Compatibility of Structural Steels with Heavy Liquid Metals (HLMs) for Nuclear and Fusion Applications

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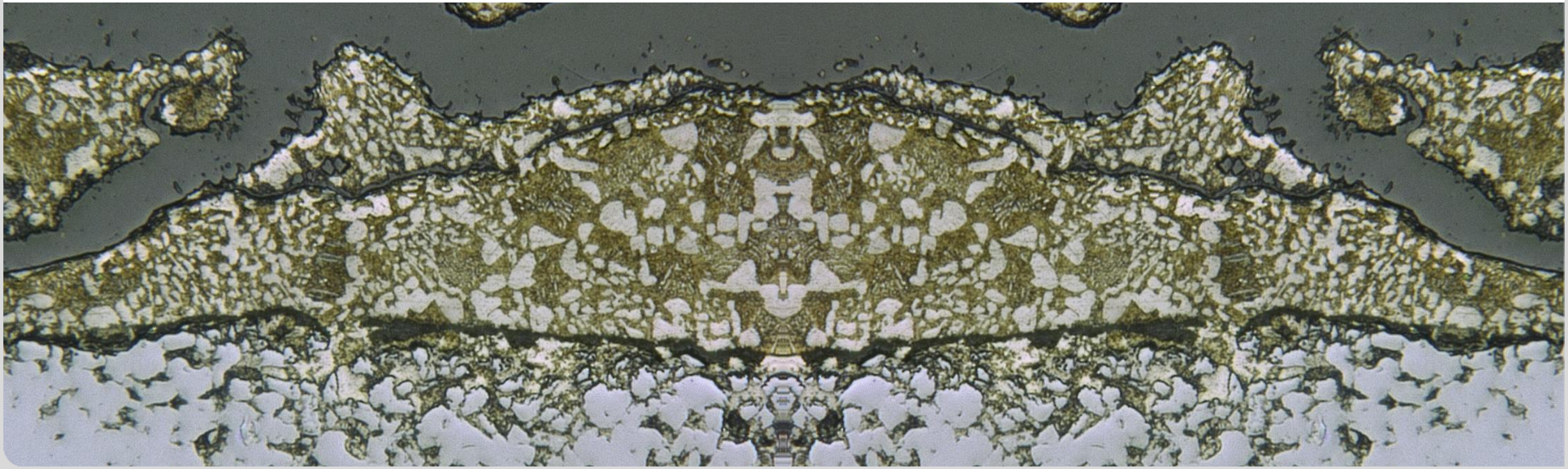

Outline

- HLMs for Nuclear and Fusion applications
- HLM chemistry: role of oxygen .....
- Corrosion of ferritic and austenitic steels in LBE
- Dependency on oxygen concentration
- Corrosion of RAFM-steels in Pb-16Li
- Conclusions

Some Specific Properties of Liquid Metals

		UNIT	$Pb^{45}Bi^{55}$	Pb-16Li	LITHIUM	WATER
Melting Point at 0.1 MPa		[°C]	125	235	180.5	0
Boiling Point at 0.1 MPa		[°C]	2516	-	1317	100
			300°C	**300°C**	**300°C**	**25°C**
Density	ρ	[kg/m^3]	10325	9988	505	1000
Heat Capacity	c_ρ	[J/(kgK)]	146.33	200.22	4279	4180
Kinematic Viscosity	ν	[m2/s] $\cdot 10^{-7}$	1.754	1.3	9	9.1
Heat Conductivity	λ	[W/(m K)]	12.68	45.2	29.2	0.6
Electric Conductivity	σ_{el}	[A/(V m)] $\cdot 10^5$	8.428	12.67	33.5	$2 \cdot 10^{-4}$ (tap)
Thermal Expansion Coefficient	α	[K^{-1}] $\cdot 10^{-6}$	6.7	41.2	43.6	6
Surface Tension	σ	[N/m] $\cdot 10^{-3}$	410	430	421	52 (tap)

Lead-cooled Nuclear Reactors/Systems

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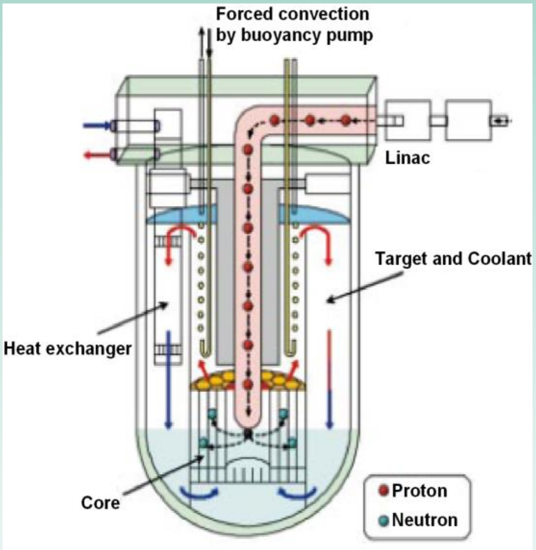
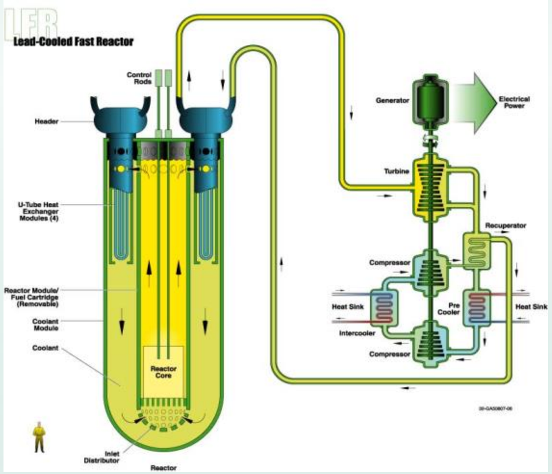


Accelerator Driven (Subcritical) System

- 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)

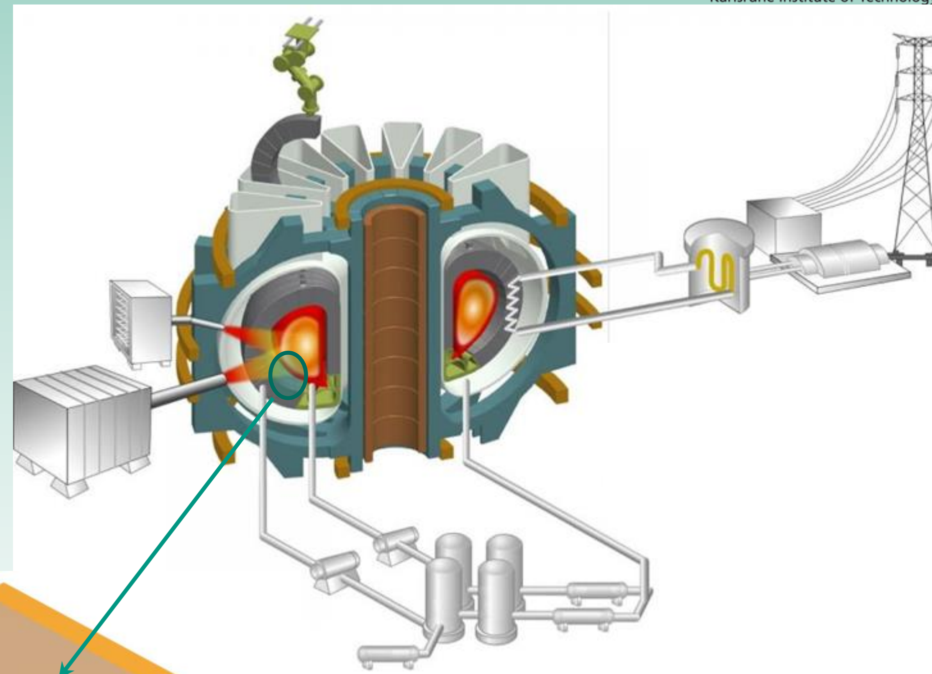
Lead-Cooled Fast Reactor

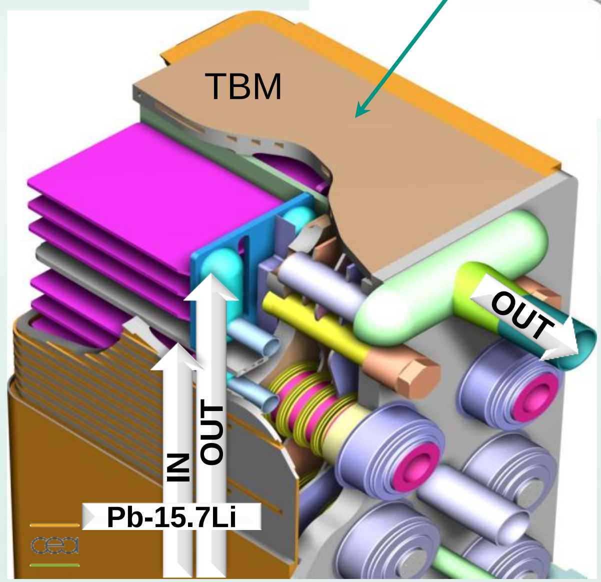
- One of the concepts for the 4th generation of nuclear power plants (Gen IV)
- In the long-term, Pb as primary coolant at maximum ca. 800°C
- Short- to mid-term: Pb- or LBE-cooled at 450 – 550°C



The HCLL (He-PbLi) TBM (and DEMO) Blanket

DEMO HCLL MAIN FEATURES
2m x 2m modules
RAFM steel (e.g. EUROFER)
He (8 MPa, 300-500°C)
Liquid Pb-16Li (eutectic) as breeder and multiplier
PbLi slowly re-circulating (10/50 rec/day)
90% ^{6}Li in PbLi Pb-Li velocities in breeding unit ~ 1 cm/s range
TBR = ≤1.15 with 550mm Breeder radial depth
Lifetime 7.5 MWy/m^{2}





Blanket for energy conversion

Heavy Liquid-metal – steel interactions

- **Corrosion**
  - Solution of steel elements with preferential (Ni, Cr) rather than general removal
  - Surface recession and/or development of a near-surface depletion zone
  - 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

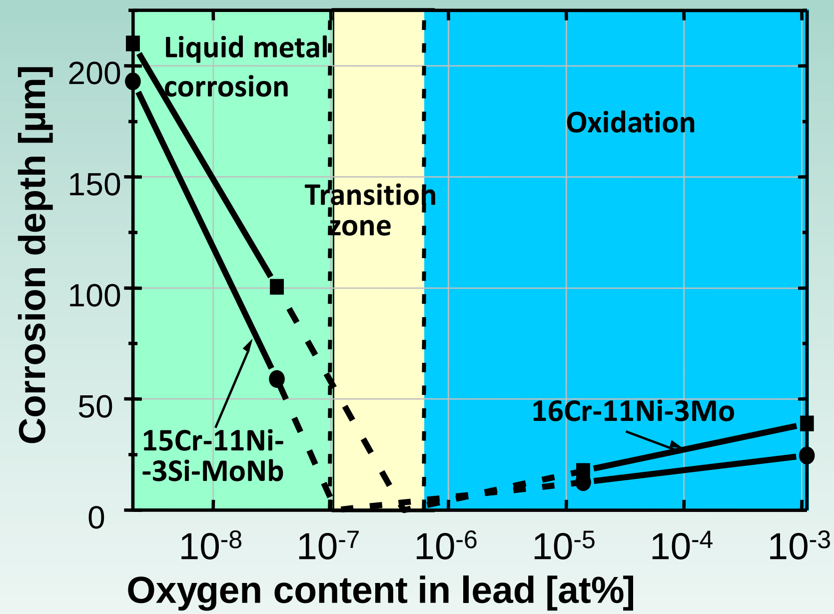
Observed on the µm-scale, accessible by light-optical microscopy (LOM), scanning-electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) …

