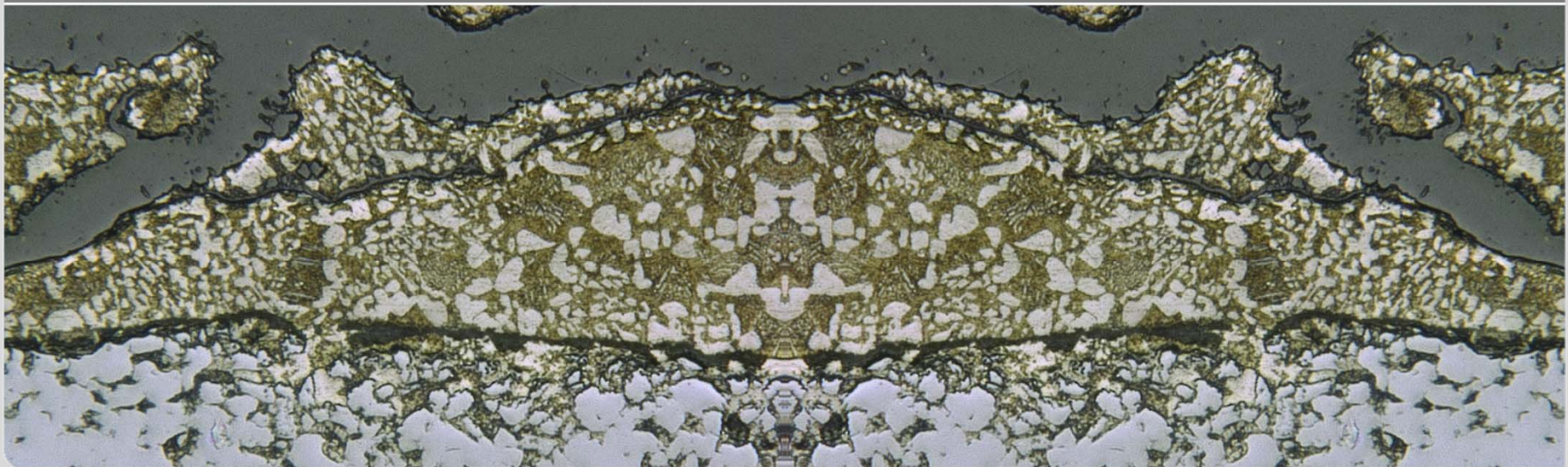# OXIDATION AND SOLUTION OF STEELS IN LIQUID LEAD-BISMUTH EUTECTIC (LBE)

Carsten Schroer

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

www.kit.edu

Background

- **Favourable properties of liquid metals**
  - High thermal conductivity and boiling point
  - Reasonably low dynamic viscosity

    → Efficient heat transfer medium/ coolant for thermal energy conversion

  - Some show minimum interaction with neutrons (e.g., sodium and lead)

    → Essential for fast neutron reactors

  - Liquid heavy metals release neutrons under proton irradiation (e.g., mercury, lead and bismuth)

    → Allows for sub-critical nuclear fuel in a proton-accelerator driven system

  - …

- **Compatibility between liquid metals and steels?**
  - Major steel elements are soluble in liquid metals
  - Formation of intermetallic phases
  - Degradation of mechanical properties
  - Still in question for lead alloys, especially lead-bismuth eutectic (LBE)

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Liquid metal/steel interactions

❑ **Corrosion**

- Solution of steel elements with preferential (Ni, Cr) rather than general removal
- Surface recession and/or development of a near-surface depletion zone
- Penetration of the depletion zone by liquid metal
- Formation of intermetallic phases on the steel surface or in a near-surface zone inside the steel

Observed on the µm-scale, accessible by light-optical microscopy (LOM), scanning-electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) …

❑ **Degradation of mechanical properties**

- Damage accumulation at the surface due to corrosion
- Or arising from phenomena below the µm-scale:
  - Processes affecting one- and two-dimensional defects (dislocations, grain boundaries, cracks)
  - Especially apparent at low temperatures
- Quantification by tensile, slow-strain rate, creep, fatigue, fracture-toughness tests performed either in or after exposure to the liquid metal

Liquid-metal embrittlement (LME), liquid-metal induced embrittlement

Impact of oxygen solved in liquid metals on steel corrosion
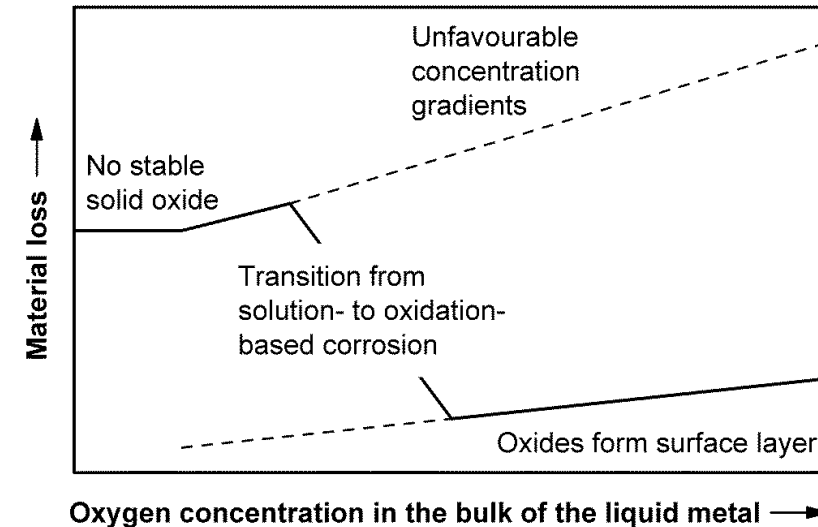
❑ **"Absence" of oxygen**
- Chemical oxygen potential too low for remarkable interactions with steel elements
- Steel elements dissolve in the liquid metal
- (Absorption of liquid metal constituents by the steel
- Formation of intermetallic phases)

❑ **Low-oxygen conditions**
- Solid oxides of steel elements are stable
- Amount of oxides formed too small for a continuous surface layer
- Concentration gradients that <u>promote</u> solution of steel elements may develop in the liquid metal

