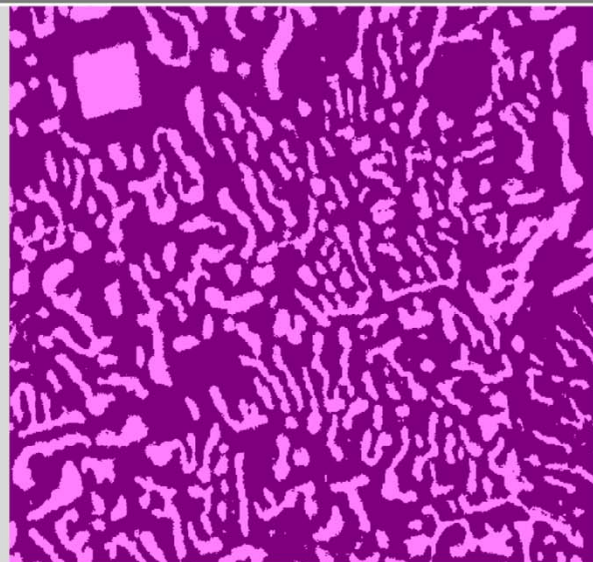


CORROSION CAUSED BY LIQUID LEAD OR LEAD ALLOYS – OVERVIEW

Carsten Schroer

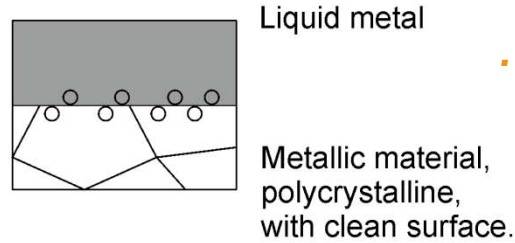
INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS (IAM-AWP)



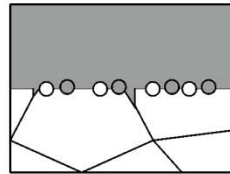
Metallic solid material in contact with liquid metal

Steel, refractory metals, ...

... lead or lead alloys

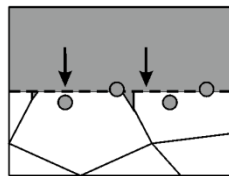


Physical interactions

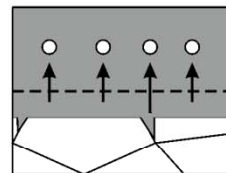


Adsorption at interface, interactions at near-surface defects, grain boundary grooving, ...

Possible reasons for degraded mechanical properties.



Transfer of elements from the liquid to the solid metal (at comparatively low mobility in the solid phase).

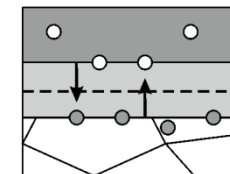


Solution of the solid metal!

Transfer of material elements to the liquid metal, limited by global saturation of the liquid.

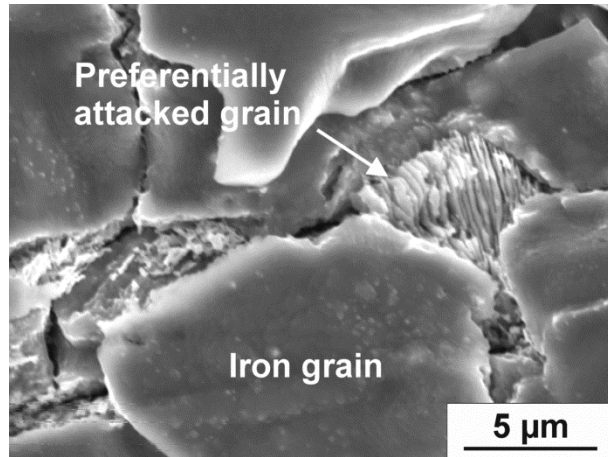
Noticable recession of the material surface or loss of material.

'Chemical reaction'

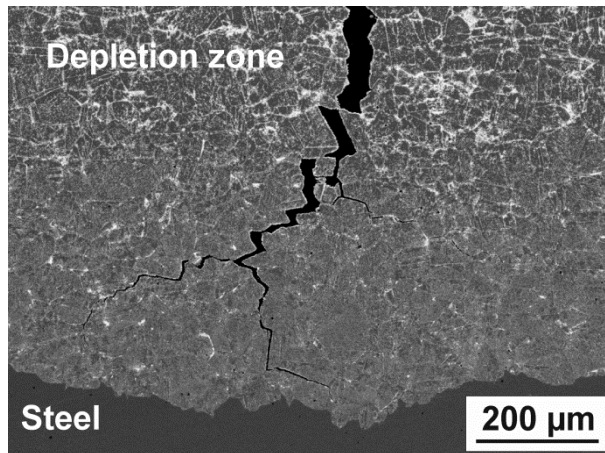


Formation of intermetallic compound, if stable and liquid metal locally saturated.