- **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, …

Impact of oxygen on steel corrosion in HLMs

- **"Absence" of oxygen (Pb-16Li)**
  - 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



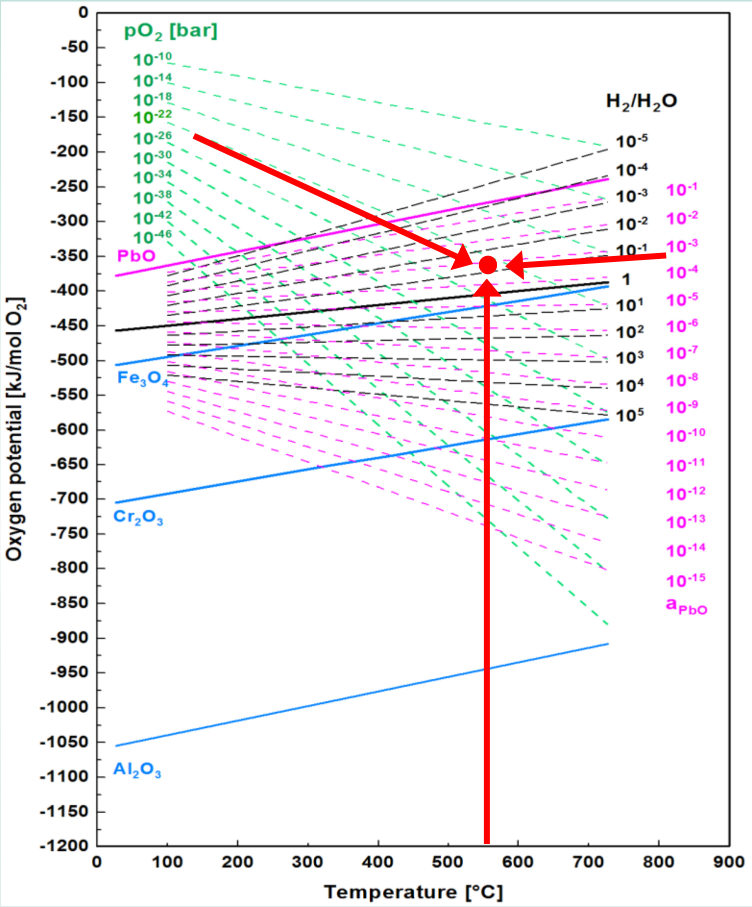
→ Transition from solution-based to oxidation-based corrosion with increasing oxygen concentration

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

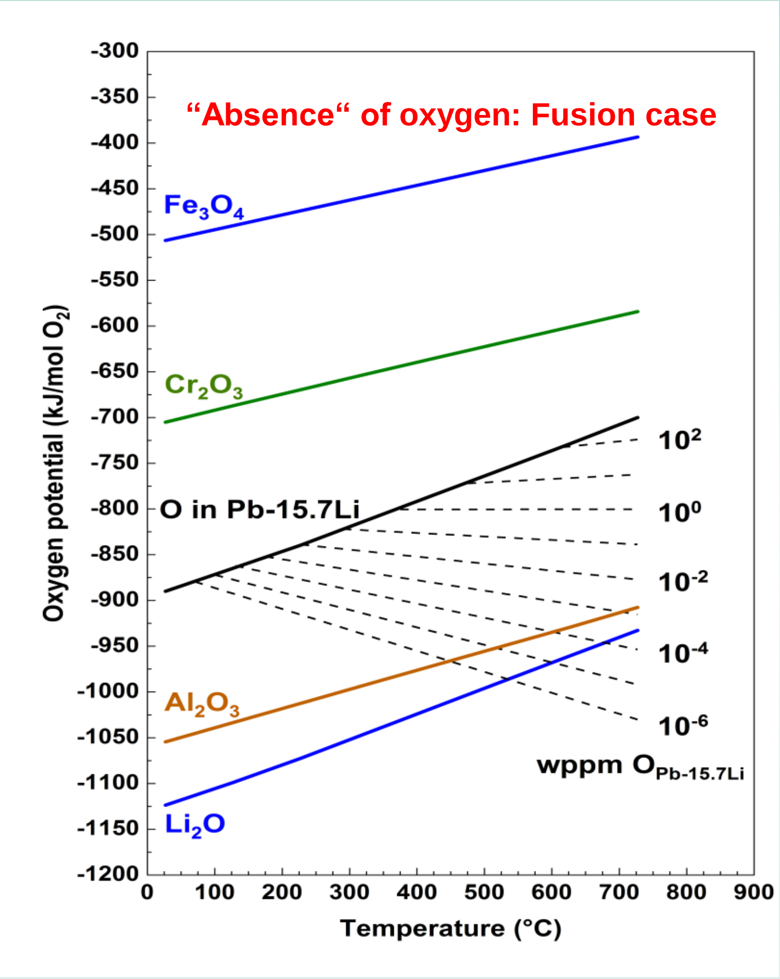
→ Locally low-oxygen conditions even when oxygen concentration in the bulk of the liquid metal is high

Oxygen Potentials of Metal/Metal-oxides, relevant for the Stability of Structural Materials in

Pb, LBE

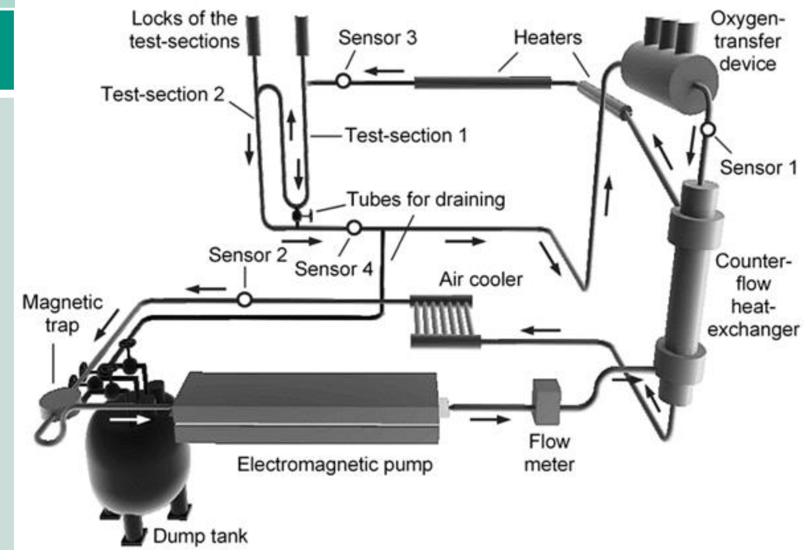


Pb-16 Li



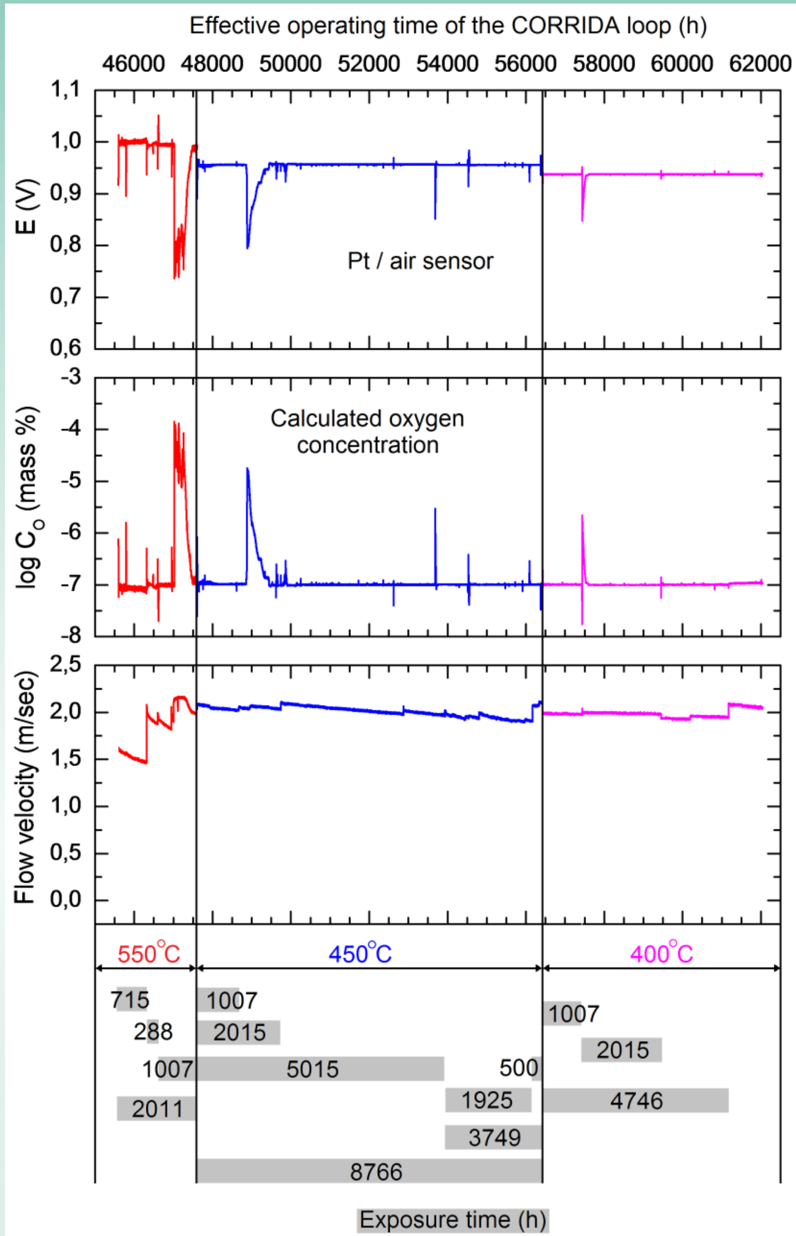
Corrosion testing in Pb or LBE for nuclear applications

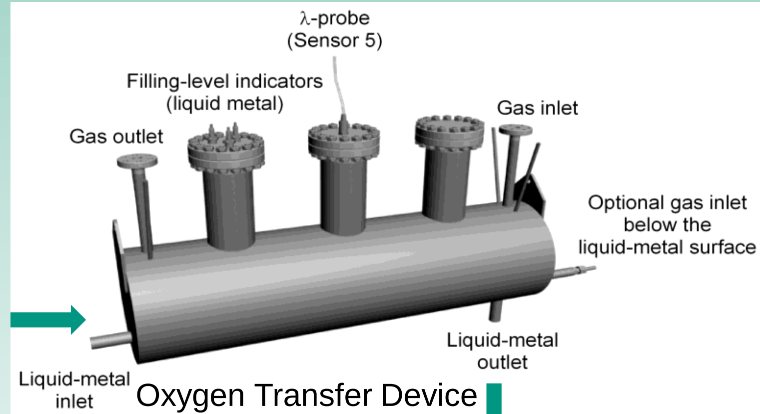
CORRIDA	
Testing characteristics	Exposure to flowing LBE, typically 2 m/s. 1000 kg circulating LBE (5.3 kg/s). Several steel samples simultaneously exposed in vertical test-sections. Oxygen control via gas with variable oxygen partial pressure. Large internal steel surface in contact with the liquid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





