17th Asian Pacific Corrosion Control Conference

KEYNOTE SPEAKER

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Present Affiliation	Karlsruhe Institute of Technology, Germany
Academic Qualification	Ph.D in Corrosion and Materials Science
Area of Specialization	• Liquid metal corrosion • High temperature corrosion • Corrosion protection by coatings
Achievements / Awards	- Honory medal of the German Association of Engineers - Long-time member of NACE, USA - Member of International Advisory Panels for the Evaluation of national research programmes in Europe, Japan and China regarding Transmutation Technology
Paper no. 17014	**Corrosion behavior of austenitic steels 1.4970 ..** **Jürgen Konys, Valentyn Tsisar, Carsten Schroer**

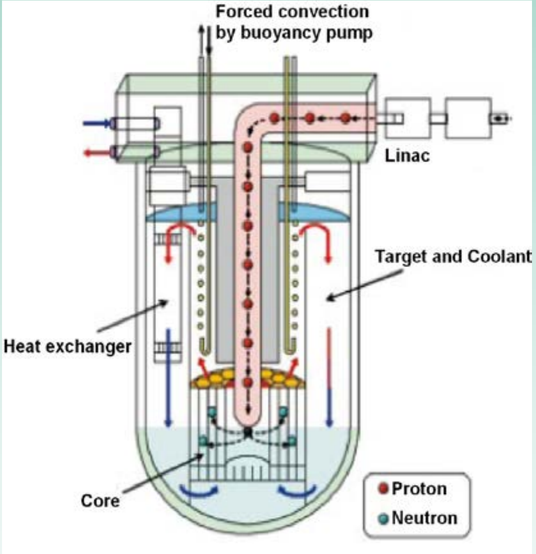
Corrosion behavior of austenitic steels 1.4970 (15-15 Cr Ni), 316L and 1.4571 (316-Ti) in flowing low-oxygen LBE with 10^{-7} mass% of oxygen at 400 to 550°C

LBE = Lead-Bismuth Eutectic)

Outline

- Heavy liquid metals for energy applications
- HLM chemistry: role of oxygen …..
- Corrosion of austenitic steels in LBE
- Quantification of corrosion attack
- Dependency on oxygen concentration
- Conclusions

Lead-cooled Nuclear Reactors/Systems

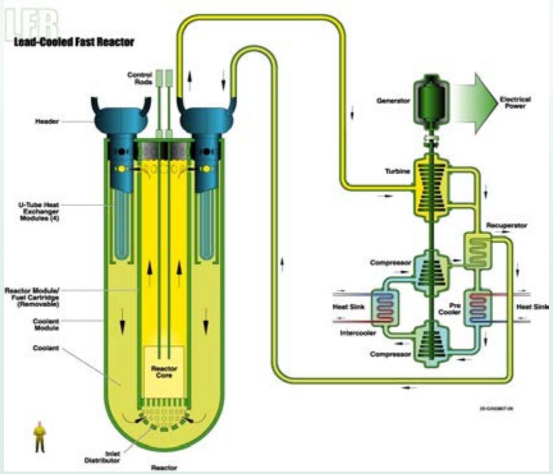


Accelerator Driven (Subcritical) System (ADS)

- Transmutation of long-lived radioactive isotopes in nuclear waste
- Power generation (Energy Amplifier)
- Liquid lead (Pb) or lead-bismuth eutectic (LBE) as spallation target and primary coolant
- Maximum temperature, typically
  - 450 – 500°C for regular operation
  - Periodically 550°C (according to plant design)

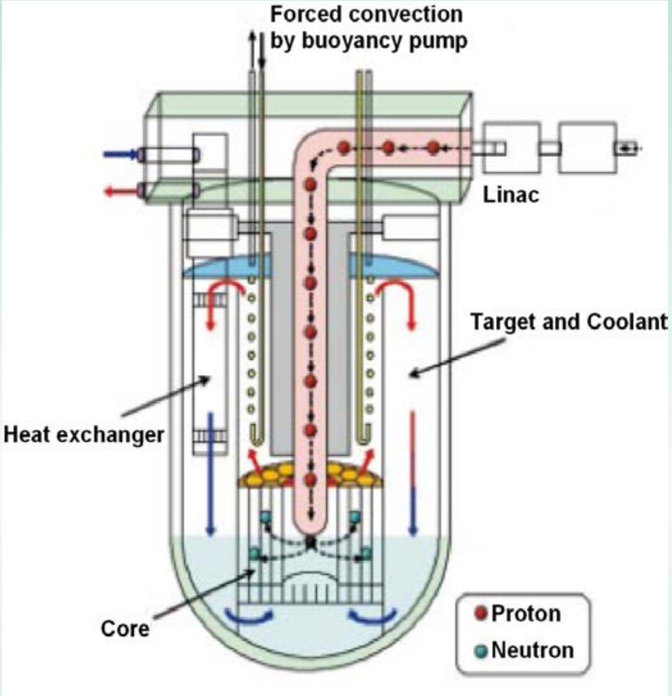
Lead-Cooled Fast Reactor (LFR)

- One of the concepts for the 4th generation of nuclear power plants (Gen-IV)
- In the long-term, Pb as primary coolant at maximum ca. 800°C
- Short- to mid-term: Pb- or LBE-cooled at 450 – 550°C



Lead-cooled Nuclear Reactors/Systems

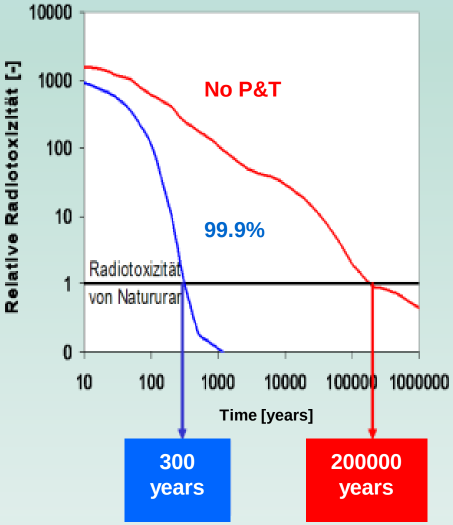
Motivation for ADS



Reduction of high-level nuclear waste

	No. NPPs		Burned Fuel (t)	
	No.	Electricity gen.	Accumulated	Per year
Worldwide	438	16%	220 000	7 000
EU	145	35%	34 500	2 500
Germany	19	30%	8 400	450

Influence of partitioning rate of Pu and MA on the radiotoxicity of burned fuel



Heavy liquid metal – steel interactions

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

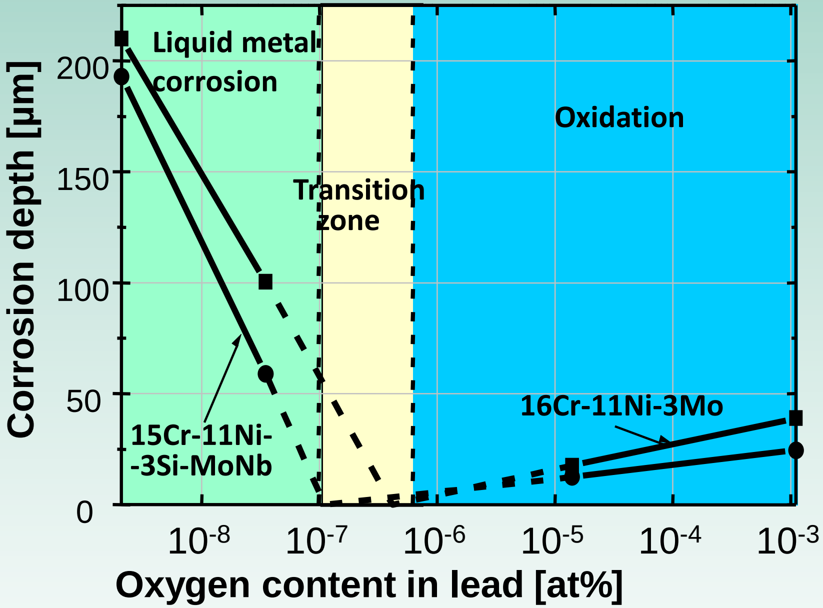
Observed on the µm-scale, accessible by light-optical microscopy (LOM), scanning-electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) …

- ❑ **Degradation of mechanical properties**
  - Damage accumulation at the surface due to corrosion
  - Or arising from phenomena below the µm-scale:
    - 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

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

Impact of oxygen on steel corrosion in HLMs

- **"Absence" of oxygen (Pb-16Li → Fusion)**
  - 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 (Pb, LBE)**
  - Solid oxides of steel elements are stable
  - But, 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 (Pb, LBE)**
  - Solid oxides of steel elements form a continuous surface layer
  - Solution of steel elements still possible, but only after diffusion through solid oxide

