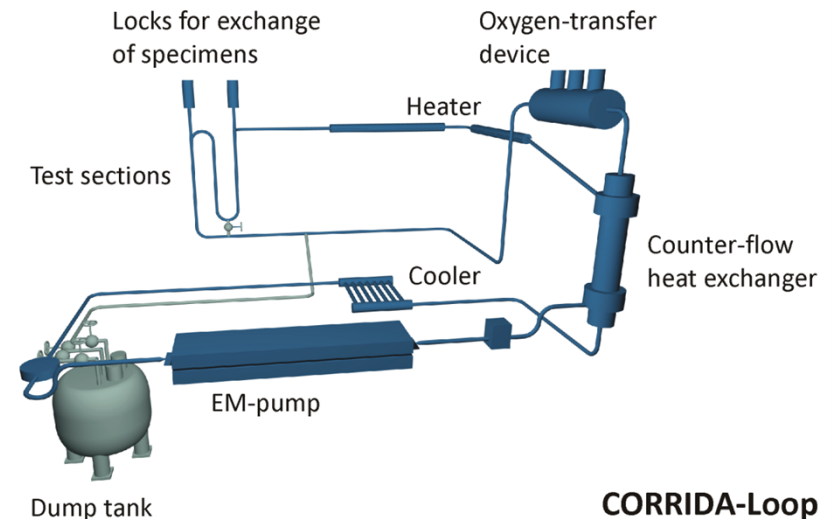
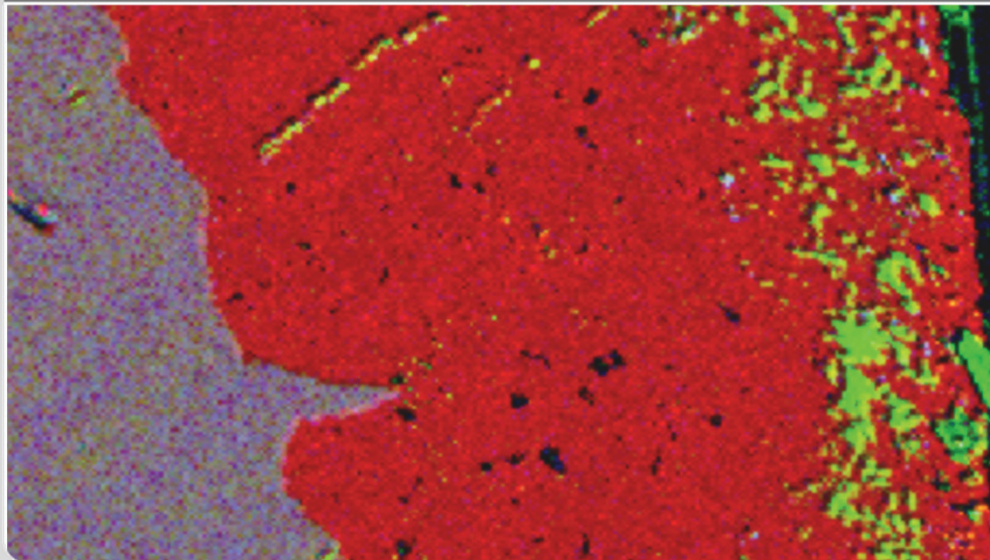


Tube failure during long-term exposure to flowing lead-bismuth eutectic (LBE)

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

INSTITUTE FOR APPLIED MATERIALS – MATERIAL PROCESS TECHNOLOGY (IAM-WPT)



Material issues for lead-cooled systems

Principal service-loading of plant components

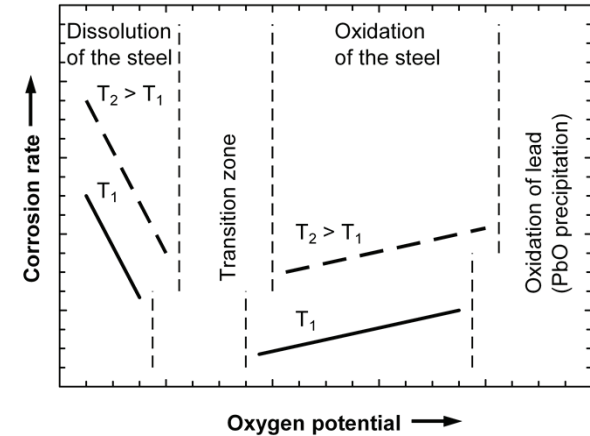
- Thermal
- Mechanic
- Irradiation
- Corrosion**
- Erosion

Materials of construction

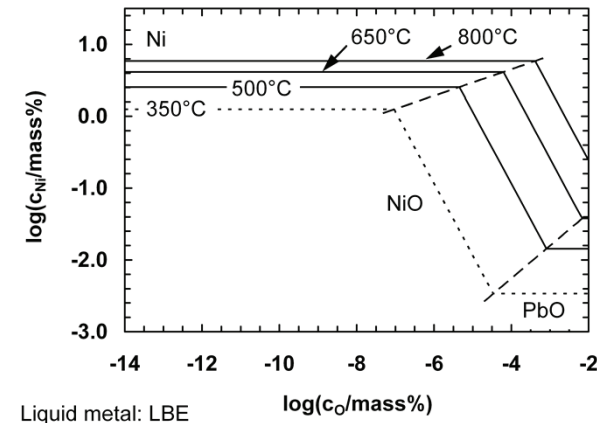
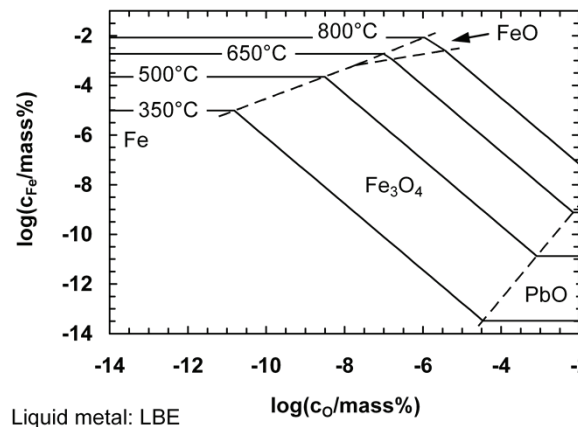
- Ferritic/martensitic steels (e.g., with 9% Cr)
- Austenitic steels
- Coated steels
- Non-ferrous metals

- 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

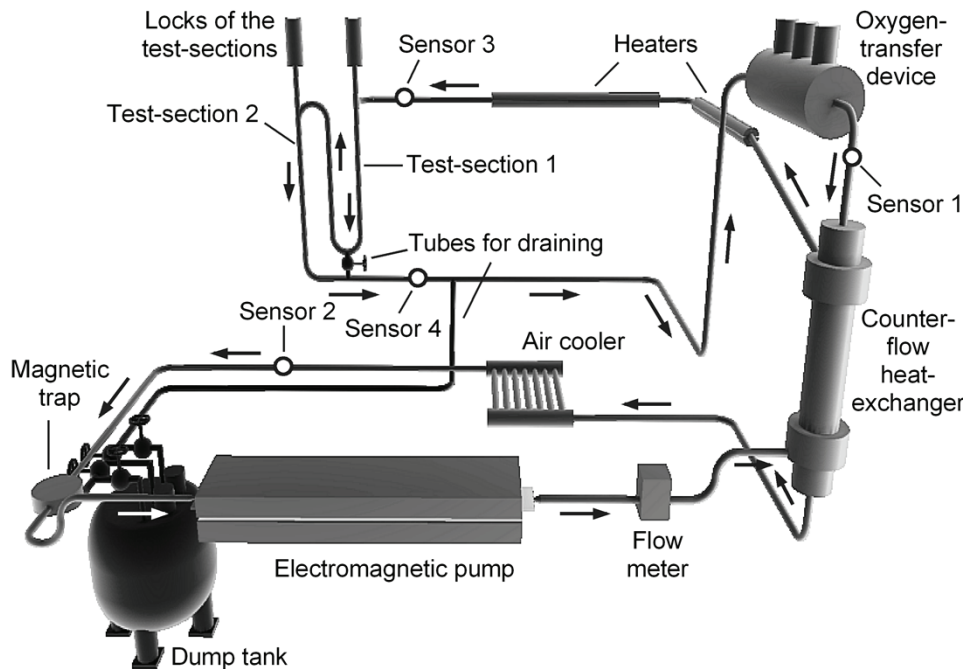


Formation of oxides on the material surface lowers the corrosion rate!