- **T = 550(+5)°C,**

  T_{min} ≈ 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} ≈ 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} ≈ 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

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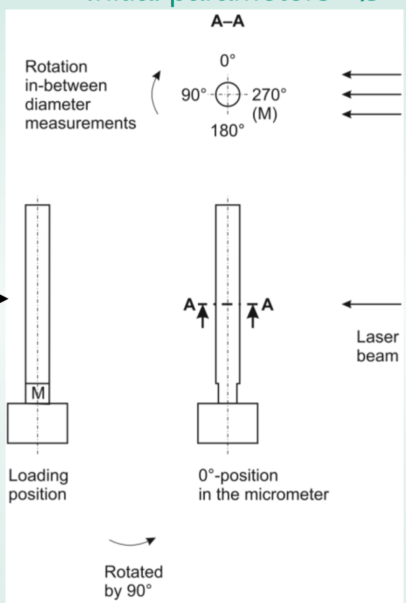
❑ Goal of quantification

- 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

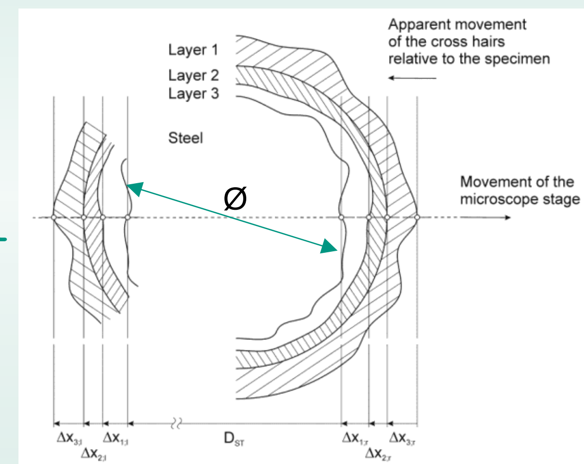
❑ Metallographic method (cylindrical specimens)

Initial parameters - Ø



- Measurement of <u>initial diameter</u> 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

9% Cr steels tested in CORRIDA loop for ADS and LFR applications

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Concentration (in mass%) of alloying elements other than Fe

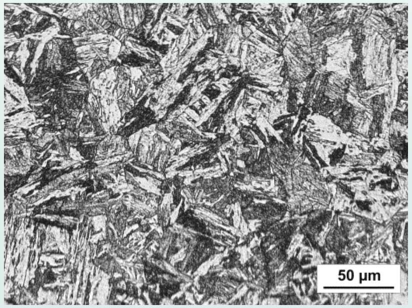
	Cr	Mo	W	V	Nb	Ta	Y	Mn	Ni	Si	C
T91-A	9.44	0.850	<0.003	0.196	0.072	n.a.	n.a.	0.588	0.100	0.272	0.075
T91-B	8.99	0.89	0.01	0.21	0.06	n.a.	n.a.	0.38	0.11	0.22	0.1025
E911*	8.50–9.50	0.90–1.10	0.90–1.10	0.18–0.25	0.060–0.100	–	–	0.30–0.60	0.10–0.40	0.10–0.50	0.09–0.13
EUROFER	8.82	<0.0010	1.09	0.20	n.a.	0.13	n.a.	0.47	0.020	0.040	0.11
EF-ODS-A	9.40	0.0040	1.10	0.185	n.a.	0.08	0.297†	0.418	0.0670	0.115	0.072
EF-ODS-B	8.92	0.0037	1.11	0.185	n.a.	0.078	0.192†	0.408	0.0544	0.111	0.067

* Nominal composition
† In the form of yttria (Y_2O_3)

Nominally 9 mass% Cr

Elements besides Cr that are likely to improve oxidation performance

Microstructure

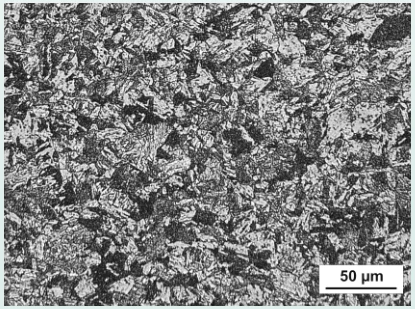


Fully martensitic: E911, T91-A

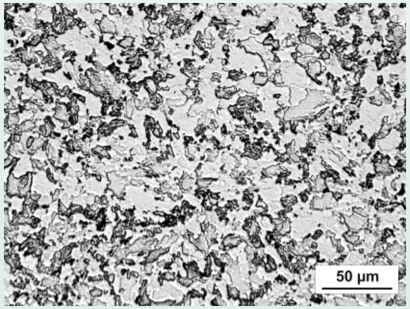
T91-B

Grain size

EUROFER



Mainly ferritic: ODS-A, ODS-B



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

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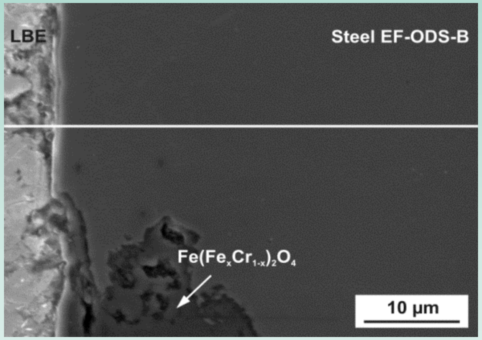
- **Protective scaling**
  - Thin Cr- (Si-) rich oxide scale (thickness ~1 µm or less)
  - Promoted by high Cr content, fine-grained structure, dispersed Y_2O_3 …
  - Favourable situation with respect to minimum material loss, but generally not of long duration (locally)

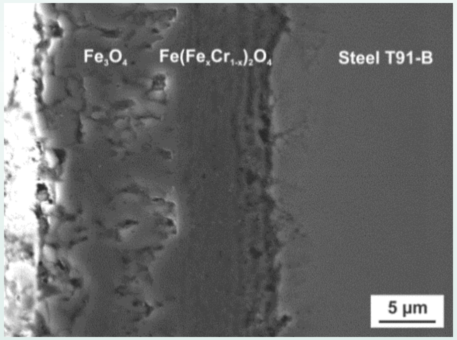


550°C

Scale failure at high local c_O (?)

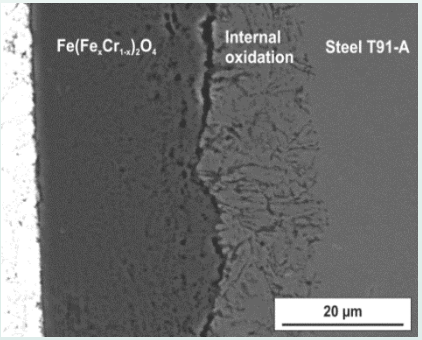
Scale failure at low local c_O (?)

- **Accelerated oxidation**



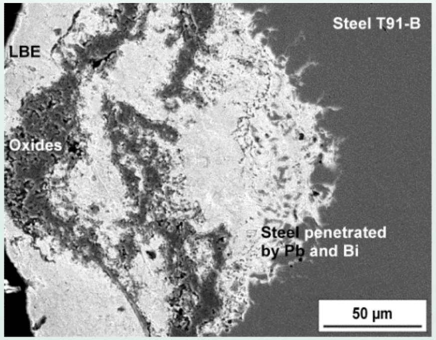
450°C

  - Typical and, finally, the general corrosion process for 9% Cr steel



550°C

- **Solution-based corrosion**
  - Steel elements first dissolve but may re-precipitate in the form of oxides
  - Intermittent solution participates in accelerated oxidation processes or solution outweighs oxidation



550°C

Flowing LBE at 550°C, 2 m/s and 10^{-7} mass% dissolved oxygen

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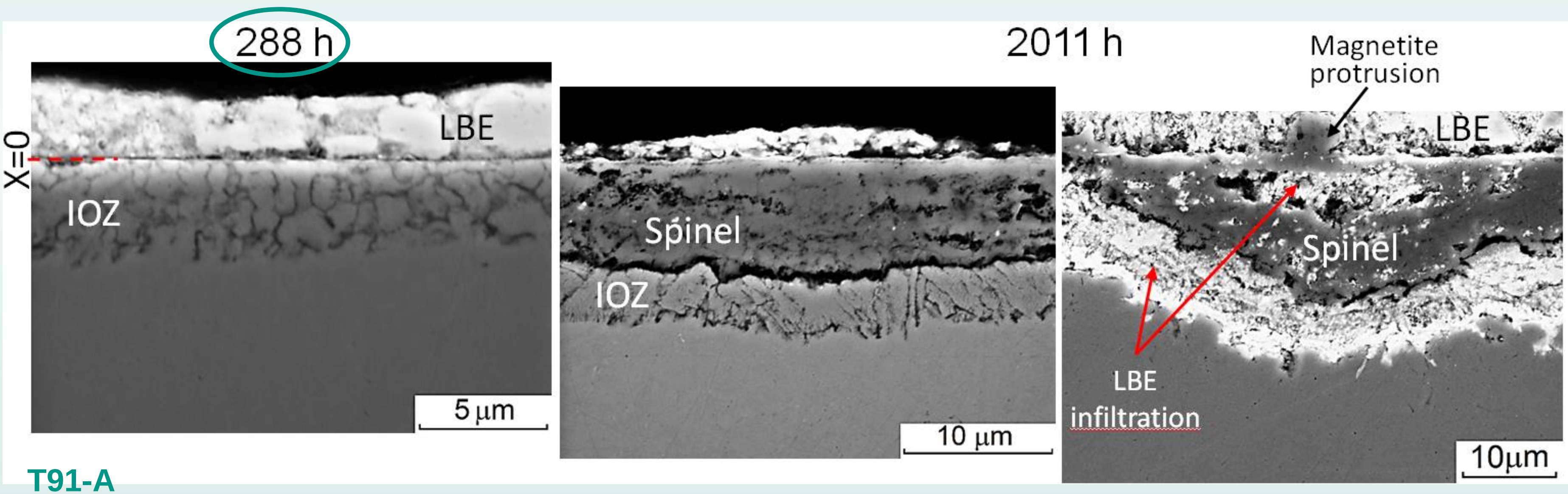
- **Accelerated oxidation**
  - Starts with internal oxidation
  - Spinel formation follows internal oxidation
  - Consumes outer part of the internal oxidation zone (IOZ) that may still grow at the IOZ/steel interface
  - General aspect of accelerated oxidation at 550°C, not only at low oxygen concentration of the LBE

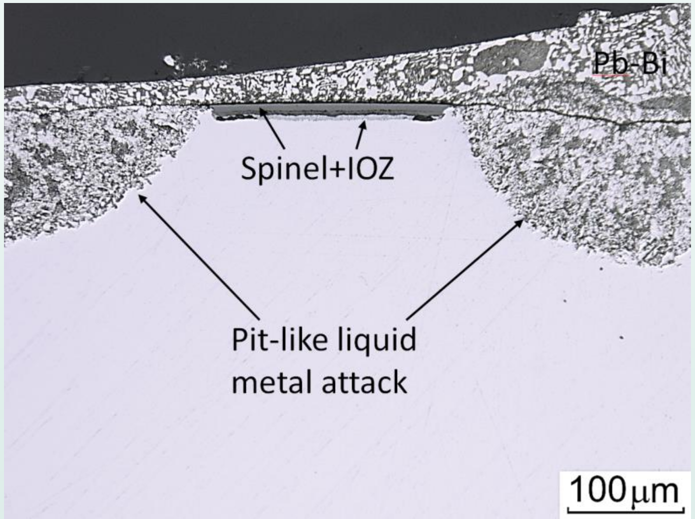
- Outer magnetite layer is missing
- Some magnetite protrusions after excursion to higher c_O
- Corresponds to previous observations at 550°C/10^{-6} mass% O
- Fe dissolves at the spinel surface rather than forming magnetite



