TOPIC 3

Fuel, Clad, Structural and Coolant Materials

Sub topic 3.3:
Compatibility of Fast Reactor Structural Materials with Liquid Metal Coolants (Part 2)

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Outline

- HLMs for Nuclear applications
- HLM chemistry: role of oxygen …..
- Corrosion of 9% Cr and austenitic steels in LBE
- Quantification of corrosion attack
- Dependency on oxygen concentration
- Conclusions

FJOH 2016 Heavy Liquid Metals for Energy Applications

- **Why: Favourable properties of liquid metals**
  - High thermal conductivity and boiling point
  - Reasonably low dynamic viscosity

  → Efficient heat transfer medium/ coolant for thermal energy conversion
  - Some show minimum interaction with neutrons (e.g., sodium and lead)

  → Essential for fast neutron reactors
  - Heavy liquid metals release neutrons under proton irradiation (e.g., mercury, lead and bismuth)

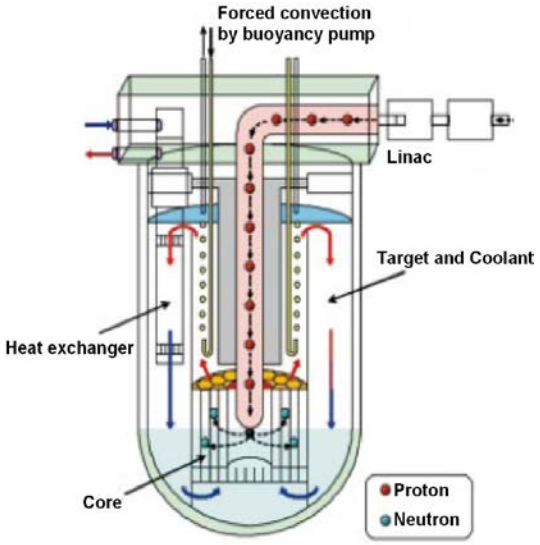
  → Allows for sub-critical nuclear fuel in a proton-accelerator driven system (ADS)

- **But: Compatibility issue between liquid metals and e.g. steels**
  - Major steel elements are (very) soluble in liquid metals (Fe, Cr, Ni)
  - Formation of intermetallic phases (Sn)
  - Degradation of mechanical properties
    - Prominent issue for lead alloys, especially lead-bismuth eutectic (LBE)

Some Specific Properties of Liquid Metals

		UNIT	$Pb^{45}Bi^{55}$	Pb-16Li	SODIUM	WATER
Melting Point at 0.1 MPa		[°C]	125	235	97.8	0
Boiling Point at 0.1 MPa		[°C]	2516	1600	881	100
			300°C	**300°C**	**300°C**	**25°C**
Density	ρ	[kg/m^3]	10325	9988	880	1000
Heat Capacity	c_ρ	[J/(kgK)]	146.33	200.22	1298	4180
Kinematic Viscosity	ν	[m2/s] · 10^{-7}	1.754	1.3	4	9.1
Heat Conductivity	λ	[W/(m K)]	12.68	45.2	77.1	0.6
Electric Conductivity	σ_{el}	[A/(V m)] · 10^5	8.428	12.67	55.5	2 · 10^{-4} (tap)
Thermal Expansion Coefficient	α	[K^{-1}] · 10^{-6}	6.7	41.2	24.2	6
Surface Tension	σ	[N/m] · 10^{-3}	410	430	175	52 (tap)

Heavy Liquid Metal-cooled Nuclear Reactors

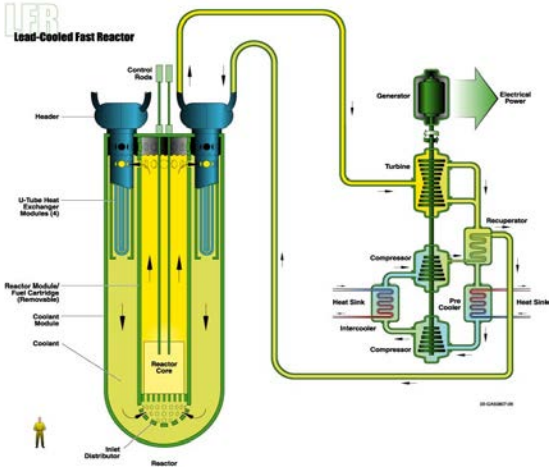


Accelerator Driven (Subcritical) System (ADS)

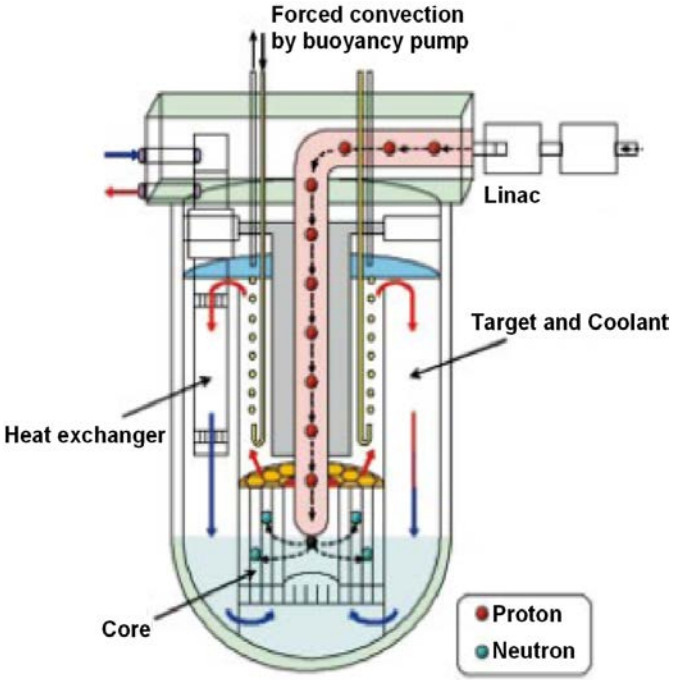
- Transmutation of long-lived radioactive isotopes in nuclear waste
- Power generation (Energy Amplifier)
- Liquid lead (Pb) or lead-bismuth eutectic (LBE) as spallation target and primary coolant
- Maximum temperature, typically
  - 450 – 500°C for regular operation
  - Periodically 550°C (according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



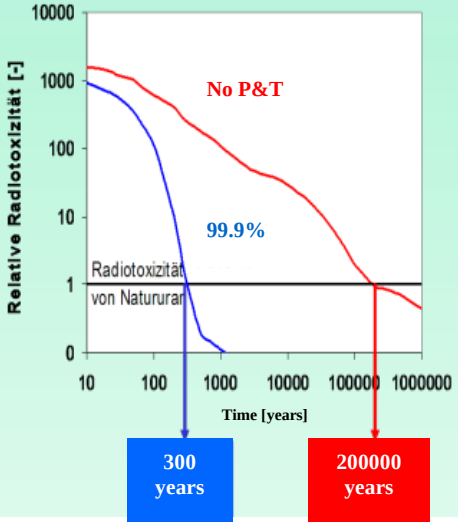
Heavy Liquid Metal-cooled Nuclear Reactors



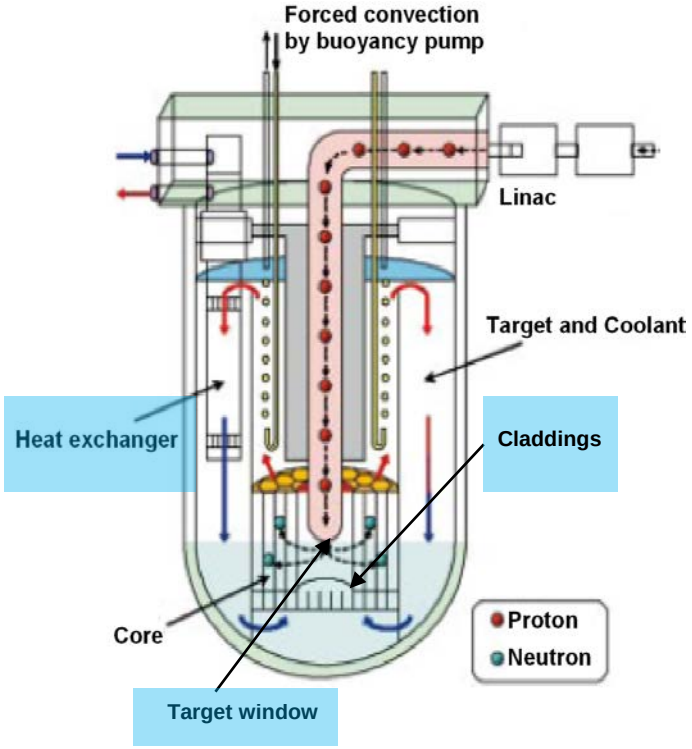
Reduction of high-level nuclear waste

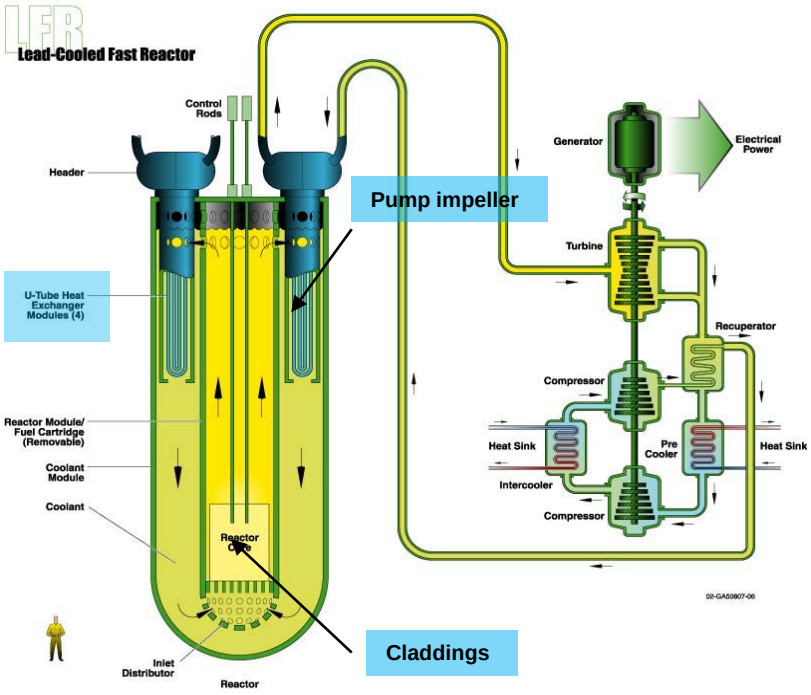
	No. NPPs		Burned Fuel (t)	
	No.	Electricity gen.	Accumulated	Per year
Worldwide	438	16%	220 000	7 000
EU	145	35%	34 500	2 500
Germany	19	30%	8 400	450

