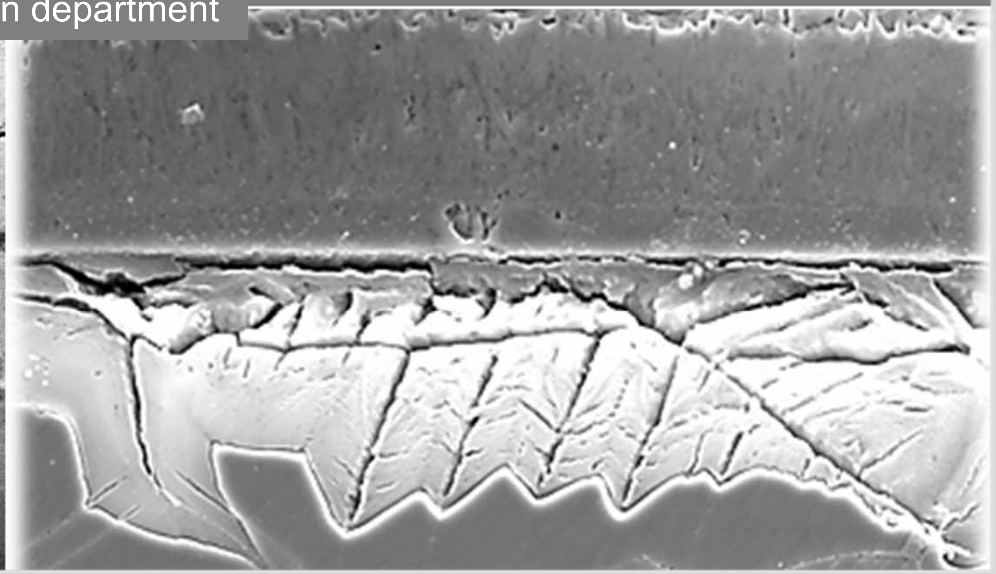
Kyoto Univ. Nov. 27 and 28

EXPERIMENTAL ACTIVITY IN KARLSRUHE INSTITUTE OF TECHNOLOGY TOWARDS CORROSION PERFORMANCE OF STEELS IN Pb-Bi EUTECTIC

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

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

Corrosion department

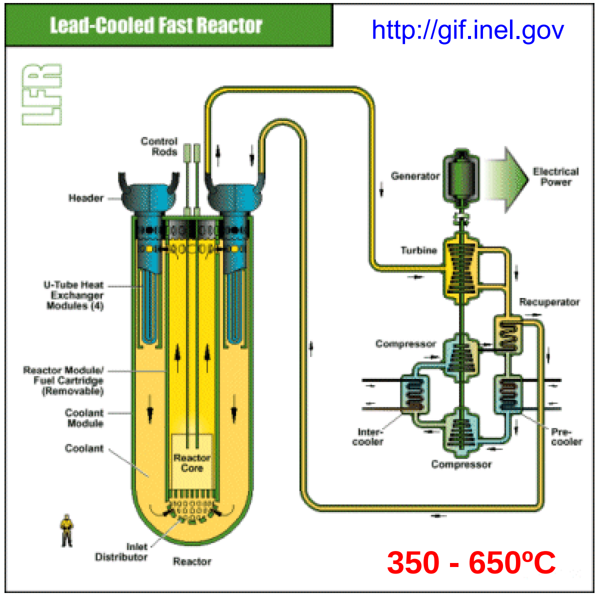


Outline

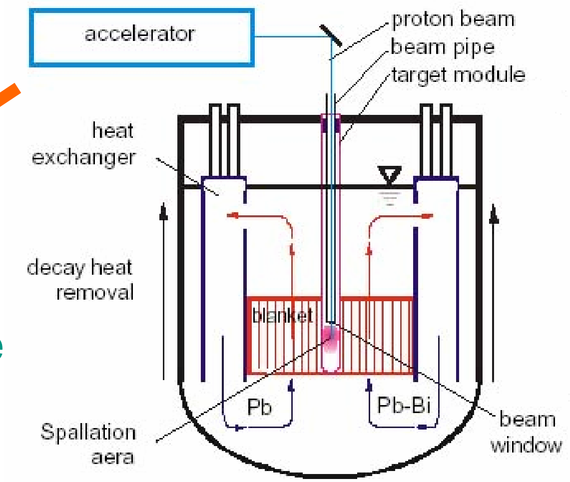
- BACKGROUND ON COMPATIBILITY OF STEELS IN CONTACT WITH HEAVY-LIQUID METALS AS APPLIED FOR GEN-IV REACTORS AND ADS
- GENERALIZATION OF RESULTS ON CORROSION OF STEELS IN FLOWING Pb-Bi – KIT ACTIVITY
- PRECIPITATIONS FOUND IN THE CORRIDA LOOP AFTER 113,000 h OPERATION
- PERFORMANCE OF ALUMINUM ALLOYED STEELS IN STATIC Pb-Bi AT 550°C FOR 1000 h

LIQUID-METALS AS A FUNCTIONAL MEDIA FOR NOVEL REACTORS

GENERATION IV



Accelerator Driven System



http://nucleartimes.jrc.nl

Liquid Metal Systems as a common area of knowledge and investigations

Blanket of fusion reactor

Li/V (Japan)

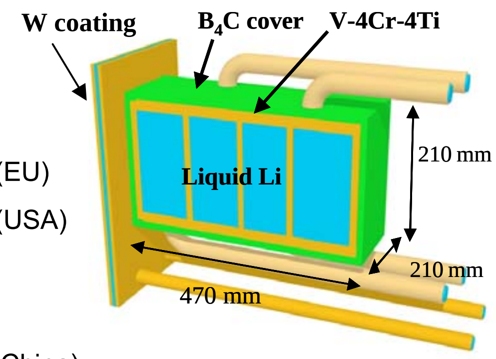
HCLL [He/LiPb/RAFM] (EU)

DCLL [He/LiPb/RAFM] (USA)

Li/He/RAFM (Korea)

Li/Be/V (Russia)

DFLL [He/LiPb/RAFM] (China)



Concentrating Solar Power

Effect of oxygen on the corrosion modes in steel / HLM system

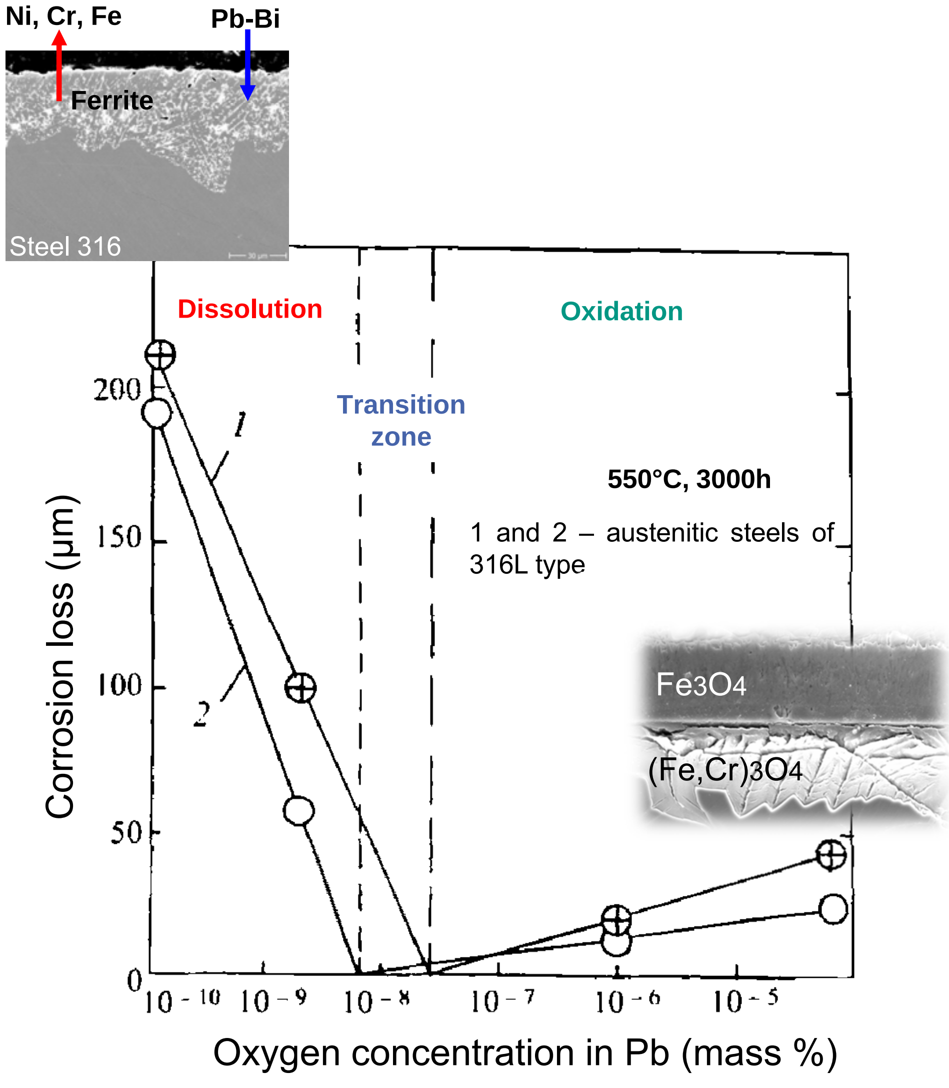
Positive effect of non-metallic impurity on corrosion

Issue!

- Dissolution of Ni, Cr and Fe from the steel by liquid metal:
  - Formation of week corrosion zone with ferrite structure on initially austenitic matrix
  - Liquid metal penetrates into the ferrite

Solution !?

