MATTER Final Workshop

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Rome, Italy

Investigating steel corrosion caused by liquid lead or lead–bismuth eutectic

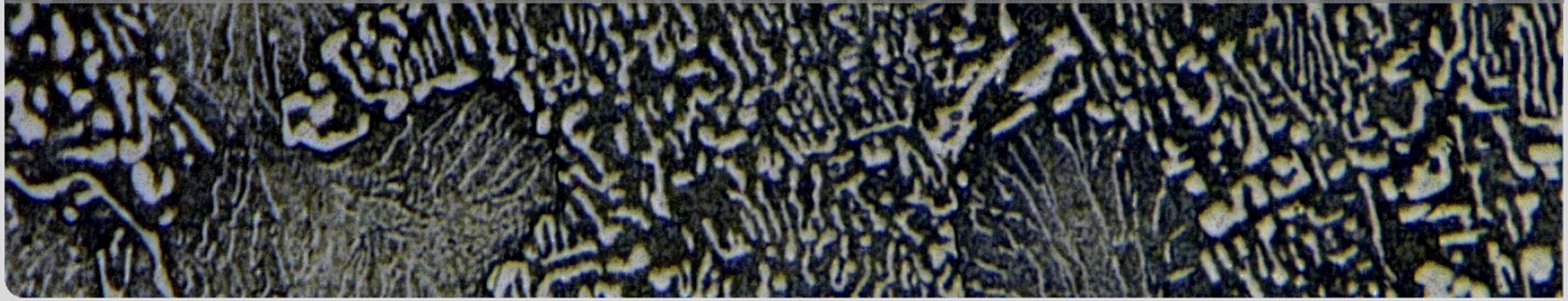
Carsten Schroer [a], Valentyn Tsisar [a], Annette Heinzel [a], Alfons Weisenburger [a], Konstantina Lambrinou [b], Serguei Gavrilov [b], Rebeca Hernández Pascual [c], Marta Serrano García [c], Alessandro Gessi [d]

[a] Karlsruher Institut für Technologie (KIT), Eggenstein-Leopoldshafen, Germany

[b] Studiecentrum voor Kernenergie•Centre d'Etude de l'Energie Nucléaire (SCK•CEN), Mol, Belgium

[c] Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid, Spain

[d] Agenzia Nationale per le Nuove Tecnologie, l'Energia e lo Sviluppo Economico Sostenibile (ENEA), Brasimone, Italy



Objectives

- **Improve understanding steel corrosion in Pb/LBE**
  - Analyse corrosion modes that occur
  - Identify potential factors of influence
  - Understand discrepancies in corrosion as observed in different laboratories*/ by different testing procedures

- **Define best practices for corrosion testing and evaluation**
  - Pre-test characterisation of corrosion samples
  - Monitoring and control of experimental conditions
  - Data on thermo-physical or chemical properties to use
  - Post-test examination and quantification* of corrosion

- **Produce new data on steel corrosion in liquid Pb/LBE**
  - At 400–550°C and 10^{-8} to 10^{-6} mass% solved oxygen
  - Static and flowing liquid metal
  - With and without pre-oxidation of the tested steel
  - Focus on 15-15Ti, 316L and T91

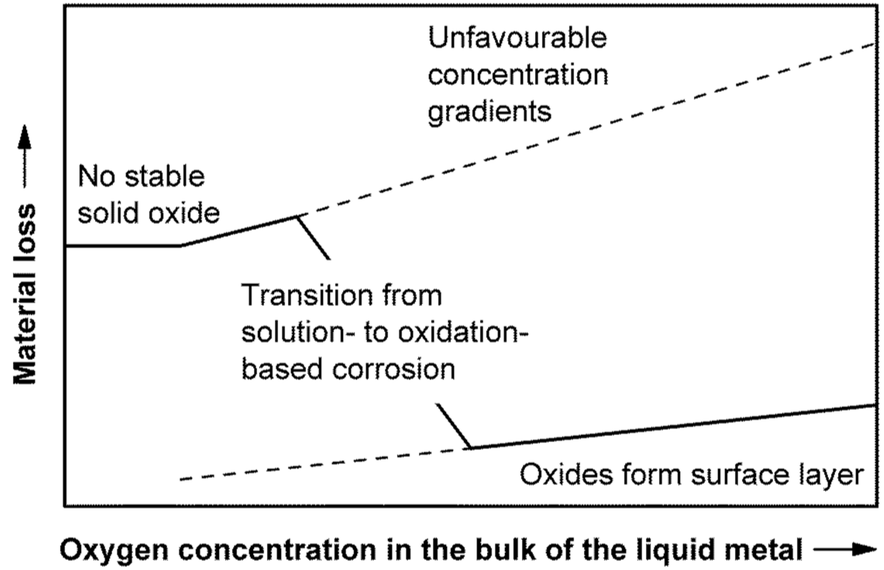
*** Addressed by the round robin on steel corrosion**

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, generally or selectively (Ni, Cr)
  - (Or form 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

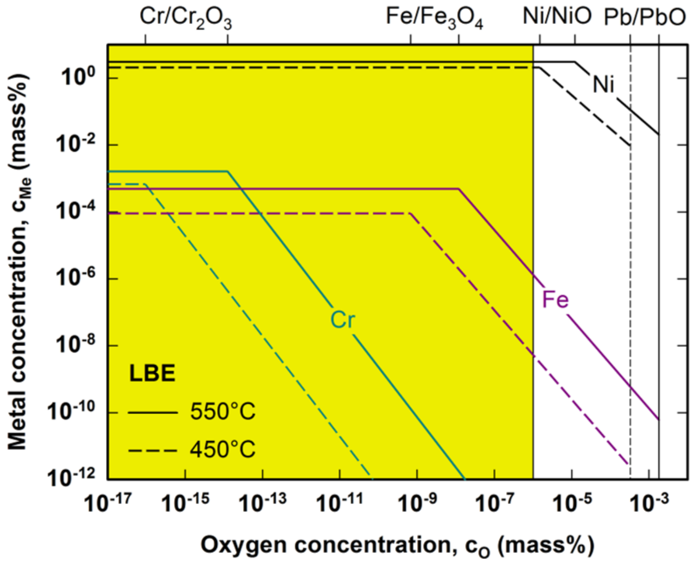


→ Transition from solution-based to oxidation-based corrosion with increasing oxygen concentration

→ Low-oxygen conditions may locally occur even when oxygen concentration in the bulk of the liquid metal is high

Effect of oxygen on the solution of steel elements

- **Unfavourable concentration gradients**
  - 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



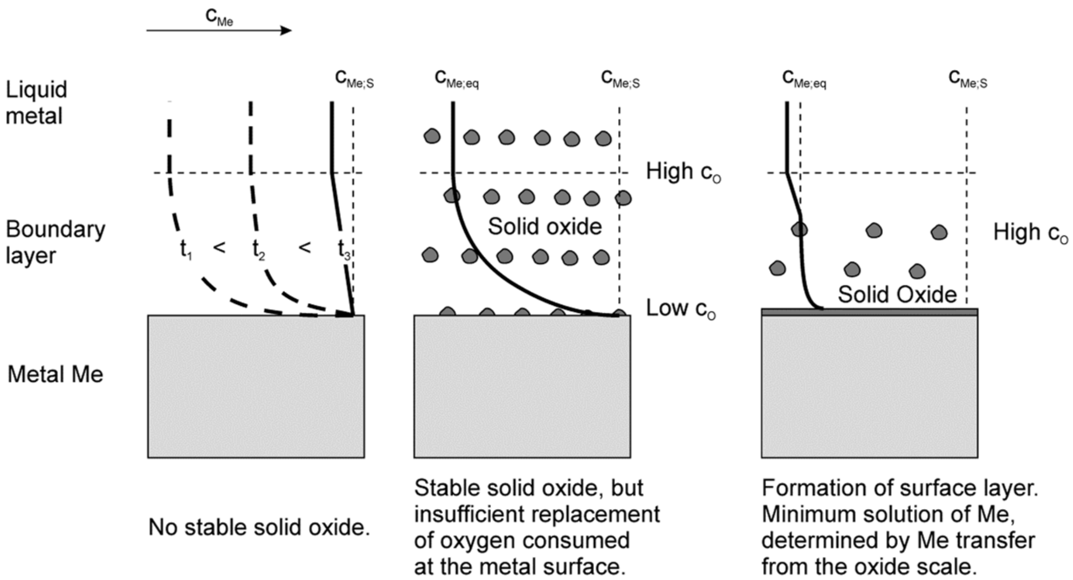
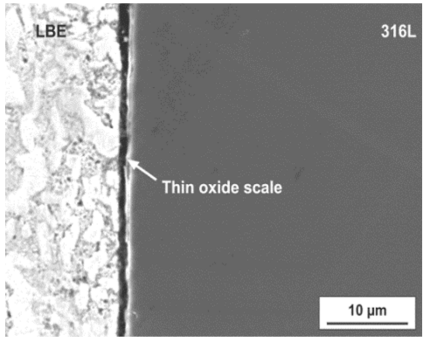


