Materials Testing and Rules (MATTER)

Workshop on

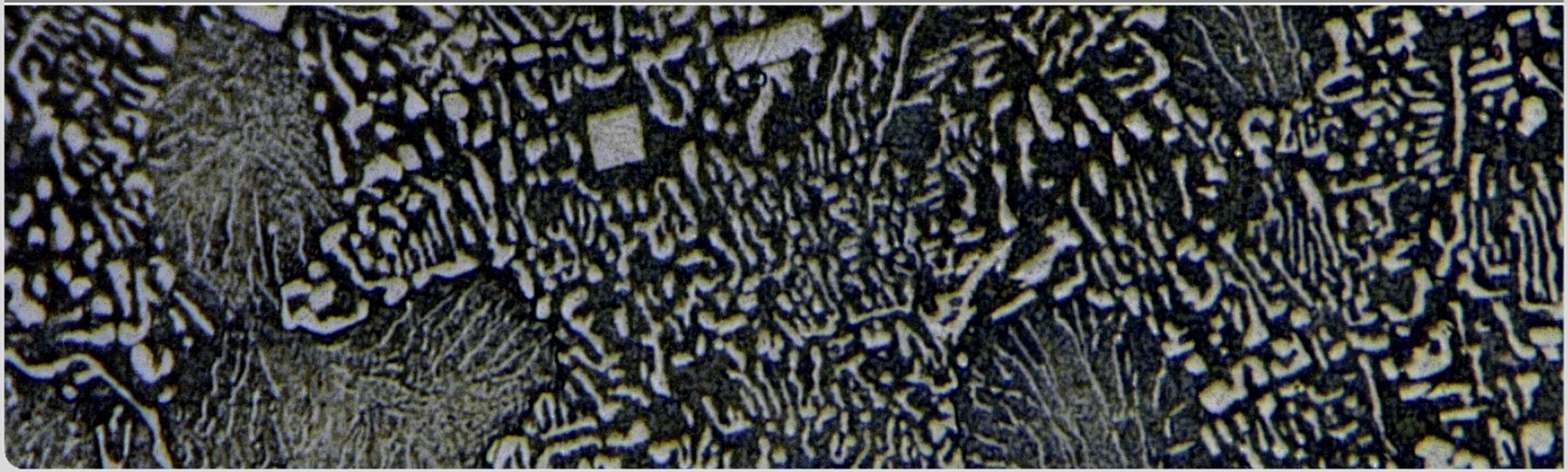
Heavy-Liquid Metal Environmental Degradation Effects and Design Rules

January 28 – 29, 2014, JRC-IET, Petten, The Netherlands

Liquid-metal corrosion of steels in oxygen-containing LBE or Pb and effects on creep

Carsten Schroer, Mariya Yurechko

Insitute for Applied Materials – Material Process Technology (IAM-WPT), Corrosion Department



Liquid-metal/steel interactions

- **Solution of steel constituents**
  - Preferential (Ni, Cr) rather than general dissolution
  - Surface recession and/or development of a near-surface depletion zone
  - Penetration of the depletion zone by liquid metal
  - Loss of load-bearing material cross-section
  - Quantification by exposure to flowing or static liquid metal

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

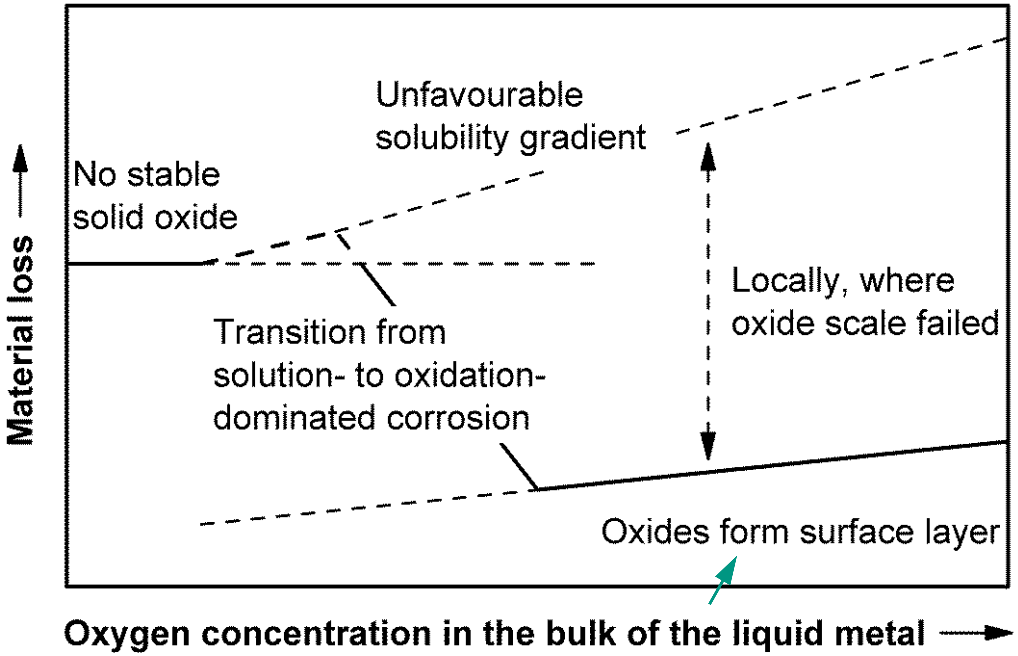
- **Degradation of mechanical properties**
  - Damage accumulation at the surface as a result of corrosion
  - Or arising from phenomena below the µm-scale:
    - Processes affecting one- and two-dimensional defects (dislocations, grain boundaries, cracks)
    - Especially apparent at low temperatures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

