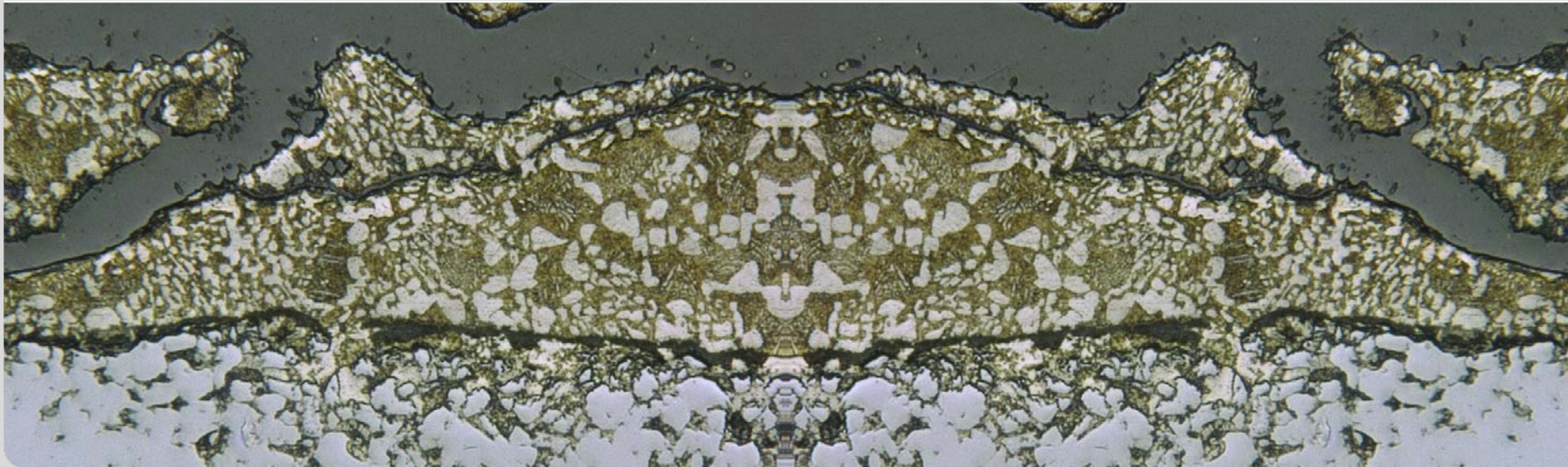



Materials Compatibility in Heavy Liquid Metals for ADS Applications

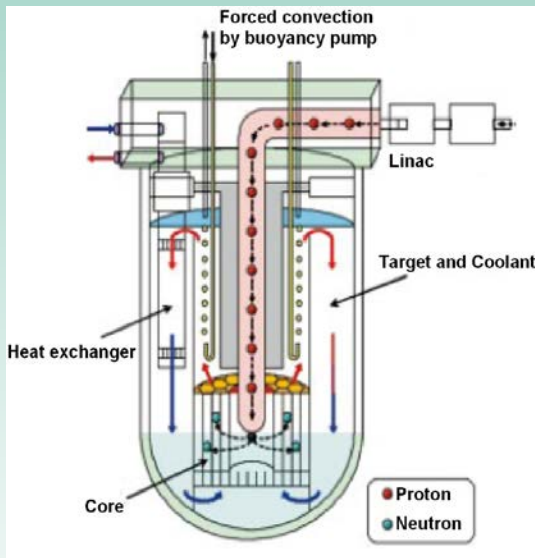
Jürgen Konys

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



Outline

- 
- Introduction
 - HLM chemistry
 - European support for MYRRAH
 - Corrosion of 9% Cr steels in LBE
 - Corrosion of austenitic steels in LBE
 - Conclusions

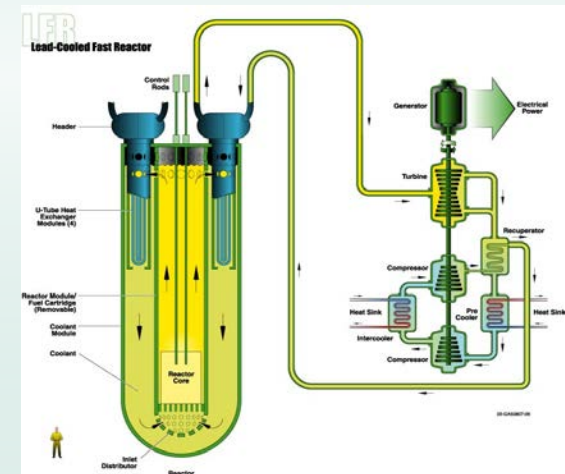


Accelerator Driven (Subcritical) System

- 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



Application of Heavy Liquid Metals (HLMs)

❑ Favourable properties of liquid metals

- ❑ High thermal conductivity and boiling point → Efficient heat transfer medium/coolant for **thermal energy conversion**
- ❑ Reasonably low dynamic viscosity
- ❑ Some show minimum interaction with neutrons (e.g., sodium and lead) → Essential for **fast neutron reactors**
- ❑ Liquid heavy metals release neutrons under proton irradiation (e.g., mercury, lead and bismuth) → Allows for sub-critical nuclear fuel in a **proton-accelerator driven system**
- ❑ Liquid breeder and coolant for fusion application → As eutectic Pb-16Li alloy in **fusion**



❑ Compatibility between liquid metals and steels?

- ❑ Major steel elements are soluble in liquid metals
- ❑ 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

Impact of oxygen on steel corrosion in HLMs

❑ “Absence” of oxygen (Pb-16Li)

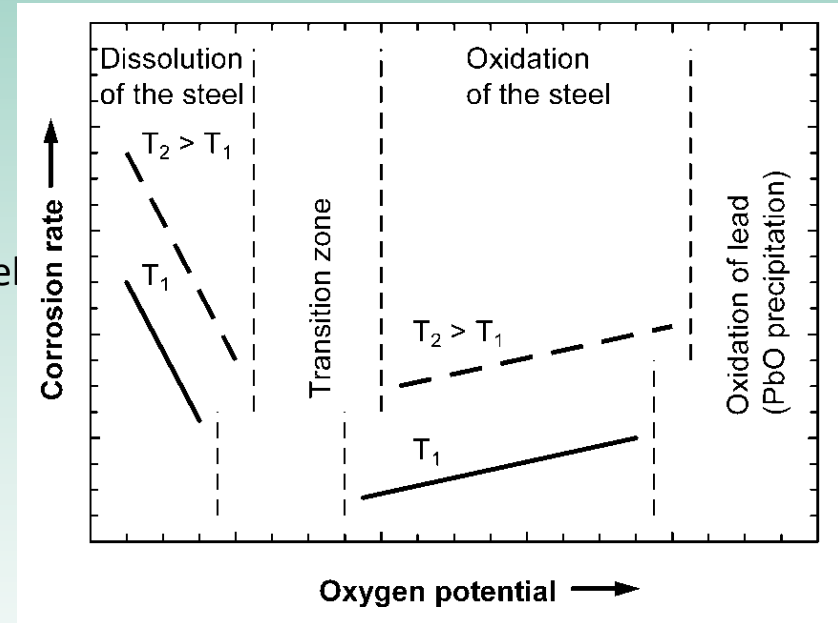
- Chemical oxygen potential too low for remarkable interactions with steel elements
- Steel elements dissolve in the liquid metal
- Absorption of liquid metal constituents by the steel
- Formation of intermetallic phases

❑ 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

CORRIDA

Testing characteristics

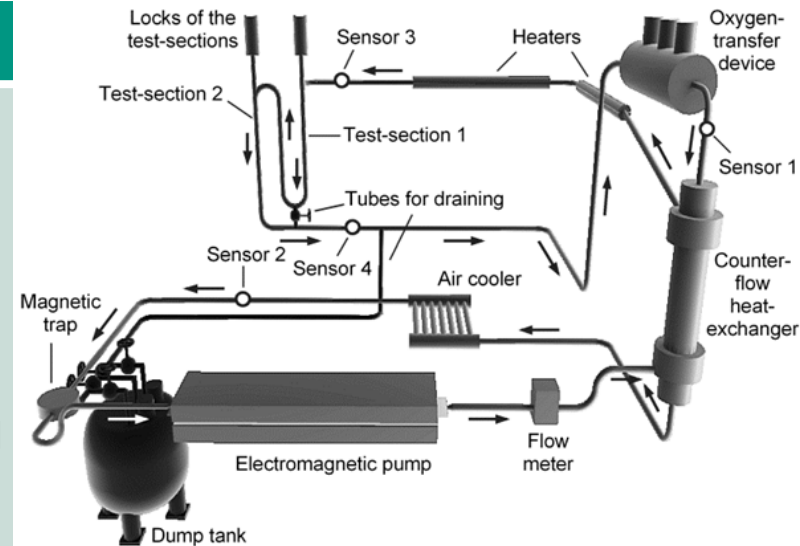
Exposure to flowing LBE, typically 2 m/s. 1000 kg circulating LBE (5.3 kg/s)
Several steel samples simultaneously exposed in vertical test sections.
Oxygen control via gas with variable oxygen partial pressure. Large internal steel surface in contact with the liquid metal. Temperature difference along the loop of ~100–150°C.