Illustration of concentration profiles that are decisive for diffusion of Me in the liquid metal (qualitatively)

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

- **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)

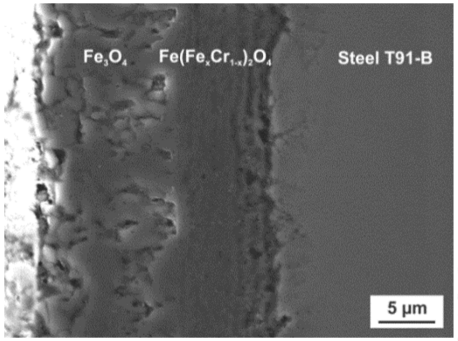


550°C

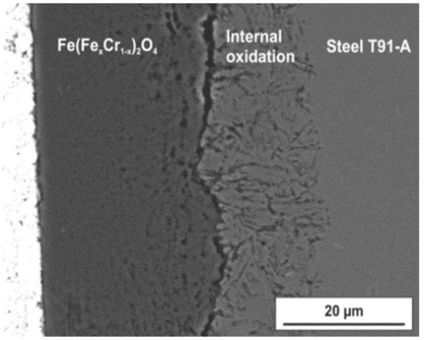
Scale failure at high local c_O (?)

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



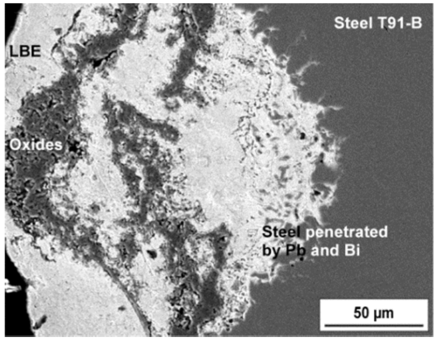
450°C

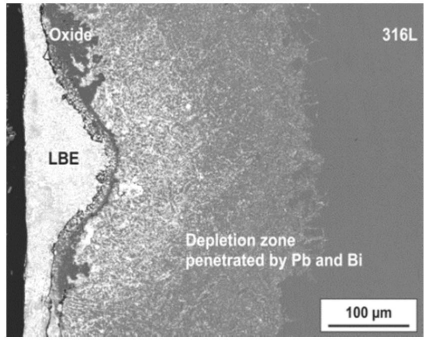


550°C

- **Solution-based 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





Factors potentially influencing the results from corrosion tests on steels in liquid metals

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Temperature	Thermo-physical and chemical properties of liquid metal and steel (elements) like solubility limits or oxide stability. Kinetics of corrosion processes and diffusion in the liquid metal.
Concentration of solved oxygen (in the bulk of the liquid metal)	Relative driving force for solution or oxidation of steel elements. Correspondingly strong impact on corrosion mechanisms.
Flow velocity	Mass transfer coefficients. Convective transport. Erosion.
Liquid-metal volume/ mass or mass flow	Capacity for solution of steel elements.
Free liquid-metal surface with cover gas/ gas composition	Potential sink or source of non-metals (oxygen). Precipitation of solved elements by reaction with gas components to form solid compounds.
Concentration of solved steel elements	Driving force for solution processes.
Experimental device, e.g., liquid-metal containment	Source of contamination of the liquid metal. Potential sink for solved steel elements and oxygen.

Monitoring/ controlling/ reporting experimental conditions

Temperature	Monitor and control to ±3°C at T<600°C or ±4°C at 600°C<T< 800°C where specimens reside. Report temperature gradients in the testing device/ facility and significant deviations from nominal conditions.
Concentration of solved oxygen (in the bulk of the liquid metal)	Monitoring during the experiment highly recommended. Control possible to ±2 mV in potentiometric oxygen sensor output. Report type of oxygen sensor used and actual sensor output as a function of time.
Flow velocity	Monitor and control. Report significant deviations from nominal conditions.
Liquid-metal volume/ mass or mass flow	Needs to be appropriate in respect of exposed surface area of steel samples and non-inert components of the experimental set-up. Report.
Free liquid-metal surface with cover gas/ gas composition	Monitor the actual cover gas composition, at least report the type of gas used. Report size of surface area.
Concentration of solved steel elements	Report concentration before and after the experiment. May be estimated from observed corrosion in some cases.
Experimental device, e.g., liquid-metal containment	Report materials and geometry. Operating history possibly decisive.

Oxygen measurement with potentiometric sensors

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- **Oxygen chemical potential**
  - Sufficient for characterising experimental conditions with respect to oxide stability
  - Fully defined by output voltage, type of reference electrode and temperature
  - Related quantities like oxygen activity or equivalent partial pressure follow from calculations using only universal constants

- **Oxygen concentration (mass%, kg/m³, …)**
  - Mandatory to calculate only when oxygen transfer, transport or consumption is to be assessed
  - Oxygen saturation concentration in Pb or LBE is required input

Different equations for estimating oxygen saturation concentrations were proposed and have been used in the past!

Characterisation of samples

Material tested	Analysed chemical composition. Final thermal or mechanical treatment. Microstructure.
Sample geometry	Geometric dimensions. Resulting volume and mass. Exposed surface area.
Surface finish	Final machining step. Peak-to-trough roughness (R_t) and centre line average roughness (R_a)
Cleaning procedure, storage/ handling after preparation	

- **Recommendations***
  - Geometry with mainly flat surfaces, minimum of corners and length of edges per unit surface area exposed (e.g., discs).
  - Smallest geometric dimension minimum 2 mm.
  - Provide a surface area (minimum) between 4–6 cm².
  - Round off corners and edges slightly.
  - Geometric dimension used for quantification should be assessed with ± 5 µm overall accuracy

→ **Depends on available sample material.**

* From guidelines for high-temperature corrosion testing.

Post-test examinations

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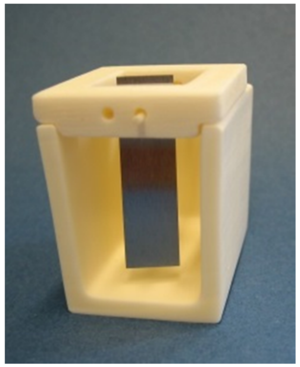
- **Corrosion phenomena**
  - Structure and composition of corrosion scales
  - Topography of interfaces, e.g., instantaneous steel surface
  - Assessment on the µm-scale by LOM, SEM+EDX, XRD, …
  - AES, XPS or TEM required when sub-micron resolution is required

- **Quantification**
  - Gravimetry vs. metallography
  - Full quantification required, i.e., loss of sound steel <u>and</u> 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

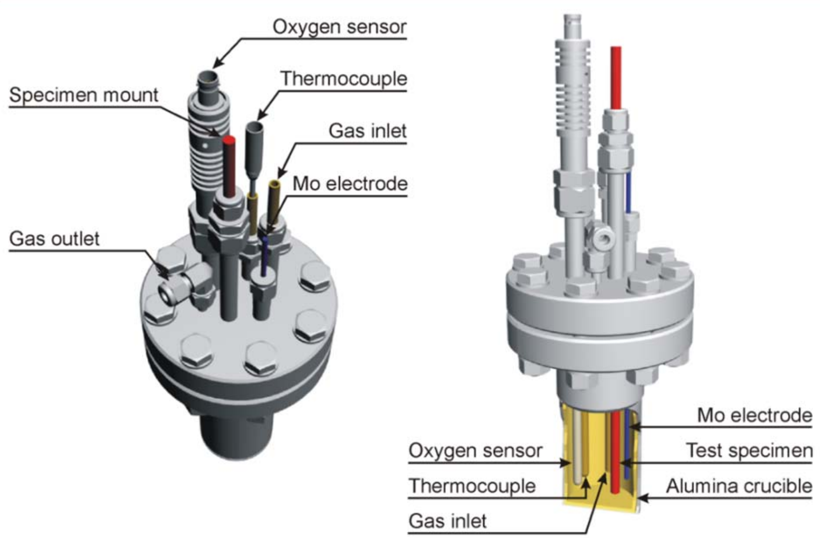
COSTA

Testing characteristics	Exposure to static liquid metal. Ceramic crucible containing 14 cm^3 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 cm^2 exposed to liquid metal.
Determination of oxygen content	From equilibrium with oxygen-containing gas. Appropriate sensors under development.