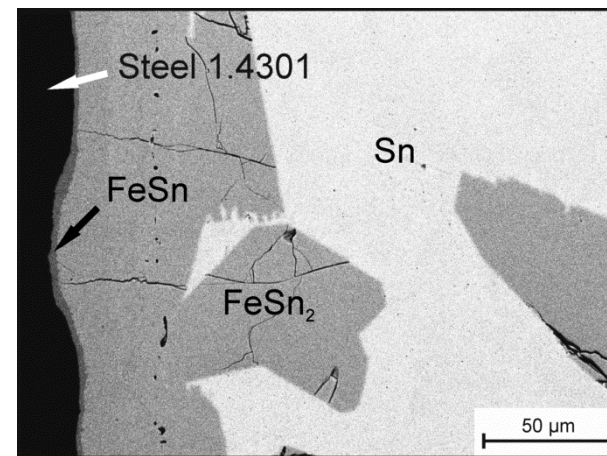
Solution and formation of intermetallics



Surface of technically pure iron after solution caused by flowing lead–bismuth eutectic at 400 °C^[1].



Selective leaching of nickel from the tubing of the CORRIDA loop (austenitic steel, lead–bismuth eutectic)^[2].



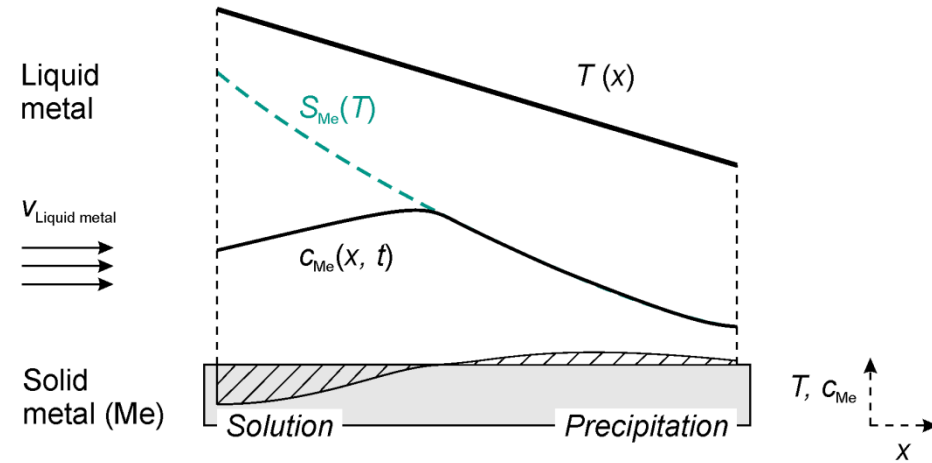
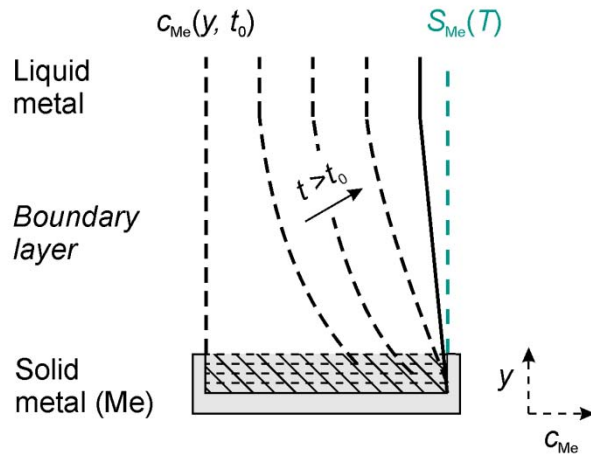
Intermetallics FeSn and FeSn₂ as found in austenitic steel after exposure to tin at around 500 °C^[3].

[1] Schroer et al., “Corrosion in iron and steel T91 caused by flowing lead–bismuth eutectic at 400 °C and 10⁻⁷ mass% dissolved oxygen”, *J. Nuclear Rad. Sci.* (2018). doi: 10.1115/1.4040937.

[2] Schroer et al., *Corros. Sci.* 84 (2014) 113–124.

[3] Emmerich & Schroer, *Corros. Sci.* 120 (2017) 171–183.