Sample geometry

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

Determination of oxygen content

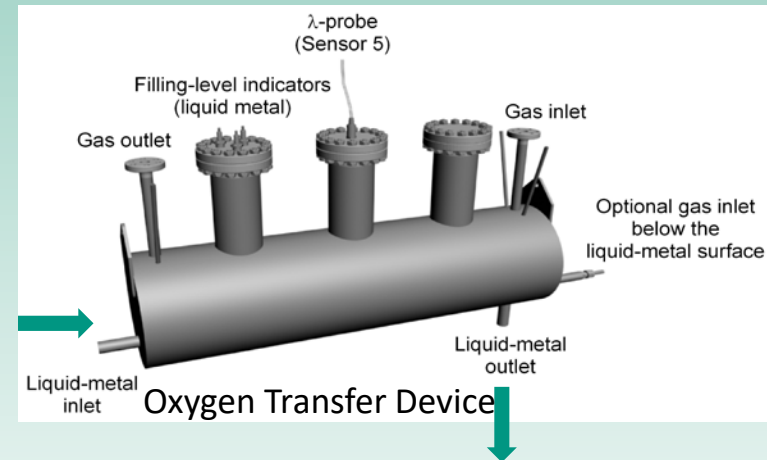
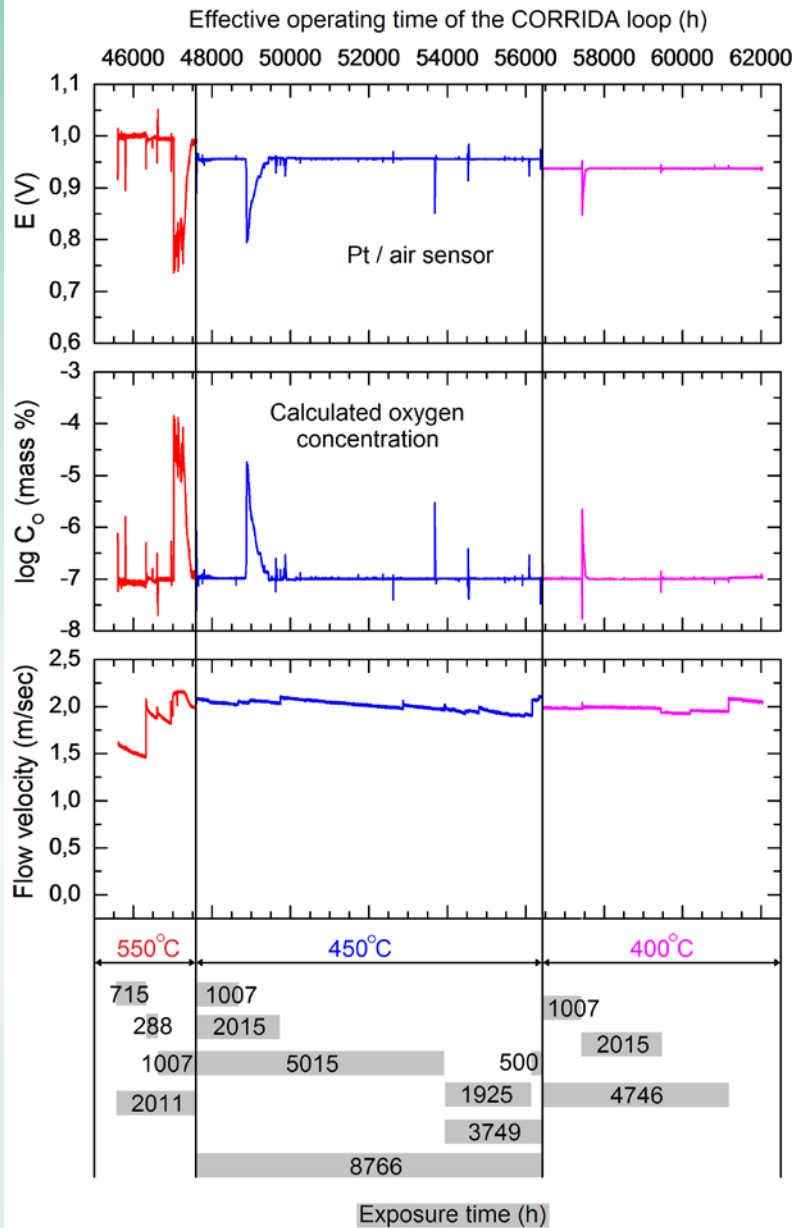
Four potentiometric oxygen sensors distributed along the loop.



Constructed and operated at KIT's

Institute for Applied Materials – Corrosion Department → current operational time: ca. 90,000 hours

Monitoring of test parameters



□ **T = 550(+5)°C,**

$T_{\min} \approx 385^\circ\text{C}$, $c_{\text{O}} = 10^{-7}$ mass%, excursion to 10^{-4} – 10^{-5} mass% O,
 $v = 2(+/-0.2)$ m/s, initially 1.5–1.6 m/s,
 $t = 288; 715; 1007; 2011$ h

□ **T = 450(+5)°C,**

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

□ **T = 400(+5)°C,**

$T_{\min} \approx 350^\circ\text{C}$, $c_{\text{O}} = 10^{-7}$ mass%,
 $v = 2(+/-0.2)$ m/s,
 $t = 1007; 2015; 4746$ h; still continuing up to 10,000h

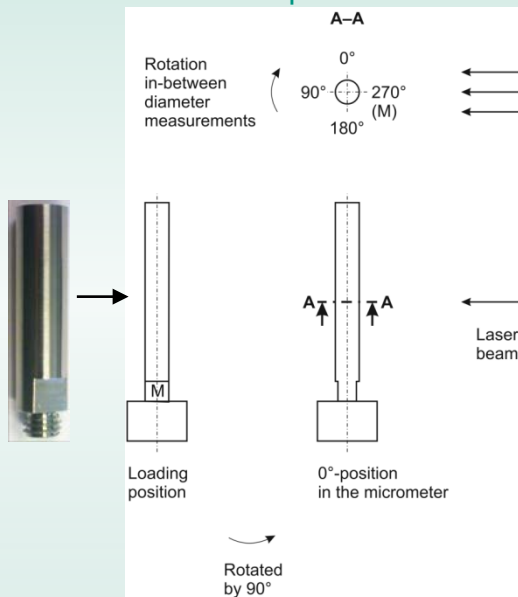
Quantification of corrosion loss (very important!!)

□ 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

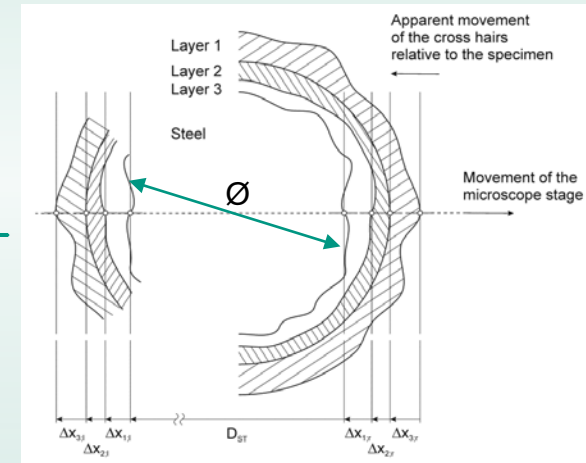
□ Metallographic method (cylindrical specimens)

Initial parameters - \emptyset



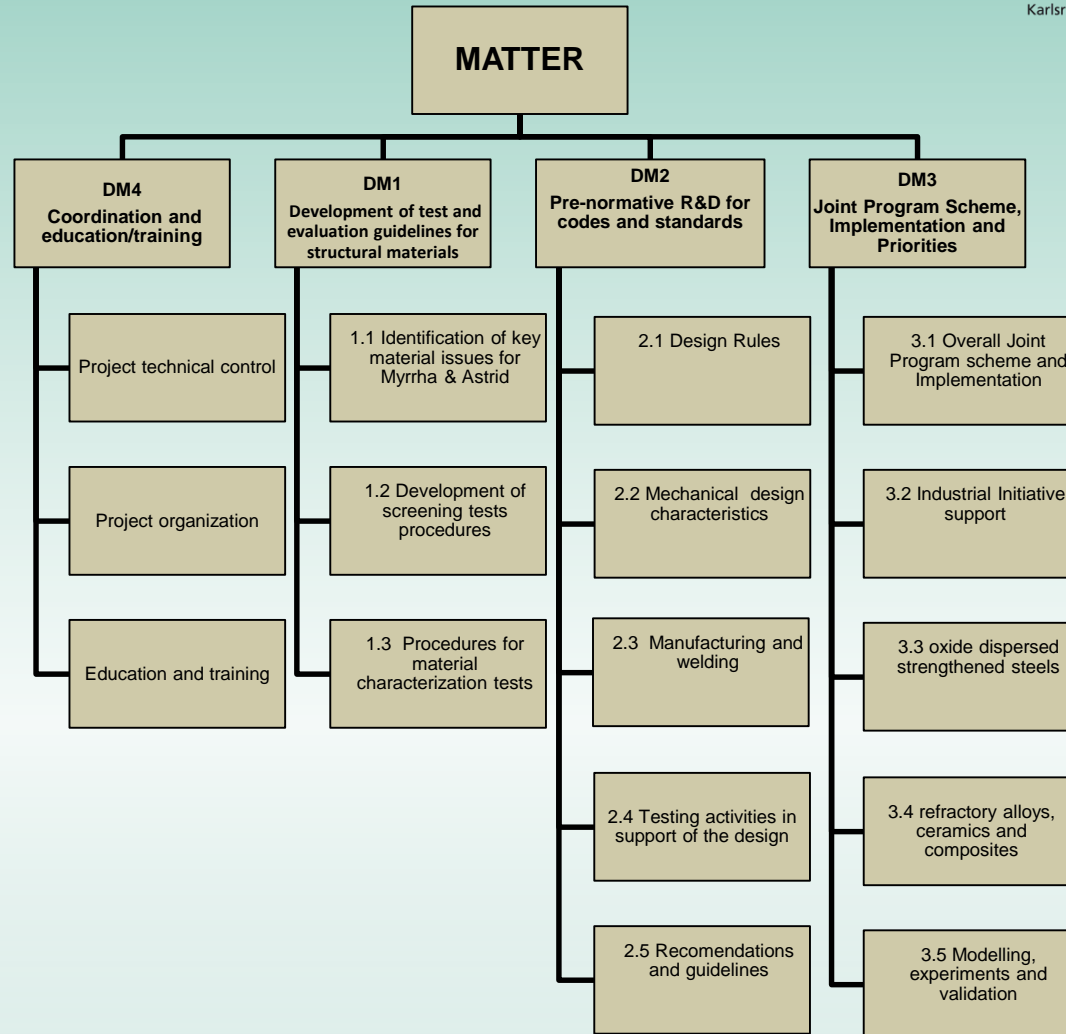
- Measurement of initial diameter in a laser scanner with $0.1 \mu\text{m}$ res.
- Diameter of unaffected material (12 measm. with rotation angle 15°) and thickness of corrosion zones determined in a microscope (LOM) with $1 \mu\text{m}$ resolution
- Occurrence of different corrosion modes on opposing sides of the re-measured diameter is considered in the evaluation (% of surface circumference)