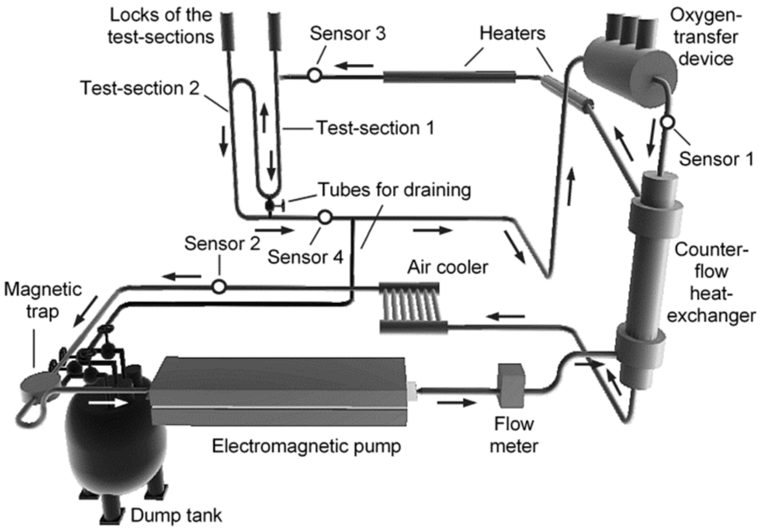
Round robin testing device

Testing characteristics	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.
Sample geometry	Typically, cylindrical specimen with ~10 cm² exposed to liquid metal.
Determination of oxygen content	Potentiometric oxygen sensor.



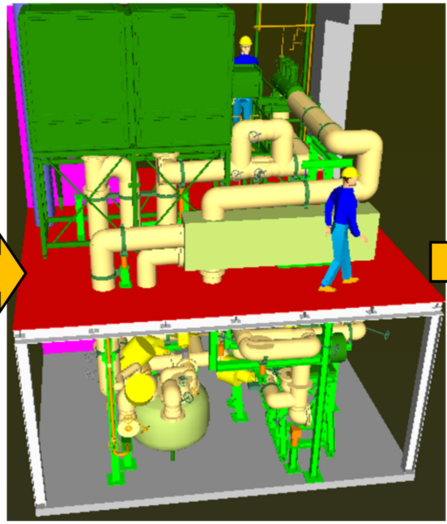
CORRIDA loop

Testing characteristics	Exposure to flowing LBE, typically 2 m/s. 1000 kg LBE circulating at typically 5.3 kg/s. Several steel specimens 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 gradient between hot (test sections) and cold leg.
Sample geometry	Typically, cylindrical specimen with 7.5 cm^2 exposed to liquid metal.
Determination of oxygen content	Four potentiometric oxygen sensors distributed along the loop.

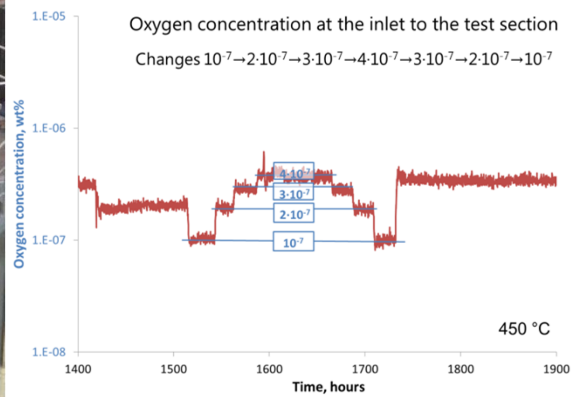


CRAFT loop

Testing characteristics	4000 kg of LBE circulation at typically 6 kg/s. Specimens are exposed in two vertical test sections. Test rigs with the specimens are extracted for specimen replacement and examination to the glove box with low oxygen environment. Flow controlled with replaceable insert in the test section, which can be adjusted for simultaneous exposure with different flow velocities. One test section is replaceable and made for instrumented tests.
Sample geometry	Typically cylindrical specimens
Oxygen control system	Oxygen control in hot and cold legs at 4 positions 3 sensors each. Conditioning with gas.



Oxygen control



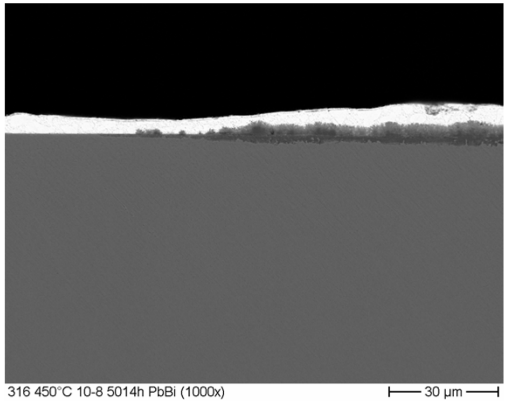
Experiments performed in COSTA

Materials	316 L (plate), 1.4970 (rod), 1.4970 (tube)					
Liquid metal	LBE					
Temperature /°C	400	450	500	550*	450	500
Oxygen concentration (max.) /mass%	4×10^{-8}				4×10^{-6}	
Exposure time /h	1000 and 5000					

* Only 316L, exposure for 800, 2000 and 5000 h

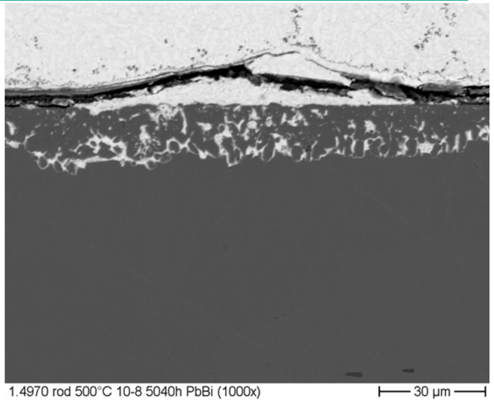
❑ **400/450°C**

- Protective scaling or accelerated oxidation
- Gain in importance of AO with increasing T, increasing c_O and for longer exposure time
- Higher susceptibility to AO of 1.4970 tube when compared to the other materials
- 450°C/ 4×10^{-6}%: 3 and locally 7 µm thick oxide scale on 1.4970 tube after 1000 and 5000 h, resp.