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

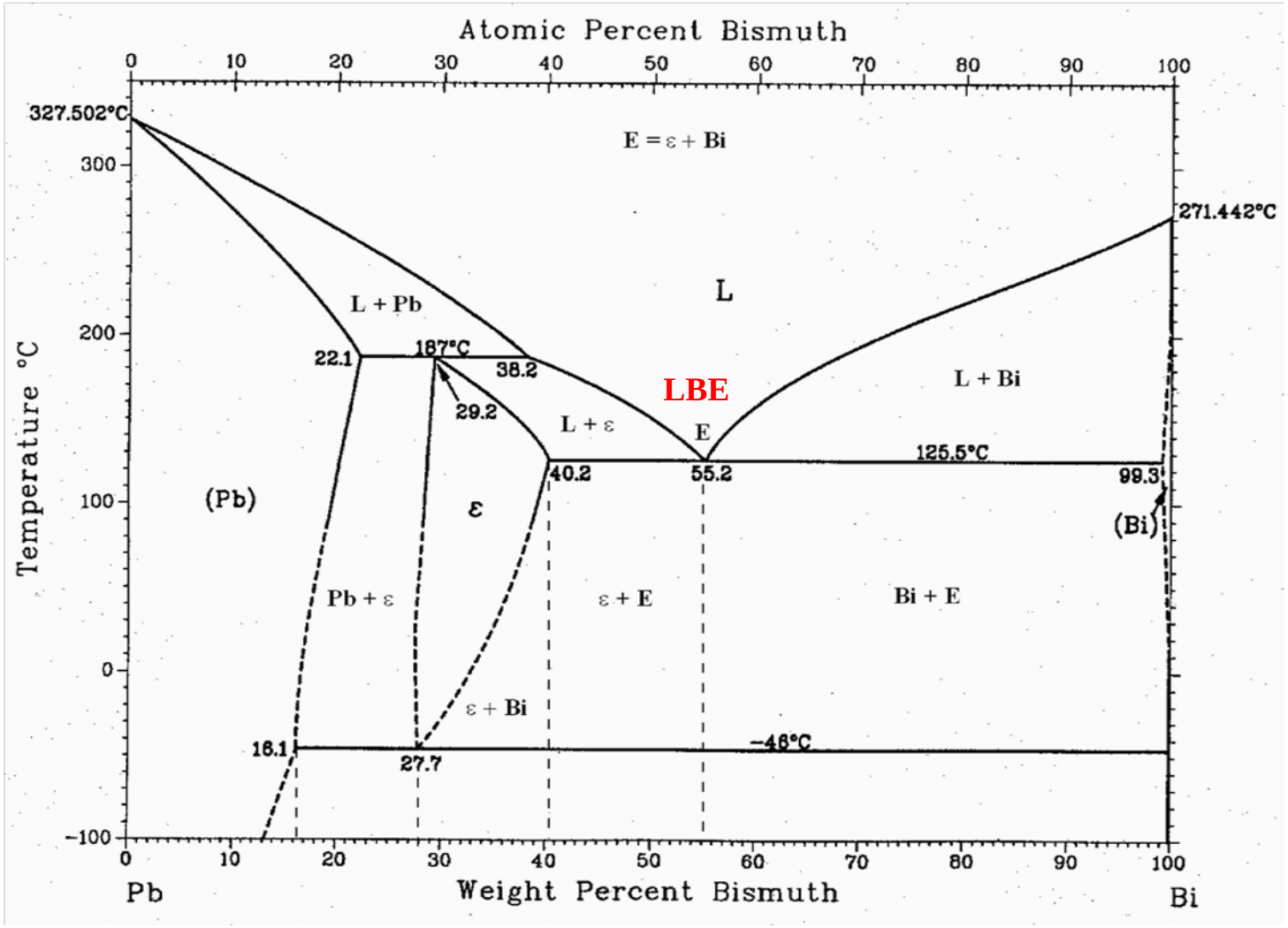


Critical Components of Heavy Liquid Metal-cooled Nuclear Reactors/Systems





FJOH 2016 Phase Diagram Lead – Bismuth Eutectic (LBE)



FJOH 2016 Heavy Liquid Metal (HLM) – 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

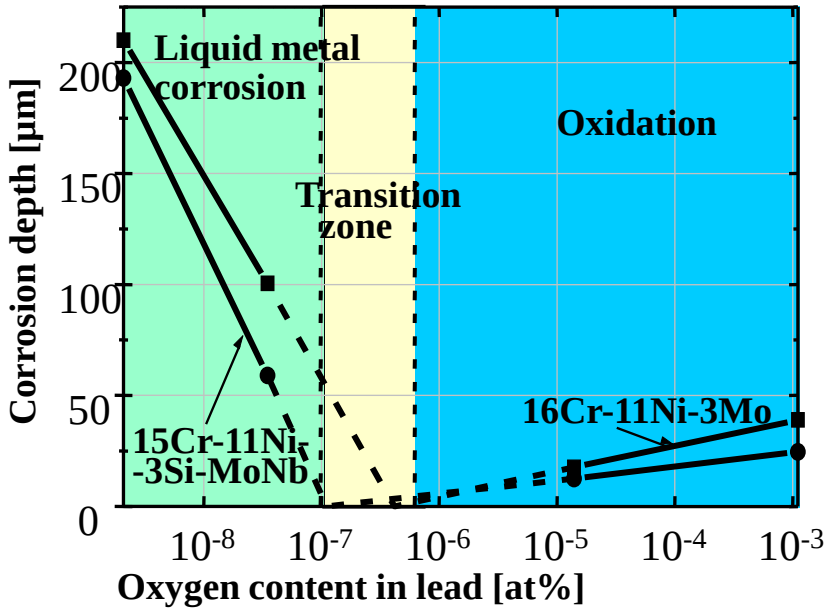
Observed on the µm-scale, accessible by light-optical microscopy (LOM), scanning-electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) …

- **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, oxidation..

FJOH 2016 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

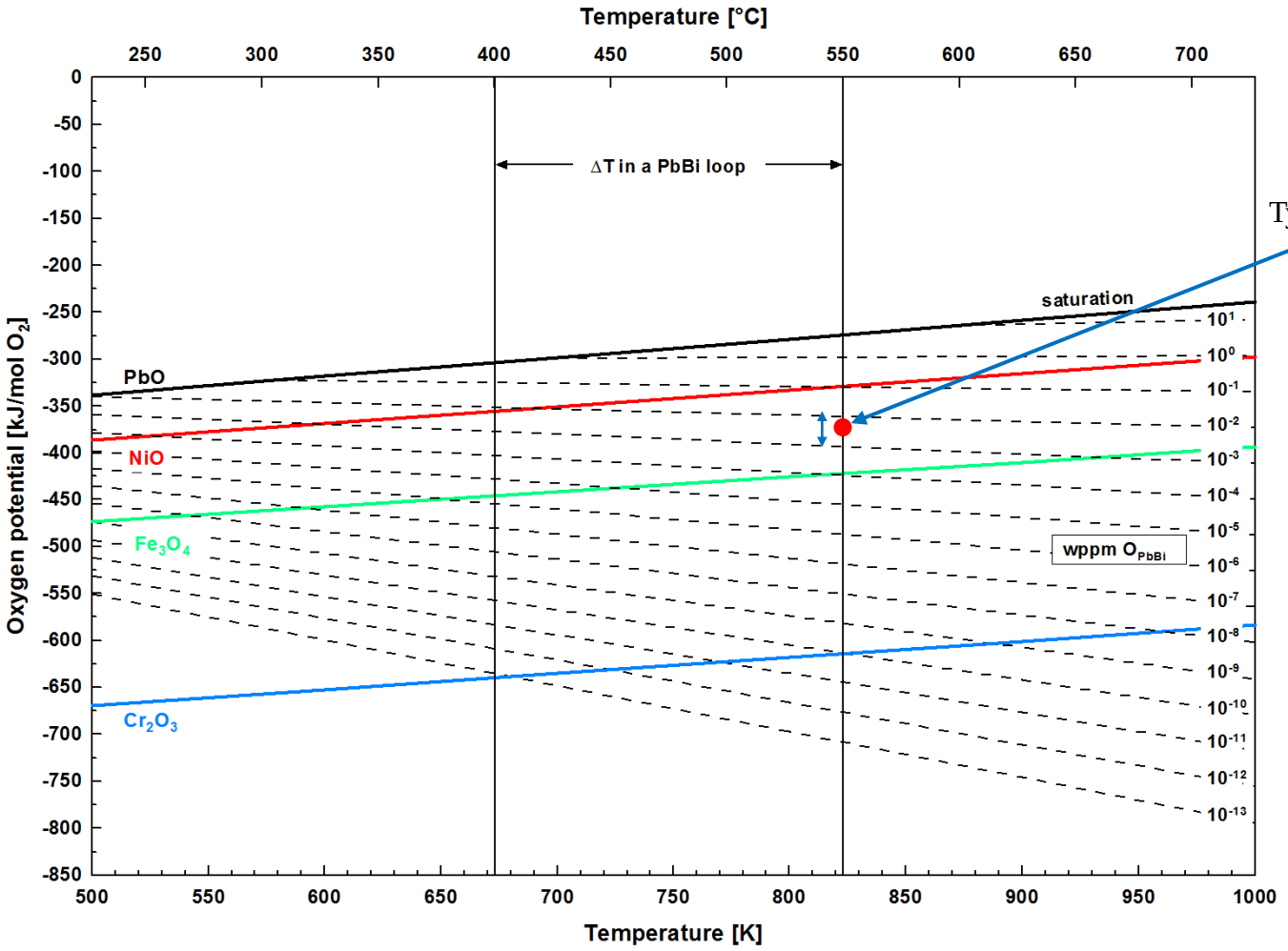


→ Transition from solution-based to oxidation-based corrosion with increasing oxygen concentration

→ **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

FJOH 2016 Oxygen Chemistry: Oxygen Potentials in HLMs



FJOH 2016 Components of an Oxygen Control System

Sensors for on-line monitoring

Electrochemical oxygen monitoring

- Solid electrolyte on the basis of yttria-stabilized zirconia (YSZ)
- Metal/metal-oxide or Pt/gas reference electrode

Issues to be addressed (in general)

- Compatibility with the use in Pb alloys (YSZ/steel joint)
- Accuracy
- Long-term reliability

Licensing for nuclear application

- Structural stability of the YSZ product used
- Risk of contamination in case of electrolyte cracking