Post-test examination



Transverse circular cross-section

Support for MYRRHA: EU-funded Projects



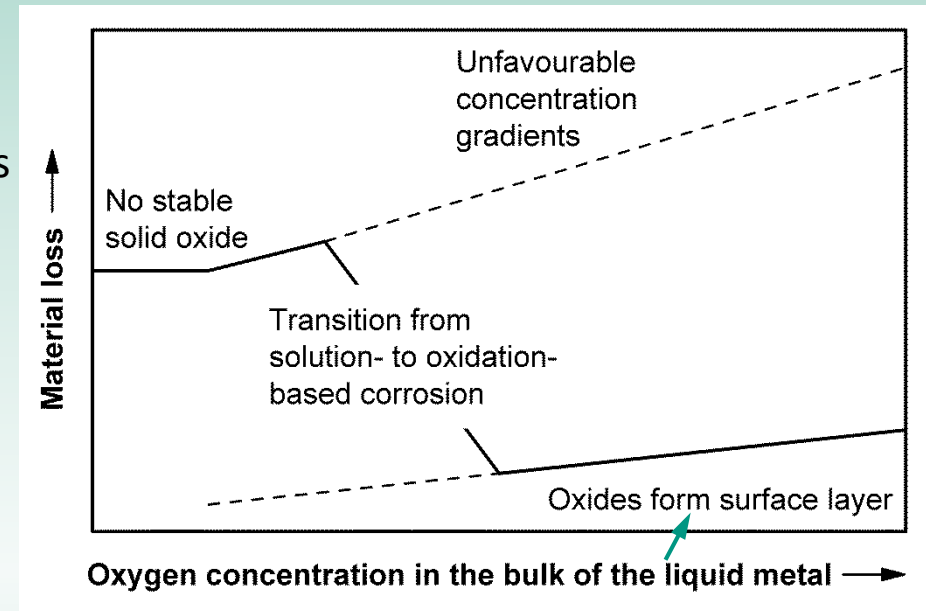
- **MATTER**
Materials **T**esting and **R**ules
- **MatISSE**
Materials **I**nnovations for a
Safe and **S**ustainable nuclear
in **E**urope
- **ESNII+**
Preparatory phase for ESNII:
European **S**ustainable **N**uclear
Industrial **I**ntiative

□ Process medium

- Lead-bismuth eutectic (LBE)
- Addition of oxygen so as to favour oxidation over solution of material elements
- Oxygen activity or concentration required is material- and temperature-dependent

□ Materials

- Austenitic steels:
316L for the main structural components,
15-15Ti in the core
- 9Cr ferritic/martensitic steels:
T91 for parts of the core support and
spallation target assembly



Goal of deliberate oxygen addition

MYRRHA design data used

Design operating parameters

Material	Temperature (°C)	Surface area (m ²)	Oxygen conc. (mass%)	Average flow velocity (m/s)
316L	400	120	~10 ⁻⁷	To be specified
	350	419 (360)		
	310	125		
	270	1697 (1596)		
15-15Ti	410	194	~10 ⁻⁷	To be specified
	270	1150		
T91	450	4	~10 ⁻⁷	To be specified
	350	(59)		
	270	1 (102)		

	Duration (days)	Temperature (°C)	
Start-up	180	270°C	
1st Power cycle	90	Components at design operating temperature; temperature transients	
Downtime	90	270°C	
Early operating stages	2nd Power cycle	90	As above

□ Estimation of corrosion product formation in respect of

- Solution of steel elements by the LBE → **May re-precipitate and contribute to floating solid oxides or plugging**
- Oxygen consumption, i.e., depletion if oxygen is not replaced → **Input for dimensioning appropriate oxygen-transfer devices**
- Uptake/precipitation of solid oxides → **Contributes to deposition of solid matter; input for dimensioning filters or other to remove floating oxides**

□ Work performed

- Analysis of availability of required corrosion data: mechanisms, rate laws, activation energies, incubation times, surface area affected by local processes → **Available data is incomplete, requiring a number of assumptions and simplifications!**
- Simplified spread sheet calculations for design operating conditions of **MYRRHA**, separately for the corrosion modes to be considered
- Specific calculations for reactor start-up and first power cycles

9% Cr-steels tested in the CORRIDA 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–	0.90–	0.90–	0.18–	0.060–	–	–	0.30–	0.10–	0.10–	0.09–
	9.50	1.10	1.10	0.25	0.100	–	–	0.60	0.40	0.50	0.13
EUROFER	8.82	<0.001 0	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 (Y₂O₃)



Elements besides Cr that are likely to improve oxidation performance

Microstructure

Nominally 9 mass% Cr

Fully martensitic:

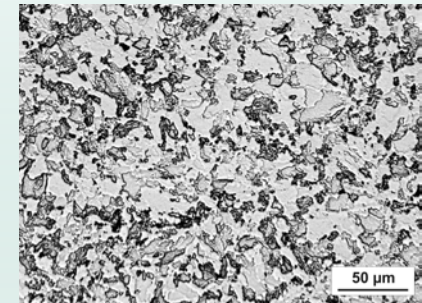
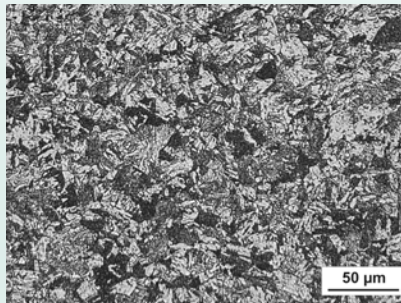
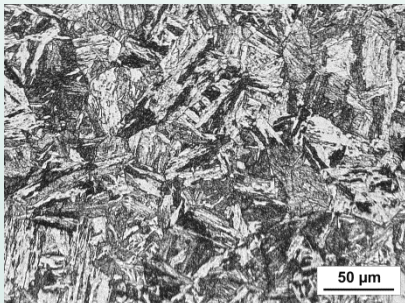
E911, T91-A

T91-B

Grain size

EUROFER

Mainly ferritic: ODS-A, ODS-B



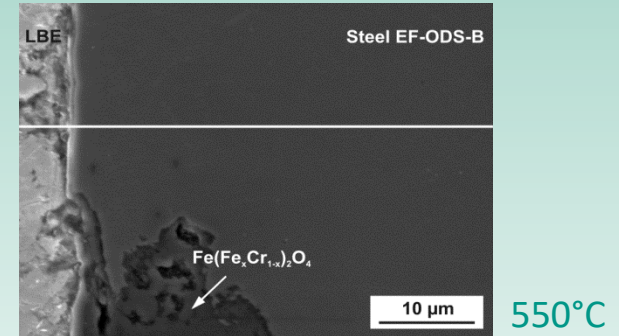
Typical phenomena observed in flowing LBE on 9Cr steels at 450–550°C, 2 m/s and 10^{-6} mass% dissolved oxygen

□ Protective scaling → ideal case!!

- 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)

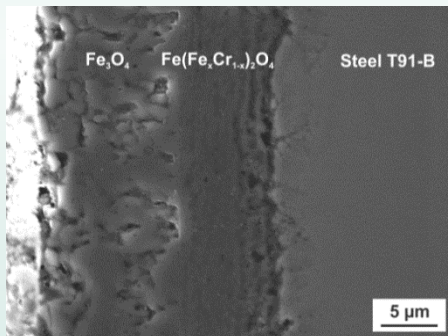
↓ Scale failure at high local c_O (?)

↓ Scale failure at low local c_O (?)