T91-A

Flowing LBE at 550°C, 2 m/s and 10^{-7} mass% dissolved oxygen

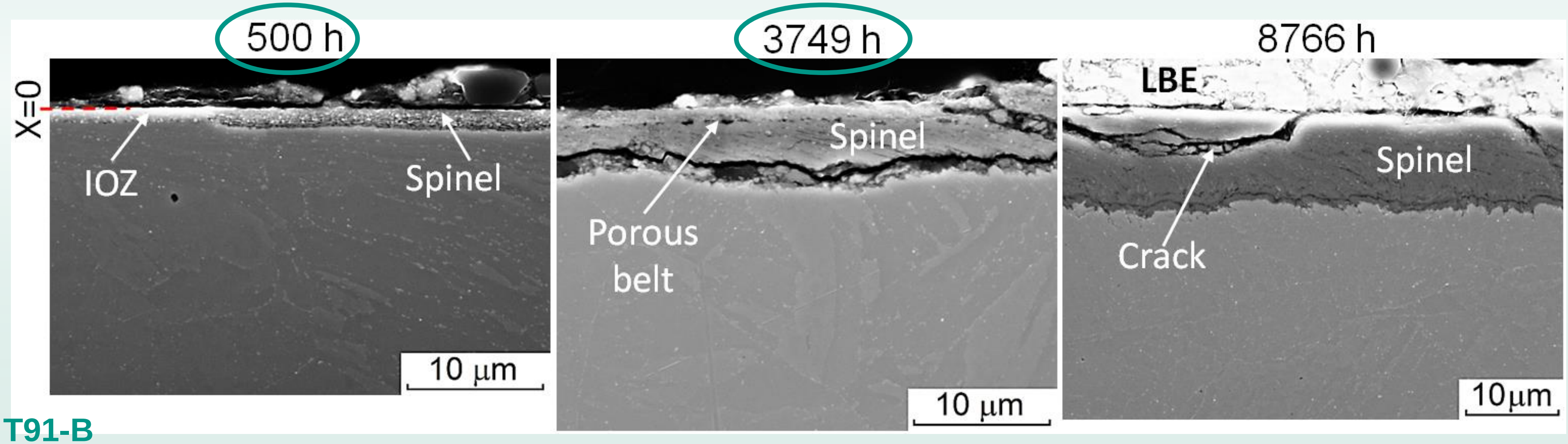
- **Solution-based corrosion**
  - Typically, affected site has pit-shape appearance
  - Non-selective dissolution of steel elements rather than selective leaching (Cr)
  - Either spinel layer or thin Cr-rich scale is present
  - Appears after failure of the thicker oxide scale formed after accelerated oxidation
  - Also, alternatively to accelerated oxidation after failure of the thin protective oxide



T91-A after exposure for 1007 h with temporary increase in c_O after ~450 h

Flowing LBE at 450°C, 2 m/s and 10^{-7} mass% dissolved oxygen

- **Accelerated oxidation**
  - Internal oxidation less pronounced than at 550°C
  - In general, only spinel layer observed
  - Pores in the outer part due to Fe diffusion towards the spinel surface
  - No magnetite at constantly 10^{-7} mass% O
  - Threshold oxygen concentration for magnetite formation between 10^{-7} and 10^{-6} mass% O at 450°C

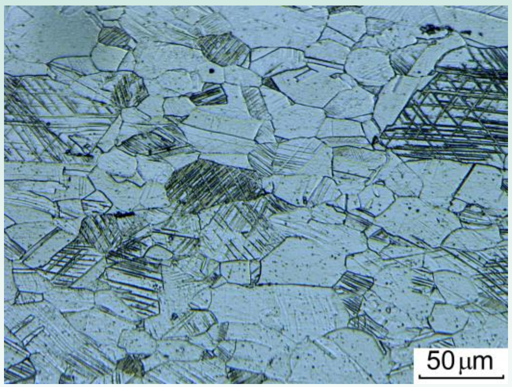


T91-B

Austenitic Cr Ni steels tested in CORRIDA loop

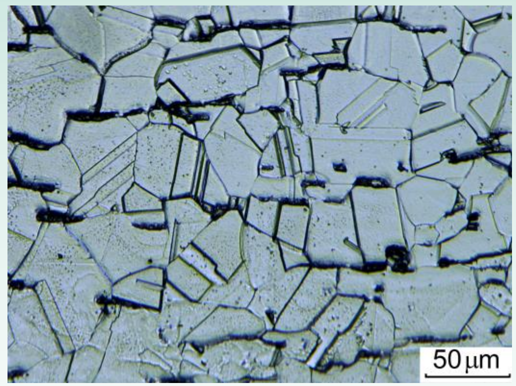
Austenitic steels	Cr	Ni	Mo	Mn	Si	Cu	V	W	Al	Ti	C	N	P	S	B
316L	16.73	9.97	2.05	1.81	0.67	0.23	0.07	0.02	0.018	-	0.019	0.029	0.032	0.0035	-
1.4970	15.95	15.4	1.2	1.49	0.52	0.026	0.036	< 0.005	0.023	0.44	0.1	0.009	< 0.01	0.0036	< 0.01
1.4571 (316-Ti)	17.50	12	2.0	2.0	1.0	-	-	-	-	0.70	0.08	-	0.045	0.015	-

1.4970 (15-15Ti)



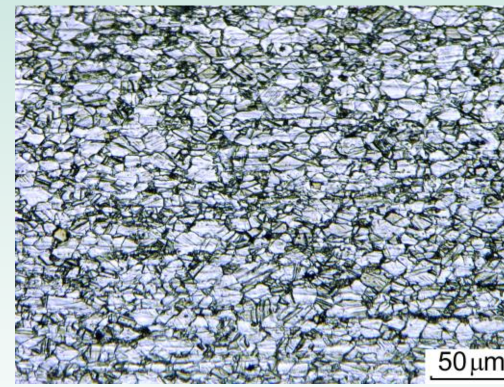
- HV_{30} = 253;
- Grain size ranged from 20 to 65 µm;
- Intersecting deformation twins.

316L



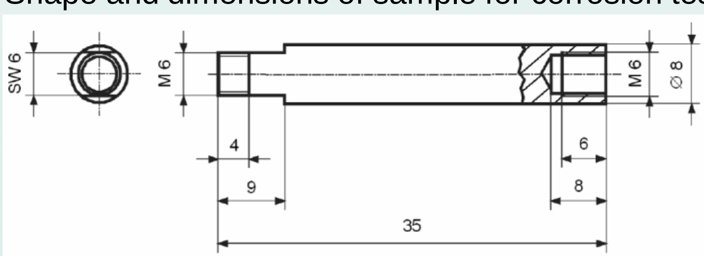
- HV_{30} = 132;
- Grain size averaged 50 µm (G 5.5);
- Annealing twins.

1.4571

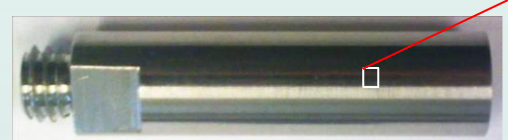


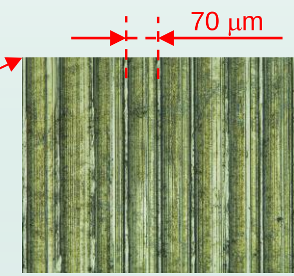
- HV_{30} = 245;
- Grain size averaged 15 µm (G 9.5).

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 between 400 and 550°C

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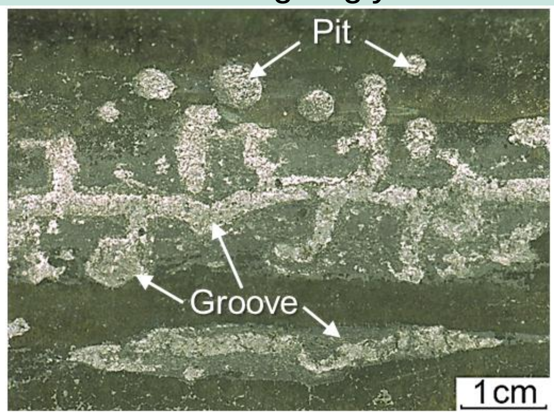
Surface examinations - general corrosion appearance

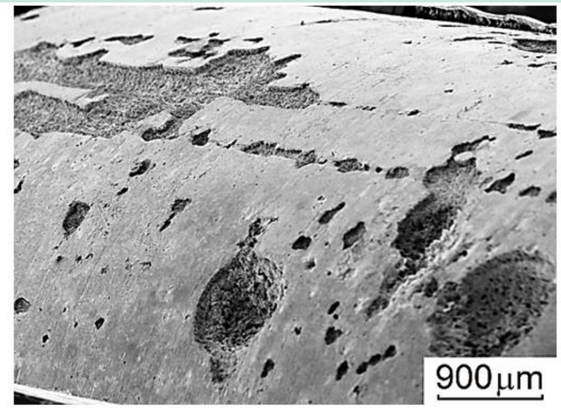
1.4970, 550°C

After cleaning in glycerin



1007 h

After chemical cleaning

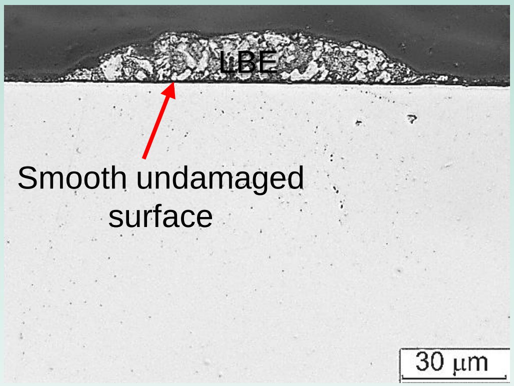


2011 h

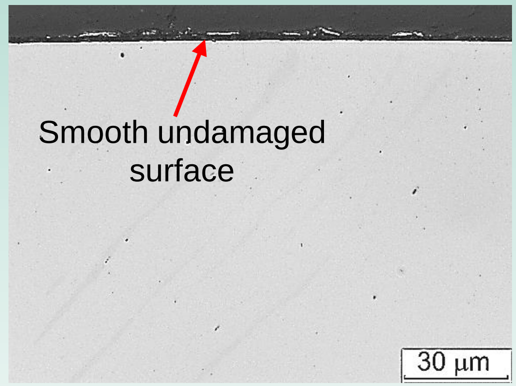
- ❑ Oxidation – formation of golden-colored oxide film (shorter test) and green-colored oxide film (longer test)
- ❑ Light areas with exfoliated oxide film;
- ❑ Severe local solution-based corrosion attack in the form of hemispherical pits and longitudinal and transversal grooves;
- ❑ The surface area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

Cross-section appearance of austenitic steels after test in flowing oxygen-containing LBE (~ 2 m/s, ~ 10^{-7} mass % O) at 400°C for 4746 h.

