Selective leaching of nickel and chromium from Type 316 austenitic steel in oxygen-containing lead-bismuth eutectic (LBE)

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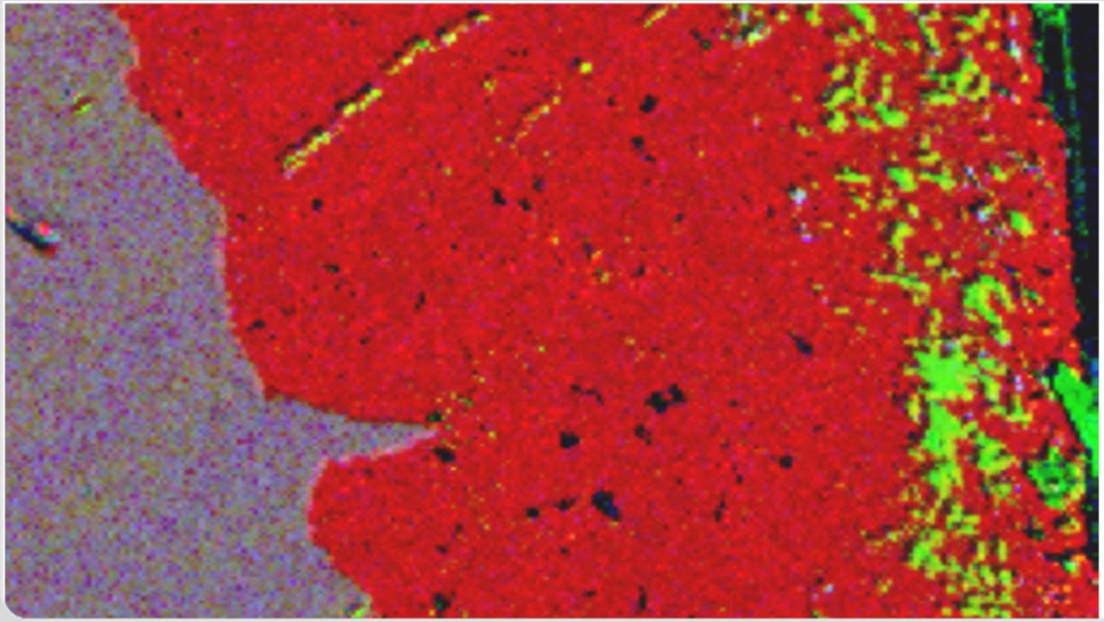
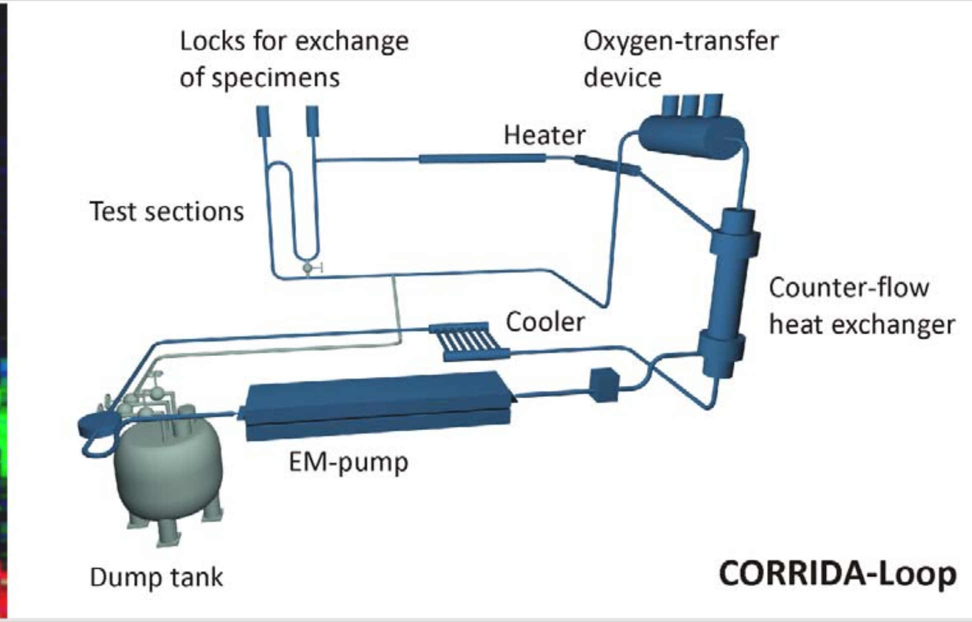