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

CORRIDA: Corrosion testing in dynamic lead alloys



□ Technical data

- Material: 17-12 Cr-Ni steel (1.4571)
- Developed length: 36 m
- Liquid metal: ~1000 kg LBE
- Mass flow: 5.3 kg/s (steady state), corresponding to 2 m/s in the test-sections loaded with \varnothing 8mm specimens
- $T_{\max} = 550^{\circ}\text{C}$ (test-sections)
- $T_{\min} = \sim 350^{\circ}\text{C}$ (inlet of EM-pump)
- Gas/liquid oxygen transfer: Gas with adjustable p_{O_2} introduced at T_{\max}

□ Monitoring of oxygen dissolved in the circulating LBE

- Sensor 1: After oxygen-transfer device; Pt/air reference electrode
- Sensor 2: Cold leg; Pt/air reference electrode
- Sensor 3: Inlet of first test-section; Pt/air reference electrode
- Sensor 4: After second test-section; Pt/air reference electrode

□ Milestones

- Commissioning in February 2003 (first filling with LBE)
- Start of first material tests (effective operation) in July 2003
- Modification of gas/liquid oxygen control from Ar-H₂-H₂O to Ar-H₂-H₂O + air after 3500 h of effective operation
- Optimized manual air addition after 17,500 h of effective operation
- Implementation of automatic air addition to Ar or Ar-H₂ after 41,000 h of effective operation

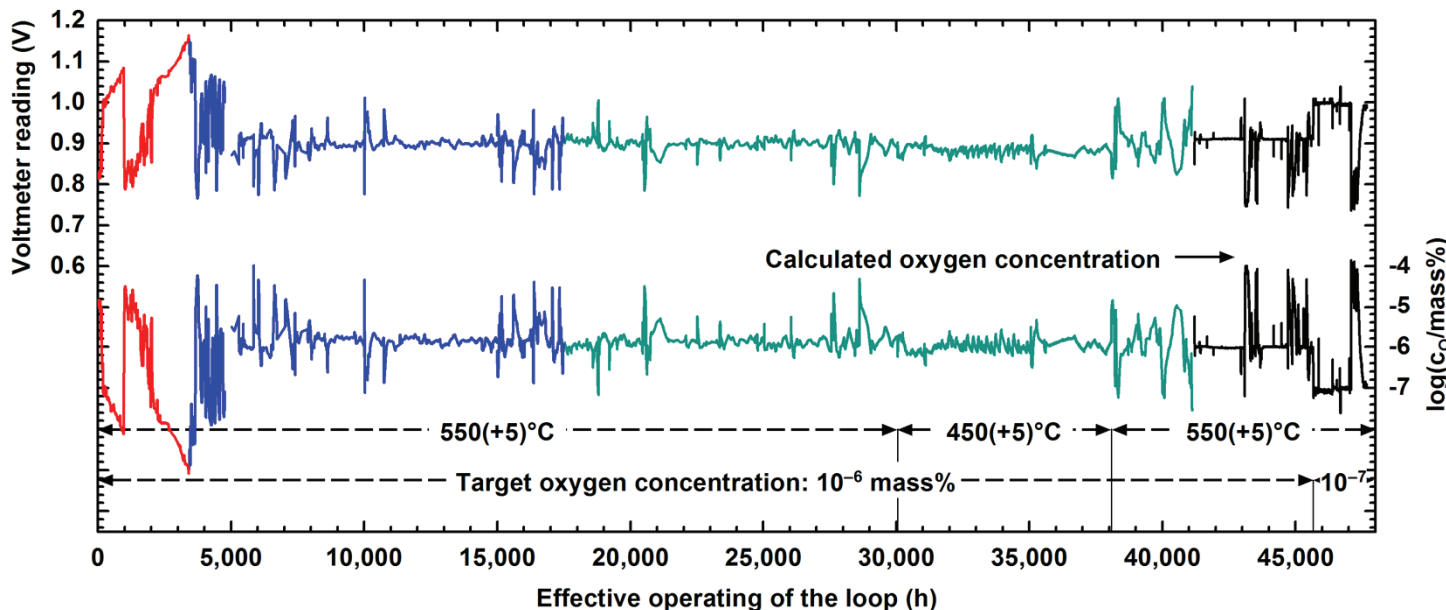
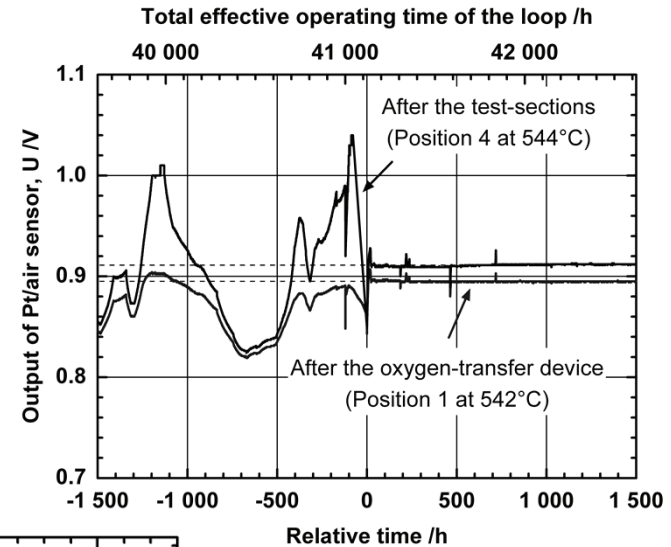
□ Material performance (1.4571, similar to 316Ti)

- Probing of the tubing of the loop after ~23,000, 29,000 and 40,000 h of total operation, i.e., 15,000, 21,000 and 30,000 h of effective operation at 550°C and nominally 10⁻⁶ mass% oxygen
- Tube failure at the inlet of the second test-section after 29,000 h total operation
- Tube failure close to the bottom end of first test-section after ~66,000 h total or 46,311 h effective operation
- Probing of the tubing in connection with the second tube failure