- Oxidation instead of dissolution:
  - Formation of continuous and protective oxide layer
  - Long-term operation of scale in protective mode



I.V. Gorynin et al. Met. Sci. Heat Treat. 41 (9) (1999) 384–388

TODAYS ACTIVITY TOWARDS HLM TECHNOLOGIES

- **Principal understanding of corrosion phenomena** taking place in the steel / Heavy Liquid Metals system **does not free from the experimental activity!**
- **Main aim** of the corrosion tests is to **determine the optimum temperature-oxygen concentration parameters** for save and long-term operation of structural materials in contact with liquid Pb and Pb-Bi eutectic
- **Todays task** is to produce the **reliable quantitative data on corrosion loss based on the long-run tests** performed in liquid metals with controlled oxygen concentration

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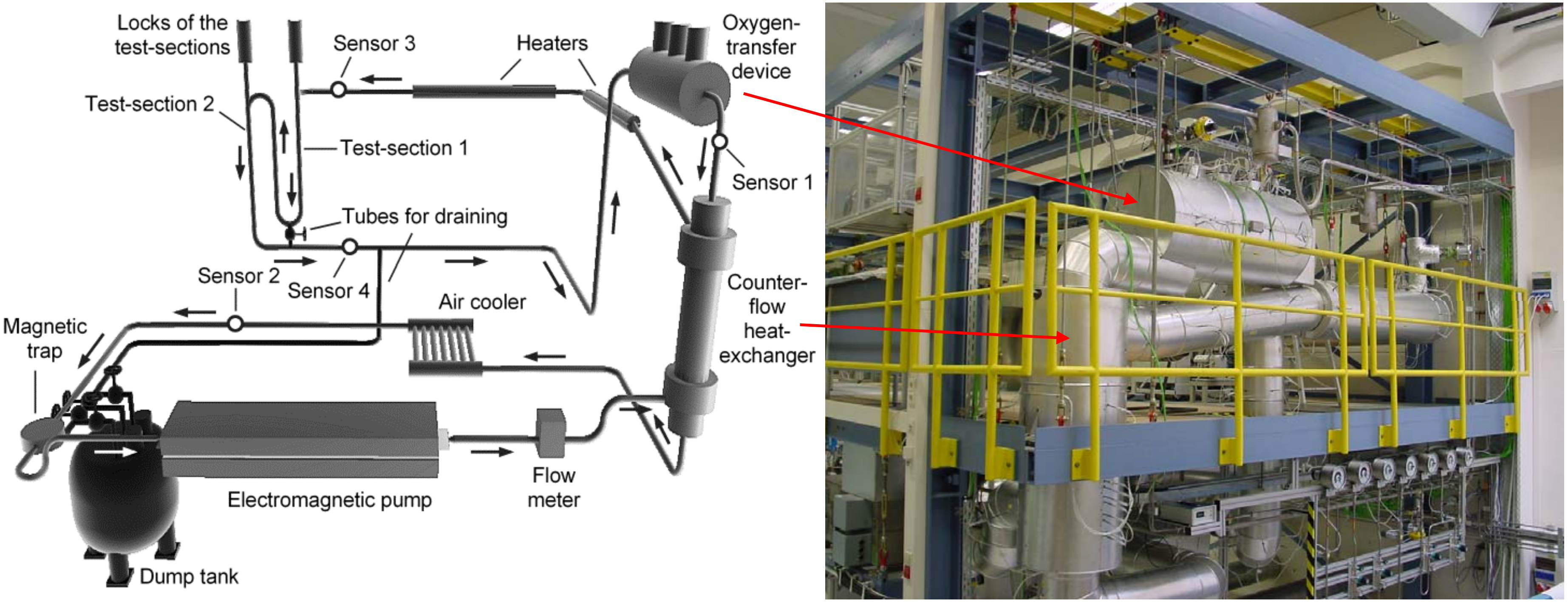
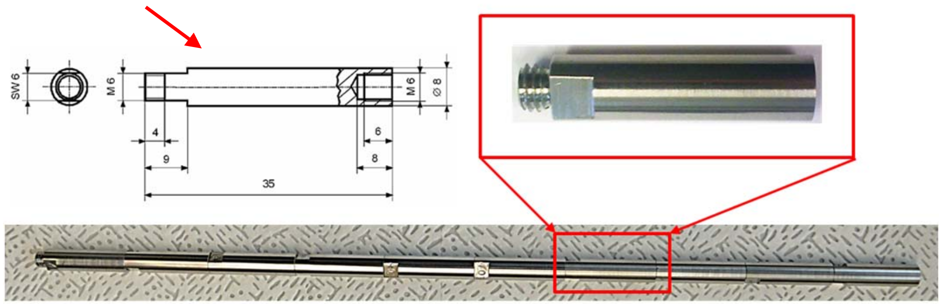
Facilities for dynamic corrosion tests in liquid metals

***CORR**osion **I**n **D**ynamic lead **A**lloys - **CORRIDA** loop*



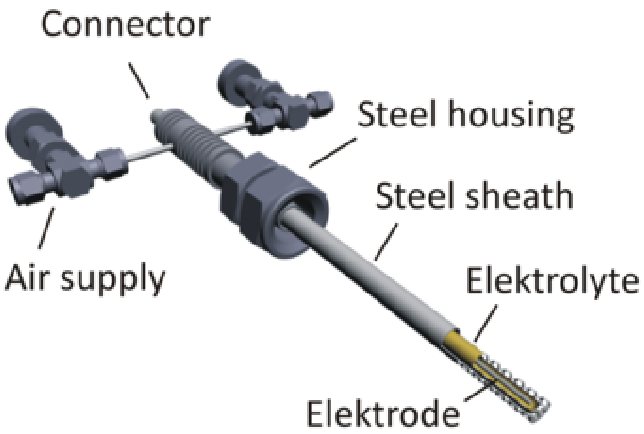
The CORRIDA facility – a forced-convection loop made of austenitic stainless steel (1.4571) designed to expose material (steel) specimens to flowing (2 m/s) Pb-Bi eutectic (~1000 kg) <u>with controlled oxygen concentration</u>.



C

Oxygen-Control System (OCS)

Pt/air oxygen sensor

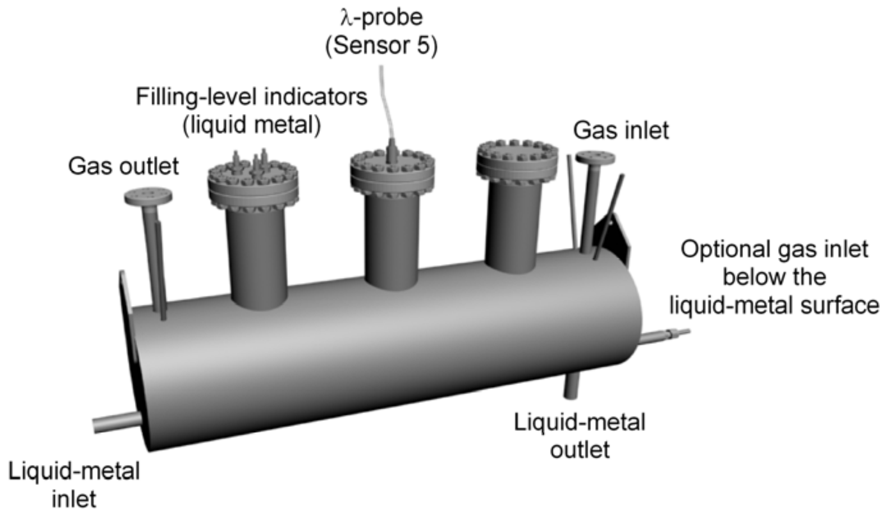


- Transformation of a difference in the chemical potential of oxygen into a difference in the electrochemical potential of electrons
- Transmission to a voltmeter and indication as electric voltage
- Calculation of the unknown oxygen potential from the known potential at the reference electrode:

$$log(CO_{Pb-Bi}) = -3.2837 + \frac{6949.8}{T} - 10080\frac{E}{T}$$

- Conversion to partial pressure, concentration of dissolved oxygen, etc.

Oxygen-transfer device



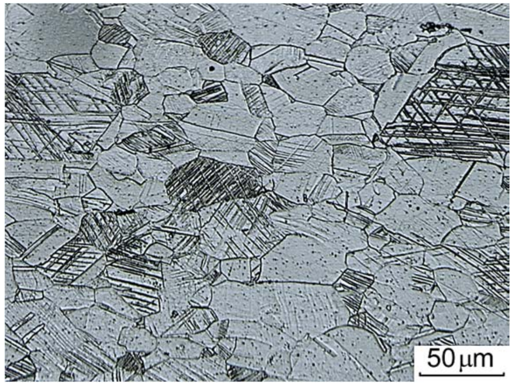
- Ar-carrier gas with automated air addition
- Optional humidification of the gas
- $Ar\text{-}H_2$ for removal oxygen from the liquid Pb-Bi

EXPERIMENTAL DATA ON CORROSION OF STEELS IN HLM

Austenitic steels tested in the CORRIDA loop

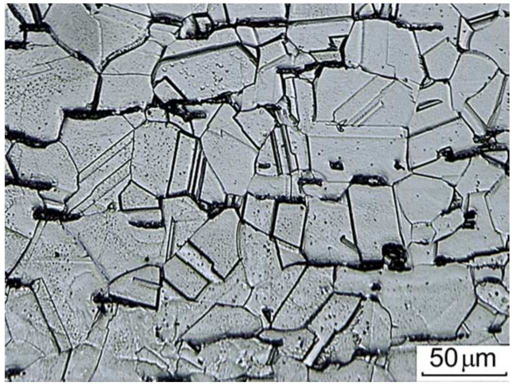
(Fe – Bal.)	Cr	Ni	Mo	Mn	Si	Cu	V	W	Al	Ti	C	N	P	S	B
316L	16.73	9.97	2.05	1.81	0.67	0.23	0.07	0.02	0.018	-	0.019	0.029	0.032	0.0035	-
1.4970	15.95	15.4	1.2	1.49	0.52	0.026	0.036	< 0.005	0.023	0.44	0.1	0.009	< 0.01	0.0036	< 0.01
1.4571	17.50	12	2.0	2.0	1.0	-	-	-	-	0.70	0.08	-	0.045	0.015	-

1.4970 (15-15Ti)



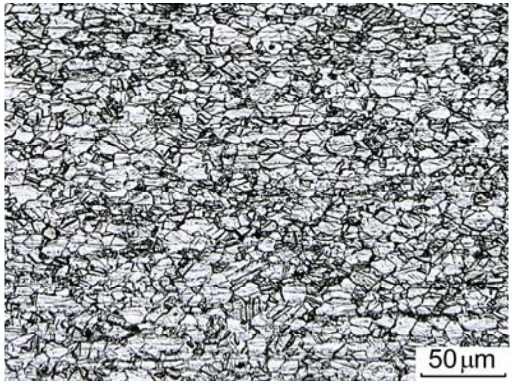
- HV_{30} = 253;
- Grain size ranged from 20 to 65 µm;
- Intersecting deformation twins.