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

Impact of oxygen dissolved in liquid Pb or LBE on material loss caused by corrosion (qualitatively)

- Bold lines:

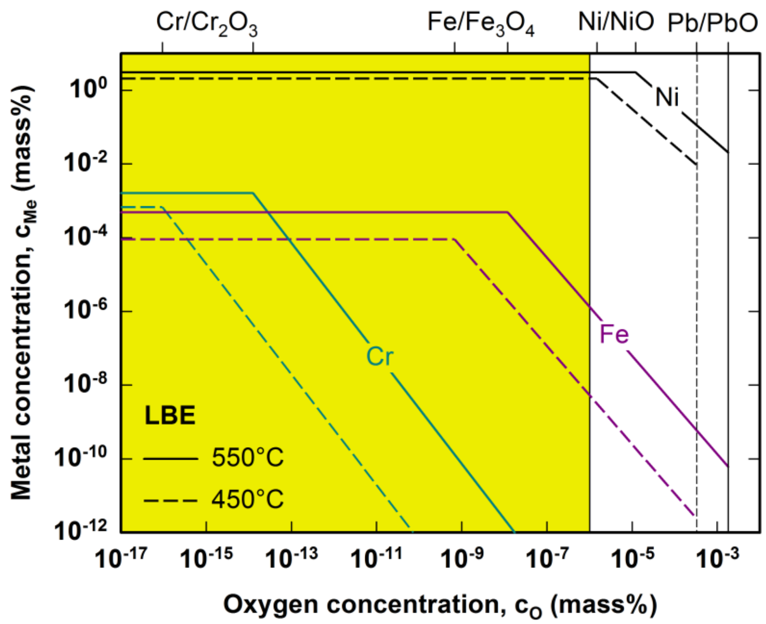
  Average material loss (solution regime, transition region) or loss due to general corrosion (oxidation regime)
- Continuous oxide layer on the steel surface results in spatial separation of steel and liquid metal – reduced solution rates or risk of LME – at the cost of a growing oxide scale
- Solution-dominated corrosion may still occur where oxide scale locally failed
- Adverse effect of oxygen expected when solid oxides form away from the steel surface (unfavourable gradient of solubility)



Goal of deliberate oxygen addition

Effect of oxygen on the solution of steel elements

- **Gradient of solubility**
  - May establish if dissolving metal Me forms stable solid oxides
  - Solubility of Me then decreases with increasing c_O (following from the solubility product of the oxide)
  - Unfavourable solubility gradient if c_O decreases with increasing distance from the steel surface



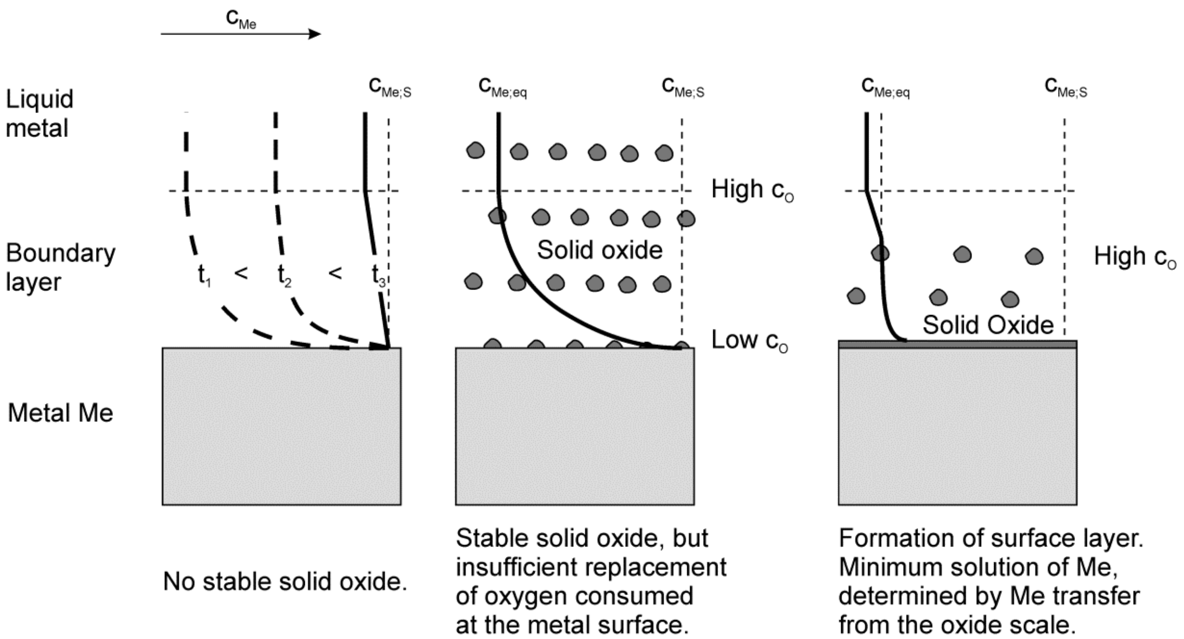
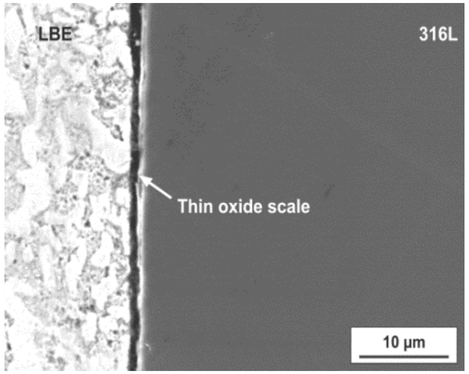