❑ **500/550°C**

- Occurrence of selective leaching (SL) after >5000 h at 500°C and 4×10^{-6}% oxygen
- SL after >1000 h and <800 h at 500°C/ 4×10^{-8}% and 550°C/ 4×10^{-8}%, resp.
- 14–22 µm depth of SL after 5000 h at 500°C/ 4×10^{-8}%; maximum for 1.4970 rod
- 110 µm on 316L after 5000 h at 550°C/ 4×10^{-8}%
- ~30 µm oxide (AO) after 5000 h at 500°C/ 4×10^{-6}%

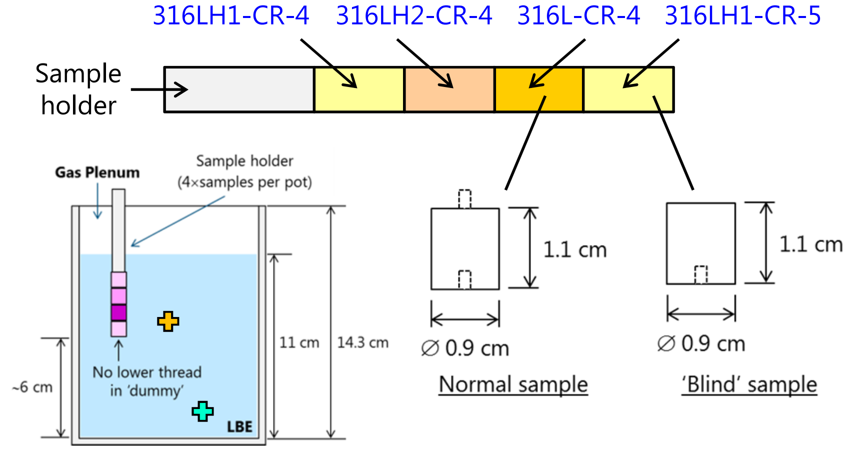


Test Rationale & Overview

❖ Goal: understand 316L dissolution behavior in static LBE as function of *exposure conditions (T, [O], t)* and *steel microstructure*

➢ Test Overview in Static LBE:
- Low [O] level ([O] < 10^{-8} mass%)
- Exposure conditions *(nominal T & t)*:
  - 400°C, 1000/2000/3000 h
  - 450°C, 1000/2000/3000 h
  - 500°C, 250/500/1000/2000/3000 h
  - 550°C, 250/750/1000 h

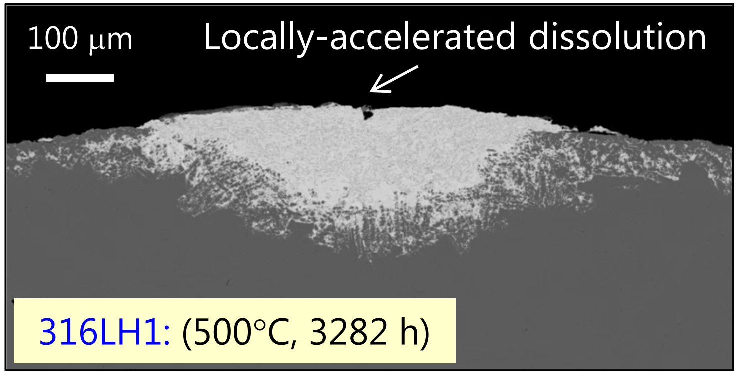
❖ Example of sample sequence (500°C, 1003 h):

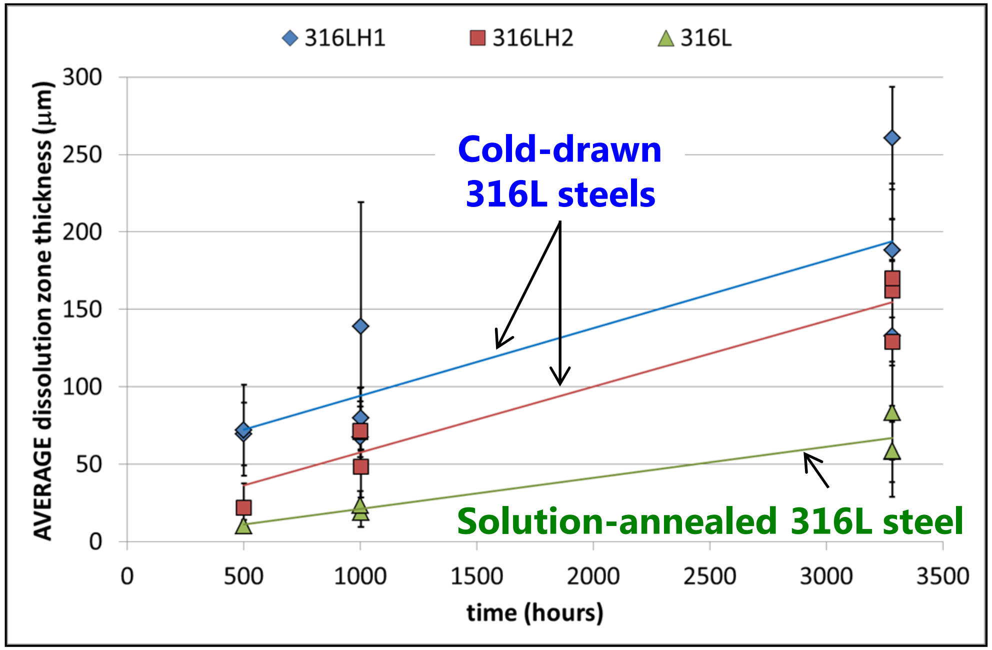


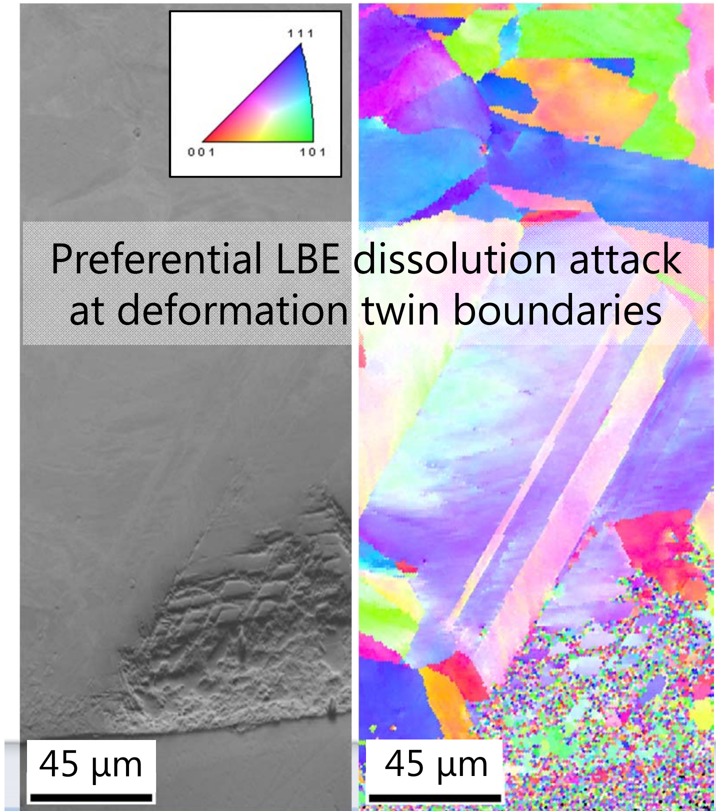
- Five 316L steel heats: 1 solution-annealed heat (316L – DEMETRA) & 4 cold-drawn heats (316LH1/316LH2/316LH3/316LH4)
- [O] monitored by electrochemical oxygen sensors (Bi/Bi_2O_3 ref. electr.)
- No automatic oxygen control system (AOCS)

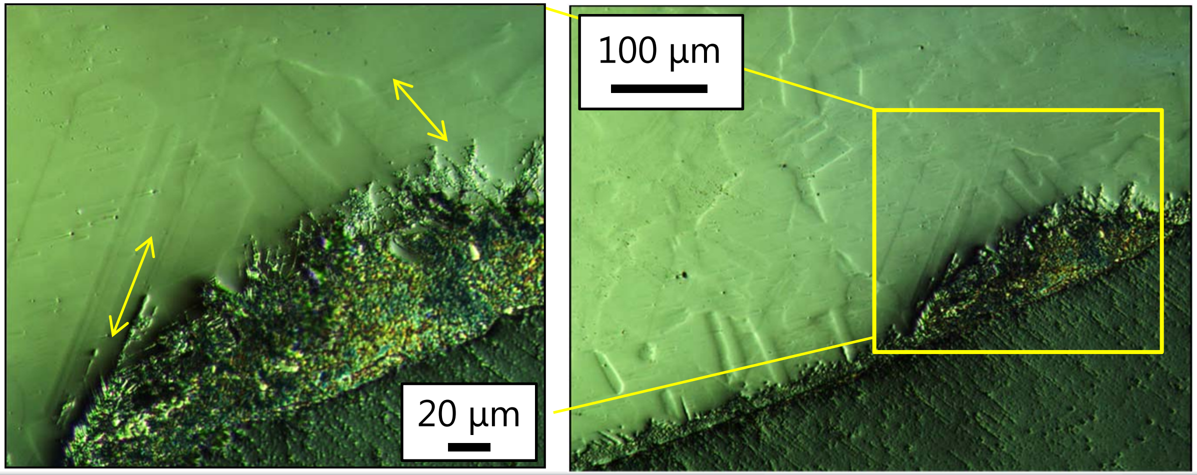
➢ Material characterisation by LOM, SEM/EDS, EBSD, FIB & t-EBSD, TEM