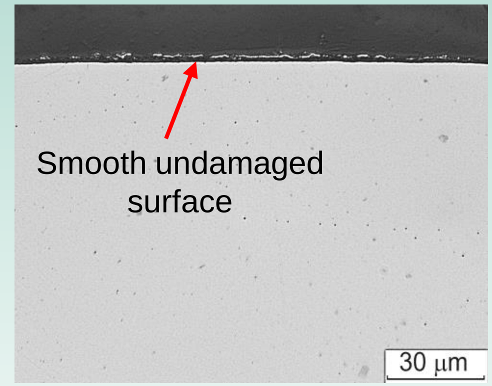
1.4970



316L

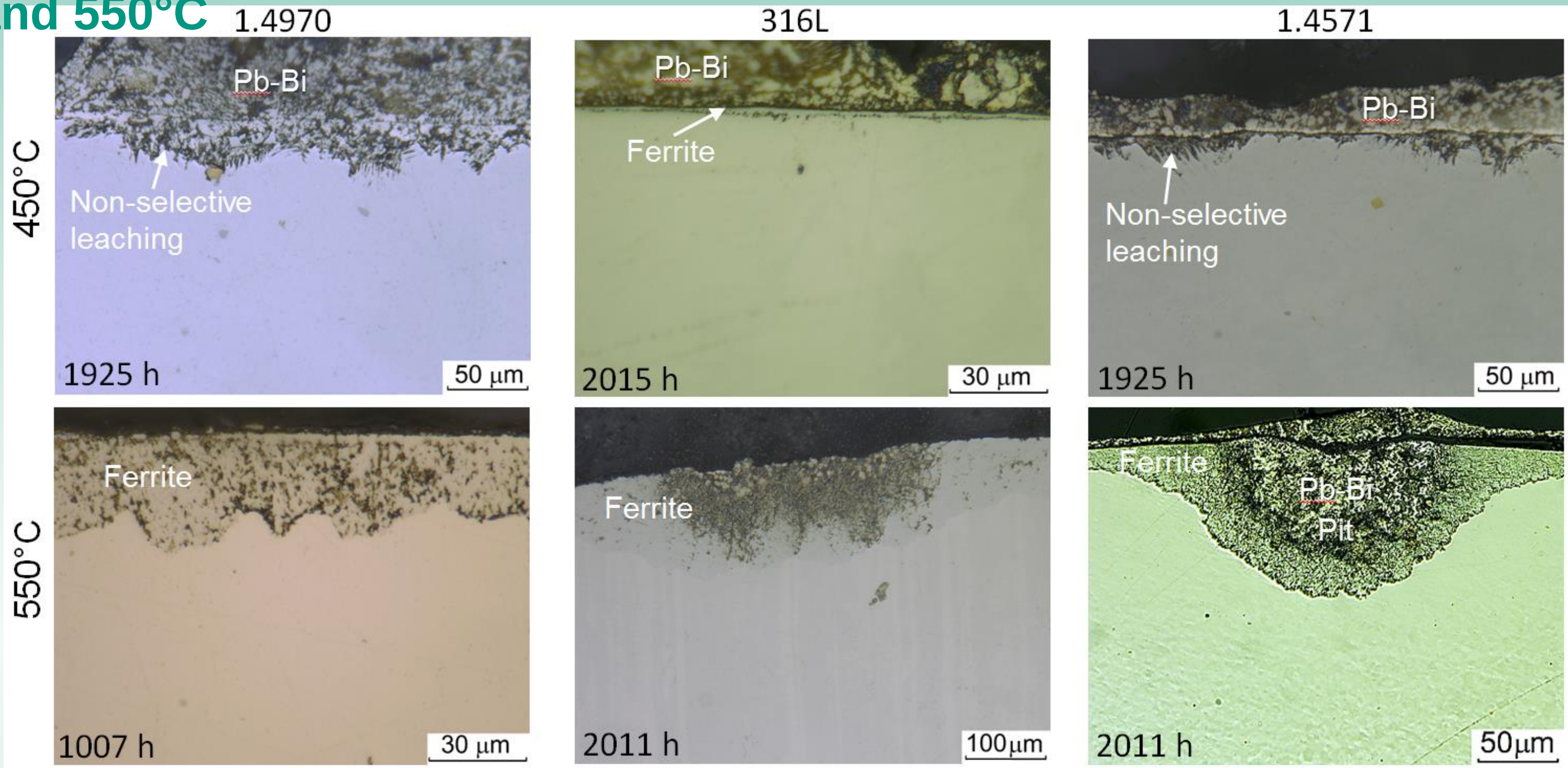


1.4571



- 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.

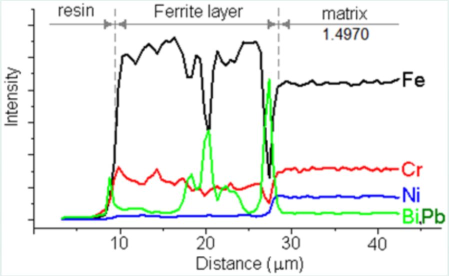
Cross-section appearance of austenitic steels in flowing oxygen-containing LBE (~ 2 m/s, ~ 10^{-7} mass % O) at 450 and 550°C



1.4970

550°C

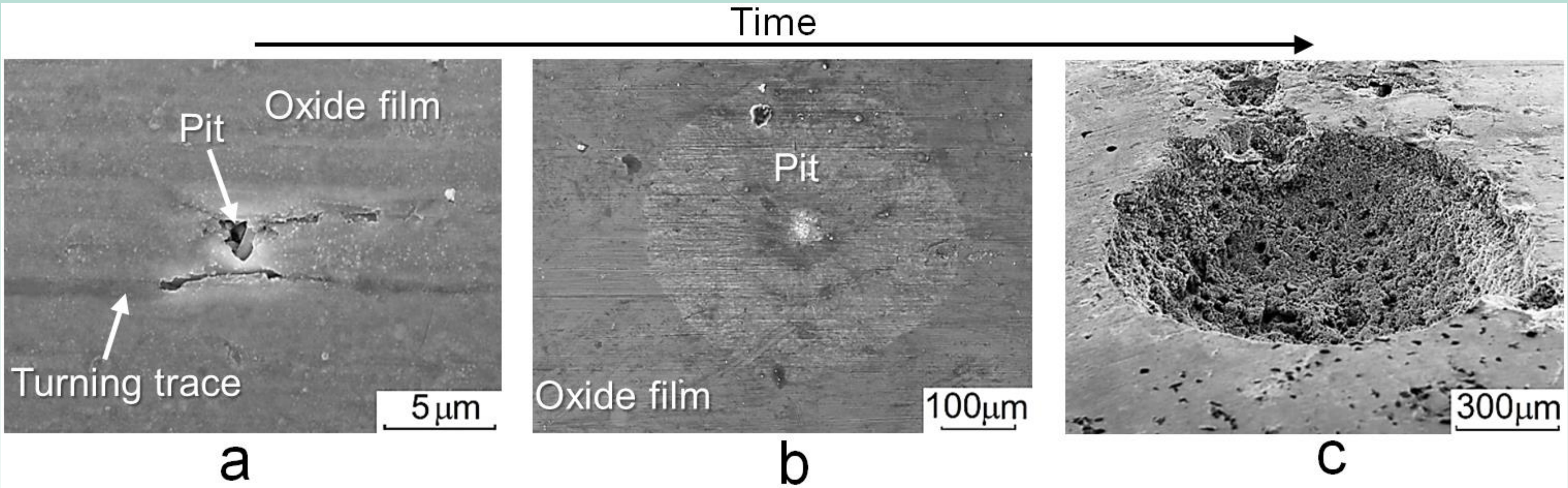
2011 h



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

Local pit-type corrosion attack

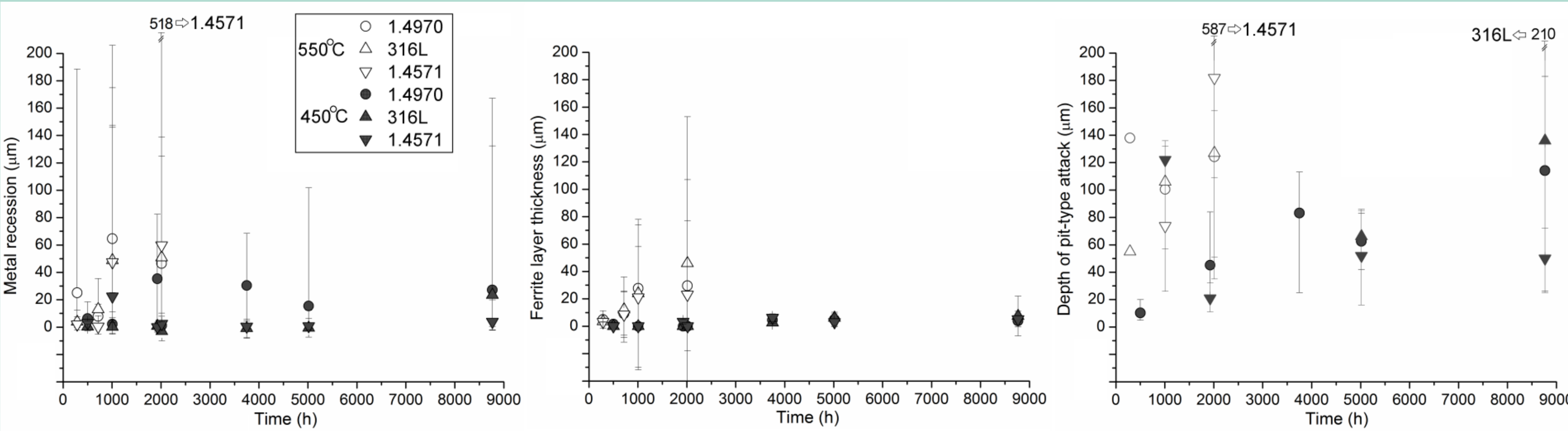
Expected sequence of evolution of corrosion pits wit time



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 (c)	13.95	8.90	29.62	0.97	5.87	40.49

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

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 %.

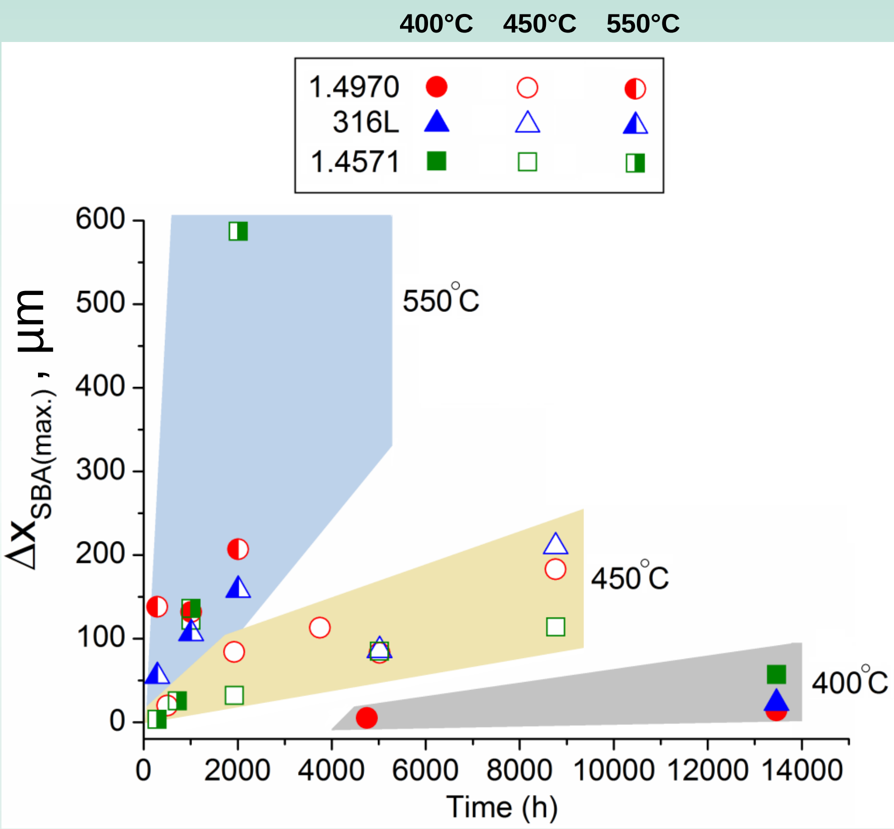
550°C:

- ❑ 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 ($\Delta X_{SBA(max)}$)



Observed corrosion phenomena at:

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.

