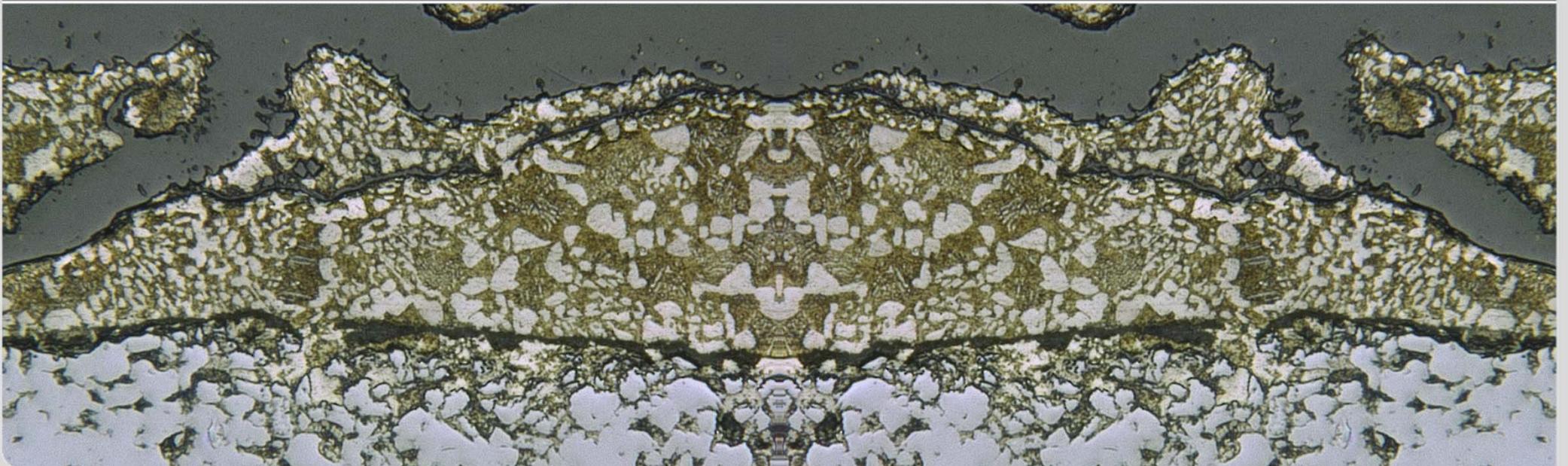


LIQUID-METAL CORROSION OF STEEL IN HLM

with emphasis on corrosion caused by liquid lead-bismuth eutectic (LBE)

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❑ Favourable properties of liquid metals

- ❑ High thermal conductivity and boiling point
- ❑ Reasonably low dynamic viscosity
- ❑ Some show minimum interaction with neutrons (e.g., sodium and lead)
- ❑ Liquid heavy metals release neutrons under proton irradiation (e.g., mercury, lead and bismuth)
- ❑ ...

→ Efficient heat transfer medium/
coolant for thermal energy conversion

→ Essential for fast neutron reactors

→ 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
- ❑ Prominent issue for lead alloys, especially lead-bismuth eutectic (LBE)

Base loadings from particular function

Temperature

- Constant or alternating
- Reversible expansion/contraction
- Thermal ageing

Mechanical stress/strain

- Static or dynamic
- Elastic or plastic deformation
- Risk of cracking or fracture

Wear

- Solid/solid friction
- Surface deterioration

Impact of service environment

Irradiation

- Swelling
- Hardening
- Activation

**Affects primarily
the material volume**

**Surface or
near-surface effects**

Corrosion

- Physico-chemical transformations
- Loss of material
- Change in properties

Abrasion

- Impingement of particles
- Solid/liquid friction

- ❑ A specific component may be affected by the simultaneous action of several forms of load.
- ❑ In the ideal case, the superimposition of singular effects is non-synergistic.
- ❑ Some loadings are, however, interactive.

- ❑ **Corrosion tends to achieve global thermodynamic equilibrium between material and corrosive medium.**
 - ❑ Allows for identifying possible corrosion processes and estimating driving forces.
 - ❑ The fastest process is likely to dominate, especially in the initial stages.
 - ❑ The outcome of corrosion in the long run is, in general, hard to predict.
- ❑ **Each corrosion process involves minimum one mass transfer across an interface and mass transport in the neighbouring phase.**
 - ❑ The slowest elementary step is rate-determining for the particular process.
 - ❑ Boundary conditions for mass transport (diffusion) follow from the assumption of local thermodynamic equilibrium at interfaces.
- ❑ **The presence of a continuous and dense surface scale on the material is of particular importance.**
 - ❑ Facilitated by the stability of solid corrosion products.
 - ❑ Spatial separation of material and corrosive medium increases the number of necessary transfer and transport processes.
 - ❑ Especially slow mass transport through oxide scales considerably reduces overall corrosion rates, may practically stop any further corrosion.
 - ❑ Such a surface oxide may be $\ll 1 \mu\text{m}$ thick and exist on the material before first contact with the corrosive medium.
 - ❑ Passivation of so-called stainless steel is a prominent example.

Factors of potential influence on corrosion

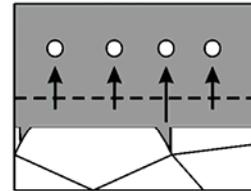
Material	Composition ^{*)} . Microstructure. Geometry.
Corrosive medium	Composition ^{*)} . Available mass/volume per unit material surface area. Static or flowing.
Temperature	Thermo-physical and chemical properties, e.g., solubility limits and phase stabilities. Kinetics of corrosion processes or elementary steps like mass transfer and diffusion.
Temperature gradients	Local differences in characteristics mentioned above. Influence on long-range mass transfer or deposition.
Flow velocity	Mass transfer coefficients. Convective transport. Abrasion.
...	...

^{*)} Impurities may be as important as major constituents.

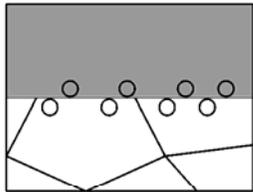
Solid metal in contact with liquid metal

Transfer of material elements onto the liquid metal as long as global saturation of the liquid is achieved

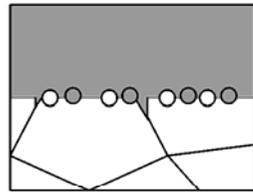
Causes for noticeable recession of the material surface or loss of material



Liquid metal



Metallic material, polycrystalline

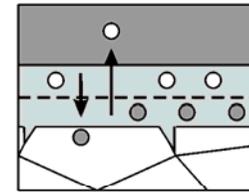


Surface interaction like adsorption, grain boundary grooving

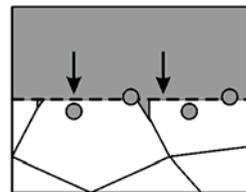
Physical interactions

Possible causes for degraded mechanical properties especially observed at relatively low temperature

Chemical reaction



Formation of intermetallic compounds, depending on transport in the liquid metal or material, and stability of such new phases



Transfer of elements from the liquid onto the material, but mobility in the solid phase is comparatively low