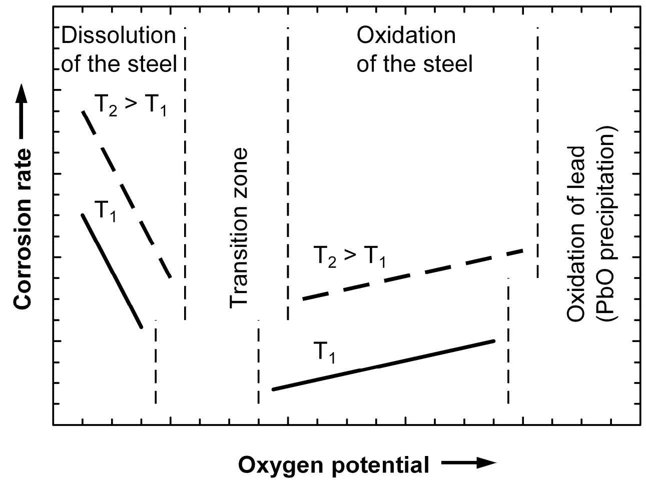
Material issues for lead-cooled systems

Principal service-loading of plant components

- Thermal
- Mechanic
- Irradiation
- **Corrosion**
- Erosion

Materials of construction

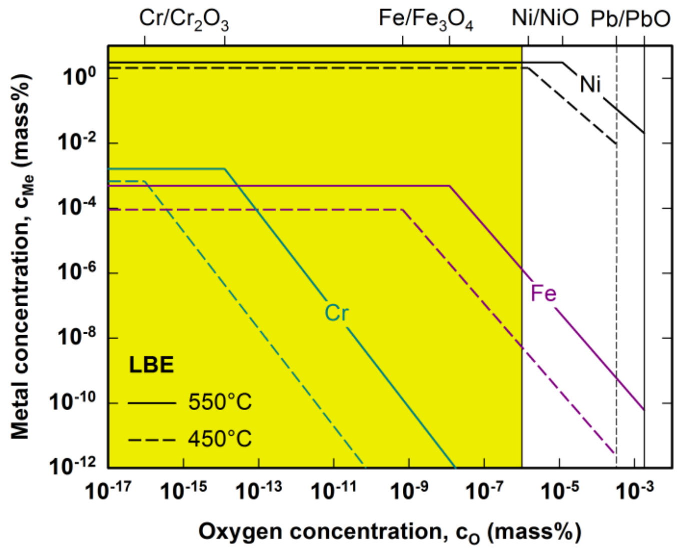
- Ferritic/martensitic steels (e.g., with 9% Cr)
- Austenitic steels
- Coated steels
- Non-ferrous metals



Formation of oxides on the material surface lowers the corrosion rate!

- Dissolution in liquid Pb or LBE
- Degradation of mechanical properties

- Mitigation by oxygen addition to the liquid metal
- Formation of (thin) oxide on the material surface



Solubility of metals less-noble than Pb is a function of oxygen concentration!

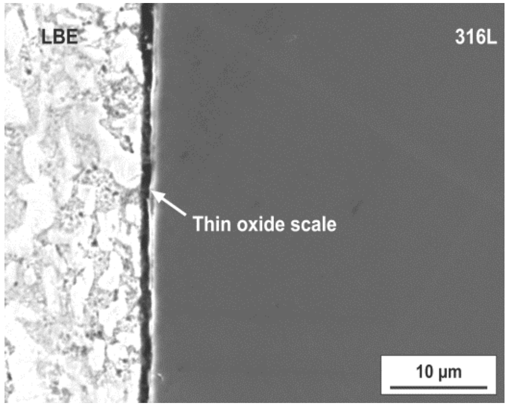
Characteristics of corrosion of austenitic steels (Type 316) in oxygen-containing Pb alloys (LBE)

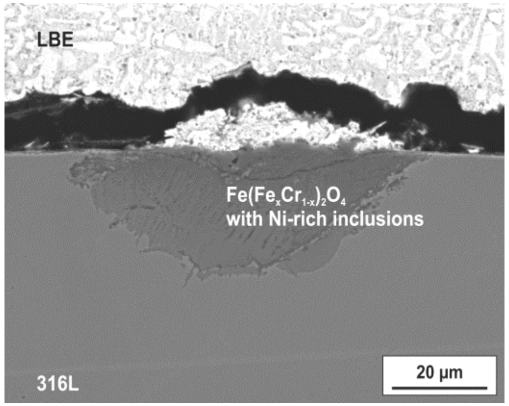
❑ Protective scaling

- ❑ Thin oxide scale (< 1 µm) consisting of Cr- or Si-rich oxide layers
- ❑ Locally long-lasting phenomenon at 450/550°C, 10^{-6} mass% O

❑ Accelerated oxidation

- ❑ Starts locally where the thin oxide scale lost integrity or did not form
- ❑ The thicker scale spreads on the steel surface with time and becomes partially continuous