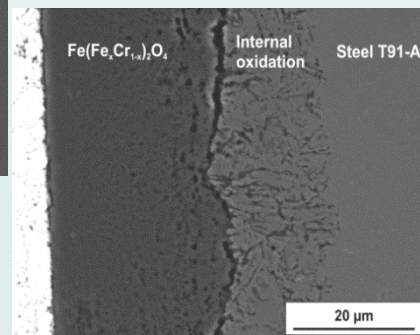


□ Accelerated oxidation → most common

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



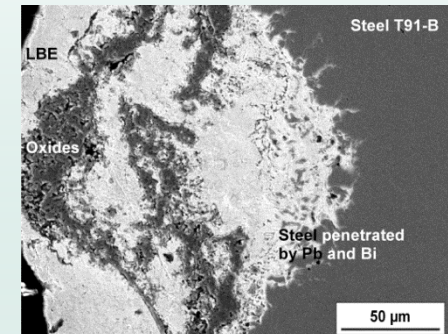
450°C



550°C

□ Solution-based corrosion → seldom, but can happen

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



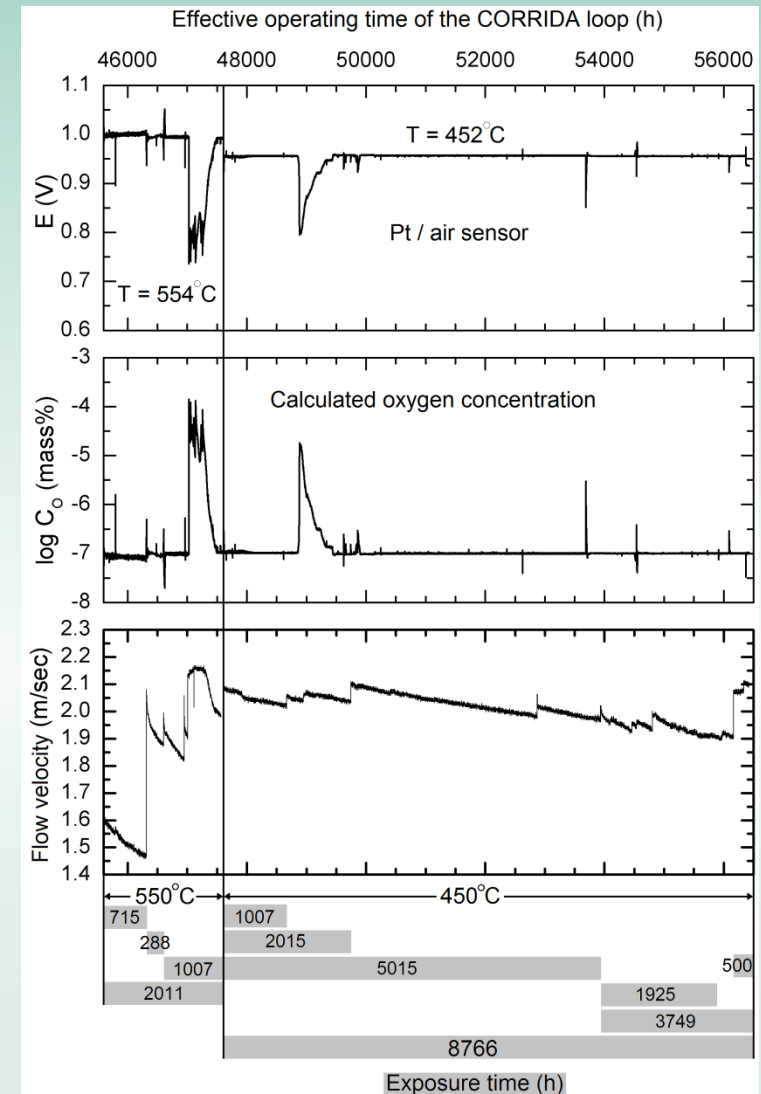
550°C

Exposure to flowing LBE at 450 or 550°C, 2 m/s and 10^{-7} mass% dissolved oxygen (nominal conditions)

Materials T91-A and T91-B (same supplier)

- T = 550(+5)°C
 $T_{\min} \approx 385^\circ\text{C}$
 $c_{\text{O}} = 10^{-7}$ mass%, excursion to 10^{-4} – 10^{-5} mass%
 $v = 2(+/-0.2)$ m/s, initially 1.5–1.6 m/s
 $t = 288; 715; 1007; 2011$ h

- T = 450(+5)°C
 $T_{\min} \approx 350^\circ\text{C}$
 $c_{\text{O}} = 10^{-7}$ mass%, excursion to 10^{-5} mass%
 $v = 2(+/-0.2)$ m/s
 $t = 500; 1007; 1925; 2015; 3749; 5015; 8766$ h



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

Accelerated oxidation

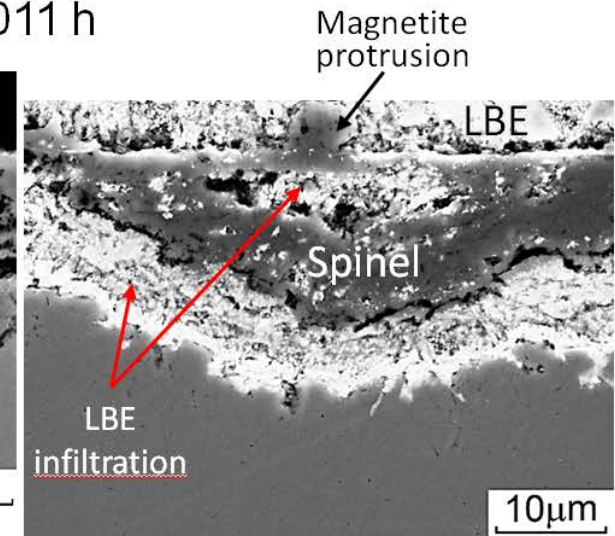
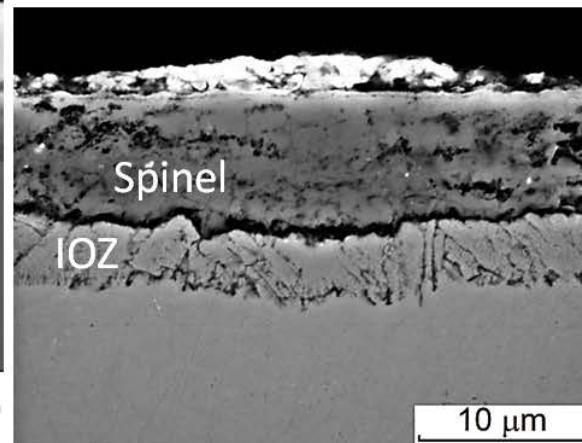
- Starts with internal oxidation
- Fe-Cr spinel formation follows internal oxidation
- Consumes outer part of the internal oxidation zone (IOZ) that may still grow at the IOZ/steel interface
- General aspect of accelerated oxidation at 550°C, not only at low oxygen concentration of the LBE
- Outer magnetite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

288 h



T91-A

2011 h

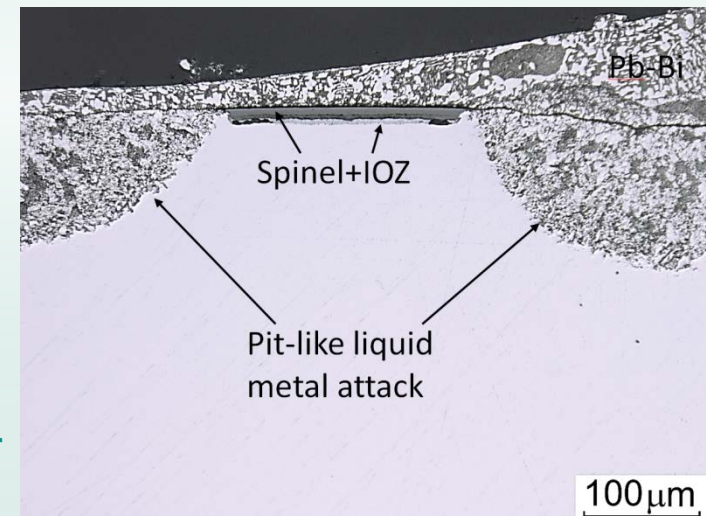


Flowing LBE at 550°C, 2 m/s and 10⁻⁷ mass% dissolved oxygen (nominal conditions)

□ 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

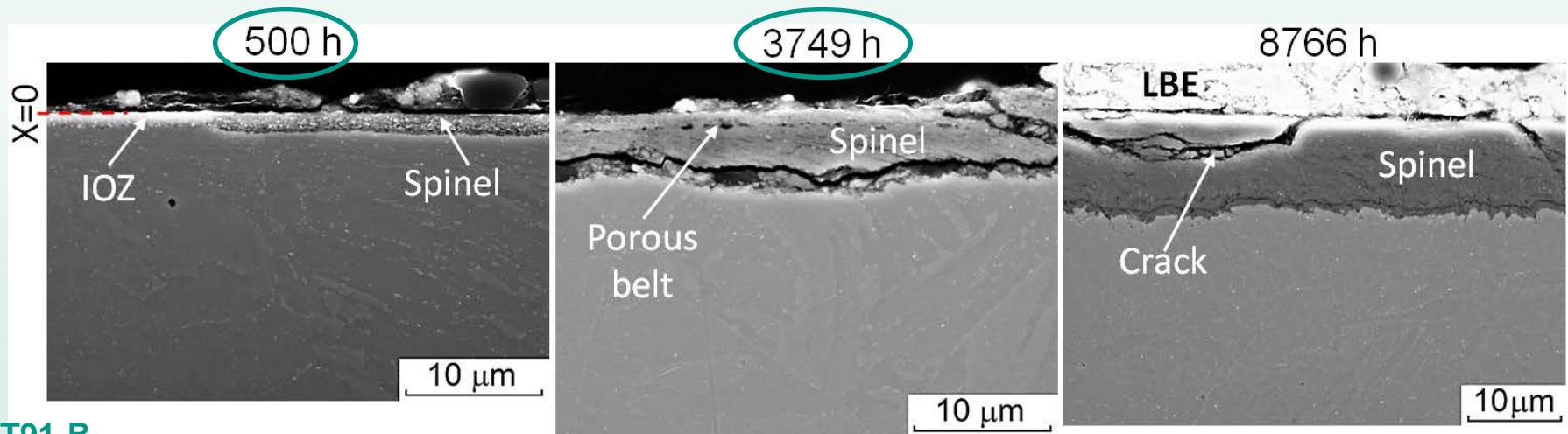
**T91-A after exposure for 1007 h
with temporary increase in c_O after
~450 h**



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

□ Accelerated oxidation

- Internal oxidation less pronounced, compared to 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



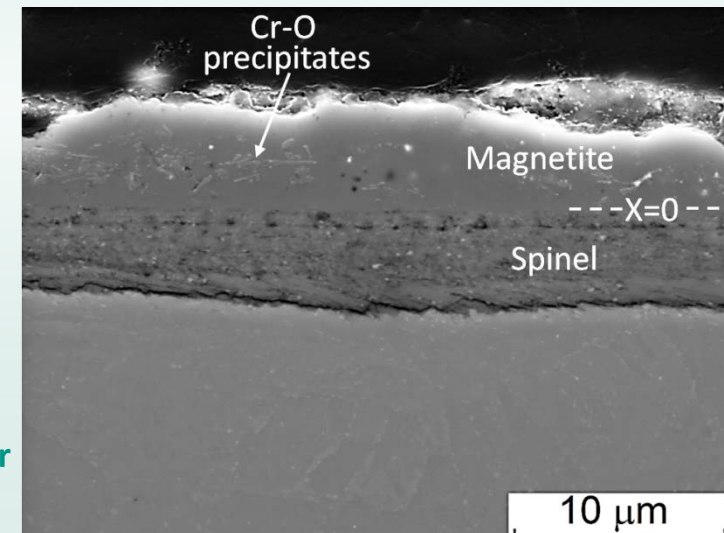
T91-B

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

❑ Magnetite formation

- Magnetite, in general, not present
- Forms during temporary increase in oxygen concentration from 10⁻⁷ to ~10⁻⁵ mass%
- Is not observed anymore some time after return to 10⁻⁷ mass% O
- Metals in deposited magnetite may stem from simultaneously exposed specimens or tubing of the experimental facility