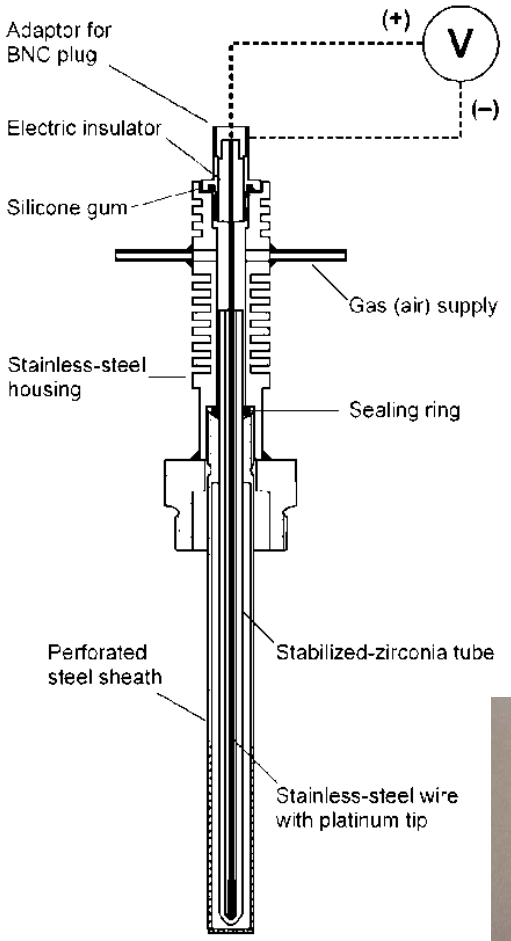
Oxygen-transfer device(s)

"Classic" mass transfer across the interface between oxygen source/sink and the liquid metal

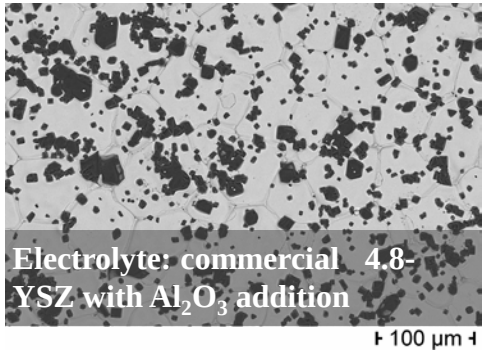
Type	Oxygen source	Oxygen sink
Solid-liquid	PbO	(less noble metals)
Gas-liquid	Ar, H_2O, air	Ar-H_2

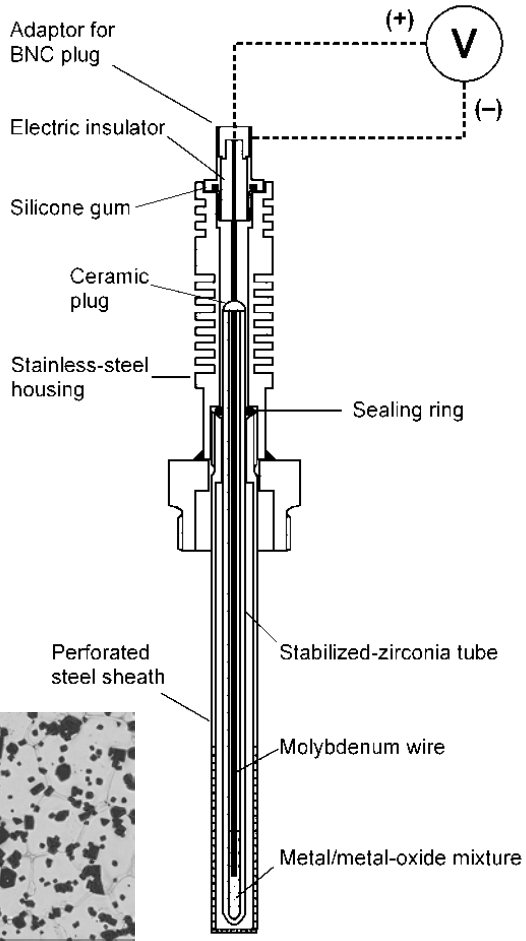
Long-term experience from operating experimental facilities for testing materials (steels) in oxygen-containing Pb alloys exists

Most Common Oxygen Sensors



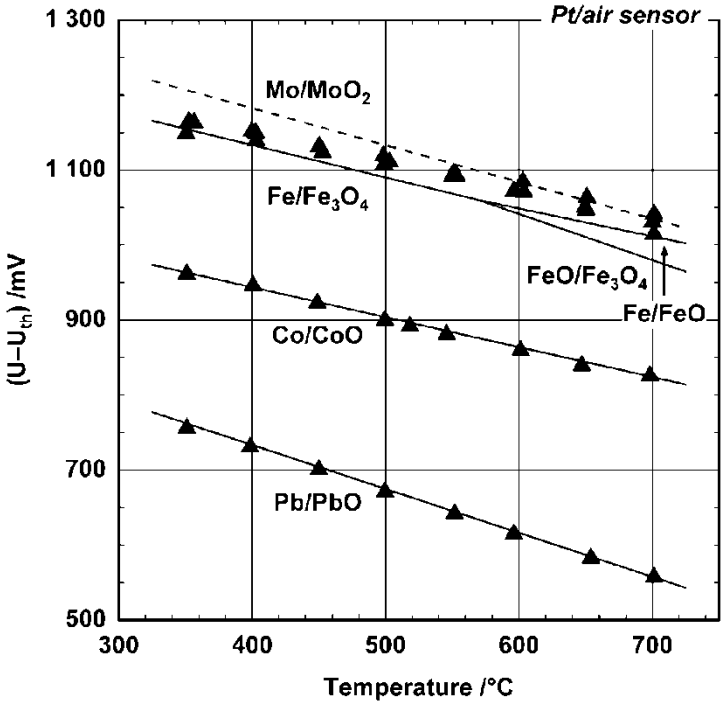
- Long electrolyte tube (Ø 6×255 mm)
- Polymer sealing ring in sufficient distance from the liquid metal
- Cooling fins for reducing the thermal load on the sealing ring
- Steel sheath for protecting the electrolyte from shear forces, serving as electric lead on the liquid-metal side
- Reference electrodes
  - (Steel)Pt/air
  - (Mo)Bi/Bi_2O_3





Calibration of Pt/air Sensor

Accuracy of measurement resulting from comparison with metal/metal-oxide equilibria adjusted in LBE



Fe oxide equilibria

- Stepwise cooling or heating
- Ar-15% H_2 bubbling continuously through the LBE (5 ml/min) or quasi-stagnant
- Oxygen potentials move from Fe-oxide to Mo/MoO_2 equilibrium with temperature variation (Mo comes from wire submerged in the LBE)

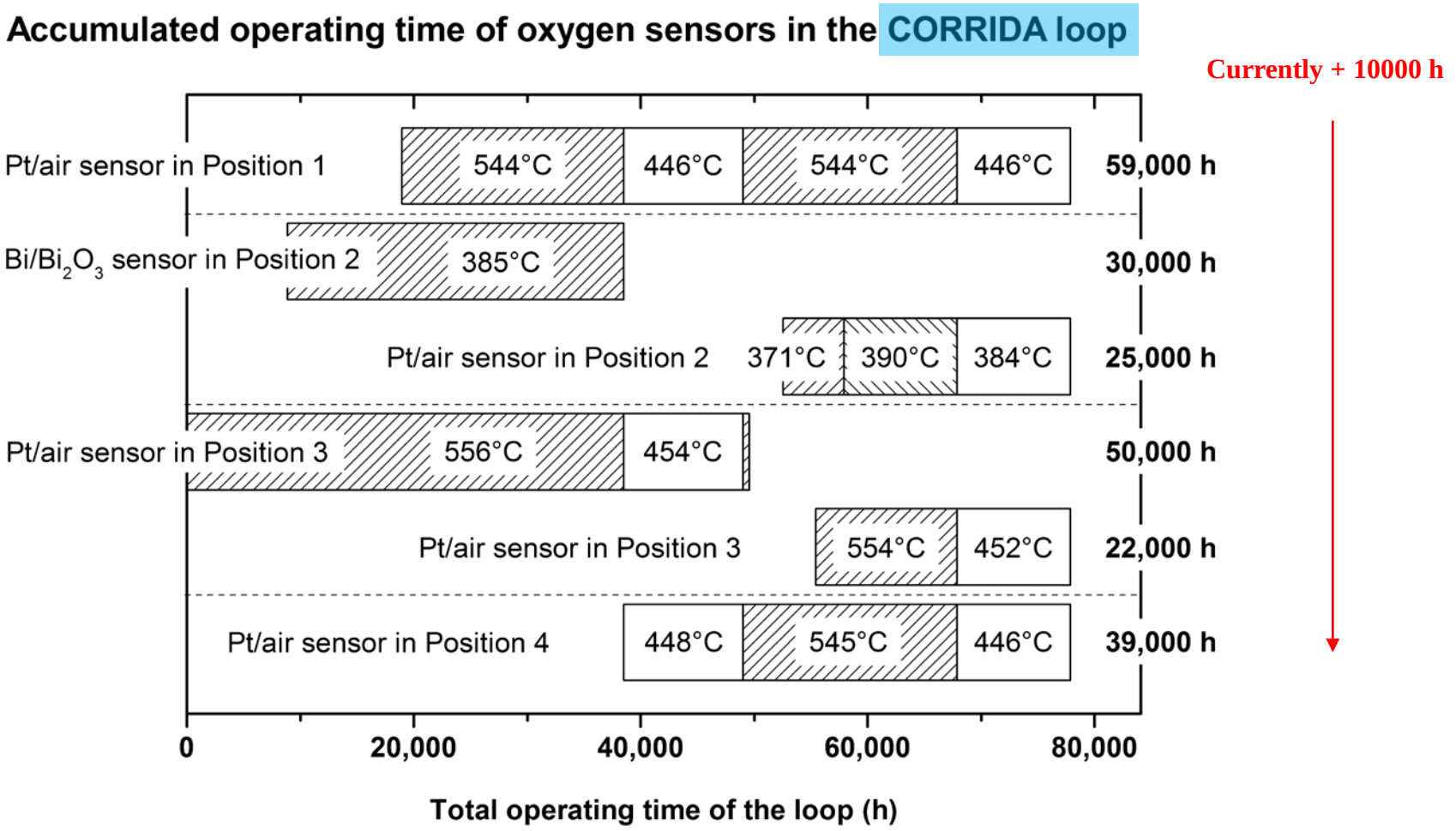
Co/CoO

- Stepwise cooling
- Ar 5.0 bubbling continuously through the LBE (5 ml/min)
- Periodically addition of air (5 ml/min) at 700 and 650°C
- Maximum deviation from theoretical prediction < 6 mV

Pb/PbO

- Stepwise cooling
- Ar 5.0 bubbling continuously through the LBE (5 ml/min)
- Maximum deviation from theoretical prediction < 4 mV