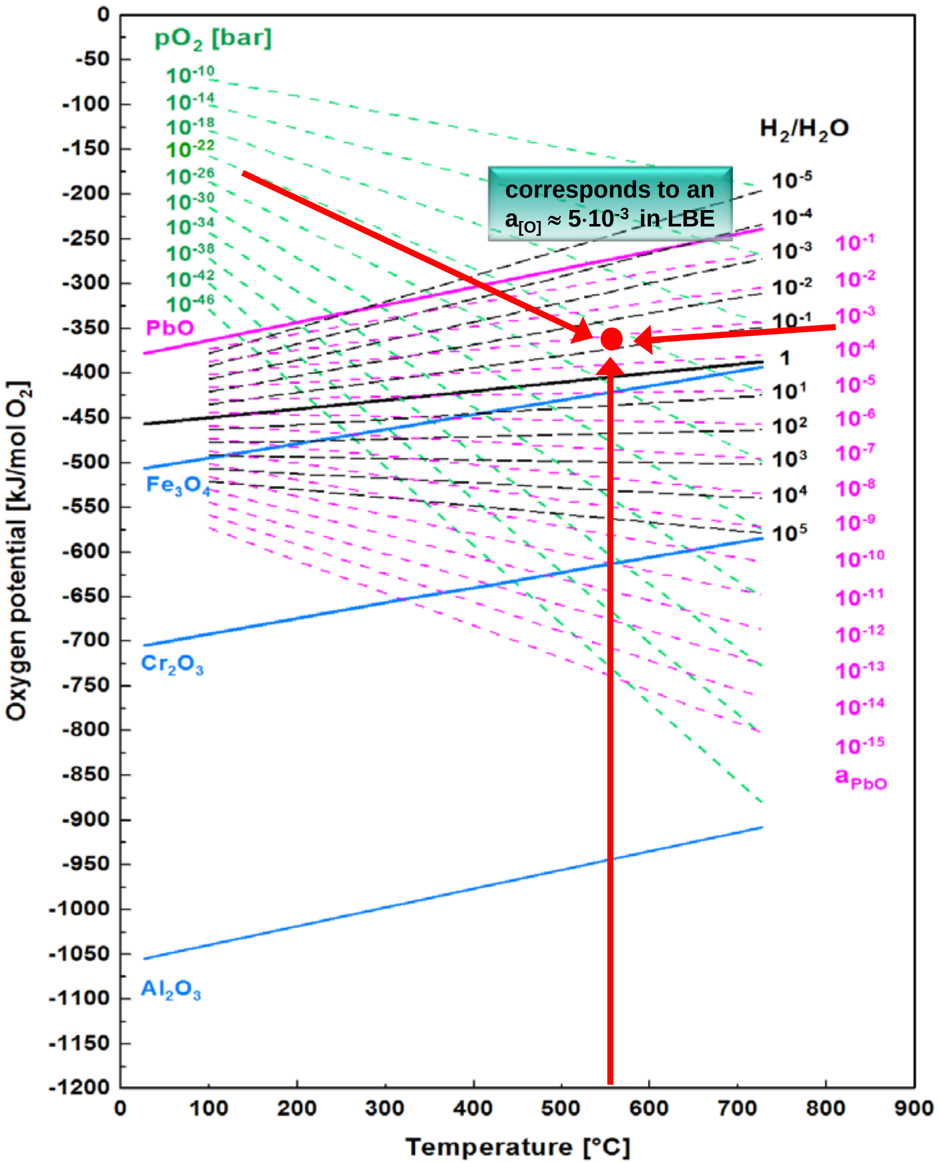


→ Transition from solution-based to oxidation-based corrosion with increasing oxygen concentration

→ **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

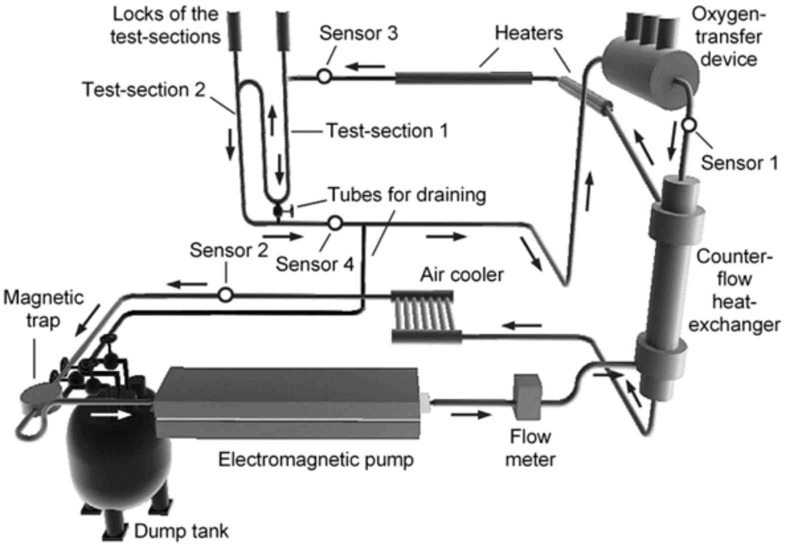
Oxygen chemistry: relevant oxygen potentials in Pb, LBE



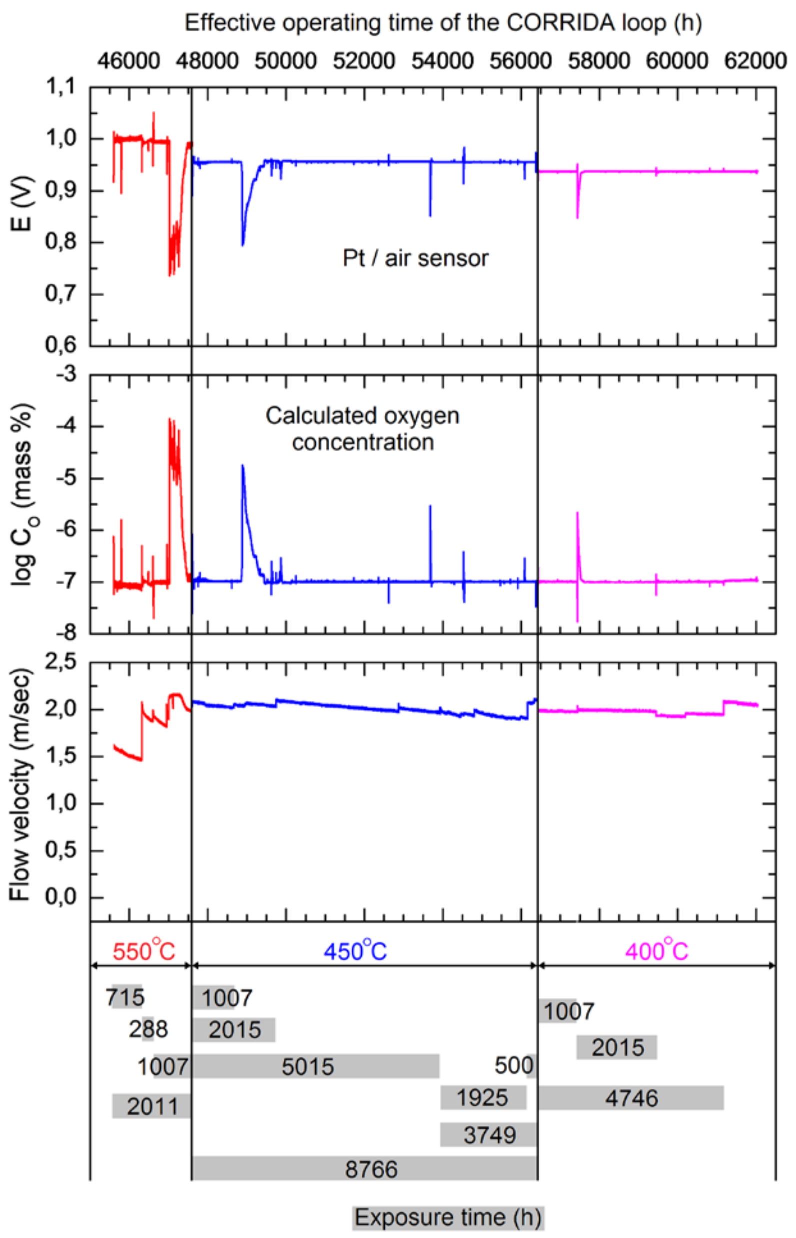
corresponds to an $a_{[O]} \approx 5 \cdot 10^{-3}$ in LBE