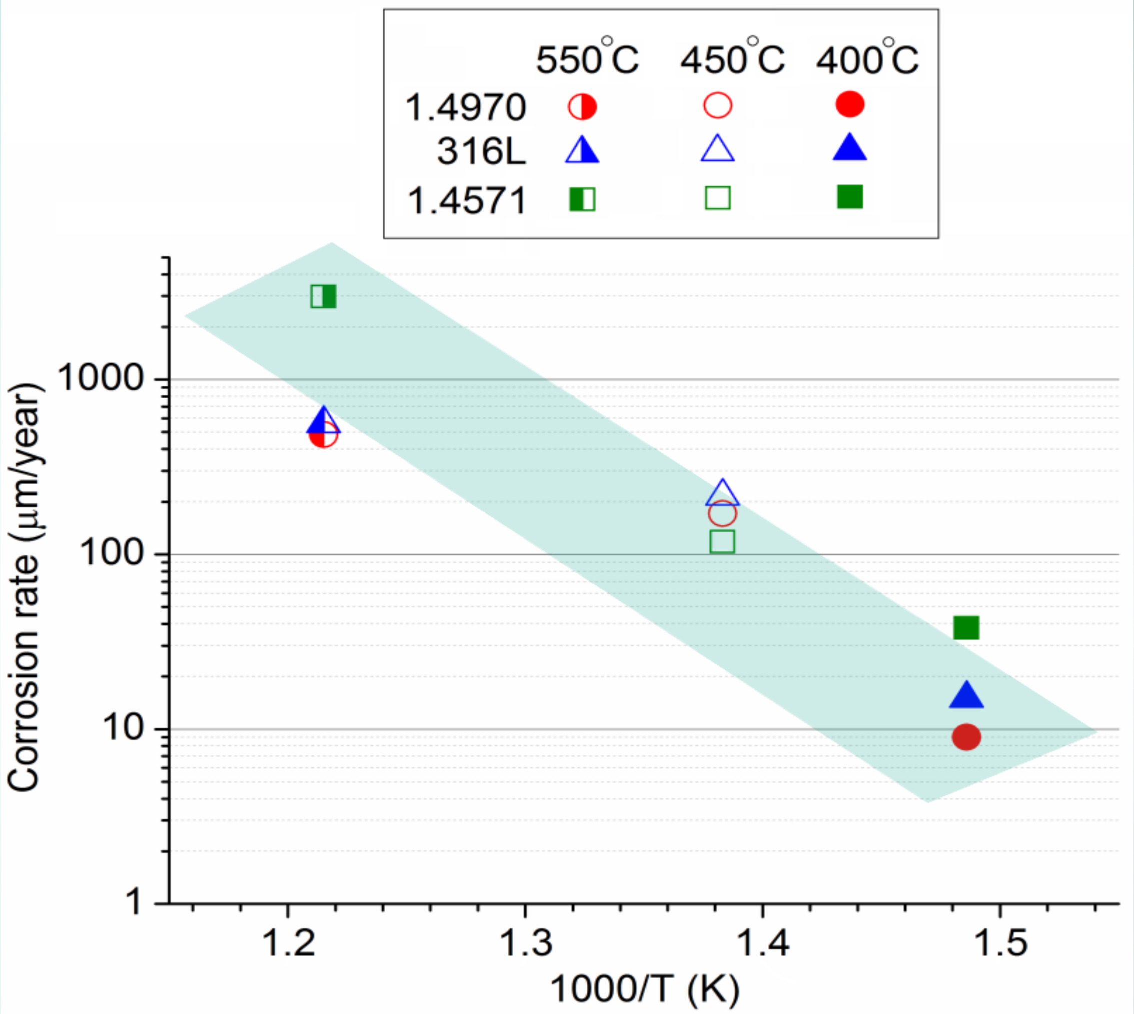
400°C:
- ✓ Oxidation – thin Cr-based oxide film;
- ✓ Rare local pit-type solution-based corrosion attack;
- ✓ In-situ formed oxide film protects steels against solution-based attack at 400°C.

Maximum corrosion loss:

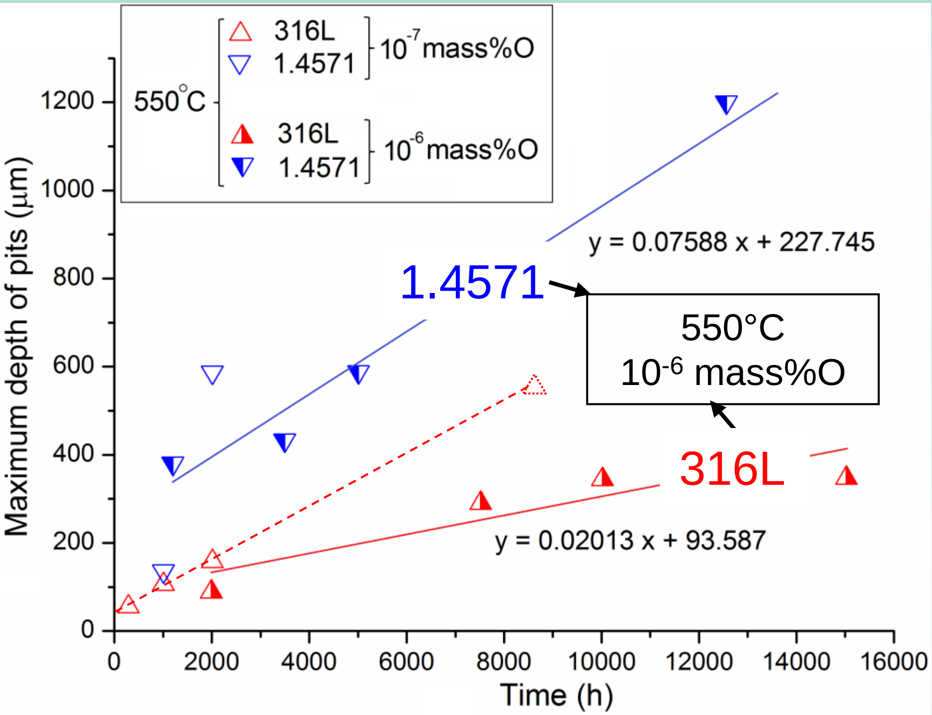
- ✓ 400°C: 15-60 µm after ~13000 h;
- ✓ 450°C: 120-220 µm after ~9000 h;
- ✓ 550°C: 150-600 µm after ~2000 h.

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



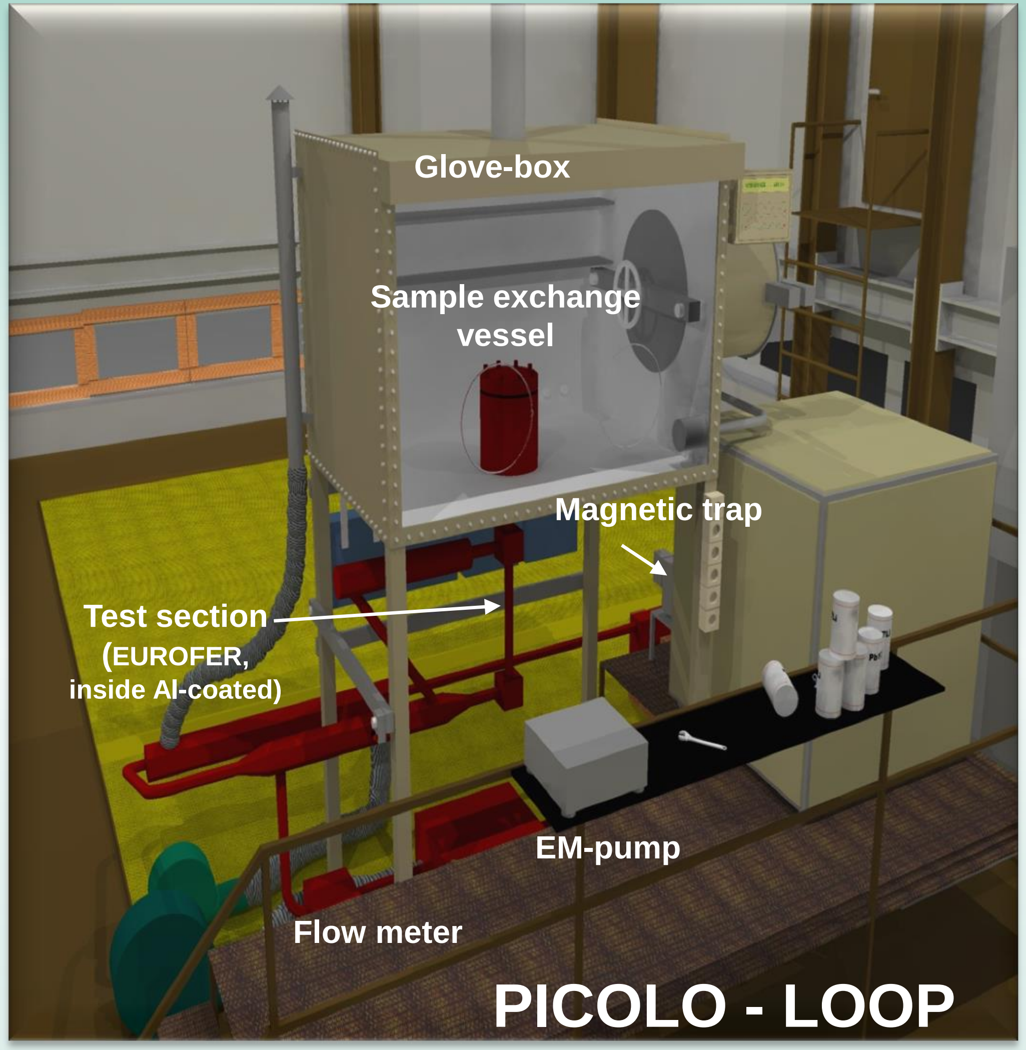
Comparison of results at 10^{-7} and 10^{-6} mass% O (CORRIDA experiments)



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

- ❑ 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).