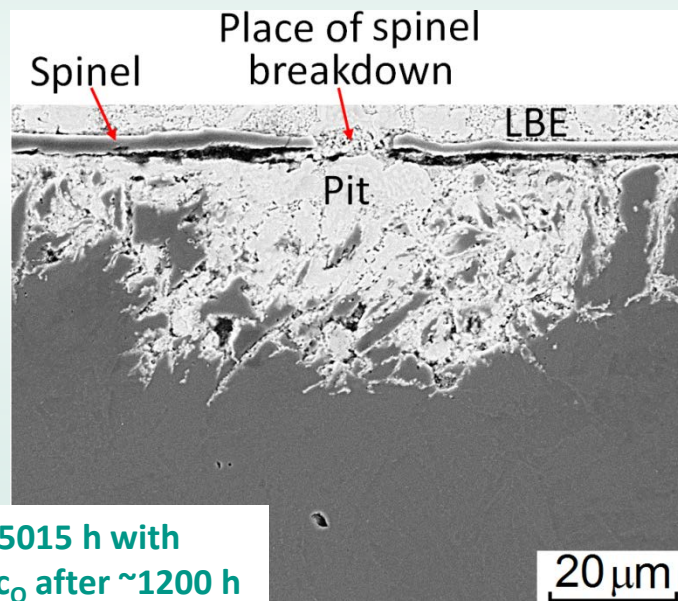
T91-B after exposure for 2015 h with intermittent increase in c_o after ~1200 h



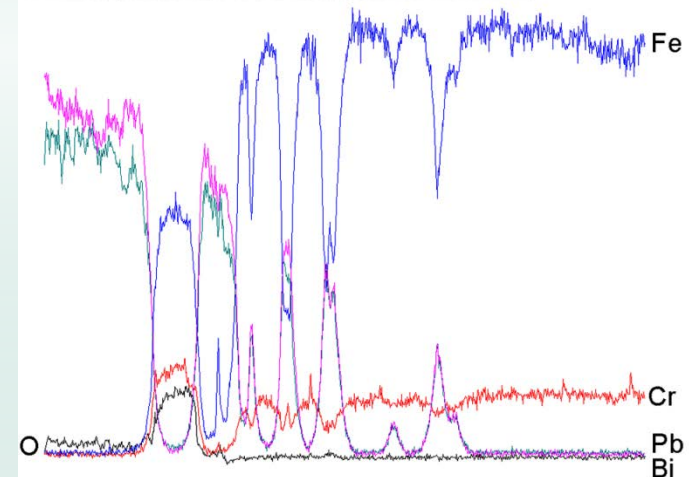
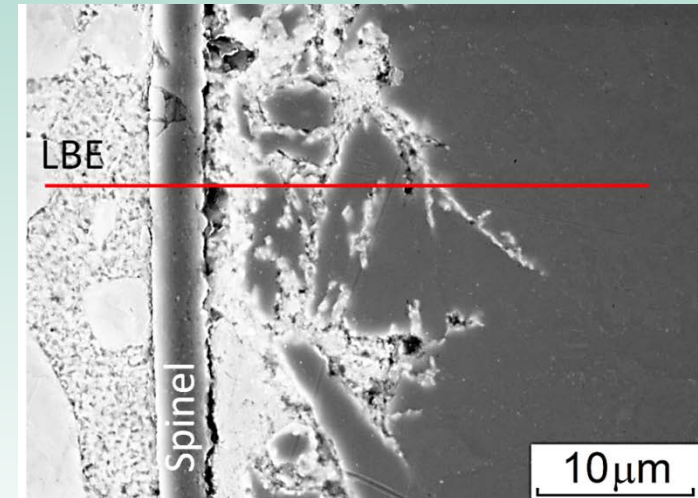
Flowing LBE at 450°C, 2 m/s and 10⁻⁷ mass% dissolved oxygen (nominal conditions)

□ Solution-based attack

- Where spinel scale failed
- Non-selective dissolution of steel elements



T91-A after exposure for 5015 h with intermittent increase in c_o after ~1200 h

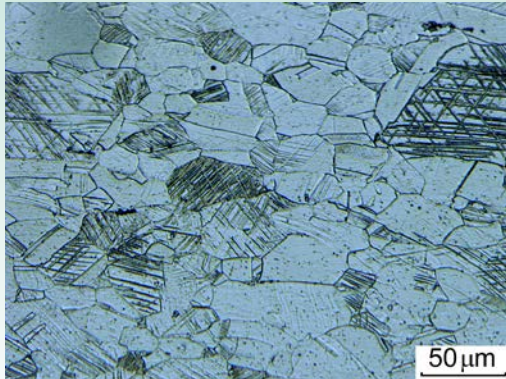


Austenitic steels tested in the CORRIDA loop

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	17.50	12	2.0	2.0	1.0	-	-	-	-	0.70	0.08	-	0.045	0.015	-

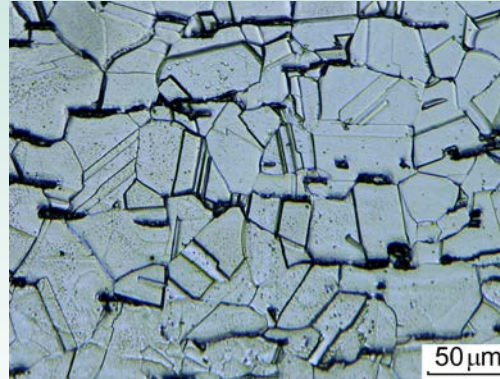
(Fe – Bal.)

1.4970 (15-15Ti)



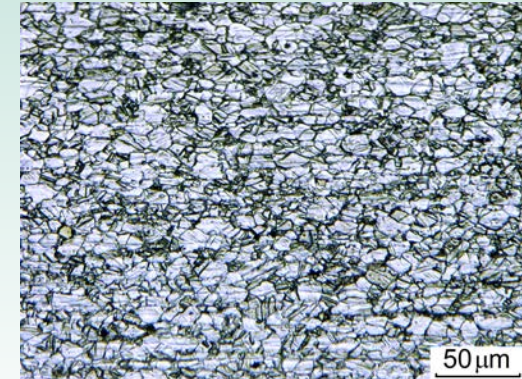
- HV₃₀ = 253;
- Grain size ranged from 20 to 65 μm;
- Intersecting deformation twins.

316L



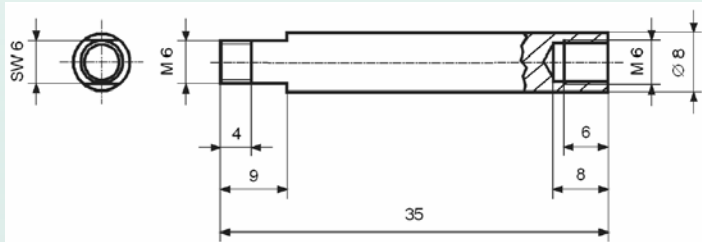
- HV₃₀ = 132;
- Grain size averaged 50 μm (G 5.5);
- Annealing twins.

1.4571

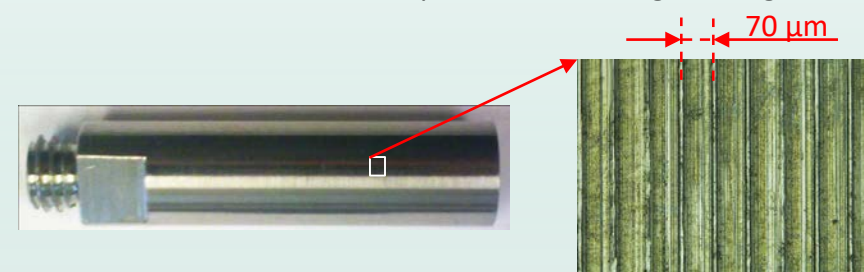


- HV₃₀ = 245;
- Grain size averaged 15 μm (G 9.5).