❑ **High-oxygen conditions**
- Solid oxides of steel elements form a continuous surface layer
- Solution of steel elements still possible, but only after diffusion through solid oxide
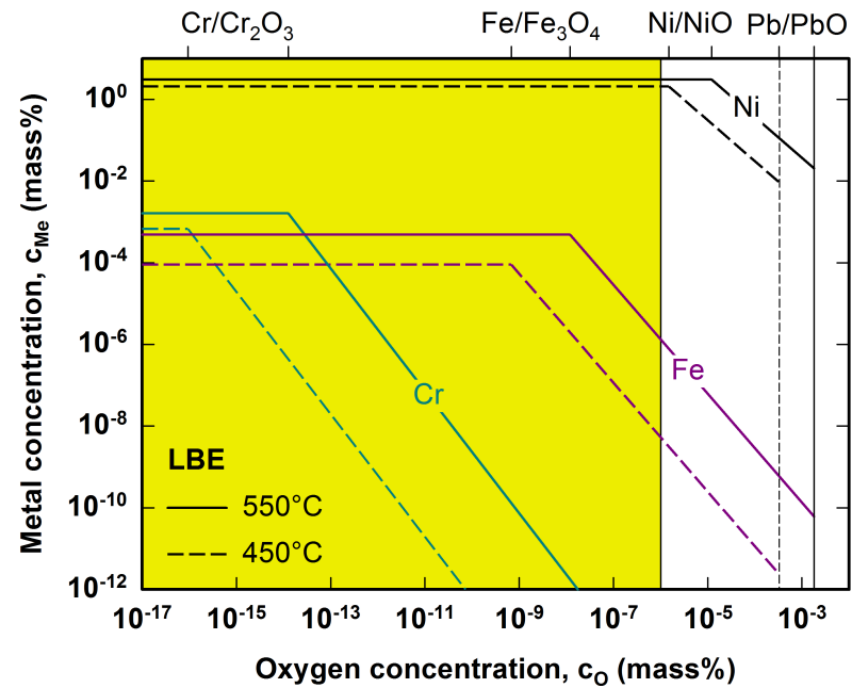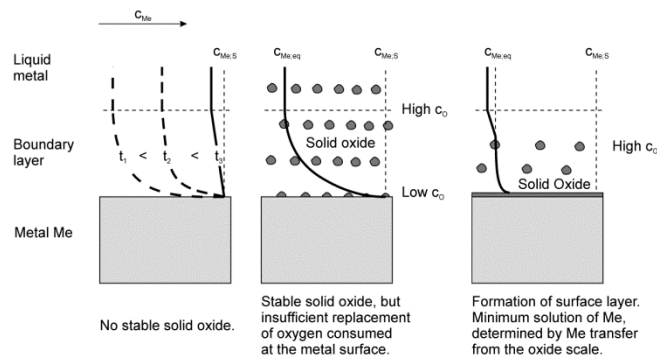

Material loss ↑

No stable solid oxide

Unfavourable concentration gradients

Transition from solution- to oxidation-based corrosion

Oxides form surface layer

Oxygen concentration in the bulk of the liquid metal →

➡ Transition from solution-based to oxidation-based corrosion with increasing oxygen concentration

➡ **Continuous oxide layer is the goal of deliberate oxygen addition (Pb, LBE)**

➡ Locally low-oxygen conditions even when oxygen concentration in the bulk of the liquid metal is high

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Effect of oxygen on the solution of steel elements

❑ **Unfavourable concentration gradients**

- ▪ May establish if dissolving metal Me forms stable solid oxides
- ▪ Equilibrium concentration of solved Me then decreases with increasing c_O (following from the solubility product of the solid oxide)
- ▪ Unfavourable solubility gradient if c_O increases ($c_{Me;eq}$ decreases) with increasing distance from the steel surface

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Effect of oxygen on the solution of steel elements
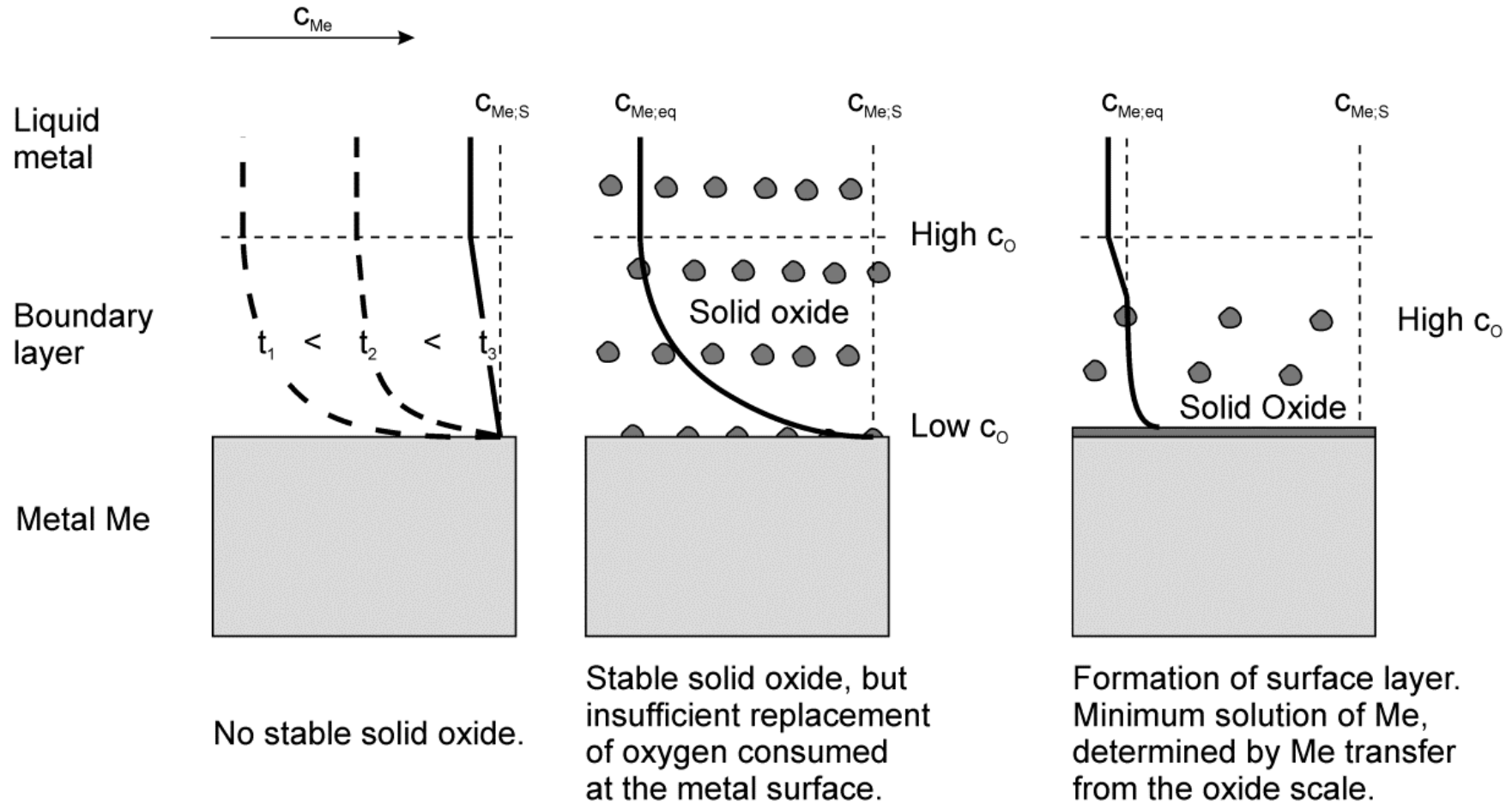
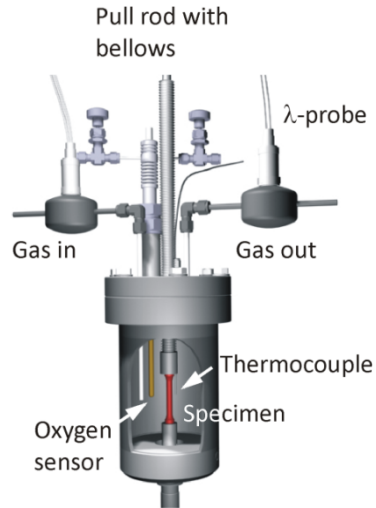Illustration of concentration profiles that are decisive for diffusion of Me in the liquid metal