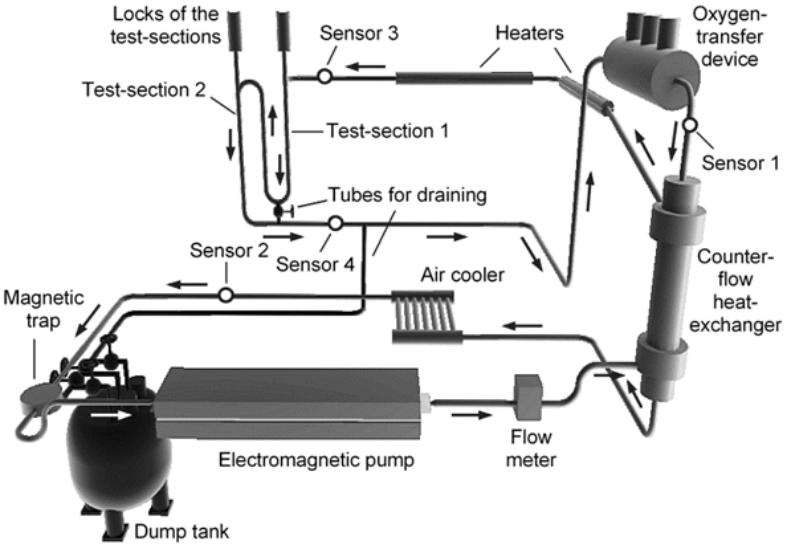
Lifetimes of Oxygen Sensors



Corrosion testing in HLMs

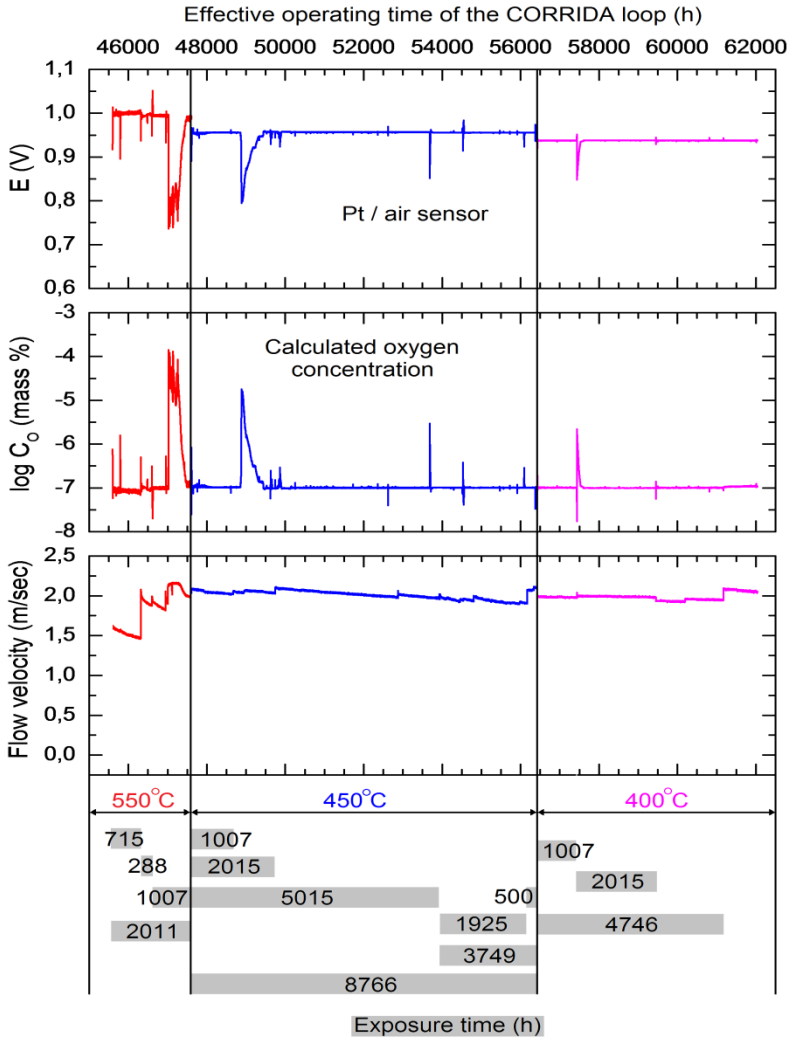
CORRIDA

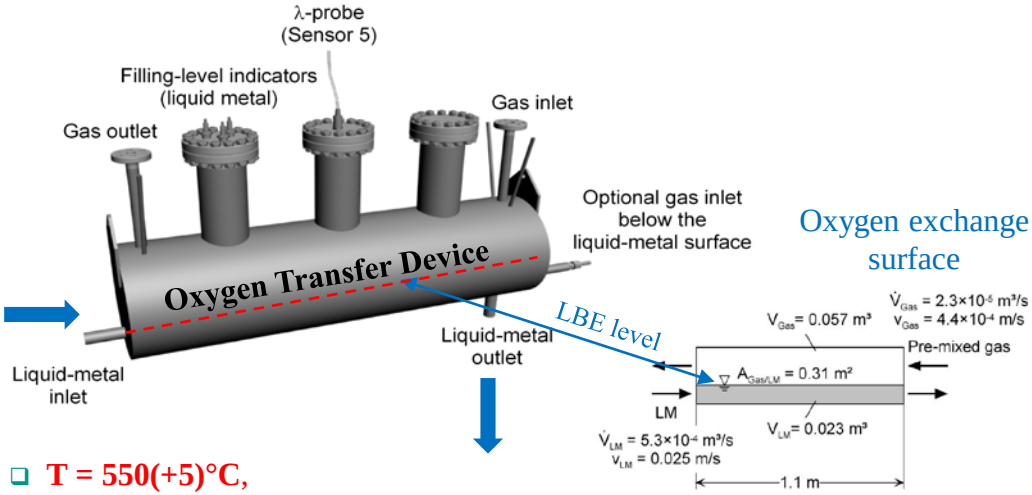
Testing characteristics	Exposure to flowing LBE, typically 2 m/s. 1000 kg circulating LBE (5.3 kg/s). Several steel samples simultaneously exposed in vertical test-sections. Oxygen control via gas with variable oxygen partial pressure. Large internal steel surface in contact with the liquid metal. Temperature 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 since mid 2003

Gas Phase Oxygen Transfer





- **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

FJOH 2016 Relevant 9% Cr Steels for ADS and LFR

Concentration (in wt%) 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
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)

Elements besides Cr that are likely to improve oxidation performance

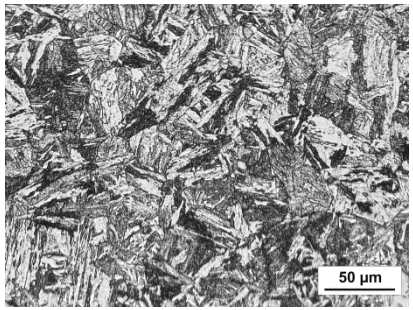
Microstructure

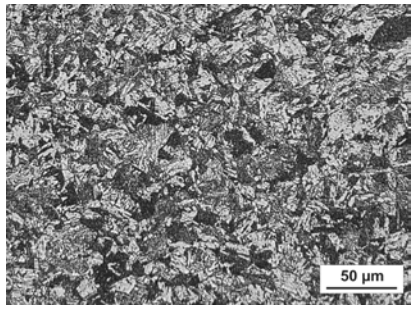
Fully martensitic: E911, T91-A

T91-B

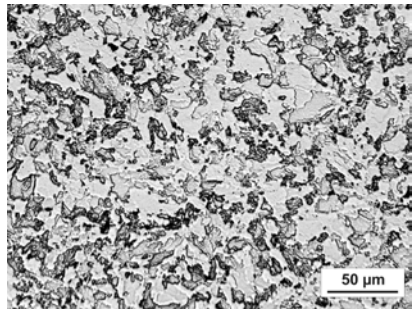
Grain size

EUROFER





Mainly ferritic: ODS-A, ODS-B

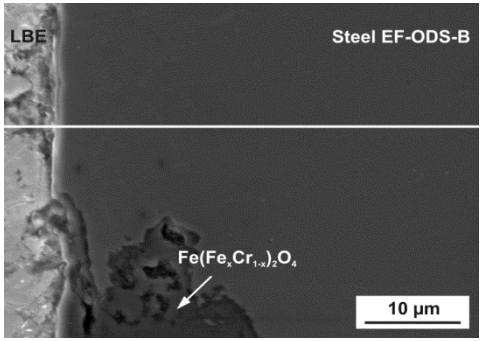


Corrosion Phenomena of 9% Cr Steels in LBE

T = 450 -550°C, v = 2 m/s, 10^{-6} wt% O

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)

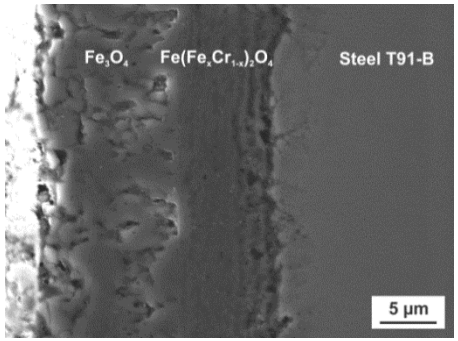


550°C

Scale failure at high local c_O (?)

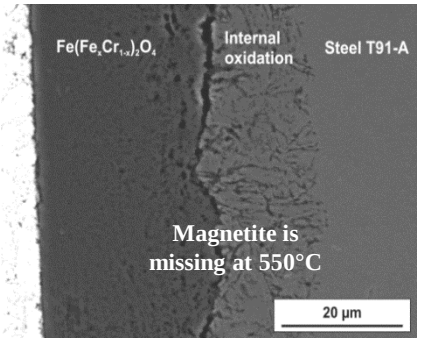
Scale failure at low local c_O (?)

Accelerated oxidation



450°C

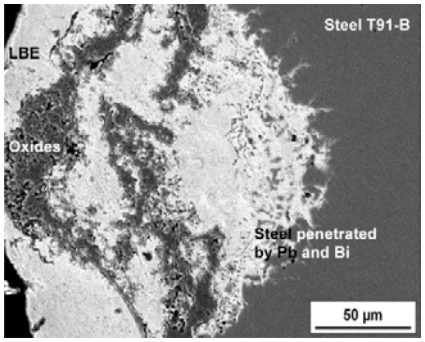
- Typical and, finally, the general corrosion process for 9% Cr steel



550°C

Solution-based corrosion

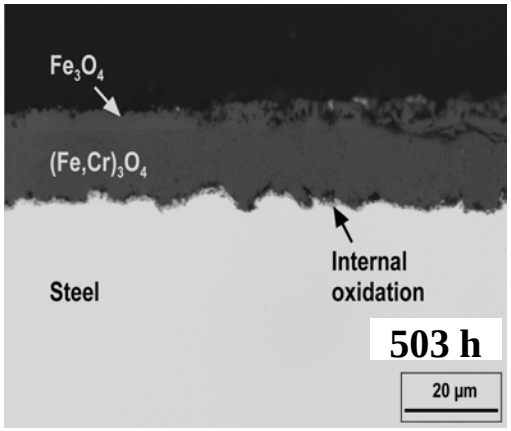
- Steel elements first dissolve but may re-precipitate in the form of oxides
- Intermittent solution participates in accelerated oxidation processes or solution outweighs oxidation
- Substantial loss of material!