Illustration of concentration profiles that are decisive for diffusion of Me in the liquid metal (qualitatively)

Phenomena observed in flowing LBE on 9Cr or Type 316 steels at 450–550°C, 2 m/s and 10^{-6}% dissolved oxygen

Karlsruhe Institute of Technology

- **Protective scaling**
  - Thin Cr- (Si-) rich oxide scale (thickness ~1 µm or less)
  - Promoted by high Cr content, fine-grained structure, dispersed Y_2O_3 …
  - Favourable situation with respect to minimum material loss, but generally not of long duration (locally)

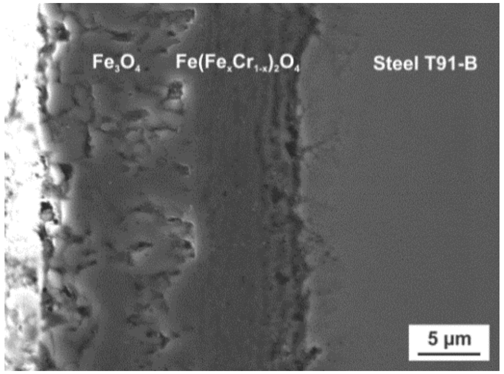


550°C

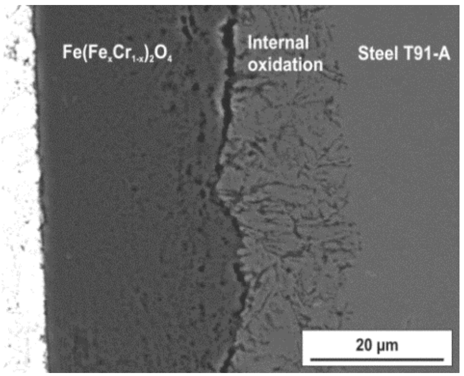
Scale failure at high local c_O (?)

Scale failure at low local c_O (?)

- **Accelerated oxidation**
  - Typical and, finally, the general corrosion process for 9Cr steel
  - Locally observed for Type 316 at 550°C



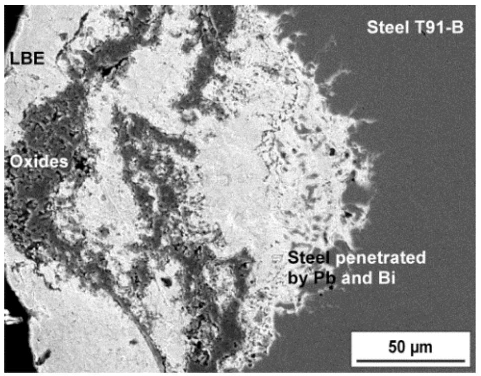
450°C

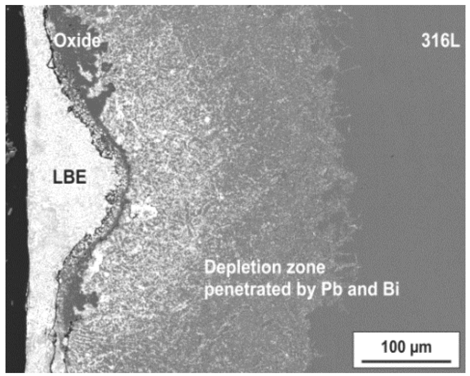


550°C

- **Solution-assisted corrosion**
  - Type 316: Primarily selective leaching of Ni or Cr
  - 9Cr: Intermittent solution participates in accelerated oxidation processes or solution outweighs oxidation