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Research at KIT/IAM-WPT related to liquid Pb or LBE

❑ Long-term corrosion in oxygen-containing lead-bismuth eutectic (LBE)
- ❑ At a flow velocity of 2 m/s
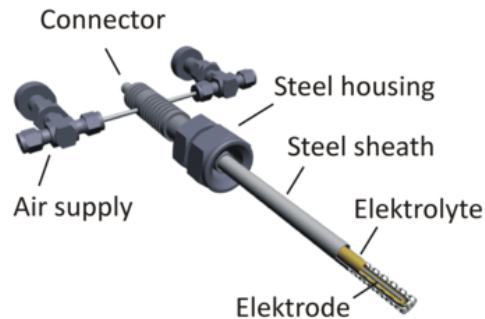- ❑ T = 400–550°C
- ❑ $c_O = 10^{-7}–10^{-6}$ mass%

Locks for exchange of specimens
Oxygen-transfer device
Heater
Test sections
Cooler
Counter-flow heat exchanger
EM-pump
Dump tank

CORRIDA-Loop

❑ Creep and stress rupture in oxygen-containing Pb alloys
- ❑ Static Pb or LBE
- ❑ T = 450–650°C
- ❑ $c_O = <<10^{-8}–10^{-6}$ mass%

Pull rod with bellows
λ-probe
Gas in
Gas out
Thermocouple
Oxygen sensor
Specimen

CRISLA

Connector
Steel housing
Steel sheath
Air supply
Elektrolyte
Elektrode
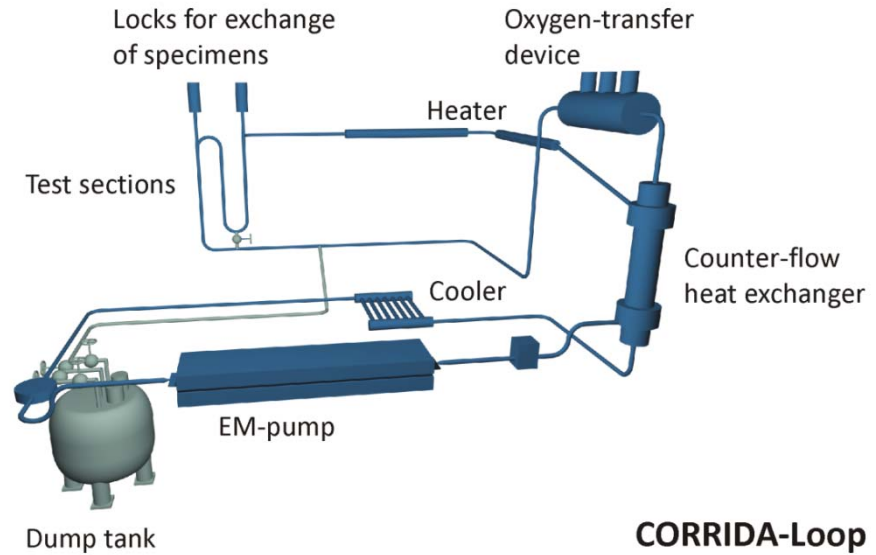
❑ Instruments and methods of controlling solved oxygen in Pb alloys
- ❑ Via oxygen-containing gas (gas/liquid oxygen transfer)
- ❑ Potentiometric oxygen sensors

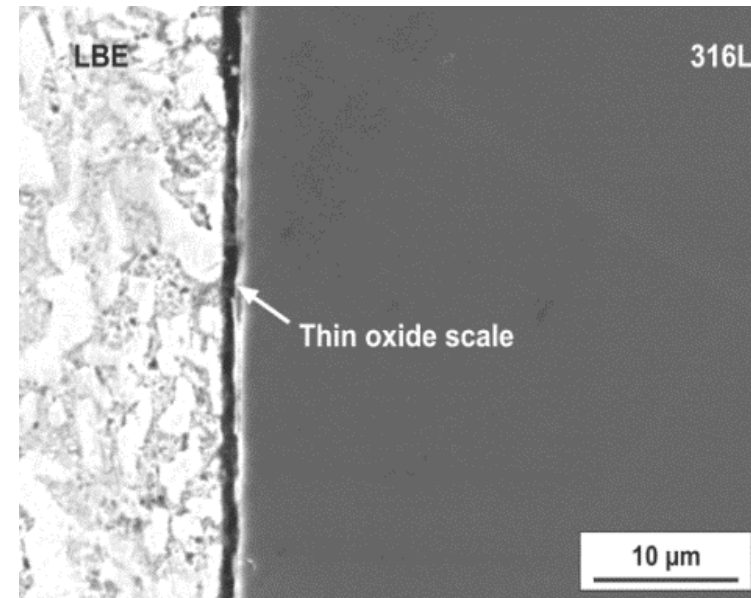# Long-term corrosion studies in flowing oxygen-containing LBE conducted in the CORRIDA loop

