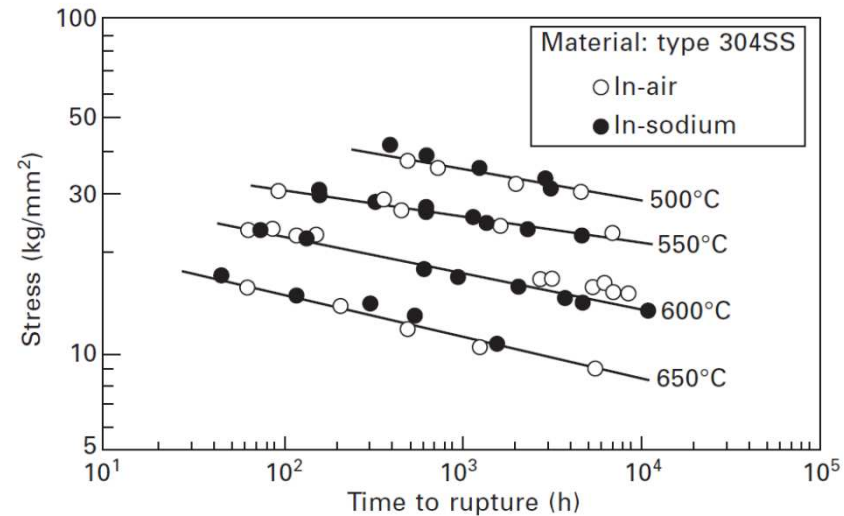


Fig. 4. Comparison of the force versus cross-head displacement of tensile tests of T91 steel at 573 K and $2.5 \times 10^{-7} \text{ m s}^{-1}$ in sodium. "T91 Na" stands for test in low saturated sodium, and "T91 Ar" stands for test in argon of vacuum aged specimen (48 h at 723 K).

From Hémy, S. & al., 2013, Corrosion Science 76, 441–452.