Both at 550°C

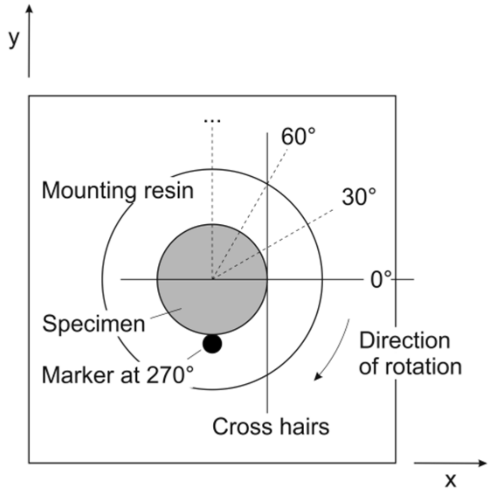




Quantification of corrosion

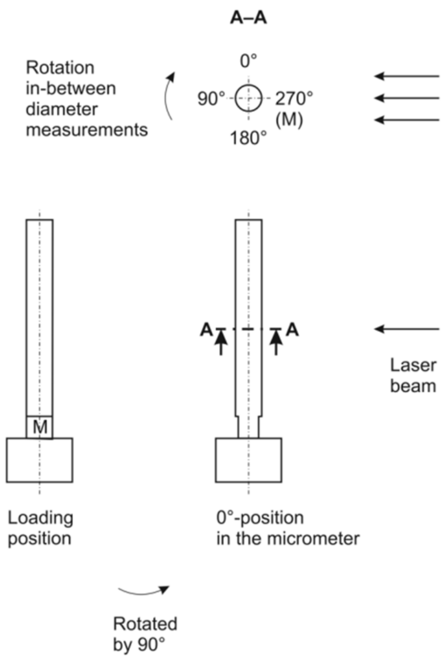
Goal of quantification

- 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

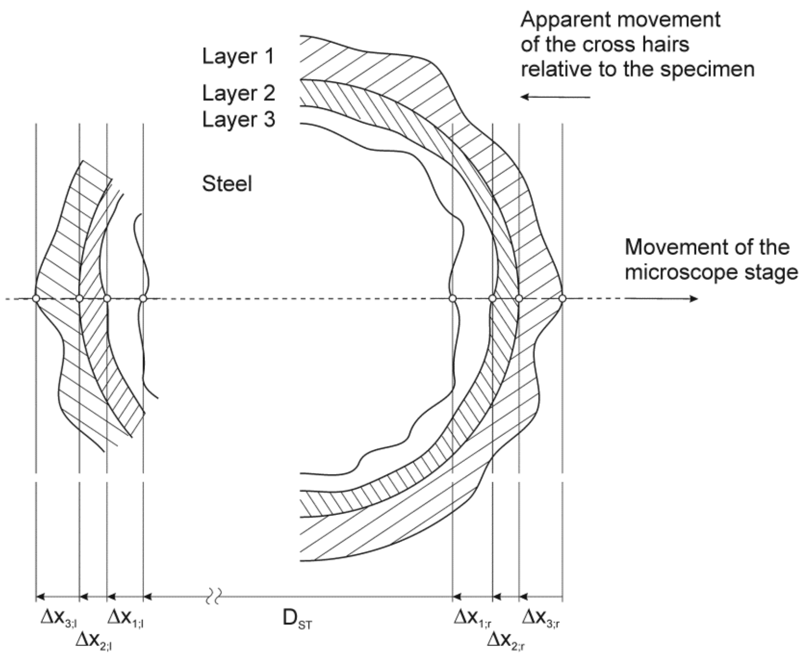


Metallographic method (cylindrical specimens)

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



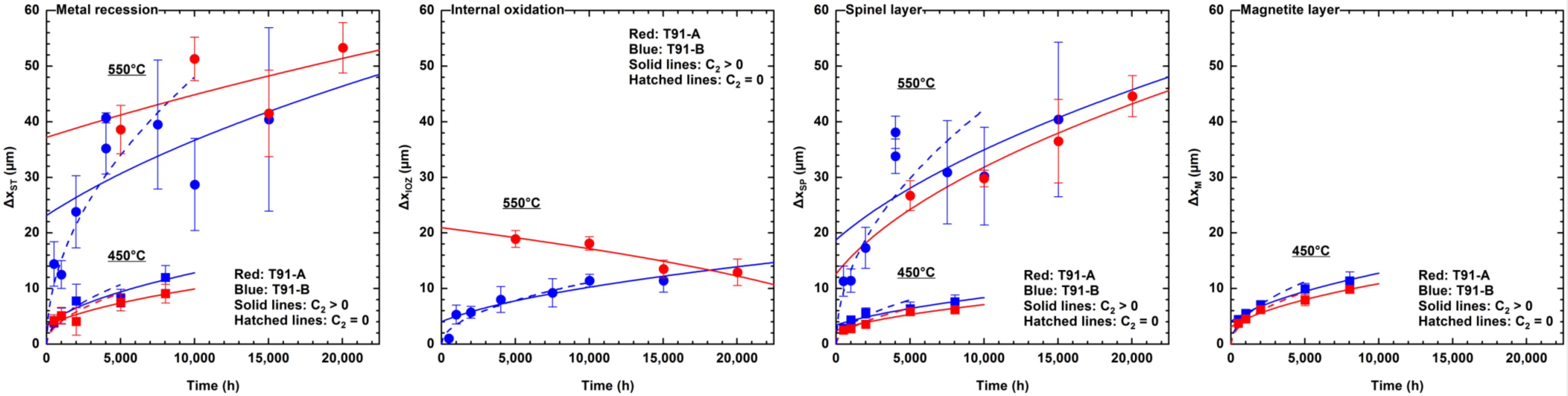
- Diameter of unaffected material and thickness of corrosion scales determined in a microscope (LOM) at ×500 magnification, with 1 µm resolution
- Occurrence of different corrosion modes on opposing sides of the re-measured diameter is considered in the evaluation
- Verification of the method in MATTER Task 3.2



Institute for Applied Materials – Material Process Technology (IAM-WPT)
Corrosion Department

Quantitative results from experiments in the CORRIDA loop: T91 in LBE at 450–550°C, 2 m/s and 10^{-6}% dissolved oxygen

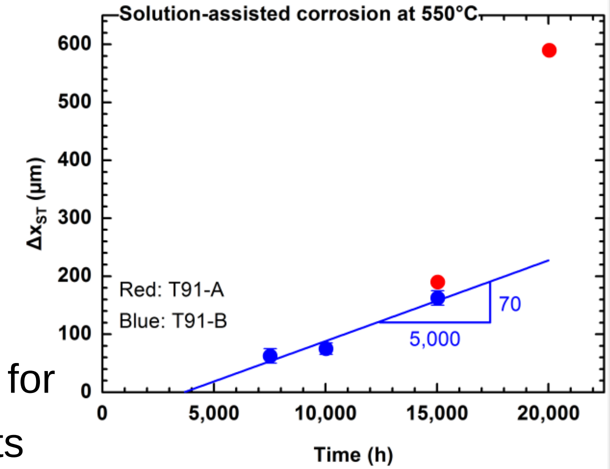
❑ Accelerated oxidation



- Thickness of magnetite approximates the overall increase in specimen radius
- Dissolved Fe from balancing the mass consumed and present in oxides
- Extrapolation of data naturally depends strongly on the type of rate law assumed

