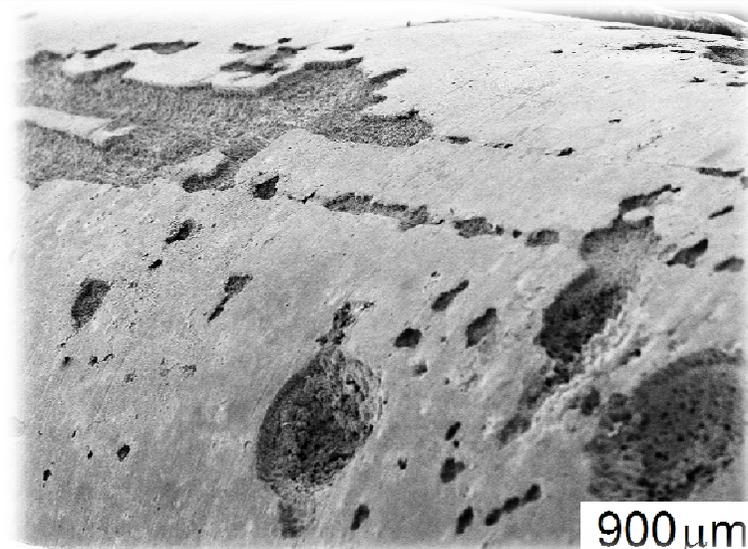


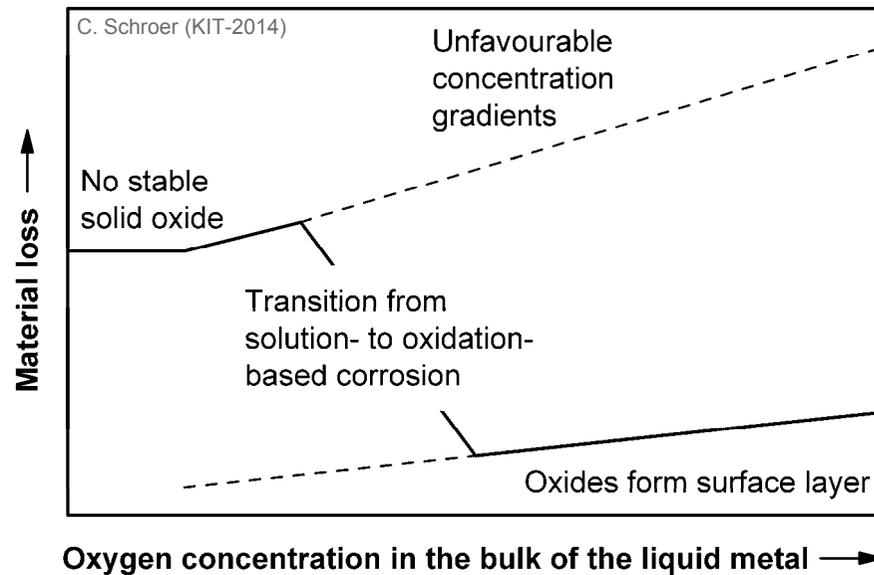
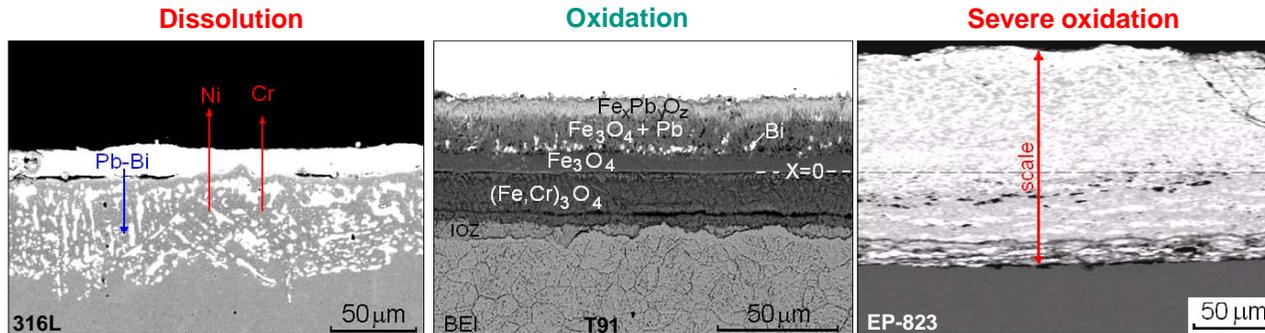
Corrosion response of 1.4970, 316L and 1.4571 austenitic steels to flowing LBE with 10^{-7} mass % dissolved oxygen at 400, 450 and 550°C

Valentyn Tsisar, Carsten Schroer, Olaf Wedemeyer, Aleksandr Skrypnik, Jürgen Konys

INSTITUTE FOR APPLIED MATERIALS – MATERIAL PROCESS TECHNOLOGY (IAM-WPT)



In-situ technology of Pb and Pb-Bi melt doping with oxygen in order to form the protective oxide layer on the surface of steel



Scheme of corrosion (material) loss and interaction modes of steels in Pb/Pb-Bi melts depending on the oxygen concentration in the liquid metal at fixed time and temperature
 (modified based on the experimental graph of I. Gorynin et al., *Metal Science and Heat Treatment*, 41, No 9-10, 1999, 384)

BASIS of Pb-Bi technology

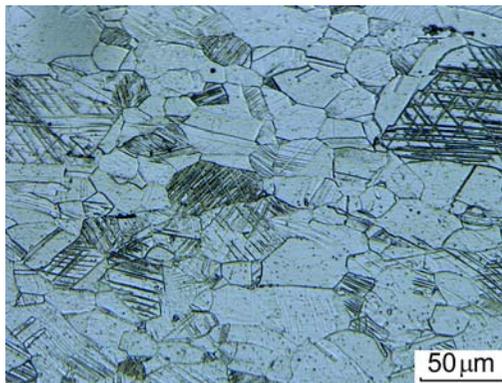
- ❑ Pb / Pb-Bi dissolves and transports the oxygen;
- ❑ Components of steels (Si, Cr, Fe...) have high affinity to oxygen than Pb or Bi.

Materials

(Fe – Bal.)

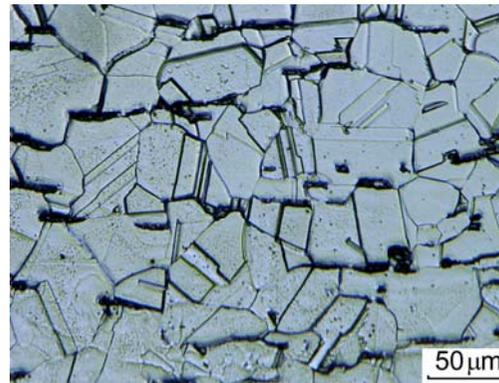
Austenitic steels	Cr	Ni	Mo	Mn	Si	Cu	V	W	Al	Ti	C	N	P	S	B
316L	16.73	9.97	2.05	1.81	0.67	0.23	0.07	0.02	0.018	-	0.019	0.029	0.032	0.0035	-
1.4970	15.95	15.4	1.2	1.49	0.52	0.026	0.036	< 0.005	0.023	0.44	0.1	0.009	< 0.01	0.0036	< 0.01
1.4571	17.50	12	2.0	2.0	1.0	-	-	-	-	0.70	0.08	-	0.045	0.015	-

1.4970 (15-15Ti)



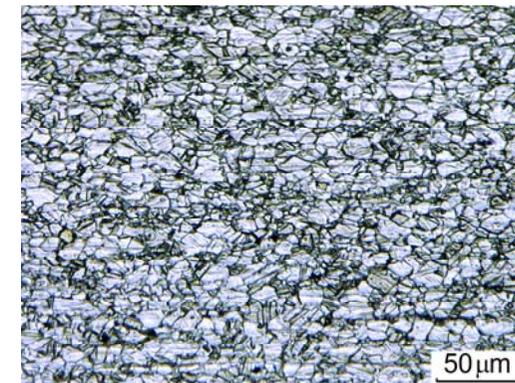
- HV₃₀ = 253;
- Grain size ranged from 20 to 65 μm;
- Intersecting deformation twins.