Performance of the oxygen-control system

Gas composition/control strategy

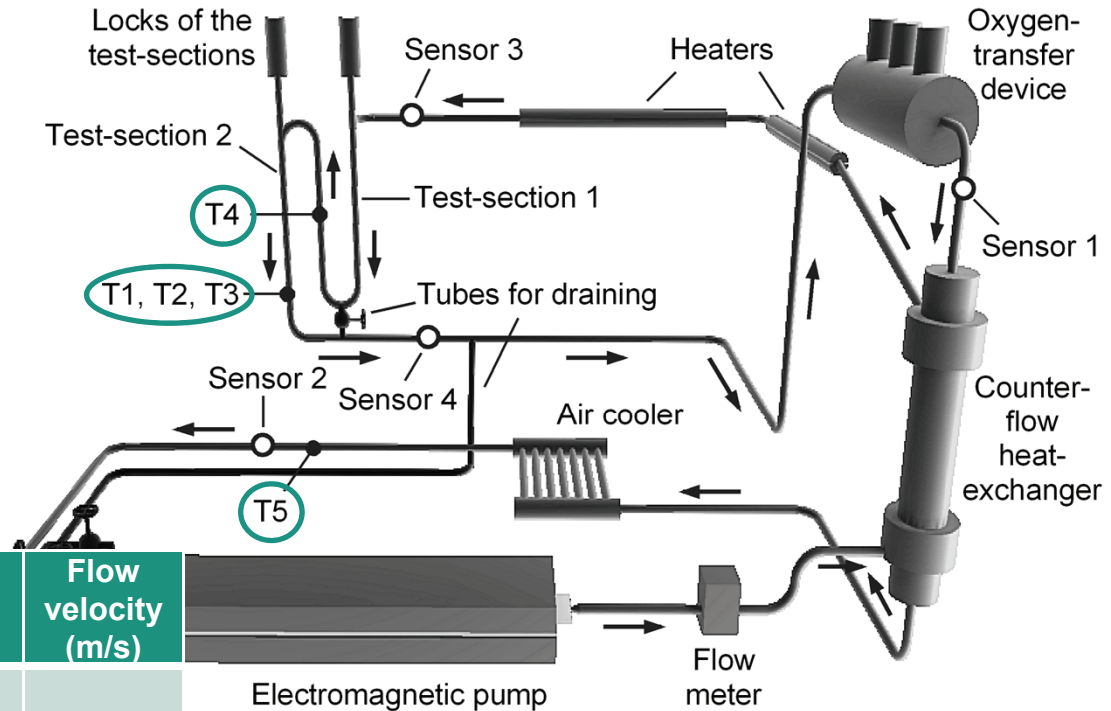
- ❑ Ar-H₂-H₂O corresponding to equilibrium at target oxygen concentration
- ❑ Ar-H₂-H₂O, Ar-H₂O or Ar with varying air addition
- ❑ Optimized manual air addition to Ar-H₂O
- ❑ After implementation of automatic air addition to Ar or Ar-H₂



Before and after automatic air addition has been implemented.

Probing of the tubing of the loop (1)

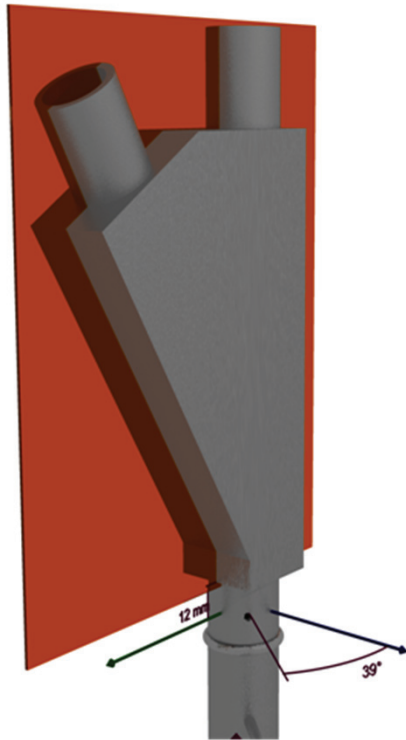
- ❑ Tube samples were pre-oxidised in the loop before first filling with LBE, except for T3
- ❑ Exposure during experiments and pre-conditioning for experiments at 550°C/10⁻⁶ mass% oxygen
- ❑ Periods of low c_O in the beginning of the exposure, except for T3



	Exposure time (h)	Temperature (°C)	Dimensions (mm)	Flow velocity (m/s)
T1	23,000	550°C	Ø25 × 2.5	1.7
T2	29,000			
T3*)	6000			
T4	40,000			
T5	40,000	385°C	Ø33.7 × 3.6	1

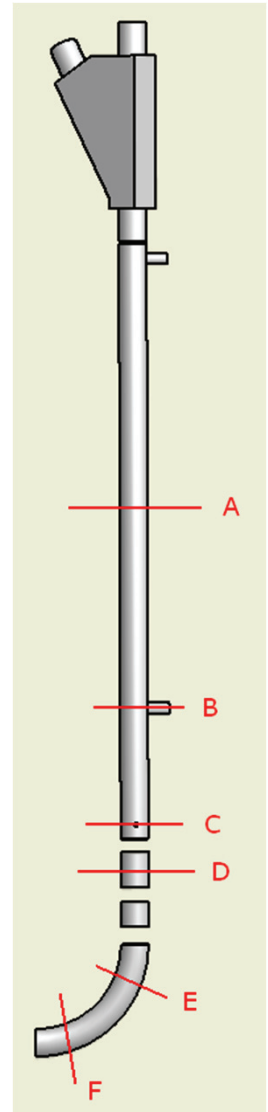
*) : The tube replaced the part removed after ~23,000 h and was not pre-oxidized before operation

Probing of the tubing of the loop (2)



❑ Failure cases

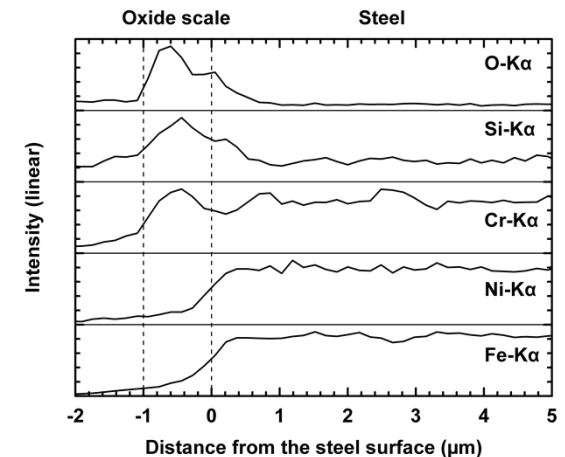
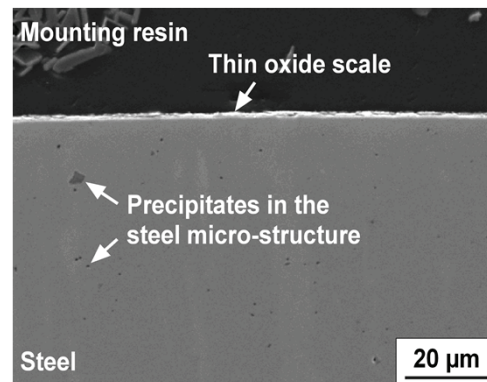
- ❑ At the inlet of the second test-section after ~29,000 h total operation (~20,000 h effective operation)
- ❑ Close to the bottom end of the first test-section after ~66,000 h total operation (46,311 h effective operation)
- ❑ Probing of the removed test-section in various positions, including the site of failure



Corrosion of type 316 austenitic steels in oxygen-containing LBE (1)

□ Protective scaling

- Thin oxide scale ($< 1 \mu\text{m}$) consisting of Cr- or Si-rich oxide layers
- Might have evolved from thin films already existing on the steel surface before exposure
- Similar to the scale formed by pre-oxidation in dry gas (Ar)
- Locally long-lasting phenomenon on specimens exposed at $450/550^\circ\text{C}$, 10^{-6} mass% O in the test-sections of the loop
- Not observed on tube samples taken from the hot leg of the loop; effect of long exposure time and varying c_{O} (?)