❑ Solution-assisted corrosion

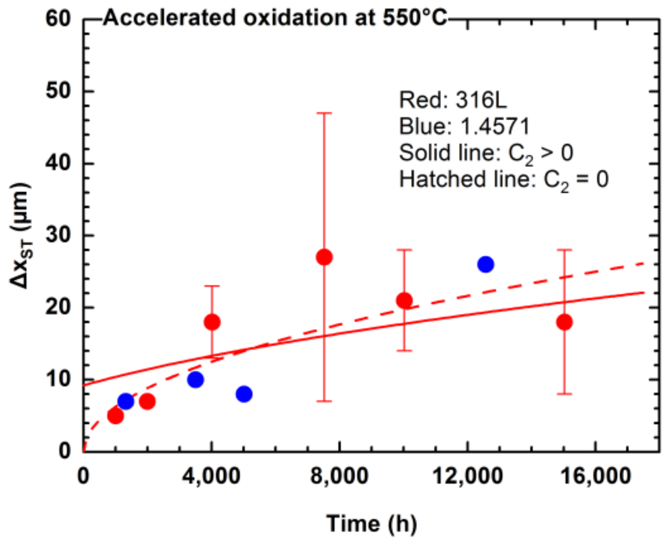
- Significantly increased material loss
- Comparatively small database for kinetic analysis
- Underlying corrosion mechanisms may differ for the particular data points



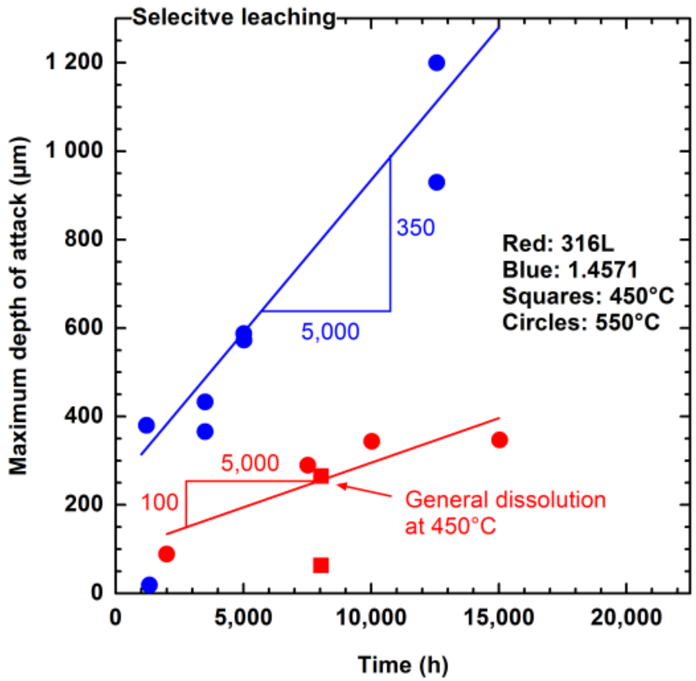
Quantitative results from experiments in the CORRIDA loop: Type 316 in LBE at 450–550°C, 2 m/s and 10^{-6}% dissolved oxygen

Karlsruhe Institute of Technology

- **Accelerated oxidation**
  - Observed locally at 550°C
  - In parts continuous scale after long exposure time
  - Not observed at 450°C



- **Solution-assisted corrosion**
  - Only few sites on investigated specimens may be affected
  - Mostly selective leaching of Ni and Cr
  - But also general dissolution of all steel elements at 450°C
  - Incubation time decreases from around 5000 h at 450°C to 1000 h at 550°C



Long-term corrosion studies in flowing oxygen-containing LBE conducted in the CORRIDA loop at KIT/IAM-WPT

Karlsruhe Institute of Technology

Temperature	Flow velocity	Nominal oxygen concentration	Maximum exposure time	Tested materials
550 (+5)°C	2 (±0.2) m/s	10^{-6} mass%	~ 20,000 h	CSEF (T91, E911, EUROFER), ODS steels, 316SS, surface alloyed steels (Al), ...
450 (+5)°C	2 (±0.2) m/s	10^{-6} mass%	~ 8000 h	CSEF (T91, E911), pure Fe, 316SS, ...

In the framework of MATTER Task 3.2:

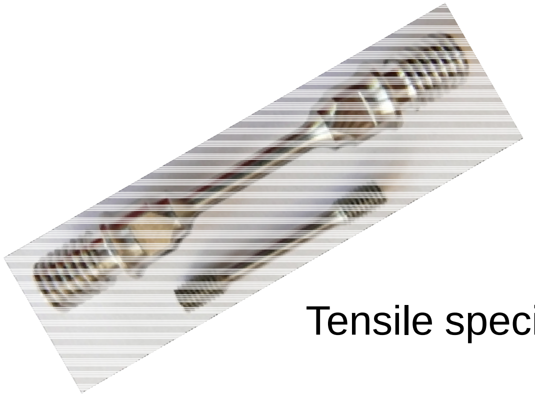
550°C (+5)°C	2 (±0.2) m/s	10^{-7} mass%	~ 2000 h	T91, E911, P92, 316SS, 15-15Ti (1.4970), …
450°C (+5)°C	2 (±0.2) m/s	10^{-7} mass%	~ 8800 h	
400°C	2 m/s	10^{-7} mass%	Ongoing	

→

- **Empirical Δx for general and local corrosion**
  - As a function of T (400–550°C) and c_O (10^{-6}–10^{-7} mass%)
  - For specific materials (T91, 316L, …)
  - For material groups (9Cr, Type 316, …), if appropriate