Solution of metallic materials caused by liquid metals



□ Isothermal (temperature $T = \text{const.}$)

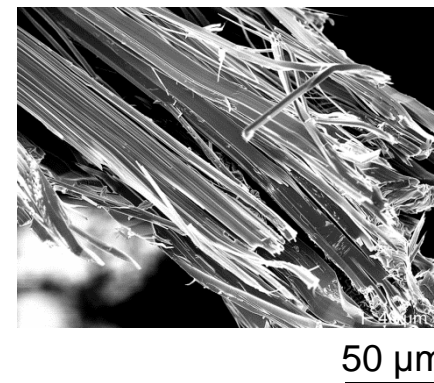
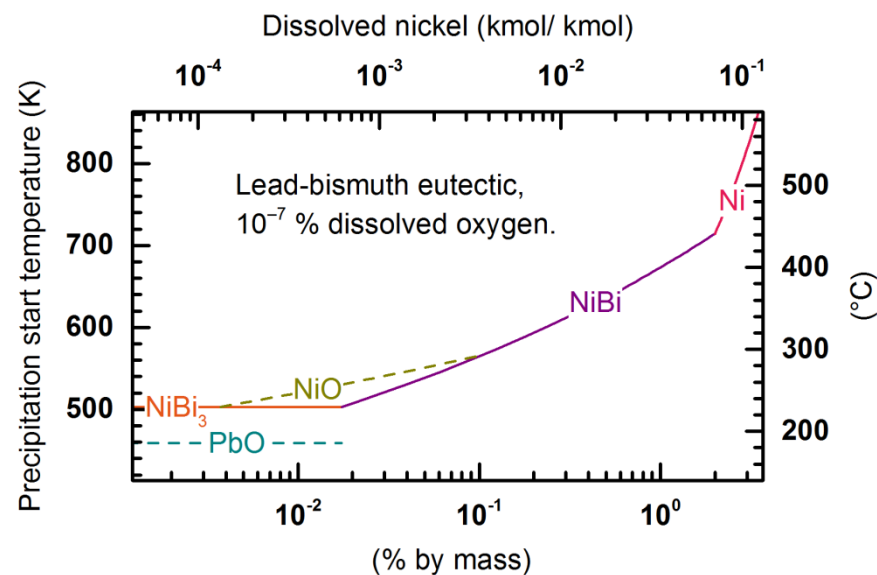
- Solution is limited by the solubility $S_{\text{Me}}(T)$.
- Solution rate decreases as saturation with the dissolved material elements is approached.

□ Non-isothermal system

- Re-deposition of material elements where the local solubility would be passed otherwise.
- Particularly noticeable in combination with convection of the liquid metal in the direction of decreasing temperature.
- Counteracts saturation of the liquid metal in a loop-type system.
- Risk of plugging of narrow paths of the liquid metal in the colder parts of the system.

Deposition of intermetallic compound

Relevant to nickel dissolved in lead–bismuth eutectic, e. g. from austenitic steel.



Nickel–bismuth compound found in the cold leg of the CORRIDA loop. Energy-dispersive X-ray spectroscopy supplemented by X-ray diffraction suggests NiBi₃.

Prediction of simplified calculations for pure nickel, based upon thermochemical data that includes the experimental solubility S_{Ni} in the nickel^[1] and NiBi domains^[2]. Precipitation of NiBi₃ is anticipated at <503 K (230 °C).

[1] Rosenblatt & Wilson, in: Draley & Weeks, "Corrosion by Liquid Metals", 1969.

[2] Martinelli et al., J. Nucl. Mater. 400 (2010) 232–239.

Iron–Bismuth:

- Hardening and embrittlement at 350°C.
- Softening and plastification at 550°C.