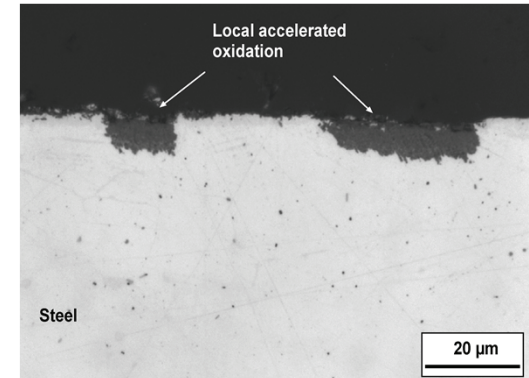
1.4571 specimen in the test-section of the loop after exposure for 3495 h to oxygen-containing flowing LBE at 550°C and $c_{\text{O}} \approx 10^{-6}$ mass%

Corrosion of type 316 austenitic steels in oxygen-containing LBE (2)

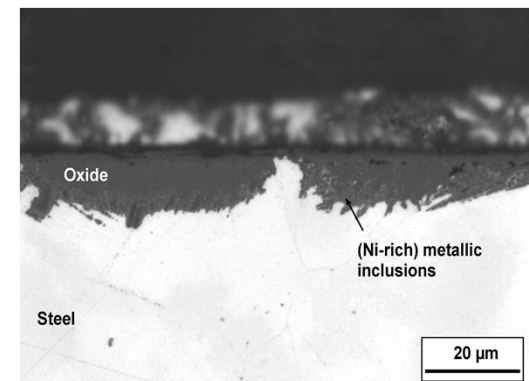
□ Accelerated oxidation

- Starts locally where the thin oxide scale lost integrity or did not form
- Formation of $\text{Fe}(\text{Fe}_x\text{Cr}_{1-x})_2\text{O}_4$, Fe_3O_4 and an internal oxidation zone; the latter two depending on oxygen content, temperature (or flow velocity)
- The thicker scale spreads on the steel surface with time and becomes partially continuous
- Varying c_{O} (mostly lower than 10^{-6} mass%) seems to promote accelerated oxidation

1.4571 specimens in the test-sections of the loop:



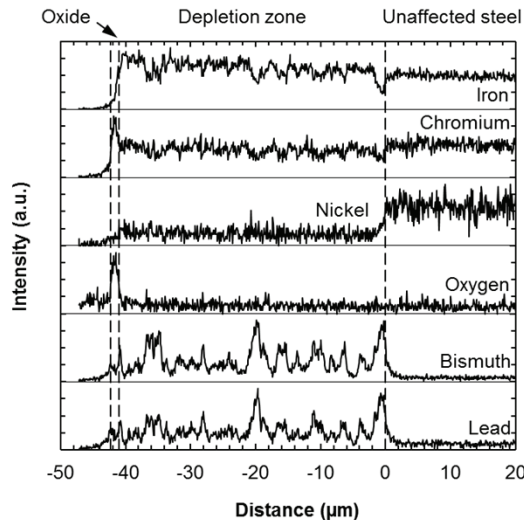
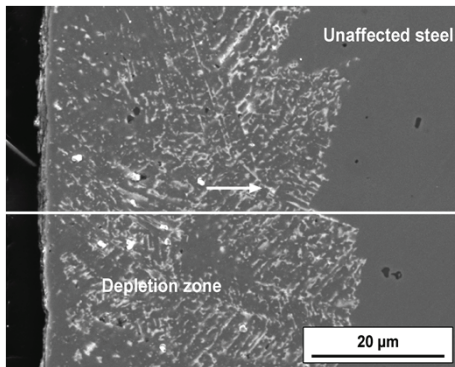
After exposure for 3495 h at 550°C and $c_{\text{O}} \approx 10^{-6}$ mass%



After exposure for 10,006 h at 550°C and varying c_{O}

Corrosion of type 316 austenitic steels in oxygen-containing LBE (3)

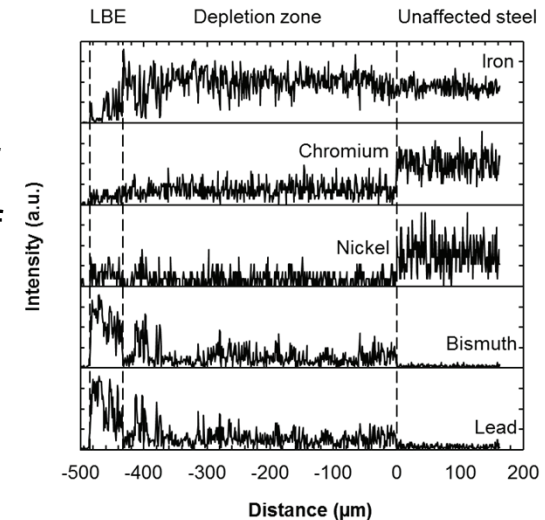
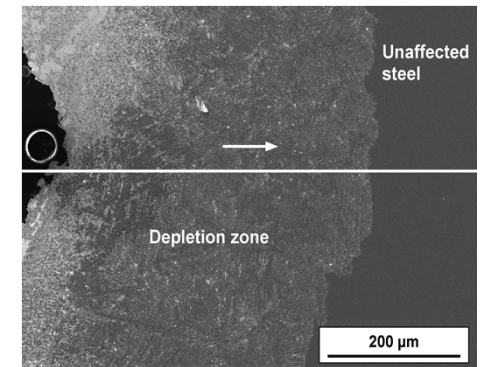
1.4571 after exposure for 5012 h at 550°C and $c_O \approx 10^{-6}$ mass%



□ Selective leaching (Ni, Cr)

- Starts locally with preferential dissolution of Ni and penetration of Pb and Bi into the depletion zone
- Phase transition from austenite into ferrite resulting from Ni depletion
- Dissolution of Cr after oxygen depletion in the liquid metal penetrating the steel (critical penetration depth)
- In general, insignificant amounts of Cr oxide inside or on the surface of the depletion zone
- Removal of loosened steel grains by the liquid-metal flow in a later stage of severe selective leaching

1.4571 after exposure for 5012 h at 550°C and $c_O \approx 10^{-6}$ mass%



Corrosion of type 316 austenitic steels in oxygen-containing LBE (4)

Basic mechanism of selective leaching

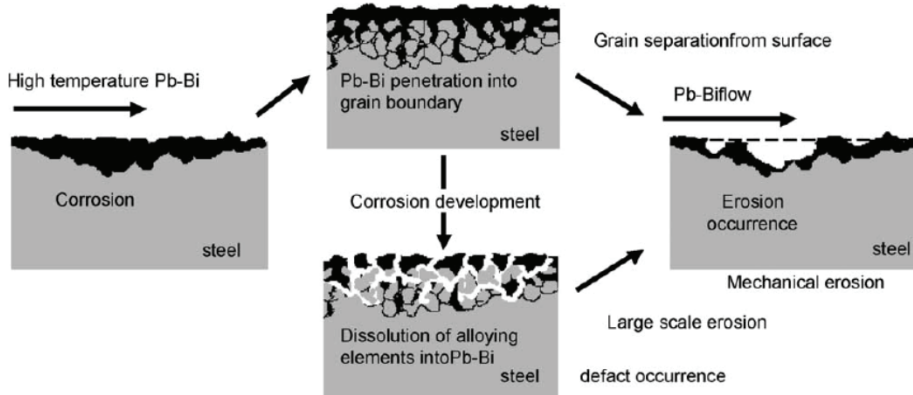
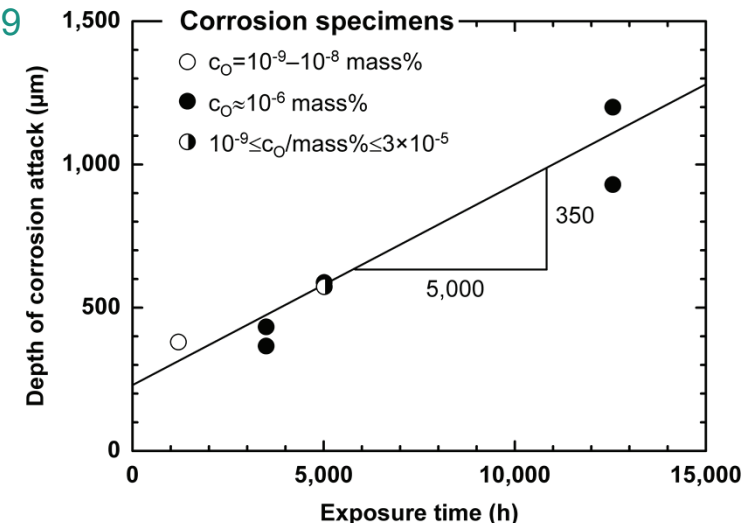