Temp. (°C)	Flow v. (m/s)	Oxygen (mass%)	Max. time (h)	Tested materials
Almost completely evaluated:				
550 (+5)	2 (±0.2)	~10^{-6}	~ 20,000	CSEF (T91, E911, EUROFER), ODS steels, Si-containing F/M steel, Type 316SS, surface alloyed steels (Al), ...
450 (+5)	2 (±0.2)	~10^{-6}	~ 8000	CSEF (T91, E911), EUROFER-ODS, Si-containing F/M steel, pure Fe, Type 316SS
Evaluation in progress:				
550 (+5)	2 (±0.5)	~10^{-7}	~ 2000	CSEF (T91, E911, P92), Si-containing F/M steel, Type 316SS, 15-15Ti, aluminide coatings
450 (+5)	2 (±0.2)	~10^{-7}	~ 9000	CSEF (T91, E911, P92), Si-containing F/M steel, Type 316SS, 15-15Ti
400 (+5)	2 (±0.2)	~10^{-7}	~ 10,000 (indicative)	CSEF (T91, E911, P92), Si-containing F/M steel, pure Fe, Type 316SS, 15-15Ti

Oxidation of 9Cr ferritic/martensitic and austenitic steels in oxygen-containing LBE
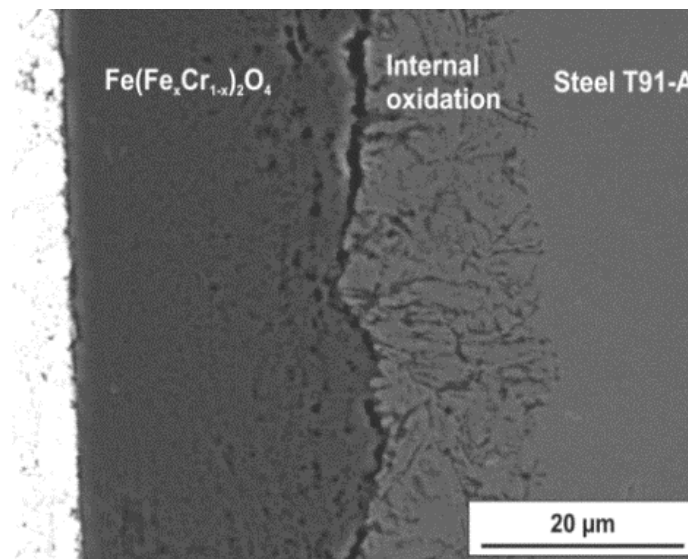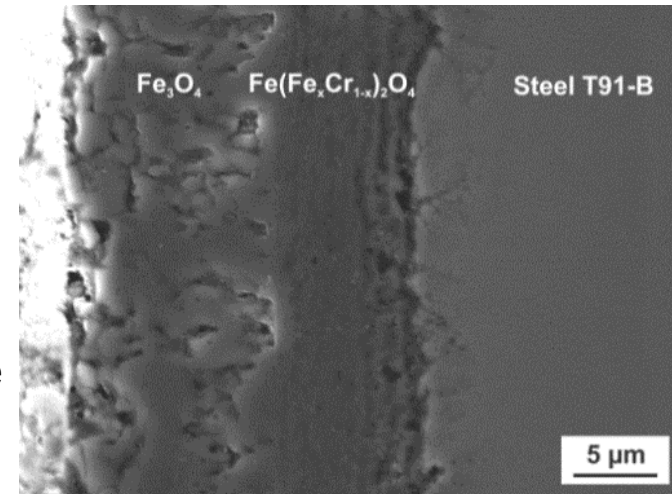
□ **Protective scaling**
- Thin Cr- (Si-) rich oxide scale (thickness ~1 µm or less)
- Precursors of this scale are likely to be present already on the original material
- Insignificant growth in thickness with increasing exposure time
- Release of Fe, Ni and other steel elements to the liquid metal is likely to be negligible
- Local degradation gives way to faster corrosion processes
- Dominant oxidation process for Type 316 steels and 15-15Ti, especially at T≤ 450°C and c_O≤ 10^{-6} mass%

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Oxidation of 9Cr ferritic/martensitic and austenitic steels in oxygen-containing LBE
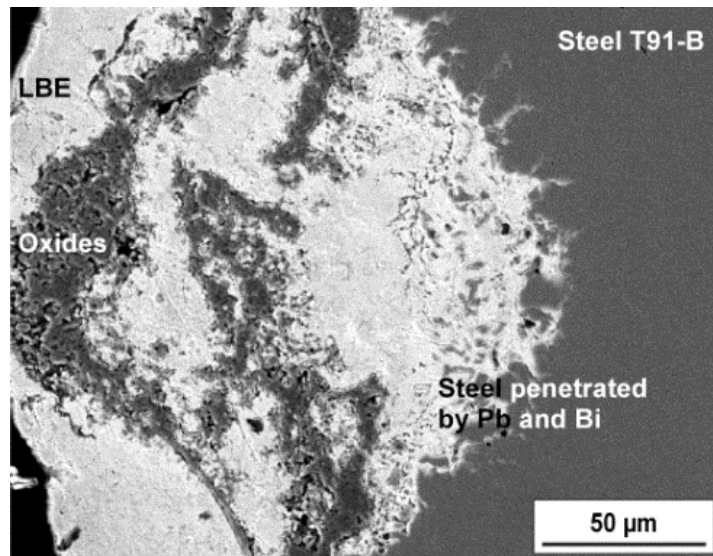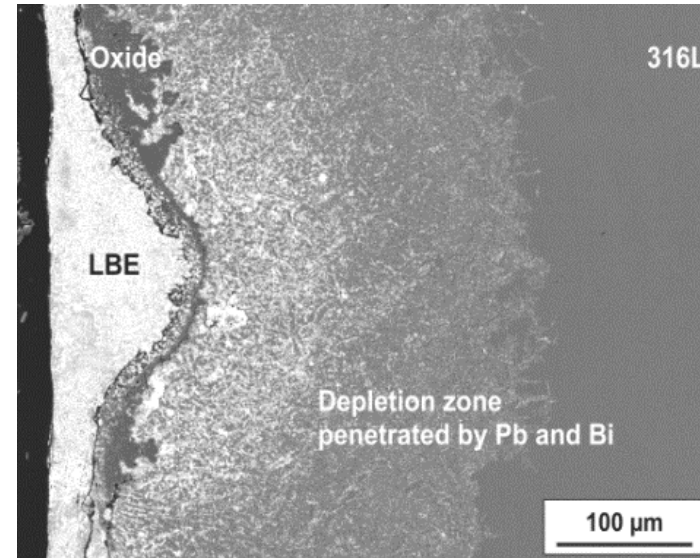
❑ **Accelerated oxidation**
- Typical for and, finally, the general corrosion process of 9Cr steels, after failure of the thin Cr-rich scale
- Less frequent occurrence on austenitic steels, especially at T≤ 450°C and c_O≤ 10^{-6} mass%
- Comparatively thick scales generally consisting of Fe_3O_4, $Fe(Fe_xCr_{1-x})_2O_4$ and an internal oxidation zone
- Release of Fe to the LBE at the oxide scale surface
- Fe_3O_4 is missing at high T
  and low c_O
  (or high flow velocity)