Corrosion testing in PICOLO loop for fusion applications



Parameters of Pb-16Li Loop PICOLO

Test temperature:	480-550°C
T_{max} in test section:	550°C
T_{low} at EM-pump:	350°C
Pb-15.7Li volume:	20 litres
Flow velocity range:	0.01 - 1 m/s
Test velocity up to 2007:	0.22 m/s
Loop materials:	
Cold legs:	18 12 CrNi steel
Hot legs:	10 % Cr steel
Total loop operation:	
at 480°C	> 125,000 h
at 550°C	> 25,000 h

Test conditions since 2008

Pb-15.7Li velocity 0.1 m/s

Compromise to laminar/turbulent flow regimes, data for modeling and TBM requirements

RAFM steels tested in the PICOLO loop

Concentration (in mass%) of alloying elements other than Fe

	Cr	Mo	W	V	Nb	Ta	Y	Mn	Ni	Si	C
T91-A	9.44	0.850	<0.003	0.196	0.072	n.a.	n.a.	0.588	0.100	0.272	0.075
T91-B	8.99	0.89	0.01	0.21	0.06	n.a.	n.a.	0.38	0.11	0.22	0.1025
E911*	8.50–9.50	0.90–1.10	0.90–1.10	0.18–0.25	0.060–0.100	–	–	0.30–0.60	0.10–0.40	0.10–0.50	0.09–0.13
EUROFER	8.82	<0.0010	1.09	0.20	n.a.	0.13	n.a.	0.47	0.020	0.040	0.11
EF-ODS-A	9.40	0.0040	1.10	0.185	n.a.	0.08	0.297†	0.418	0.0670	0.115	0.072
EF-ODS-B	8.92	0.0037	1.11	0.185	n.a.	0.078	0.192†	0.408	0.0544	0.111	0.067

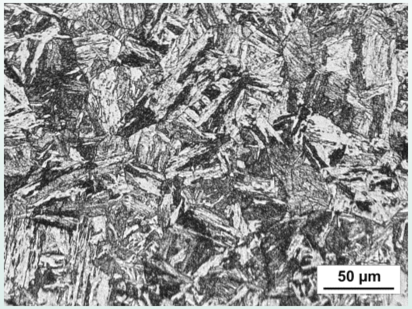
Microstructure

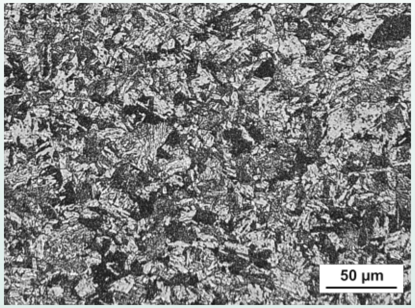
Fully martensitic:
E911, T91-A

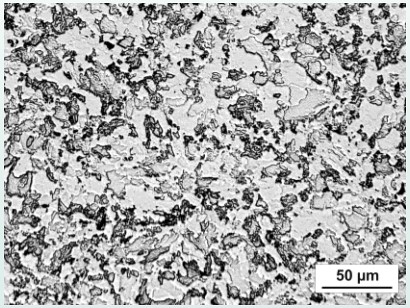
T91-B

EUROFER

Mainly ferritic: ODS-A, ODS-B



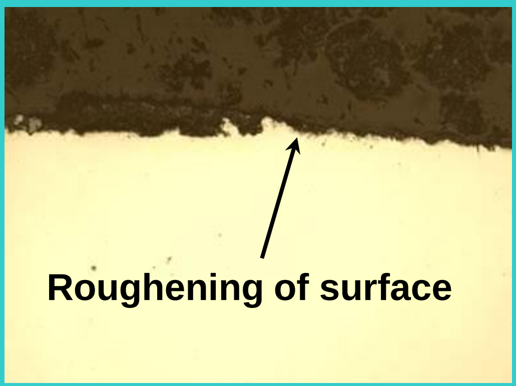




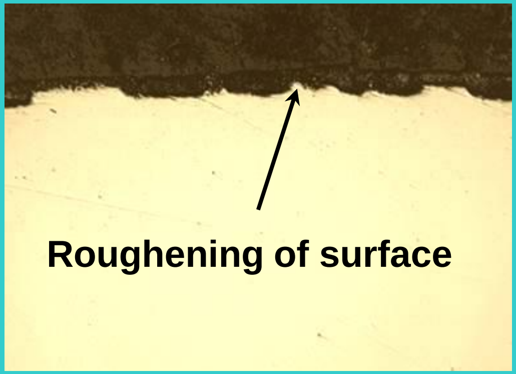
Microstructure analysis after Pb-16Li short-term exposure at 550°C

Karlsruhe Institute of Technology

500 h

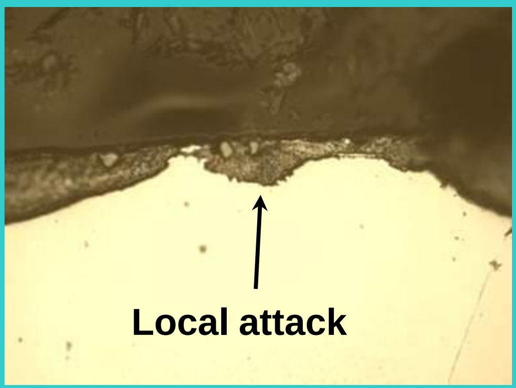


(200×)



(200×)

1,000 h



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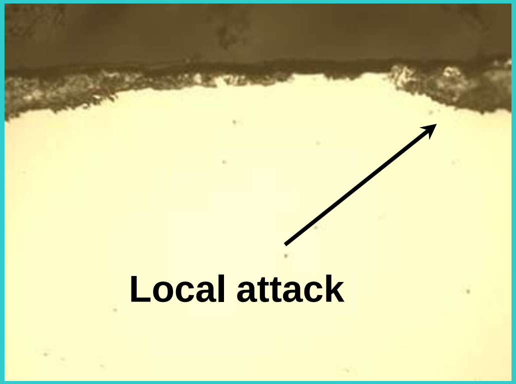


(500×)

1,500 h

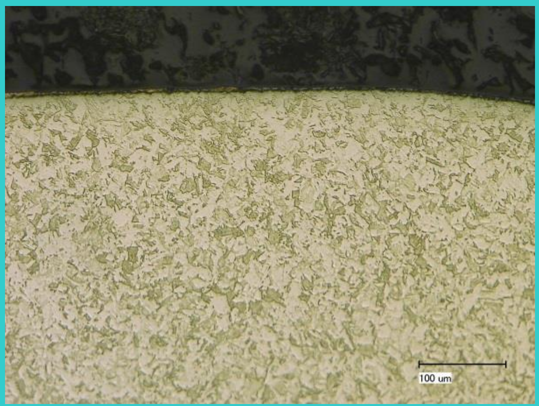
(200×)

EUROFER

(200×)

Microstructure analysis after Pb-16Li long-term exposure at 550°C

7,500 h



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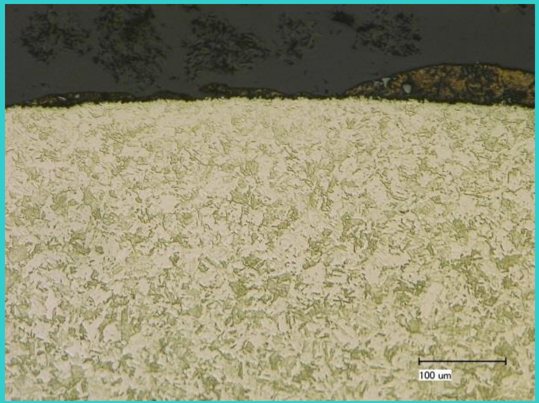
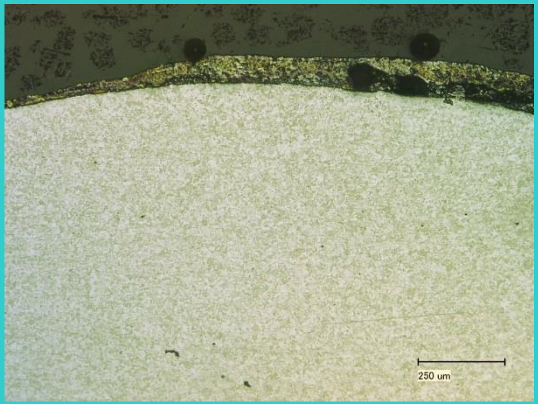


(500×)

12,000 h



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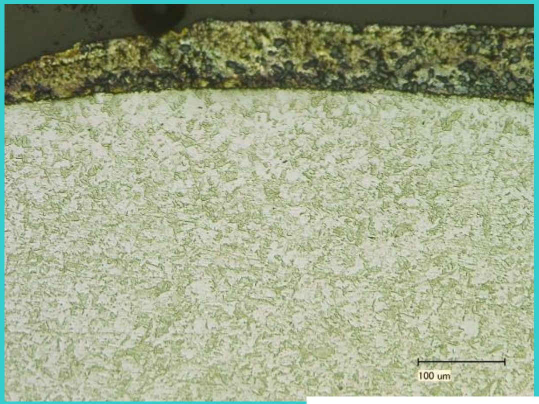

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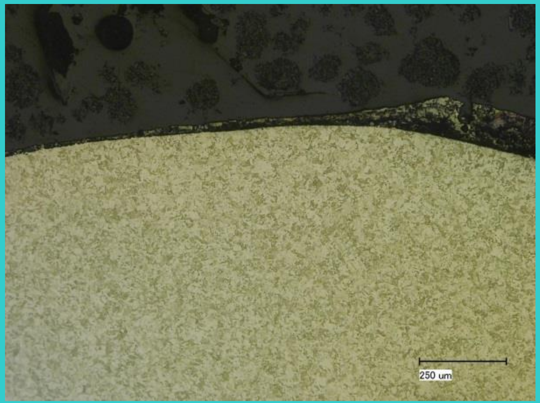
EUROFER