Figure taken from Kondo, et al., J. Nucl. Mater. 343 (2005) 349–359

Maximum corrosion depth on 1.4571

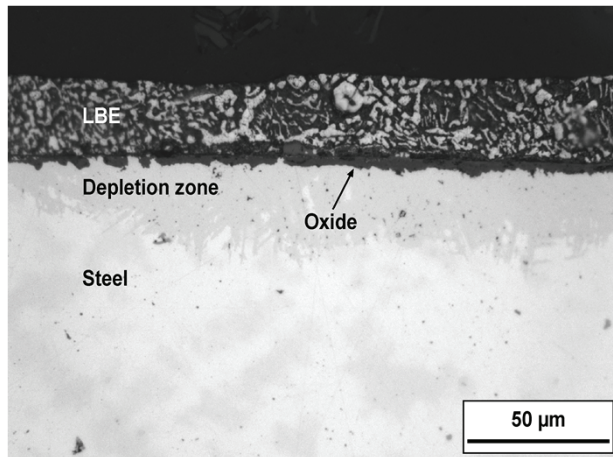
- ❑ At 550°C and 2 m/s flow velocity
- ❑ Observed on cylindrical specimens exposed in the test-sections of the CORRIDA loop
- ❑ Maximum attack observed on tube samples from the loop is significantly less



Corrosion of type 316 austenitic steels in oxygen-containing LBE (5)

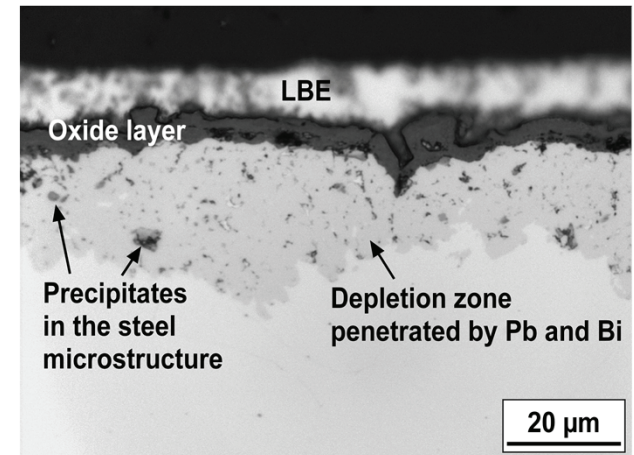
□ “Mixed mode”

- Depletion zone penetrated by Pb and Bi underneath an oxide scale
- Oxide is Cr-rich in comparison to the $\text{Fe}(\text{Fe}_x\text{Cr}_{1-x})_2\text{O}_4$ layer formed by accelerated oxidation
- Result of the transition from selective leaching to oxidation (?)
- Formation of Cr-rich oxide scale can stop selective leaching (?)



- Typical scale observed for some of the tube samples from the CORRIDA loop

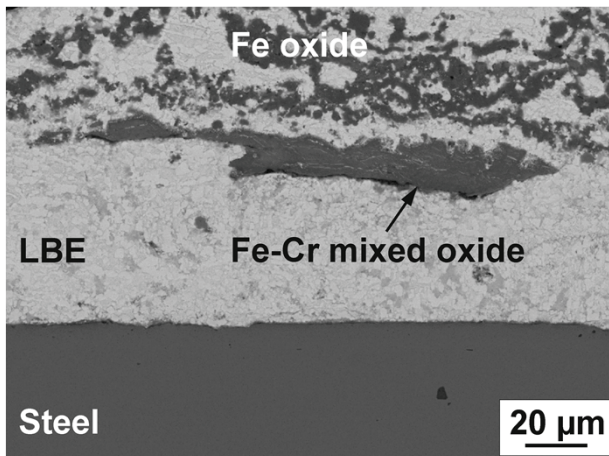
1.4571 specimen exposed in the test-sections after 3495 h at 550°C and $c_{\text{O}} \approx 10^{-6}$ mass%



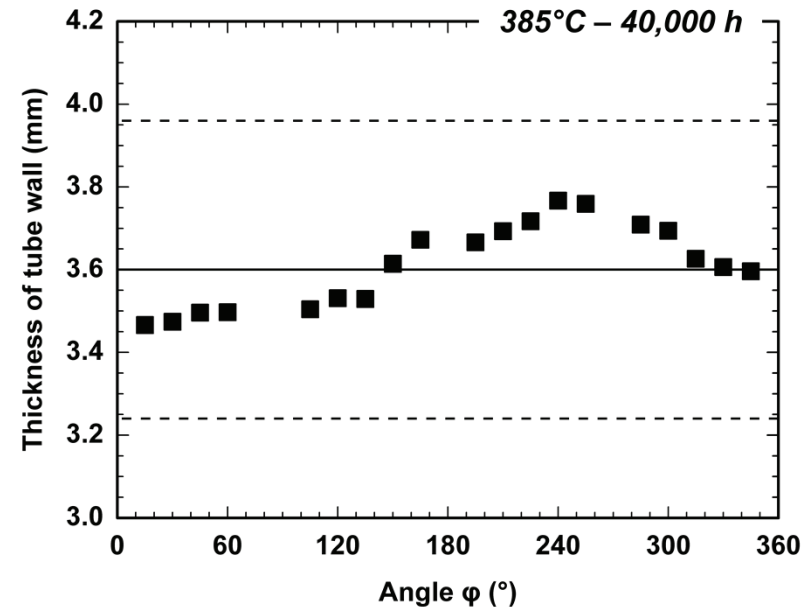
Tube sample taken from the CORRIDA loop after exposure for ~23,000 h to flowing oxygen-containing LBE at 550°C

□ Sample T5 after 40,000 h at 385°C

- Position after the cooler, before magnetic trap
- No significant change in wall thickness after the long-term exposure
- Oxide deposits in adherent solidified LBE, but only in some distance from the tube wall
- Neither deposits nor significant amounts of oxide on the surface