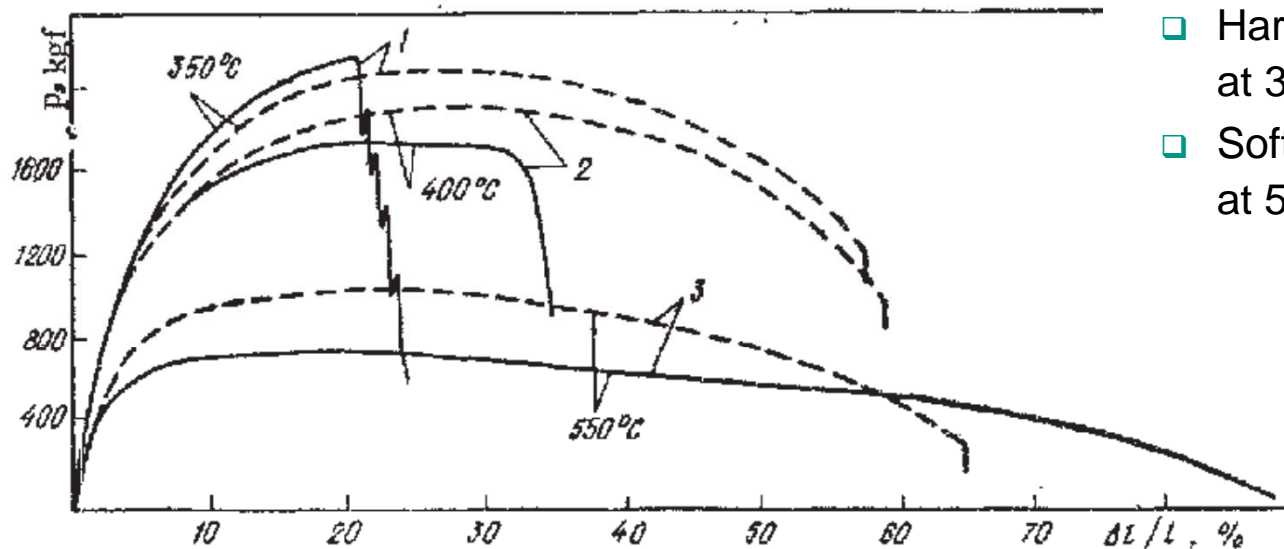
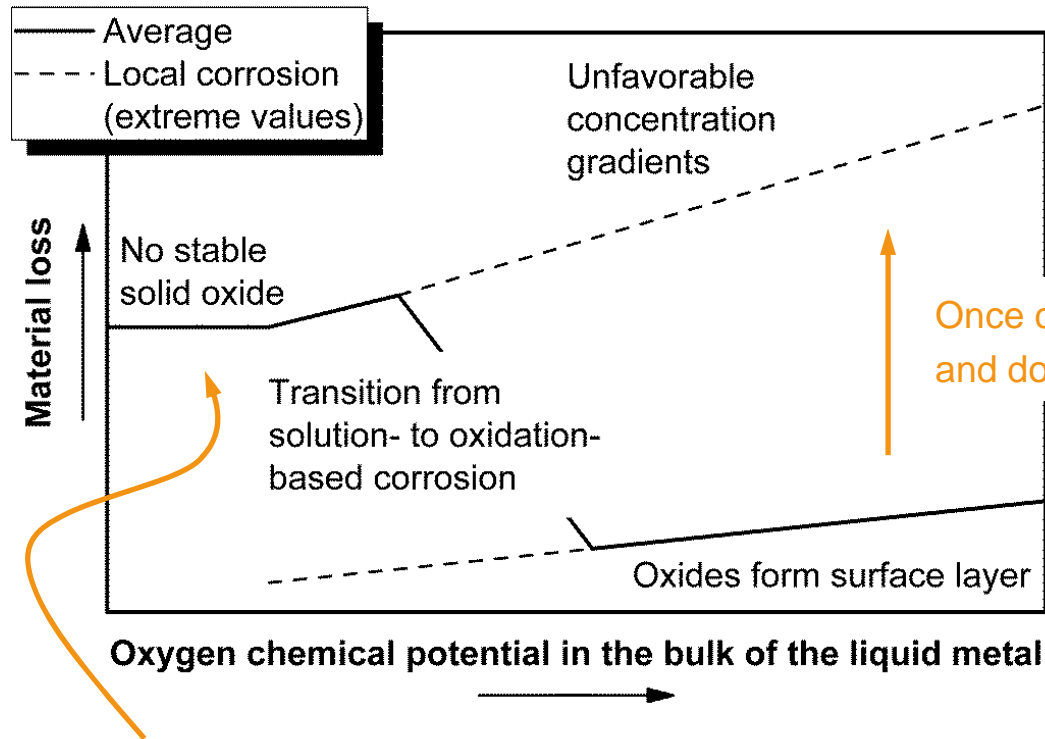


Fig. 2. Tensile load–strain diagrams of Armco iron specimens tested in bismuth (continuous lines) and in vacuum (dashed lines) at 350°C (1), 400°C (2), and 550°C (3).

Source: V.V. Popovich, I.G. Dmukhovskaya, Soviet materials science a transl. of Fiziko-khimicheskaya mekhanika materialov / Academy of Sciences of the Ukrainian SSR 14 (1978) 365–370.

Especially relevant to ferritic/ martensitic steel in contact with lead–bismuth eutectic.

Role of dissolved oxygen for material recession



No or discontinuous surface layer. Oxide formation in some distance from the solid surface promotes the solution of elements.^[1]

Once continuous layer locally fails and does not heal on its own terms.

Spatial separation between solid and liquid metal. Degradation of the solid determined by

- growth of the oxide layer and
- solution after diffusion through the oxide layer.