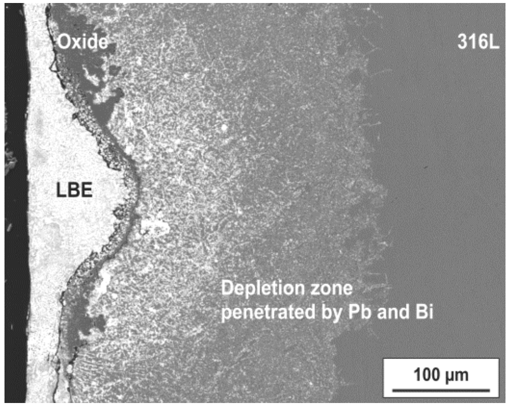


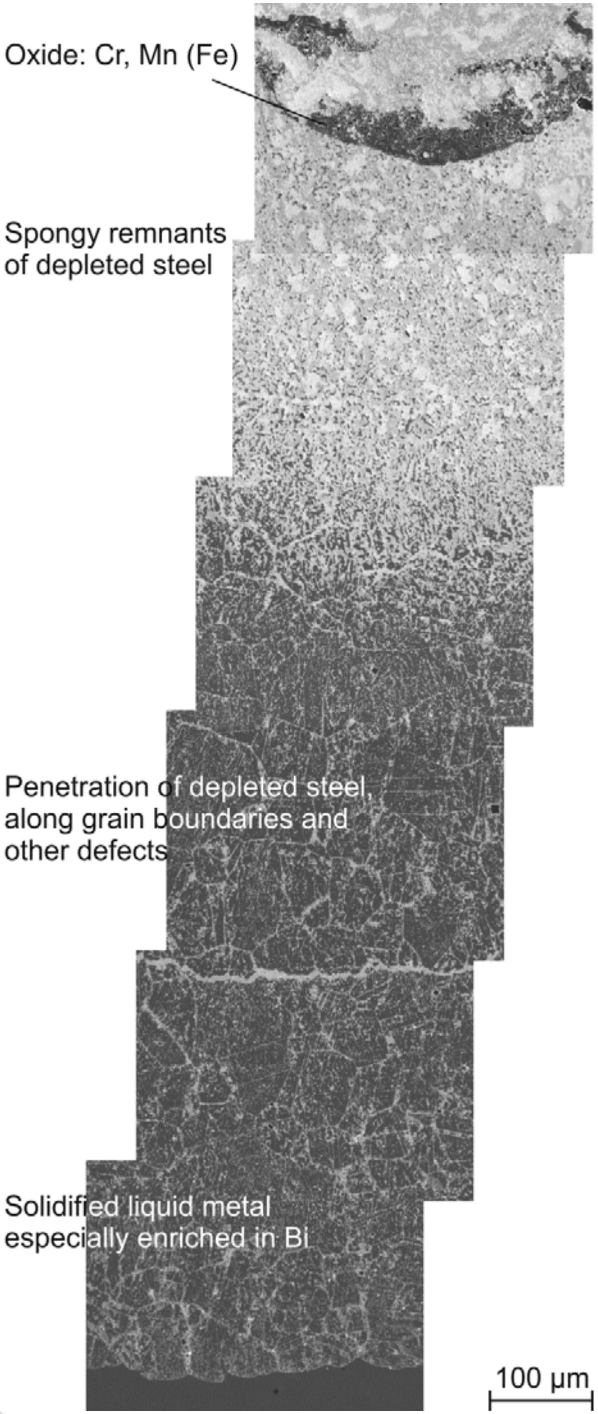
316L after exposure to flowing LBE:

- ❑ 550°C
- ❑ 10^{-6} mass% O
- ❑ 2 m/s
- ❑ 10,021 h

❑ Selective leaching

- ❑ Starts locally with preferential removal of Ni, Cr, …
- ❑ Phase transition from austenite into ferrite in the originating depletion zone
- ❑ Penetration of Pb and Bi into the depletion zone

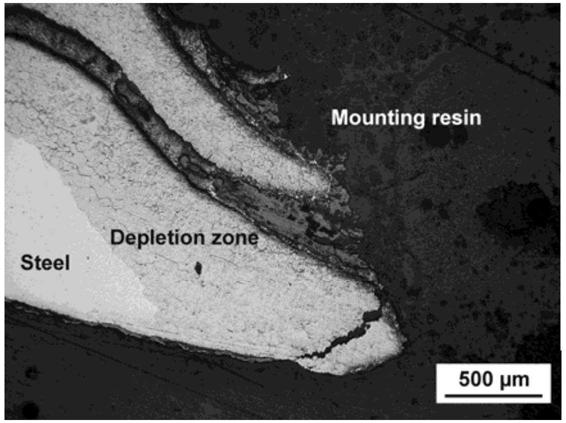




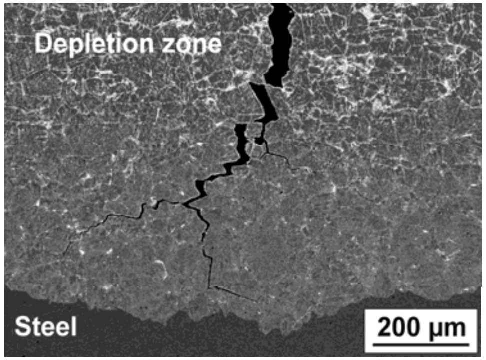
Tube failure associated with selective leaching in a LBE loop (CORRIDA)