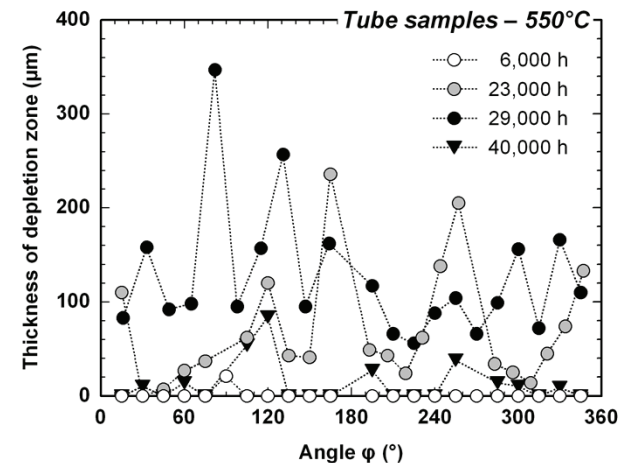
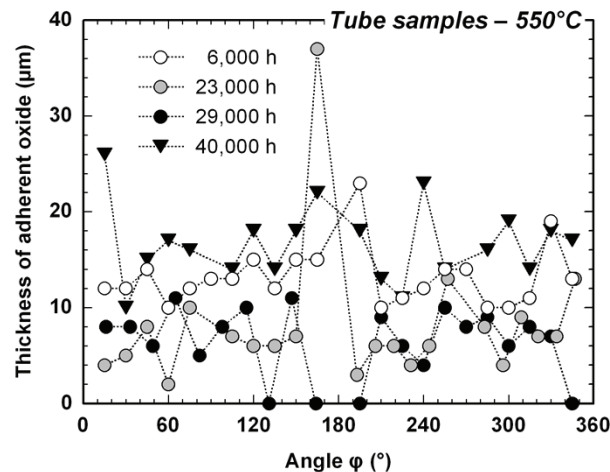
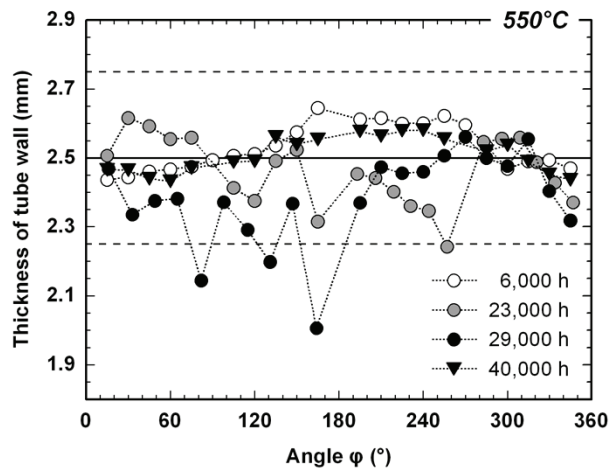
Electron-optical micrograph (BSE)



Results from measuring the residual wall thickness in the microscope

□ Samples from different positions in the hot leg (550°C)

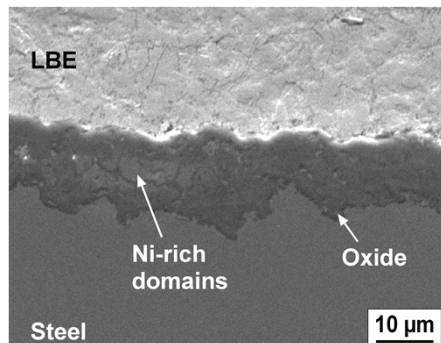
- After exposure for up to 40,000 h
- Non-distinctive results as a function of exposure time for residual wall thickness, oxide scale and depletion zone
- Only few data points for residual wall thickness below the manufacturing tolerance of the used tubes
- No clear conclusions on the benefit of pre-oxidation possible



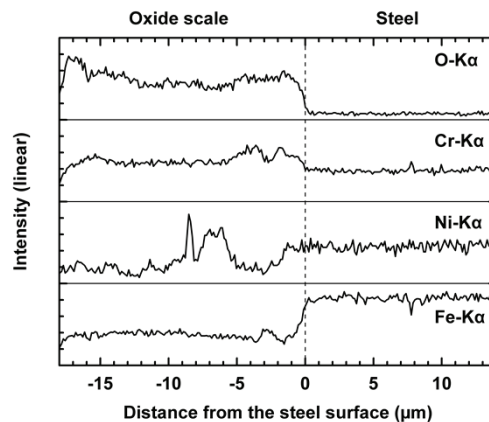
Results from quantitative measurements in the light-optical microscope

Corrosion scales formed in the hot leg (550°C)

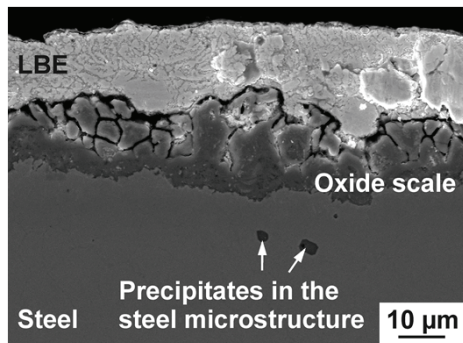
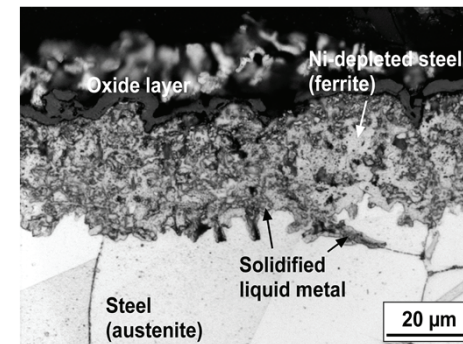
- T3 (6000 h) and T4 (40,000 h) mainly show oxidation; T3 was not pre-oxidised
- T1 (23,000 h) and T2 (29,000 h) show significant selective leaching



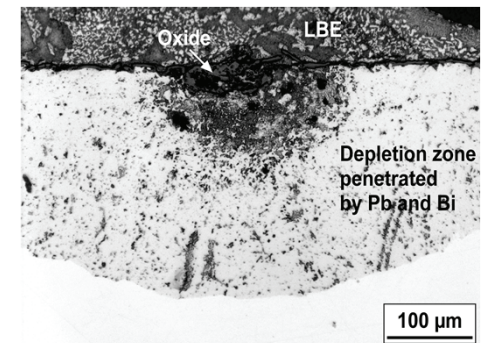
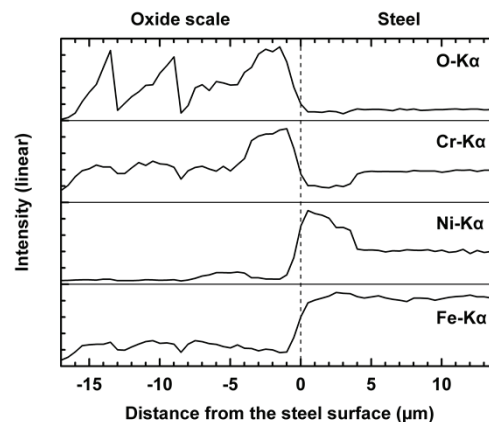
Oxide scale on T3