Corrosion testing in Pb or LBE for nuclear applications

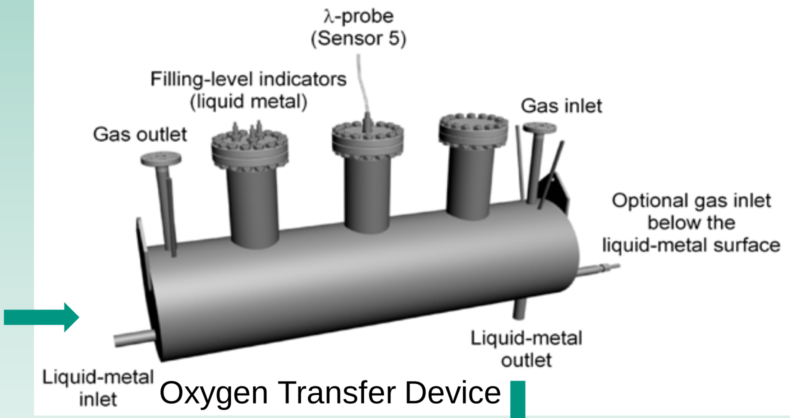
CORRIDA	
Testing characteristics	Exposure to flowing LBE, typically 2 m/s. 1000 kg circulating LBE (5.3 kg/s). Several steel samples simultaneously exposed in vertical test-sections. Oxygen control via gas with variable oxygen partial pressure. Large internal steel surface in contact with the liquid 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 Institute for Applied Materials – Corrosion Department



Test campaigns



Oxygen Transfer Device

- **T = 550(+5)°C,**

  $T_{min} \approx 385°C$, $c_O = 10^{-7}$ mass%, excursion to 10^{-4}–10^{-5} mass%O,

  v = 2(+/–0.2) m/s, initially 1.5–1.6 m/s,

  t = 288; 715; 1007; 2011 h

- **T = 450(+5)°C,**

  $T_{min} \approx 350°C$, $c_O = 10^{-7}$ mass%, excursion to 10^{-5} mass% O
  v = 2(+/–0.2) m/s,
  t = 500; 1007; 1925; 2015; 3749; 5015; 8766 h

- **T = 400(+5)°C,**

  $T_{min} \approx 350°C$, $c_O = 10^{-7}$ mass%,

  v = 2(+/–0.2) m/s,
  t = 1007; 2015; 4746 h; still continuing up to 10,000h

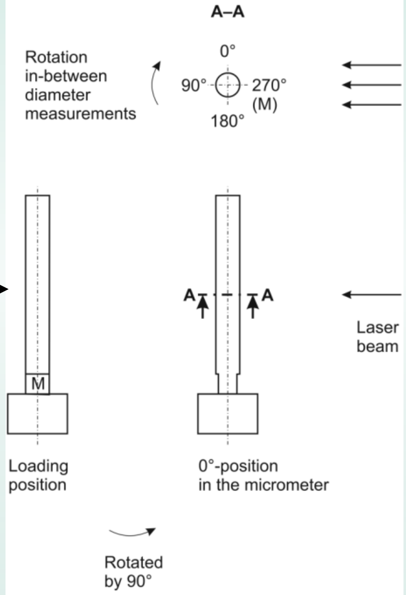
Quantification of corrosion attack

❑ 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

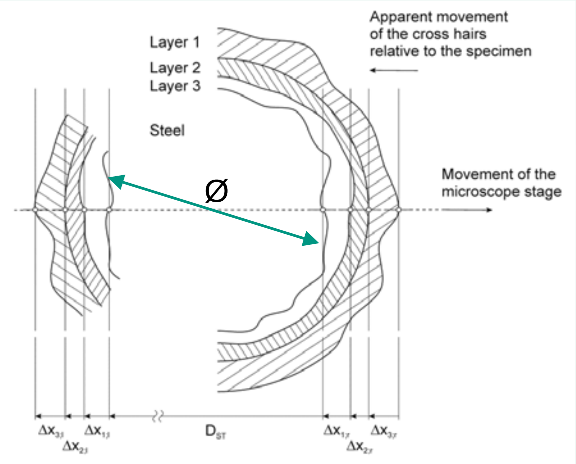
❑ Metallographic method (cylindrical specimens)

Initial parameters - Ø



- Measurement of initial diameter in a laser scanner with 0.1 µm resolution
- Diameter of unaffected material (12th measurements with rotation angle 15°) and thickness of corrosion zones determined in a microscope (LOM) with 1 µm resolution
- Occurrence of different corrosion modes on opposing sides of the re-measured diameter is considered in the evaluation (% of surface circumference)

Post-test examination



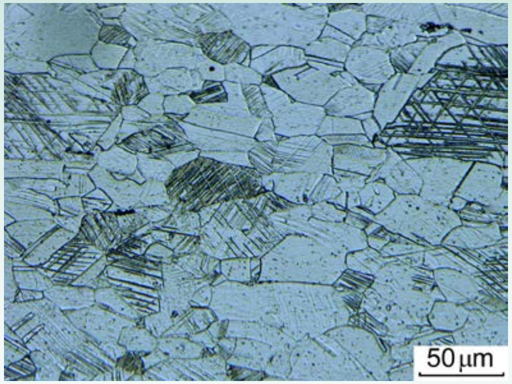
Transverse circular cross-section

Investigated materials

(Fe – Bal.)

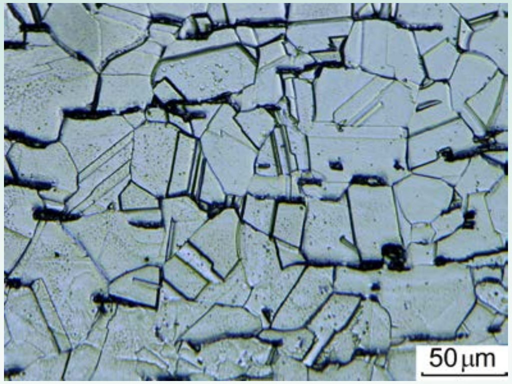
Austenitic steels	Cr	Ni	Mo	Mn	Si	Cu	V	W	Al	Ti	C	N	P	S	B
316L	**16.73**	**9.97**	**2.05**	**1.81**	**0.67**	**0.23**	**0.07**	**0.02**	**0.018**	**-**	**0.019**	**0.029**	**0.032**	**0.0035**	**-**
1.4970	**15.95**	**15.4**	**1.2**	**1.49**	**0.52**	**0.026**	**0.036**	**< 0.005**	**0.023**	**0.44**	**0.1**	**0.009**	**< 0.01**	**0.0036**	**< 0.01**
1.4571 (316-Ti)	**17.50**	**12**	**2.0**	**2.0**	**1.0**	**-**	**-**	**-**	**-**	**0.70**	**0.08**	**-**	**0.045**	**0.015**	**-**

1.4970 (15-15Ti)



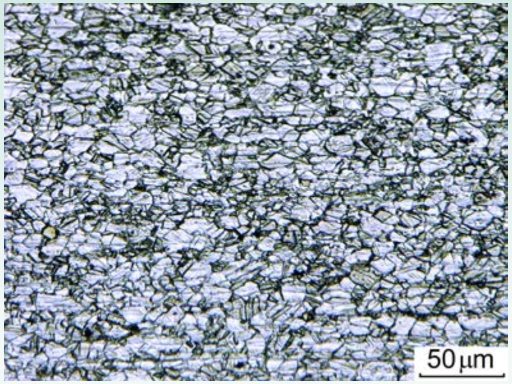
- HV_{30} = 253;
- Grain size ranged from 20 to 65 µm;
- Intersecting deformation twins.

316L



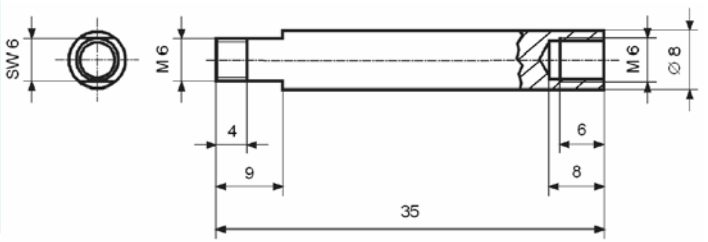
- HV_{30} = 132;
- Grain size averaged 50 µm (G 5.5);
- Annealing twins.