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Solution-based corrosion in oxygen-containing LBE

□ **Type 316 steels, 15-15Ti**

- Selective leaching of Ni and Cr
- Formation of a ferritic depletion zone that is penetrated by the liquid metal
- Occasionally oxide (precipitated) on the surface, but transfer of removed elements to the LBE dominates
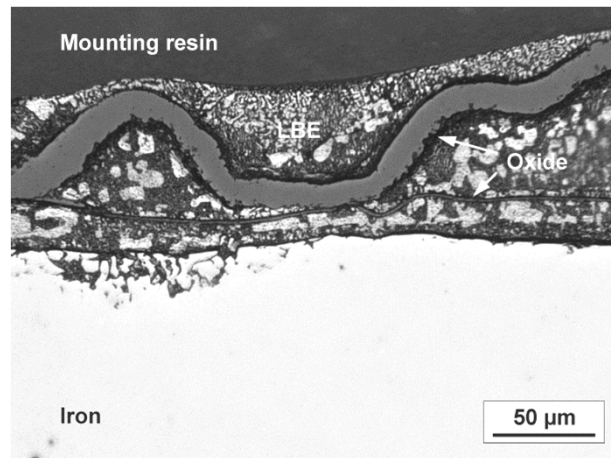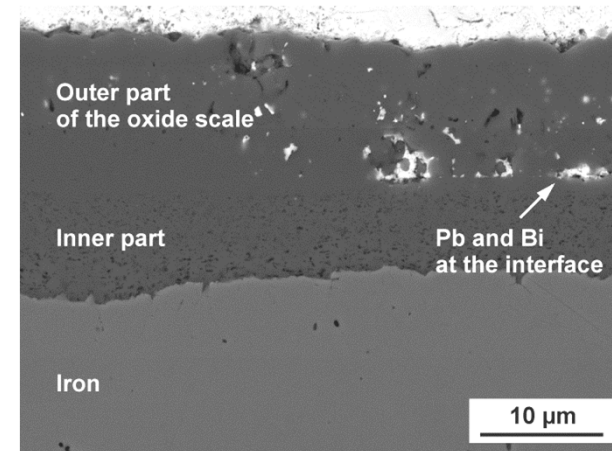- Starts locally from failure of the thin Cr-scale
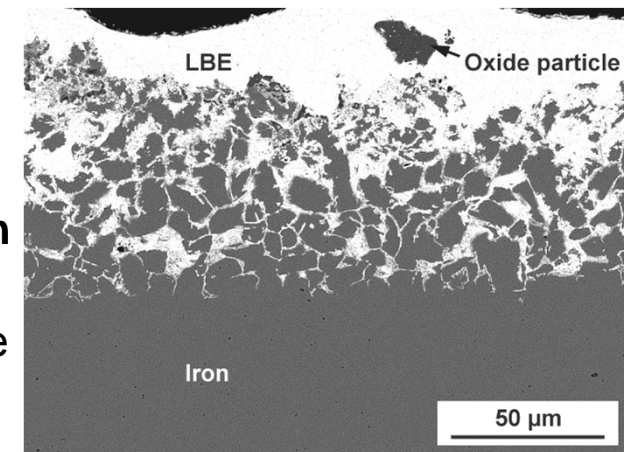

□ **9Cr ferritic/martensitic steel**

- Probably starts from penetration of LBE into the oxide scale formed during accelerated oxidation
- Steel elements may be selectively (Cr) or generally removed, depending on local conditions
- Predominance of steel element release over accumulation in oxides not always clear

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Performance of Fe in flowing oxygen-containing LBE at 450°C, 2 m/s and 10^{-6} mass% oxygen

❑ **No protective scaling**

❑ **Accelerated oxidation**

- A porous inner magnetite (Fe_3O_4) layer replaces the spinel ($Fe(Fe_xCr_{1-x})_2O_4$) found in Cr steels
- Oxidation not significantly faster, but scale integrity poorer than for Cr steels
- Magnetite scale detaches, buckles and finally fails more frequently in comparison to Cr steels

❑ **Solution-based corrosion**
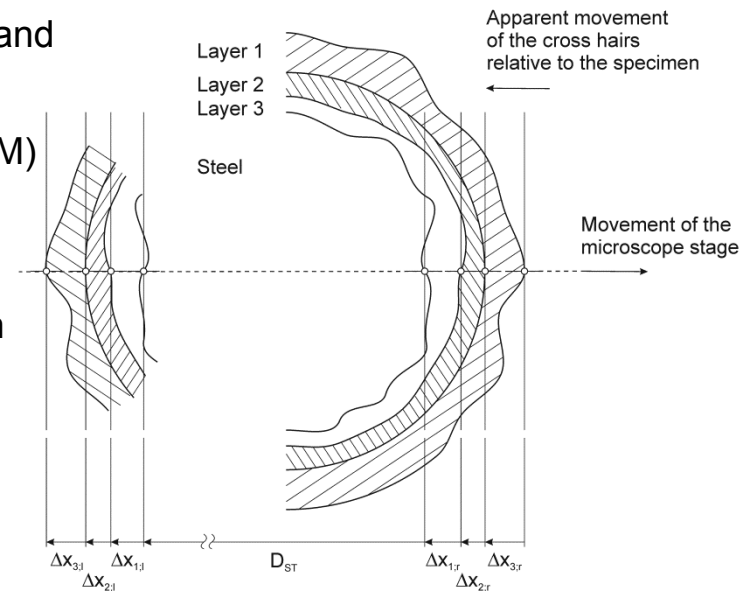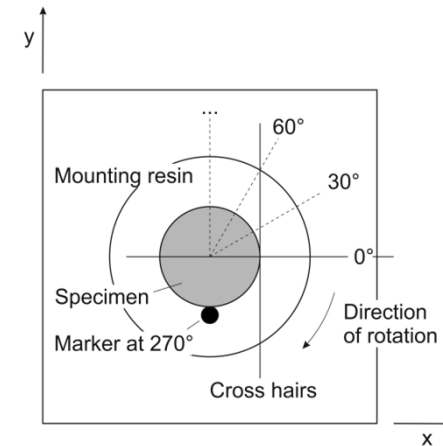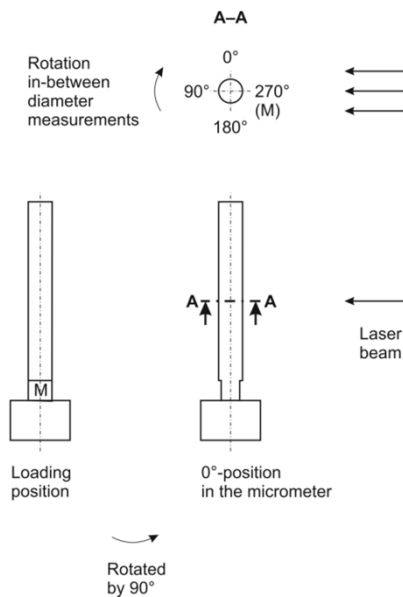
- Underneath or in the absence of buckled scale