316L



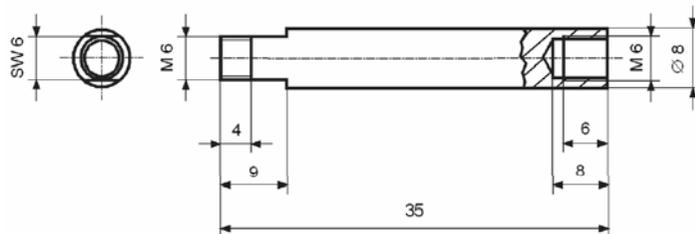
- HV₃₀ = 132;
- Grain size averaged 50 μm (G 5.5);
- Annealing twins.

1.4571 (material of CORRIDA loop)

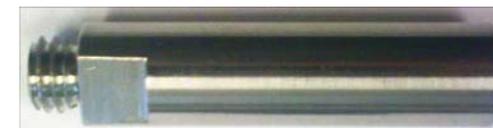


- HV₃₀ = 245;
- Fine-grained structure with grain size averaged 15 μm (G 9.5).

Shape and dimensions of sample for corrosion tests

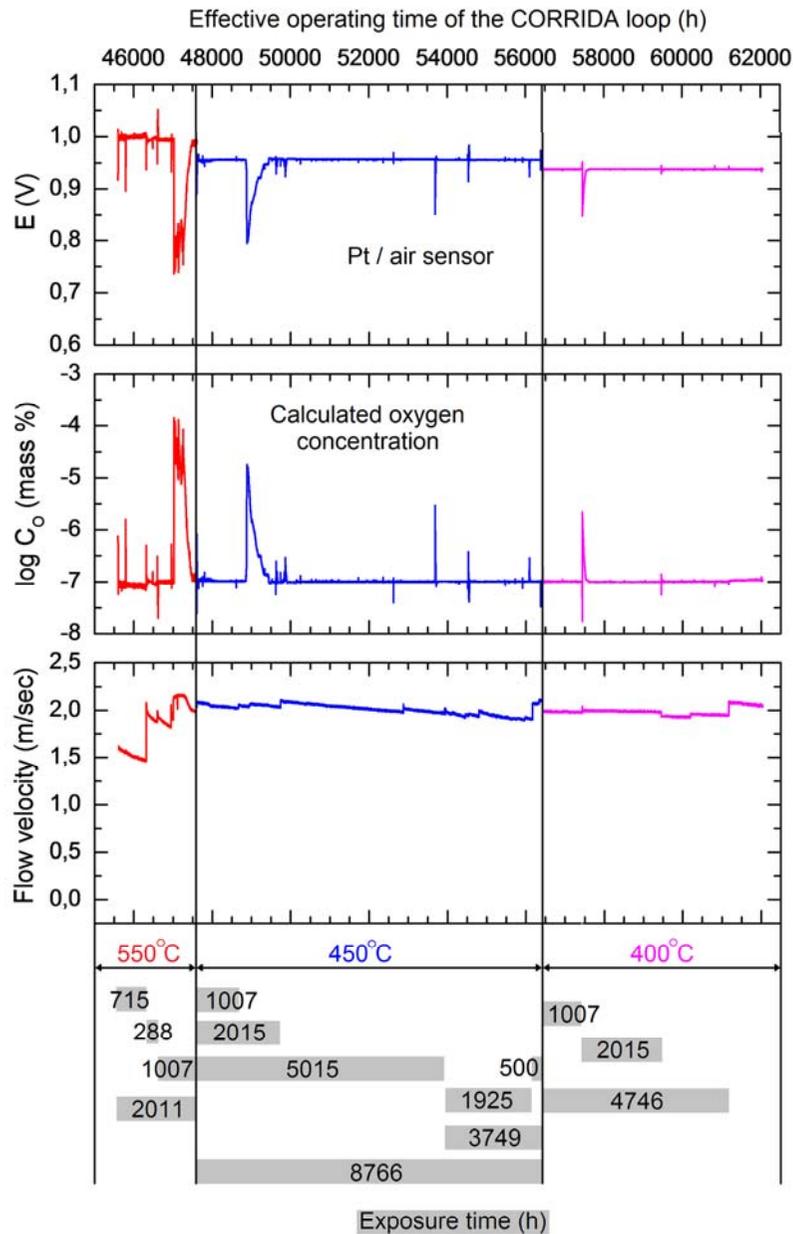


General view of initial sample



Manufacturing procedure:
Electric Discharge Machining (EDM) + finishing turning

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,

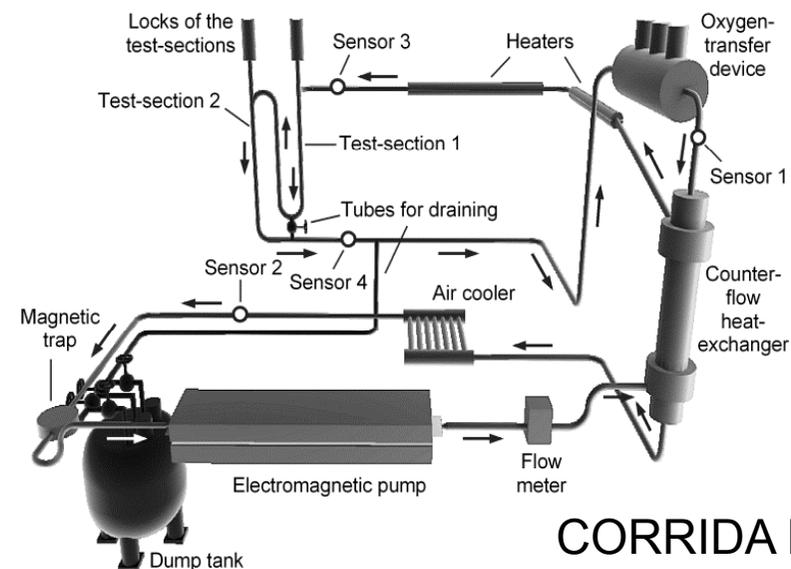
$t = 500; 1007; 1925; 2015; 3749; 5015; 8766$ h

□ **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 10000h



CORRIDA loop

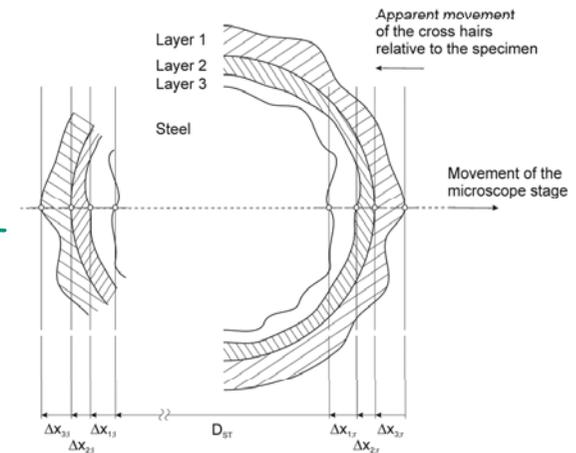
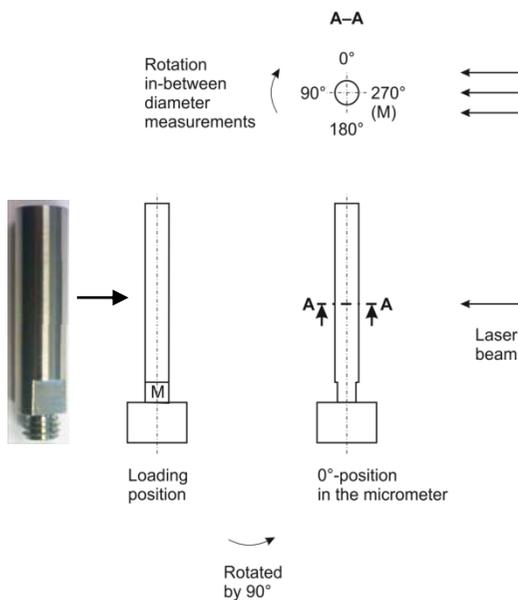
Quantification of corrosion loss