1.4571

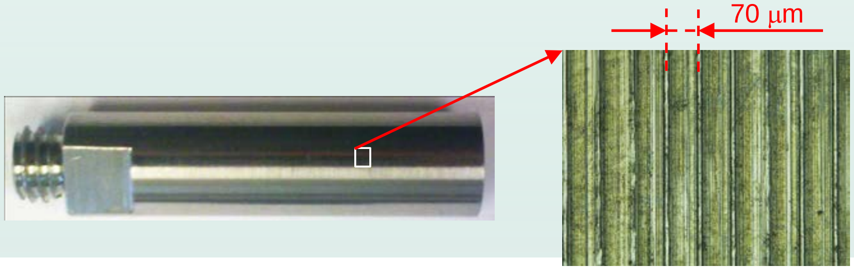


- HV_{30} = 245;
- Grain size averaged 15 µm (G 9.5).

Shape and dimensions of sample for corrosion tests

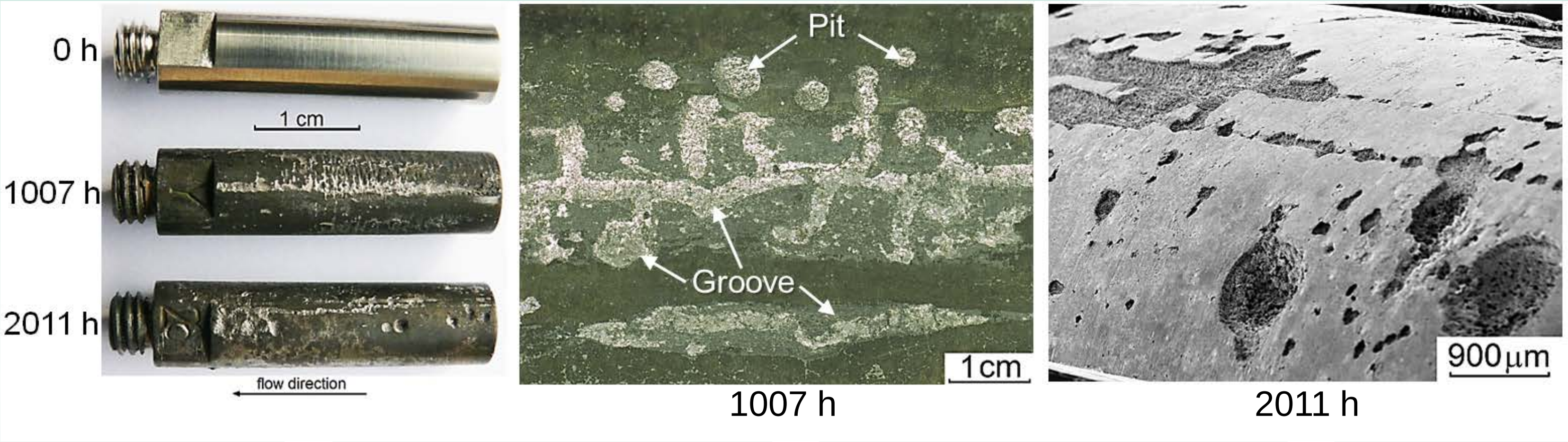


General view of initial sample after finishing turning



Qualification of corrosion modes on surface of austenitic steels after exposure to flowing LBE with 10^{-7} mass% O at 450 and 550°C

Surface examinations - general corrosion appearance



1.4970, 550°C

After cleaning in glycerin

After chemical cleaning

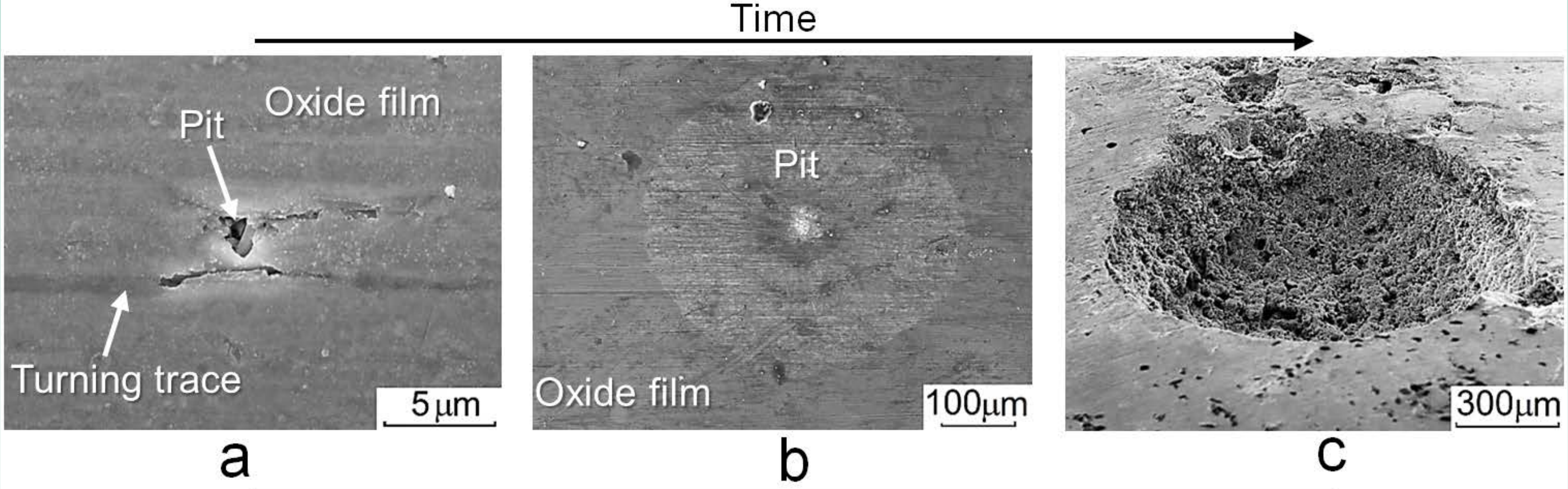
1007 h

2011 h

- Oxidation – formation of golden-colored oxide film (shorter test) and green-colored oxide film (longer test)
- Light areas with exfoliated oxide film;
- Severe local solution-based corrosion attack in the form of hemispherical pits and longitudinal and transversal grooves;
- The surface area covered by the oxide film decreases with exposure time in LBE, while the number of sites affected by local corrosion attack respectively increases.

Local pit-type corrosion attack

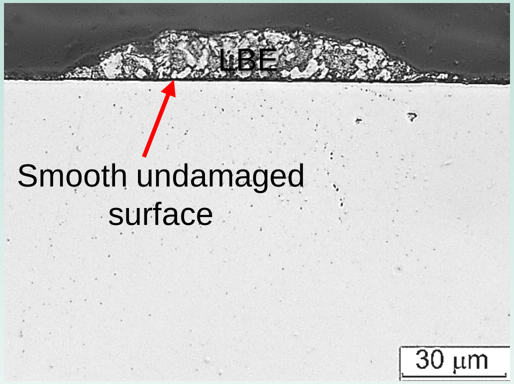
Expected sequence of evolution of corrosion pits wit time



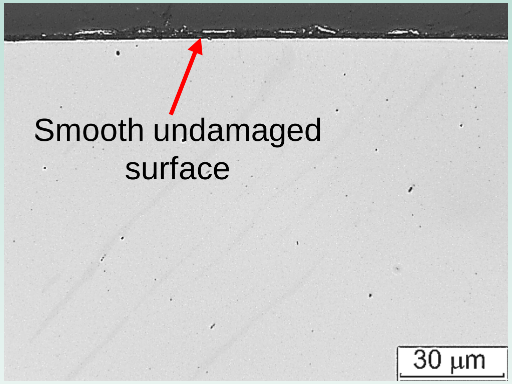
Object analyzed	mass %					
	O	Cr	Fe	Ni	Pb	Bi
Oxide film (a)	10.68	16.36	54.06	14.57	1.86	1.30
Oxide film (b)	7.21	16.08	63.17	10.23	2.21	-
Pit (b)	13.95	8.90	29.62	0.97	5.87	40.49

Cross-sections of austenitic steels after test in flowing oxygen-containing LBE (~ 2 m/s, ~ 10^{-7} mass % O) at 400°C for 4,746 h