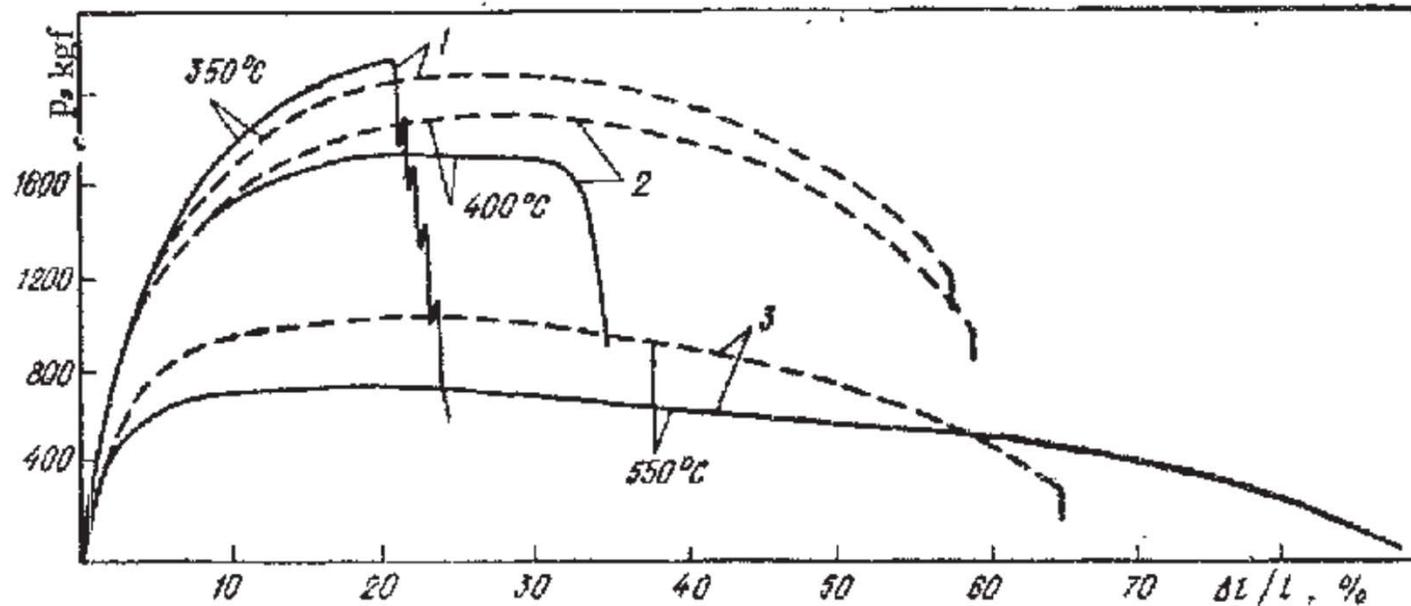


Fig. 2. Tensile load–strain diagrams of Armco iron specimens tested in bismuth (continuous lines) and in vacuum (dashed lines) at 350°C (1), 400°C (2), and 550°C (3).

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.

- **Iron–Bismuth:**
 - Hardening and embrittlement at 350°C.
 - Softening and plastification at 550°C.

- Effects depend on the specific pair of solid and liquid metal.

❑ 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) ...

Liquid-metal embrittlement (LME), softening, ...

❑ Degradation of mechanical properties

- Damage accumulation at the surface due to corrosion
- Or arising from phenomena below the μm -scale:
 - Adsorption of liquid-metal elements
 - Subsequent processes affecting near-surface defects (dislocations, grain boundaries, cracks)
- Quantification by tensile, slow-strain rate, creep, fatigue, fracture-toughness tests performed either in or after exposure to the liquid metal

□ “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

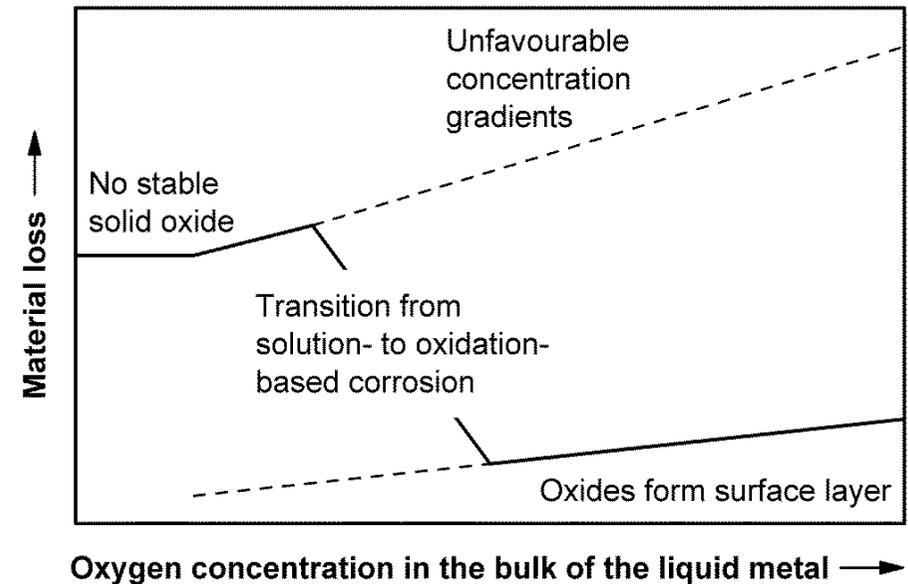
(▪ Formation of intermetallic phases)

□ Low-oxygen conditions

- Solid oxides of steel elements are stable
- Amount of oxides formed too small for a continuous surface layer
- Concentration gradients that promote solution of steel elements may develop in the liquid metal

□ High-oxygen conditions

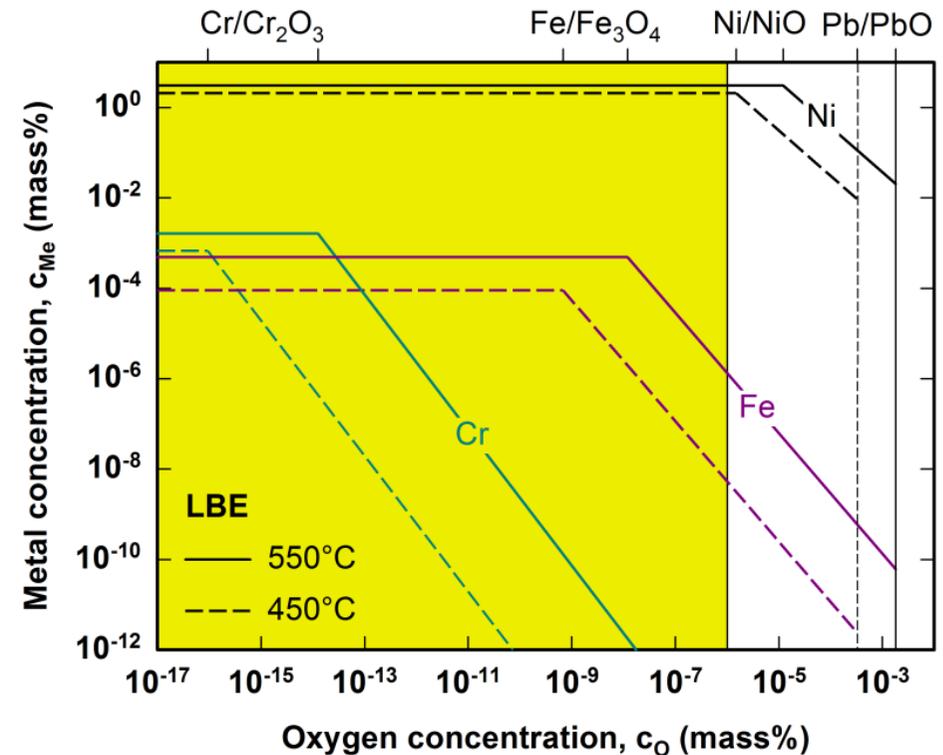
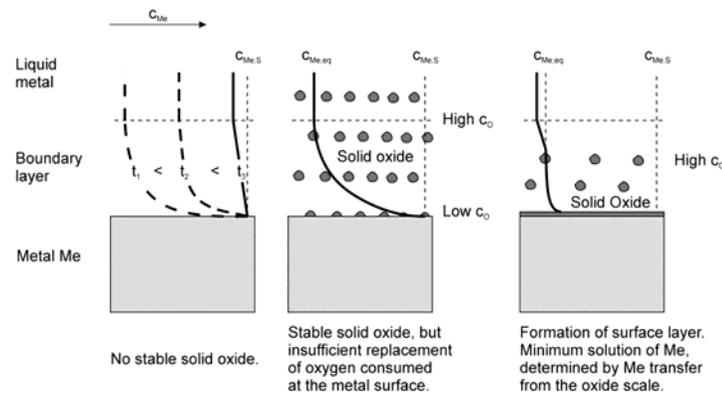
- Solid oxides of steel elements form a continuous surface layer
- Solution of steel elements still possible, but only after diffusion through solid oxide



- ➔ 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

□ 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 gradient if $c_{Me;eq}$ decreases (due to increasing c_O) with increasing distance from the steel surface