□ 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

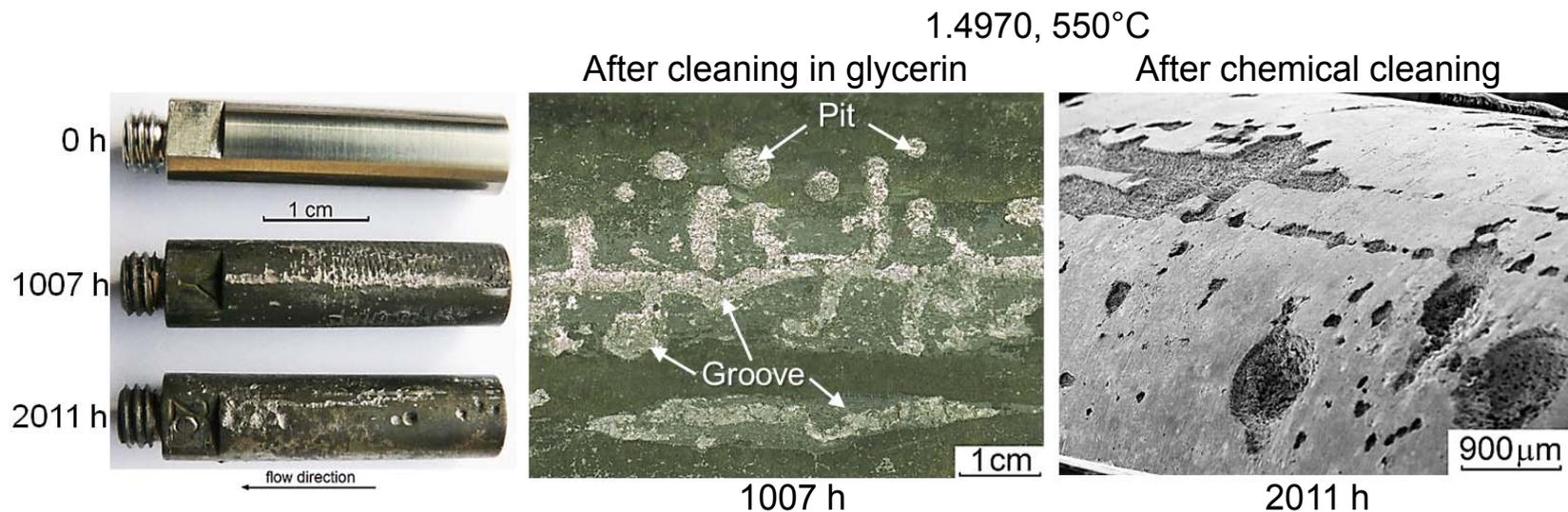
□ Metallographic method (cylindrical specimens)

- Measurement of initial diameter in a laser micrometer with 0.1 μm resolution
- Diameter of unaffected material and thickness of corrosion zones determined in a microscope (LOM) with 1 μm resolution
- Occurrence of different corrosion modes on opposing sides of the re-measured diameter is considered in the evaluation



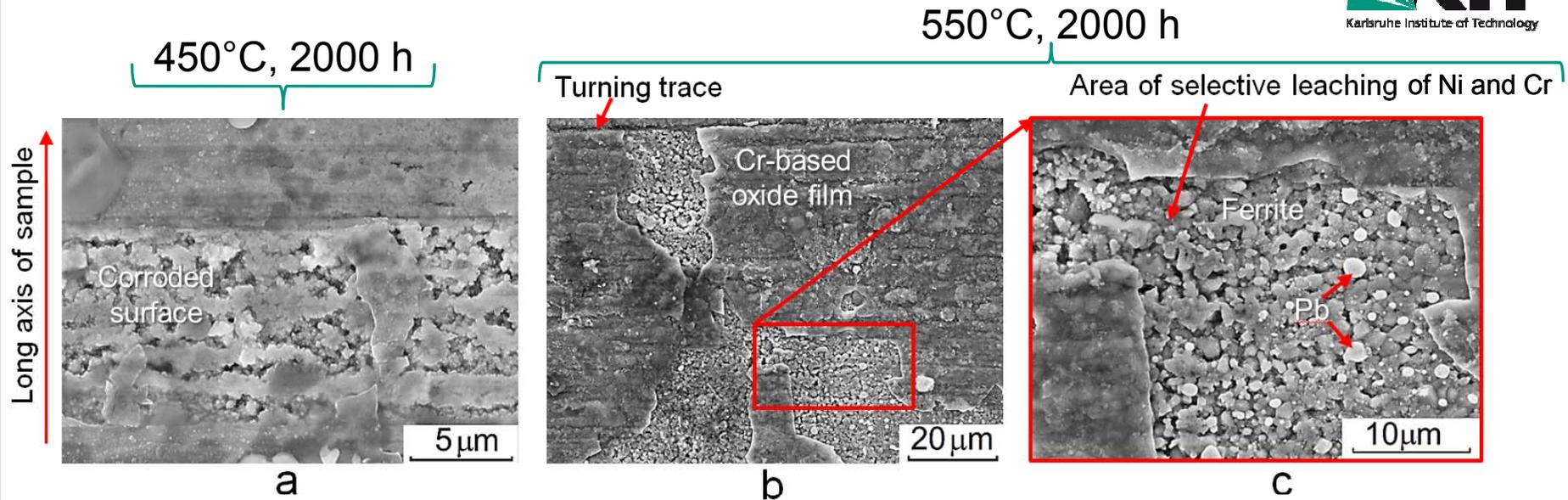
Qualification of corrosion modes on surface of austenitic steels after exposure to flowing LBE with 10^{-7} mass% O at 450 and 550°C

Surface examinations - general corrosion appearance



- ❑ 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.

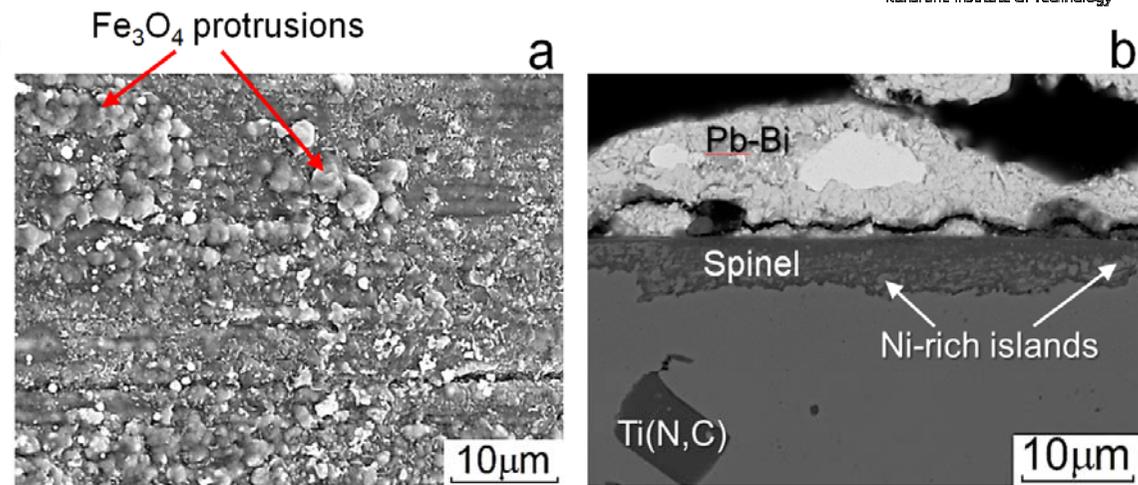
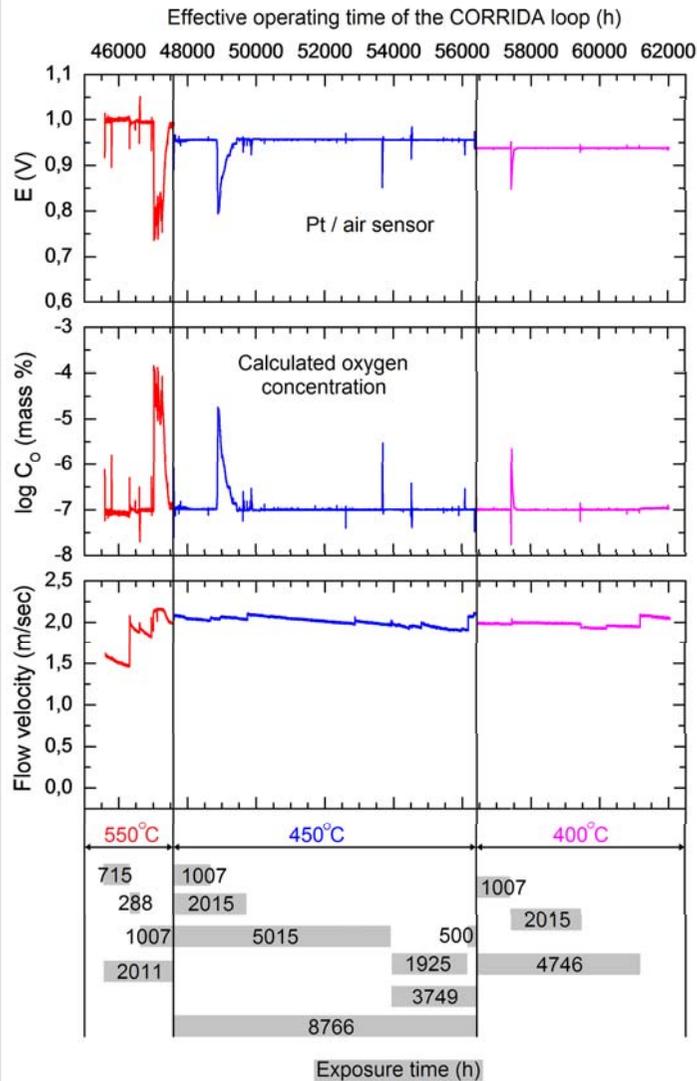
Surface examinations of tested steels