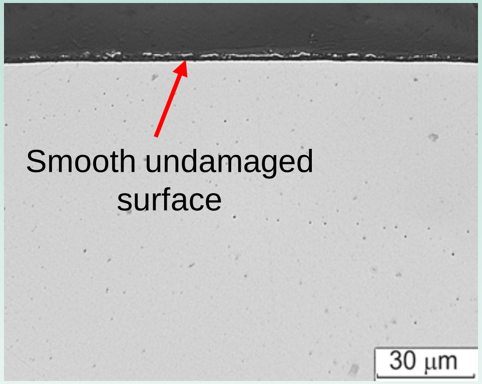
1.4970



316L

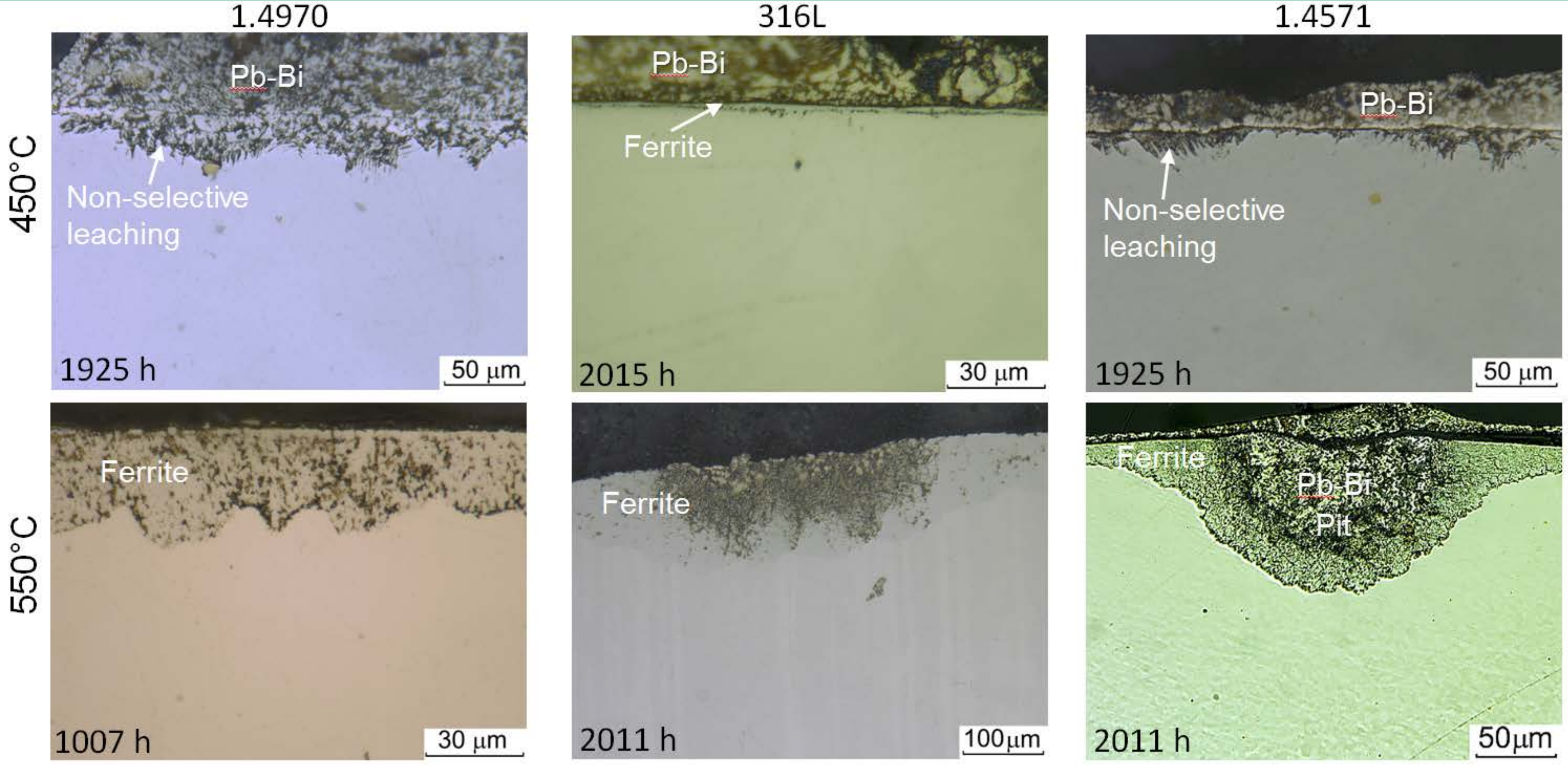


1.4571

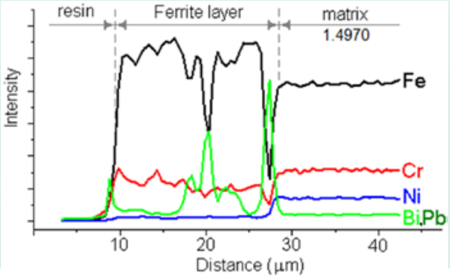


- Smooth undamaged surface is observed on the cross-section of samples;
- Selective leaching attack is not detected under the given duration of test - 4746h;
- Samples revealed golden-colored oxide film - protective scaling;
- Corrosion tests are still continuing with expected max. duration about 10000h.

Cross-sections of austenitic steels in flowing oxygen-containing LBE (~ 2 m/s, ~ 10^{-7} mass % O) at 450 and 550°C



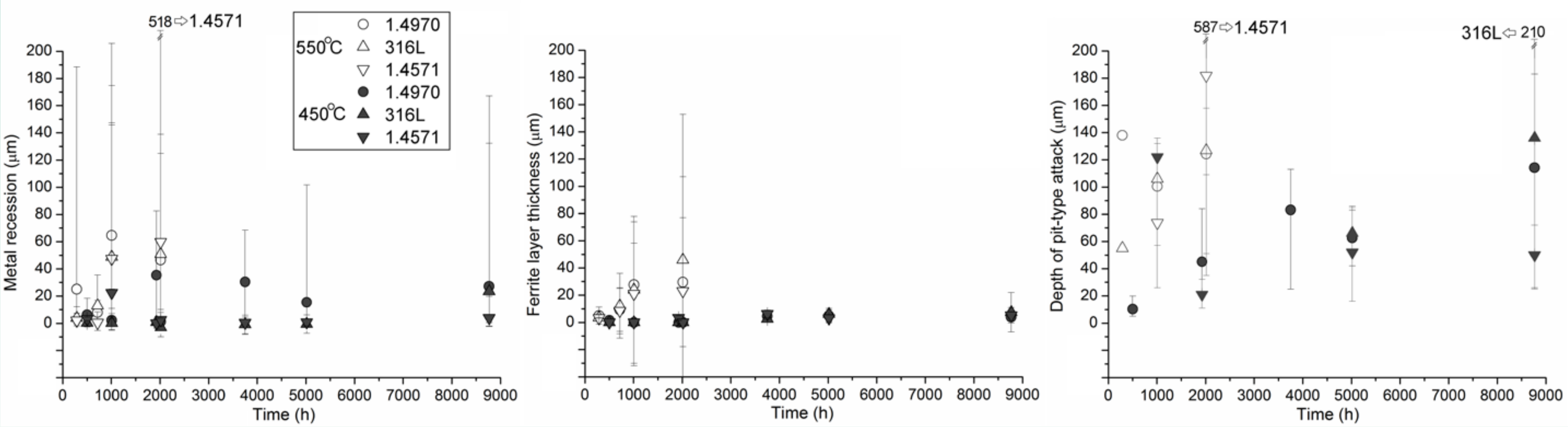
1.4970
550°C
2011 h



Steel	Ferrite layer composition (mass %)				
	Ni	Cr	Fe	Pb	Bi
1.4970	1.85	6.76	84.47	-	3.12
316L	1.10	8.13	86.48	-	1.95
1.4571	1.61	6.15	69.15	6.45	13.75

Overview of quantification of corrosion attack at 450 and 550°C in LBE with 10^{-7} mass% dissolved oxygen

Average corrosion loss of steels, expectedly, increase with rise in test temperature from 450 to 550°C



450°C:

❑ Metal recession (change in diameter) does not exceed 4, 27, and 26 µm after 8,766 h for 1.4571, 1.4970 and 316L steels, respectively;

❑ Thickness of layer-type attack (ferrite) averaged 5, 7 and 4 µm after 8,766 h for 1.4571, 1.4970 and 316L steels, respectively;

❑ Depth of pit-type attack average 50, 114 and 136 µm correspondingly. The percentage of circumference affected by selective leaching increases with time and after 8,766 h reached 100 %.