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

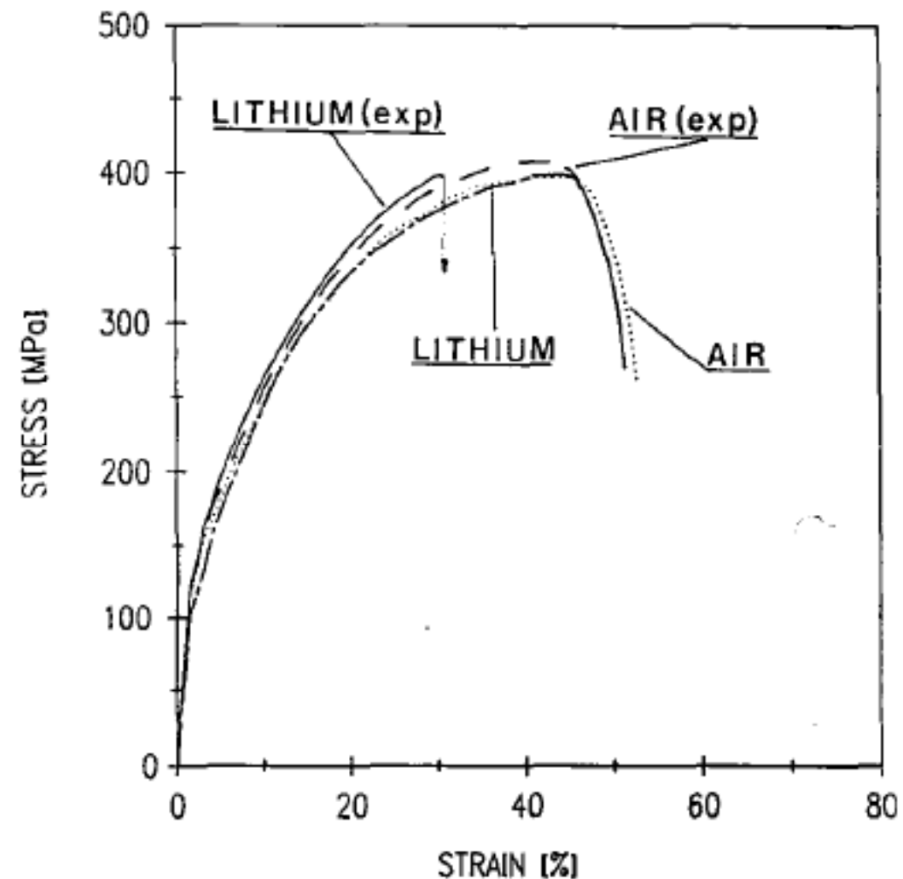
In liquid lithium

- 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

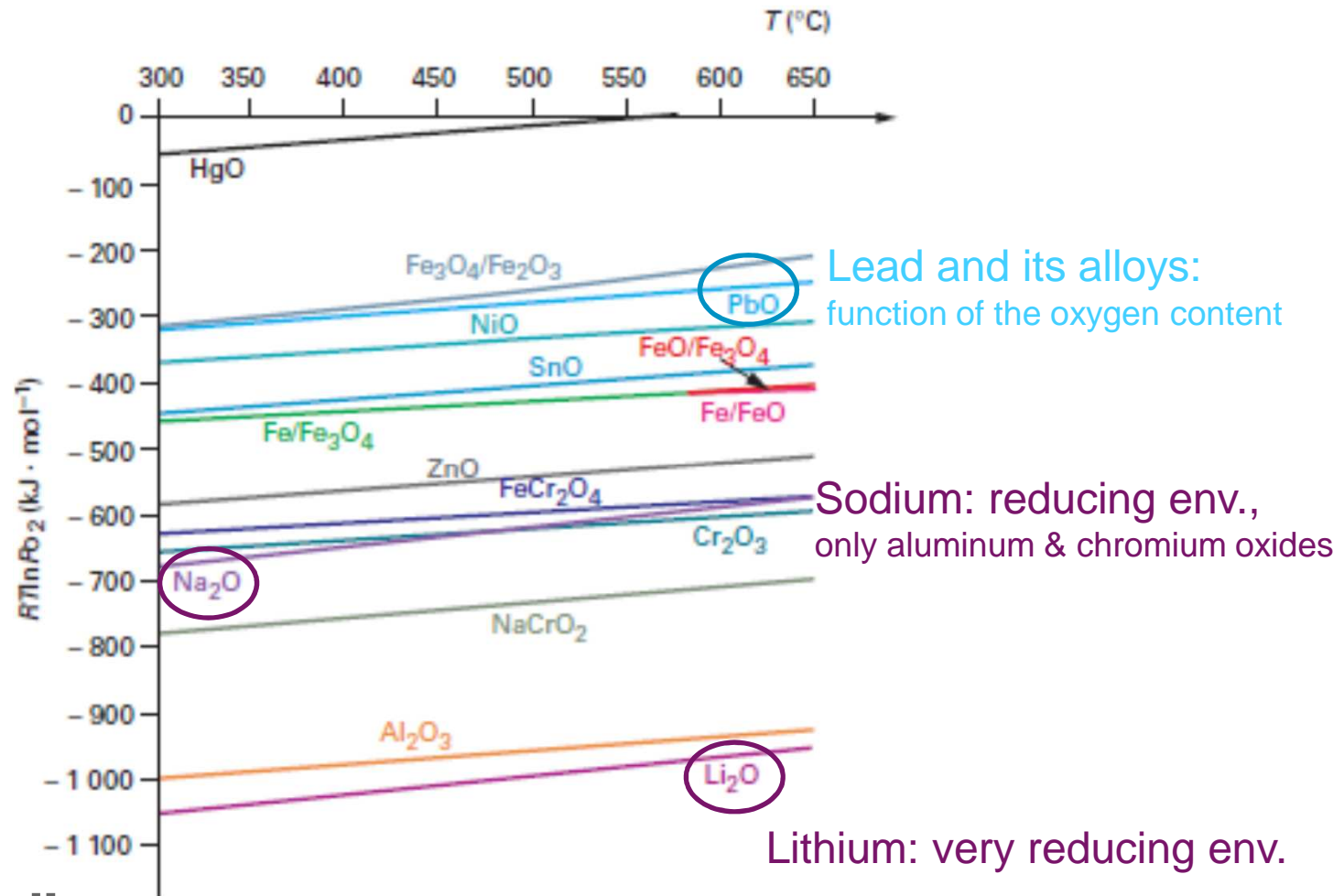
- Ferritic/martensitic steels, including ODS,
 - are **susceptible in lead and its alloys** (PbLi and PbBi)
 - some susceptibility observed in sodium and in lithium at low temperatures
- Austenitic stainless steels
 - Some susceptibility observed at low temperature in liquid lithium
 - Low (negligible?) 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