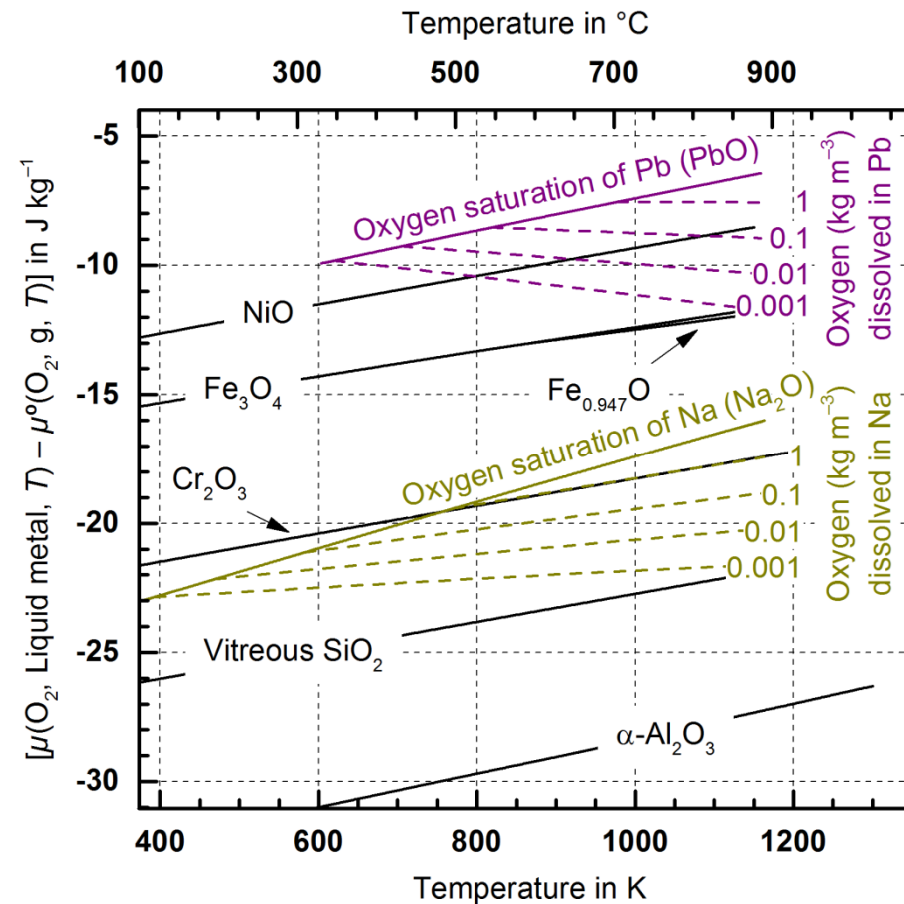
No or minor influence of dissolved oxygen if solid oxides are unstable at any temperature of interest.

Likely to be beneficial also with respect to the conservation of mechanical material properties in the presence of liquid metal.

[1] Recently confirmed experimentally (also) for steels in contact to oxygen-containing lead-bismuth eutectic. O. Klok, Doctoral Thesis, Vrije Universiteit Brussels, March 2018.

- **Liquid metals with low affinity to oxygen**
 such as lead (Pb) or lead–bismuth eutectic (LBE)
 - Chemically more noble than the elements in typical steels or nickel-based alloys.
 - Oxygen chemical potential sufficient for the formation of solid binary oxides of nickel, iron, chromium ... is passed before oxygen saturation of the liquid metal.

- **Liquid metals with high affinity to oxygen**
 such as sodium (Na) or lead–lithium (Pb17Li)
 - Fairly high amount of oxygen (kg m^{-3}) may generally be available, but with only low chemical potential.
 - Thresholds for the formation of solid binary oxides of the parent element in steels and nickel alloys cannot be passed.
 - Possible acceleration of corrosion (solution) due to the formation of ternary oxides from elements in the metallic material and elements of the liquid metal.



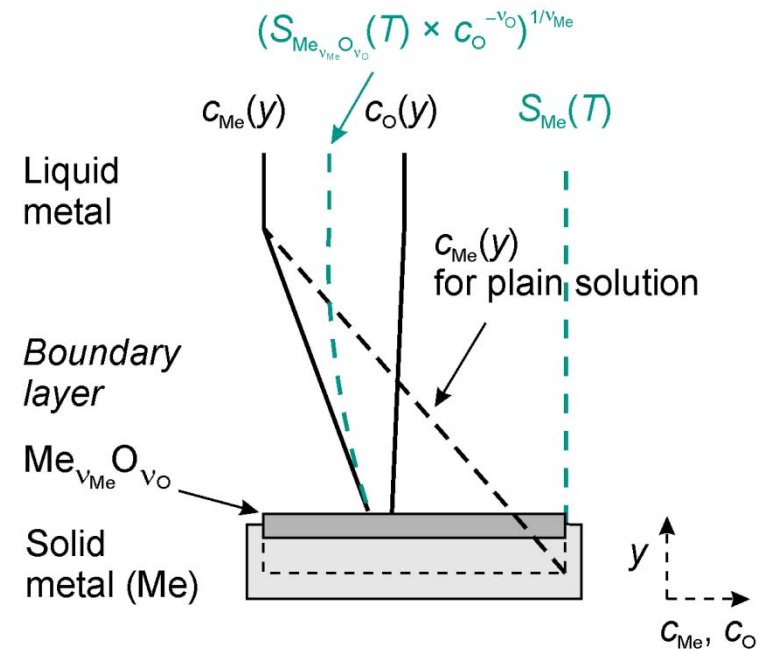
Sources of thermochemical data:
 Pankratz, *Thermodynamic properties of elements and oxides*, 1982; Noden, *J. Brit. Nucl. Ener. Soc.*, 1973 (oxygen solubility in Na); Ganesan et al., *J. Nucl. Mater.*, 2006 (oxygen solubility in Pb).