550°C:

❑ Metal recession averaged ~ 60, 46 and 51 µm after 2011 h for 1.4571, 1.4970 and 316L steels, respectively;

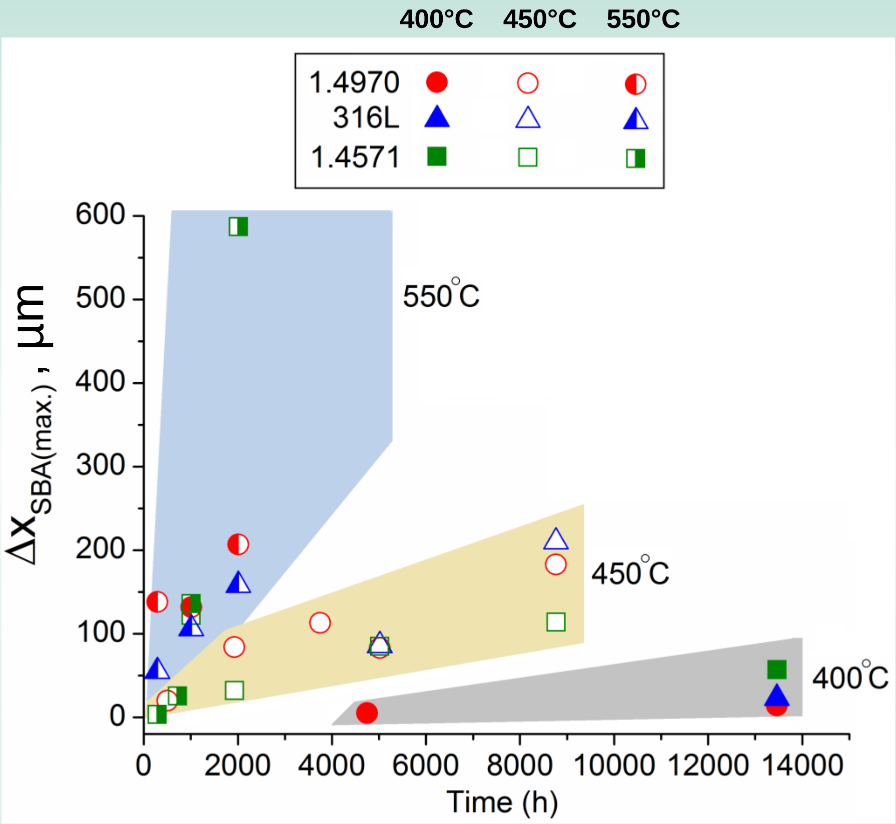
❑ Layer-type attack averaged 23, 30 and 46 µm;

❑ Depth of pit-type attack averaged 182, 124 and 127 µm.

Maximum depth of solution-based attack, seems to most adequately reflect corrosion losses of austenitic steels and therefore could be used as parameter for evaluation of corrosion rates using linear kinetics!

Corrosion behaviour of austenitic steels at 400, 450 and 550°C in flowing LBE (~ 2 m/s) with 10^{-7} mass% dissolved oxygen

Maximum depth of solution-based corrosion attack observed ($\Delta X_{SBA(max)}$)



<u>Observed corrosion phenomena at:</u>

450 and 550°C:

- ✓ Oxidation – thin Cr-based oxide film;
- ✓ Solution-based corrosion attack – ferrite layer;

In-situ formed oxide film is not a sufficient protective barrier against solution-based corrosion attack at 450 and 550°C.

400°C:

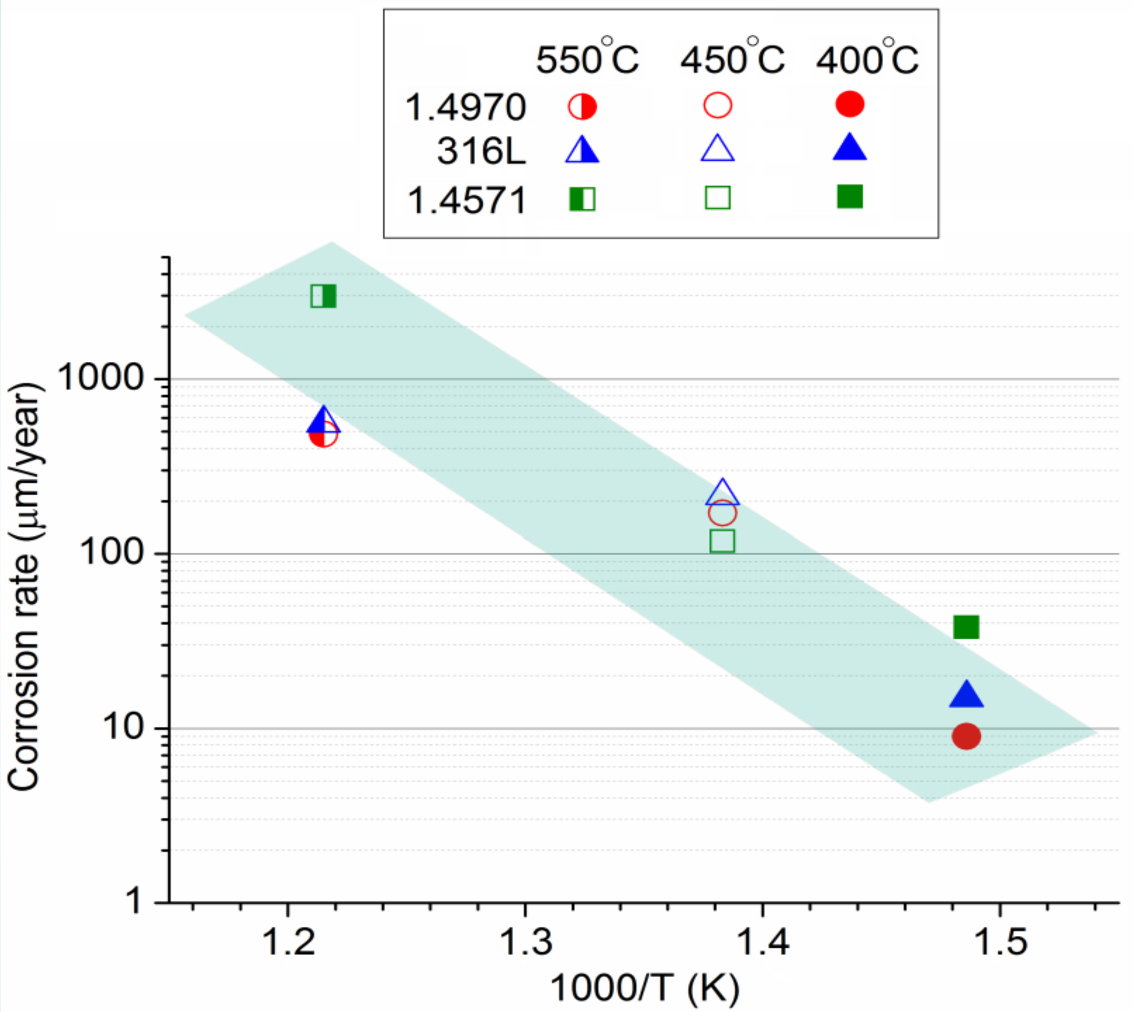
- ✓ Oxidation – thin Cr-based oxide film;
- ✓ Rare local pit-type solution-based corrosion attack;
- ✓ In-situ formed oxide film protects steels against solution-based attack at 400°C.

<u>Maximum corrosion loss</u>:

- ✓ 400°C: 15-60 µm after ~13000 h;
- ✓ 450°C: 120-220 µm after ~9000 h;
- ✓ 550°C: 150-600 µm after ~2000 h.

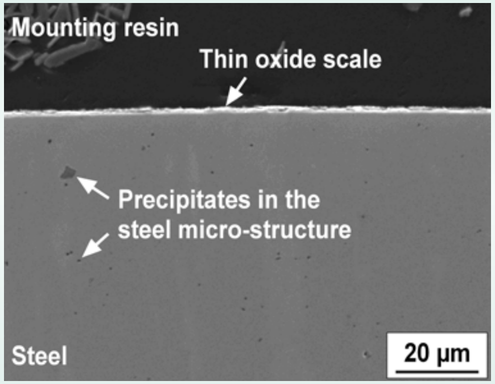
Incubation time required for initiation of solution-based attack decreases with increasing temperature from about 4500 h at 400°C to ~500 – 4000 h at 450°C and to ≤ 200 h at 550°C.