T (°C)	mass %	O	Si	Ti	Cr	Fe	Ni	Pb	Bi
450	Surface area scan (a)	15.89	0.84	0.58	19.84	48.91	10.39	2.38	1.17
	Corroded surface (a)	-	0.61	0.07	6.58	42.25	4.00	22.70	23.79
550	Cr-based oxide film (b)	31.89	0.63	0.55	39.05	19.39	0.22	3.50	4.78
	Ferrite (c)	-	0.77	0.28	12.92	78.21	0.84	1.73	3.42

- ❑ Surface of austenitic steels are covered by thin ($\leq 0.5 \mu\text{m}$) Cr-based oxide film;
- ❑ Porous corroded surface markedly depleted in Cr and Ni and penetrated with Pb and Bi is also observed.

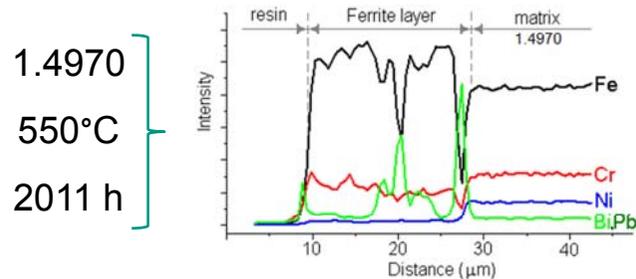
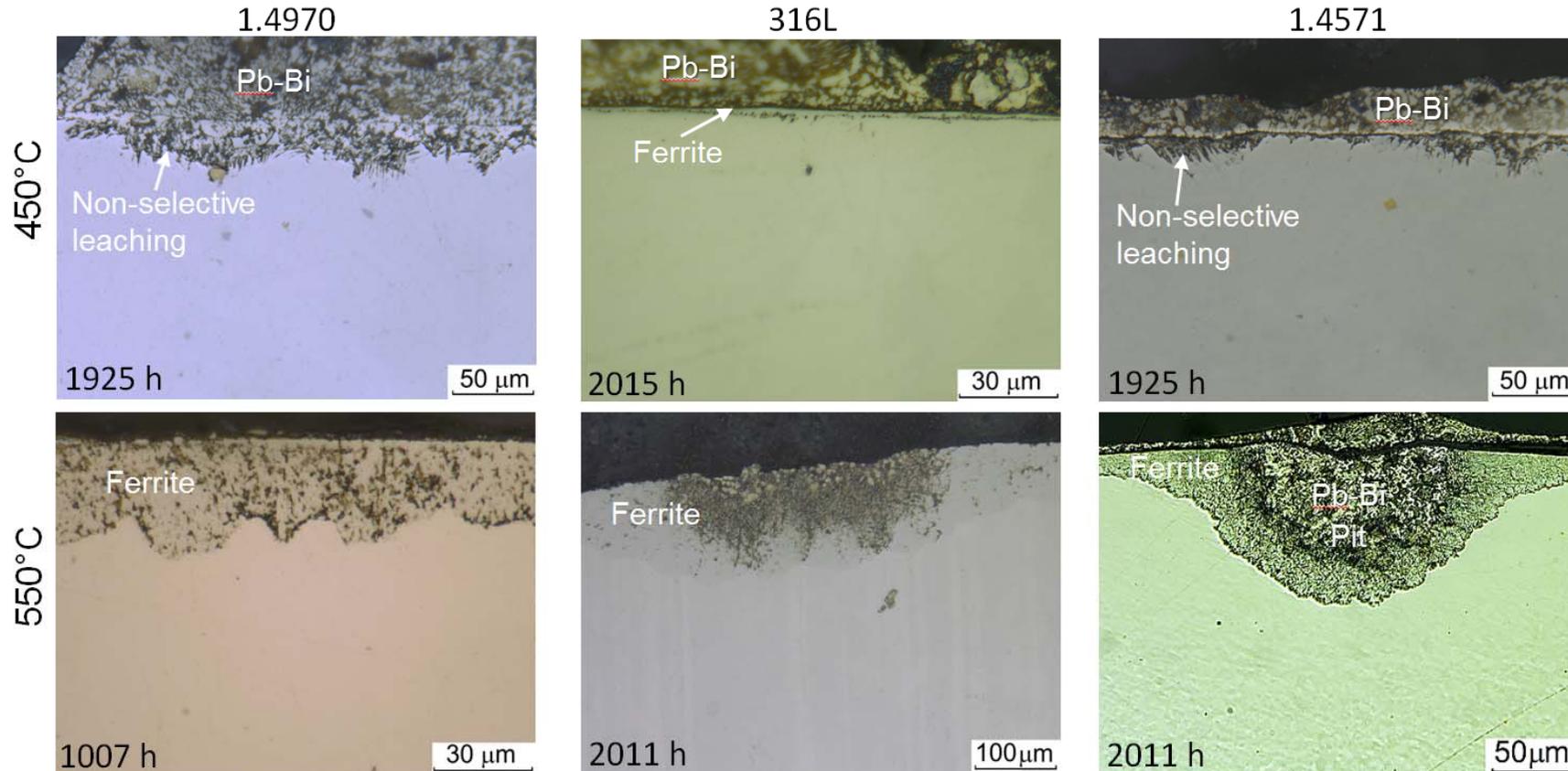
Effect of temporal increase in oxygen concentration in LBE



Object analyzed	mass %			
	O	Cr	Fe	Ni
Protrusions	27.63	2.46	69.43	-
Spinel	21.16	25.21	38.70	2.89
Ni-rich islands	2.85	8.96	59.73	20.05

- ❑ Growth of rare magnetite protrusions on the surface of 316L steel (550°C, 1007 h) (Fig. a);
- ❑ Formation of islands of Fe-Cr spinel (1.4970 exposed at 550°C (Fig. b).

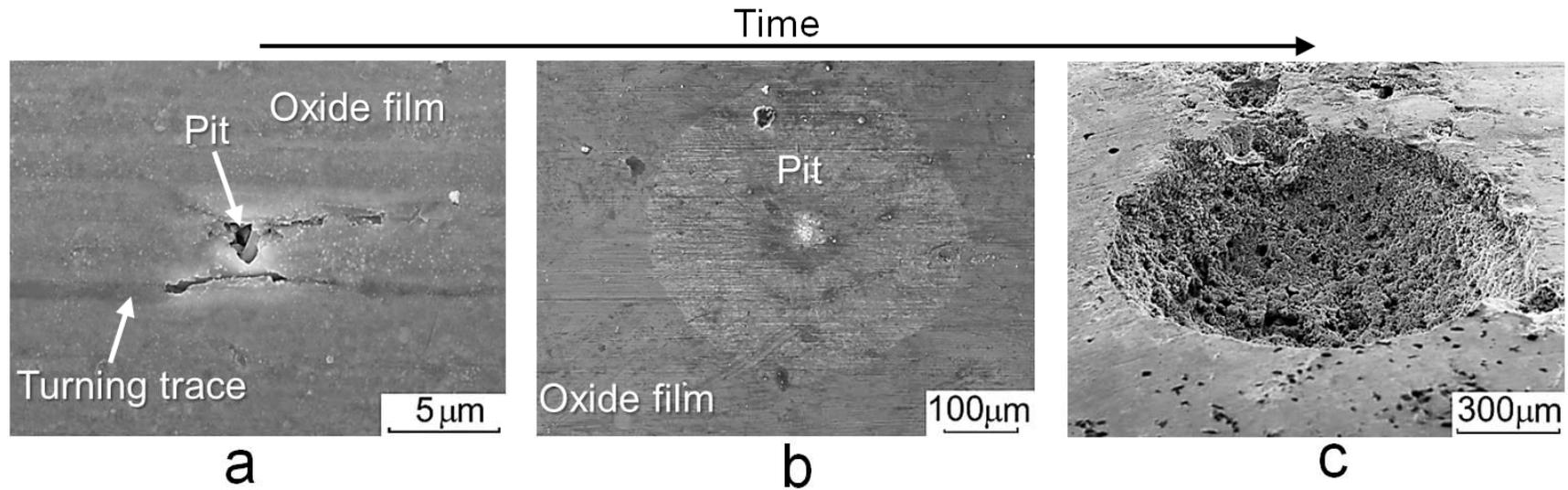
Cross-section examination of tested steels