316L



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

1.4571 (material of CORRIDA loop)



- HV_{30} = 245;
- Fine-grained structure with grain size averaged 15 µm (G 9.5).

F/M steels tested in the CORRIDA loop

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

(Fe – Bal.)	Cr	Mo	W	V	Nb	Ta	Mn	Ni	Si	C
T91-A	9.44	0.850	<0.003	0.196	0.072	n.a.	0.588	0.100	0.272	0.075
T91-B	8.99	0.89	0.01	0.21	0.06	n.a.	0.38	0.11	0.22	0.1025
P92	8.99	0.49	1.75	0.20	0.06	-	0.43	0.12	0.26	0.11
E911*	8.50-9.50	0.90-1.10	0.90-1.10	0.18-0.25	0.06-0.10	-	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	0.47	0.020	0.040	0.11

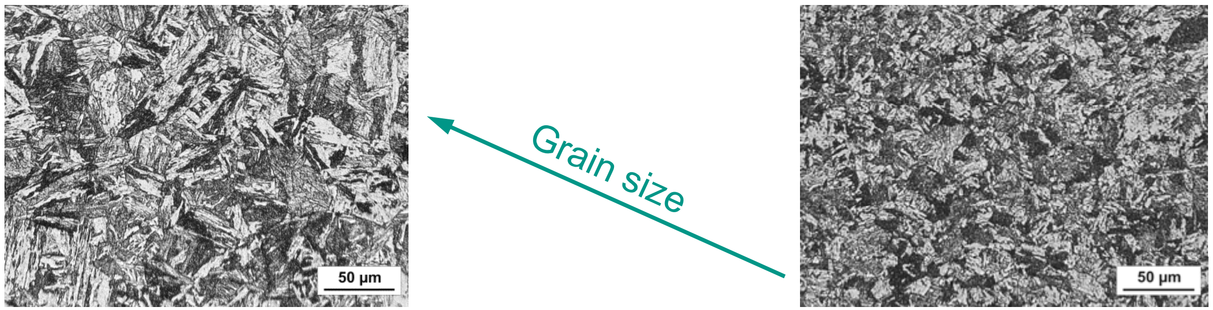
*nominal composition

⇧ Nominally 9 mass% Cr

⇧ Element besides Cr that improves oxidation resistance

Martensitic microstructure of F/M steels

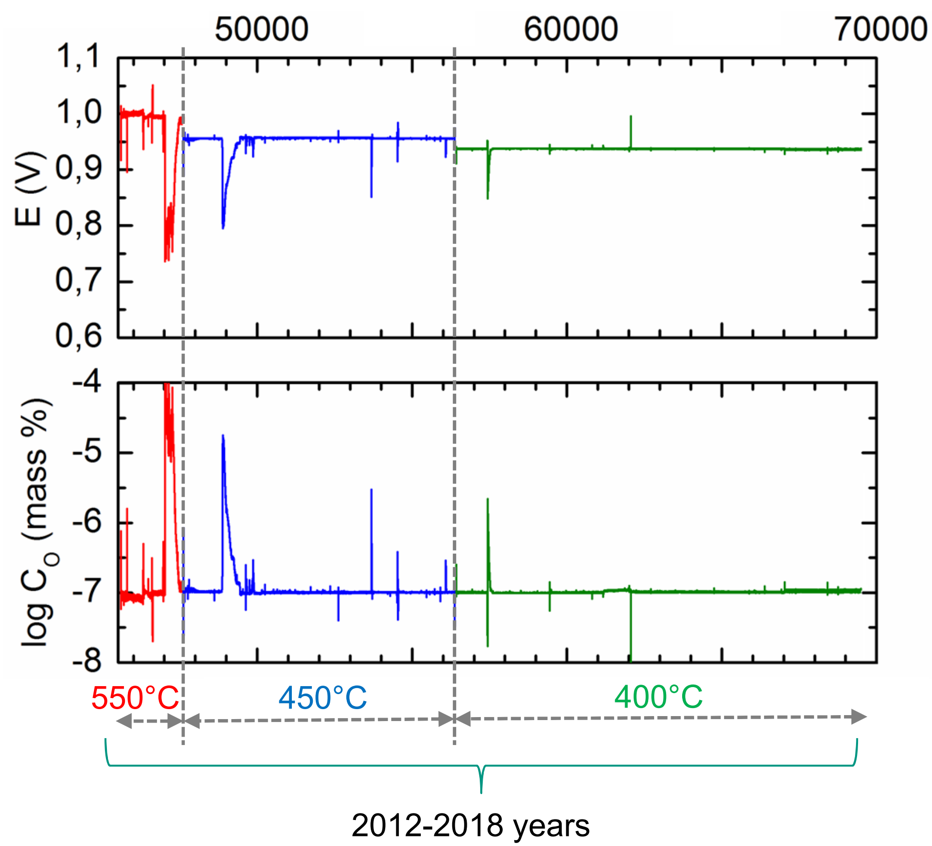
E911, T91-A, T91-B, P92



EUROFER

Corrosion tests performed for period from 2012 to 2018 years

Effective operating time of CORRIDA loop (h)



Flow velocity 2 m/s

Target oxygen concentration in Pb-Bi = 10^{-7} mass%

- **T = 550°C**

  excursion to 10^{-4}–10^{-5} mass%O

  t = 288; 715; 1007; 2011 h

- **T = 450°C**

  excursion to 10^{-5} mass% O

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

- **T = 400°C**

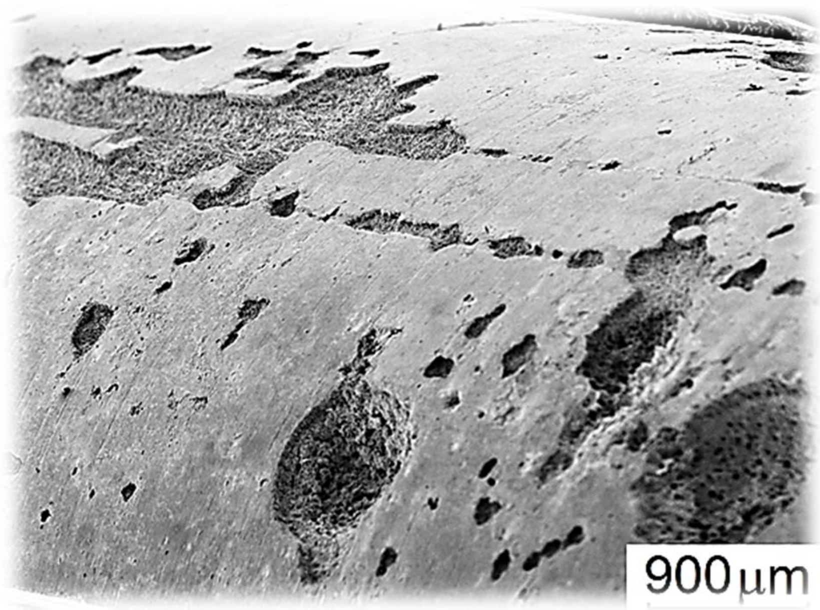
  t = 1007; 2015; 4746; 13194 h

Corrosion response of austenitic steels

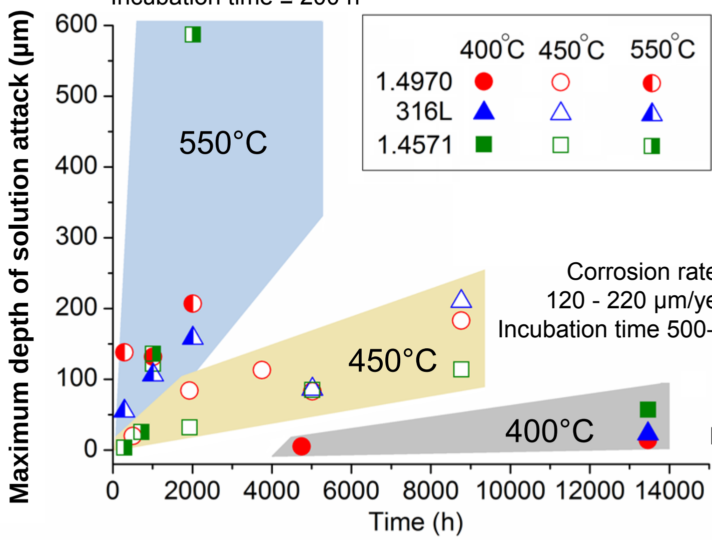
Flowing Pb-Bi (2 m/s), 10^{-7} mass% O, 400-550°C