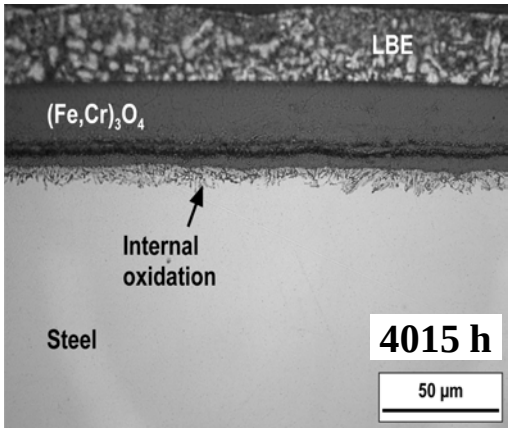


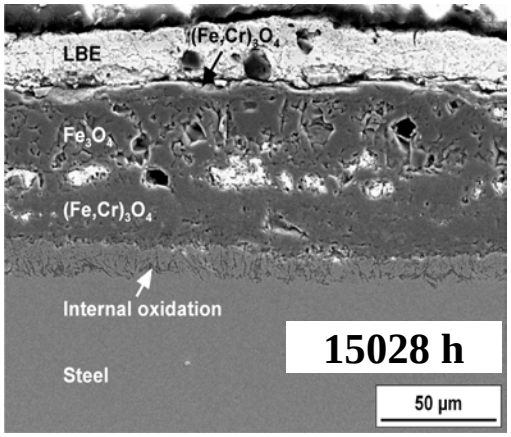
550°C

Corrosion Phenomena of 9% Cr Steels in LBE

T = 550°C, v = 2 m/s, 1.6×10^{-6} wt% O





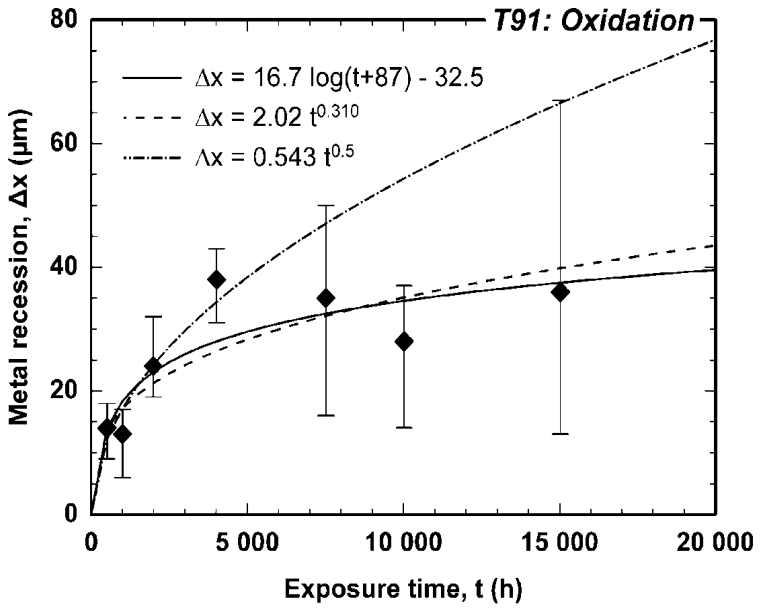


- **Oxidation**
- **Oxide scale consists of**
  - **Magnetite (Fe_3O_4)**
  - **Cr-deficient spinel ($Fe(Fe_xCr_{1-x})_2O_4$)**
  - **Internal Oxidation Zone (IOZ)**
- **Magnetite is mostly missing, i. e., Fe is partially dissolved in the liquid metal (or eroded after Fe_3O_4 formation?)**
- **Inclusions of Pb and Bi inside the scale, espesially after long exposure times**

Corrosion Phenomena of 9% Cr Steels in LBE

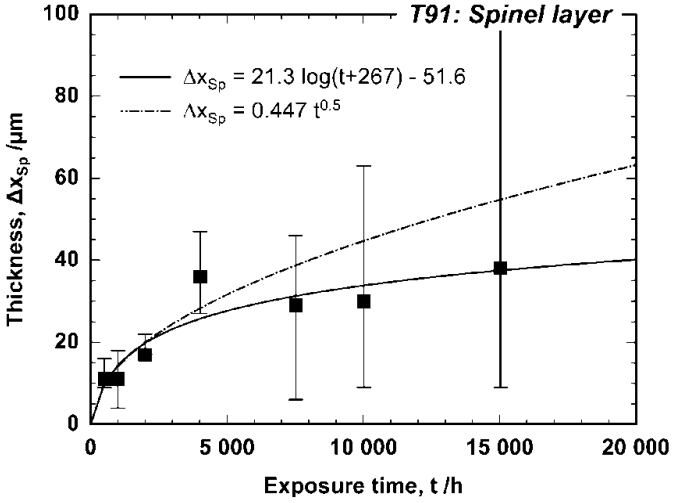
T = 550°C, v = 2 m/s, 1.6×10^{-6} wt% O

- **Metal recession (loss of cross-section)**
- **Compromises the structural integrity of plant components**
- **Determined from measurements in the LOM (generally six measurements per investigated cross-section)**
- **Includes internal oxidation**
- **Local variation significantly increases with increasing exposure time**
- **Optimistic prediction: 50–70 µm after 100,000 h**
- **Worst-case: 100 µm after 4 years**



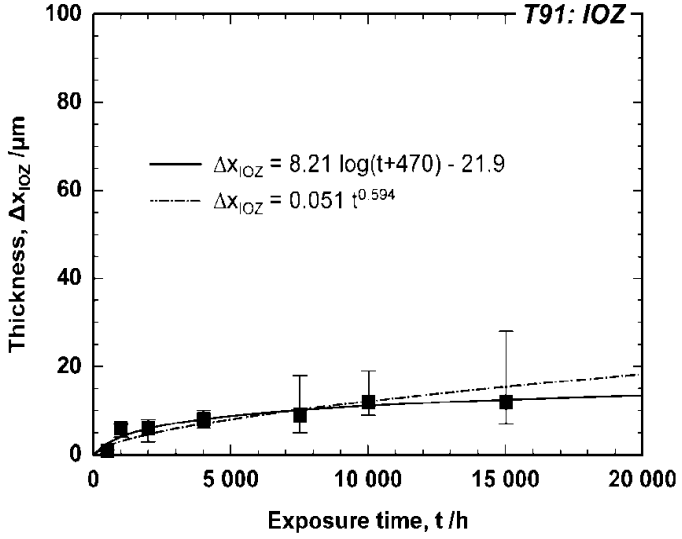
Corrosion Phenomena of 9% Cr Steels in LBE

T = 550°C, v = 2 m/s, 1.6x10^{-6} wt% O



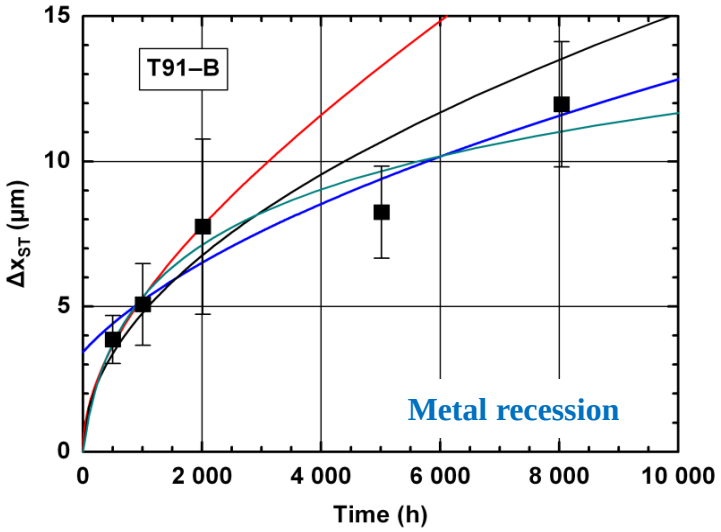
- Thickness of different layers of the oxide scale
- May affect heat transfer in the case of thermally-loaded plant components
- Generally twelve measurements per investigated cross-section
- Thickness of spinel layer significantly varies locally with increasing exposure time
- Average thickness of the spinel layer is in the order of the metal recession

Fe flux into the LBE can be estimated from the spinel layer thickness



Corrosion Phenomena of 9% Cr Steels in LBE

T = 450°C, v = 2 m/s, 1.6x10^{-6} wt% O



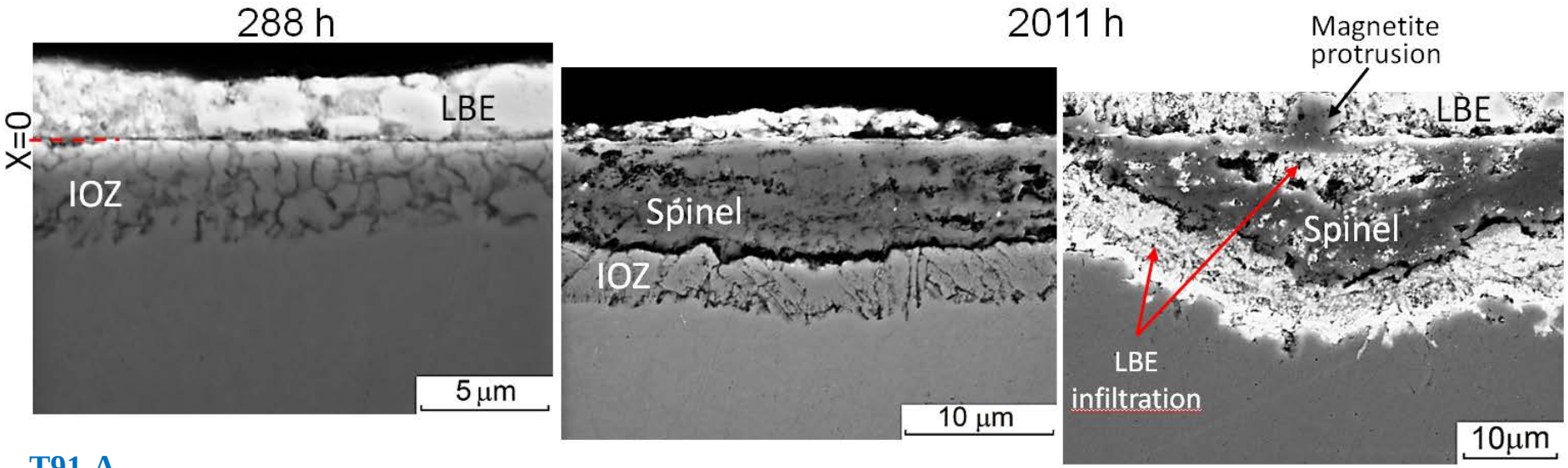
Parabolic:	**$\Delta x^2 = k_2 t$**
Parabolic after faster kinetics:	$\Delta x^2 = k_2 t + C_2$
Paralinear model of oxide scale growth	
Logarithmic:	$\Delta x = k_{log} (t + t_0) + C_{log}$