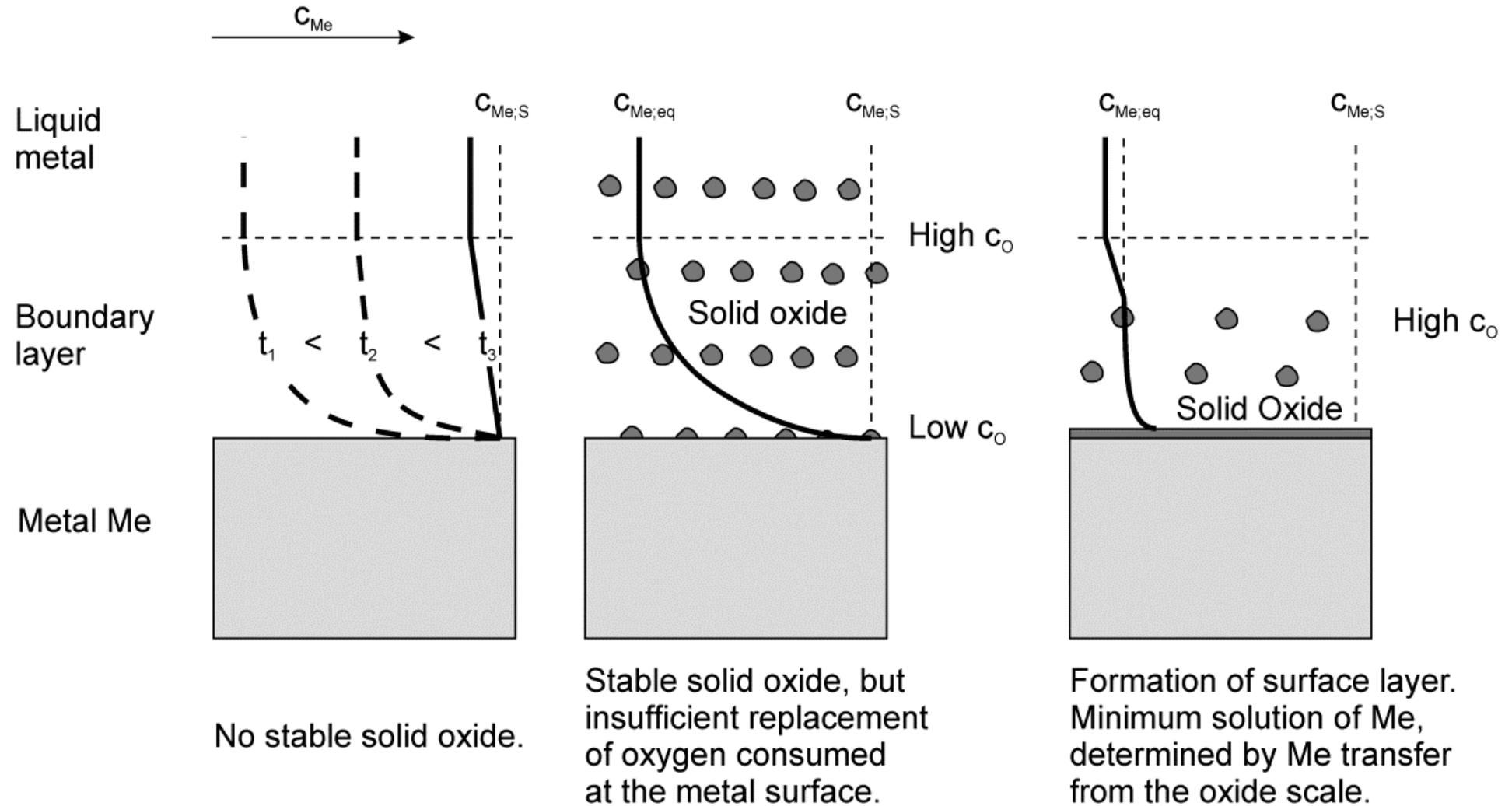


Illustration of concentration profiles that are decisive for diffusion of Me in the liquid metal

COSTA

Testing characteristics

Exposure to static liquid metal. Ceramic crucible containing 14 cm³ liquid metal. One specimen per crucible, partially submerged. Simultaneous exposure of several crucibles to flowing gas with controlled oxygen partial pressure in a glass tube. Homogeneous liquid metal temperature.

Sample geometry

Typically, rectangular specimens with 5.6 cm² exposed to liquid metal.

Determination of oxygen content

From equilibrium with oxygen-containing gas. Appropriate sensors under development.

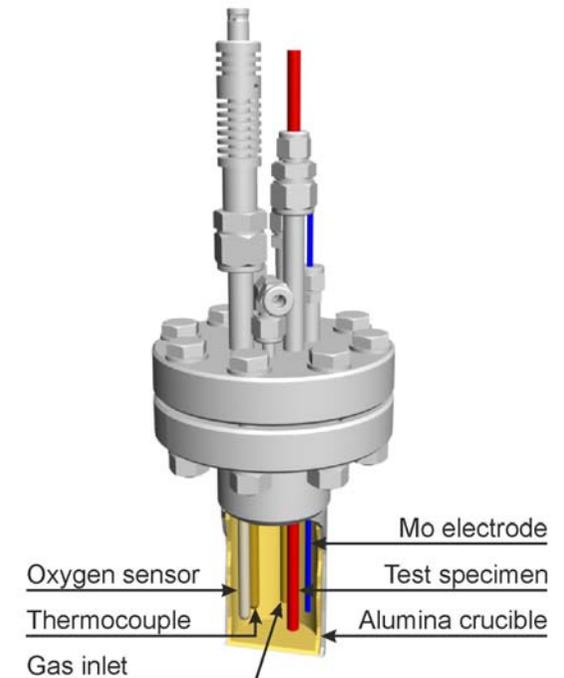
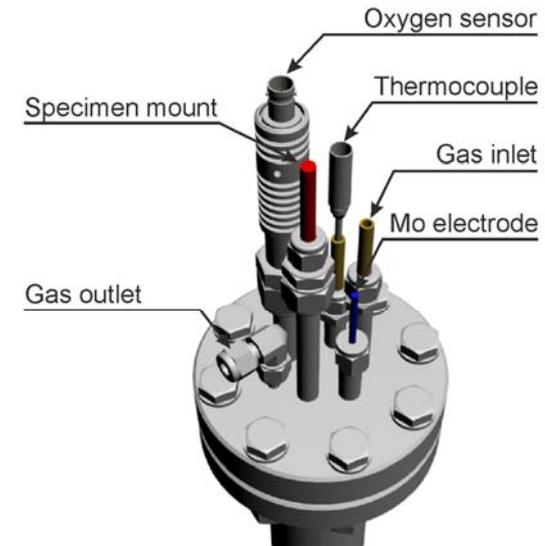


Constructed and operated at KIT's
Institute for Pulsed Power and Microwave Technology (IHM)

Corrosion testing in Pb or LBE

<p>Testing characteristics</p>	<p>Exposure to static liquid metal. Ceramic crucible containing 70 cm³ liquid metal. One specimen, partially submerged. Option to introduce oxygen-lean or -rich gas into the steel capsule that houses the crucible. Quasi-static when bubbling the gas through the liquid metal. Temperature gradient along the crucible height.</p>
<p>Sample geometry</p>	<p>Typically, cylindrical specimen with ~10 cm² exposed to liquid metal.</p>
<p>Determination of oxygen content</p>	<p>Potentiometric oxygen sensor.</p>

Designed at KIT's Institute for Applied Materials – Applied Materials Physics (IAM-AWP)



Corrosion testing in Pb or LBE

CORRIDA

Testing characteristics

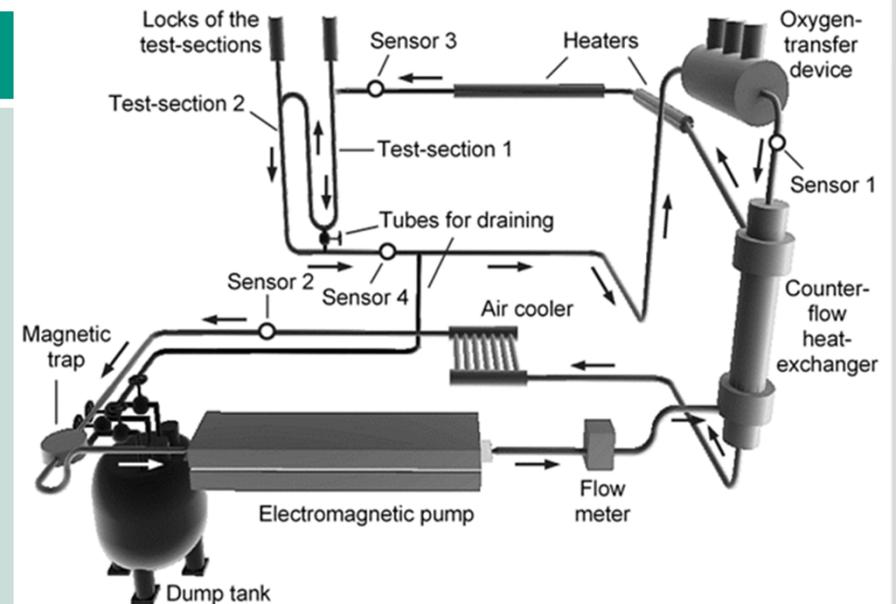
Exposure to flowing LBE, typically 2 m/s. 1000 kg circulating LBE (5.3 kg/s). Several steel samples simultaneously exposed in vertical test-sections. Oxygen control via gas with variable oxygen partial pressure. Large internal steel surface in contact with the liquid metal. Temperature difference along the loop of ~100–150°C.