Oxidation + Local pit-type dissolution attack

Local solution-based corrosion attack



Time-temperature dependence of local attack

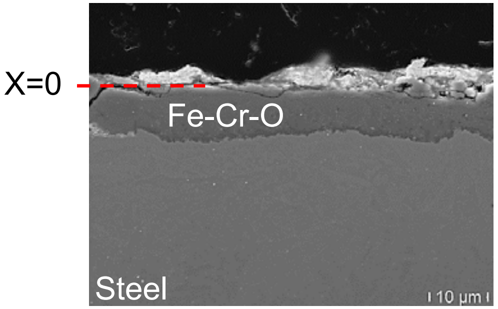


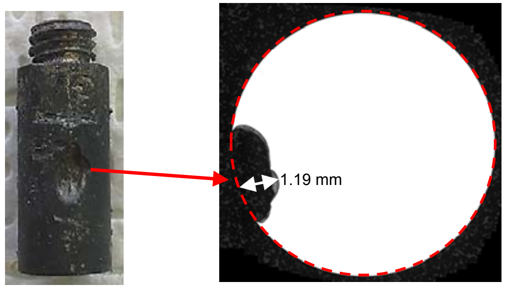
- 10% of wall thinning for cladding tube - corrosion criterion suggested for “steel / sodium” system
- Corrosion limit for 450 μm thick cladding tube made of 1.4970 steel is 45 μm
- 550 and 450°C could not be a working temperatures in Pb-Bi with 10^{-7} mass% O
- At 400°C, corrosion limit for 1.4970 could be reached for about 33000 h (~4 years) that is probably within an appropriate time for life-time of cladding tube made of 1.4970 (15-15 Ti) steel

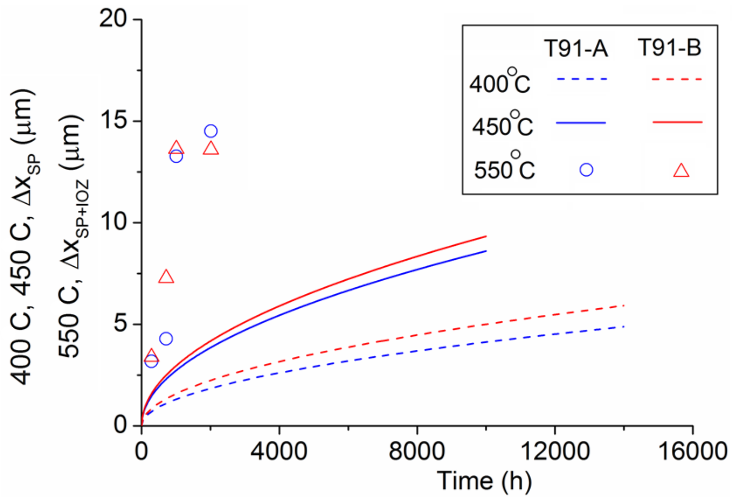
Corrosion response of F/M steels

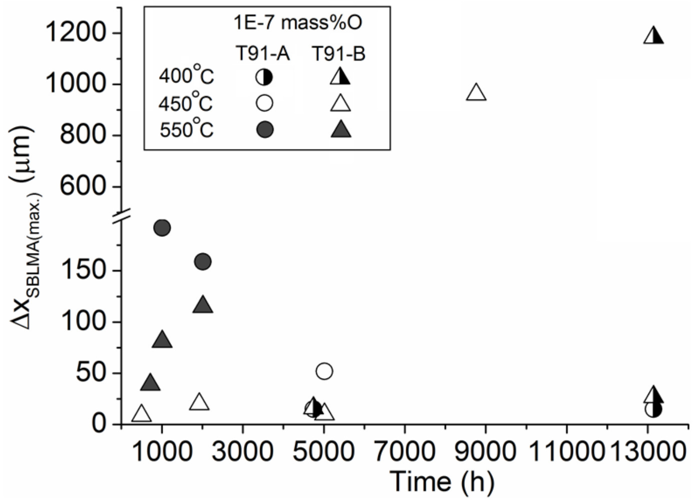
Flowing Pb-Bi (2 m/s), 10^{-7} mass% O, 400-550°C

General corrosion trend: oxidation	Local corrosion trend: leaching of steel constituents (Fe, Cr)







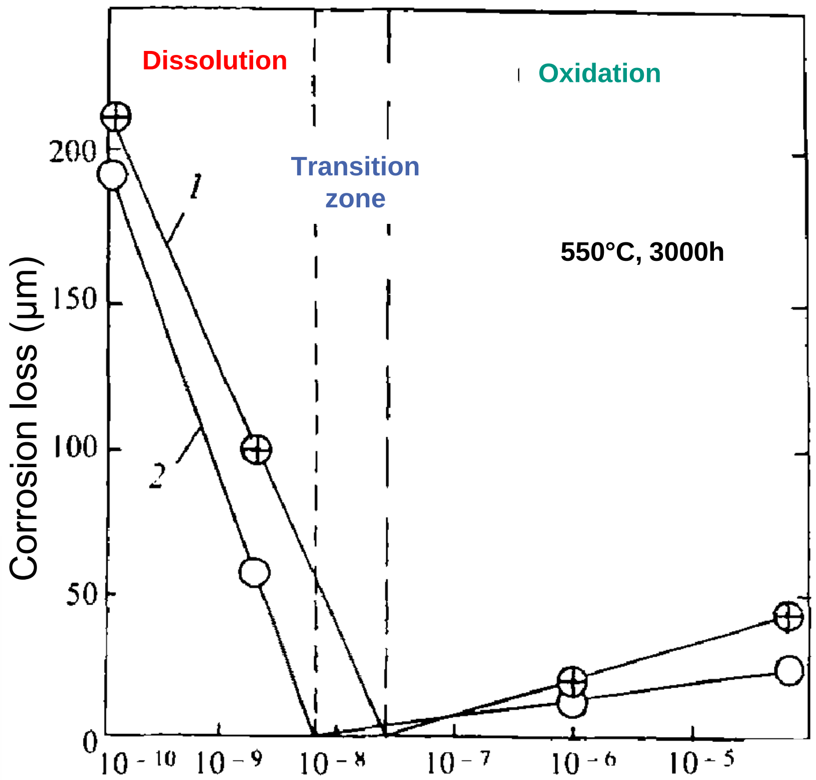


- In comparison to 450 or 550°C the oxidation is significantly reduced at 400°C
- Severe local dissolution attack, as a result of scale failure, occurs

Comparison of earlier findings and today's vision !

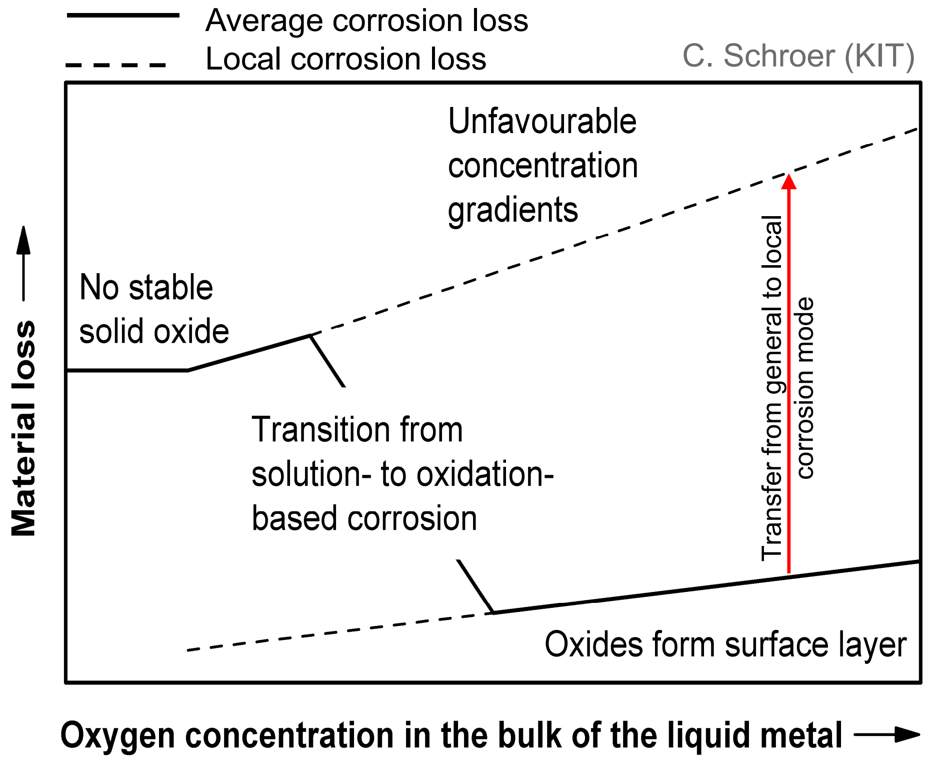
Earlier findings ! → Today`s vision !

I.V. Gorynin et al. Met. Sci. Heat Treat. 41 (9) (1999) 384–388.



1 and 2 – austenitic steels of 316L type

- In general correct
- In particular - too idealistic !



- In the oxide-protection regime the failure of scale might result in local and severe solution-based corrosion attack instead of expected re-oxidation of steel surface!
- Local solution-based attack is a critical factor affecting corrosion resistance of steels in Pb-Bi !!!