Exposure time (years)	**1**	**5**	**10**
T91-A → Upper limit of Cr content specified for T9			
Δx_M (µm)	10	13 – 22	13 – 31
Δx_{SP} (µm)	7	8 – 14	8 – 20
Δx_{ST} (µm)	9	20	28
T91-B → Lower limit of Cr content specified for T91			
Δx_M (µm)	12	15 – 26	15 – 36
Δx_{SP} (µm)	8	10 – 16	10 – 23
Δx_{ST} (µm)	12	26	37

Corrosion Phenomena of 9% Cr Steels in LBE

T = 550°C, v = 2 m/s, 10^{-7} wt% O

- **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

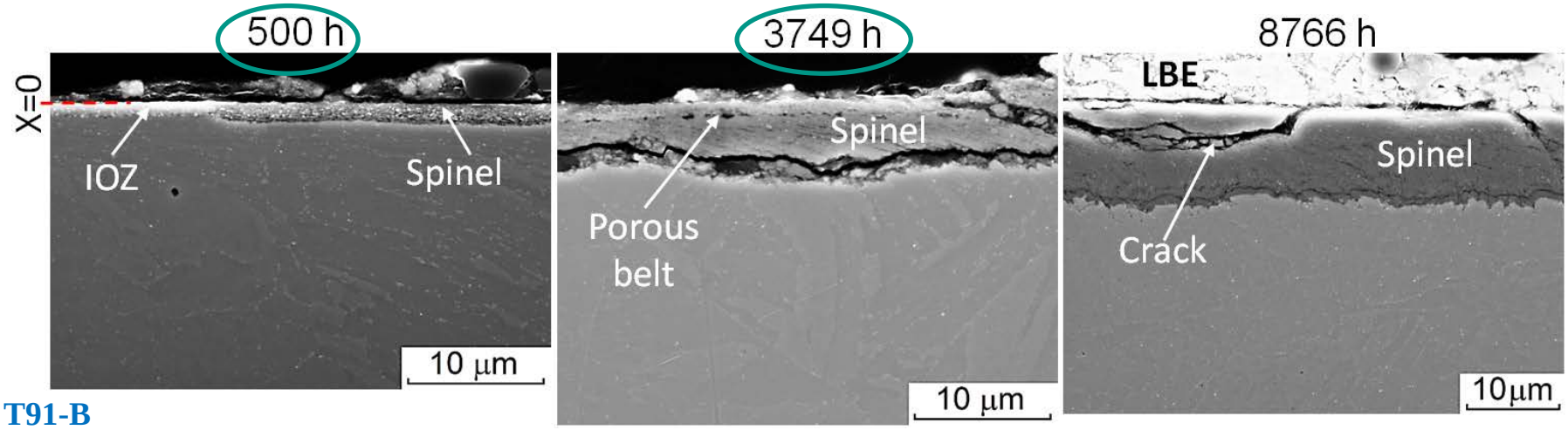


T91-A

Corrosion Phenomena of 9% Cr Steels in LBE

T = 450°C, v = 2 m/s, 10^{-7} wt% O

- **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



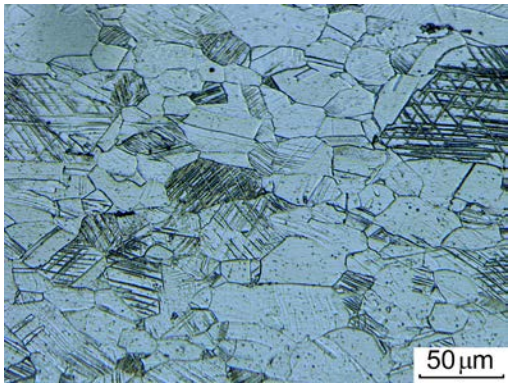
T91-B

Relevant Austenitic Steels for ADS and LFR

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

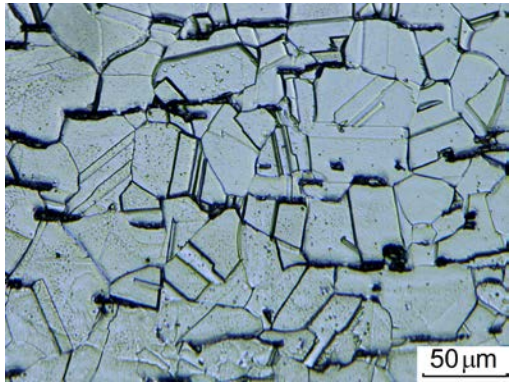
Austenitic steels	Cr	Ni	Mo	Mn	Si	Cu	V	W	Al	Ti	C	N	P	S	B
316L	16.73	9.97	2.05	1.81	0.67	0.23	0.07	0.02	0.018	-	0.019	0.029	0.032	0.0035	-
1.4970	15.95	15.4	1.2	1.49	0.52	0.026	0.036	< 0.005	0.023	0.44	0.1	0.009	< 0.01	0.0036	< 0.01
1.4571 (316-Ti)	17.50	12	2.0	2.0	1.0	-	-	-	-	0.70	0.08	-	0.045	0.015	-

1.4970 (15-15 Cr Ni)



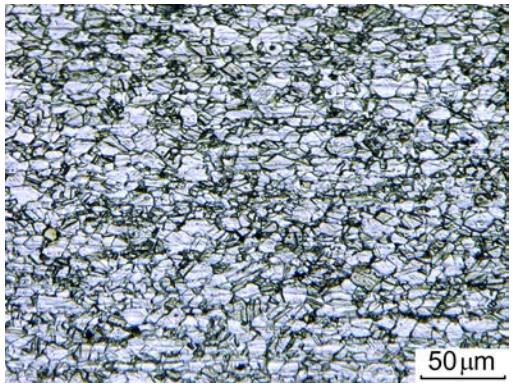
- HV_{30} = 253;
- Grain size ranged from 20 to 65 µm;
- Intersecting deformation twins.

316L



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

1.4571 (316-Ti)



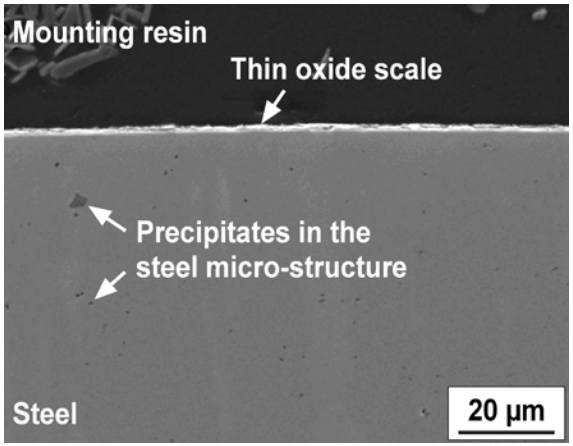
- HV_{30} = 245;
- Grain size averaged 15 µm (G 9.5).

Corrosion Phenomena of Austenitic Steels in LBE

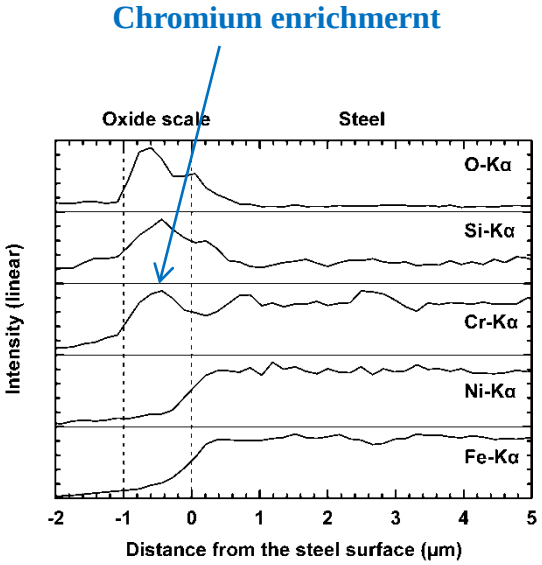
T = 550°C, v = 2 m/s, 10^{-6} wt% O

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} wt% 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 (?)*



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



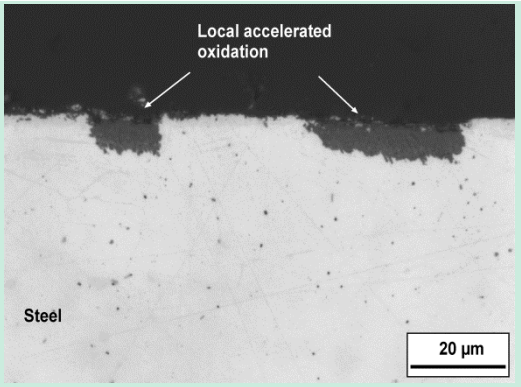
Corrosion Phenomena of Austenitic Steels in LBE

T = 550°C, v = 2 m/s, 10^{-6} wt% O

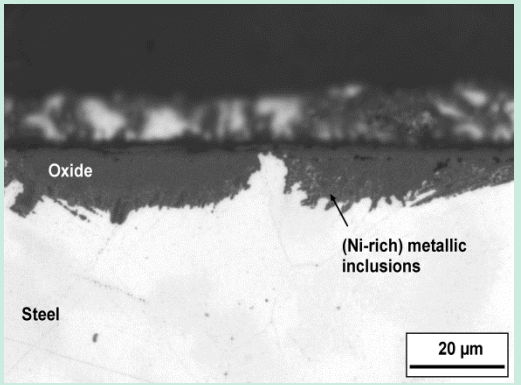
Accelerated oxidation

- 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 $c_O \approx 10^{-6}$ wt%



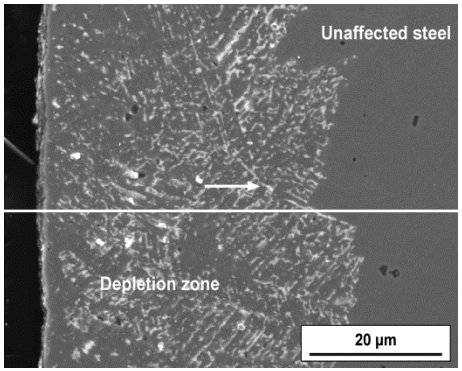
After exposure for 10,006 h at 550°C and variying c_O