Beneficial effect of solid oxide formation

□ Continuous oxide scale

- Acts as a diffusion barrier for further solution of the metal Me.
- Maximum enrichment of Me is limited by the temperature-dependent **solubility product**

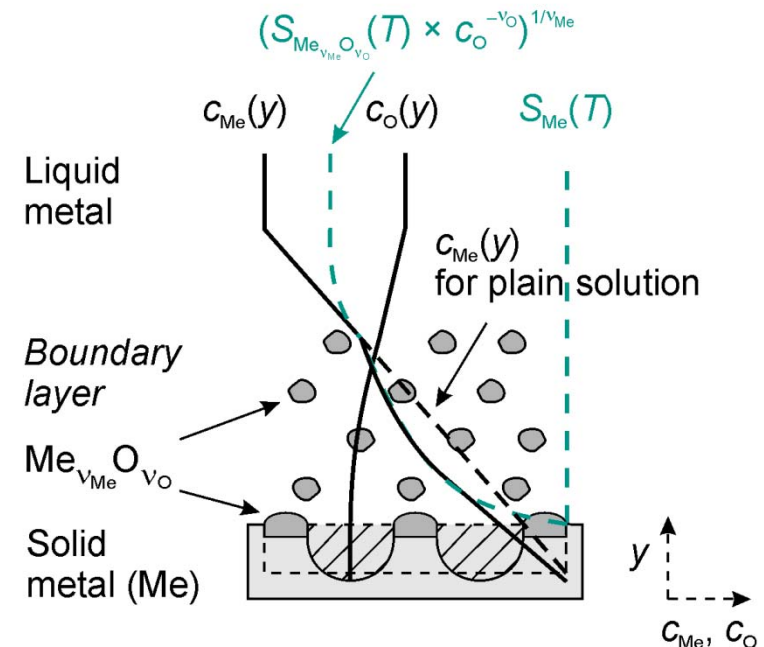
$$S_{\text{Me}_{v_{\text{Me}}}\text{O}_{v_{\text{O}}}}(T) = c_{\text{Me}}^{v_{\text{Me}}} \times c_{\text{O}}^{v_{\text{O}}}.$$
- High oxygen concentration at the scale surface if the oxide grows only slowly.
- Relatively slight enrichment of Me in the liquid metal at the interface with the scale, the gradient of c_{Me} between oxide surface and liquid metal volume is respectively shallow.
- Most favorable situation as to minimum material consumption and minimum accumulation of Me in the liquid metal.
- **But: Solution is unlikely to be zero as long as a gradient of c_{Me} exists!**



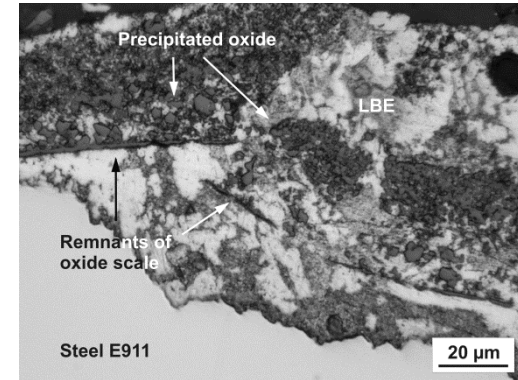
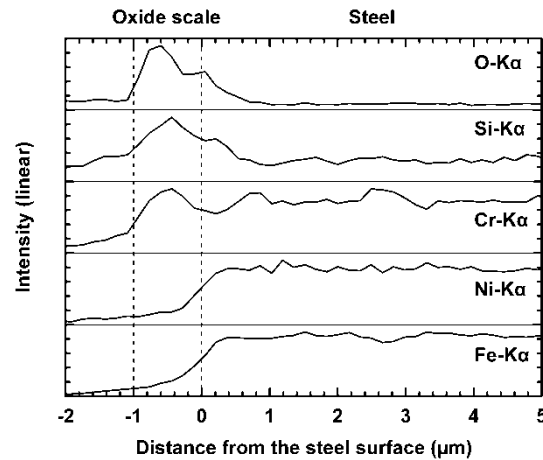
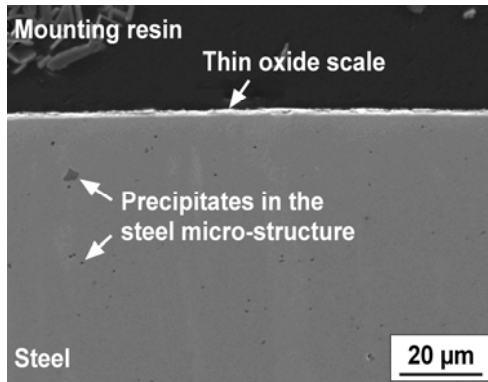
Adverse effect of solid oxide formation