Sample geometry

Typically, cylindrical specimen with 7.5 cm² exposed to liquid metal.

Determination of oxygen content

Four potentiometric oxygen sensors distributed along the loop.



Constructed and operated at KIT's
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❑ Corrosion phenomena

- Structure/composition of corrosion scales
- Topography of interfaces, e.g., instantaneous steel surface
- Assessment on the μm -scale by LOM, SEM+EDX, XRD, ...
- AES, XPS or TEM required when sub-micron resolution is required

❑ Quantification

- Gravimetry vs. metallography
- Full quantification required, i.e., loss of sound steel and thickness of corrosion scales
- Element transfer to the liquid metal may then be calculated
- Local assessment of corrosion needed



❑ Mechanisms and kinetics

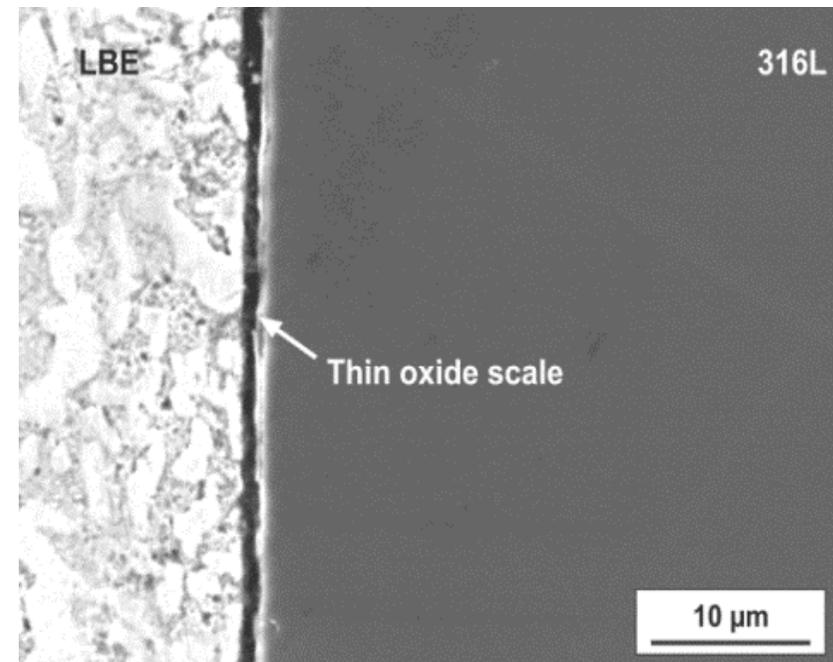
- Deeper understanding
- Increased reliability of predictions
- Input to corrosion models
- Transfer to in-plant conditions

Oxidation in oxygen-containing LBE

of 9Cr ferritic/martensitic and austenitic steels

□ Protective scaling

- Thin Cr- (Si-) rich oxide scale (thickness $\sim 1 \mu\text{m}$ 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 $T \leq 450^\circ\text{C}$ and $c_{\text{O}} \leq 10^{-6}$ mass%

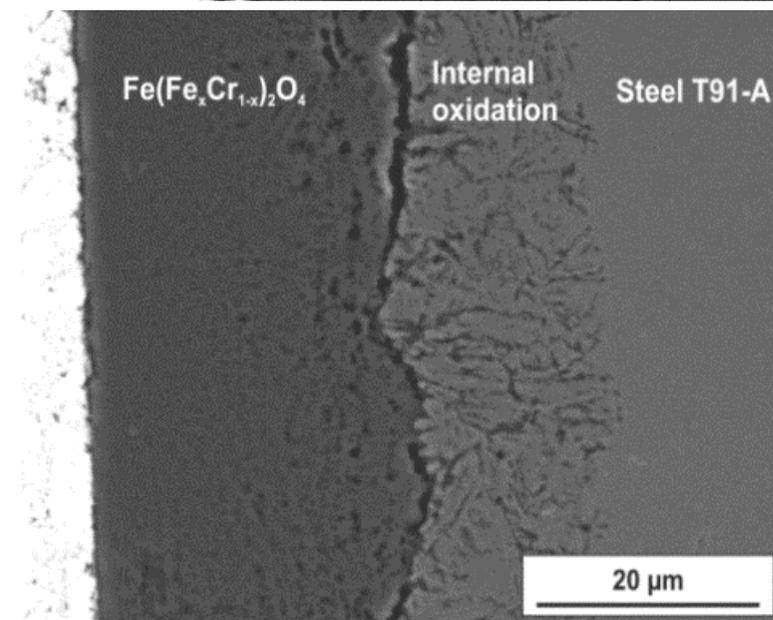
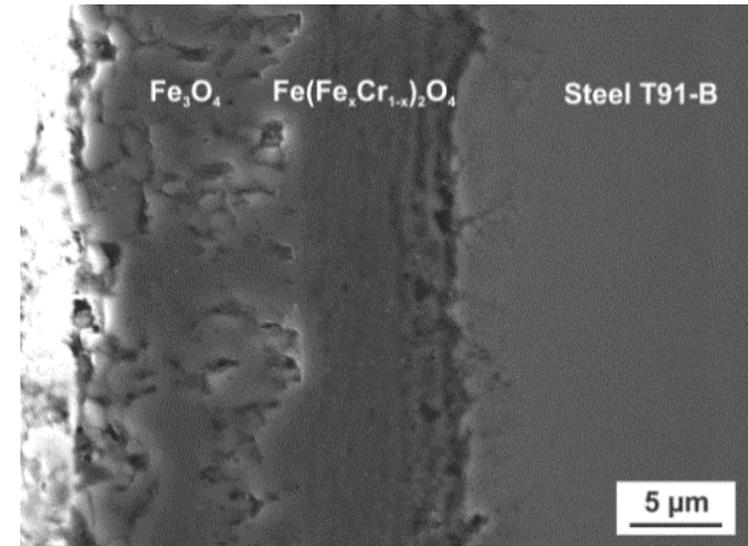