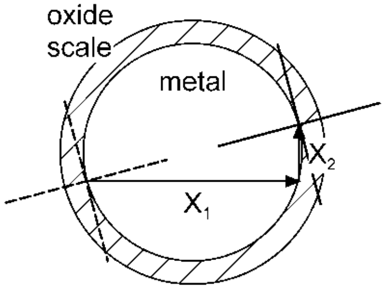
Institute for Applied Materials – Material Process Technology (IAM-WPT)
Corrosion Department

Creep-rupture testing in oxygen-containing static liquid metal as performed at KIT/IAM-WPT



Tensile specimen

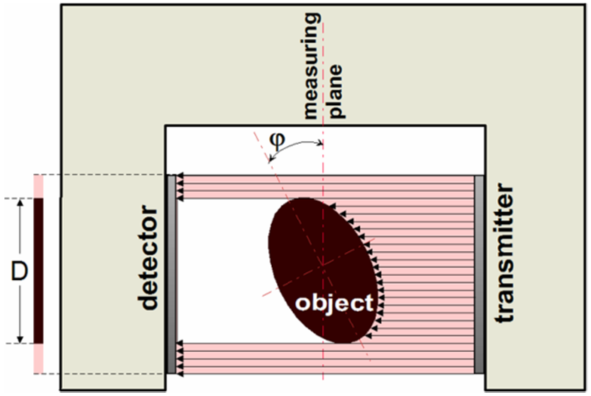
Pre-test characterization



$$D = \sqrt{X_1^2 + X_2^2}$$

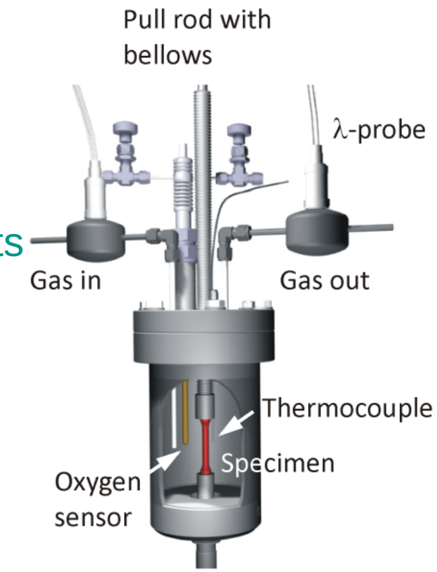
Quantitative microscopy
- Performed at ×500
- Resolution: 1 µm
- Diameter of unaffected steel
- Corrosion scale thickness

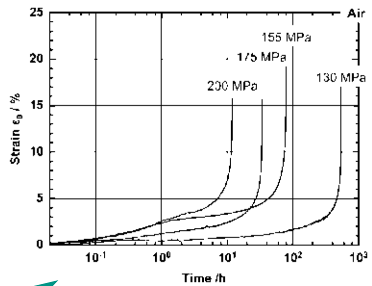
Post-test measurements



Laser micrometer
- Diameter (Res.: 0.1 µm)
- Gauge length (Res.: 0.1 mm)
- Necking, strain at rupture after the test

Creep test





Analysis of recorded creep curves

CRISLA

- In liquid metal with oxygen control
- In air as reference atmosphere
- At constant load
- Specimen elongation identified with the movement of the pull rod

Potential interactions of liquid-metal corrosion and creep

Karlsruhe Institute of Technology

- **Impact of corrosion on creep or stress rupture of steels**
  - General or local thinning of steel cross-section versus overall strengthening by a stiff corrosion scale
  - Corrosion-induced vacancies, pores or surface damage (notches, pits, grooves …)

  Not specific for corrosion in liquid metal

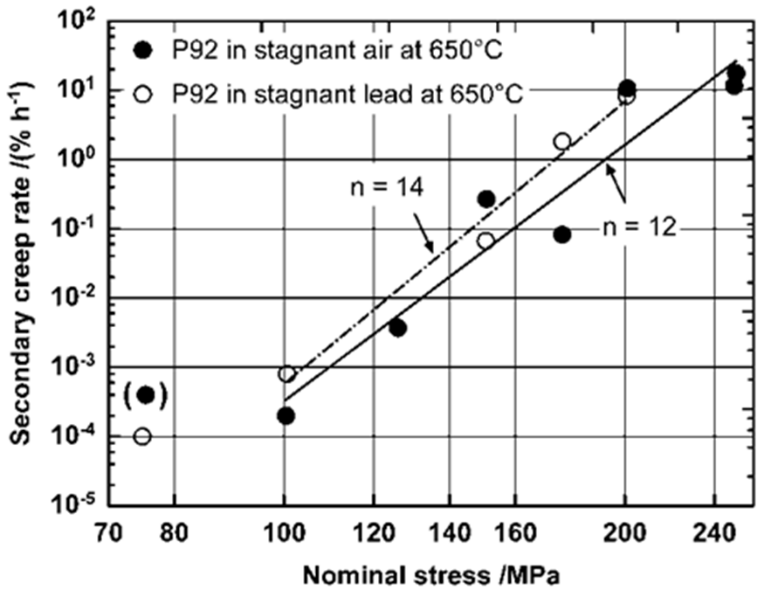
  - Weakening or embrittlement due to liquid-metal/steel interactions at near-surface dislocations, grain boundaries, cracks …

  May be suppressed by any dense oxide scale on the surface

- **Impact of tensile stress or creep on steel corrosion**
  - Stress-enhanced re-distribution of near-surface vacancies in the material volume promoting solution in (or penetration of) liquid metal as well as steel oxidation
  - Local failure of the corrosion scale (oxides) induced by unfavourable stress state or deformation of underlying steel relative to the scale