Corrosion rates of 1.4970, 316L and 1.4571 at 10^{-7} mass% oxygen at 400, 450 and 550°C

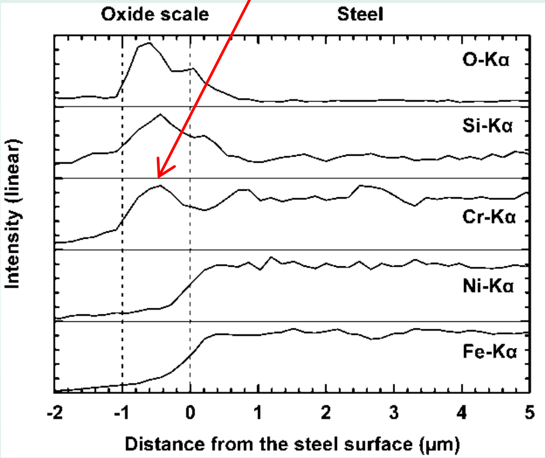


Corrosion behaviour of austenitic steel 1.4571 at 550°C in flowing LBE (~ 2 m/s) with 10^{-6} mass% dissolved oxygen

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



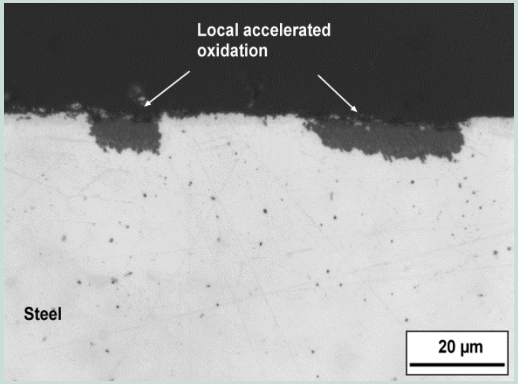
chromium enrichmernt



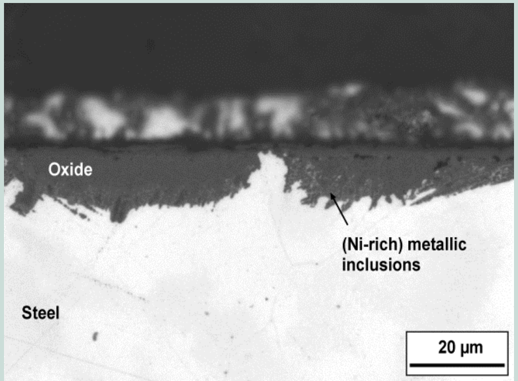
Corrosion behaviour of austenitic steel 1.4571 at 550°C in flowing LBE (~ 2 m/s) with 10^{-6} mass% dissolved oxygen

- **Accelerated oxidation**
  - Starts locally where the thin oxide scale lost integrity or did not form
  - Formation of $Fe(Fe_xCr_{1-x})_2O_4$, Fe_3O_4 and an internal oxidation zone; the latter two depending on oxygen content, temperature (or flow velocity)
  - The thicker scale spreads on the steel surface with time and becomes partially continuous
  - Varying c_O (mostly lower than 10^{-6} mass%) seems to promote accelerated oxidation

1.4571 specimens in the test-sections of the loop:



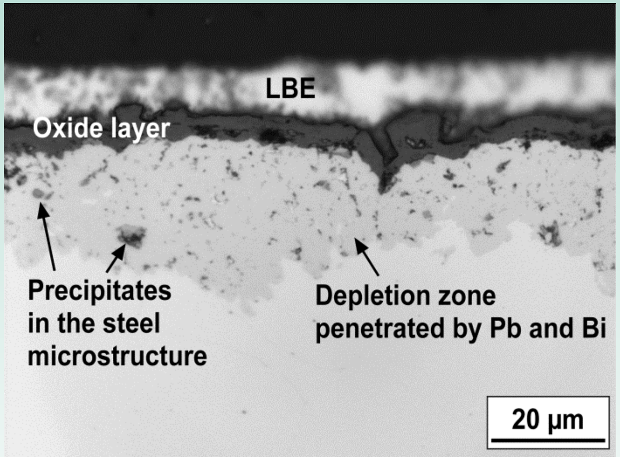
After exposure for 3,495 h at 550°C and $c_O \approx 10^{-6}$ mass%



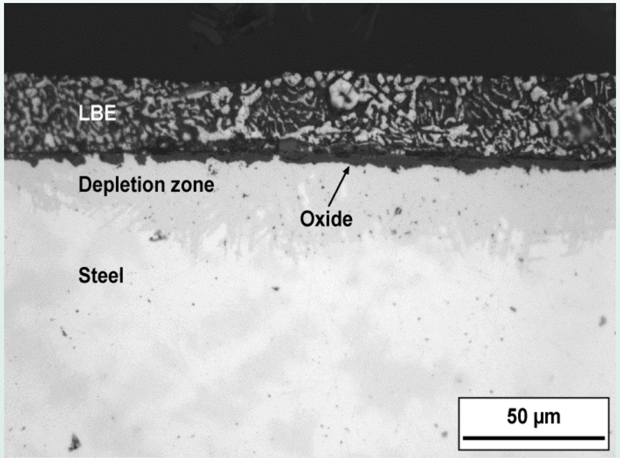
After exposure for 10,006 h at 550°C and variying c_O

Corrosion behaviour of austenitic steel 1.4571 at 550°C in flowing LBE (~ 2 m/s) with 10^{-6} mass% dissolved oxygen

- **"Mixed mode"**
  - Depletion zone penetrated by Pb and Bi underneath an oxide scale
  - Oxide is Cr-rich in comparison to the Fe $(Fe_xCr_{1-x})_2O_4$ layer formed by accelerated oxidation
  - Result of the transition from non-selective leaching to oxidation (?)
  - Formation of Cr-rich oxide scale can stop non-selective leaching (?)



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

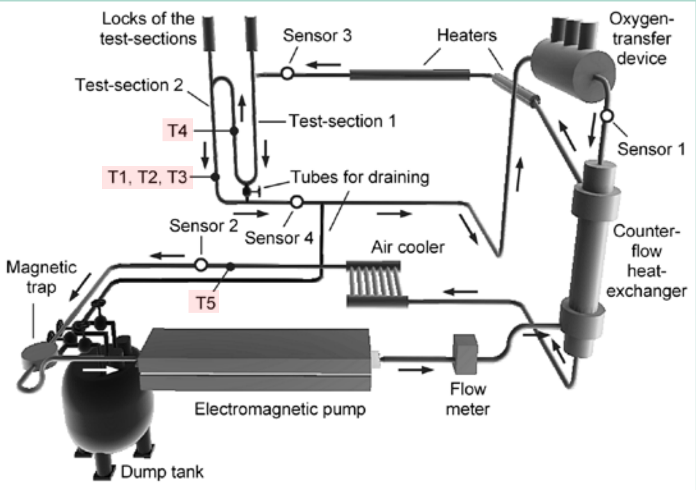


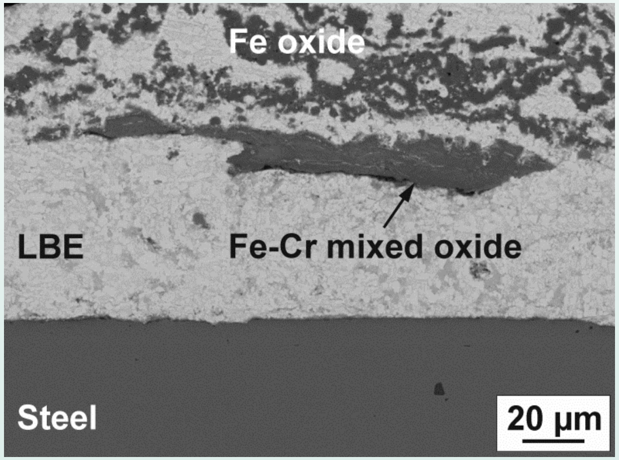
- Typical scale observed for some of the tube samples from the CORRIDA loop

1.4571 specimen exposed in the test sections after 3,495 h at 550°C and $c_O \approx 10^{-6}$ mass%

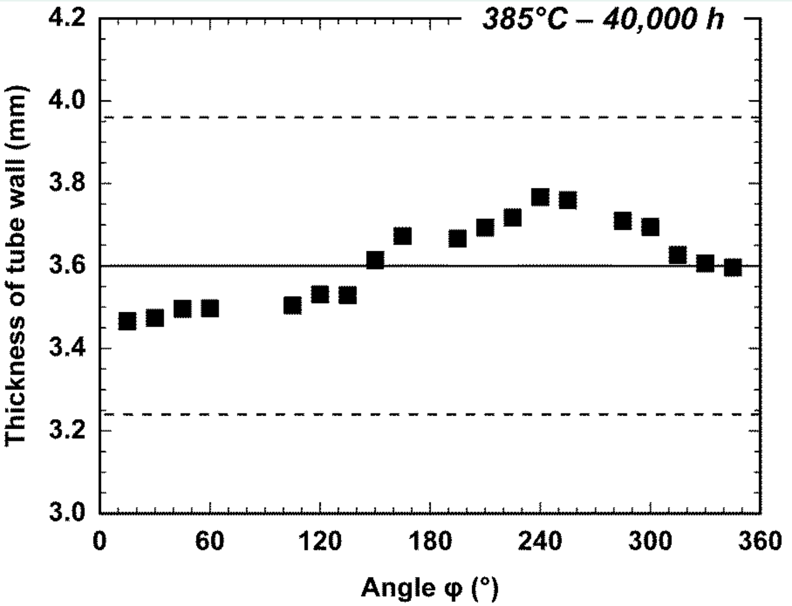
Performance of the tubing of CORRIDA loop
(10^{-6} mass% O)