Corrosion in liquid metals oxidation

Structural materials: mainly steels and nickel based alloys



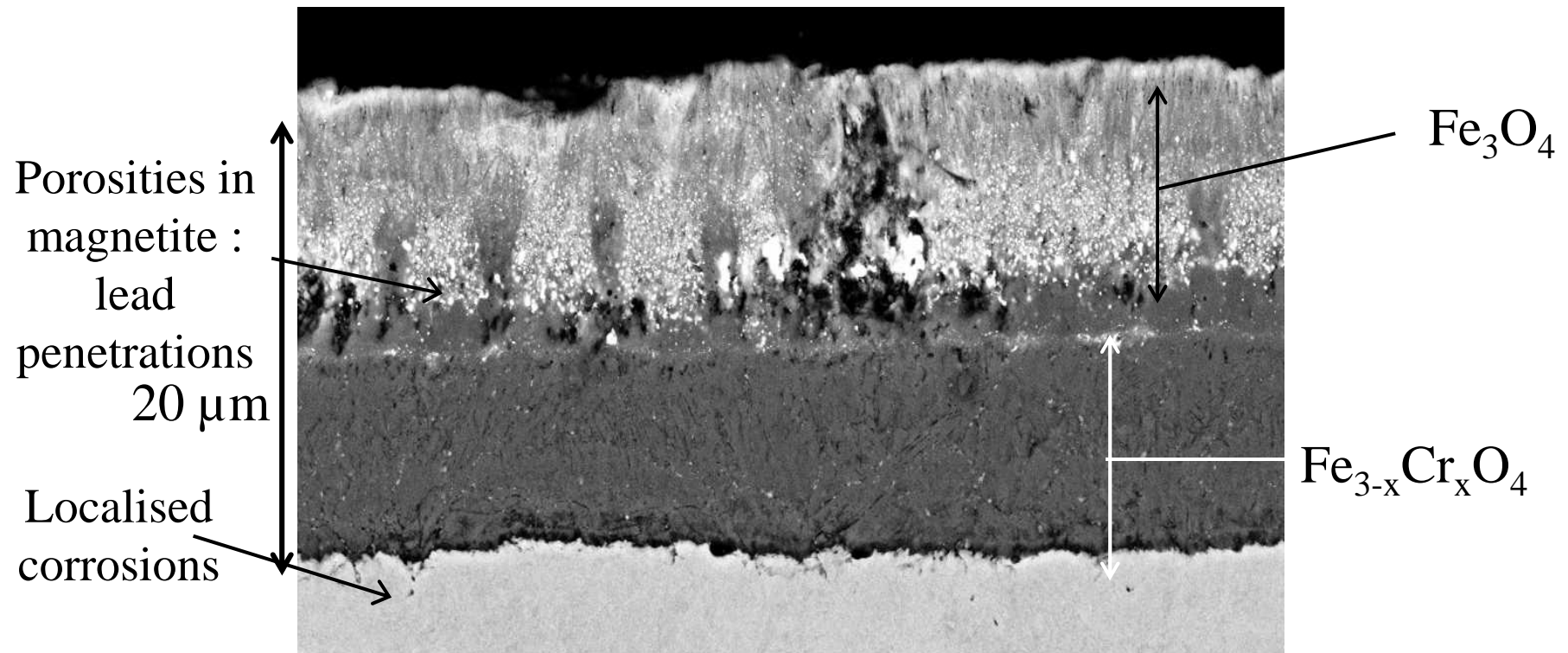
Ellingham diagram

Corrosion in liquid metals oxidation

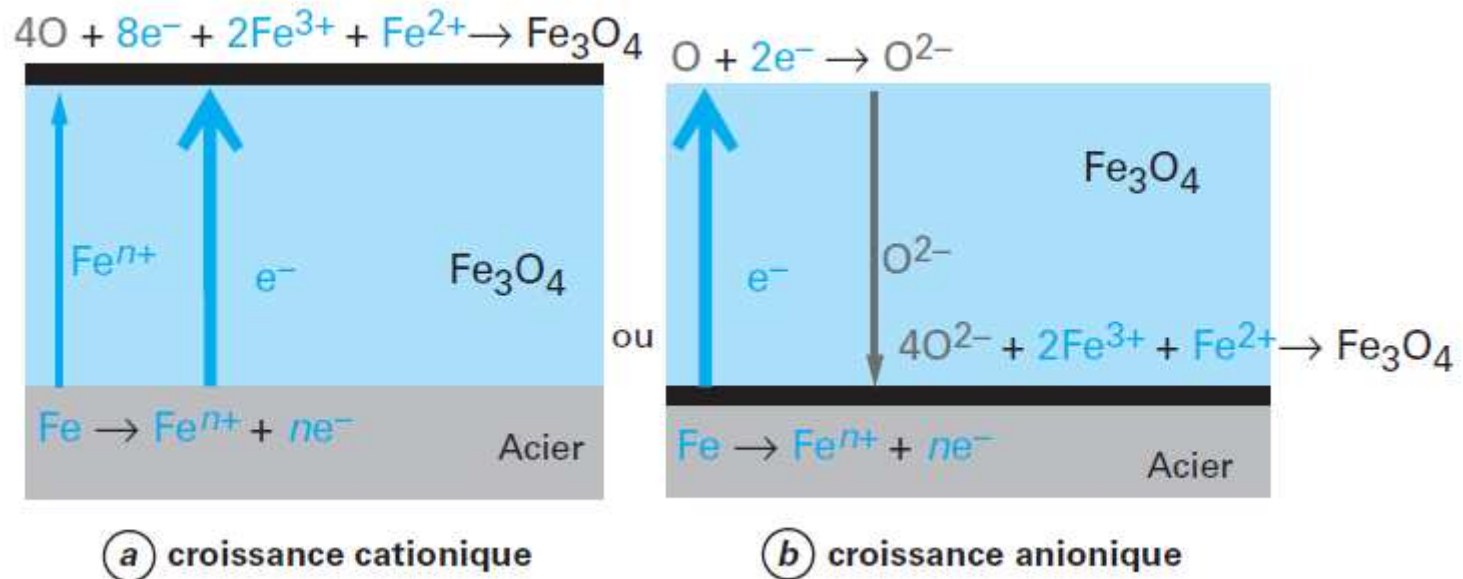
CORROSION IN LIQUID LEAD-BISMUTH SATURATED WITH OXYGEN