❑ Failure case

- Tube material: 1.4571 (~316Ti)
- Wall thickness: 2.5 mm
- Ø10 mm leak at the bottom end of a vertical tube after operation for ~66,000 h



Site of failure



In a cross-section nearby the site of failure

❑ Failure analysis

- Severe selective leaching along nearly the complete inner tube surface
- Depletion zone locally reaches the outer tube surface
- Ultimate cause of failure: Cracking of the mechanically unstable depletion

Basis for the analysis of selective leaching

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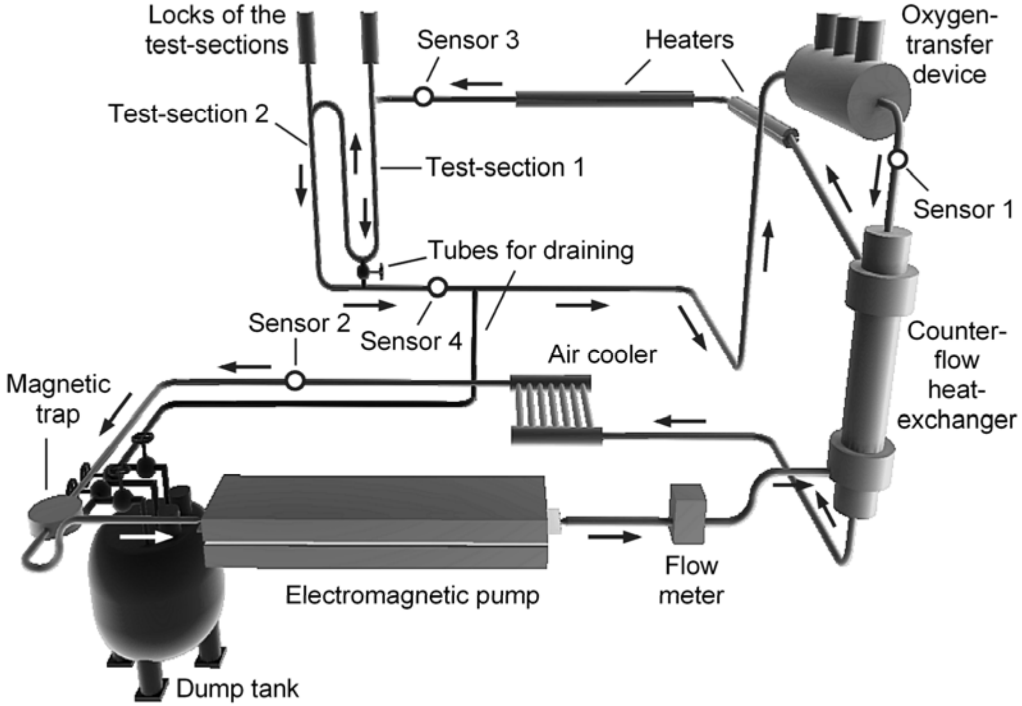
❑ Experimental

- Materials: 316L, 1.4571/316Ti
- Cylindrical specimens exposed to flowing LBE in the CORRIDA loop at 450°C/10^{-6}% O or 550°C/10^{-6}% O
- Samples taken from the tubing (1.4571) of the CORRIDA loop
- Published studies on the performance of austenitic steels in flowing/static Pb alloys

CORRIDA loop operated at KIT since 2003

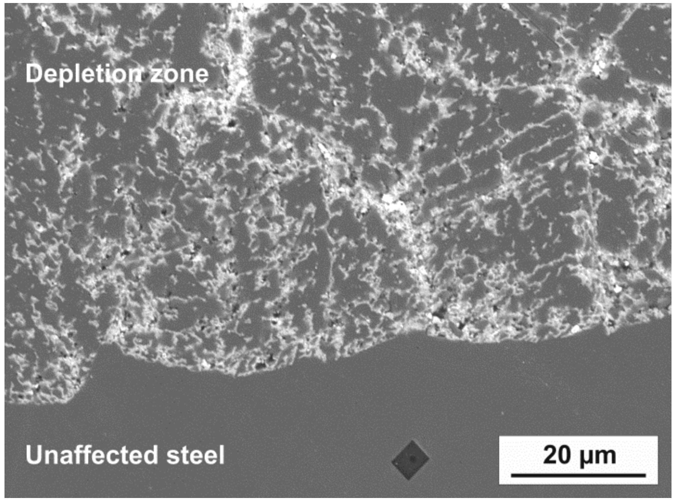


❑ Analogy to selective leaching of Zn from brass

- Proposed mechanisms:
  (a) Non-selective dissolution followed by re-precpitation of less soluble Cu;
  (b) Preferential dissolution of Zn in combination with solid-state diffusion of Zn in the Cu-Zn alloy
- However, selective leaching of brass is an electrochemical process, i.e., metals dissolve in the form of ions