❑ Discontinuous surface oxide

- ❑ Material locally remains prone to solution.
- ❑ Oxide precipitation where dissolved Me meets sufficiently high c_O .
- ❑ Resulting oxygen depletion increases the possible enrichment of Me in the liquid metal, promoting solution and subsequent oxide precipitation.
- ❑ Gradient of c_{Me} at the material surface may be steeper than for plain solution, i.e. solution may locally be faster than in the absence of oxygen.
- ❑ Formed oxides are generally prone to solution at the material surface and transition to the bulk of the liquid metal.
- ❑ Also applies to local failure of a once continuous oxide scale.



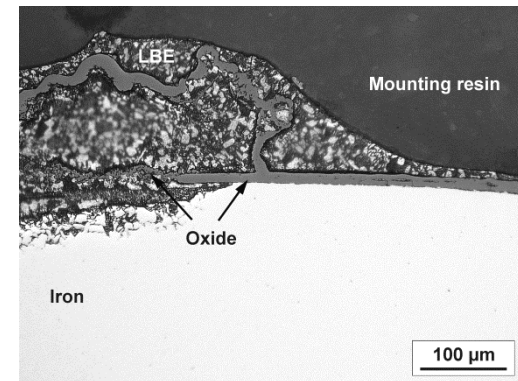
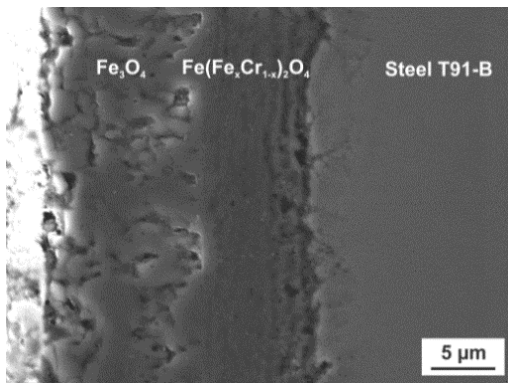
Examples from exposure to oxygen-containing LBE



Thin protective oxide scale on austenitic steel after exposure at 450 °C and 10⁻⁶ % oxygen^[1] ...

... and thicker, but still protective to some degree, oxide scale on martensitic steel^[2].

Solution and oxide precipitation in martensitic steel^[3] and iron^[4] for same exposure conditions.



- [1] Schroer et al., J. Nucl. Mater. 418 (2011), 8–15.
- [2] Schroer et al., J. Nucl. Mater. 431 (2012), 105–112.
- [3] Schroer et al., Nucl. Eng. Des. 280 (2014) 661–672.
- [4] Schroer et al., Corros. Sci. 61 (2012) 63–71.

Principal corrosion modes observed in steels after exposure to oxygen-containing liquid lead or lead alloys

SOLUTION-BASED

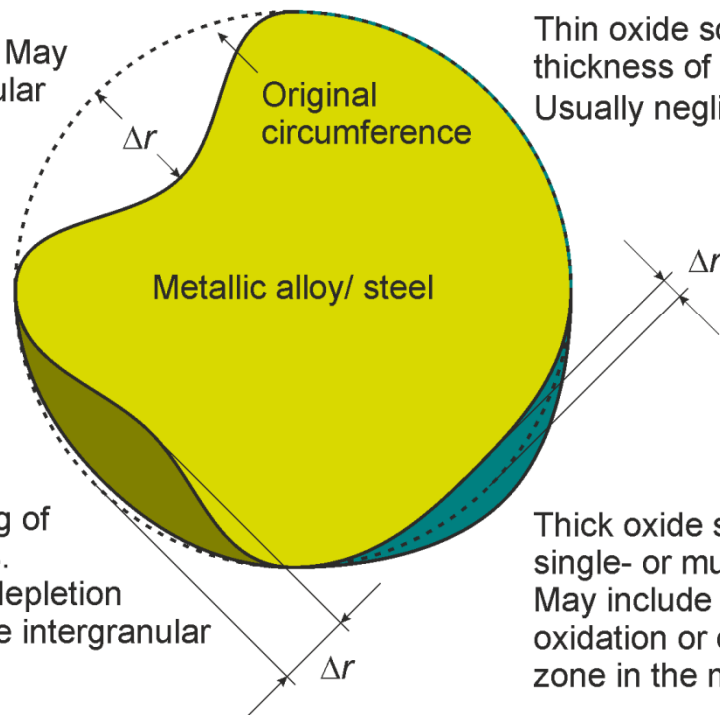
General solution. May include intergranular penetration.

