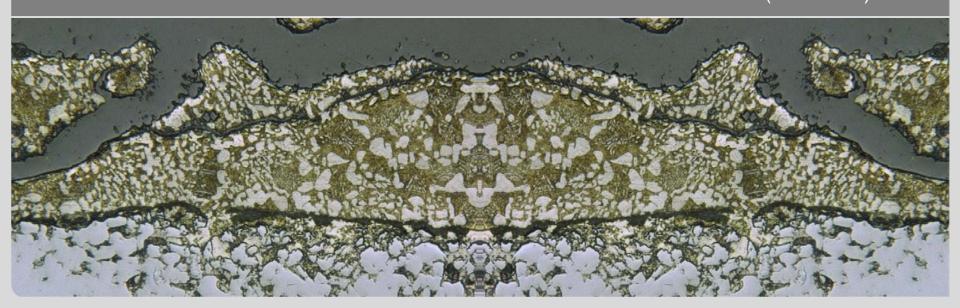


Compatibility of Structural Steels with Heavy Liquid Metals (HLMs): From a Cross-cutting View

Jürgen Konys

INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS (IAM-AWP)

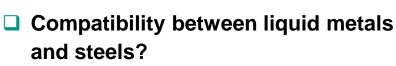


Compatibility with (Heavy) Liquid Metals



■ Favourable properties of liquid metals

- High thermal conductivity and boiling point
- Reasonably low dynamic viscosity
- Some show minimum interaction with neutrons (e.g., sodium and lead)
- Heavy liquid metals release neutrons under proton irradiation (e.g., mercury, lead and bismuth)
- Liquid breeder and coolant for fusion application



 Major steel elements are soluble in liquid metals

Efficient heat transfer medium/

coolant for thermal energy conversion

Essential for fast neutron reactors

Allows for sub-critical nuclear fuel in

a proton-accelerator driven system

As eutectic Pb-16Li alloy in fusion

- Formation of intermetallic phases
- Degradation of mechanical properties
- Prominent issue for lead alloys, especially lead-bismuth eutectic (LBE)
- Chemistry is different for Pb/LBE and Pb-16Li





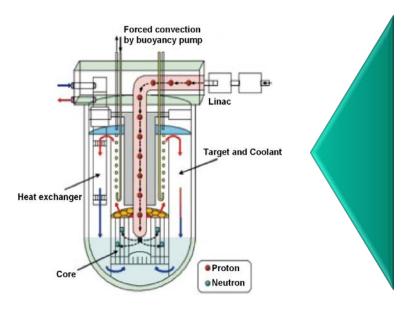
Some Specific Properties of Liquid Metals



		UNIT	Pb ⁴⁵ B ⁱ⁵⁵	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	\mathbf{c}_{p}	[J/(kgK)]	146.33	200.22	4279	4180
Kinematic Viscosity	ν	[m2/s] · 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 _e	[A/(V m)] · 10 ⁵	8.428	12.67	33.5	2 · 10 ⁻⁴ (tap)
Thermal Expansion Coefficient	α	[K ⁻¹] · 10 ⁻⁶	6.7	41.2	43.6	6
Surface Tension	σ	[N/m] · 10 ⁻³	410	430	421	52 (tap)

Lead-cooled Nuclear Reactors/Systems



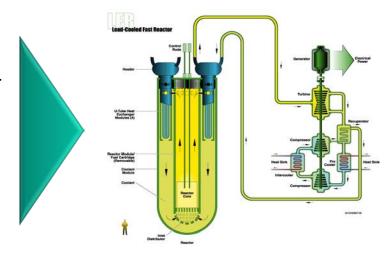


Accelerator Driven (Subcritical) System

- Transmutation of long-lived radioactive isotopes in nuclear waste
- Power generation
- 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-15.7Li (eutectic) as breeder and multiplier

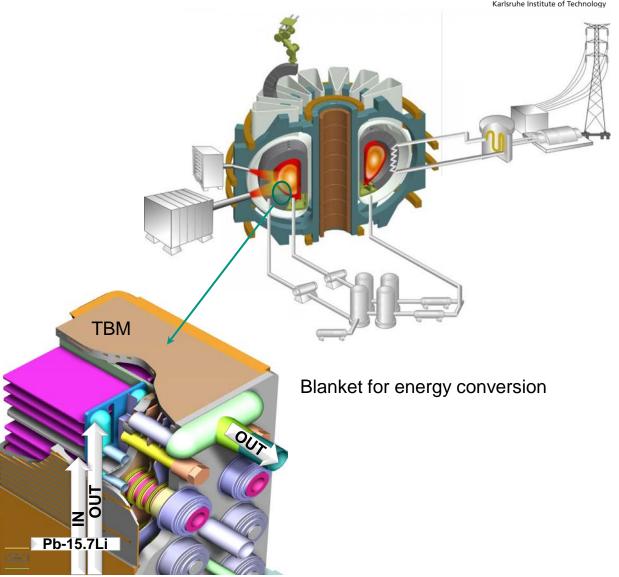
PbLi slowly re-circulating (10/50 rec/day)

90% ⁶Li in PbLi

Pb-Li velocities in breeding unit ~ 1 cm/s range

TBR = ≤1.15 with 550mm Breeder radial depth

Lifetime 7.5 MWy/m²



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 nearsurface 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) ...