Basic mechanism of selective leaching

- **Elementary processes involved in the dissolution/removal of steel elements**
  - The actual dissolution in the sense of mass transfer from the steel to the liquid-metal phase
  - Transport of the steel elements in the liquid phase, away from the site of transfer
- **From examining the depletion zone/steel interface**
  - Missing gradient in the steel composition beyond the deepest penetration of liquid metal implies **non-selective transfer** of steel elements
  - Preferential removal of Ni and Cr results from **selective transport** in the liquid phase
  - Fe and Cr partially re-precipitate in the form of ferrite
  - Volume decrease from loss of metal outweighs volume increase from austenite-to-ferrite transformation
  - Decreasing volume of solid metal allows for penetration of LBE



1.4571 sample taken from the tubing of CORRIDA after about 66,000 h of operation

Detailed mechanisms in the absence of oxygen (I)

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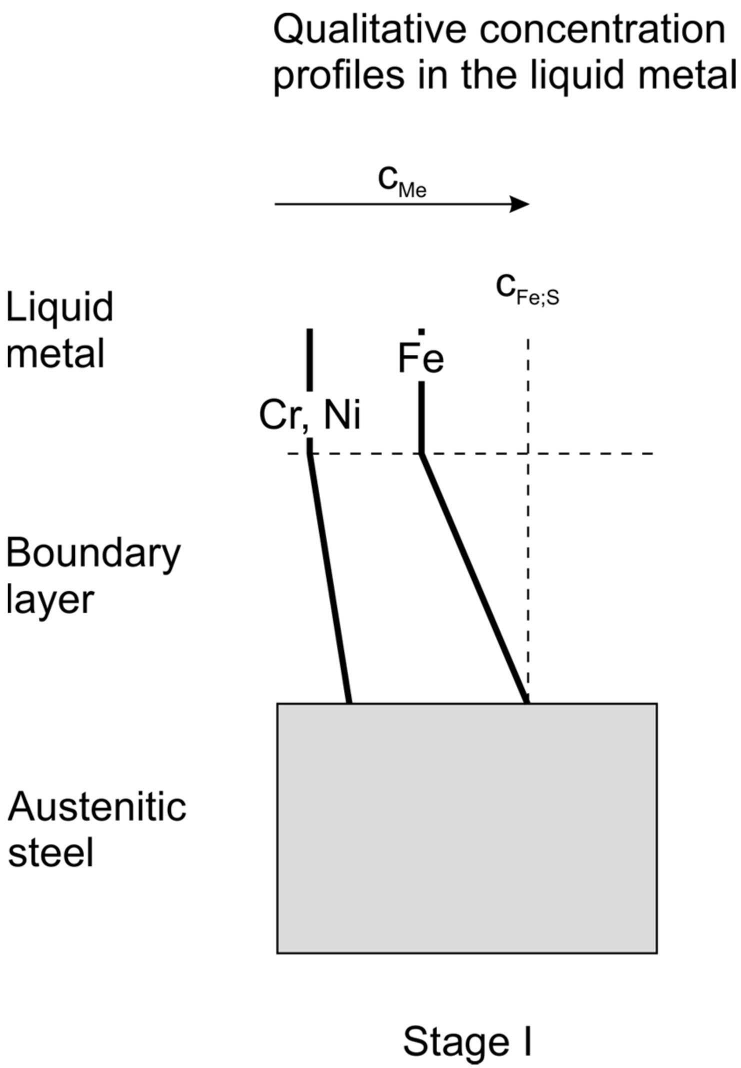
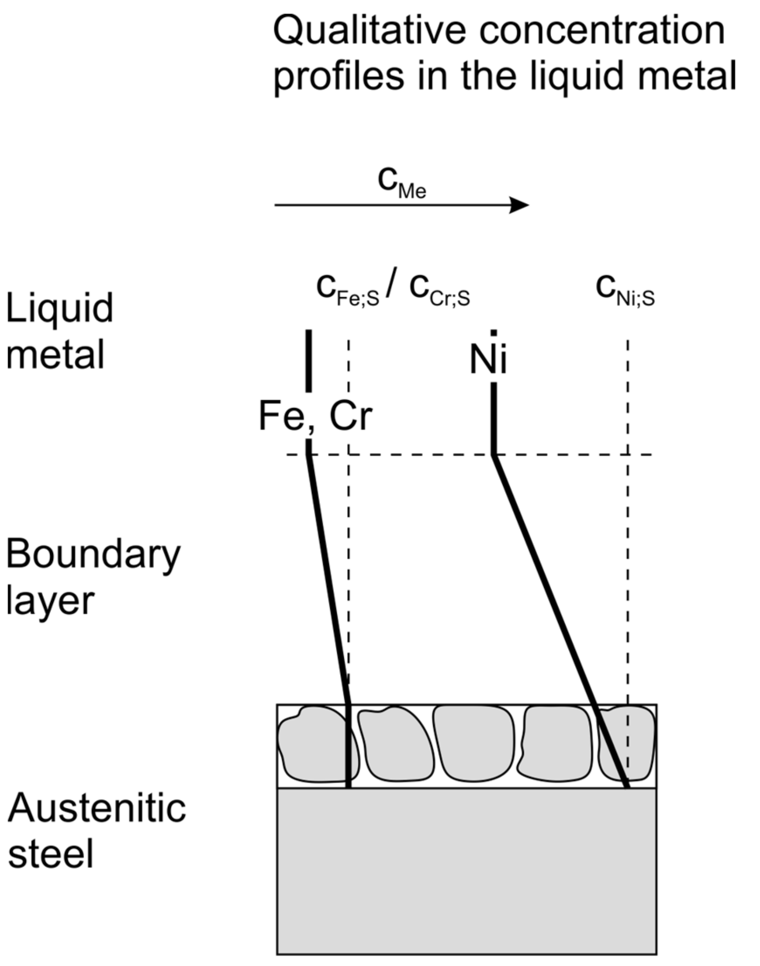