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Quantification of corrosion
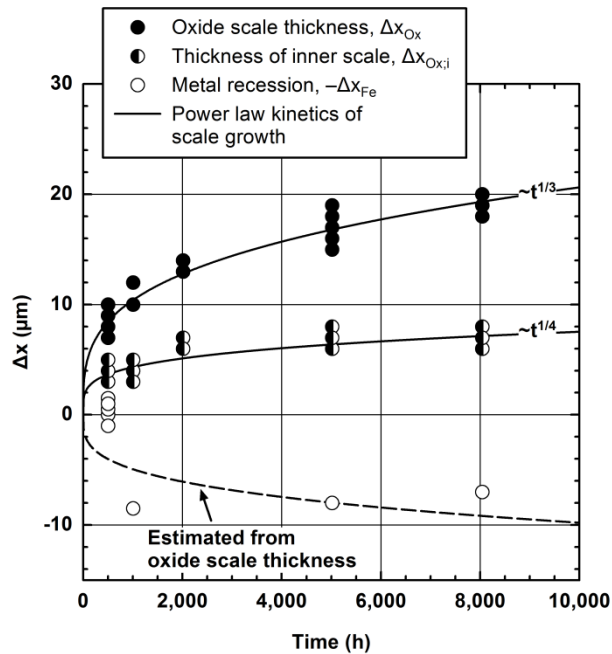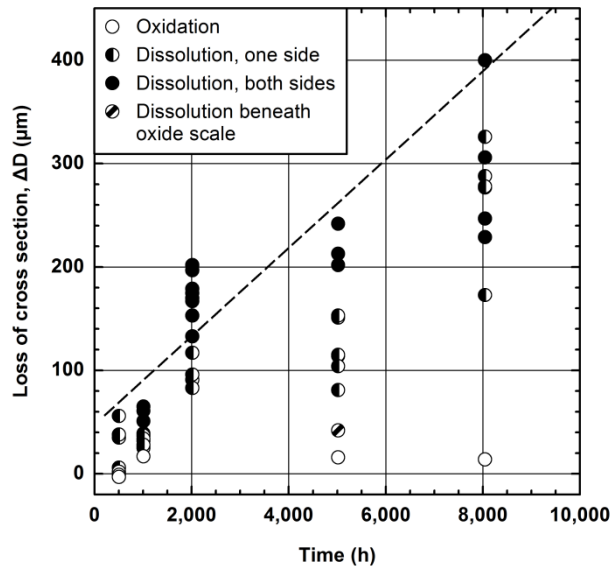
- ❑ **Goal of quantification**

  - ▪ Material loss, average of general corrosion and maximum of local corrosion
  - ▪ Thickness of adherent (oxide) scale
  - ▪ Overall change in dimensions, including the scale
  - ▪ Amount of metals transferred to the liquid metal

- ❑ **Metallographic method (cylindrical specimens)**

  - ▪ Measurement of initial diameter in a laser micrometer with 0.1 µm resolution

    - ▪ Diameter of unaffected material and thickness of corrosion scales determined in a microscope (LOM) at minimum ×500 magnification, with 1 µm resolution
    - ▪ Occurrence of different corrosion modes on opposing sides of the re-measured diameter is considered in the evaluation

