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

Carsten Schroer, Olaf Wedemeyer, Josef Novotny, Aleksandr Skrypnik, Jürgen Konys
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

- 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

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

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

- **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

**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
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

Analogy to selective leaching of Zn from brass

- Proposed mechanisms:
  - Non-selective dissolution followed by re-precipitation of less soluble Cu;
  - 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)

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

- 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**
  - 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

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

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

The construction and operation of the CORRIDA loop was financially supported by the Nuclear Safety Programme of KIT.

The analysis of selective leaching of austenitic steels is part of the SEARCH project that has received funding by the 7th Framework Program of the EU (Grant Agreement No. 295736).