Oxidation in oxygen-containing LBE

of 9Cr ferritic/martensitic and austenitic steels

□ Accelerated oxidation

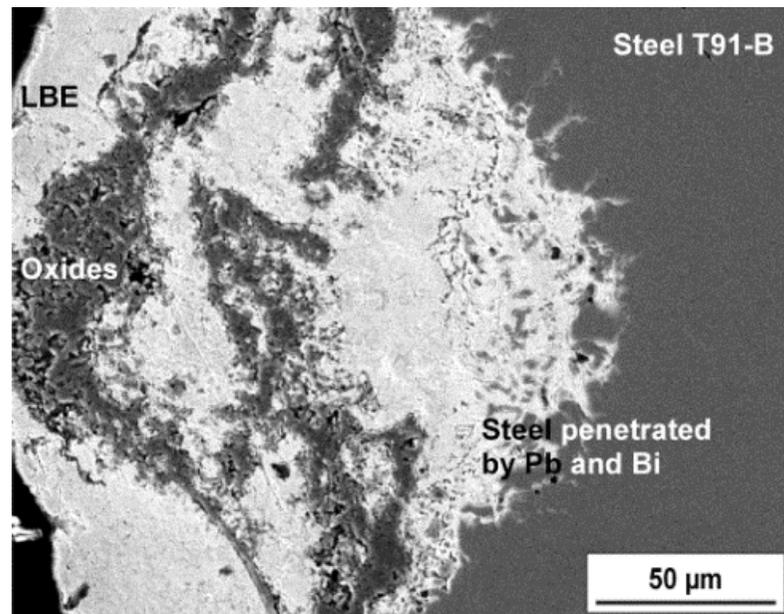
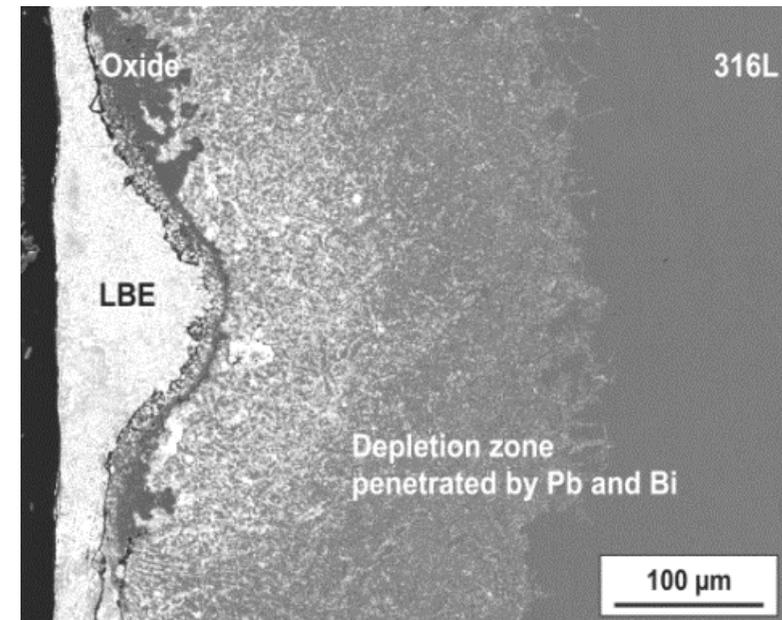
- Typical for and, finally, the general corrosion process of 9Cr steels, after failure of the thin Cr-rich scale
- Less frequent occurrence on austenitic steels, especially at $T \leq 450^\circ\text{C}$ and $c_{\text{O}} \leq 10^{-6}$ mass%
- Comparatively thick scales generally consisting of Fe_3O_4 , Fe–Cr spinel*) 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



*) Notation $\text{Fe}(\text{Fe}_x\text{Cr}_{1-x})_2\text{O}_4$ implies that the formed spinel is based on FeCr_2O_4 (regular spinel structure) but deficient in Cr. Alternatively, the formed spinel may derive from Fe_3O_4 (inverse spinel structure) with solved Cr, i.e., $\text{Fe}(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_4$.

□ 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



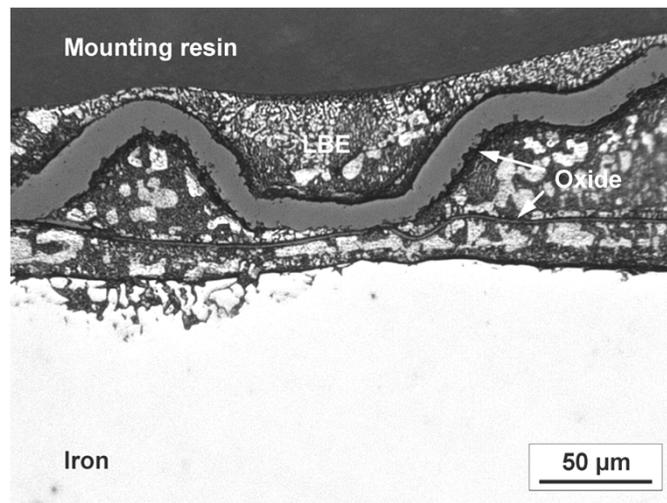
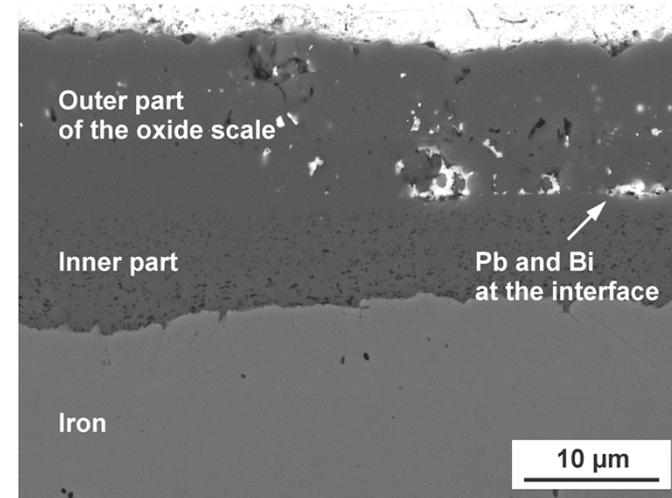
□ 9Cr ferritic/martensitic steel

- 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

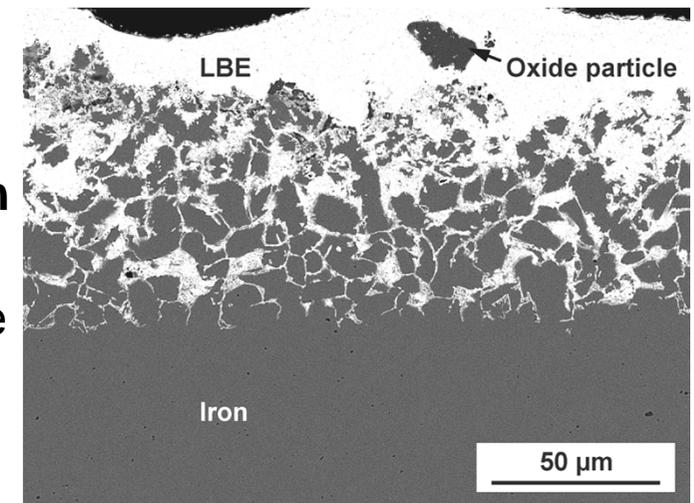
Performance of Fe in oxygen-containing LBE

at 450°C, 2 m/s and 10⁻⁶ mass% oxygen

- ❑ No protective scaling
- ❑ Accelerated oxidation
 - A porous inner magnetite layer replaces the Fe–Cr spinel found in 9Cr steels
 - Oxidation not significantly faster, but scale integrity poorer
 - Magnetite scale detaches, buckles and finally fails more frequently than scales observed for 9Cr steels