Shape and dimensions of sample for corrosion tests



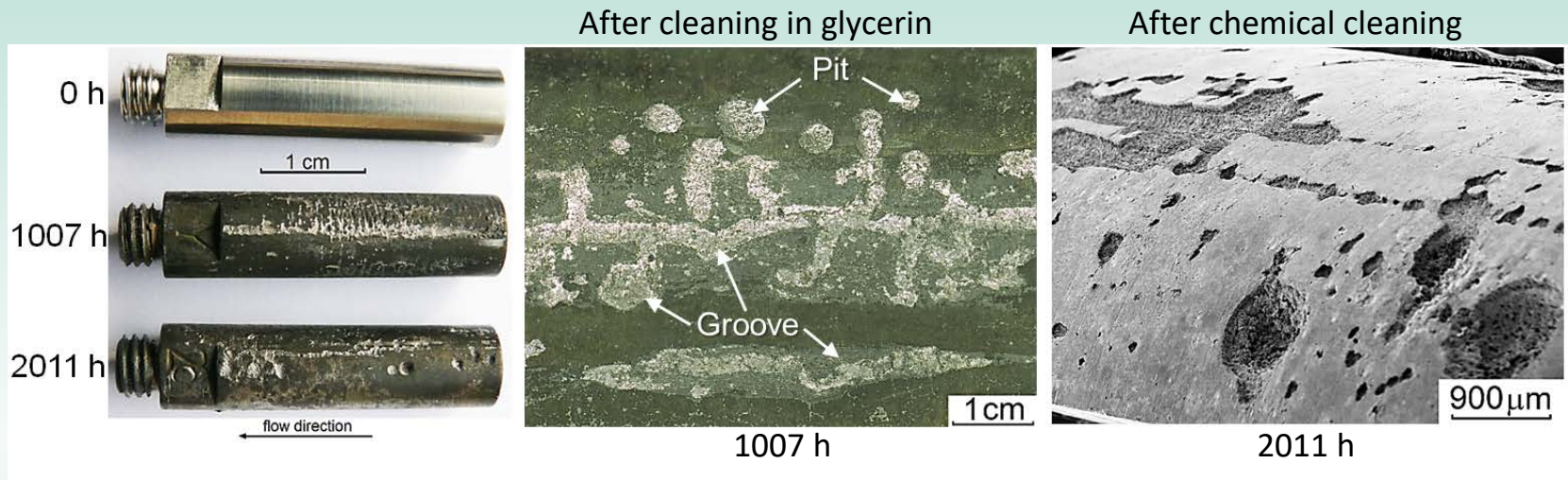
General view of initial sample after finishing turning



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

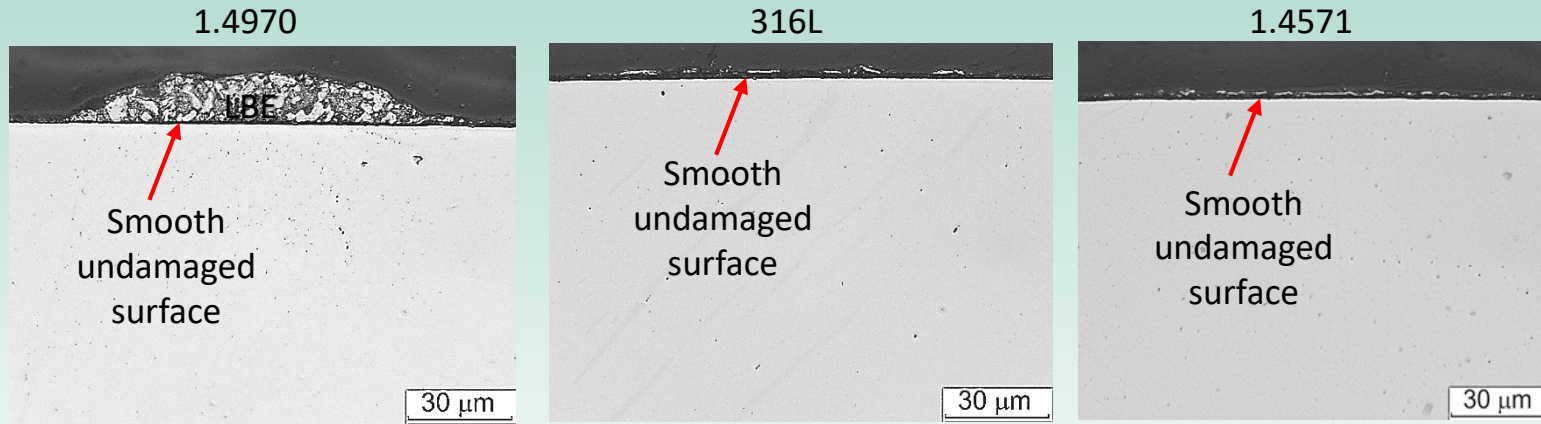
Surface examinations - general corrosion appearance

1.4970, 550°C



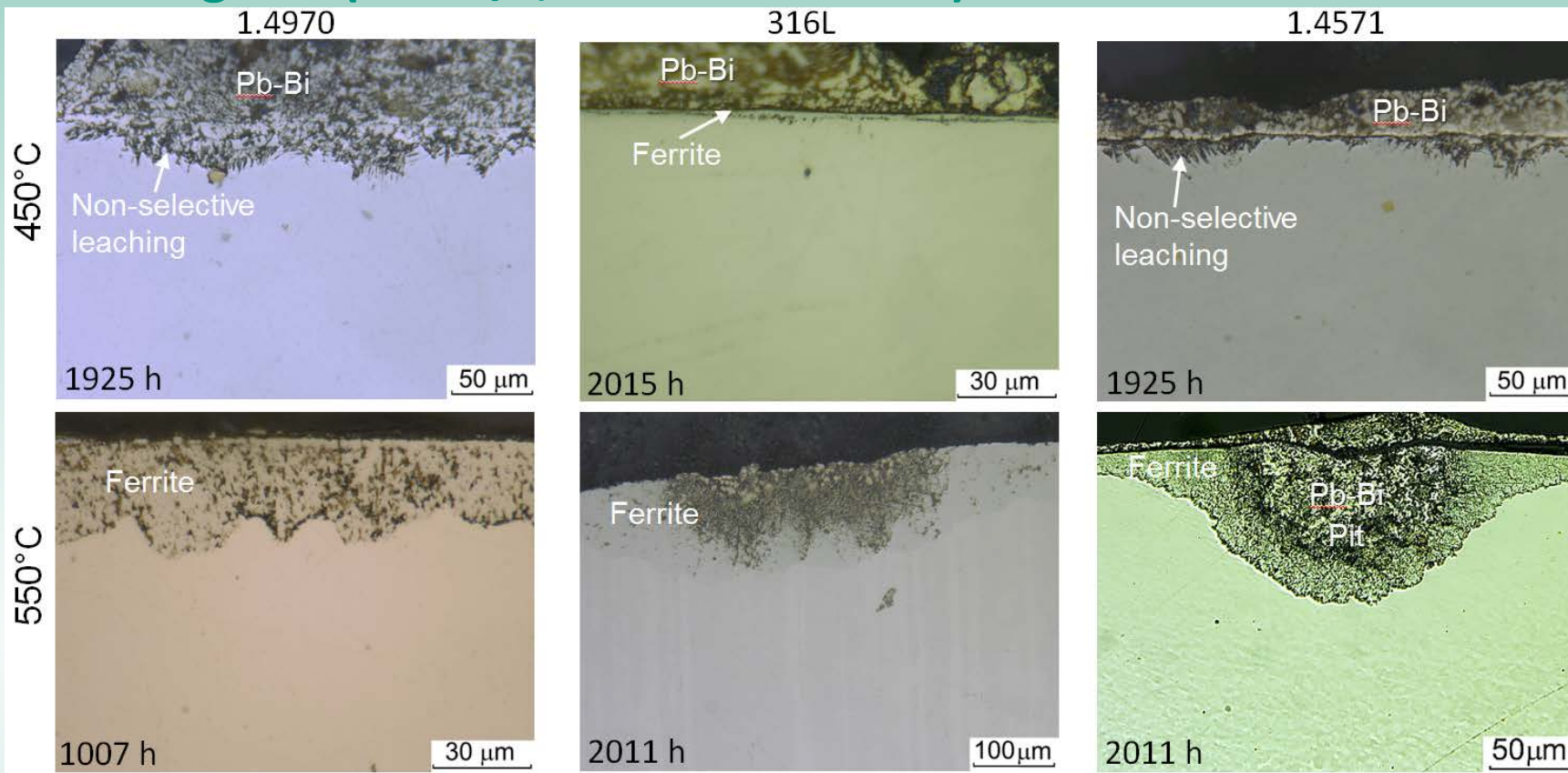
- Oxidation – formation of golden-colored oxide film (shorter test) and green-colored oxide film (longer test)
- Light areas with exfoliated oxide film;
- Severe local solution-based corrosion attack in the form of hemispherical pits and longitudinal and transversal grooves;
- The surface area covered 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, $\sim 10^{-7}$ mass % O) at 400°C for 4746 h.

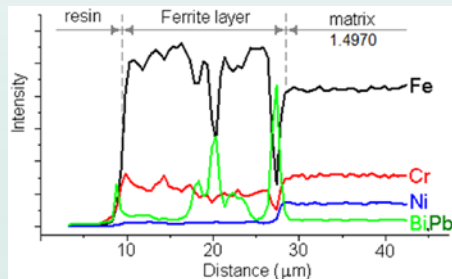


- Smooth undamaged surface is observed on the cross-section of samples;
- Selective leaching attack is not detected under the given duration of test - 4746h;
- Samples revealed golden-colored oxide film - protective scaling;
- Corrosion tests are still continuing with expected max. duration about 10000h.