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

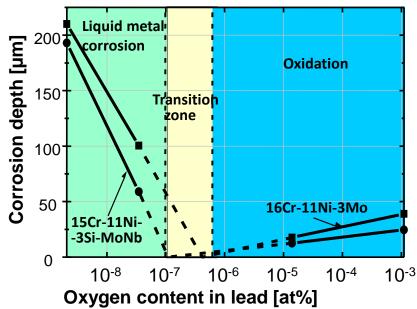
Degradation of mechanical properties

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

Impact of oxygen on steel corrosion in HLMs



- □ "Absence" of oxygen (Pb-15.7Li)
 - 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 <u>promote</u> 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

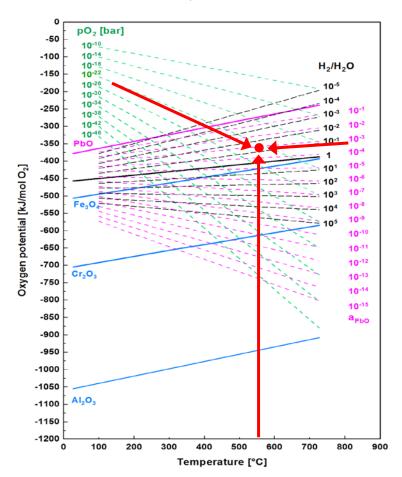


- Transition from solution-based to
 → oxidation-based corrosion with increasing oxygen concentration
- Continuous oxide layer is the goal of deliberate oxygen addition (Pb, LBE)
- Locally low-oxygen conditions even
 when oxygen concentration in the bulk of the liquid metal is high

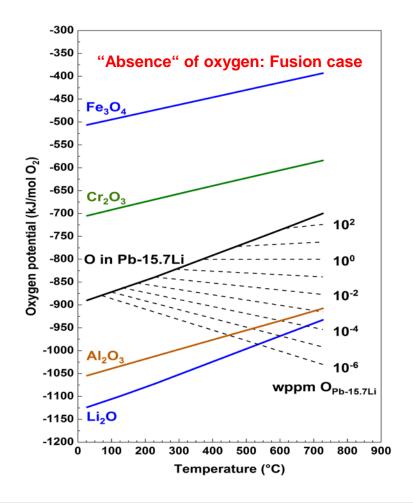
Oxygen Potentials of Metal/Metal-oxides, relevant for the Stability of Structural Materials in



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

Determination of oxygen content

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

Four potentiometric oxygen sensors distributed along the loop.

Locks of the test-sections

Test-section 2

Test-section 1

Sensor 2

Sensor 4

Air cooler

Magnetic trap

Test-section 1

Sensor 1

Sensor 2

Flow heat-exchanger

Test-section 1

Sensor 1

Sensor 1

Tubes for draining

Sensor 1

Flow heat-exchanger

Test-section 1

Sensor 1

Dump tank

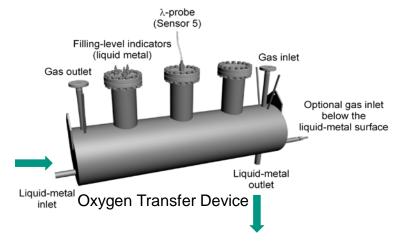


Constructed and operated at KIT'sInstitute for Applied Materials – Corrosion Department

Effective operating time of the CORRIDA loop (h) 46000 48000 50000 52000 54000 56000 58000 60000 62000 1,0 € 0,9 8,0 Pt / air sensor 0,7 0,6 -3 log C_o (mass %) Calculated oxygen -4 concentration -5 -8 Flow velocity (m/sec) 1,5 1,0 0,5 0,0 0,0 550°C 450°C 400°C 715 1007 1007 288 2015 2015 1007 5015 500 1925 4746 2011 3749 8766 Exposure time (h)

Oxygen control system





$T = 550(+5)^{\circ}C$

 $T_{min} \approx 385$ °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

\Box T = 450(+5)°C,

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

\Box 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

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



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

	Cr	Мо	W	V	Nb	Та	Y	Mn	Ni	Si	С
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