Time Dependence of 316L Steel Dissolution Corrosion at 500°C



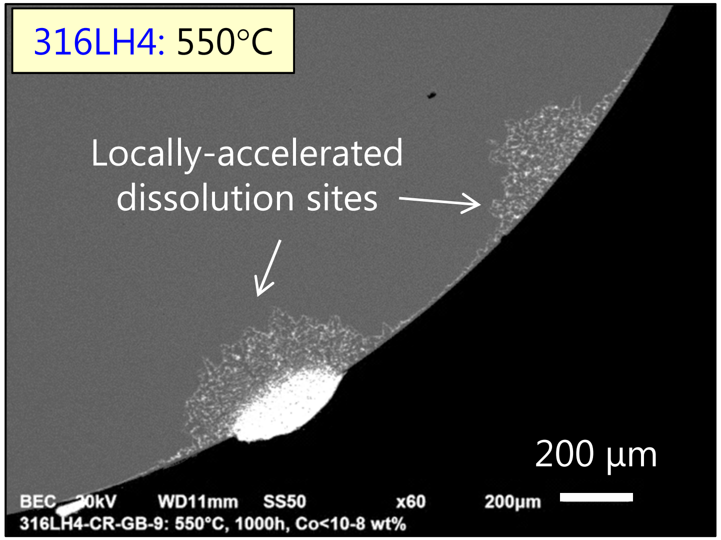


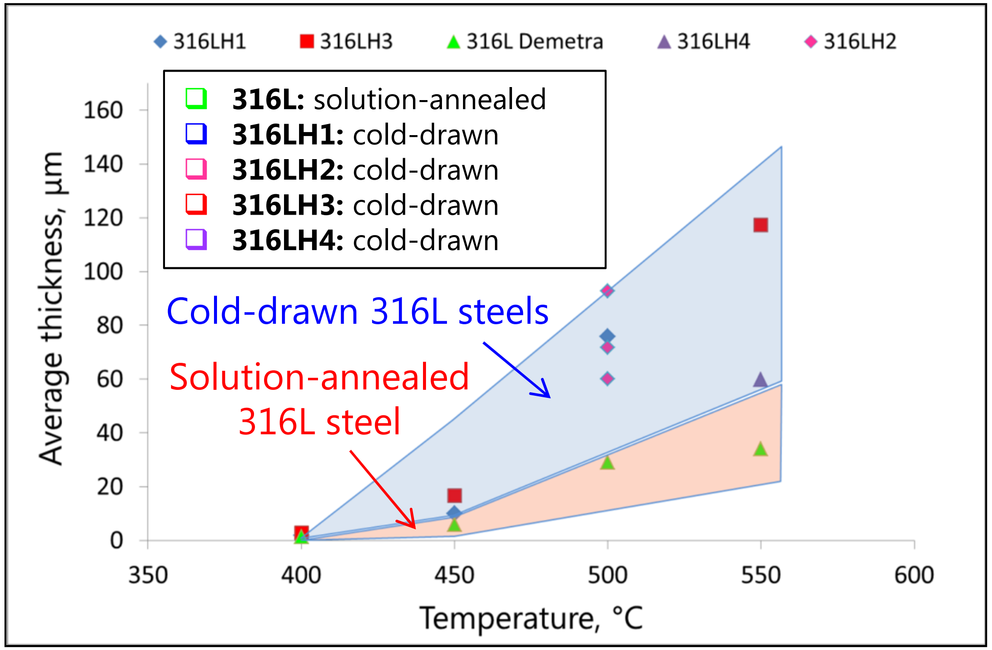


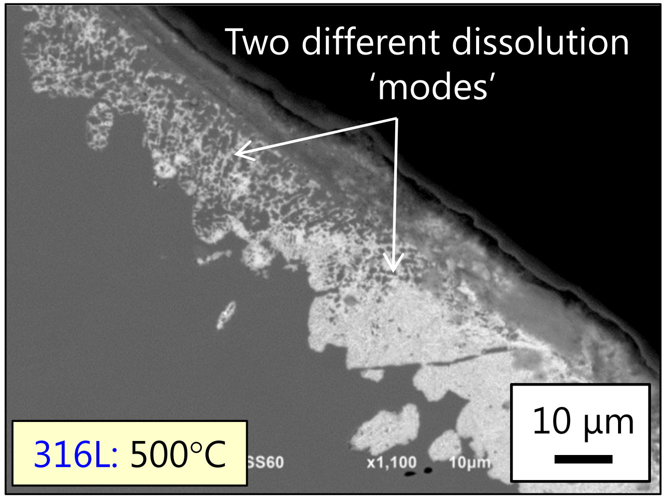


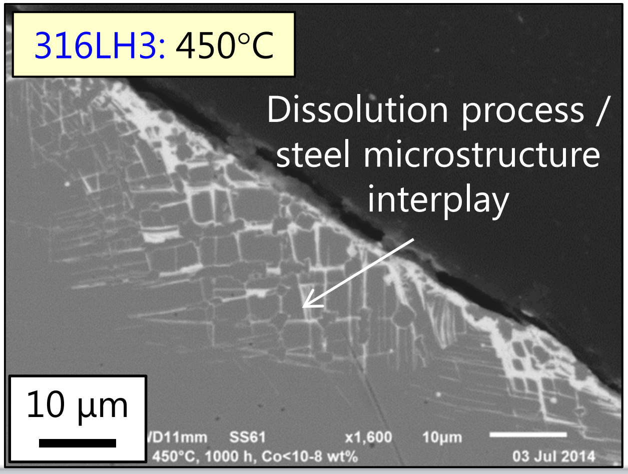
316LH2: (500°C, 1000 h)

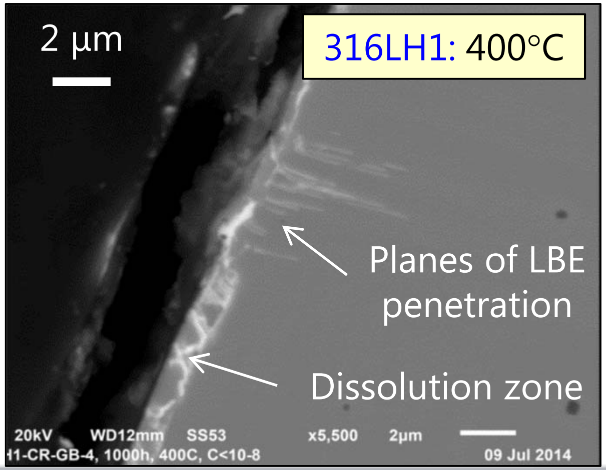
Temperature Dependence of 316L Dissolution Corrosion (400÷550°C, 1000 h)