Corrosion modeling

- Spinel interface
- Magnetite interface



Corrosion in liquid metals oxidation



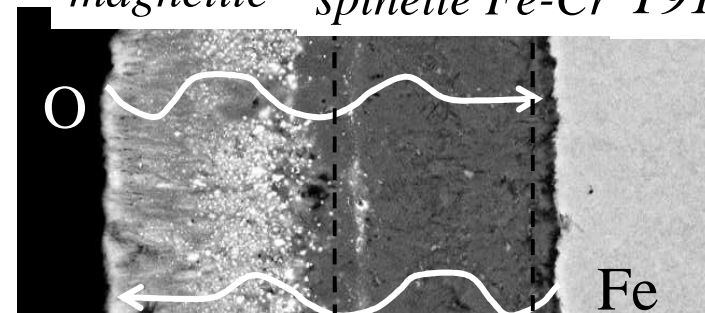
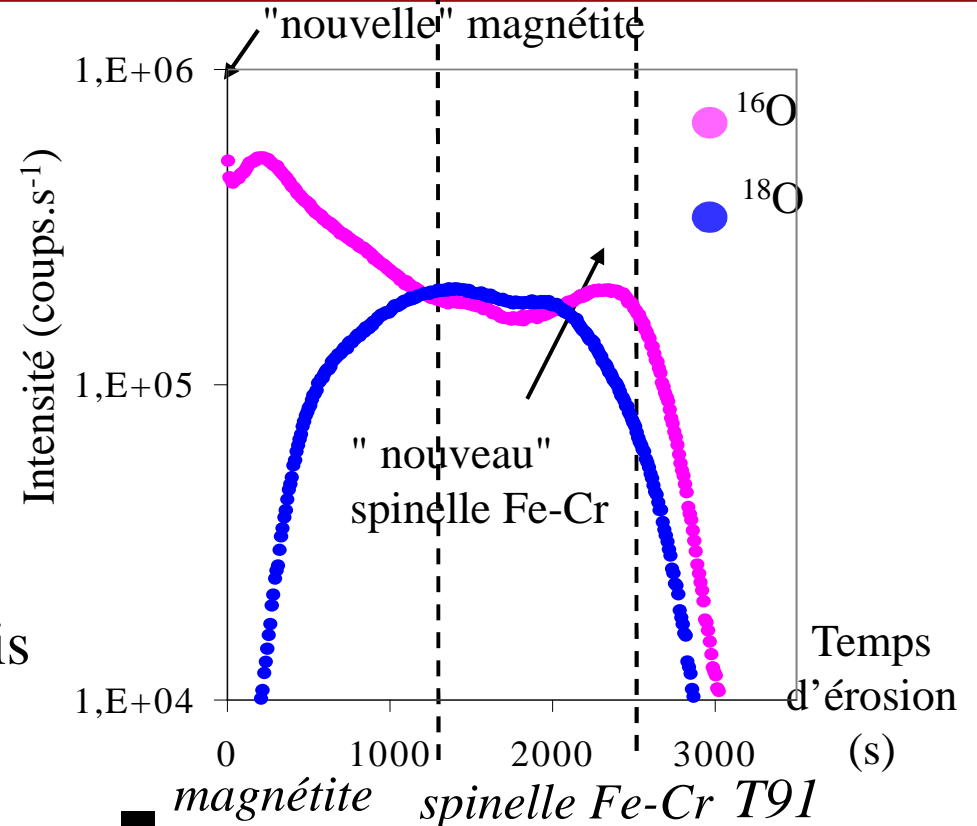
- Where does the growth occur?
- interface oxide/liquid : cationic growth
 - interface metal/oxide : anionic growth