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

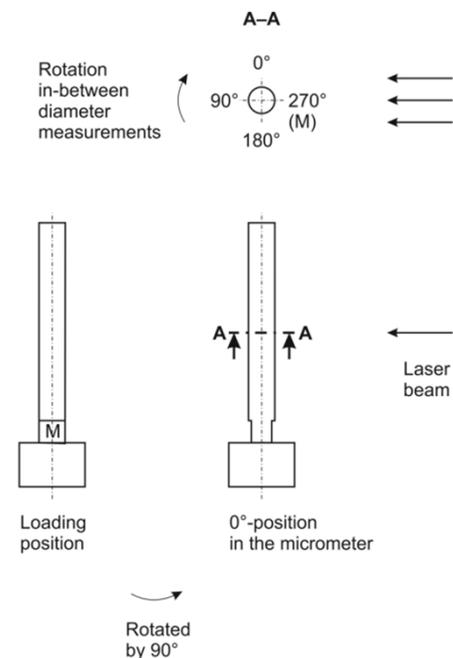


□ Goal of quantification

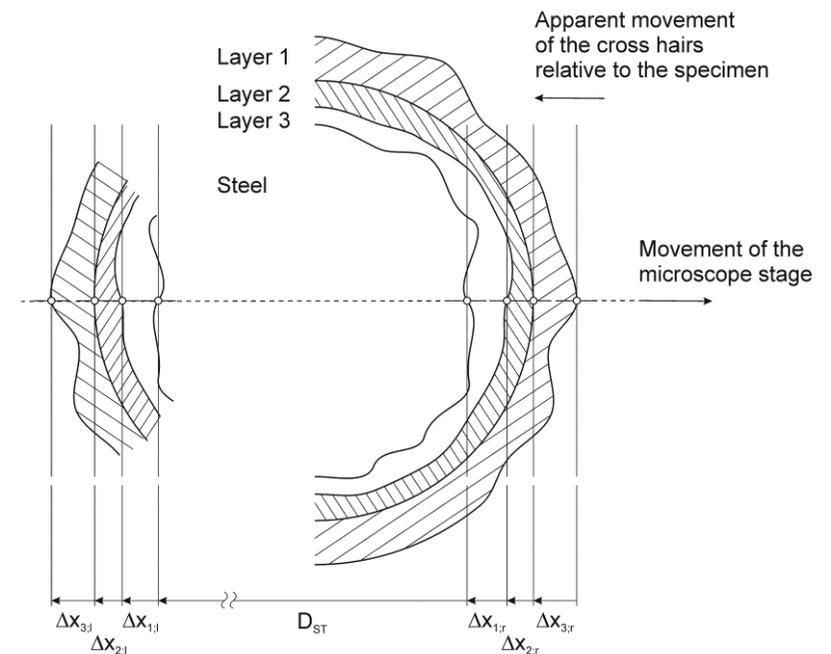
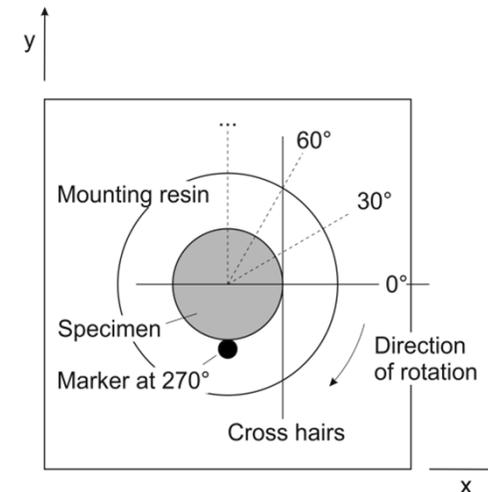
- Material loss, average of general corrosion and maximum of local corrosion
- Thickness of adherent (oxide) scale
- Overall change in dimensions, including the scale
- Frequency of occurrence of different corrosion modes
- Amount of metals transferred to the liquid metal

□ Metallographic method (cylindrical specimens)

- Initial diameter from measurement in a laser micrometer (0.1 μm resolution)



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



Example evaluation

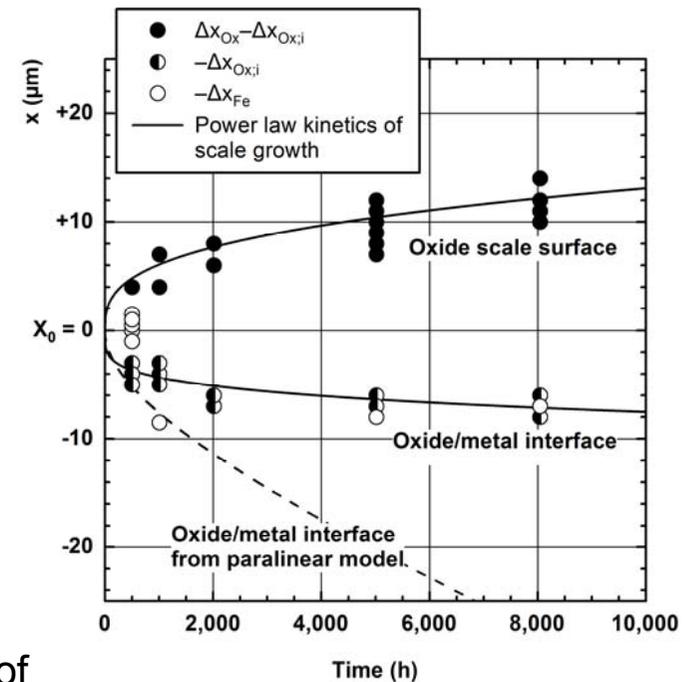
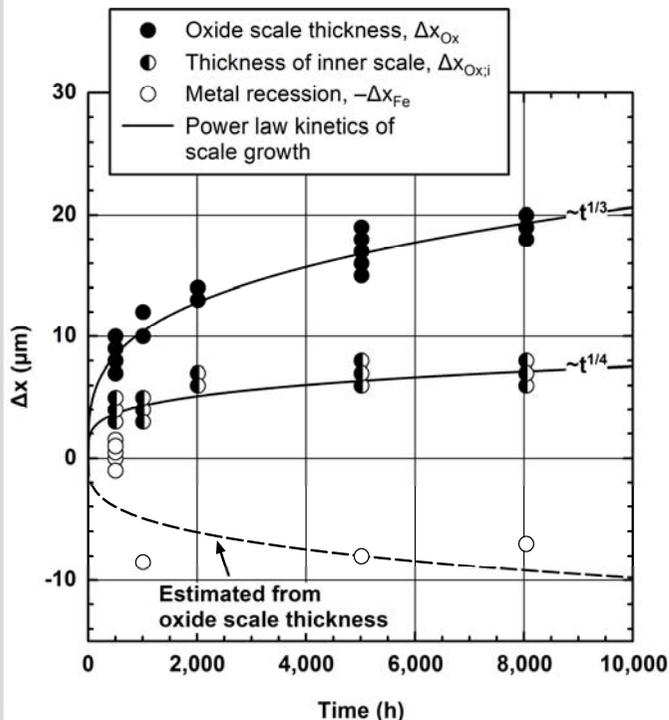
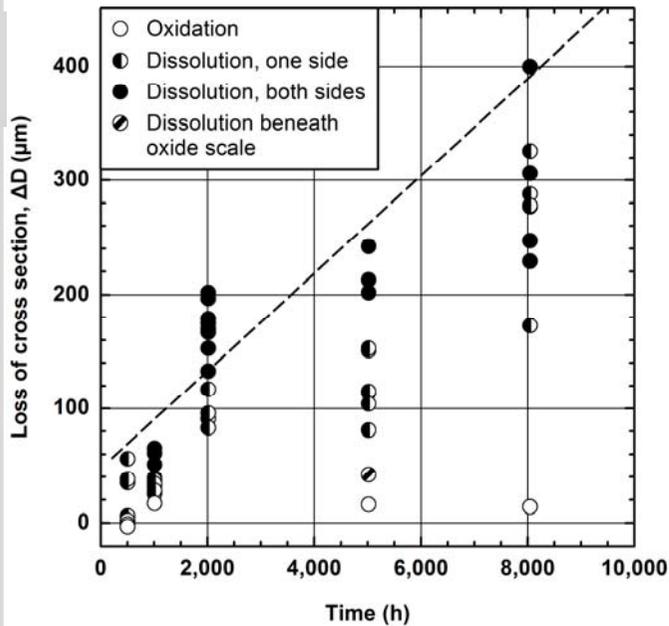
Oxidation of Fe in LBE at 450°C, 2 m/s, 10⁻⁶% oxygen

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?