Corrosion scales typically observed on T1 and T2



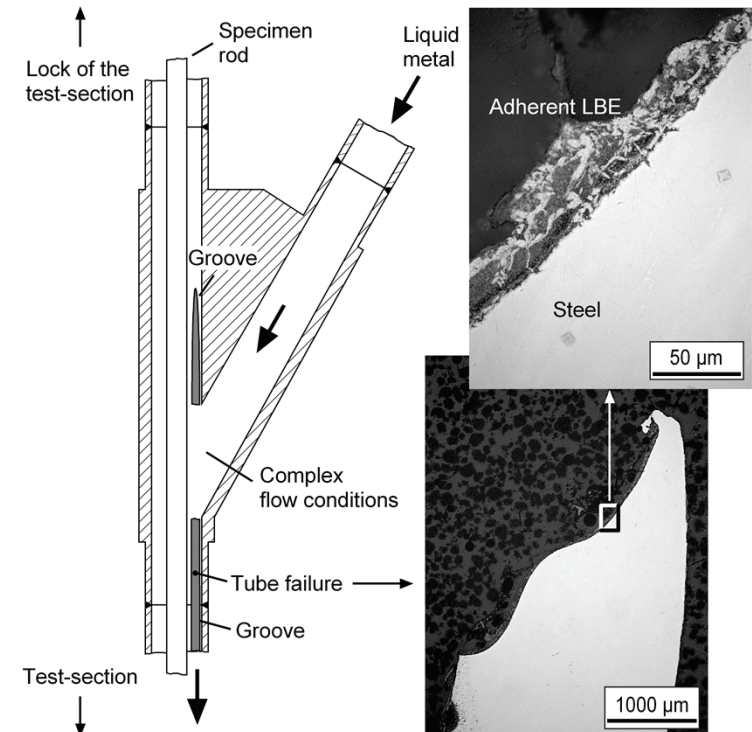
Oxide scale on T4



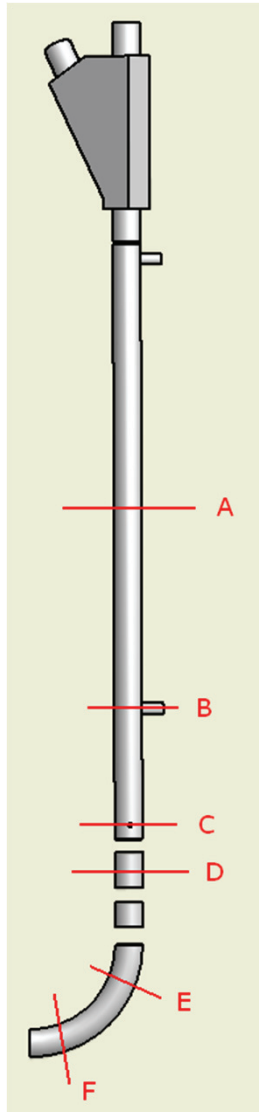
Tube failures in the hot leg of CORRIDA (1)

❑ After 29,000 h, at the inlet of the second test-section

- ❑ Hole the size of a pinhead in the straight bottom part of the approximately Y-shaped inlet piece
- ❑ Failure occurred inside a vertical groove that is interrupted at the junction where the liquid metal enters the test-section tube
- ❑ Adherent LBE observed inside the groove, but none of the corrosion scales typical for the steel
- ❑ Erosion caused by the complex liquid-metal flow in the inlet piece was identified as main reason for tube failure
- ❑ Replacement of the inlet piece by a re-designed part
- ❑ Inlet piece of the first test-section was operated for 66,000 h without major damage

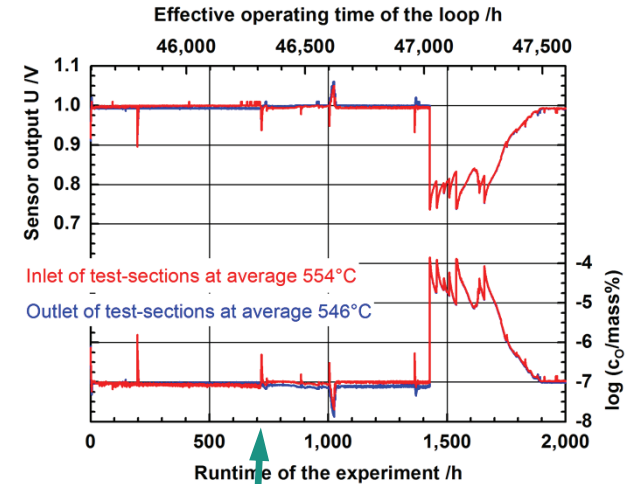


Tube failures in the hot leg of CORRIDA (2)

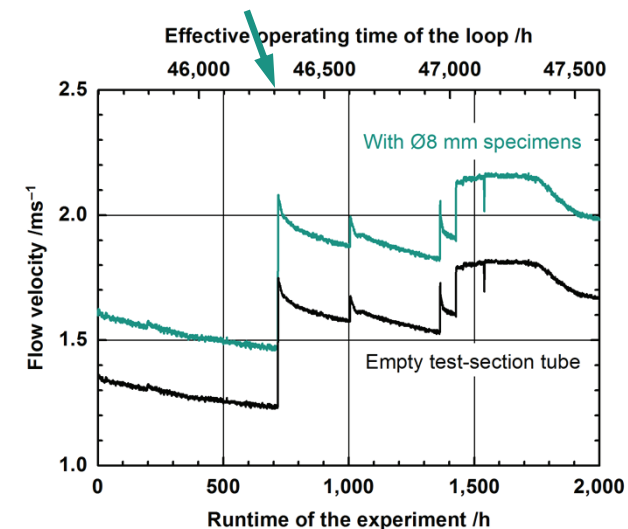


❑ Tubing of the first test-section after 66,000 h

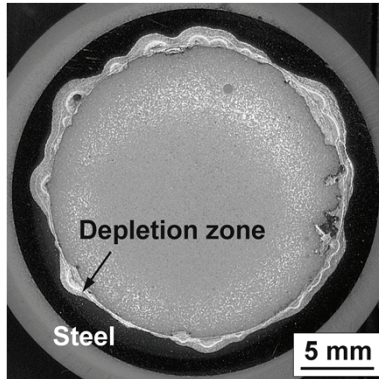
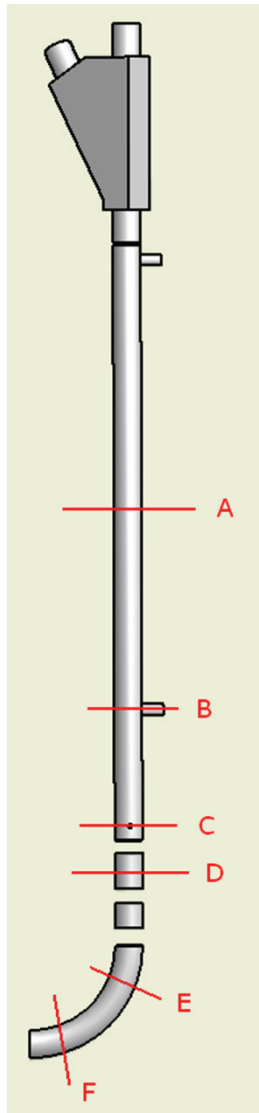
- ❑ During experiment at 550°C/10⁻⁷ mass% O
- ❑ Prior to that, experiments at 450°C and 550°C/10⁻⁶ mass% O and pre-conditioning for 550°C/10⁻⁷ mass% O
- ❑ Ø10 mm leak in Position C that corresponds to the bottom end of the specimen rod
- ❑ **The particular specimen in this position (9Cr steel) was heavily corroded!**
- ❑ Up- and down-stream specimens inconspicuous
- ❑ Oxygen sensors did not indicate excessive oxygen consumption in the test-sections
- ❑ Problems with maintaining constant flow and sudden release of oxygen into the LBE



Tube failure after 715 h of the experiment at 550°C/10⁻⁷ mass% O

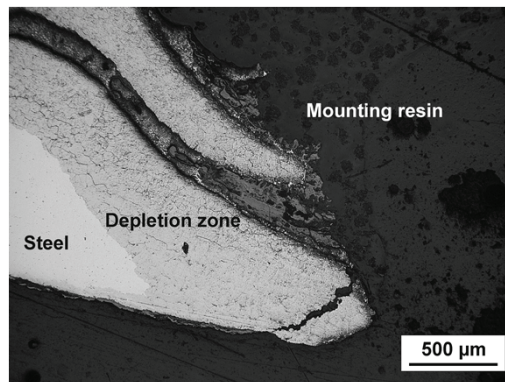


Metallographic analysis of the failed tube (1)