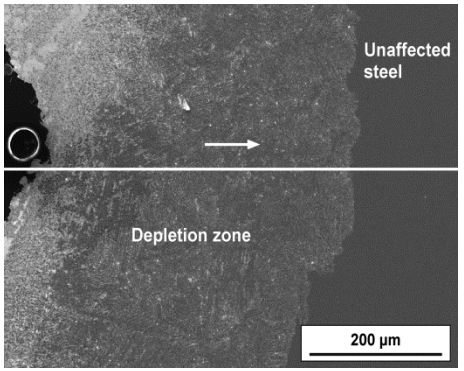
Corrosion Phenomena of Austenitic Steels in LBE

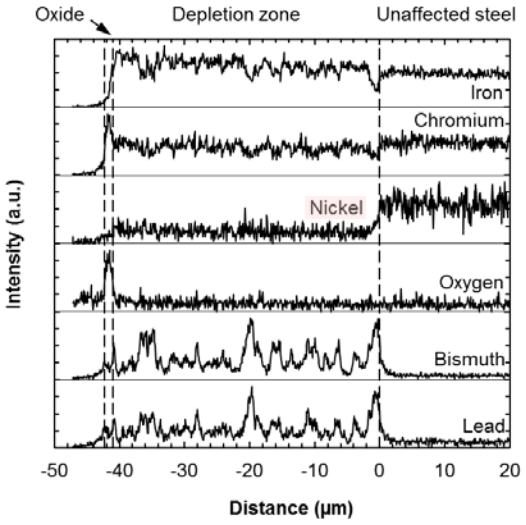
1.4571 after exposure for 5,012 h at 550°C and $c_O \approx 10^{-6}$ wt%

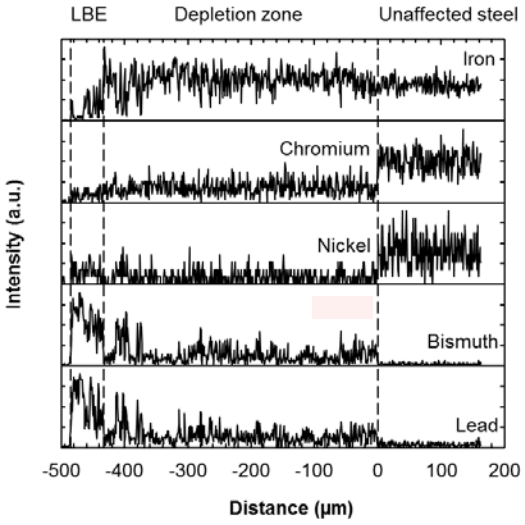
T = 550°C, v = 2 m/s, 10^{-6} wt% O

1.4571 after exposure for 5,012 h at 550°C and $c_O \approx 10^{-6}$ wt%









Non-selective leaching (Ni, Cr)

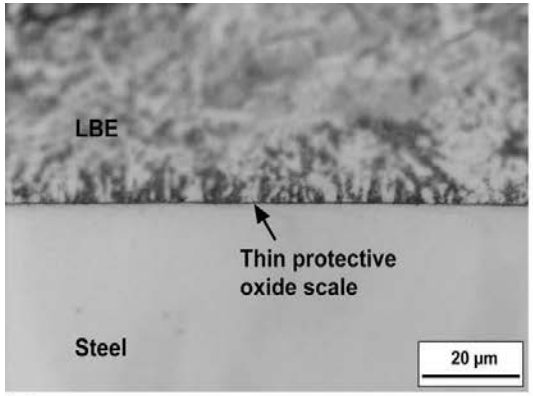
- Starts locally with preferential dissolution of Ni and penetration of Pb and Bi into the depletion zone
- Phase transition from austenite into ferrite resulting from Ni depletion
- Dissolution of Cr after oxygen depletion in the liquid metal penetrating the steel (critical penetration depth)
- In general, insignificant amounts of Cr oxide inside or on the surface of the depletion zone
- Removal of loosened steel grains bythe liquid-metal flow in a later stage of severe selective leaching

Corrosion Phenomena of Austenitic Steels in LBE

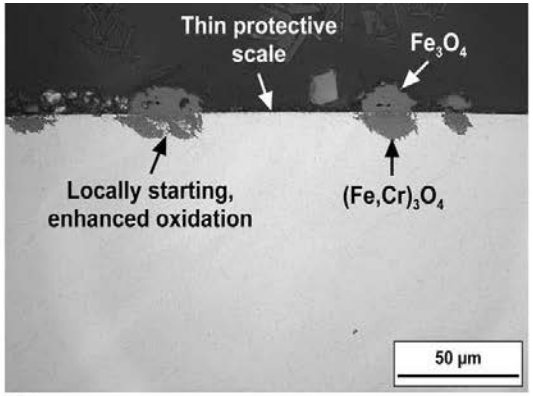
General Corrosion Appearance of Austenitic Steel Fe-17Cr-10Ni (316L) at 550°C

10^{-6} mass%O

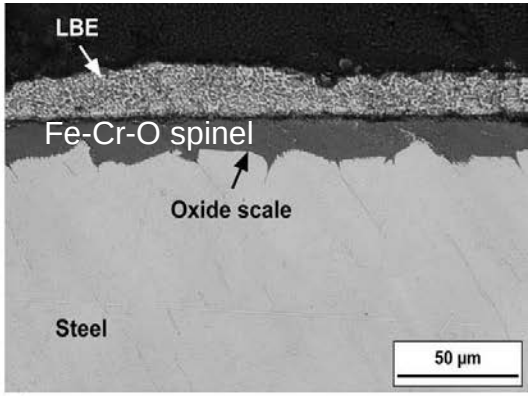
503 h



4015 h

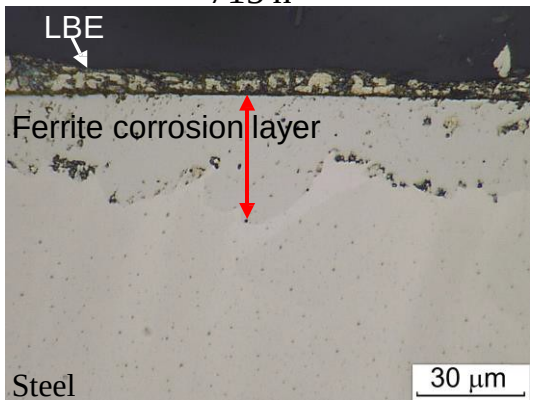


15028 h

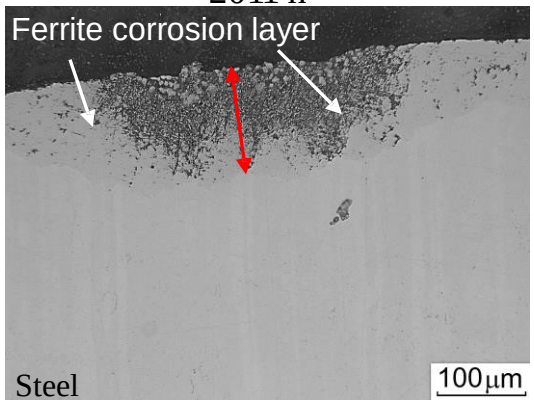


10^{-7} mass%O

715 h



2011 h



Ferrite - corrosion layer depleted in Cr and Ni and penetrated by Pb and Bi.

- **At 10^{-6} mass%O**, the **<u>oxidation</u>** – main corrosion mode resulted in general material loss of ~18µm (±10) after 15000h;
- **At 10^{-7} mass%O** – the **<u>dissolution</u>** is a main corrosion mode resulted in material loss ~51µm (±37) after 2011h.

Corrosion Phenomena of Austenitic Steels in LBE

Qualitative Corrosion Appearance of 316L at 450°C depending on Oxygen Concentration

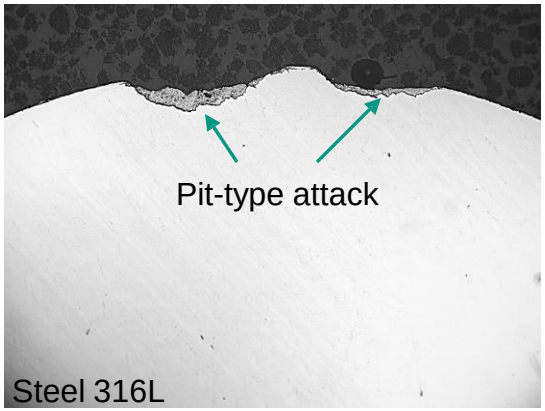
10^{-7} mass%O

- Protective scaling: Cr-based oxide film ≤1µm;
- Incubation time ~3000h;
- Solution-based attack resulted in formation of ferrite layer with general material loss of ~8µm (±6) after 8766h;
- Local corrosion attack with maximum depth of 210µm after 8766h.

10^{-6} mass%O

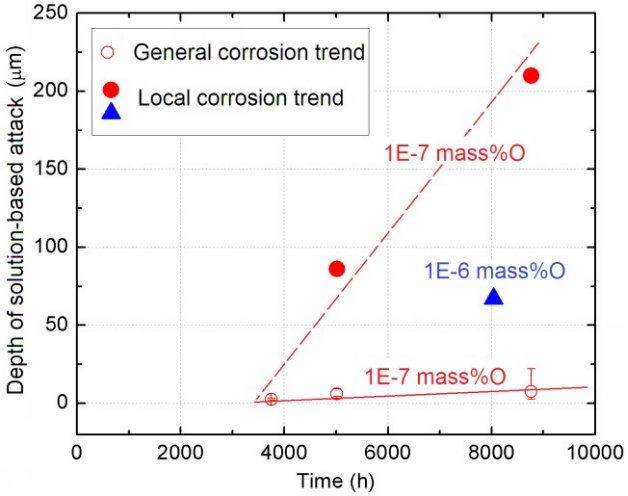
- Oxidation: Cr-based oxide and Fe-Cr spinel;
- Local deep corrosion attack with maximum depth of 67µm after 8039h.
- Incubation time for local attack is >5000h.