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

Local pit-type corrosion attack

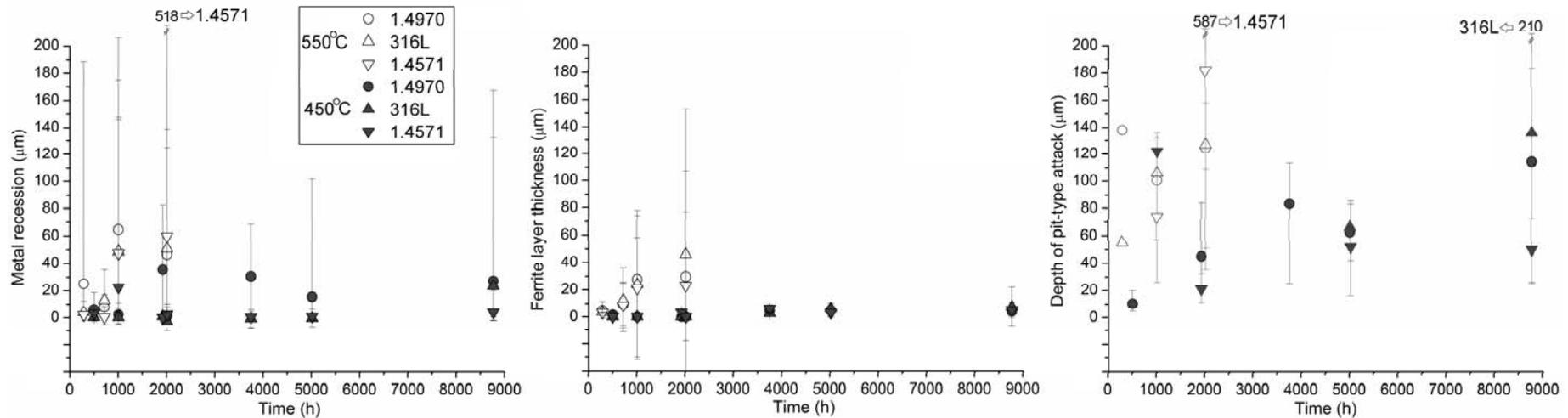
Expected sequence of evolution of corrosion pits wit time



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

Quantification of corrosion loss 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 8766 h for 1.4571, 1.4970 and 316L steels, respectively;
- ❑ Thickness of layer-type attack (ferrite) averaged 5, 7 and 4 µm after 8766 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 8766 h reached 100 %.

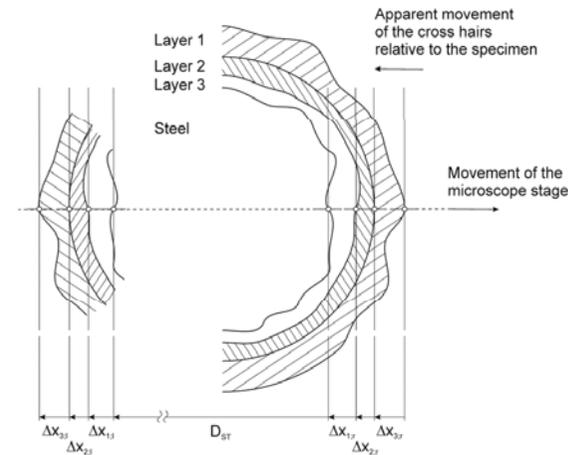
550°C:

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

Average values of metal recession, thickness of ferrite layer and depth of pit-type attack could result in underestimation of corrosion rate!

Maximum depth of solution based attack, seems to be most adequately reflects corrosion loss of austenitic steels and therefore could be used as parameter for evaluation of corrosion rate using linear law!

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	

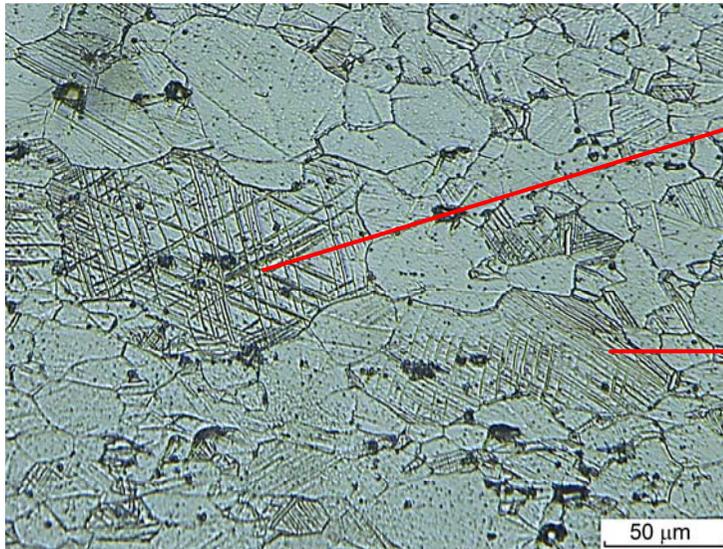
* - smooth surface covered by thin (~ 0.5 μm) protective Cr-based oxide film

** - L + P = selective leaching attack

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

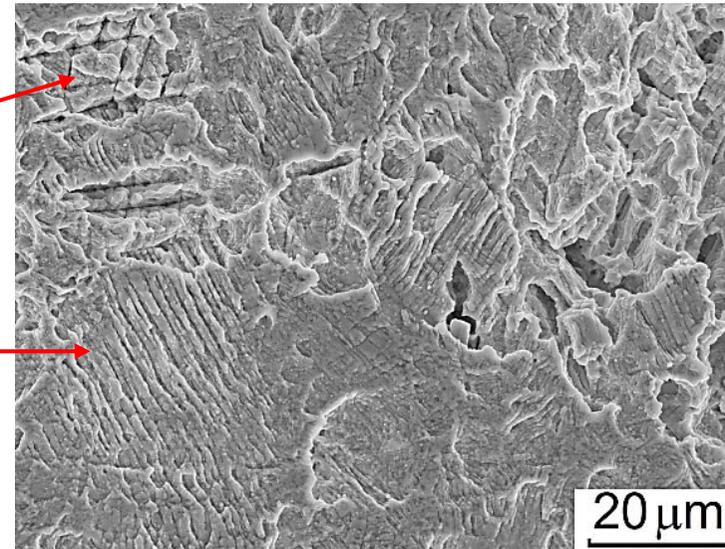
Effect of initial microstructure on the propagation depth of solution-based attack