Nominally 9 mass% Cr





Elements besides Cr that are likely to improve oxidation performance

Microstructure

50 μm

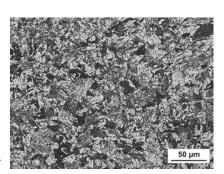
Fully martensitic:

E911, T91-A

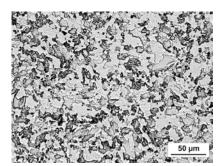
T91-B

GRANIE

EUROFER



Mainly ferritic: ODS-A, ODS-B



[†] In the form of yttria (Y₂O₃)

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

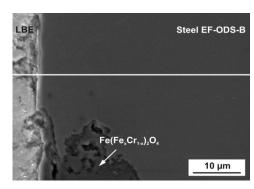


Protective scaling

- 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)

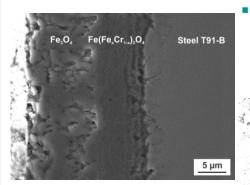
Scale failure at high local c_{Ω} (?)

Scale failure at low local c_0 (?)



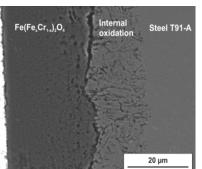
550°C

Accelerated oxidation



550°C

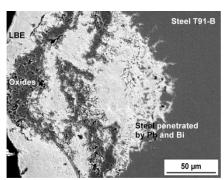
Typical and, finally, the general corrosion process for 9% Cr steel



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

450°C

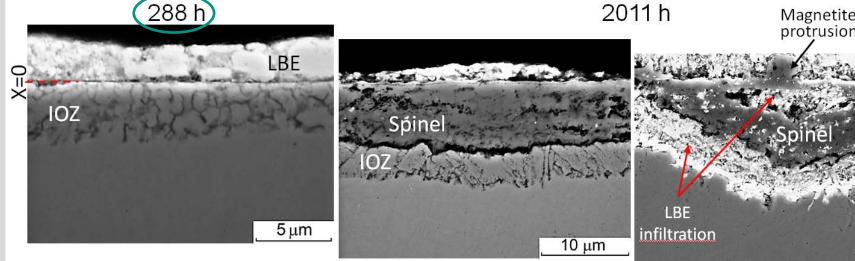
Flowing LBE at 550°C, 2 m/s and 10⁻⁷ mass% dissolved oxygen

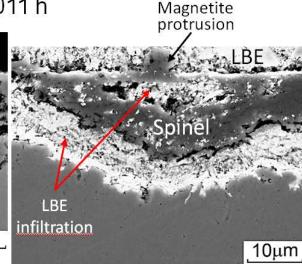


Accelerated oxidation

- 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 co
- Corresponds to previous observations at 550°C/10⁻⁶ mass% O
- Fe dissolves at the spinel surface rather than forming magnetite





T91-A

13

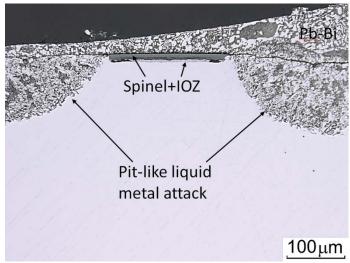
Flowing LBE at 550°C, 2 m/s and 10⁻⁷ mass% dissolved oxygen