Corrosion in liquid metals oxidation

Steel / lead-bismuth system
Localisation of the interfaces
where oxide growth occurs



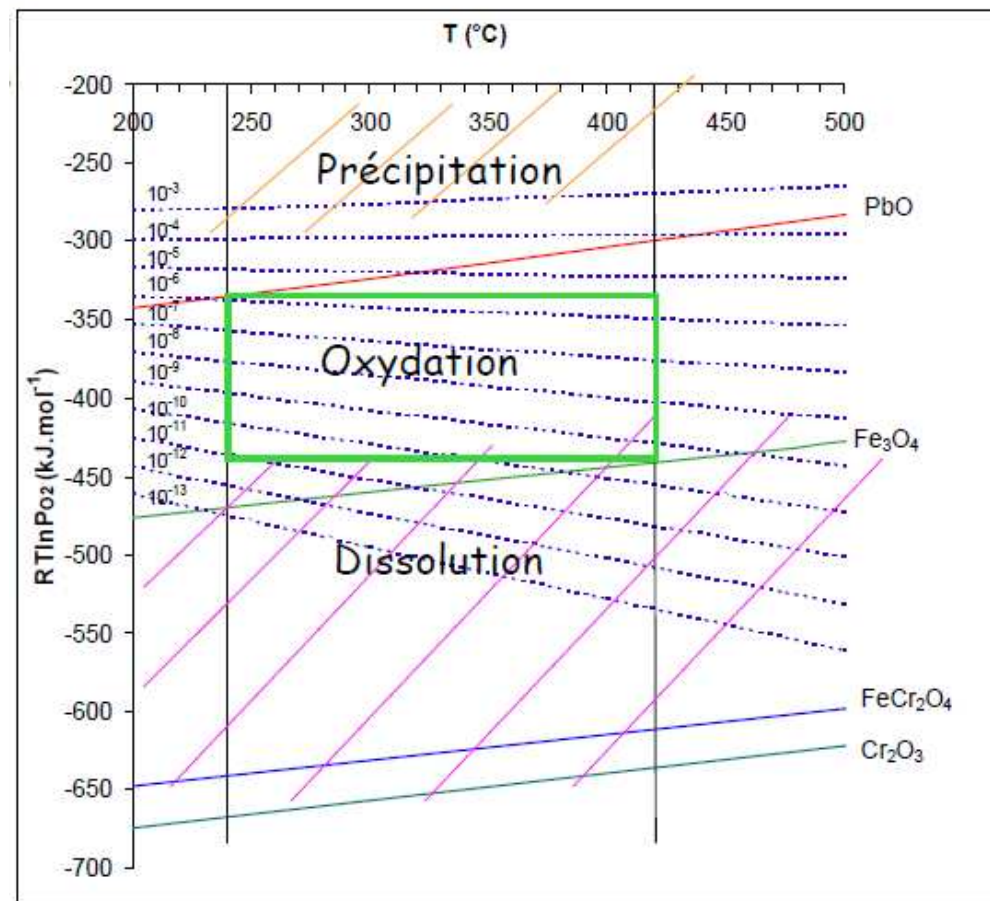
→ SIMS
analysis



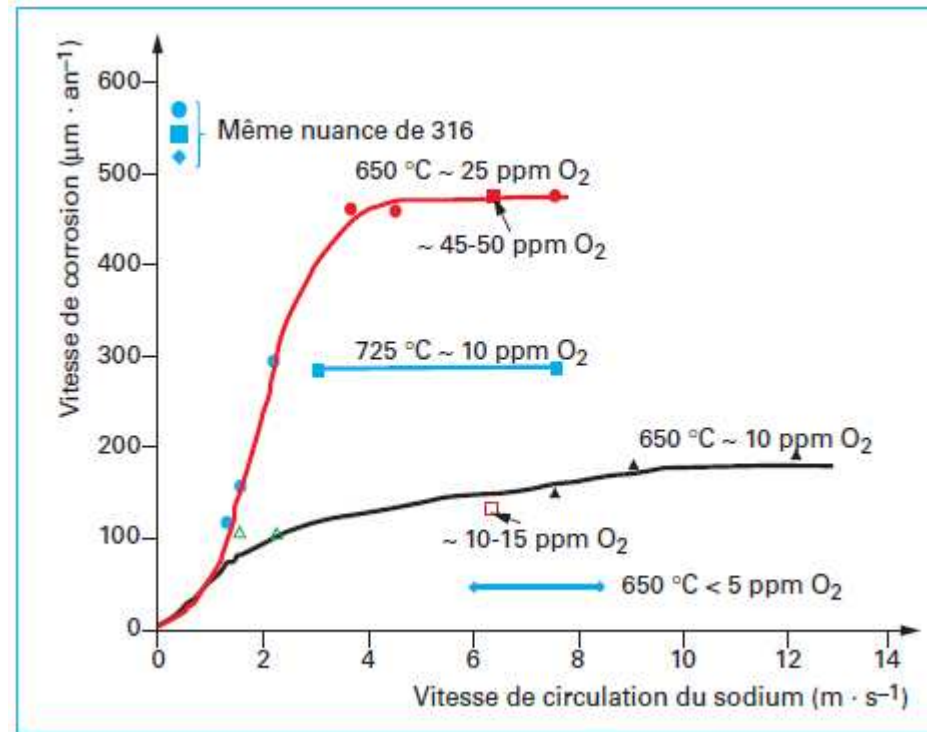
1- Oxidation in Pb-Bi saturated
with ¹⁶O-¹⁸O at 470°C

2- Oxidation in Pb-Bi saturated
with ¹⁶O at 470°C

Corrosion of T-91 (ferritic steel) in liquid lead or liquid lead-bismuth