As-received



Deformation twins in the body of grain

Exposed to LBE and chemically cleaned

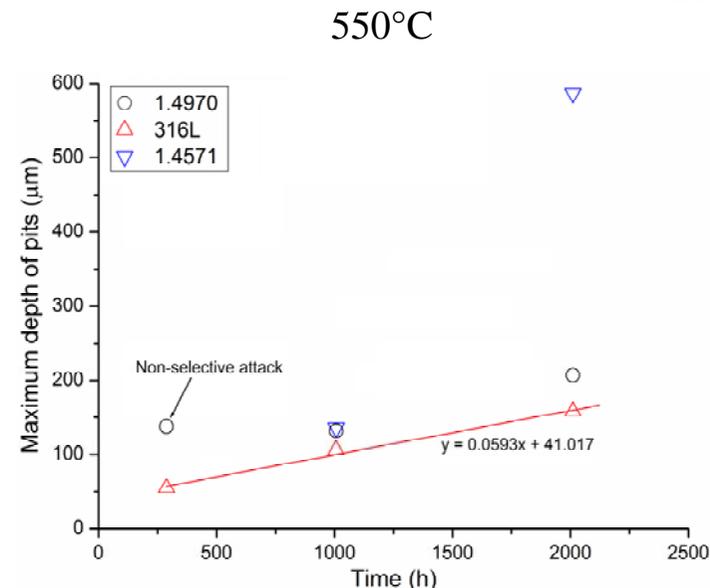
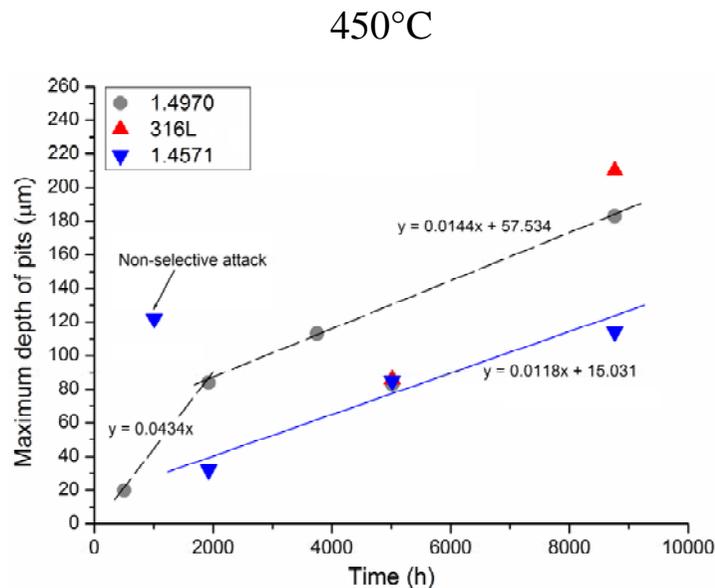


Preferential solution-based attack along twins

Micro-defects: cavities

- ❑ Pre-existing “active” diffusion paths, i.e. grain or sub-grain boundaries and twins (deformation and solution) are the preferential paths for solution-based attack via selective leaching of Ni and Cr and subsequent penetration of Pb and Bi into steel matrix.

Maximum depth of solution-based attack on austenitic steels tested at 450 and 550°C in LBE with 10⁻⁷ mass% O



450°C:

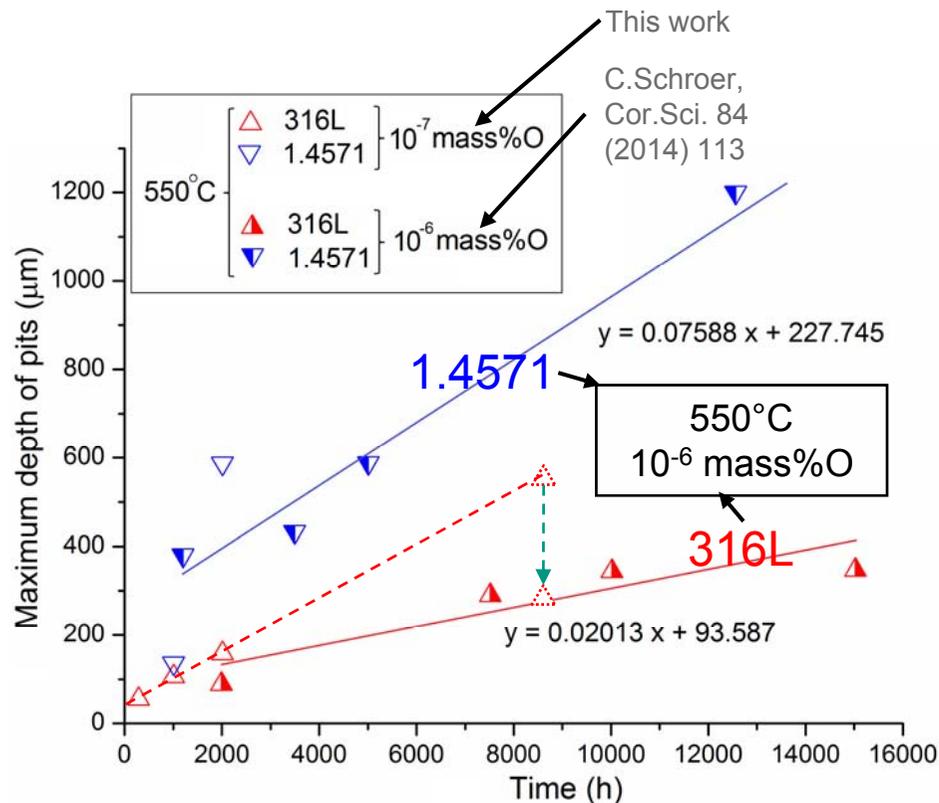
- **1.4970** – the time dependence of maximum depth of attack consists of initial transient period of faster kinetics (up to 2000 h) and steady-state period. **Corrosion rate** of calculated based on steady-state period is about **184 µm/year**;
- **1.4571** – steady-state period established after 2000 h resulted in corrosion rate **164 µm/year**;
- **316L** – available data are scarce enough to be approximated using linear law. Corrosion rate based on the nominal value after 8766h is **210 µm/year**. In comparison with 1.4970 and 1.4571 the incubation time for 316L is substantially longer, i.e. about 4000 h.

550°C:

- **1.4970** – maximum depth of attack after 2011h is **207µm**;
- **316L** – maximum depth of attack after 2011h is **158µm**;
- **1.4571** – maximum depth of attack after 2011h is **587µm**, i.e. about three times higher than those for 1.4970 and 316L.

Steel which showed the longest incubation period, i.e., 316L at 450°C and 1.4571 at 550°C, revealed afterwards the deepest attack!

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



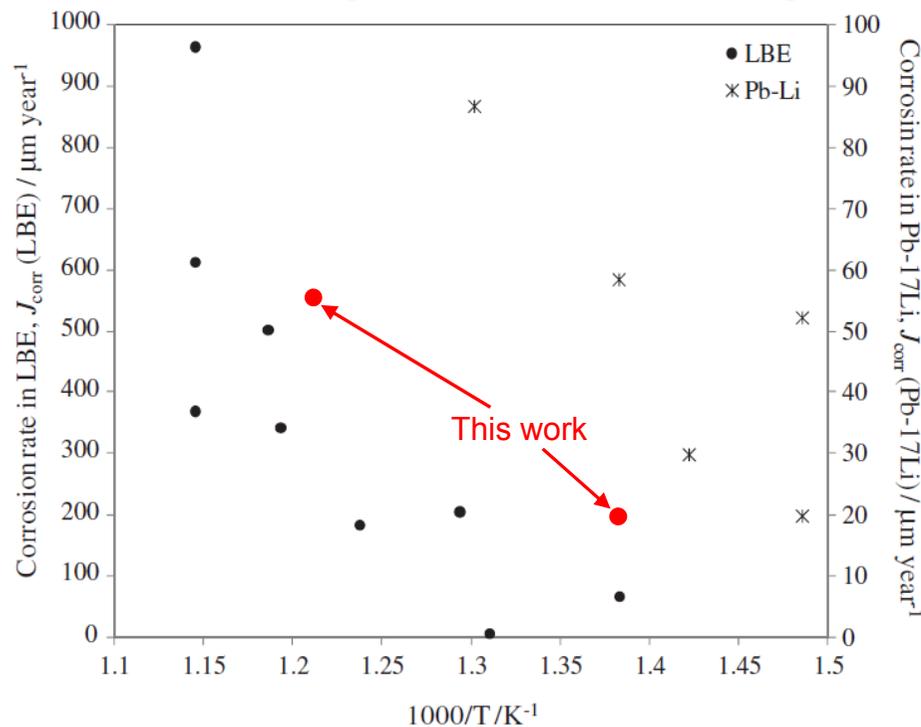
Maximum depth of pit-type corrosion attack on austenitic steels tested in flowing LBE (~ 2 m/s) depending on temperature and oxygen concentration in the melt.

- 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;
- Under the other similar conditions of test the finer grains ($15\mu\text{m}$) of steel (1.4571 **blue markers**) of steel the deeper corrosion attack (coarse-grained ($50\mu\text{m}$) 316L **red markers**).