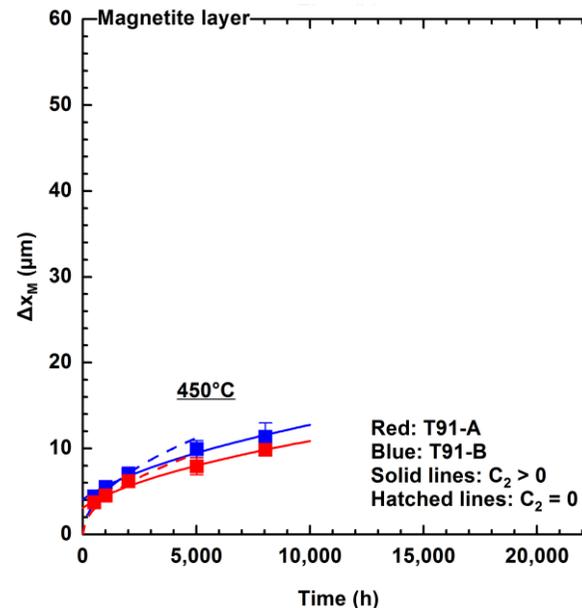
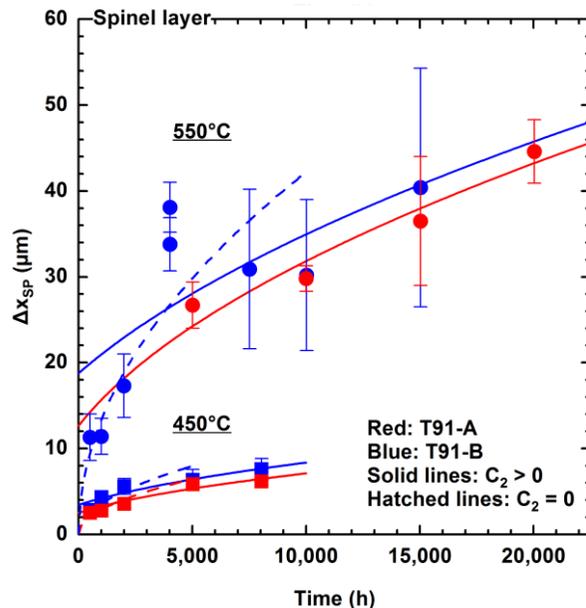
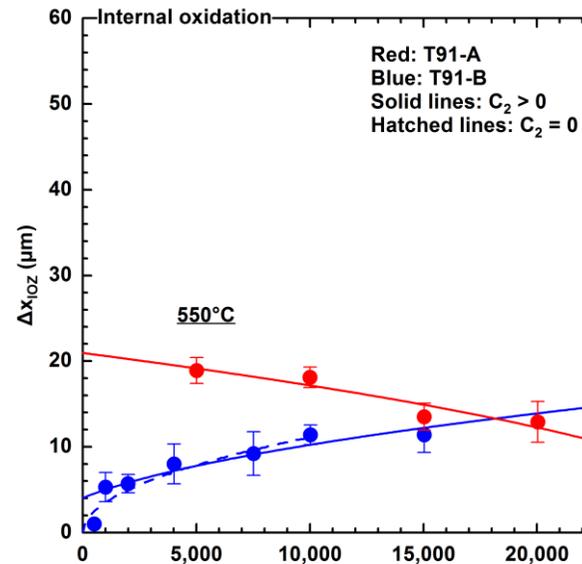
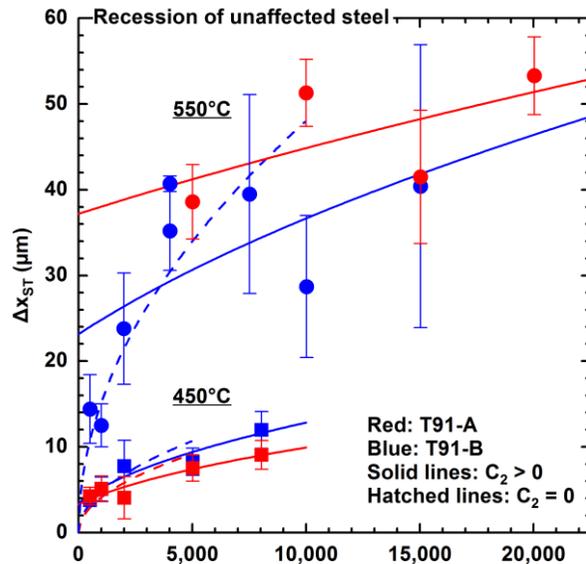
Analysis of oxidation data

- Local scale thickness and recession of solid Fe as a function of time 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



Kinetics of accelerated oxidation

of 9Cr steel 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 $\Delta x^2 = k_2 t + C_2$

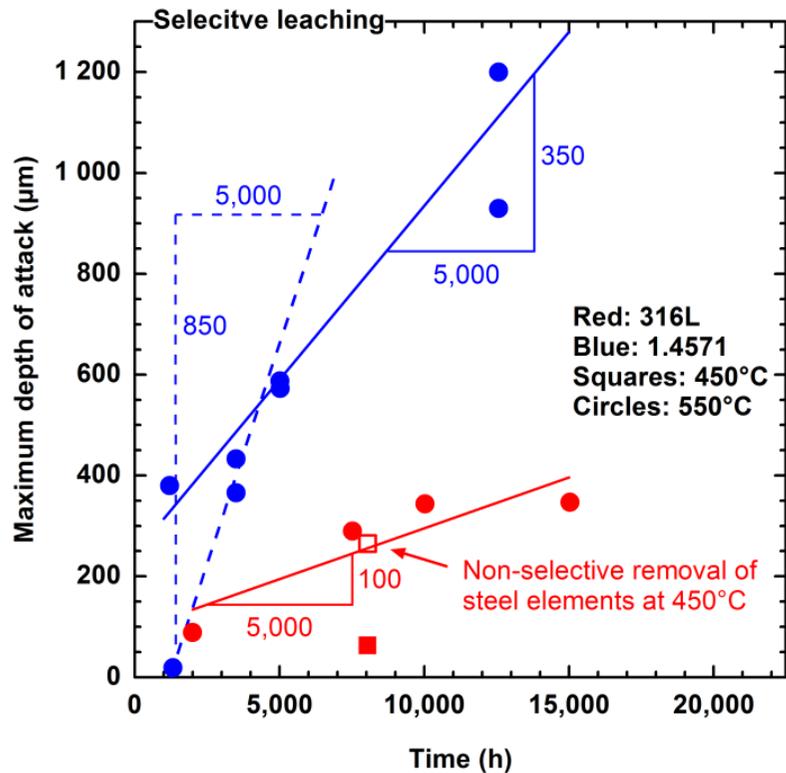
- C₂ > 0 reflects initially fast progress
- Corresponds well with both steel recession and scale growth for long term data
- Believed to be more appropriate for data extrapolation than other power laws or logarithmic approach

□ Paralinear approach $\frac{d\Delta x}{dt} = \frac{k_p}{2\Delta x} + k_1$

- Approximates the scale thickness
- Significantly overestimates metal recession

Kinetics of solution-based corrosion

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



- 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?

Mechanism of 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

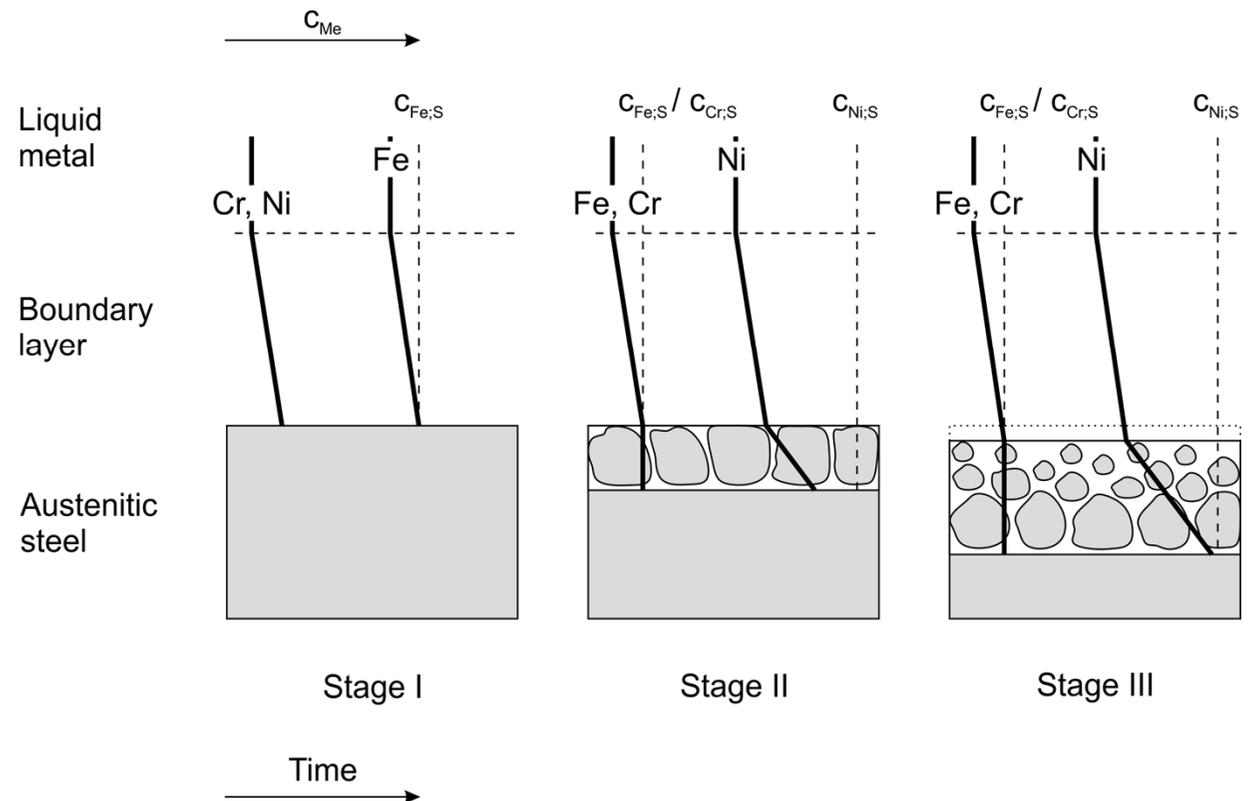
Stage II

- 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 (Cr) still dissolves and is 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

□ 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–Cr spinel (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

❑ Optimum oxygen addition to liquid Pb or LBE

- ❑ In order to keep up protective scaling
- ❑ Promote accelerated oxidation rather than solution-based corrosion if the protective scale fails
- ❑ Required c_O tends to increase with increasing temperature (and flow velocity)
- ❑ Adverse effect of oxygen if solution-based corrosion actually occurs?