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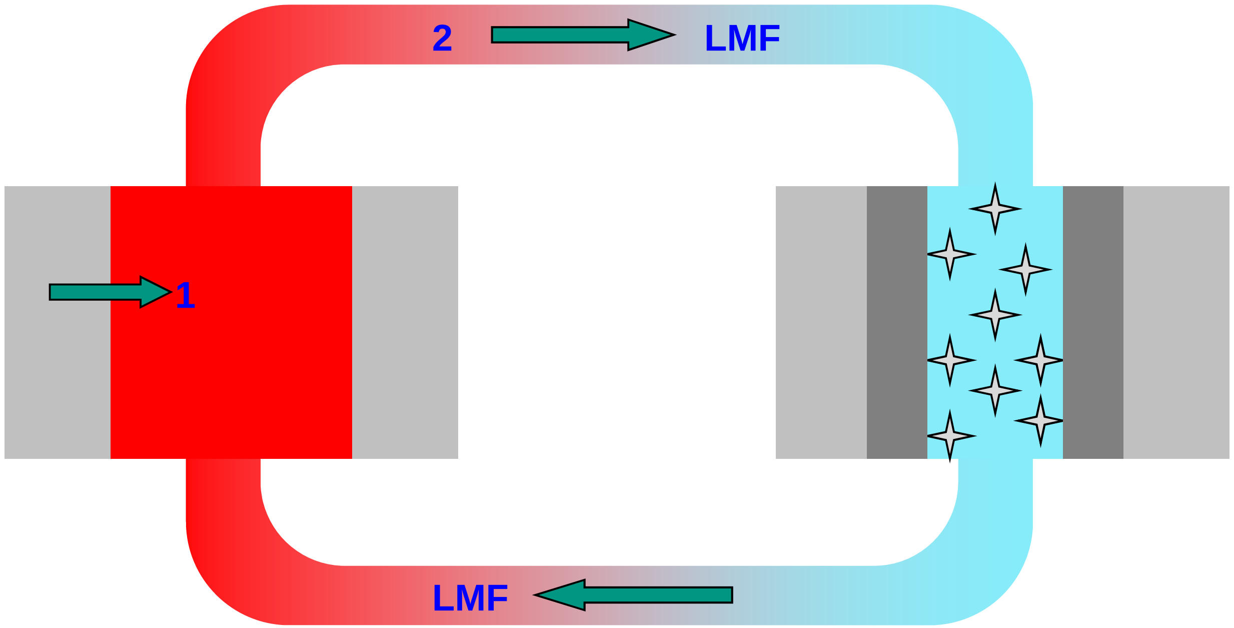
Mass transfer under temperature gradient

Simplified scheme of non-isothermal mass-transfer



Tortorelli, 1987

- Solid metal
- LMF – Liquid Metal Flow
- "Hot" zone
- "Cold" zone
1. Dissolution
2. Mass transfer
- Nucleation of crystals
- Plug formation

Operating history of the CORRIDA loop

Carsten Schroer (KIT), ICONE26

Commissioning in Feb 2003.

Start of operation at 550 °C/ 10^{-6} % oxygen in Jul 2003. Oxygen transfer with $Ar–H_2–H_2O$.

Manual air addition to $Ar–H_2–H_2O$. ☺

Optimization.

Dry gas.

Optimized manual air addition to humidified Ar. ☺ Tube failure at the inlet of the second test-section after total operation for 29,000 h. ☹

450 °C/10^{-6} % oxygen.

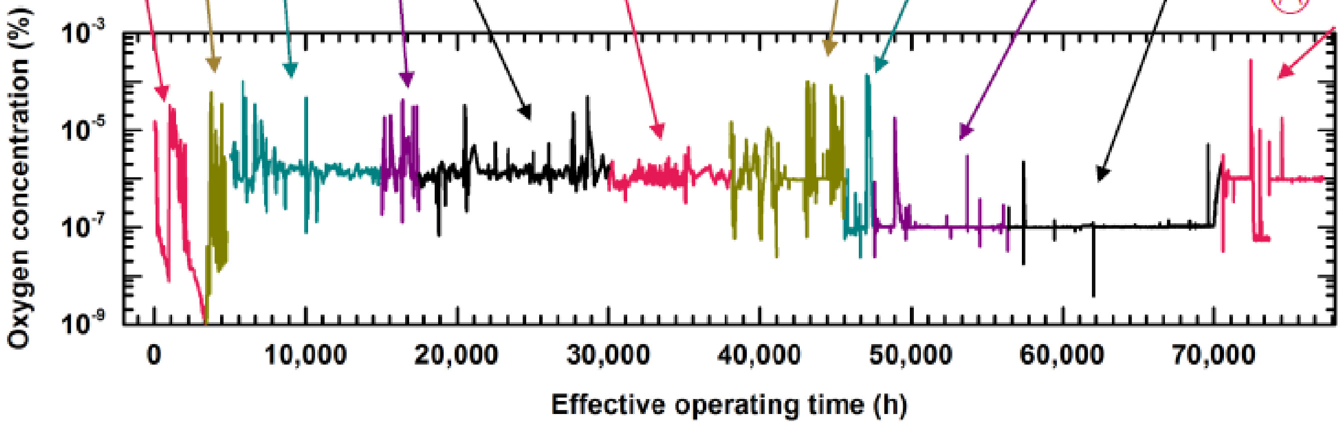
Return to 550 °C/ 10^{-6} % oxygen.
Automated air addition to Ar or $Ar–H_2$. ☺
Decreasing mass flow and mobile oxide deposits. ☹

☺ Automation of hydrogen addition.
550 °C/ 10^{-7} % oxygen.
☹ Tube failure at the bottom end of the first test-section after total operation for 66,000 h.

450 °C/ 10^{-7} % oxygen.
☹ Tube failure close to the weldment of the once replaced inlet piece after total operation for 47,500 (76,500) h.

400 °C/ 10^{-7} % oxygen.

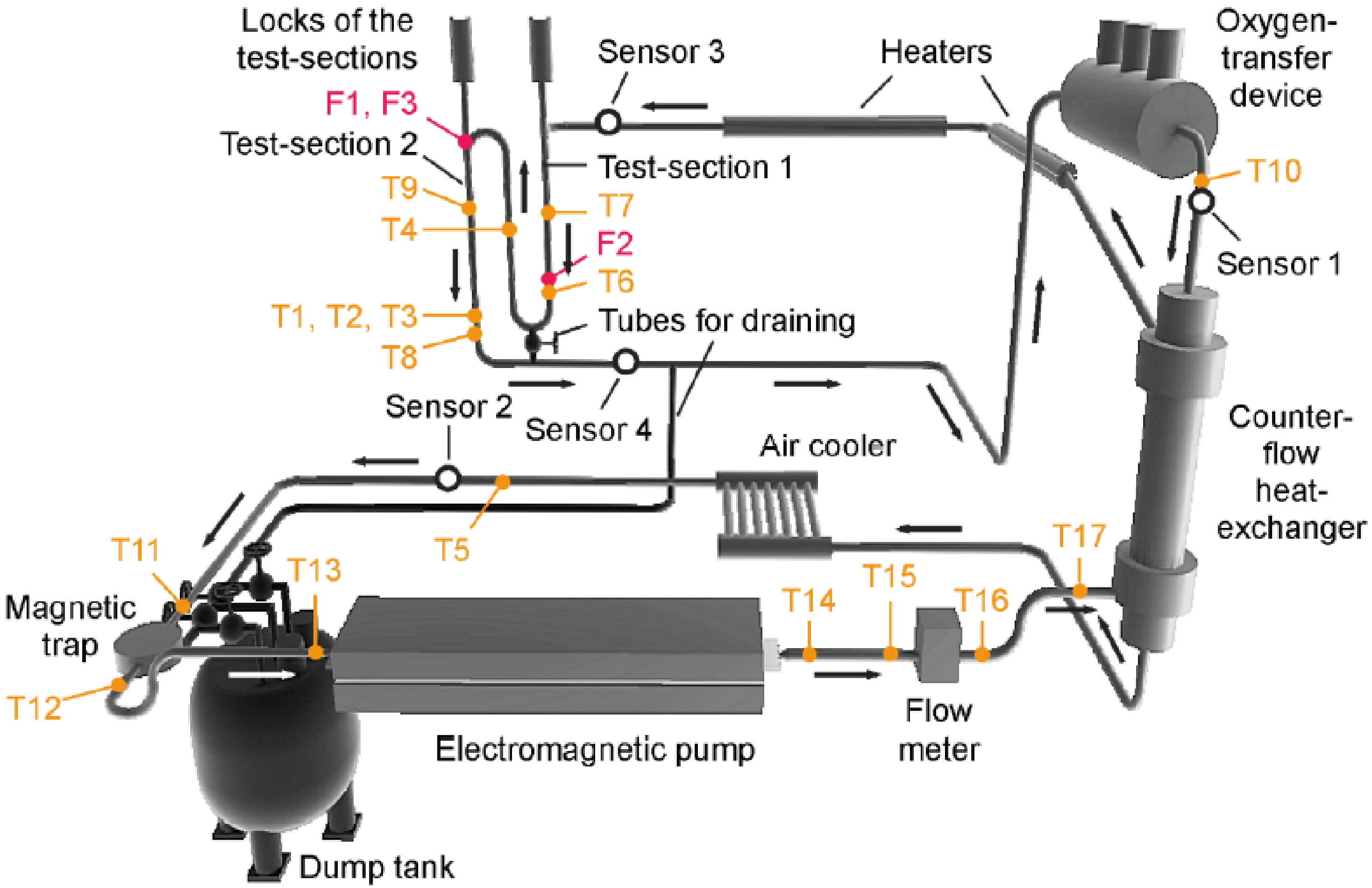
500 °C/ 10^{-6} % oxygen.
☹ Problems with mass flow return.



Total operation for 100,000 h in Feb 2016. ☺
Effective operation for 75,000 h in May 2017.