Experiments in CORRIDA

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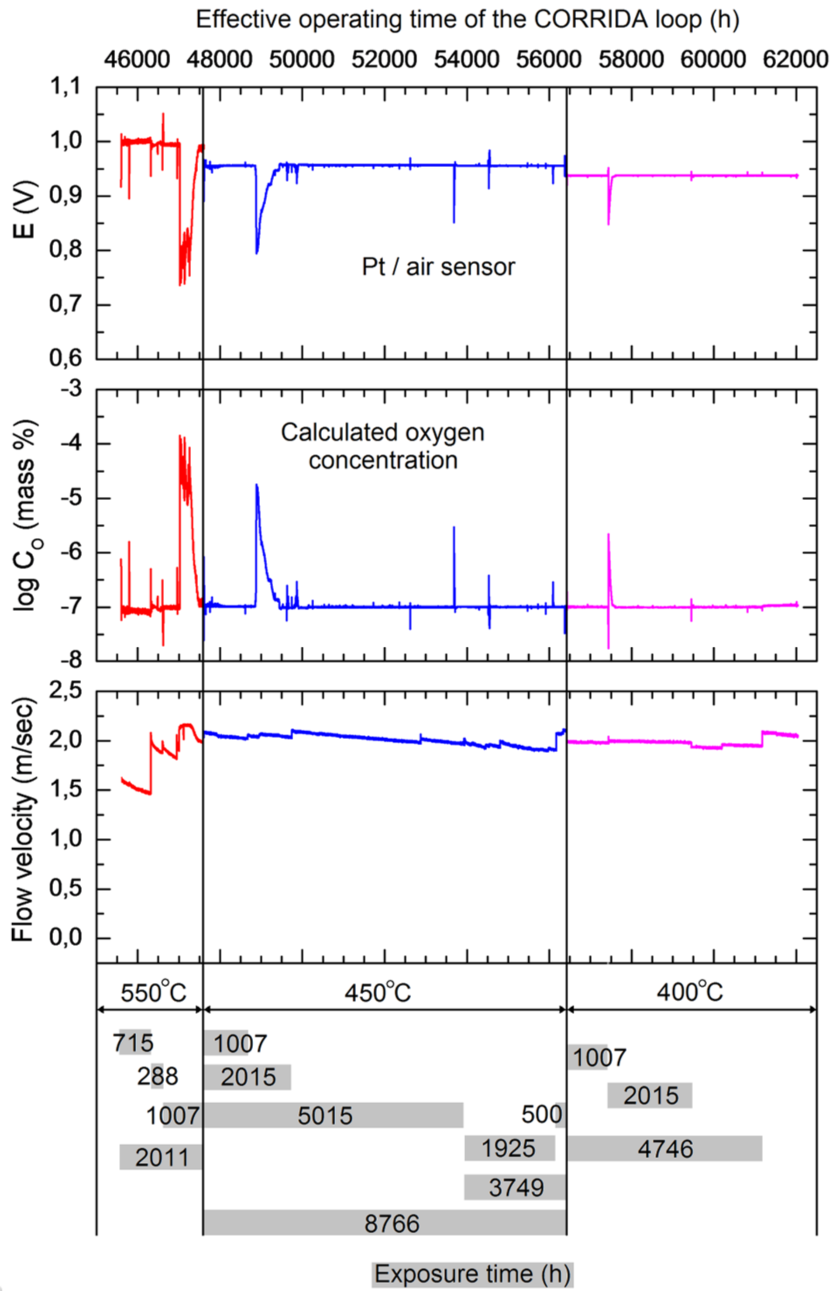


Materials	316 L (plate), 1.4571 (rod), 1.4970 (rod), T91 (two different plates)		
Liquid metal	LBE		
Temp. /°C	550	450	400
Oxygen /mass%	10^{-7}*	10^{-7}†	10^{-7}
Flow velocity /(m s^{-1})	2‡	2	
T_{min} /°C (Loop)	~385	~350	~350
Exposure time /h	~300–2000 (4 samples)	~500–9000 (7 samples)	~1000–5000 (3 samples)

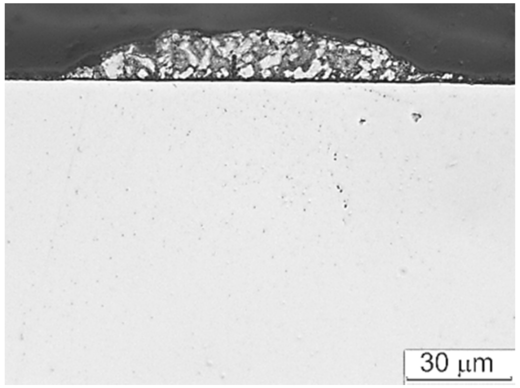
* Temporary excursion to ~10^{-4} mass% for 450 h, after 1450 h total runtime of the experiment.

† Temporary excursion to ~10^{-5} mass% for 600 h, after 1200 h total runtime of the experiment.

‡ Varying flow velocity, around 1.5 m/s during the first 700 h of total runtime of the experiment.

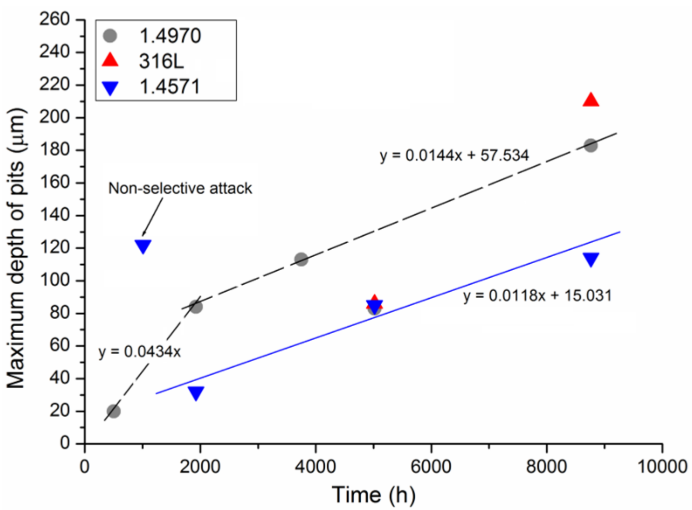
Austenitic steels after exposure in the CORRIDA loop

- **400°C/ 10^{-7} mass% oxygen**
  - Only protective scaling at up to 4766 h

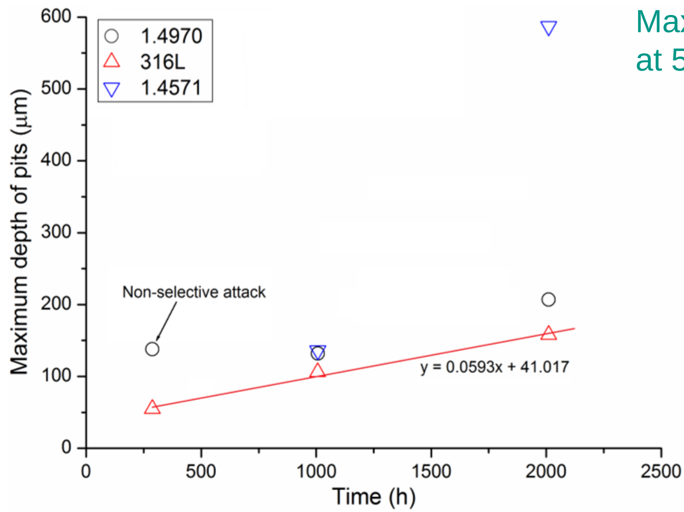


1.4970
after 4766 h
at 400°C/10^{-7}**%**

- **450 and 550°C/ 10^{-7} mass% oxygen**
  - Protective scaling and selective leaching (SL)
  - Occasionally non-selective attack (general solution) at higher rate than SL
  - Comparatively long incubation of SL seems coupled to faster progress
  - Steel that showed highest relative resistance against SL at 450°C, corrodes fastest at 550°C (1.4571), and vice versa (316L)
  - 100–200 µm local material loss after 9000 h at 450°C, 150–600 µm after 2000 h at 550°C