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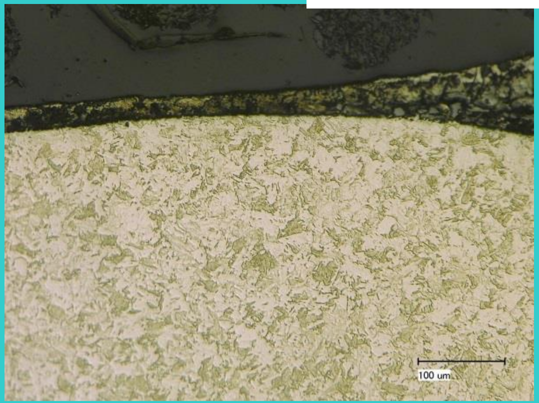
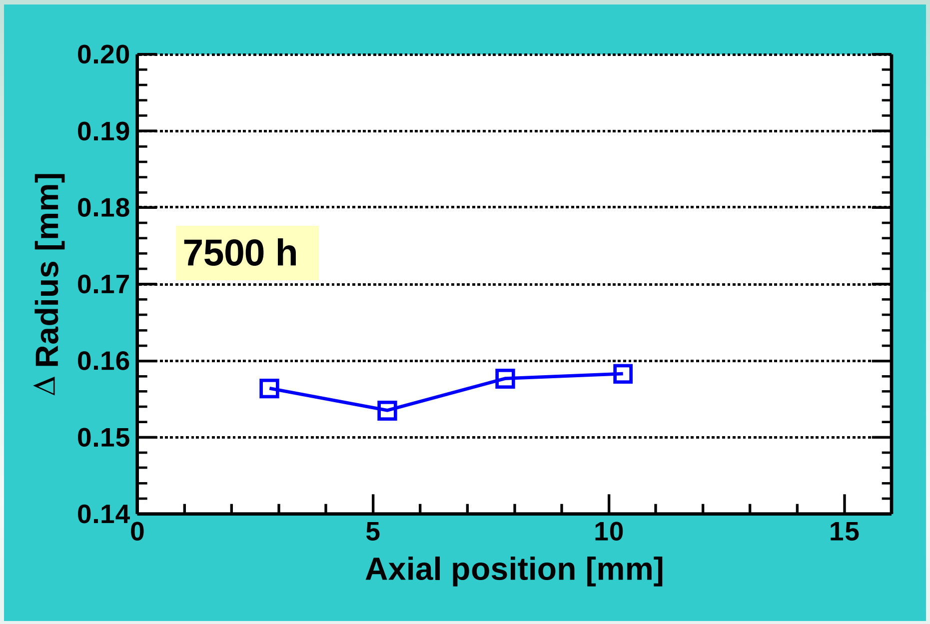
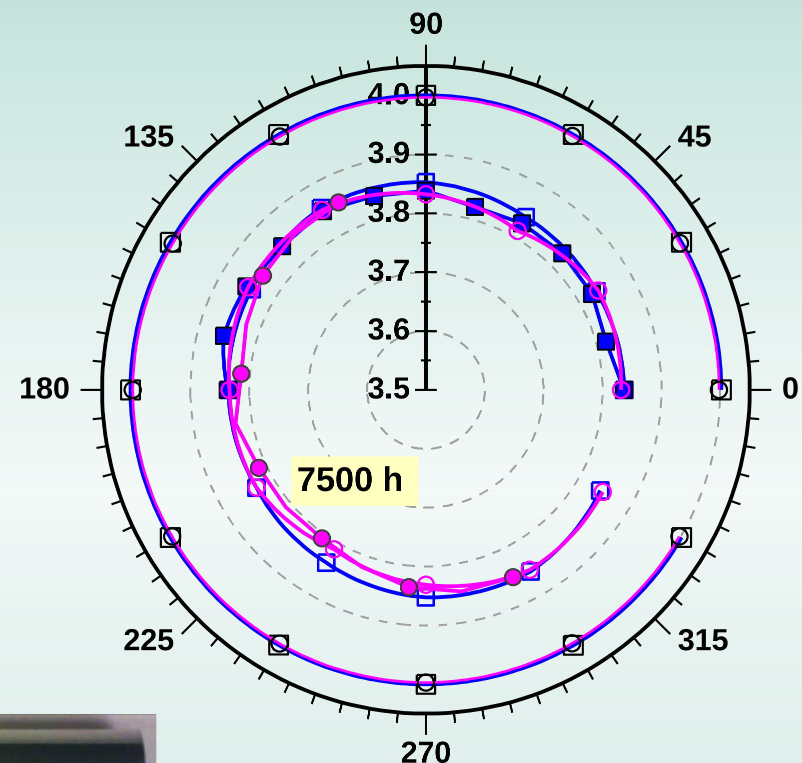


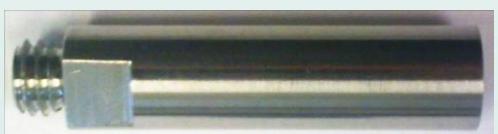
(500×)

Comparison of roundness of EUROFER steel samples after 7,500 hrs in Pb-16Li at 550°C and 10 cm/s flow velocity

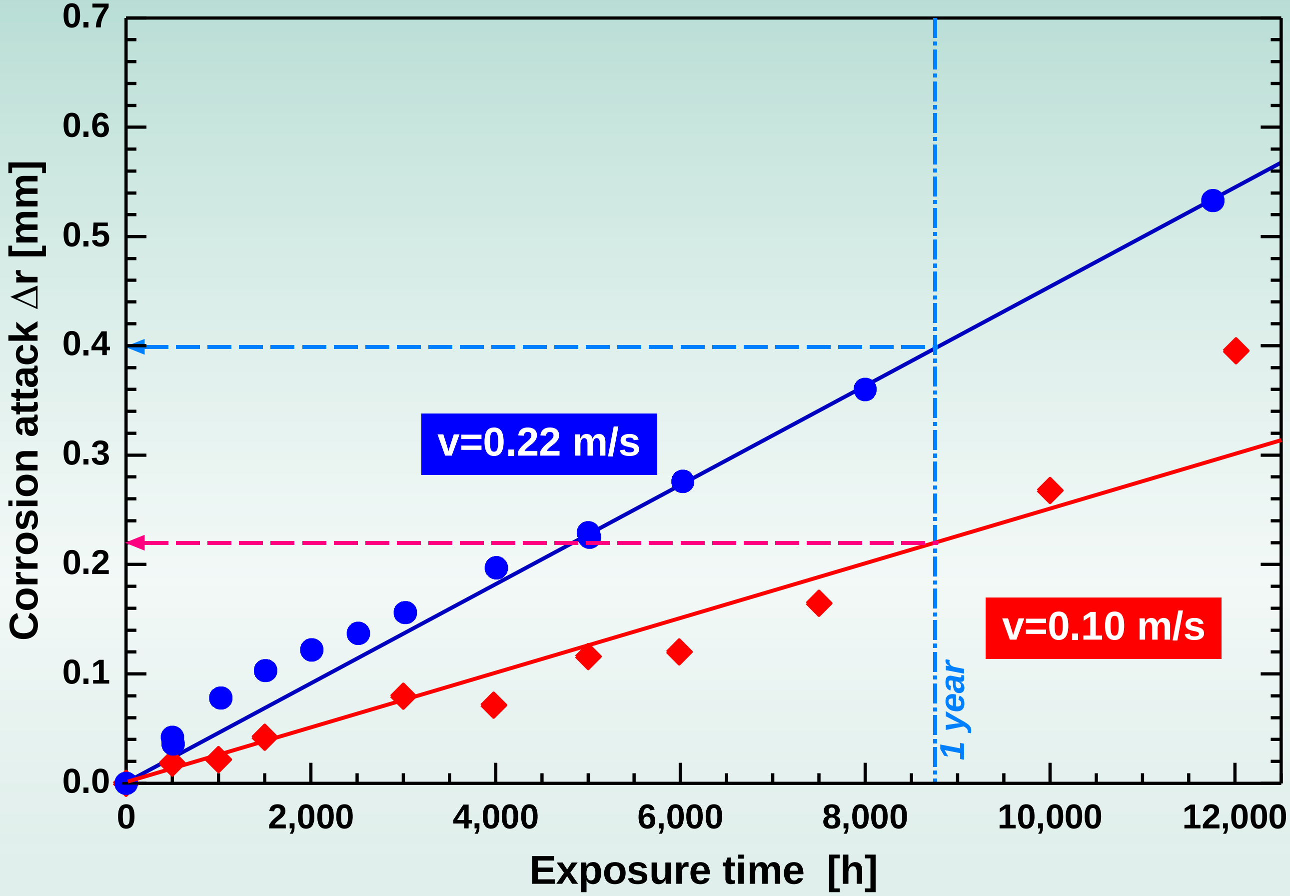




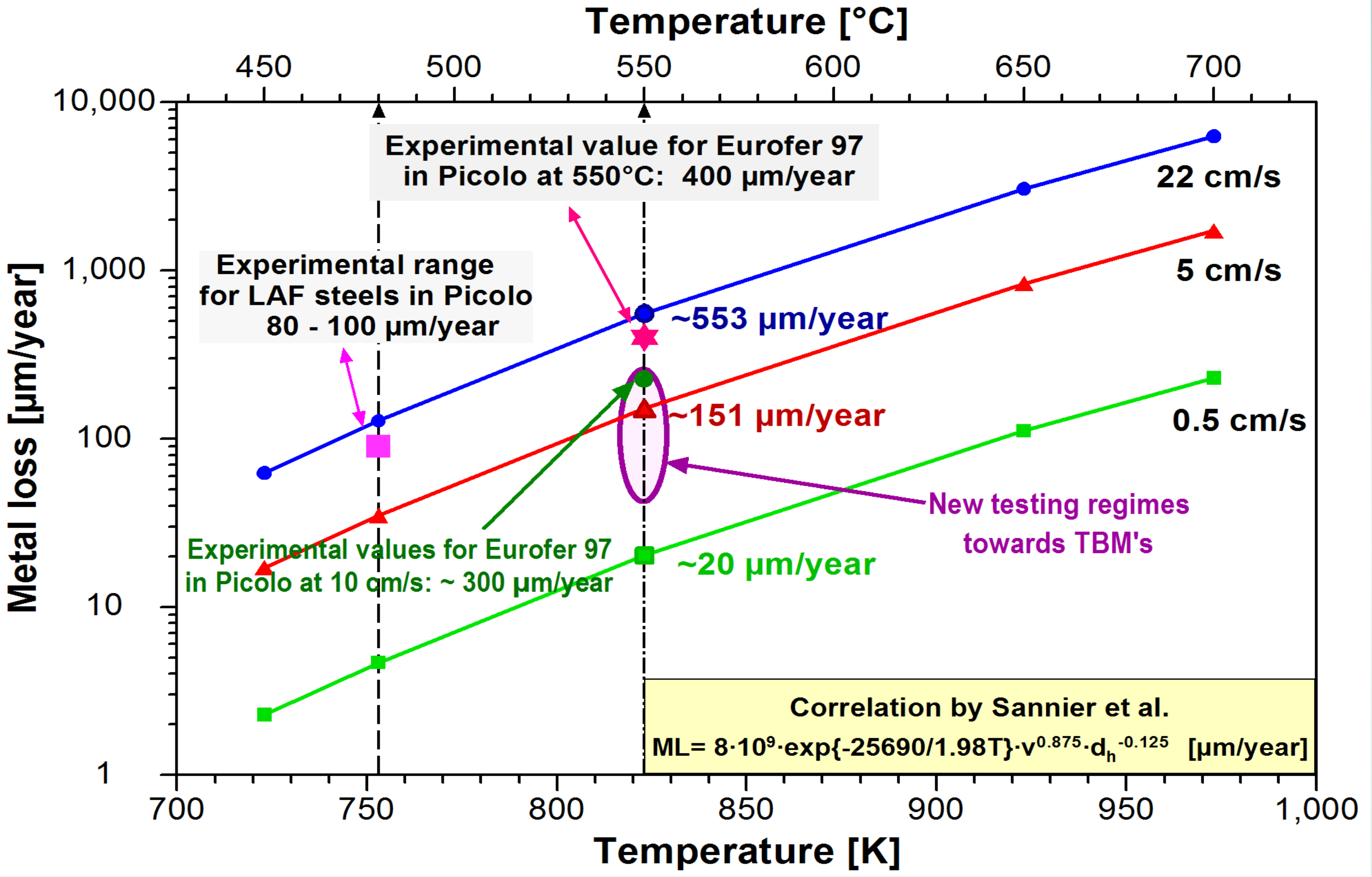
Test sample ∅ 8 mm x 35 mm



Comparison of corrosion attack of EUROFER steel in Pb-16Li at 550°C as a function of flow velocity



Flow rate dependent corrosion of FM steels in Pb-16Li



Overall summary for compatibility of structural steels in HLMs

- Heavy liquid metals, e. g. pure lead, lead-bismuth eutectic (LBE) and Pb-16Li are very appropriate coolants/targets for Nuclear and Fusion applications. European- and Worldwide organized R&D has been established to buildup databases for the compatibility behavior of potential reference materials

- Because of their favourable physical/chemical properties like e.g.,
  - Efficient heat transfer medium/coolant for thermal energy conversion
  - Essential for fast neutron reactors
  - Target/coolant for subcritical proton accelerator driven systems
  - Liquid breeder in fusion blanket concepts

  they cover the bridge between Nuclear and Fusion materials development