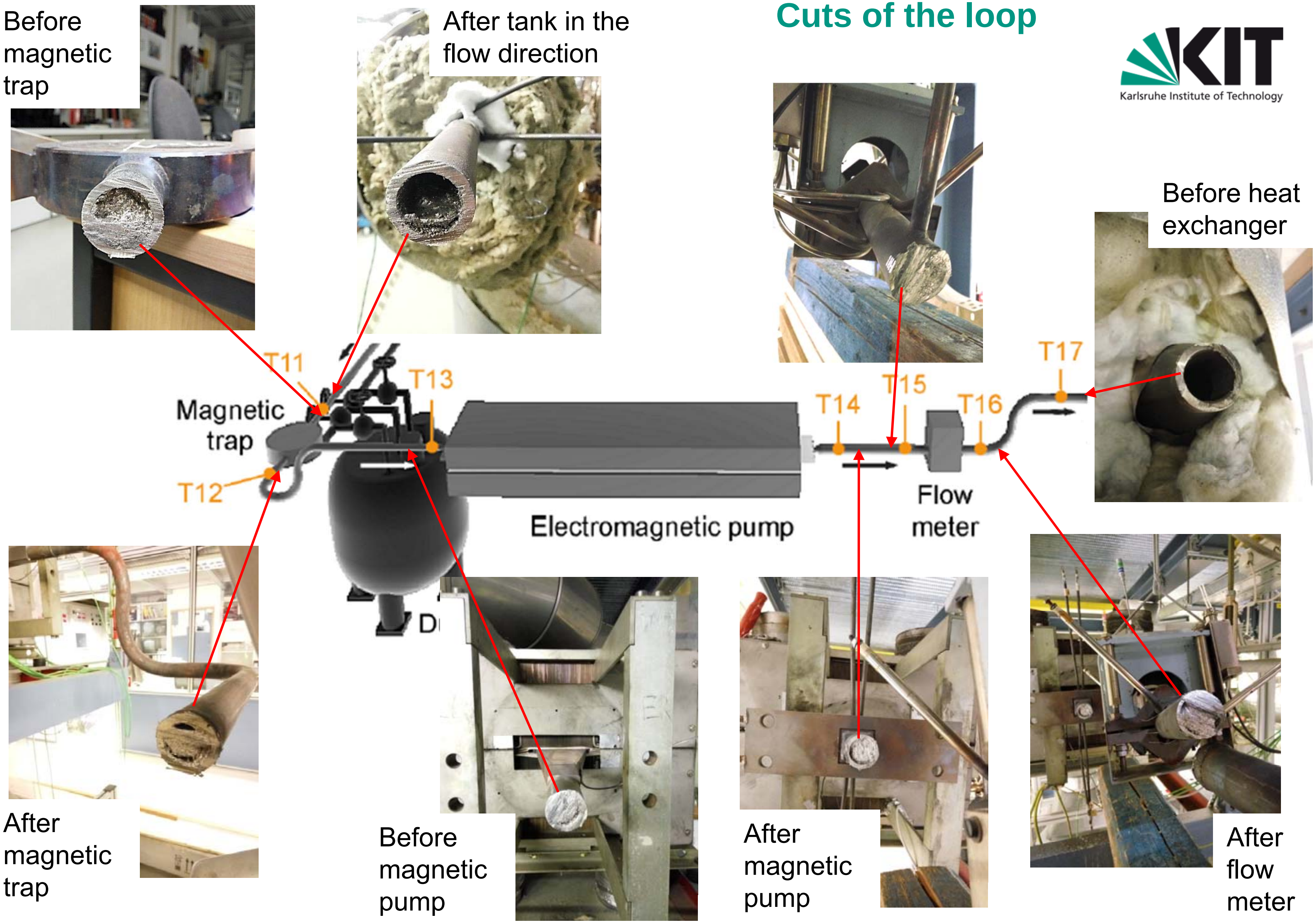
Plug in the cold leg after total operation for 113,000 h (Dec 2017): ☹
Loop cannot be refilled after LBE dump.

Localization of possible plugging areas in the loop



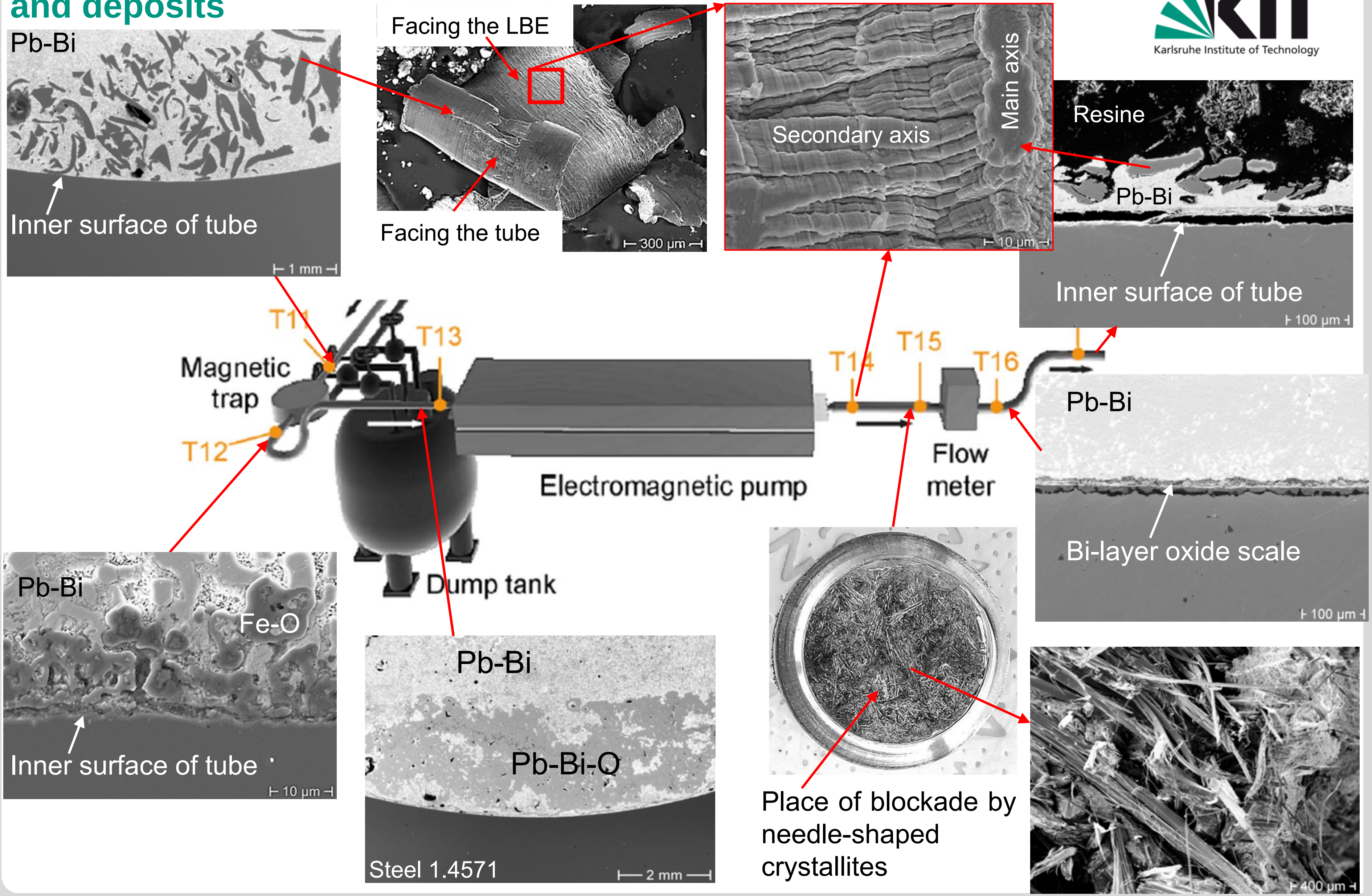
- ❑ According to the output of the thermocouples the solidified Pb-Bi is located among thermocouples T11 and T16.

Cuts of the loop



Precipitates and deposits

Fe-18Cr-10Ni dendrides (XRD →γ-Fe, magnetic !?)