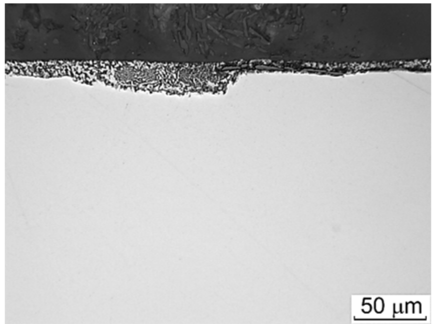
Maximum of SL
at 450°C/10^{-7}**%**



Maximum of SL
at 550°C/10^{-7}**%**

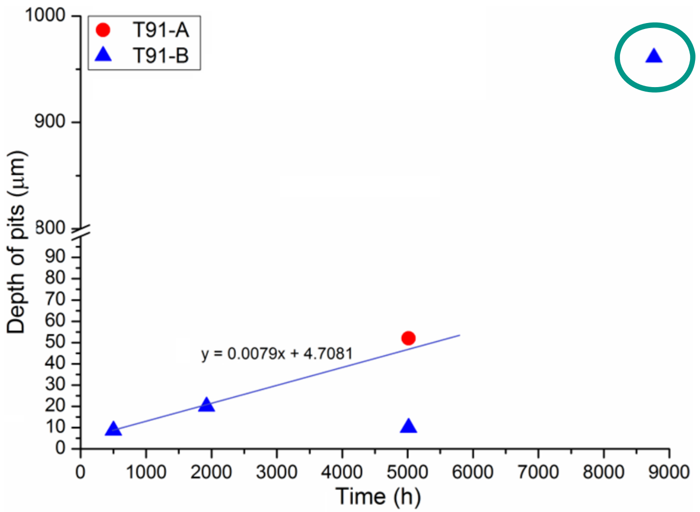
T91 after exposure in the CORRIDA loop

- **400°C/ 10^{-7} mass% oxygen**
  - Primarily accelerated oxidation (AO)
  - Flawed and partially detached oxide scale
  - Solution-based corrosion (SB) observed locally after 4766 h

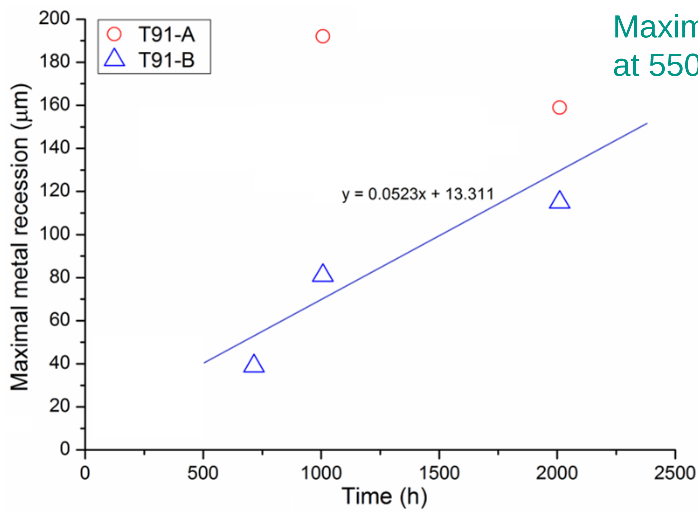


T91-B after 4766 h at 400°C/10^{-7}**%**

- **450 and 550°C/ 10^{-7} mass% oxygen**
  - Protective scaling locally still evident, especially after shorter exposure time
  - Dominant AO
  - Possible incipient stages of SB after 500, clearly observed after 5000 h at 450°C
  - At 550°C, incubation of SB between ~300 and 700 h
  - ~50 µm maximum SB after 5000 h at 450°C, exceptionally severe attack observed on T91-B (950 µm) after 8766 h
  - Maximum 190 µm after 1000 h at 550°C



Maximum of SB at 450°C/10^{-7}**%**



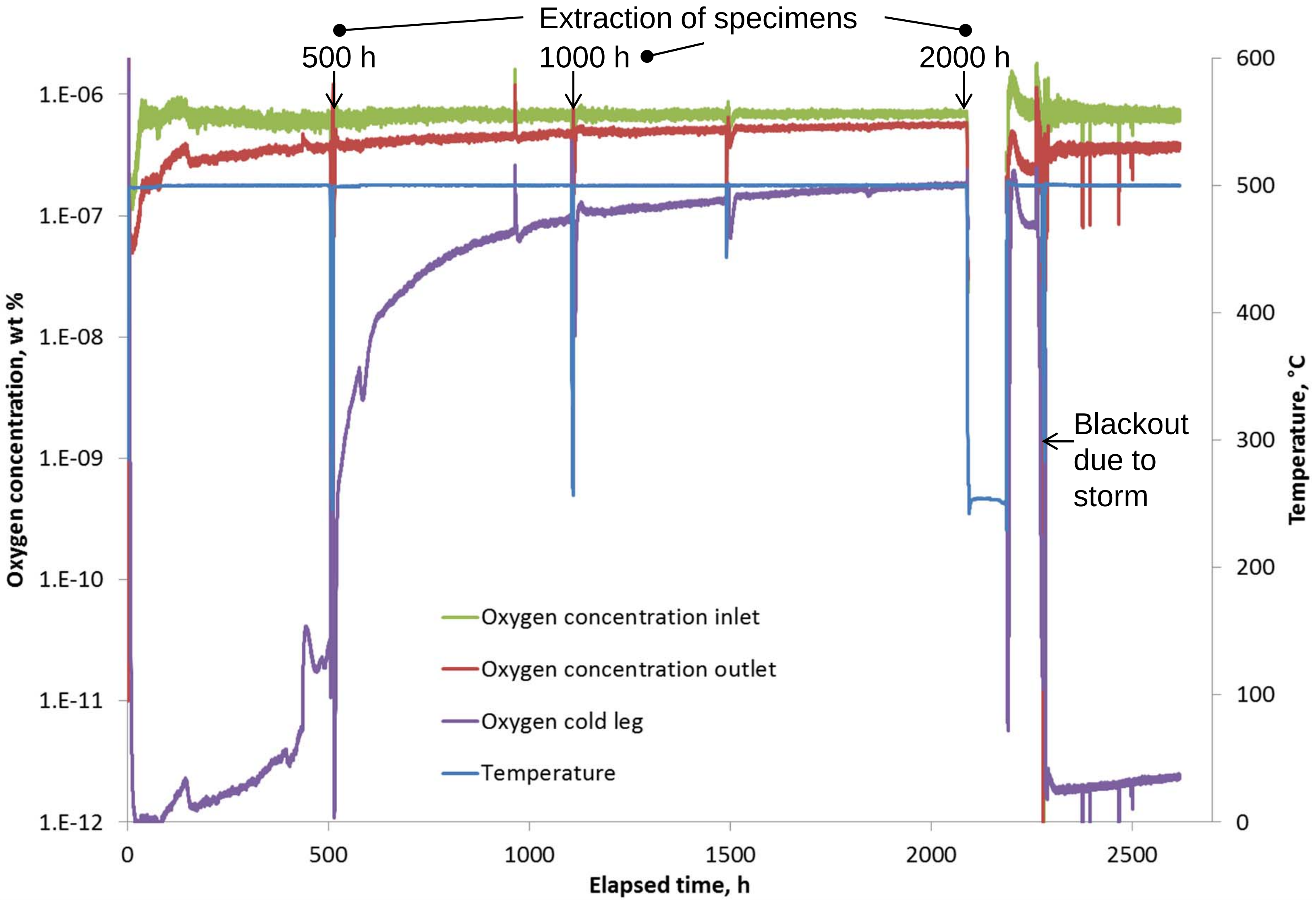
Maximum of SB at 550°C/10^{-7}**%**

Schedule of CRAFT

- End mechanical contracting →11/2012
- Process tubing →12/2012
- Glove box
  - Assembly → 12/2012
  - Leak test → 06/2013
- Wiring →03/2013
- First Filling →04/2013
- Automated Conditioning →05/2013
- Fully Commissioned →07/2013