Corrosion in liquid metals oxidation



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

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

Steels 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 Al_2O_3) 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)

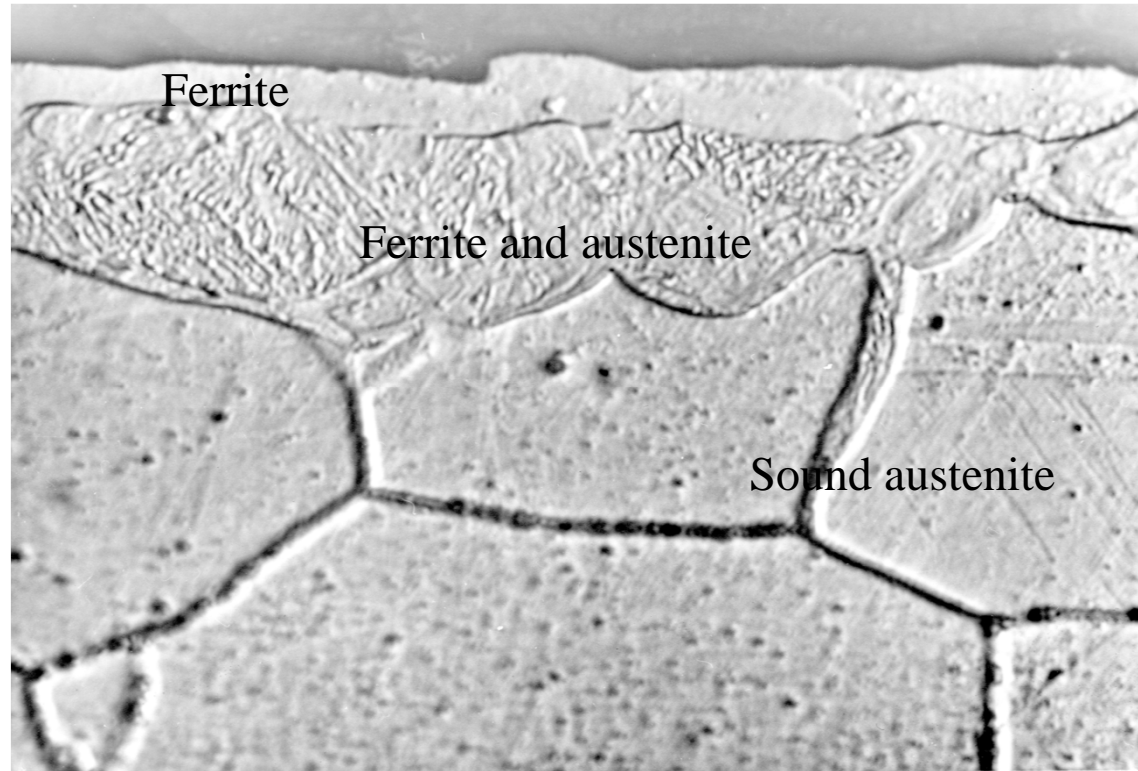
Solubility of the main alloying elements at 500°C