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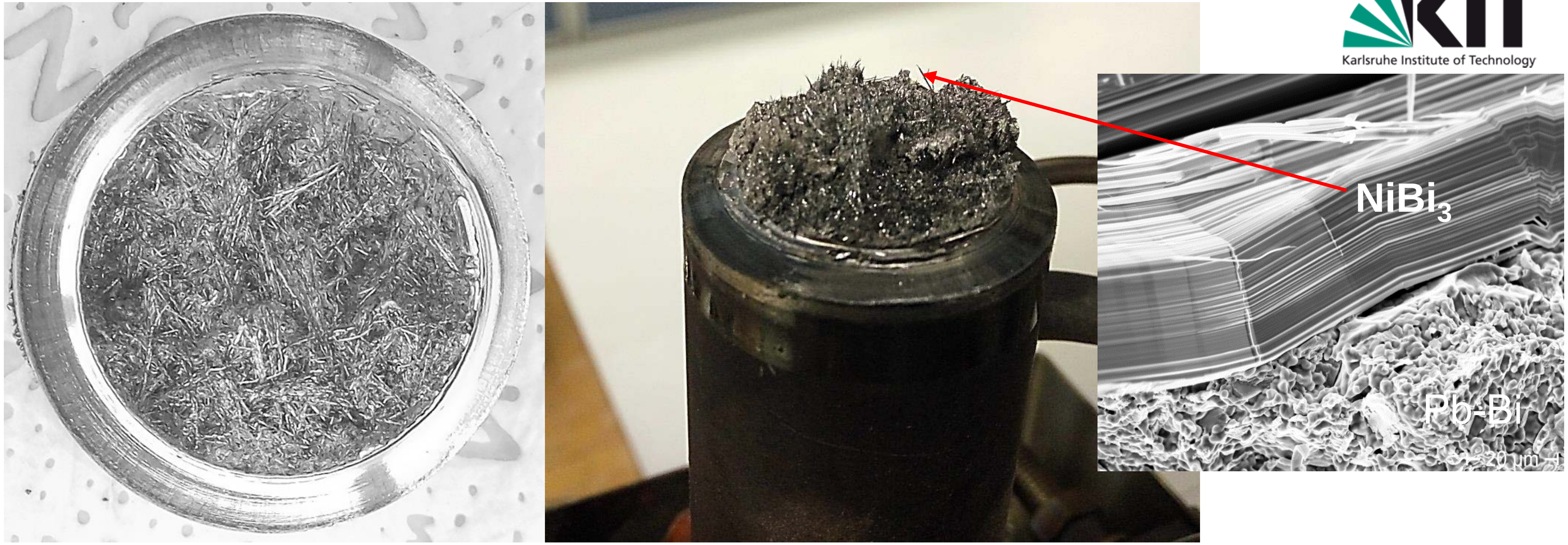
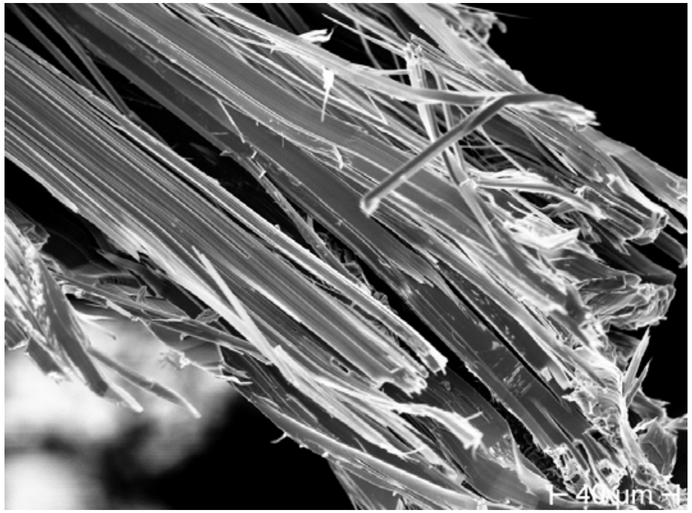
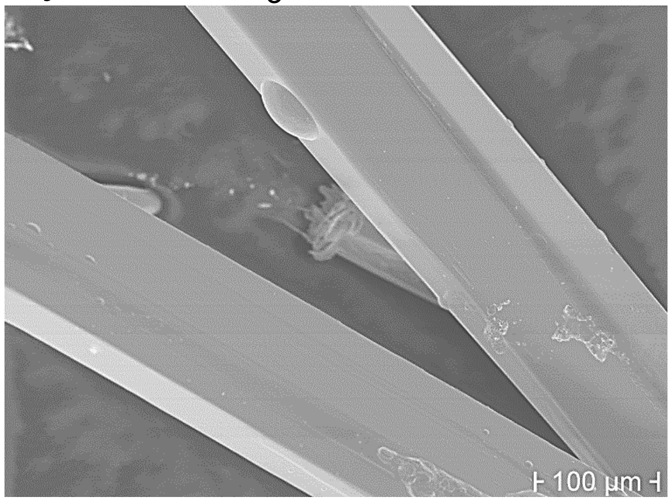


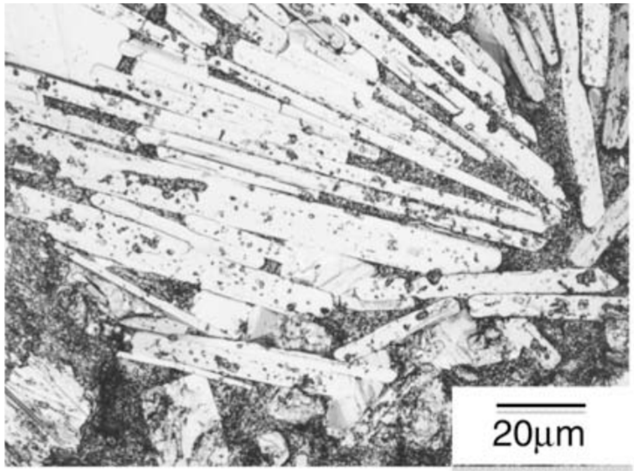
Array of needle-type crystals NiBi$_3$

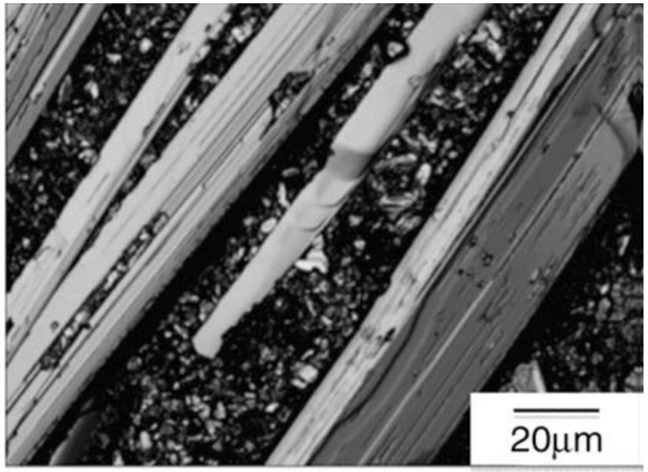




Literature data on $NiBi_3$

K. Kikuchi, S. Saito, D. Hamaguchi, M. Tezuka. K. Journal of Nuclear Materials 398 (2010) 104–108.





- $NiBi_3$ needle-type precipitates existed on the surface of solidified LBE
- A size is tens micron meters in width and over hundreds micron meters in length
- Needle-type precipitates existed at both the low temperature part of the loop and high temperature parts
- It can be assumed that Ni-rich precipitates formed on the surface of residual LBE during a cooling period

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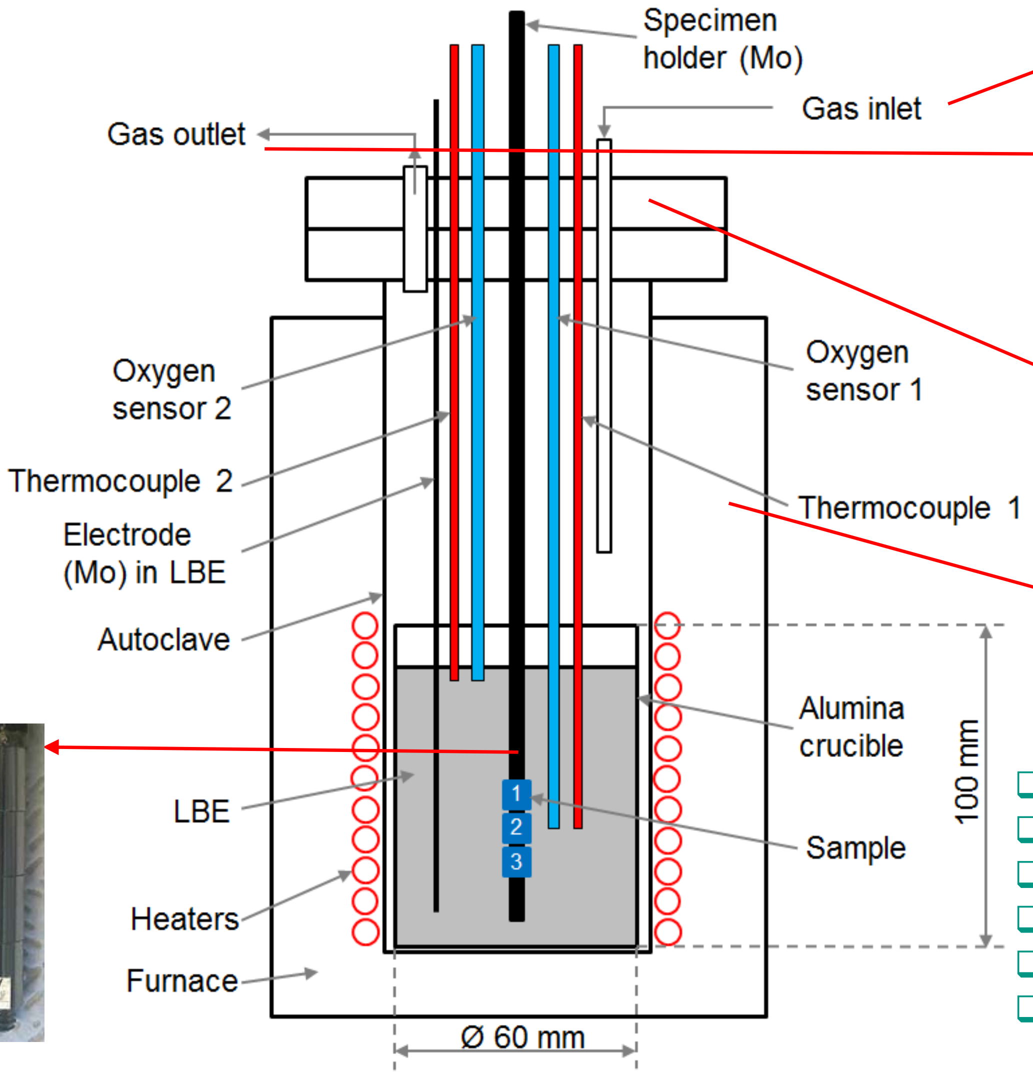
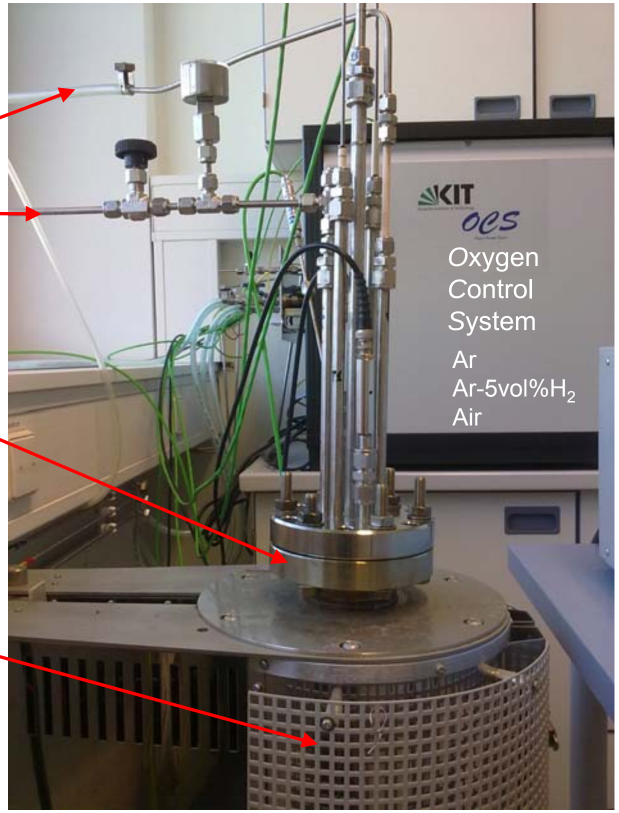
APPARATUS FOR STATIC CORROSION TESTS IN HEAVY LIQUID METALS