❑ Stage I

- ❑ Non-selective dissolution (transfer + transport)
- ❑ Steel elements dissolve in proportion to their concentration in the steel
- ❑ Fe transfer is critical for the progress of non-selective dissolution (lowest solubility, highest concentration in the steel)
- ❑ Non-measurable surface recession of the steel, if Fe transport in the liquid metal is slow (rate-determining for the overall process)
- ❑ Slow Fe transport is the pre-requisite for selective leaching to start (Stage II)

Detailed mechanisms in the absence of oxygen (II)



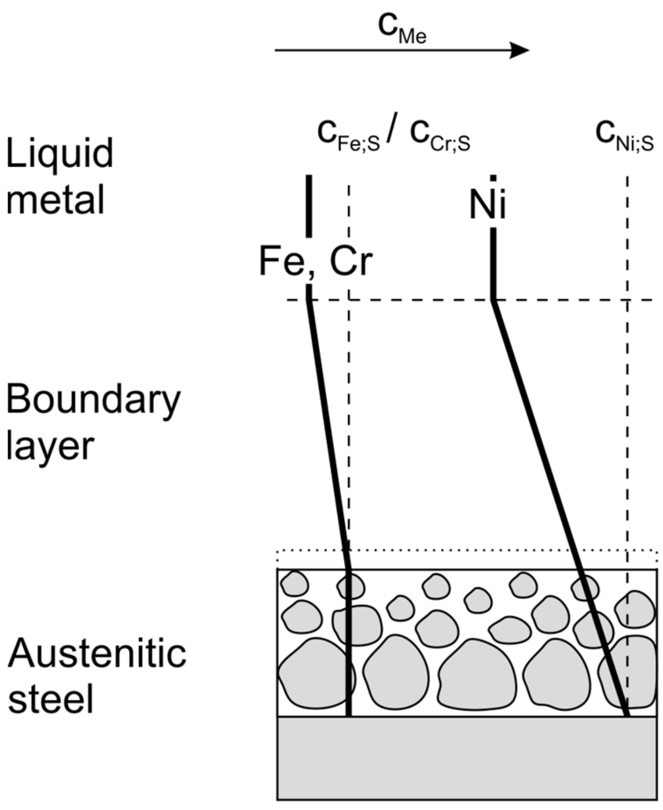
Stage II

❑ Stage II

- Partial re-precipitation of Fe (and Cr) enables further enrichment of Ni once the saturation concentration of Fe (Cr) is achieved
- Austenite-to-ferrite transition delivers an extra driving force for re-precipitation
- Ni may enrich at the depletion zone/steel interface, promoting transport in the liquid phase
- Insignificant transport of Fe (and Cr) to the surface of the depletion zone

Re-crystallisation of austenite into ferrite, facilitated by intermittent dissolution and the capacity of the liquid metal to retain Ni.