Selective leaching of alloying elements. Development of depletion zone. May include intergranular penetration.

OXIDATION-BASED

Thin oxide scale, typical thickness of $< 1 \mu\text{m}$. Usually negligible Δr .

Thick oxide scale, single- or multi-layer. May include internal oxidation or depletion zone in the material.



Mixed modes possible, notably if oxidation transitions to solution-based corrosion.

In general, the material recession Δr has to be determined directly.

Separate evaluation of Δr for each corrosion mode. Averaging over different modes not recommended.

Working hypotheses for Type 316 austenitic steels exposed to oxygen-containing liquid lead/ lead alloys

❑ Thin, highly protective oxide layer

- ❑ Typically chromium- and silicon-rich.
- ❑ Nuclei/ precursor of this scale may already exist before exposure.
- ❑ Dominates the initial performance of the steel.



❑ Failure of the protective scale

- ❑ The earlier the higher the temperature or lower the oxygen concentration in the bulk of the liquid metal.
- ❑ Not clear if this scale actually reheals because of possible chromium and silicon depletion.
- ❑ Corrosion mode transitions to either the accelerated form of oxidation or solution-based corrosion.



❑ Thick oxide scale

- ❑ Formation of relatively fast growing iron-containing oxides.
- ❑ Local oxygen concentration (activity) must be sufficient despite potential depletion at the steel surface.
- ❑ Material loss and oxide thickness may still be tolerable, but also this scale becomes prone to failure as growth continues.



❑ Solution-based corrosion

- ❑ Selective leaching, most notably of nickel but also of chromium.
- ❑ General solution if local conditions allow fast iron transport away from the steel surface e. g. due to adverse oxygen effect.
- ❑ Intolerable material degradation, the more so the higher the temperature.

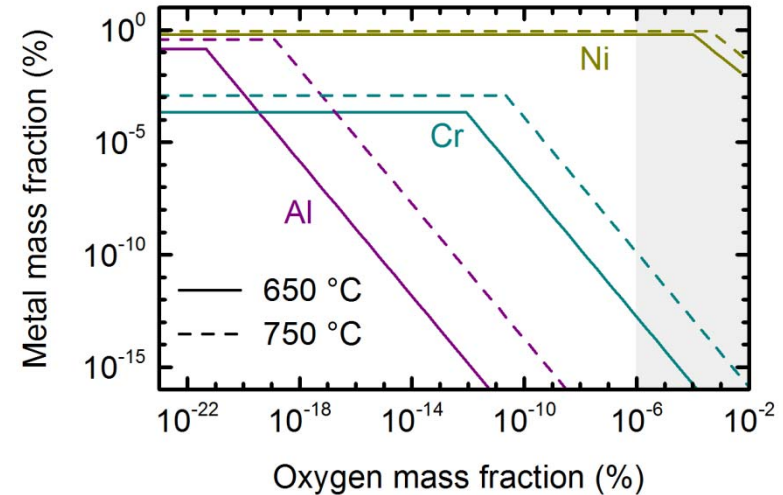
Expectations of AFA steels as concerning corrosion

caused by liquid lead/ lead alloys

- ❑ **Formation of protective oxide layer**
 - ❑ May initially still be chromium- (and silicon-) rich.
 - ❑ Aluminium-rich sub-layer significantly contributes to the protectiveness.
 - ❑ Feeding of oxygen remains essential because of considerable solubility of aluminium in oxygen-depleted liquid metal.



GOAL: Protective oxide layer will not fail at higher temperature or lower oxygen concentration in comparison to classic austenitic steels.



Enrichment of elements in equilibrium with oxygen-containing liquid lead as a function of dissolved oxygen at 650 and 750 °C.

Sources of thermochemical data:

Pankratz, Thermodynamic properties of elements and oxides, 1982; Ganesan et al., J. Nucl. Mater., 2006 (oxygen solubility in Pb); Alden et al., T. Metall. Soc. AIME, 1958 (chromium and nickel solubility); Davey & Floyd, T. I. Min. Metall. C, 1976 and Martin-Garin & Desré, C. R. Acad. Sc. Paris C, 1967 (aluminium solubility).