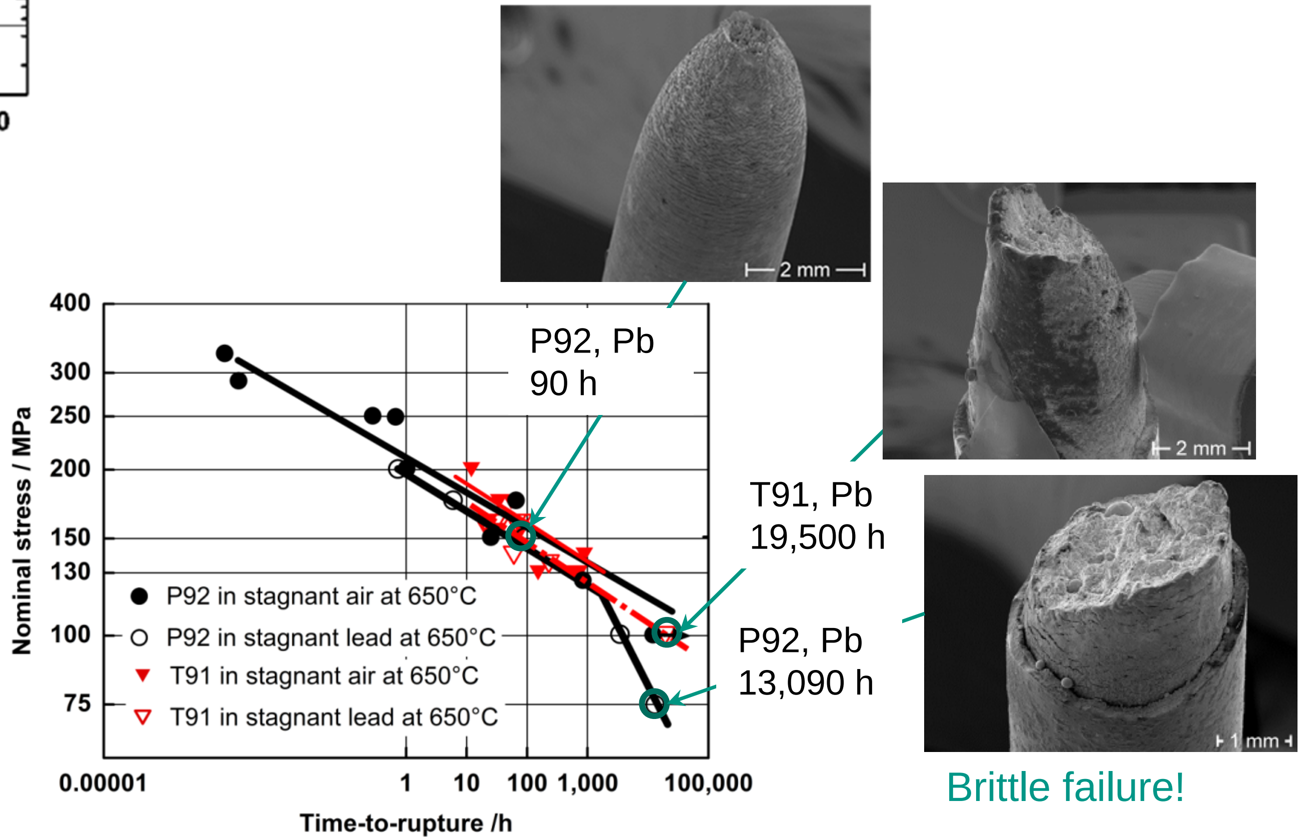
Creep and stress rupture of T91 and P92 in static Pb at 650°C and 10^{-6} mass% dissolved oxygen

KIT
Karlsruhe Institute of Technology



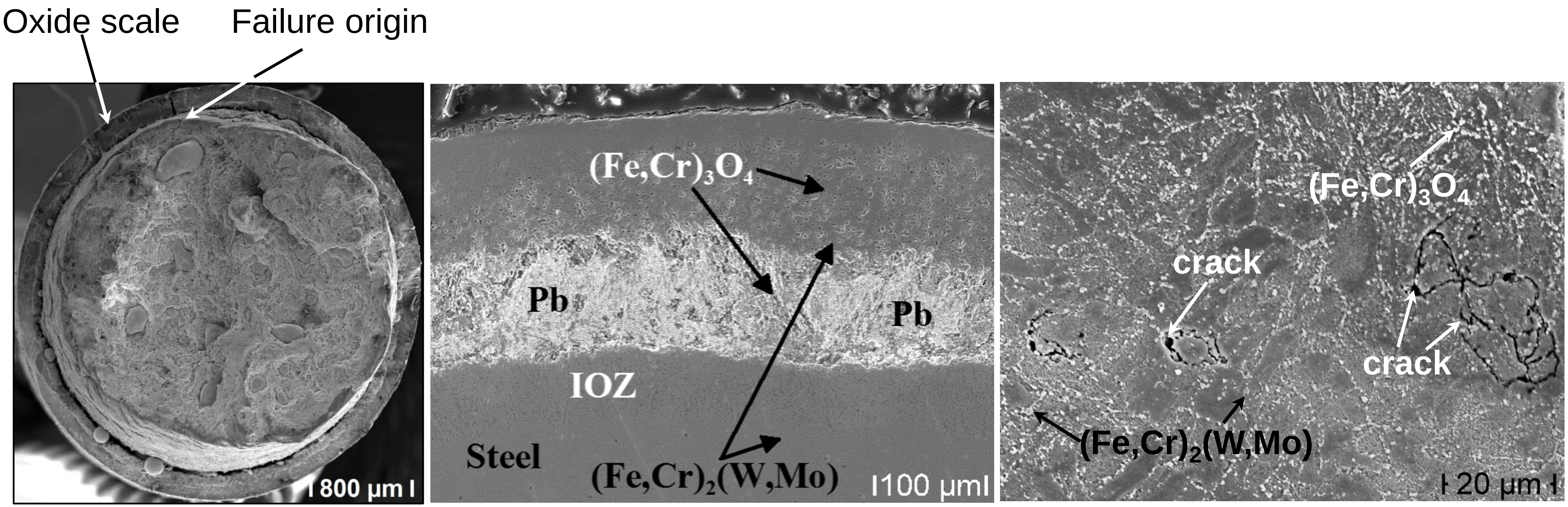
- **Secondary creep rate**
  - Creep rate in oxygen-containing Pb within or at the higher edge of the scatter band observed in air
  - Insignificant difference between exposure to Pb and air during creep test