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 $c_{\rm O}$ after ~450 h

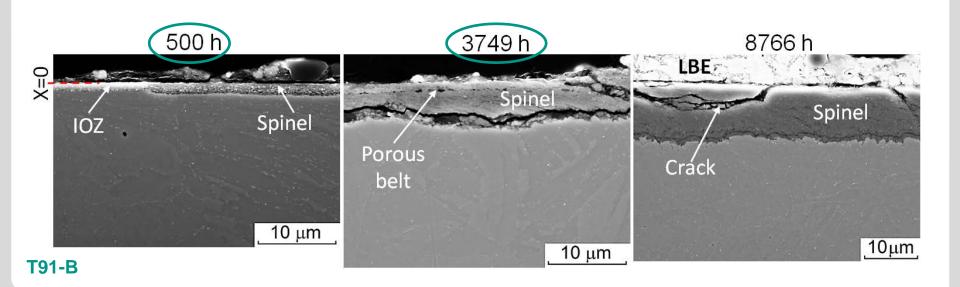


Flowing LBE at 450°C, 2 m/s and 10⁻⁷ mass% dissolved oxygen



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



Summary for corrosion of 9% Cr steels in LBE

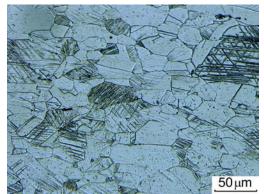


- At 450/550°C, 2 m/s and 10⁻⁻ mass% dissolved oxygen, T91 shows the three stages of corrosion typical for flowing oxygen-containing LBE:
 - □ Protective scaling short term or local phenomenon
 - Accelerated oxidation the general degradation mechanism in the long run
 - Solution-based corrosion locally, after accumulation of liquid metal underneath the oxide scale
- ☐ Marginally better overall performance with slightly higher Cr, Si and lower C content
- In comparison to 10⁻⁶ mass% O:
 - Shorter incubation especially of solution-based corrosion
 - □ Slower accelerated oxidation in terms of metal recession only at 550°C
 - Reduction of overall scale thickness at 450°C due to missing magnetite, but an equivalent amount of Fe will dissolve
 - □ In the case of T91, 10⁻⁶ mass% may be closer to optimum oxygen content in LBE than 10⁻⁷ mass%
- Quantitative corrosion data at 10⁻⁷ mass% O useful for predictive corrosion models

Austenitic Cr Ni steels tested in CORRIDA loop

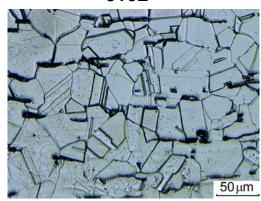
Austenitic steels	Cr	Ni	Мо	Mn	Si	Cu	V	W	Al	Ti	С	N	Р	S	В
316L	16.73	9.97	2.05	1.81	0.67	0.23	0.07	0.02	0.018	-	0.019	0.029	0.032	0.0035	-
1.4970	15.95	15.4	1.2	1.49	0.52	0.026	0.036	< 0.005	0.023	0.44	0.1	0.009	< 0.01	0.0036	< 0.01
1.4571	17.50	12	2.0	2.0	1.0	-	-	-	-	0.70	0.08	-	0.045	0.015	-

1.4970 (15-15Ti)



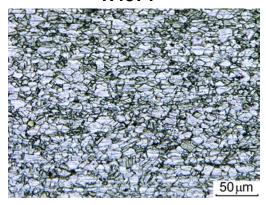
- $HV_{30} = 253$;
- Grain size ranged from 20 to 65 µm;
- Intersecting deformation twins.

316L



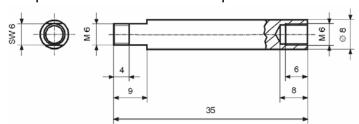
- HV₃₀ = 132;
- Grain size averaged 50 µm (G 5.5);
- Annealing twins.

1.4571

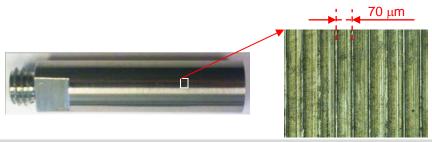


- $HV_{30} = 245$;
- Grain size averaged 15 µm (G 9.5).

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



Surface examinations - general corrosion appearance

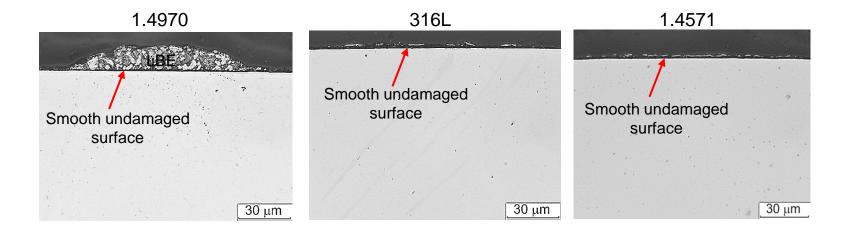
1.4970, 550°C

- ☐ 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.

18

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



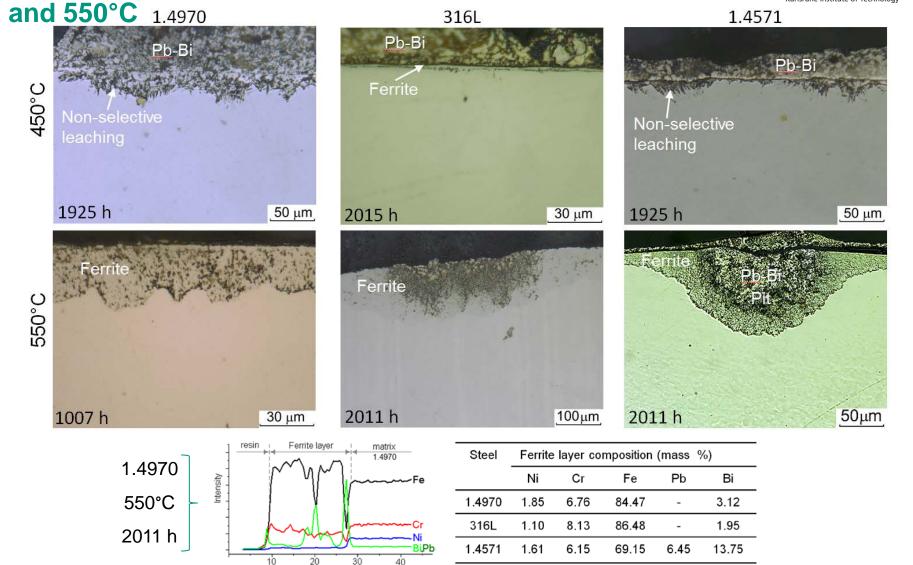




- Smooth undamaged surface is observed on the cross-section of samples;
- Selective leaching attack is not detected under the given duration of test 4746h;
- Samples revealed golden-colored oxide film protective scaling;
- Corrosion tests are still continuing with expected max. duration about 10000h.