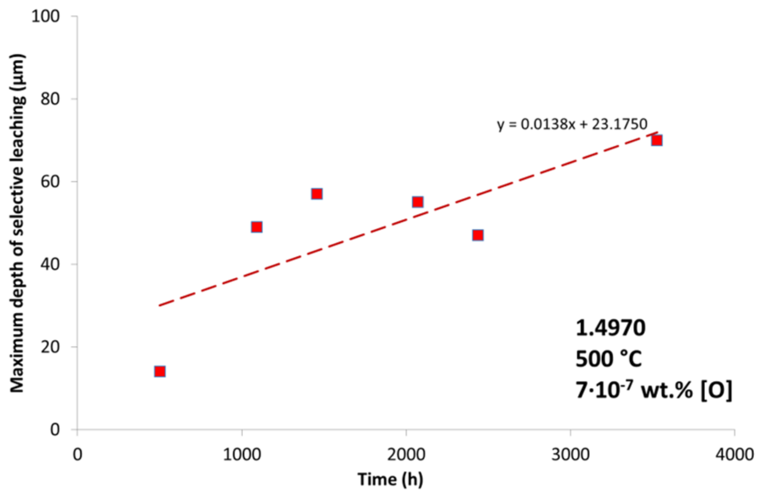
- The first corrosion tests → 09/2013 – 12/2013
- Modifications → 01/2014 – 02/2014
- The second corrosion test → 03/2014 – 09/2014

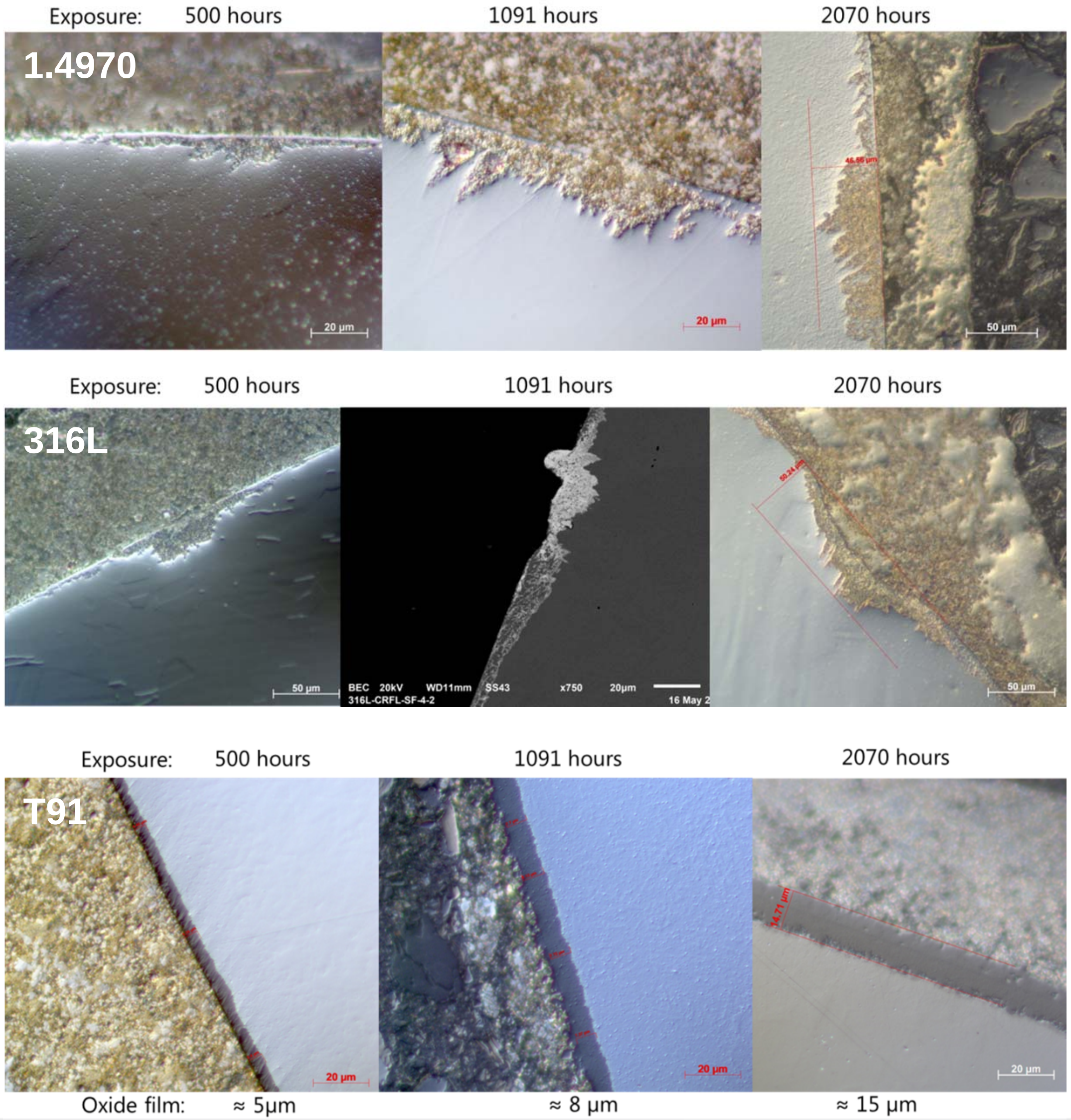
The second cycle



Preliminary results of exposure steels in CRAFT loop

- Significant variations of LMC spots sizes between different cross sections of the same specimen
- Deep localized corrosion damage was found on austenitic stainless steels at 500°C / $7{\cdot}10^{-7}$ wt.% / 2m/s due to selective leaching
- More detailed microstructural analysis of the exposed specimens will be performed and the results will be provided for the final deliverable

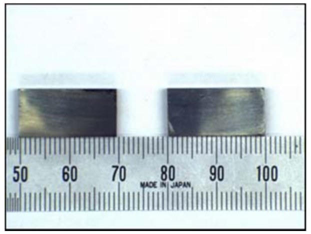


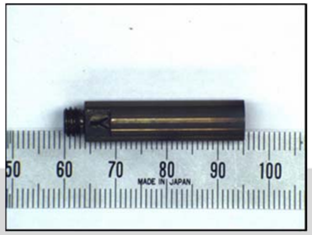


Tests on pre-oxidised steels

Materials	316 L (plate), 1.4970 (rod)
Surface finish	Fine-grinding followed by pre-oxidation at 580°C, 50 Nccm/min dry air, for 1000 h
Liq. Metal	LBE
Temp. /°C	500
c_O (max.) /mass%	10^{-6}
Time /h	500
Testing device	FELIX (similar to COSTA)

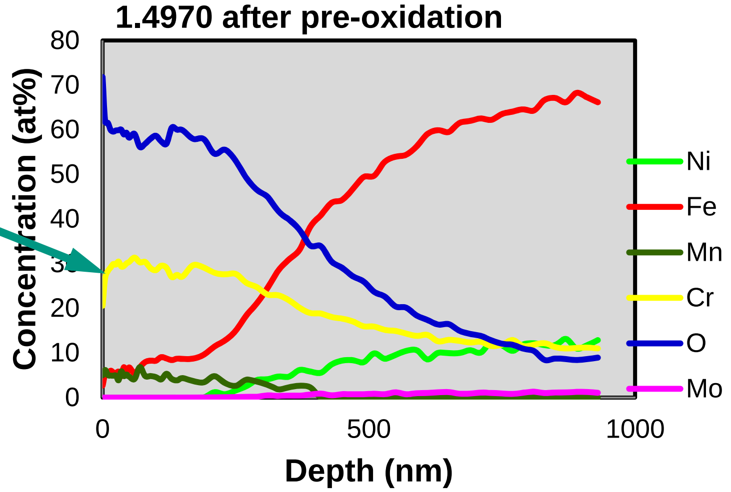
- **Pre-oxidised samples**
  - Rectangular coupons (1.4970, 316L) for tests in FELIX
  - Cylindrical samples for CORRIDA





Furnace for pre-oxidation in flowing gas

XPS after pre-oxidation: Thin Cr_2O_3.



Exposure in FELIX recently finished, evaluation on-going.

Status of Task 3.2

- **Analysis of the "State-of-the-art"**
  - Summarised in the form of best practices
  - Not all recommendations may possibly be obeyed in a particular experiment
  - Actual, not only nominal experimental conditions are to be reported

- **Round robin**
  - Separate presentation
  - Reproducibility of experiments in different laboratories
  - Qualification of metallographic quantification procedure
  - Quantification still needs to be finished

- **New corrosion data**
  - Supplements previous work especially by experiments at <500°C and $<10^{-6}$ mass% solved oxygen
  - Parts of the experiments need to be finalized

Thank you
for your attention!