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

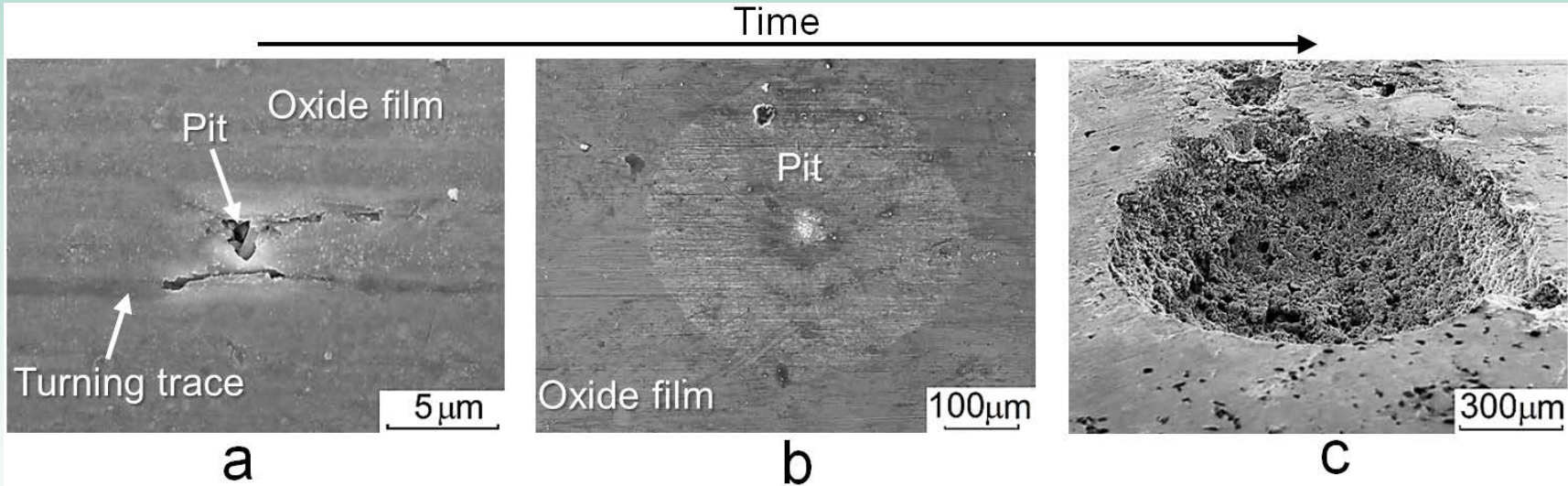


1.4970
550°C
2011 h



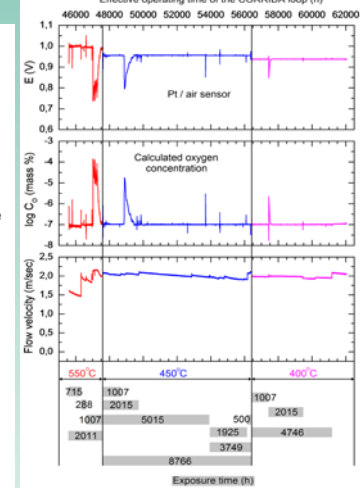
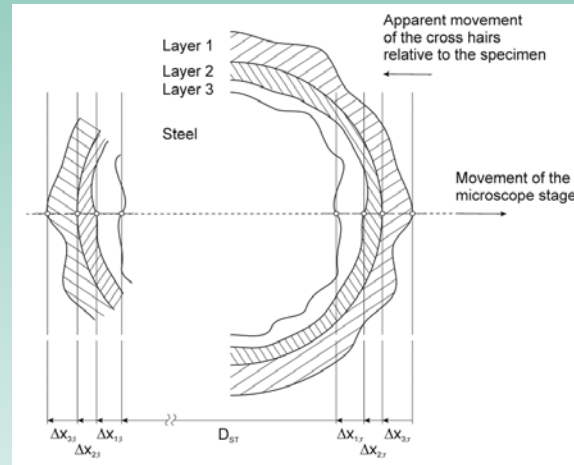
Steel	Ferrite layer composition (mass %)				
	Ni	Cr	Fe	Pb	Bi
1.4970	1.85	6.76	84.47	-	3.12
316L	1.10	8.13	86.48	-	1.95
1.4571	1.61	6.15	69.15	6.45	13.75

Expected sequence of evolution of corrosion pits with time



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

Percentage (%) of circumference affected by solution-based selective leaching attack that resulted in either formation of layer-type (L) or pit-type (P) damage



Surface appearance (%)	550°C				450°C							
	288h	715h	1007h	2011h	500h	1007h	1925h	2015h	3749h	5015h	8766h	
1.4970												
Layer-type (L)	6	43	62	75	42	*	33	*	52	23	92	
Pit-type (P)	5	-	35	16	9		46		44	11	8	
(L + P)**	11	43	97	91	51		79		96	34	100	
1.4571												
Layer-type (L)	4	46	68	42		*	17	*	100	4	98	
Pit-type (P)	-	-	7	13			1		0	3	2	
(L + P)**	4	46	75	55			18		100	7	100	
316L												
Layer-type (L)	4	58	88	82				*	100	8	92	
Pit-type (P)	4	-	8	9		*		*	0	7	8	
(L + P)**	8	58	96	91					100	15	100	

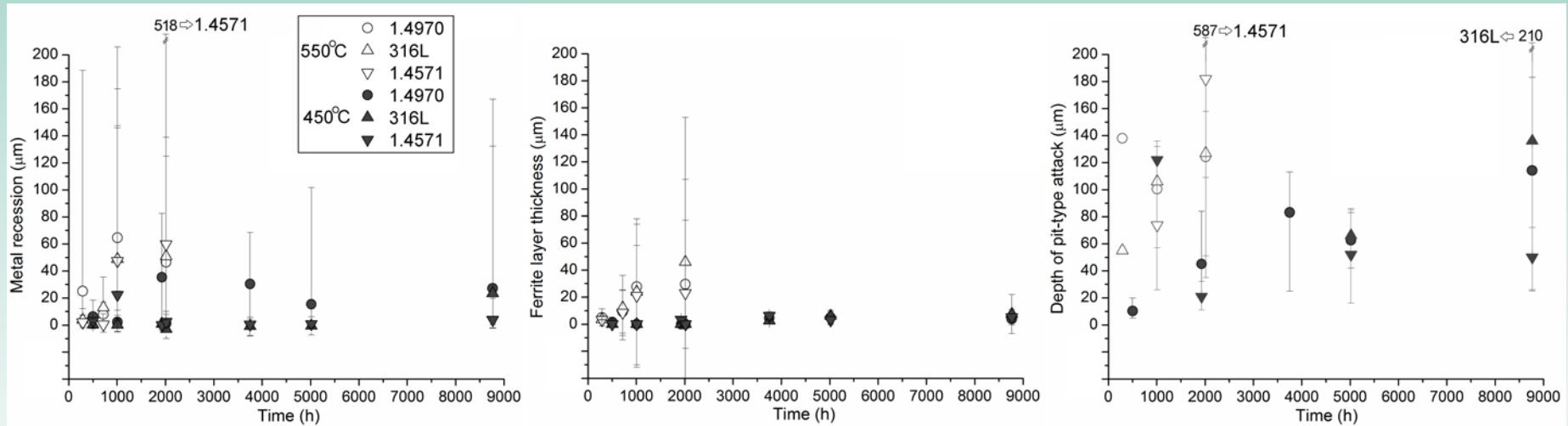
* - smooth surface covered by thin (~ 0.5 μm) protective Cr-based oxide film

** - L + P = selective leaching attack + protective scaling = 100%

□ The percentage of surface affected by selective leaching attack increases with 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 %.

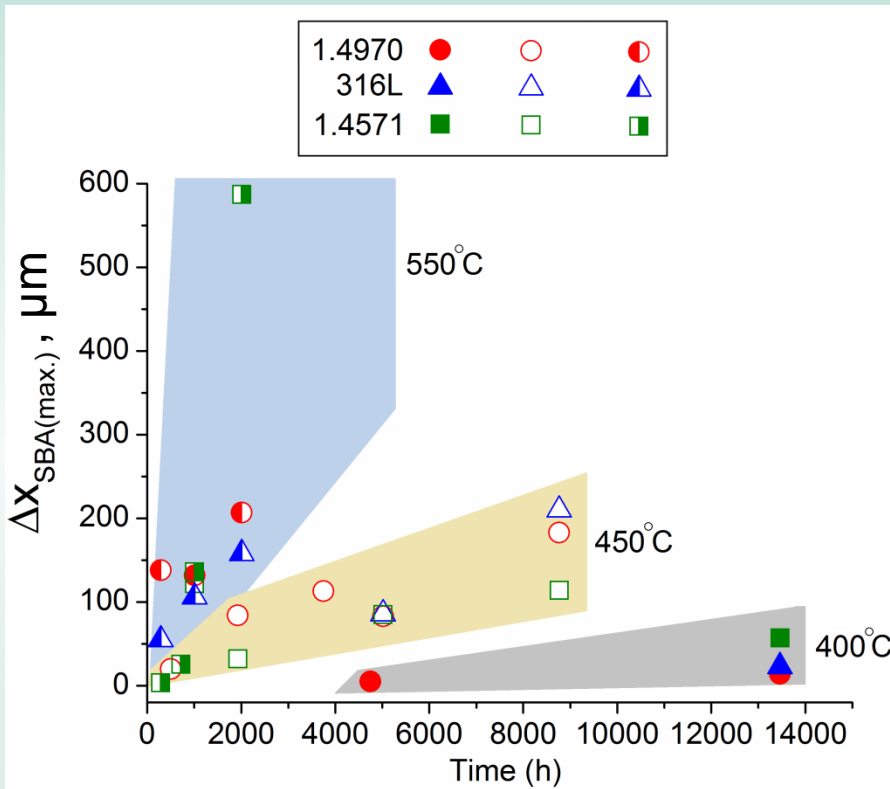
550°C:

- Metal recession averaged \sim 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:

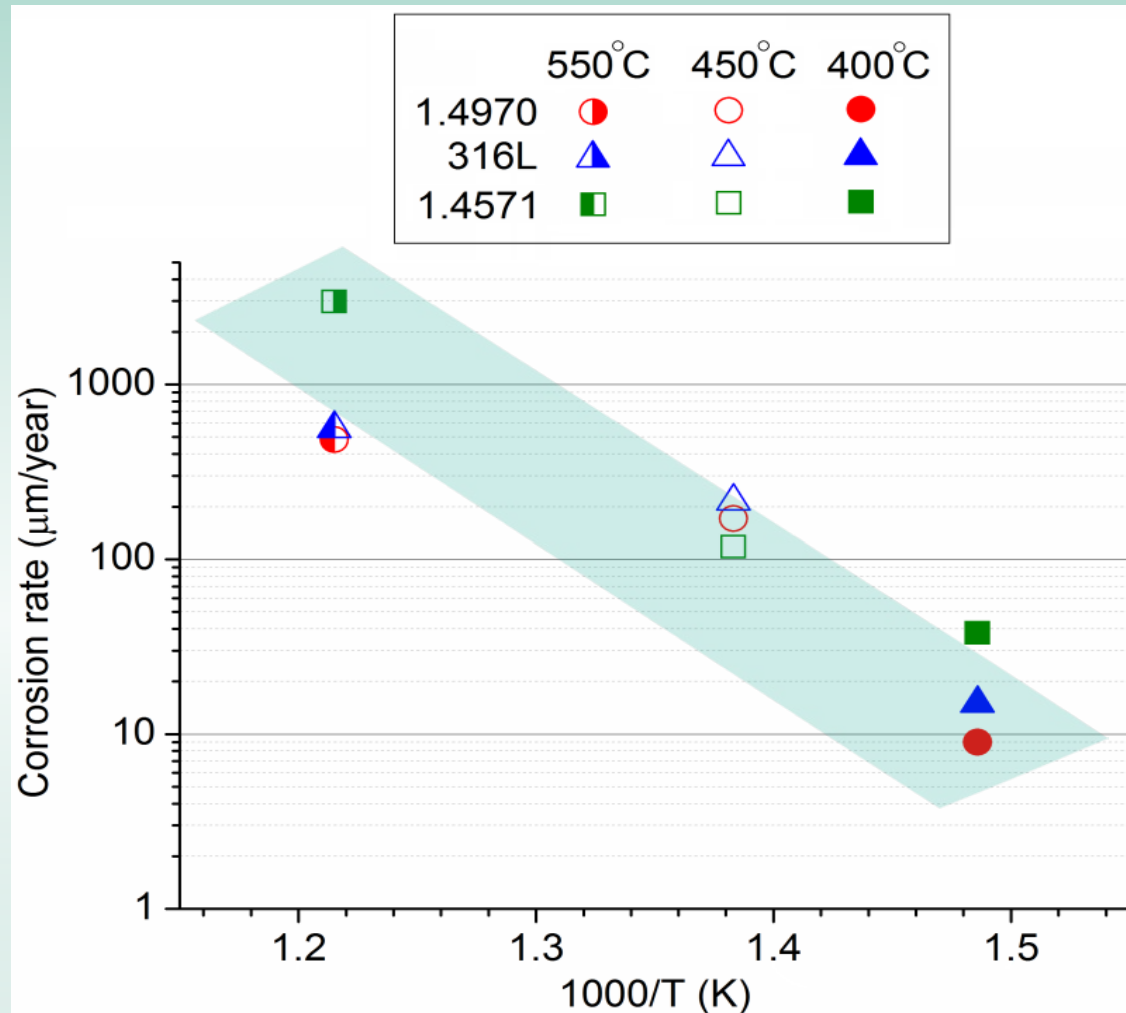
- ✓ Oxidation – thin Cr-based oxide film;
- ✓ Rare local pit-type solution-based corrosion attack;
- ✓ In-situ formed oxide film protects steels against solution-based attack at 400°C.

Maximum corrosion loss:

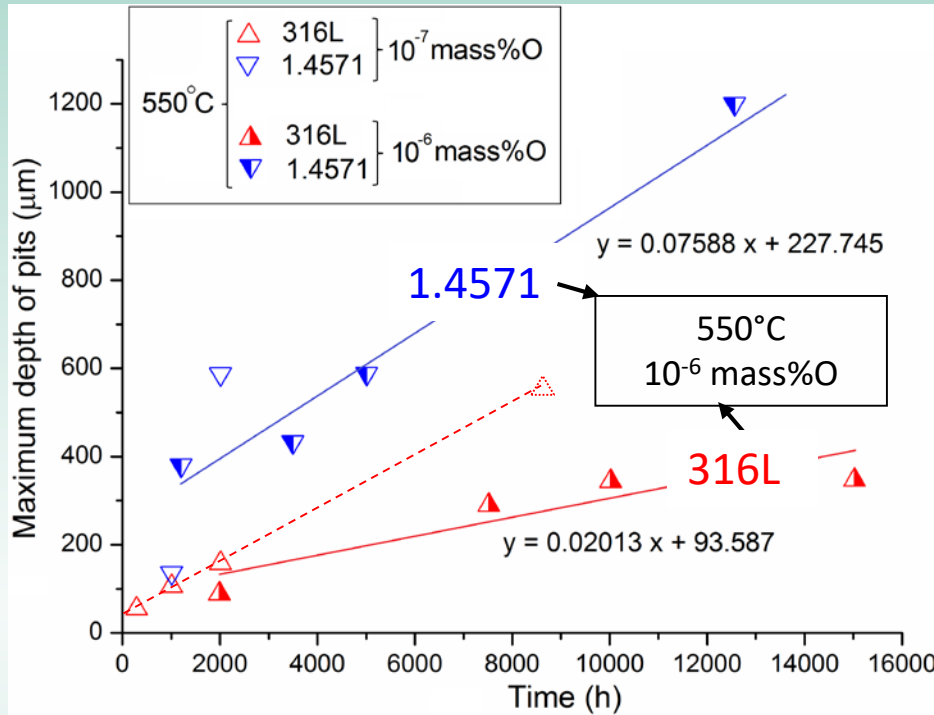
- ✓ 400°C: 15-60 μm after ~13000 h;
- ✓ 450°C: 120-220 μm after ~9000 h;
- ✓ 550°C: 150-600 μm after ~2000 h.

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)

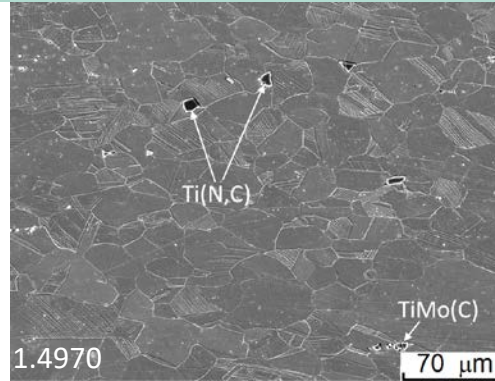
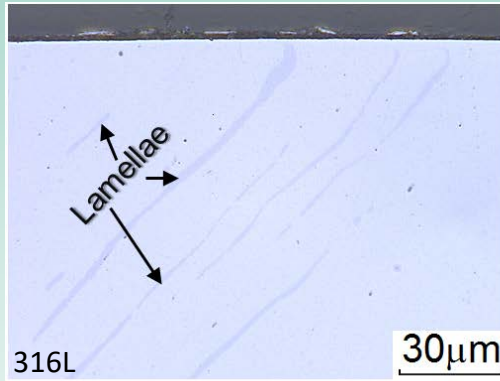


Maximum depth of pit-type corrosion attack on austenitic steels tested in flowing LBE (~ 2 m/s) depending on temperature and oxygen concentration in the melt.

- ❑ 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**).

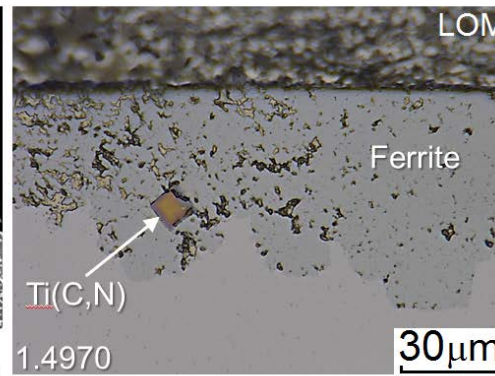
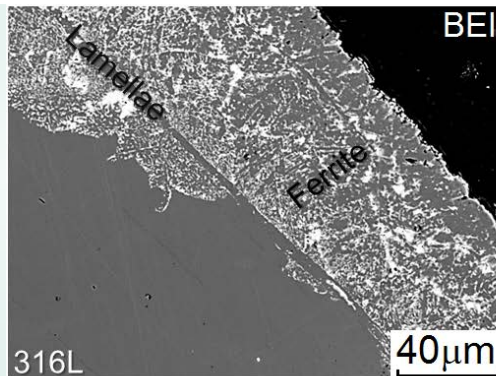
Possible effect of Ti(C,N) precipitation and Cr-rich lamellae on the preferential initiation and propagation of solution-based attack

Initial state



- Ti(C,N) precipitation in composition of 1.4970 and 1.4571
- Cr-rich lamellae (Fe-20%Cr-4%Ni) in composition of 316L (Fe-16%Cr-10%Ni)

After exposure to LBE



- Ti(C,N) precipitation and Cr-rich lamellae are corrosion resistant to LBE with 10^{-7} mass%O

Object analyzed	mass%			
	Cr	Fe	Ni	Bi
Lamellae	18.45	70.73	3.36	-
Ferrite	6.52	68.68	1.55	17.15

Conclusions (FM-steels)

□ 400°C/ 10⁻⁷ mass% oxygen

- Primarily corrosion process is **accelerated oxidation (AO)**
- Flawed and partially detached oxide scale
- **Solution-based corrosion (SB)** observed locally after 4766 h

□ 450 and 550°C/ 10⁻⁷ mass% oxygen

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

Conclusions (Austenitic steels)

❑ Interaction of austenitic steels with flowing was accompanied by **oxidation** (400, 450 and 550°C) and **solution-based liquid-metal attack** (450 and 550°C), resulted in **selective leaching of Ni and Cr** with subsequent development of ferrite zone penetrated by LBE:

❑ **400°C: oxidation** – thin Cr-based oxide film (**protective scaling**)

❑ **450°C: oxidation** – thin ($\leq 0.5 \mu\text{m}$) Cr-based oxide film

solution-based selective leaching with maximum depth of local attack 114 μm (1.4571), 183 μm (1.4970) and 210 μm (316L) for 8766h

❑ **550°C: oxidation** – thin ($\leq 0.5 \mu\text{m}$) Cr-based oxide film

solution-based selective leaching with maximum depth of local attack 587 μm (1.4571), 207 μm (1.4970) and 158 μm (316L) for 2011 h

❑ **Cr-based oxide films, formed *in-situ* on the surface of austenitic steels, are not sufficient protective barriers 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 in LBE with 10^{-6} mass% O, **oxidation is dominating!!**