Detailed mechanisms in the absence of oxygen (III)

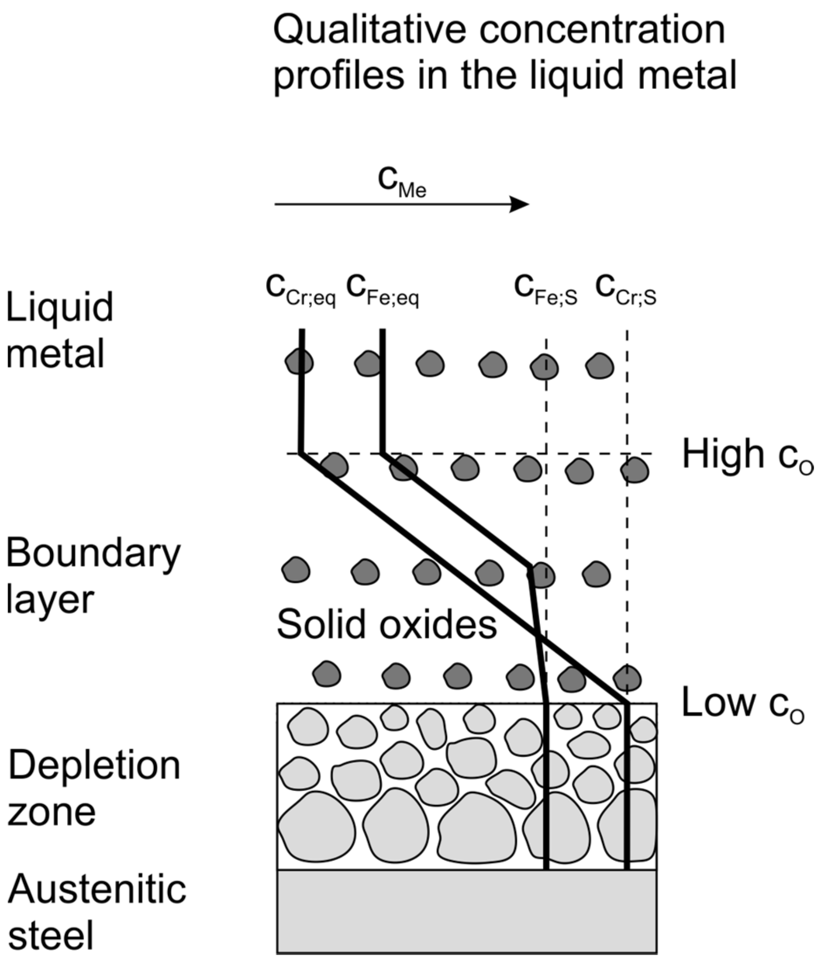


Stage III

- **Stage III**
  - Significant dissolution of ferrite at the depletion zone surface
  - Decreasing size of ferrite particles or surface recession
  - Liquid-metal volume increases/ depletion-zone thickness decreases, promoting also the removal of Ni

Selective leaching is an intermittent stage of the general dissolution of austenitic steels.

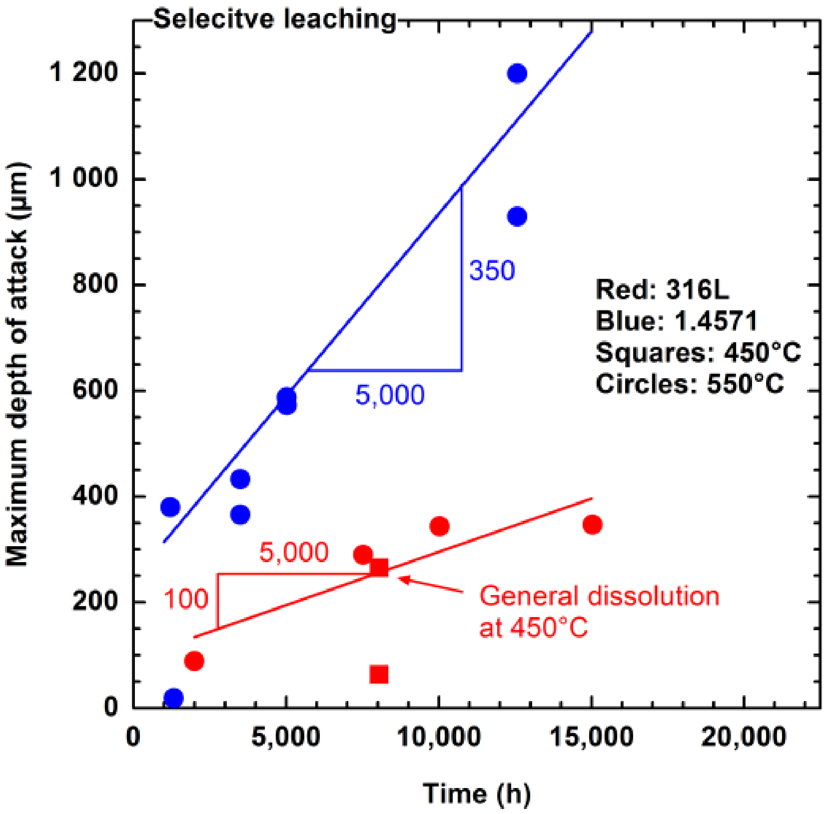
Role of oxygen dissolved in the liquid metal