Local corrosion appearance

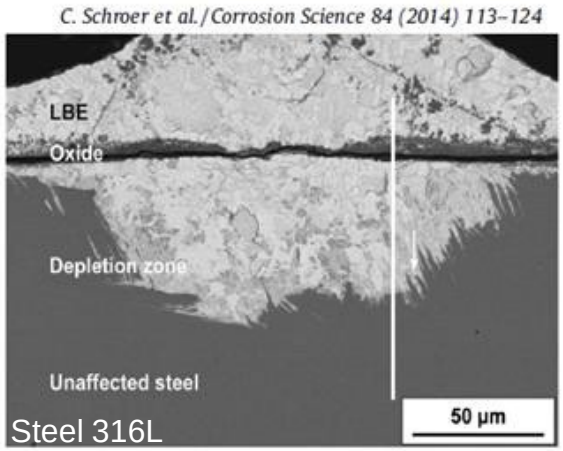


8766h

Quantitative output for solution-based corrosion attack



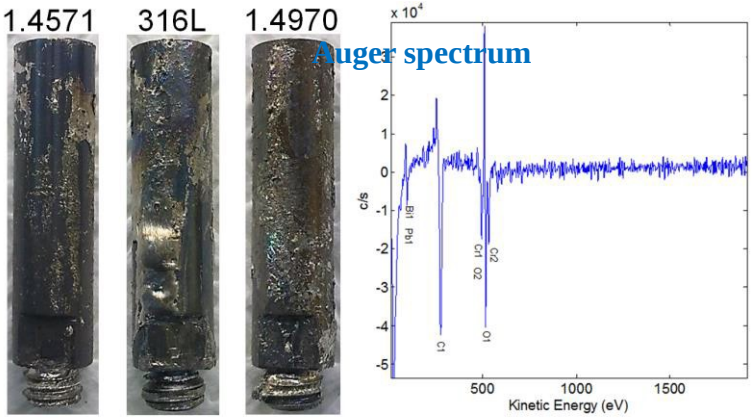
Local corrosion appearance



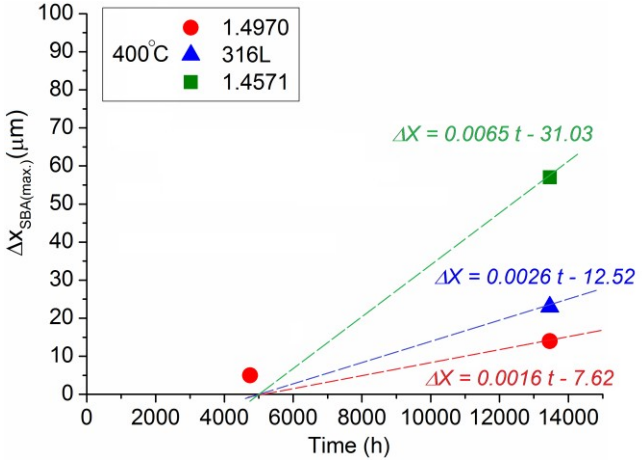
8039h

Corrosion Phenomena of Austenitic Steels in LBE

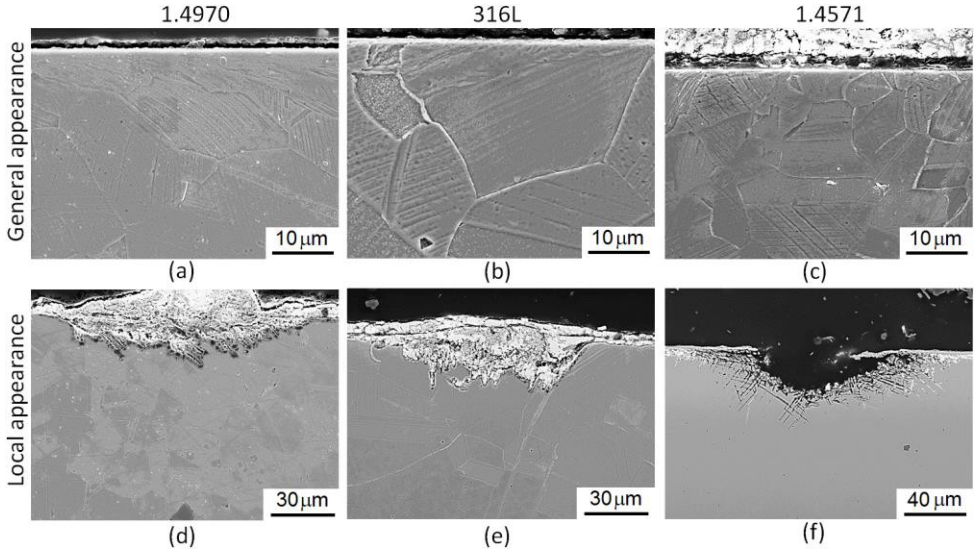
Corrosion Appearance of Austenitic steels at 400°C after 13194 h in Pb-Bi with 10^{-7} mass%O



Cr-base oxide film is formed.



Maximum depth of dissolution attack

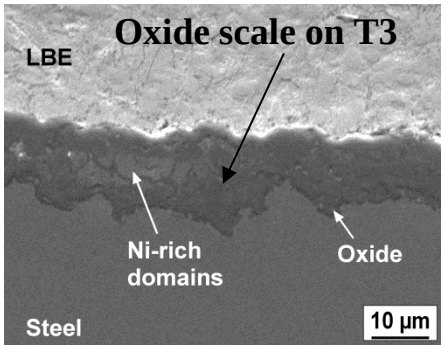


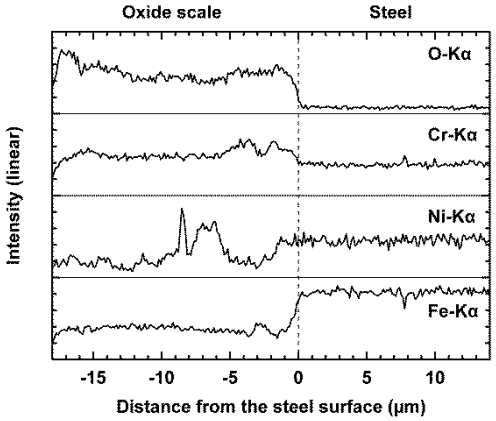
- **Steels show generally good corrosion resistance** in Pb-Bi with 10^{-7} mass%O for up to 13194 h;
- **Slight general oxidation** (Cr-based oxide film) along with very **rare local pit**-type solution-based corrosion attack are observed;
- The incubation time for pit-type attack is ~4500 h;
- After ~13194 h, the maximum pit depth observed was ~ 14, 23 and 57 µm for 1.4970, 316L and 1.4571, respectively;
- Local corrosion rate ~ 6-26 µm/year.

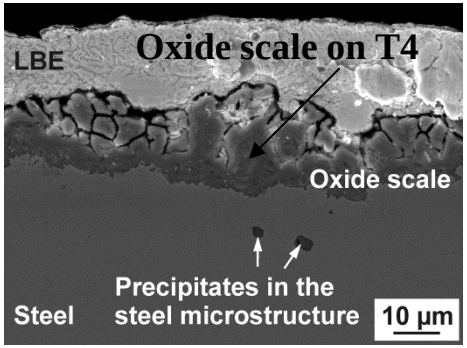
Corrosion Phenomena of Austenitic Steels in LBE

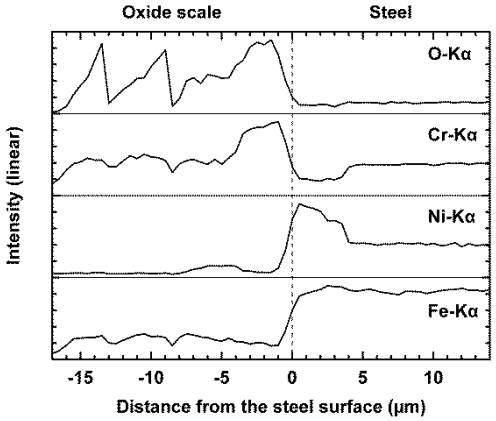
T = 550°C, v = 2 m/s, 10^{-6} wt% O

- **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

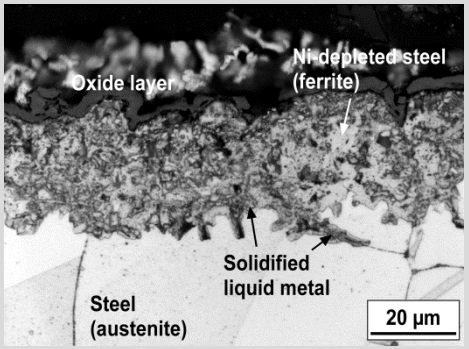


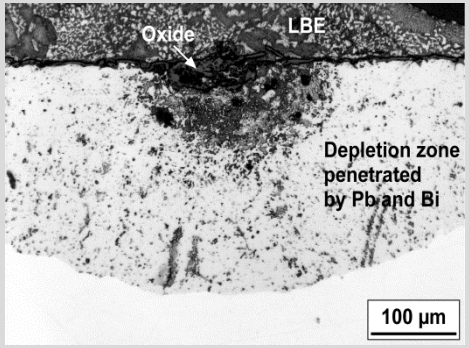






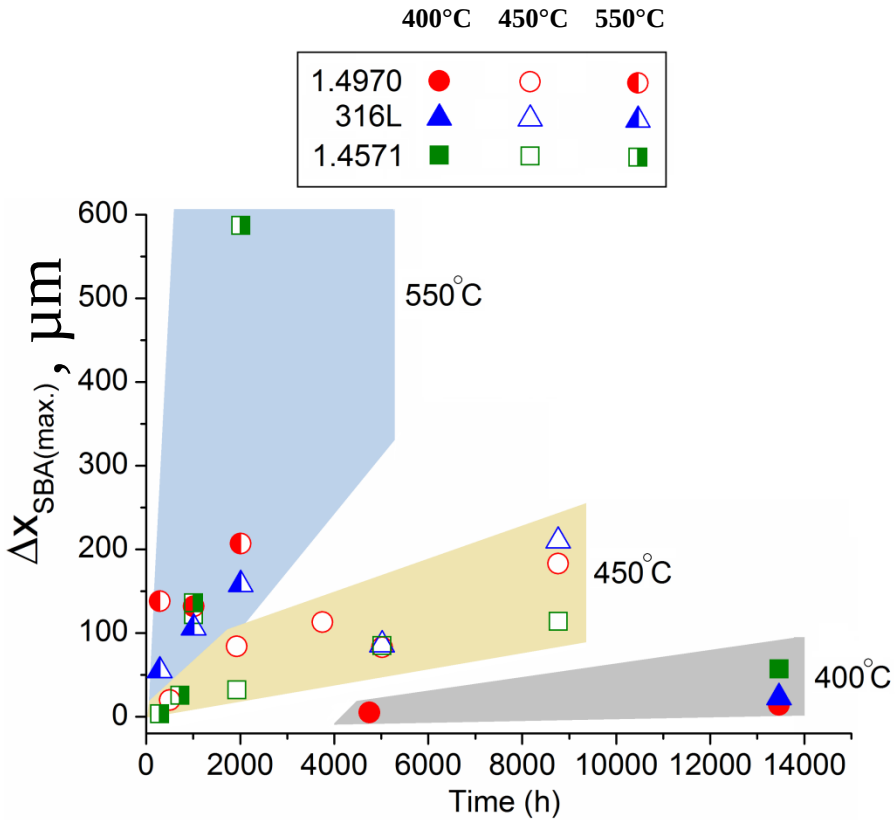
Corrosion scales typically observed on T1 and T2





Corrosion Phenomena of Austenitic Steels in LBE

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.

Thank you for your attention