Comparison of corrosion rate of 316L tested in this work with literature data

Corrosion rate of 316L versus temperature and liquid metal

Yamaki et al. [Cor. Sci. 53, 2011, 3075-3085]



$$\log J_{\text{corr}} (\mu\text{m}/\text{year}) = 6.5 - 27705 / RT$$

Corrosion rates of 316L steel in comparison with data generalized by Yamaki et al. :

450°C

- 80 μm/year - Yamaki et al.
- 210 μm/year - this work (nominal value)

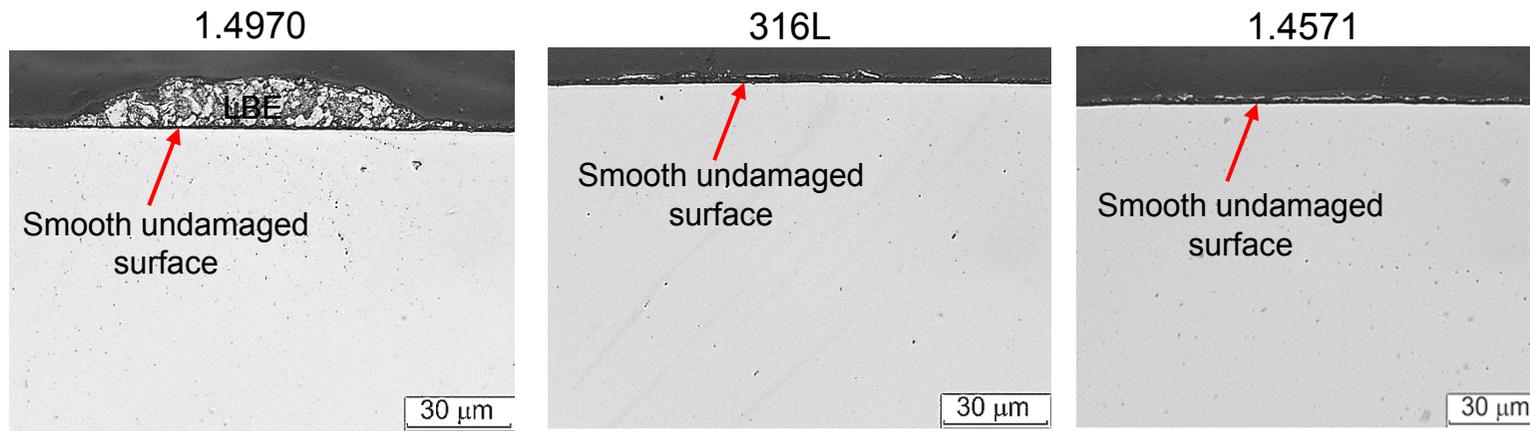
550°C

- 280 μm/year - Yamaki et al.
- 560 μm/year - this work (linear approximation)

Markedly higher corrosion loss of 316L steel in this work could be caused by:

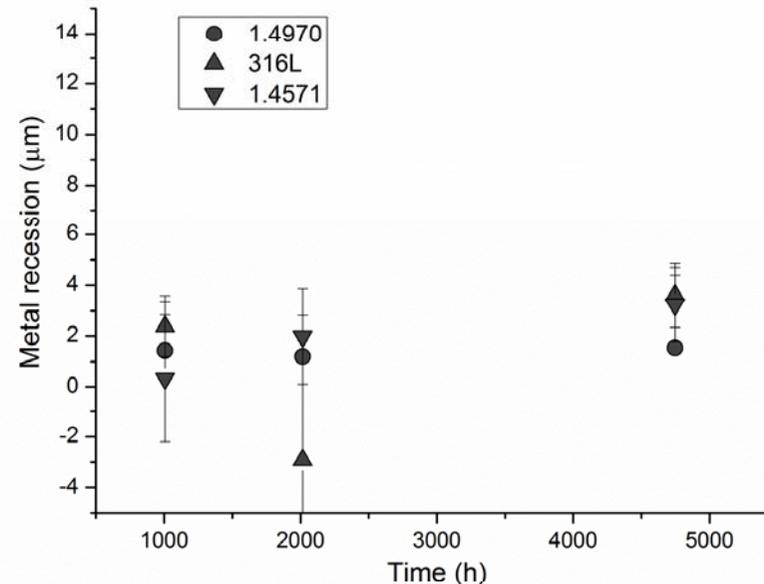
- flowing conditions in this test while data presented by Yamaki et al. correspond mainly to static conditions;
- maximum values used in this work for evaluation of corrosion loss while data presented by Yamaki et al. could correspond to averaged values.

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.

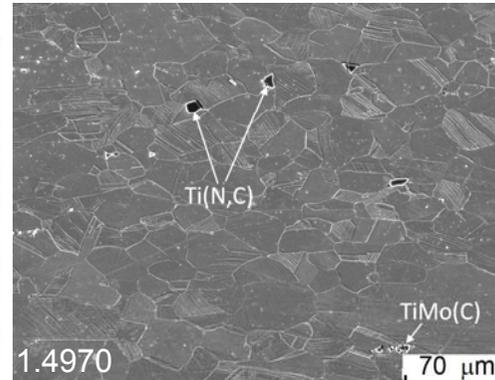
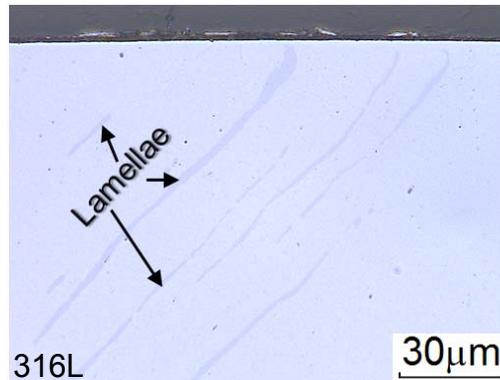
Quantification of corrosion loss of austenitic steels after exposure to flowing LBE (2 m/s) at 400°C with 10^{-7} mass% O



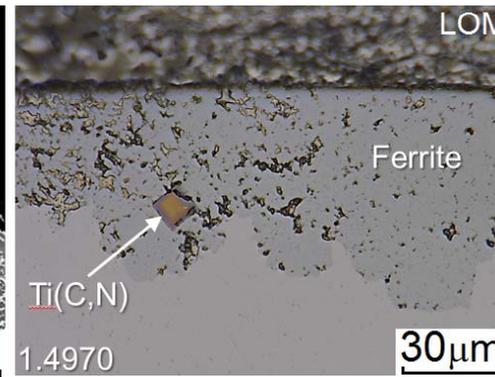
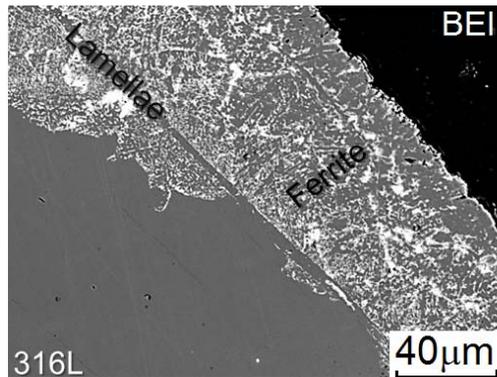
- ❑ Metal recession is in the range of error of the metallographic measurements ($\pm 2-4 \mu\text{m}$), i.e., no metal recession observed;
- ❑ Metallographic investigations clearly showed absence of solution-based attack at 400°C for duration of test 4746 h.