Liquid metal	Fe ppm	Cr ppm	Ni ppm
Li	4	4	200
Na ⁽¹⁾	0.25	0.005	1.1
Pb	0.77	0.10	31 000
Pb-17Li	1.1	0.1-10	3600
Pb-Bi	30	150	25 000

From F. Balbaud-Célérier & al., Techniques de l'ingénieur, COR640 V1, 2013
Handbook on Lead-bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal-hydraulics and Technologies », OECD/NEA, 2007
(1) Borgstedt, H.U., Mathews, C.K., 1987. Applied chemistry of the alkali metals. Plenum Press, New-York

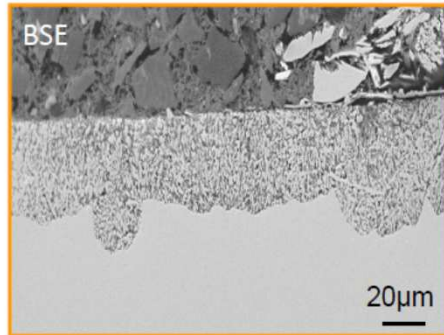
High solubility of Ni => Nickel based alloys not suitable

Steels (ferritic/martensitic/austenitic): main structural alloys

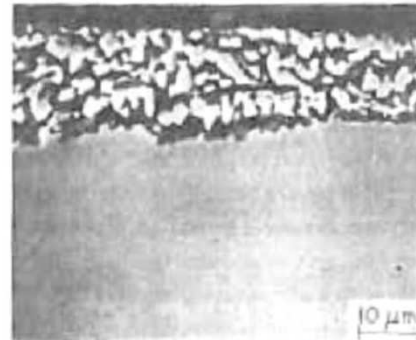


Austenitic stainless steel in **liquid sodium** (low oxygen content)
formation of a ferrite film at the surface
(ferrite/ferrite and austenite /Sound austenite)

Corrosion in liquid metals dissolution



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



Immersion de 316 ds Pb-17Li
en circulation
T = 455°C – t = 1400h
Chopra, Tortorelli, 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

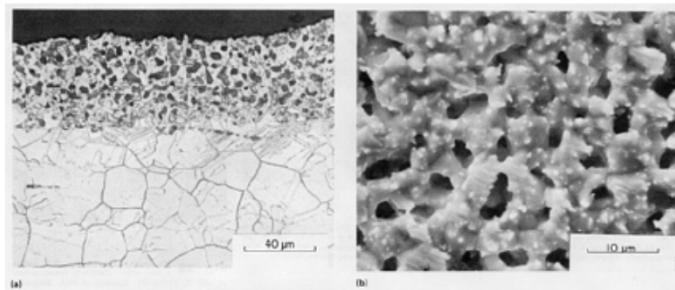


Fig. 23 Corrosion of type 316 stainless steel exposed to thermally convective lithium for 7488 h at the maximum loop temperature of 600 °C (1110 °F). (a) Light micrograph of polished and etched cross section. (b) SEM showing the top view of the porous surface. Source: Ref 6

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

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 Al_2O_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)

Corrosion in liquid metals

Conclusive remarks

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

Acknowledgements to our colleagues of the
CEA « Corrosion department »

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