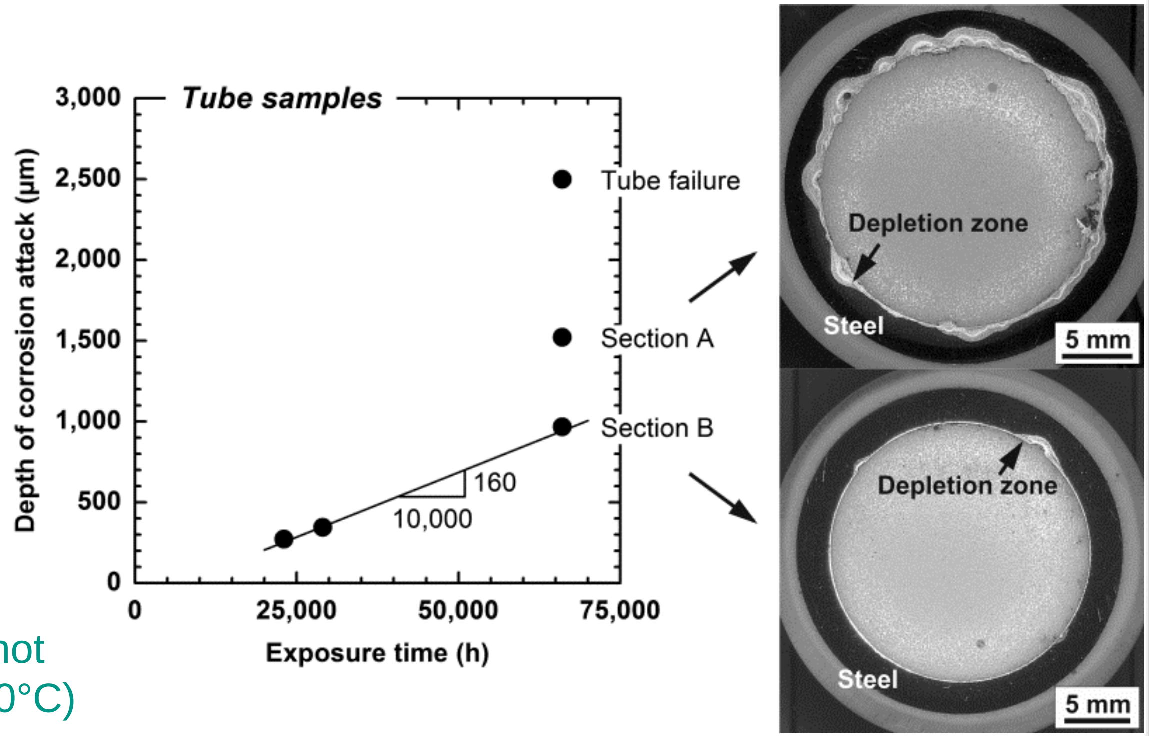
- **Impact on transport of Fe and Cr (Mn)**
  - Precipitation of solid oxides alters the concentration gradients at the depletion zone surface (become steeper)
  - Oxide formation maintains a low c_O at the depletion zone surface
  - Solid oxides are an efficient sink of dissolved metals, promoting the removal from the steel
  - Comparatively strong effect on leaching of Cr (Mn), insignificant effect on Ni removal

Formation of a continuous oxide layer will retard leaching of steel elements!

Kinetics of selective leaching in oxygen-containing LBE



Corrosion specimens exposed in the test-sections of the CORRIDA loop at 2 m/s and 10^{-6} mass% oxygen



1.4571 samples from the tubing in the hot leg of the CORRIDA loop (mainly at 550°C)

Conclusions

- **Selective leaching of Ni and Cr**
  - Critical for the performance of austenitic steel in liquid Pb alloys
  - Starts locally in the presence of dissolved oxygen (along with oxidation)
  - May cause tube failure as a result of cracking of the originating depletion zone
  - Applicable to any liquid metal

- **Mechanism for austenitic steels**
  - General transfer of steel elements to the liquid metal, but selective transport
  - Partial re-precipitation of Fe and Cr facilitates enrichment and selective transport of Ni in the liquid phase
  - Limited Fe (Cr) transport away from the site of the actual dissolution is a necessary pre-requisite
  - General dissolution at the depletion zone surface
  - Dissolved oxygen changes the boundary conditions for transport of Cr (Fe) as a result of oxide precipitation

- **Kinetics**
  - May be approached by linear rate law
  - Significantly different corrosion rates, locally or for nominally similar steels

- **Initiation**
  - Subject of future work

Acknowledgements

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