❑ Optimised steel composition and microstructure

- ❑ High content in Cr, (Si) or Al and fine-grained microstructure promote oxidation, especially protective scaling
- ❑ Low Ni content, so that the optimised steel would be ferritic (bcc structure) rather than austenitic (fcc structure)

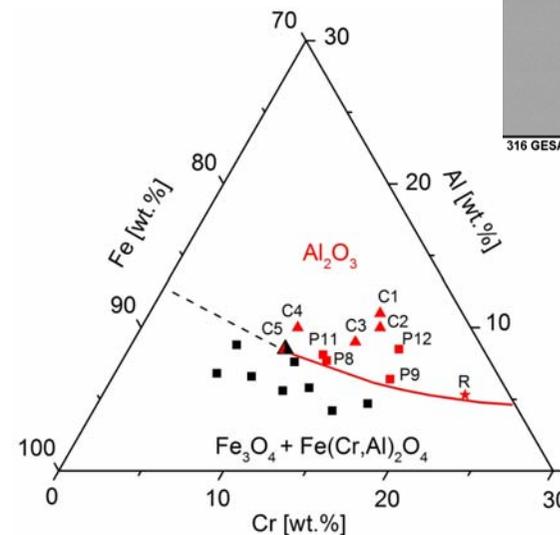
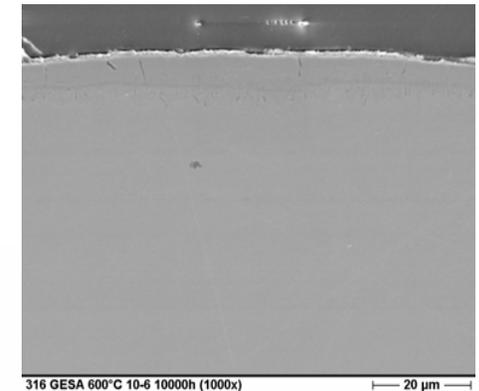
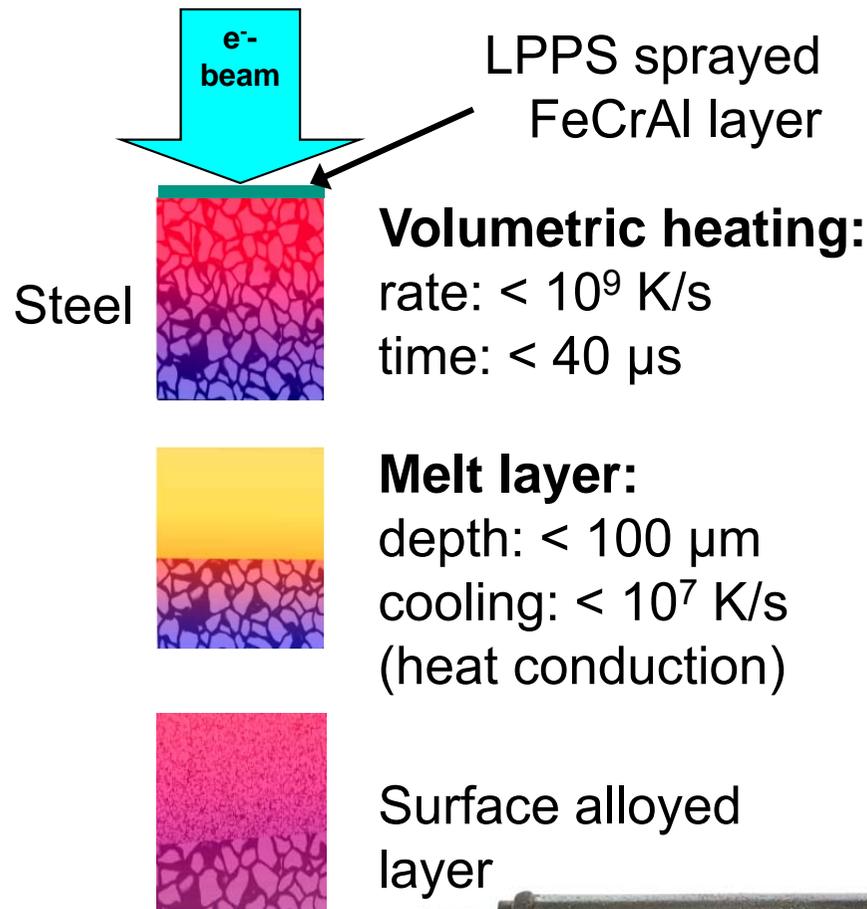
- ❑ However, the bcc structure seems more prone to embrittlement in case of oxide scale failure
- ❑ Any modification of existing steels requires time-intensive mechanical testing and qualification procedures

❑ Protective coatings

- ❑ With minimum solubility in Pb or LBE
- ❑ With optimised oxidation performance and applying oxygen addition at the same time
- ❑ Properties of the steel substrate remain unaffected as long as interdiffusion at the coating/steel interface is low
- ❑ Requires appropriate coating process
- ❑ Additional effort to be spent into manufacturing of coated components

GESA:

Surface alloying with strong oxide formers (Al) by pulsed electron beams provides corrosion protection in oxygen-containing Pb alloys at up to 700°C



Developed and operated at KIT's Institute for Pulsed Power and Microwave Technology (IHM)

- ❑ **Materials of construction, especially steels, are, in general, not stable in the service environment.**
 - ❑ Possible interactions or transformations and associated driving forces follow from equilibrium thermodynamics.
 - ❑ Actually dominating mechanisms and kinetics of degradation are hard to predict, identification requires input from previous operating experience or experiments.
 - ❑ Surface scales play an important role for the observed kinetics and, therefore, applicability of the material.
 - ❑ Such scales may form in-situ or already exist before first exposure to the operating environment.
 - ❑ Influence of other in-service loading must be considered.
- ❑ **In the presence of liquid metals, steels are prone to being solvated or mechanical properties may degrade.**
 - ❑ In the case of Pb or LBE, oxygen addition is considered an appropriate remedy for both principal degrading processes.
 - ❑ Modes of oxidation observed are protective scaling or accelerated oxidation—is the latter tolerable?
 - ❑ However, formed oxide scales tend to fail locally, and solvated oxygen may then adversely affect steel solution.
 - ❑ 9Cr steels typically show accelerated oxidation rather than protective scaling.
 - ❑ Type 316 steels: primarily protective scaling, but comparatively short incubation of solution-based attack (selective leaching).

□ Strategy accounting for interactions with LBE (Pb), for a particular steel under consideration:

- Define ranges of temperature and concentration of solved oxygen so that oxidation is tolerable and incubation of solution-based corrosion takes longer than the anticipated service time (ideal case).
- Prove that sufficient mechanical properties are maintained at contact of liquid metal with the steel after oxide scale failure.
- Consider surface alloying for improved oxidation performance, or other protective coating if limitations to operating conditions are too tight.



On the basis of empirical kinetics, derived mechanisms and corrosion models



Mechanical tests at simultaneous exposure to liquid metal, e.g., low oxygen content for investigating fundamental issues, target oxygen content for qualifying the materials



In principle, same tests as for uncoated materials, but special emphasis on interdiffusion between coating and substrate

Thank you for your attention!