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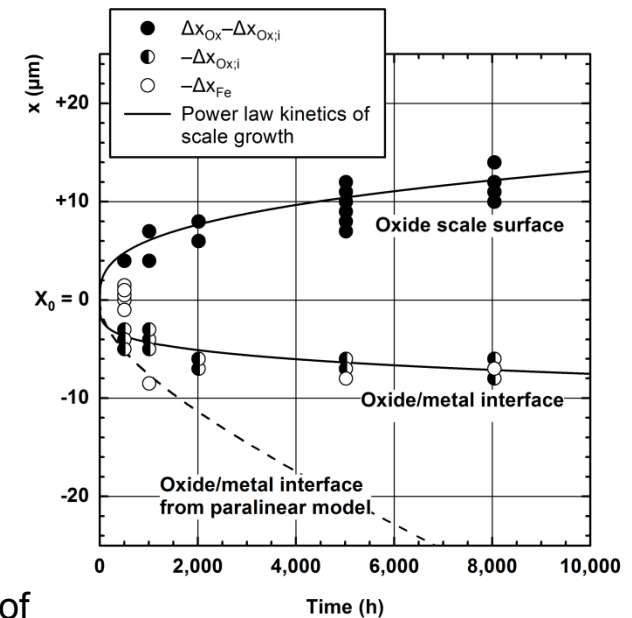
Example evaluation: Oxidation of Fe in LBE at 450°C, 2 m/s, 10^{-6}% O
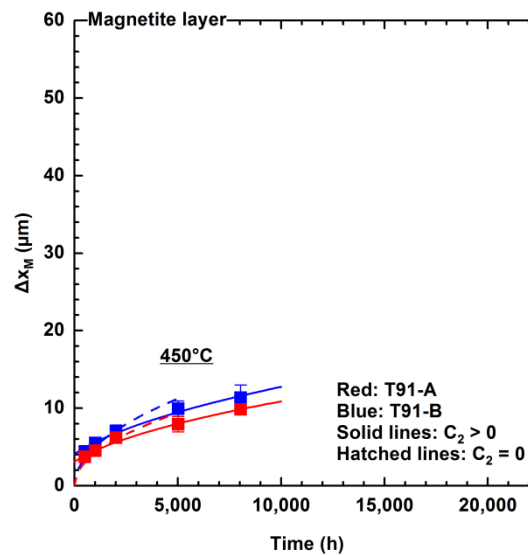
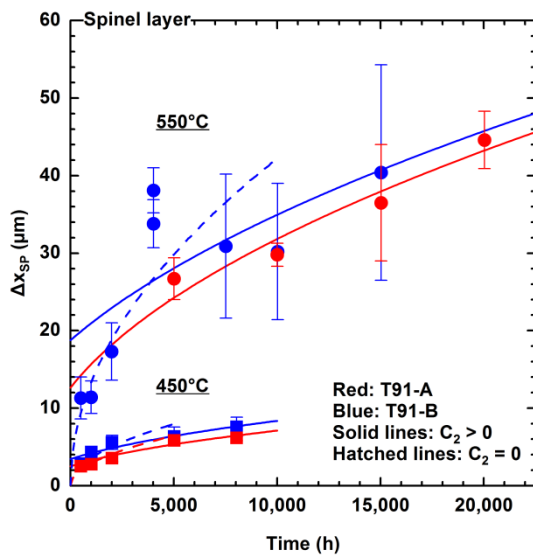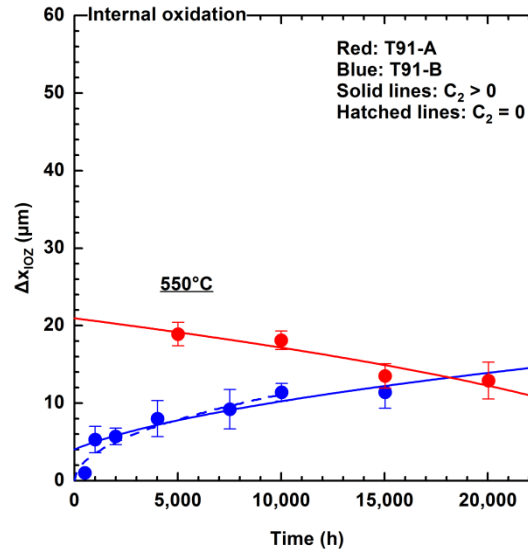❑ **Classification of local measurements**
- Only diameters with oxidation on both sides useful for determining the recession of solid Fe
- Oxide scale thickness from any evaluated site that shows oxidation
- Quality of measurements?

❑ **Analysis of oxidation data**
- Local scale thickness and recession of solid Fe as a function of are compared with typical rate laws
- Amount of Fe solved by the liquid metal estimated from Fe mass balance (if not directly linked to a parameter of the kinetics of scale growth)
- Rate laws of scale growth, solution and Fe recession need to match each other
- Estimation of the position/movement of interfaces from the determined kinetics

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Kinetics of accelerated oxidation of 9Cr steel (e.g., T91) in LBE at 450/550°C, 2 m/s, 10⁻⁶% oxygen
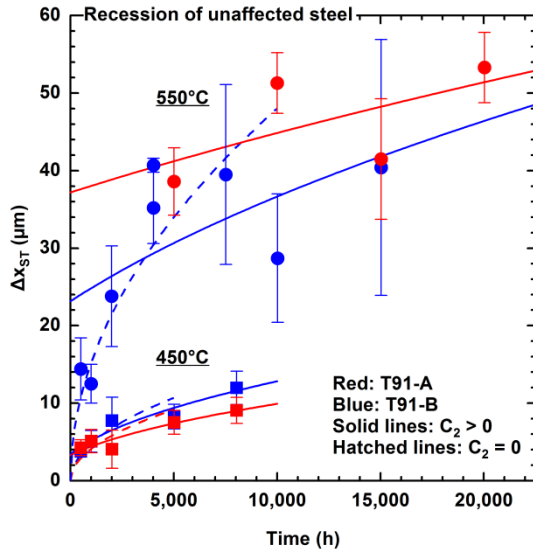
□ **Parabolic approach $\Delta x^2 = k_2 t$**
  - Good approximation for short term data
  - Overestimates steel recession and scale thickness in the long run

□ **Parabolic approach $\Delta x^2 = k_2 t + C_2$**
  - $C_2 > 0$ reflects initially fast progress
  - Corresponds well with both steel recession and scale growth for long term data
  - Believed to be more appropriate for data extrapolation than other power laws or logarithmic approach

□ **Paralinear approach** $\dfrac{d\Delta x}{dt} = \dfrac{k_p}{2\Delta x} + k_l$
  - Approximates the scale thickness
  - Significantly overestimates metal recession

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Kinetics of solution-based corrosion of Type 316 steels in LBE at 450/550°C, 2 m/s, 10⁻⁶% oxygen

Red: 316L
Blue: 1.4571
Squares: 450°C
Circles: 550°C
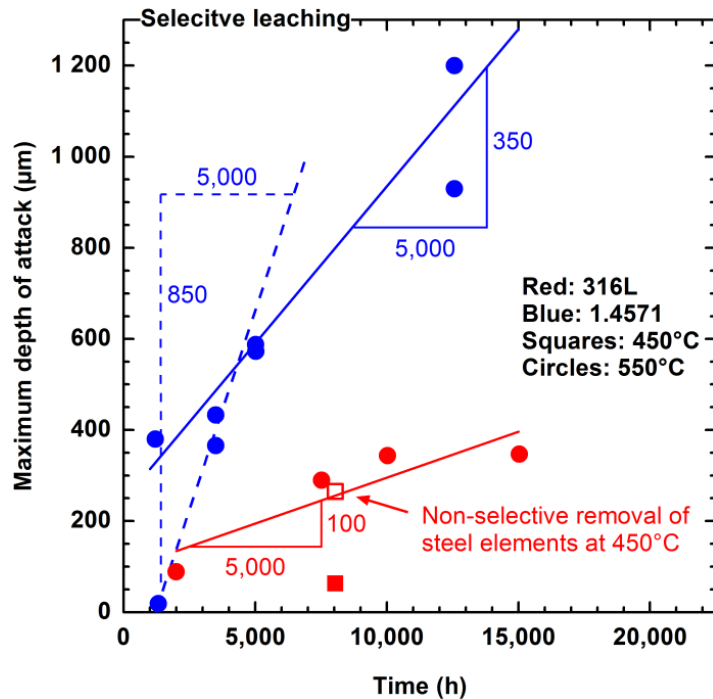
□ **In general, selective leaching of Ni and Cr**
- Only few sites on investigated specimens may be affected
- Incubation times around 5000 and 1000 h at 450 and 550°C, respectively
- Maximum depth observed on the investigated cross section is evaluated
- Approximation of the kinetics by two linear rate laws so as to account for initially faster progress

□ **In exceptional cases, non- selective removal of steel elements**
- No kinetic analysis possible so far
- Non-selective removal apparently proceeds faster (in terms of depth of attack) than selective leaching

→ Mass transfer is likely to be equally fast for all steel elements, but limited transport of one or another element in the liquid metal may render the removal selective?