Cross-section appearance of austenitic steels in flowing oxygen-containing LBE ($\sim 2 \text{ m/s}$, $\sim 10^{-7} \text{ mass } \% \text{ O}$) at 450



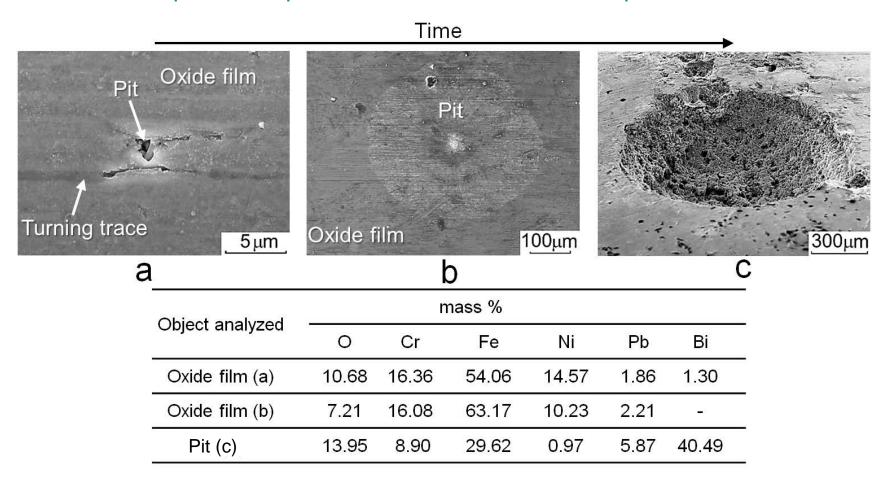


Distance (µm)

Local pit-type corrosion attack



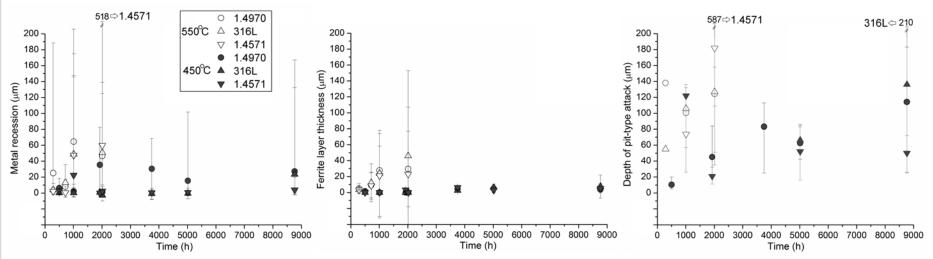
Expected sequence of evolution of corrosion pits wit time



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:

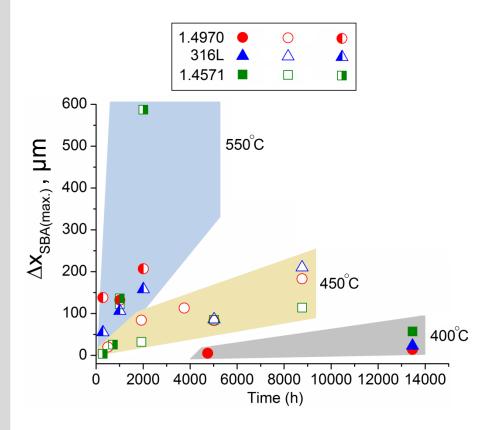
- □ Metal recession averaged ~ 60, 46 and 51 μm after 2011 h for 1.4571, 1.4970 and 316L steels, respectively;
- □ Layer-type attack averaged 23, 30 and 46 µm;
- \blacksquare Depth of pit-type attack averaged 182, 124 and 127 $\mu m.$

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.