- **Tube sample T5 after 40,000 h at 385°C**
  - Position after the cooler, before magnetic trap
  - No significant change in wall thickness after the long-term exposure
  - Oxide deposits in adherent solidified LBE, but only in some distance from the tube wall
  - Neither deposits nor significant amounts of oxide on the surface





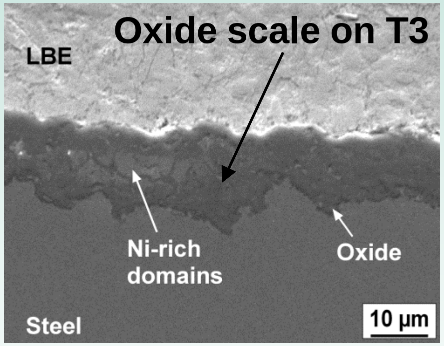
Electron-optical micrograph (BSE)

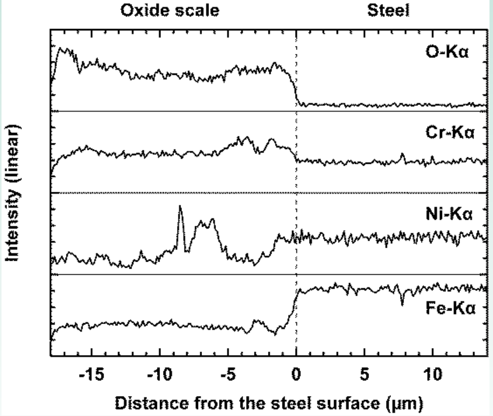


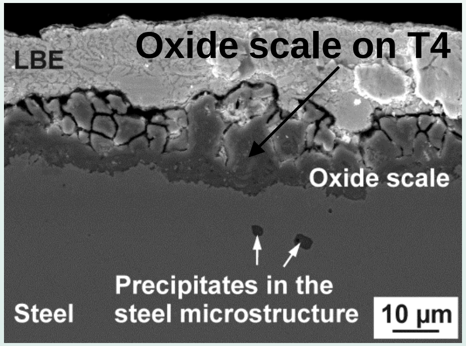
Performance of the tubing of CORRIDA loop

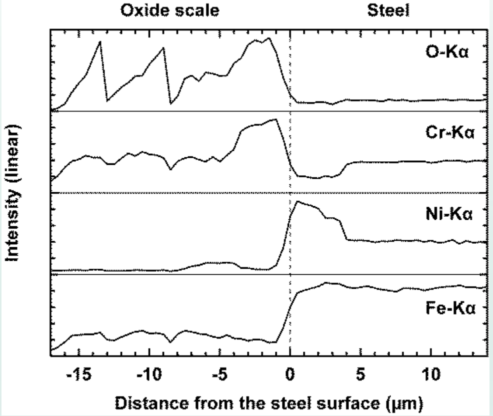
(10^{-6} mass% O)

- **Corrosion scales formed in the hot leg (550 °C)**
  - T3 (6000 h) and T4 (40,000 h) mainly show oxidation; T3 was not pre-oxidised
  - T1 (23,000 h) and T2 (29,000 h) show significant selective leaching

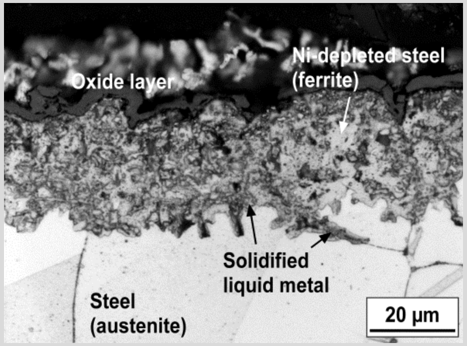


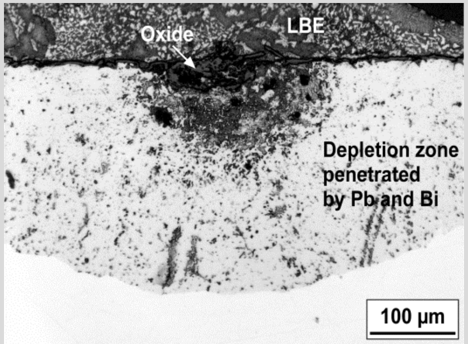




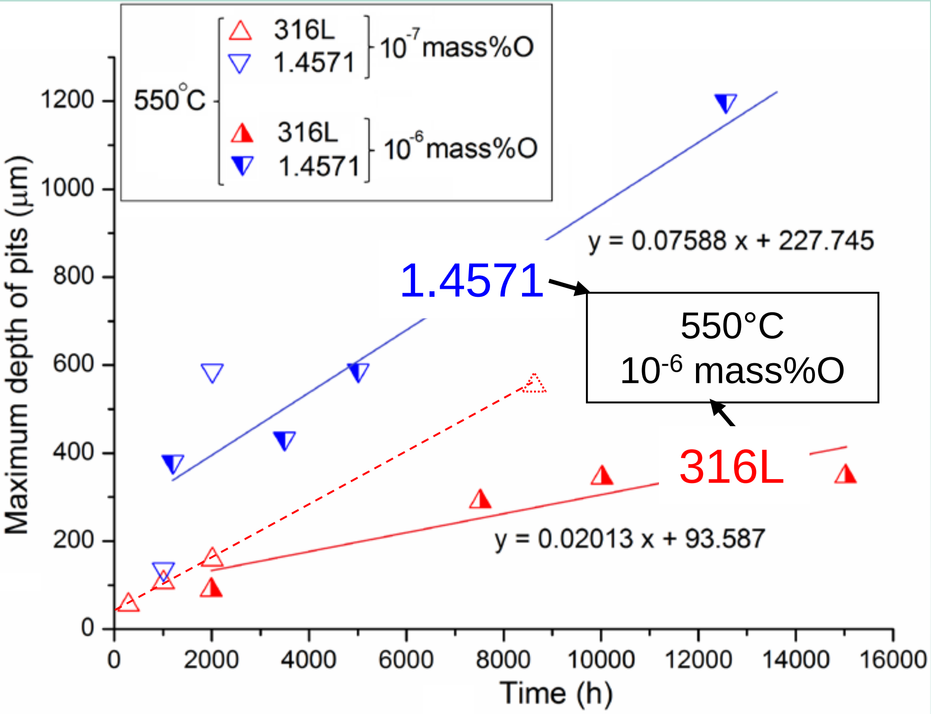


Corrosion scales typically observed on T1 and T2





Comparison of results at 10^{-7} and 10^{-6} mass% O (CORRIDA experiments)



Maximum depth of pit-type corrosion attack on austenitic steels tested in flowing LBE (~ 2 m/s) depending on temperature and oxygen concentration

- ❑ 10^{-6} mass% O – preferential oxidation (spinel formation);
- ❑ 10^{-7} mass% O – preferential solution-based selective leaching of steel constituents (Ni, Cr);
- ❑ At both concentrations the **local solution-based attack - critical factor** affecting corrosion resistance of austenitic steels in LBE;
- ❑ Incubation time for initiation of dissolution attack decreases with decreasing oxygen concentration in LBE from 10^{-7} to 10^{-6} mass%O;
- ❑ Under the similar test conditions, the finer the grain size (1.4571: 15 µm blue markers) the deeper the corrosion attack (316L: 50 µm red markers).

Conclusions

- Interaction of austenitic steels with flowing LBE with 10^{-7} mass % O was accompanied by **oxidation** and **solution-based attack,** resulted in **non-selective leaching of Ni and Cr** from the sub-oxide layers and subsequent development of ferrite zone, penetrated by LBE:
  - **<u>400°C</u>: Oxidation –** thin Cr-based oxide film (**protective scaling)**
  - **<u>450°C</u>**: **Oxidation –** thin (≤ 0.5 µm) Cr-based oxide film and **solution-based non-selective leaching** with maximum depth of local attack between 114µm and 210µm after 8,766h
  - **<u>550°C</u>: Oxidation –** thin (≤ 0.5 µm) Cr-based oxide film and **solution-based non-selective leaching** with maximum depth of local attack between 158 µm and 587µm even after 2,011 h
- **<u>Cr-based oxide films</u>, formed *in-situ* on the surface of austenitic steels, <u>are not sufficient protective barriers</u> with respect to non-selective leaching, at least at 450 and 550°C in LBE with 10^{-7} mass% O!**
- In LBE with **10^{-7} mass%O, non-selective leaching** is the main corrosion mechanism of austenitic steels causing substantial corrosion loss, while at **10^{-6} mass% O, oxidation is dominating**