- **Stress rupture**
  - In general, ductile failure
  - No clear effect of the environment, except for:
  - Slightly reduced strain at rupture of P92 in Pb (16–27% compared with 20–31% in air)
  - Premature brittle failure of P92 in Pb at 75 MPa after t_R = 13,090 h



Institute for Applied Materials – Material Process Technology (IAM-WPT)
Corrosion Department

P92 in static Pb at 650°C and 10^{-6} mass% dissolved oxygen: Brittle failure at 75 MPa after 13,090 h

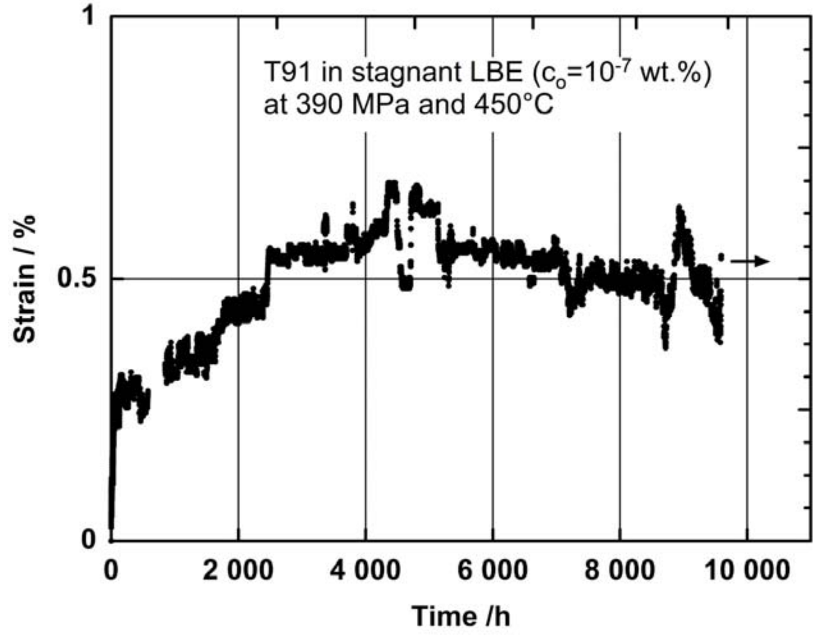


- **Indications of an environmental effect**
  - Failure origin at the surface
  - Surface cracks in the necking region
  - Solidified Pb at oxide/steel interface (observed in some distance to the site of failure)

- **Indications of thermal ageing**
  - Precipitated and coarsened Laves Phase

Creep tests performed in LBE

- **In CRISLA (as part of MATTER Task 3.3)**
  - T91 in static LBE at 450°C, 10^{-7} mass% dissolved oxygen and 390 MPa
  - Test has been running since June 2012
  - Stress rupture life of more than 10,000 h under the stated conditions
  - Continuation of testing with experiments at lower c_O



- **Tests in other laboratories**
  - T91 in static LBE at 500°C, no active oxygen control
  - Time-to-rupture at 300–320 MPa varies from several hundreds down to less than 10 h
  - Reduced creep strength in comparison with tests in air

(R. Hernández, M. Serrano, MATTER Task 3.3)

  - T91 in flowing LBE at 550°C, $c_O = 10^{-6}$ mass%, v = 0.5 m/s, 140–220 MPa
  - Increase of secondary creep rate by factor 50 in comparison to air
  - Early transition from secondary to tertiary creep
  - Surface cracks in the necking region and premature failure
  - Liquid metal at oxide/steel interface **(Jianu et al., J. Nucl. Mater., 2009)**

Accounting for effects of Pb or LBE in component design

- **Wall thinning expected for design lifetime**
  - To be added to the minimum wall thickness resulting from thermo-mechanical analysis of the component
  - For 9Cr and Type 316 steels:
    - Wall thinning is negligible for protective scaling in oxygen-containing Pb or LBE
    - However, either accelerated oxidation or solution-assisted corrosion where this scale fails
    - Both general and local corrosion need to be considered when oxide scale integrity is at risk

Define operating parameters so that incubation of solution-assisted corrosion takes longer than the design lifetime? (max. T, min. c_O …)

- **“Weakening” factor considering degraded mechanical properties**
  - Fraction of maximum load allowable in the absence of environmental effects
  - For creep of 9Cr steels:
    - Factor may approach unity for accelerated oxidation (or protective scaling)
    - <<1 for intimate contact between liquid metal and steel, e.g., solution-assisted corrosion