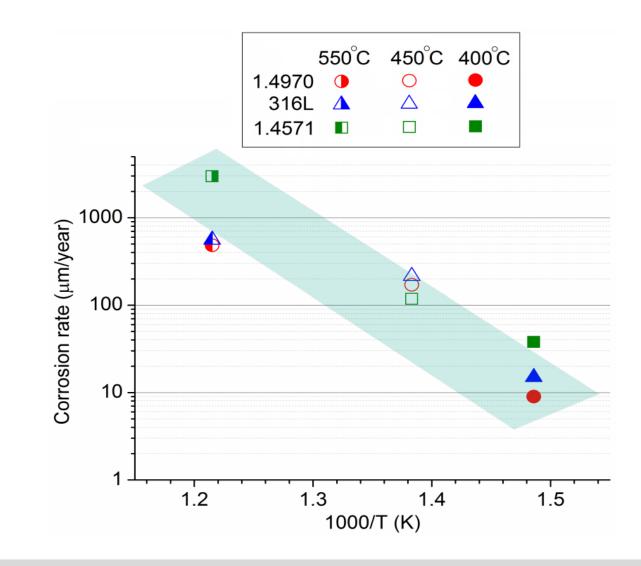
Maximum corrosion loss:

- ✓ 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 $\sim 500 - 4000 \text{ h}$ at 450°C and to $\leq 200 \text{ h}$ at 550°C .

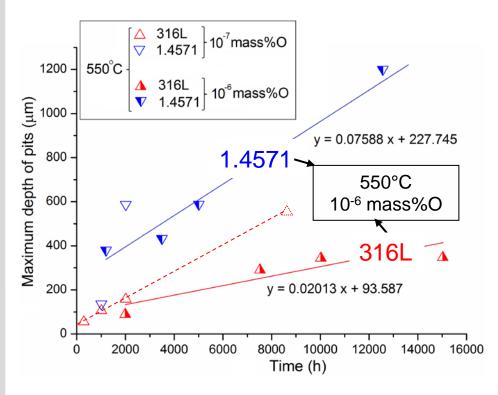
Corrosion rates of 1.4970, 316L and 1.4571 at 10⁻⁷ mass% oxygen at 400, 450 and 550°C





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 solutionbased 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).

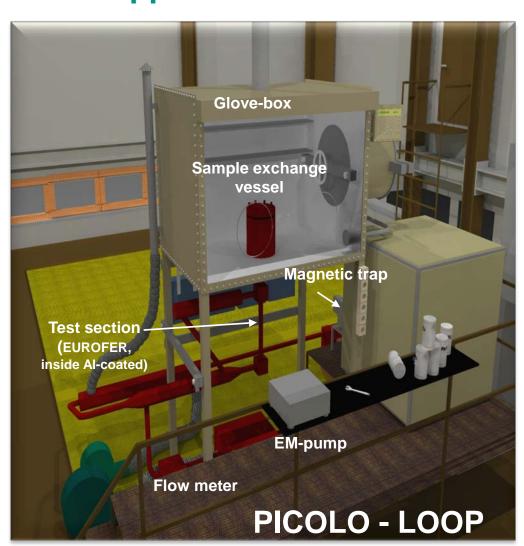
Summary for corrosion of austenitic steels in LBE



- □ Interaction of austenitic steels with flowing LBE with 10⁻⁷ mass % O was accompanied by **oxidation** and **solution-based liquid-metal attack**, resulted in **selective leaching of Ni and Cr** from the sub-oxide layers and subsequent development of ferrite zone penetrated by LBE:
 - 400°C: Oxidation thin Cr-based oxide film (protective scaling)
 - □ <u>450°C</u>: Oxidation thin (≤ 0.5 μm) Cr-based oxide film and solution-based selective leaching with maximum depth of local attack between 114μm and 210μm after 8766h
 - □ <u>550°C</u>: Oxidation thin (≤ 0.5 μm) Cr-based oxide film and solution-based selective leaching with maximum depth of local attack between 158 μm and 587μm even after 2011 h
- □ <u>Cr-based oxide films</u>, formed *in-situ* on the surface of austenitic steels, <u>are not sufficient</u> <u>protective barriers</u> with respect to selective leaching, at least at 450 and 550°C in LBE with 10⁻⁷ mass% O!
- ☐ In LBE with 10⁻⁷ mass%O, selective leaching is the main corrosion mechanism of austenitic steels causing substantial corrosion loss, while at 10⁻⁶ mass% O, oxidation is dominating

Corrosion testing in PICOLO loop for fusion applications





Parameters of Pb-15.7Li 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

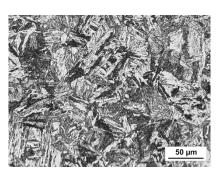
LAFM steels tested in the PICOLO loop



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

	Cr	Мо	W	V	Nb	Ta	Υ	Mn	Ni	Si	С
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

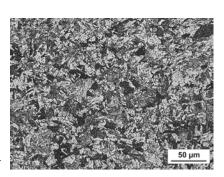


Fully martensitic:

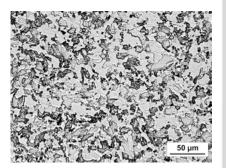
<u>E911,</u> T91-A

T91-B

EUROFER

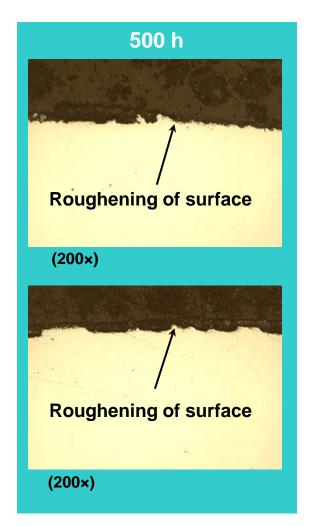


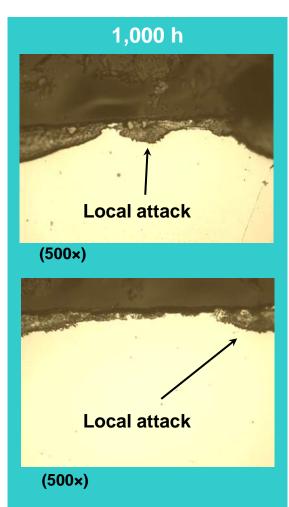
Mainly ferritic: ODS-A, ODS-B

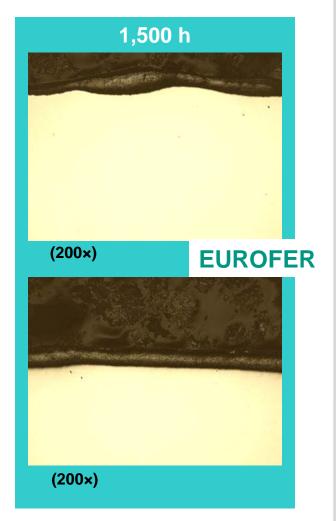


Microstructure analysis after Pb-15.7Li short-term exposure at 550°C



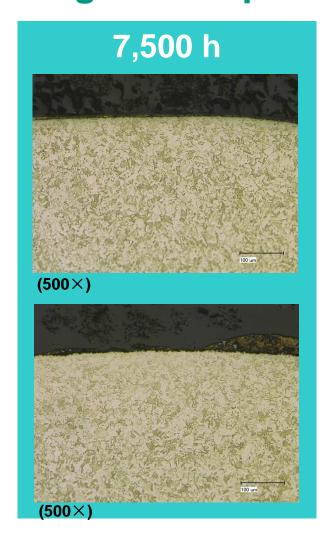


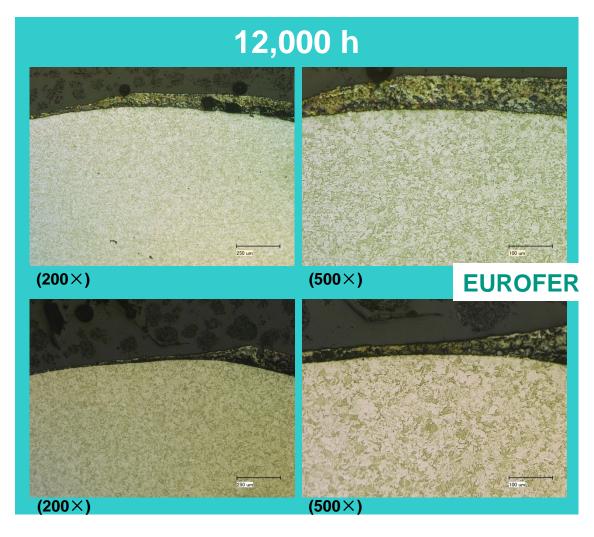




Microstructure analysis after Pb-15.7Li long-term exposure at 550°C

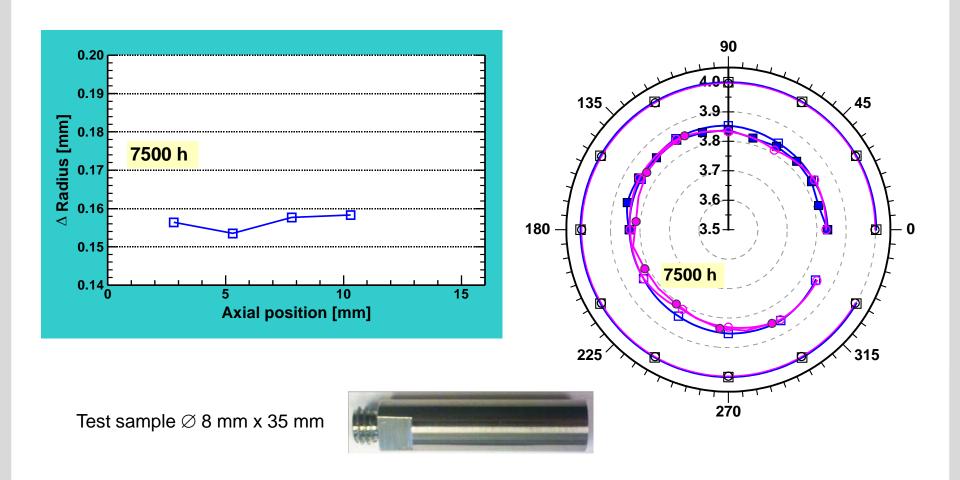






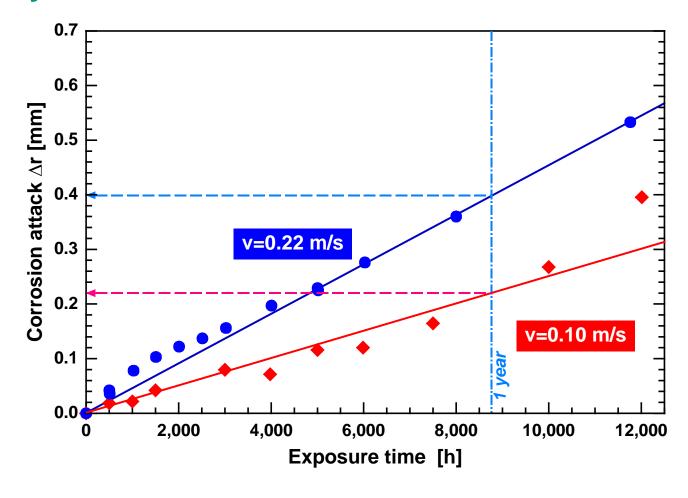
Comparison of roundness of EUROFER steel samples after 7,500 hrs in Pb-15.7Li at 550°C and 10 cm/s flow velocity





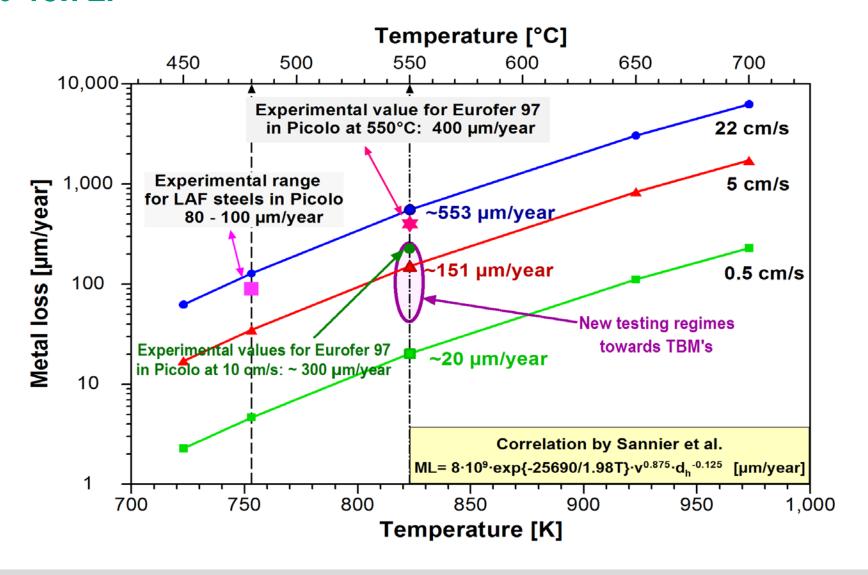
Comparison of corrosion attack of EUROFER steel in Pb-15.7Li at 550°C as a function of flow velocity





Flow rate dependent corrosion of FM steels in Pb-15.7Li





Summary for corrosion of FM- steels in Pb-16Li



- Because of the different HLM-chemistry of Pb-Li, non-metals like oxygen cannot be used for surface protection.
- The corrosion rate of RAFM steels in PbLi depend strongly on temperature and flow velocity. At "higher" flow velocity (22 cm/s) and "lower" temperature (480°C), ca. 80 μm/year for EUROFER, whereas at "lower" flow velocity (10 cm/s) and "higher" temperature (550°C), ca. 200 μm/year have been measured.
- □ Al-based coatings are the only option for both test conditions. A reduction in corrosion rate by a factor of ten has been shown in PICOLO loop of KIT

Overall summary for compatibility of structural steels in HLMs from a cross-cutting view

- Karkruhe Institute of Technology
- □ Heavy liquid metals, e. g. pure lead, lead-bismuth eutectic (LBE) and Pb-16Li are very appropriate coolants/targets for Nuclear and for Fusion applications. European- and worldwide organized R&D has been established to buildup a database for the compatibility 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 and are therefore ideal cross-cutting materials