Cross-section in Position A

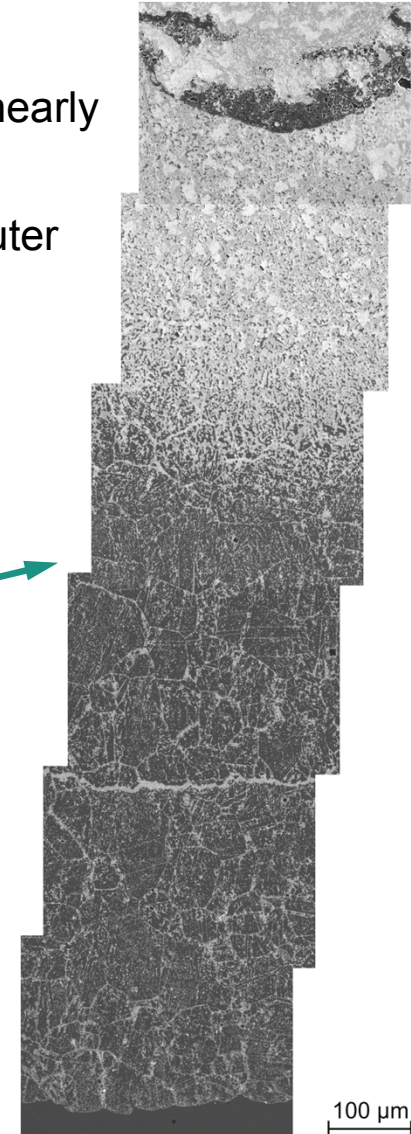
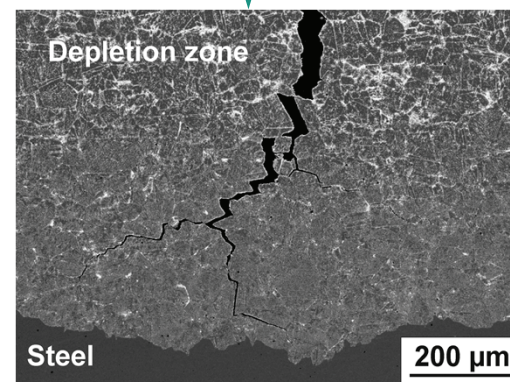
Site of failure

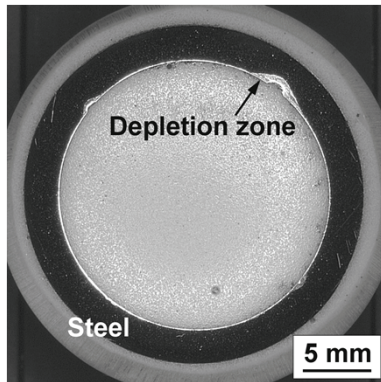
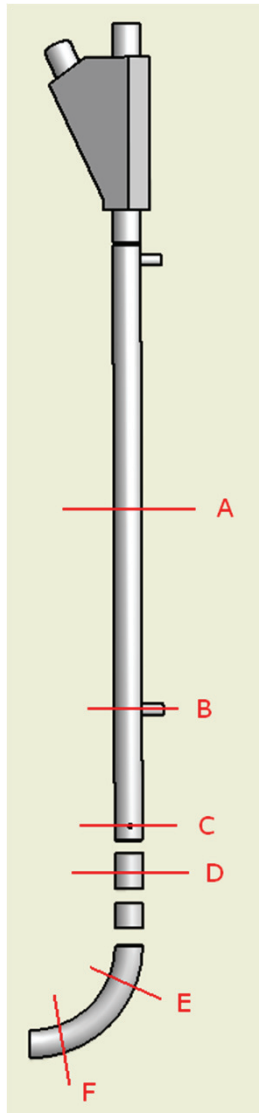


Positions A, B, C

- Severe selective leaching along nearly the complete inner tube surface
- Depletion zone locally reaches outer tube surface
- Cracking of the mechanically unstable depletion zone probably is the ultimate cause of failure in Position C

In a cross-section nearby the site of failure



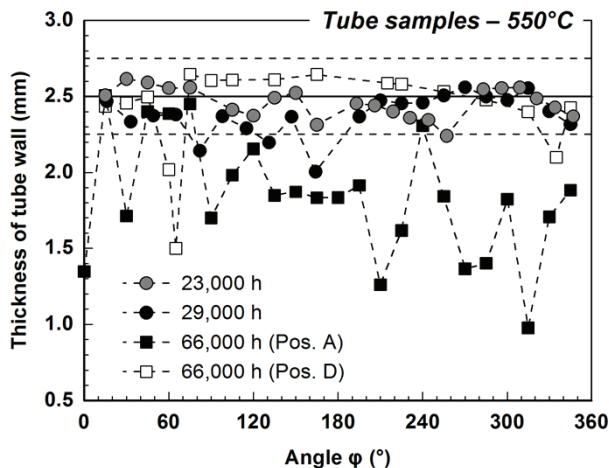


Cross-section in Position D

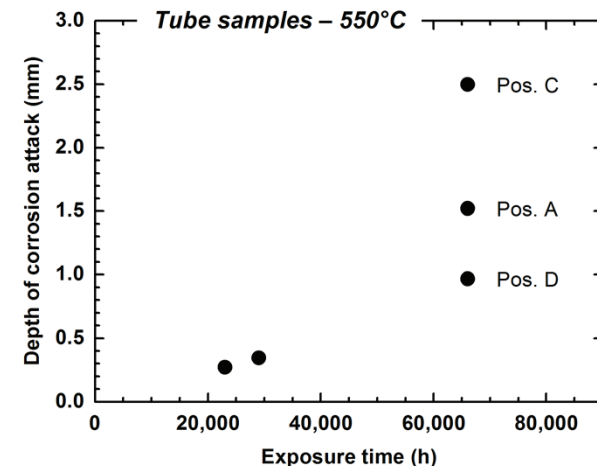
Positions D, E, F

- Severe selective leaching is a local rather than general phenomenon
- Qualitatively similar in overall appearance to tube samples T1 (23,000 h) and T2 (29,000 h)
- Absence of specimens inside the tube is the obvious difference to Positions A, B, C

Residual wall thickness



Maximum corrosion attack observed (selective leaching)



- ❑ Performance of type 316 steels (1.4571) in flowing oxygen-containing LBE is generally characterised by the interplay of three basic corrosion phenomena
 - ❑ Protective scaling – the optimum situation at negligible material degradation
 - ❑ Accelerated oxidation – still favourable if scales do not become too thick
 - ❑ Selective leaching of Ni and Cr – the critical process with high local corrosion rates

- ❑ Mixed corrosion mode: Selective-leaching and oxidation
 - ❑ Presence of significant amounts of Cr-rich (Mn-rich) oxide on the depletion zone
 - ❑ How can a return from fast selective leaching to slower corrosion underneath an oxide scale be promoted?

- ❑ Failure as a result of selective leaching is inherent to the use of type 316 steels at 550°C or higher
 - ❑ Local rather than global conditions are decisive
 - ❑ Negligible corrosion of the tubing of the CORRIDA loop after 40,000 h at 385°C (and of specimens in the test-section after 8000 h at 450°C/10⁻⁶ mass%)

- ❑ At 2 m/s average flow velocity, erosion usually follows corrosion (selective leaching)
 - ❑ Corrosion resistance is the primary material property to look at
 - ❑ Exception: complex flow patterns

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