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

Initial state



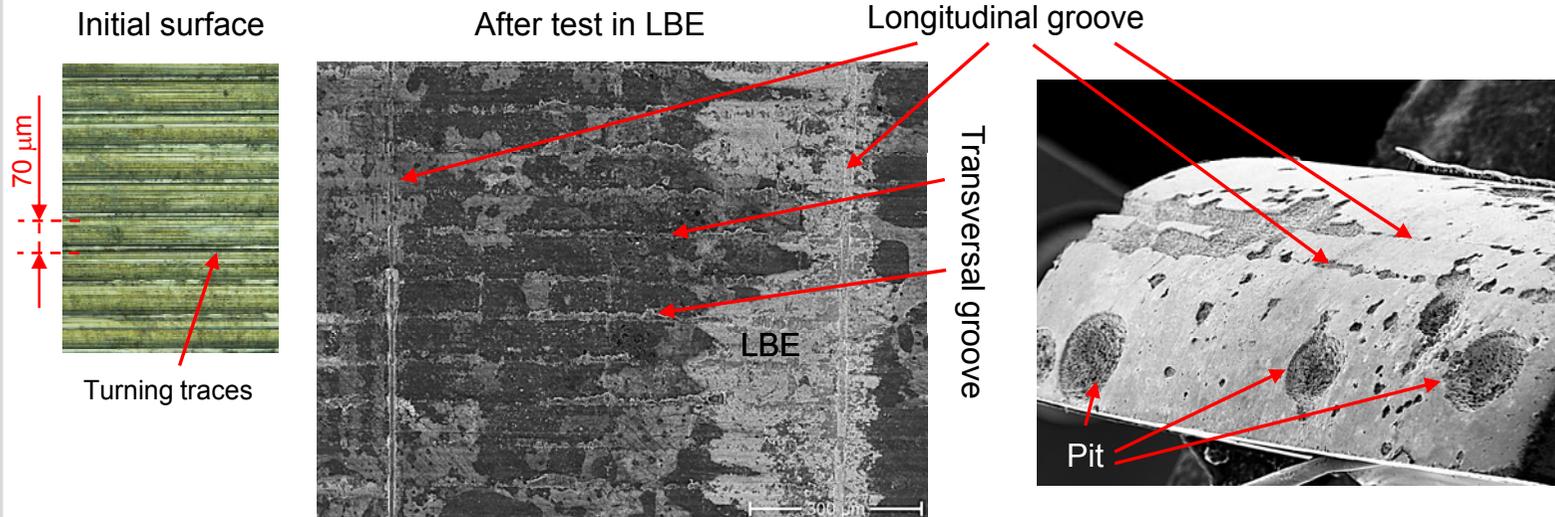
After exposure to LBE



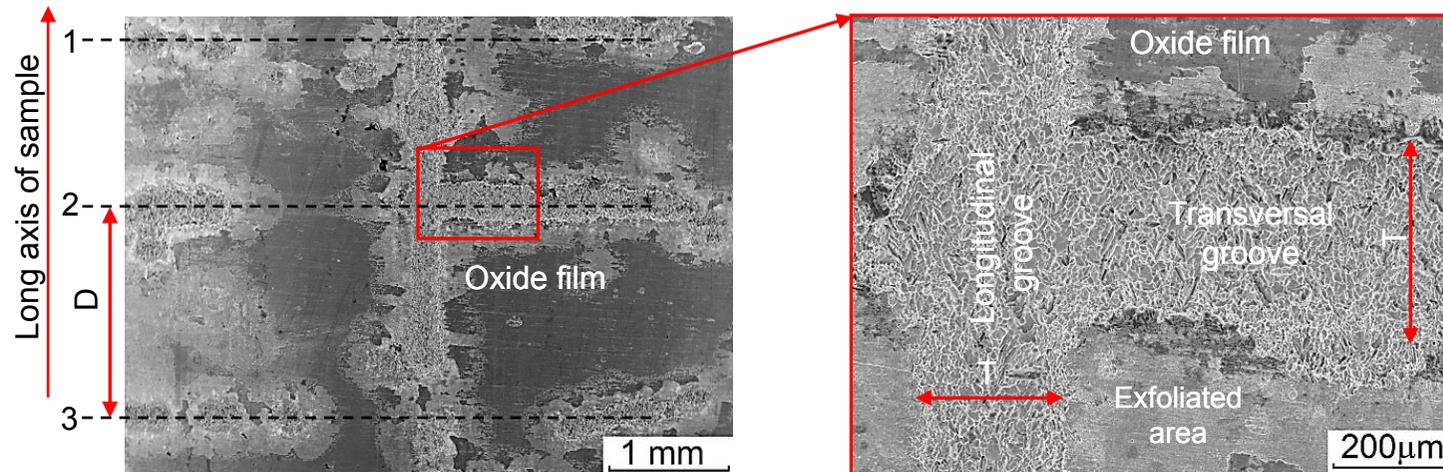
- Ti(C,N) precipitation in composition of 1.4970 and 1.4571
- Cr-rich lamellae (Fe-20%Cr-4%Ni) in composition of 316L
- Ti(C,N) precipitation and Cr-rich lamellae are corrosion resistant to LBE with 10^{-7} mass%O

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

Effect of surface preparation on the corrosion response



General surface topography of 1.4970 sample after 5015 h test in LBE at 450°C and subsequent cleaning



Macro-defects: transversal and longitudinal groves

☐ Preferential corrosion in the form of transversal and longitudinal groves is associated with surface pattern obtained after finishing turning

Effect of surface finishing on the corrosion appearance of 1.4970 steel tested in flowing oxygen-containing LBE (~ 2 m/s, ~ 10⁻⁷ mass % O) at 400°C.

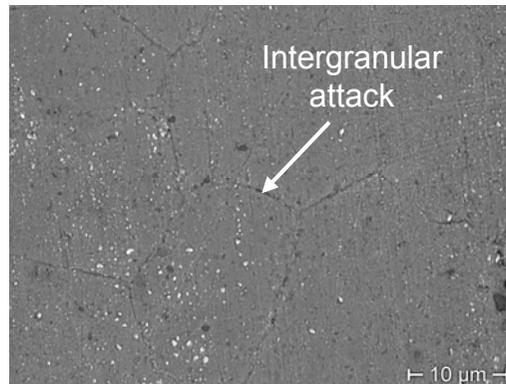
Flattened surface area of rod sample finished by:



- Grinding (500-grid SiC paper) – similar surface appearance as on the turned surface, i.e. oxidation;
- Polishing (diamond pastes 9-1µm) – origination of solution-based liquid-metal attack.

1007 h

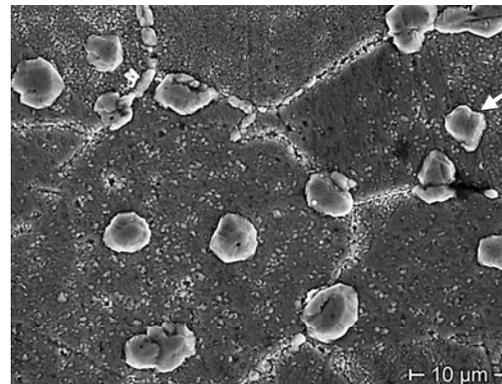
Surface



- Preferential solution-based attack along grain-boundaries (intergranular)

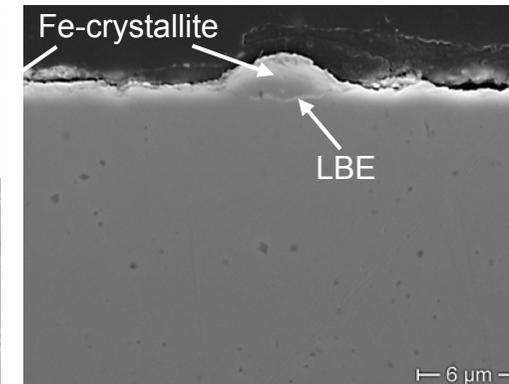
4746 h

Surface



- Solution-based attack resulted in the formation of separated Fe-based crystallites (fine and coarse);
- Composition of coarse crystallites: Fe(bal.)-3.5mass%Cr

Cross-section



- LBE is detected between Fe-crystallites and austenitic matrix;
- Volume increase due to transformation from *fcc* γ -iron to *bcc* α -iron.

Conclusions

□ Interaction of austenitic steels (1.4970, 316L and 1.4571) with flowing (2 m/s) LBE with 10^{-7} mass % O 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** from the sub-oxide layers and subsequent development of ferrite zone penetrated by LBE:

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

solution-based attack is not observed after 4746 h; test is continuing up to 10000h

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

solution-based selective leaching with maximum depth of local attack $114\mu\text{m}$ (1.4571), $183\mu\text{m}$ (1.4970) and $210\mu\text{m}$ (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 $587\mu\text{m}$ (1.4571), $207\mu\text{m}$ (1.4970) and $158\mu\text{m}$ (316L) for 2011 h

□ **Cr-based oxide film, formed *in-situ* on the surface of austenitic steels, is not a sufficient protective barrier with respect to the selective leaching attack at least at 450 and 550°C in the LBE with 10^{-7} mass%O!**

□ In the LBE with 10^{-7} mass%O the **selective leaching** is a main corrosion mechanism of austenitic steels causing substantial corrosion loss, while in LBE with 10^{-6} mass%O the **oxidation prevails**.

□ The **local deep solution-based attack due to selective leaching** of steel constituents is a **critical factor** affecting corrosion resistance of austenitic steels in oxygen-controlled LBE while **oxidation is only postpones the unavoidable start of selective leaching**.

Thank you for attention !!!

Acknowledgements

The construction and operation of the CORRIDA loop was financially supported by the Nuclear Safety Programme of KIT.

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