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A mechanism for selective leaching from austenitic steel

- ❑ **Stage I**
  - ▪ Transfer of steel elements in proportion to their concentration in the steel
  - ▪ Fe approaches saturation first, followed by Cr

- ❑ **Stage II**
  - ▪ Especially Fe partially re-precipitates as ferrite, alternatively to transport in the liquid metal
  - ▪ A ferritic depletion zone establishes, with minimum driving force for Fe (Cr) transport inside this zone
  - ▪ Further re-crystallisation of austenite into ferrite via intermittent solution in the liquid metal
  - ▪ Ni is removed via diffusion in the liquid metal that accumulates in the depletion zone

- ❑ **Stage III**
  - ▪ Fe (and Cr) still dissolve and are removed from the depletion zone surface
  - ▪ Recession of the depletion zone surface

Qualitative concentration profiles in the liquid metal
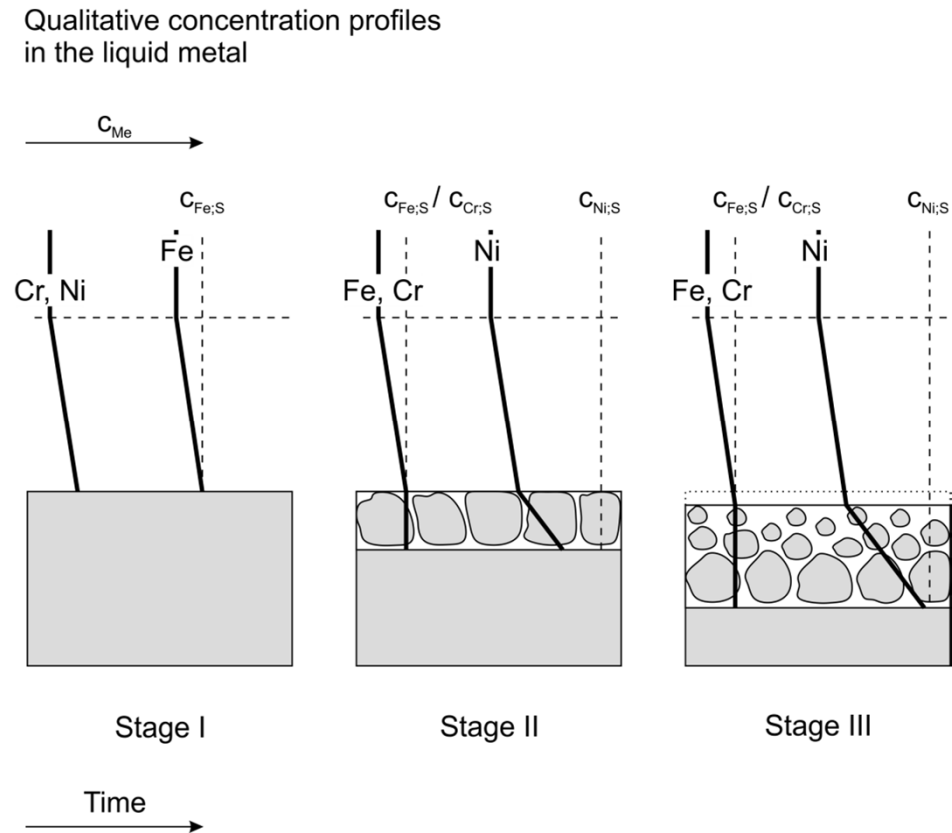
→ Selective leaching is an intermittent step in the general, non-selective removal (solution) of steel elements

→ Selectivity gets increasingly lost, the faster Fe (Cr) transport in comparison to Ni diffusion

Modelling approaches

❑ **Protective scaling**
  - Prediction of scale failure more important than scale growth
  - Approach by point defect model (e.g., developed by Macdonald et al.) seems promising
  - Experimentally observed incubation time of solution-based corrosion or accelerated oxidation may be used as quality criterion

  ❑ **Accelerated oxidation**
    - On the basis of experimental data and rate laws available for oxide growth and steel recession
    - Overall "less-than-parabolic" kinetics due to vacancy accumulation and pore formation at interfaces (point defect model) or re-distribution of Cr in the formed $Fe(Fe_xCr_{1-x})_2O_4$ (more difficult to model)
    - Growth stress or mechanical failure of the thick scale to be considered in addition to chemical failure

    ❑ **Solution-based corrosion, especially selective leaching**
      - Modification of simple mass transfer models by introducing the re-precipitation of solved steel elements in metallic form or as oxides
      - Re-precipitation of ferrite in the depletion zone based on models developed for solid-state phase transformations

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Conclusions

- **Oxidation and solution of steels in LBE**
  - Naturally linked to each other via the solubility product of solid oxides of the steel elements
  - Solid oxide formation is clearly favourable in regard of minimum corrosion if a continuous surface layer forms
  - Solid oxide formation promotes the solution of steel elements if surface oxides are discontinuous or a surface layer fails locally

    - **Phenomena observed on 9Cr and Type 316 steels**
      - Protective scaling, especially on Type 316 steels
      - Accelerated oxidation with formation of Fe_3O_4, $Fe(Fe_xCr_{1-x})_2O_4$ or an internal oxidation zone is more typical for 9Cr steels
      - Solution-based corrosion occurs either directly after failure of the thin protective oxide scale or after some time of accelerated oxidation
      - Austenitic steels generally show selective leaching of Ni and Cr after failure of the thin protective scale

        - **Kinetics and mechanisms**
          - Accelerated oxidation may be approached by two parabolic rate laws accounting for short-term and long-term behaviour, respectively
          - Selective leaching shows two phases characterised by different linear rate laws
          - A detailed mechanism of selective leaching has been proposed
          - Approaches for modelling the observed corrosion modes (separately) are available

Acknowledgements

Olaf Wedemeyer, Aleksandr Skrypnik and Josef Novotny for operation and maintenance of the CORRIDA loop as well as performing the exposure experiments in the loop.

Thank you for your attention!

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