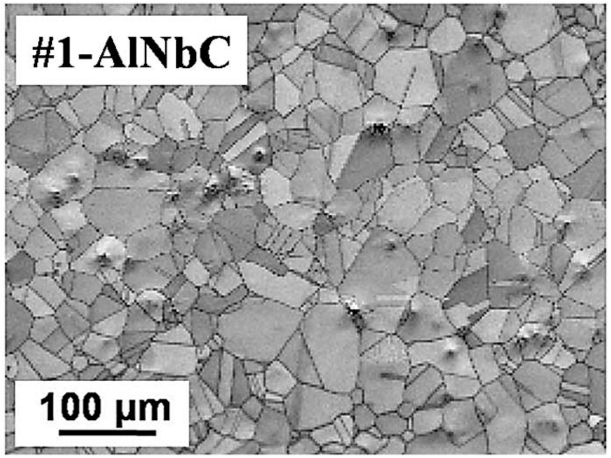
- ~2kg HLM (Pb, Pb-Bi, Sn)
- Working temperatures up to 700 ºC
- Ar+5%H2 / Ar / Air gas mixture above melt
- Two Pt/Air oxygen sensors
- Oxygen control system
- Cylindrical samples (Ø8x10 mm)

CHEMICAL COMPOSITION AND STRUCTURE OF AUSTENITIC STEELS ALLOYED BY ALUMINIUM

- Alumina-Forming Austenitic (AFA) stainless steels with improved creep resistance (strengthening with Laves phases and carbides) and oxidation resistance due to formation of Al_2O_3 at high temperatures in gaseous media are under developing (Y. Yamamoto et al., Metall and Mat Trans A 42 (2011) 922–931)
- **Applicability of AFA steels in Pb and Pb-Bi arouses interest and requires experimental investigations !**

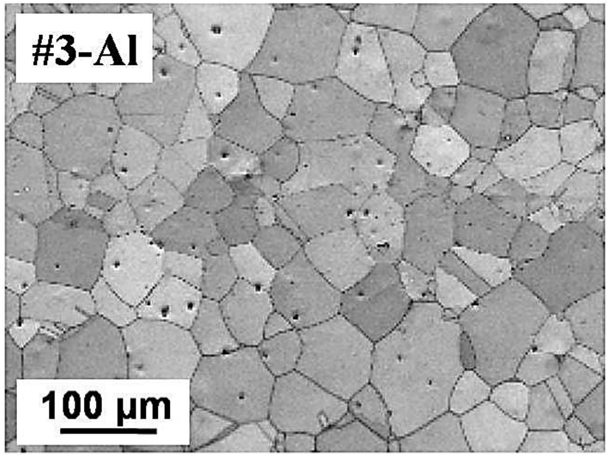
(Fe–Bal.)	Cr	Ni	Mo	Mn	Si	Al	Nb	C
# 1-AlNbC	11.7 (±0.02)	18.0 (±0.02)	1.99 (±0.003)	0.0887 (±0.0003)	0.401 (±0.0006)	2.32 (±0.008)	0.577 (±0.003)	0.0086 (±0.0003)
# 3-Al	11.7 (±0.02)	18.0 (±0.05)	2.00 (±0.007)	0.118 (±0.0005)	0.377 (±0.0009)	2.90 (±0.010)	<0.001	0.0300 (±0.0006)

Fe-18Ni-12Cr-AlNbC



Grain size →

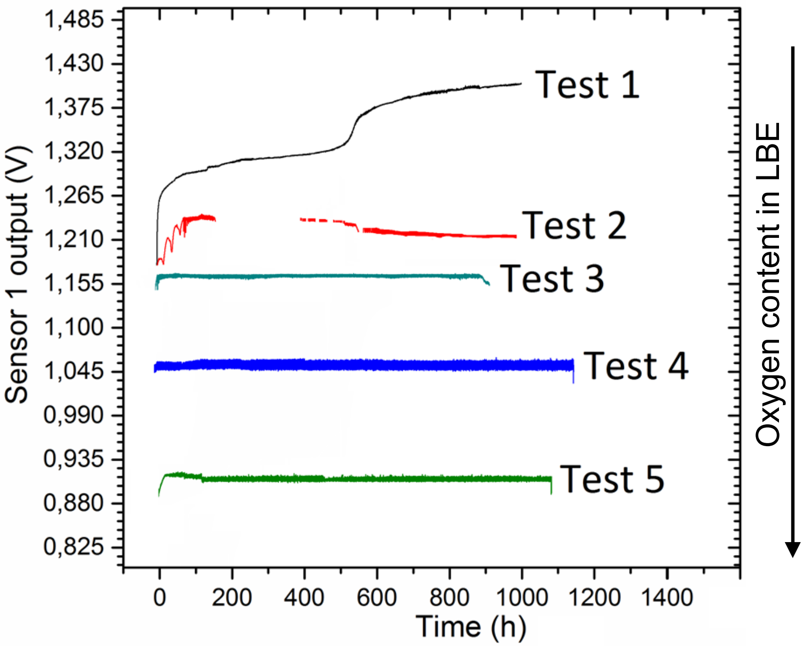
Fe-18Ni-12Cr-Al



School of Material Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

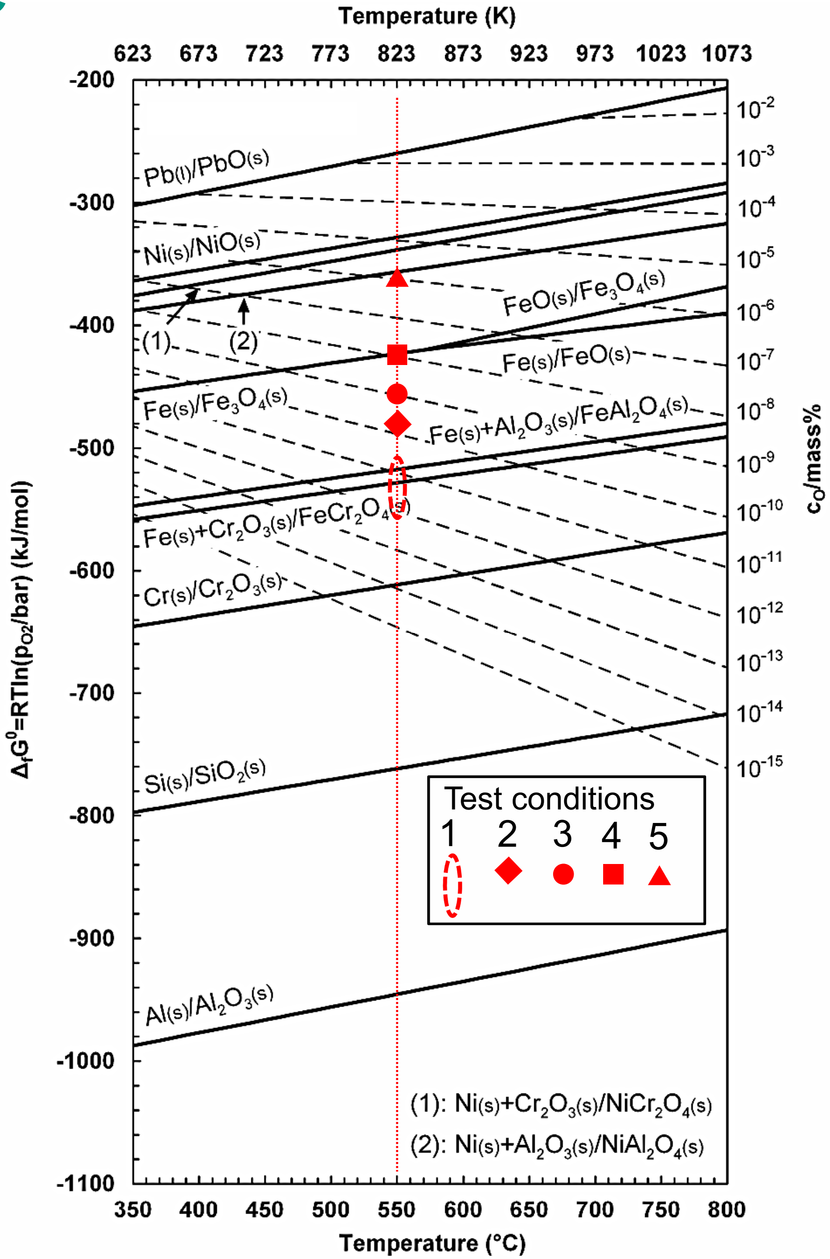
CORROSION TESTS IN Pb-Bi EUTECTIC

- Constant parameters of test:
  - volume of Pb-Bi eutectic (2 kg)
  - ratio of Pb-Bi volume to surface of samples is 25 cm
  - temperature 550°C
  - exposure time ~1000 h
- Varying oxygen concentration in Pb-Bi eutectic
  - Test 1: 10^{-11} -10^{-12} mass%O
  - Test 2: 10^{-10} mass%O
  - Test 3: 10^{-9} mass%O
  - Test 4: 10^{-8} mass%O
  - Test 5: 10^{-6} mass%O



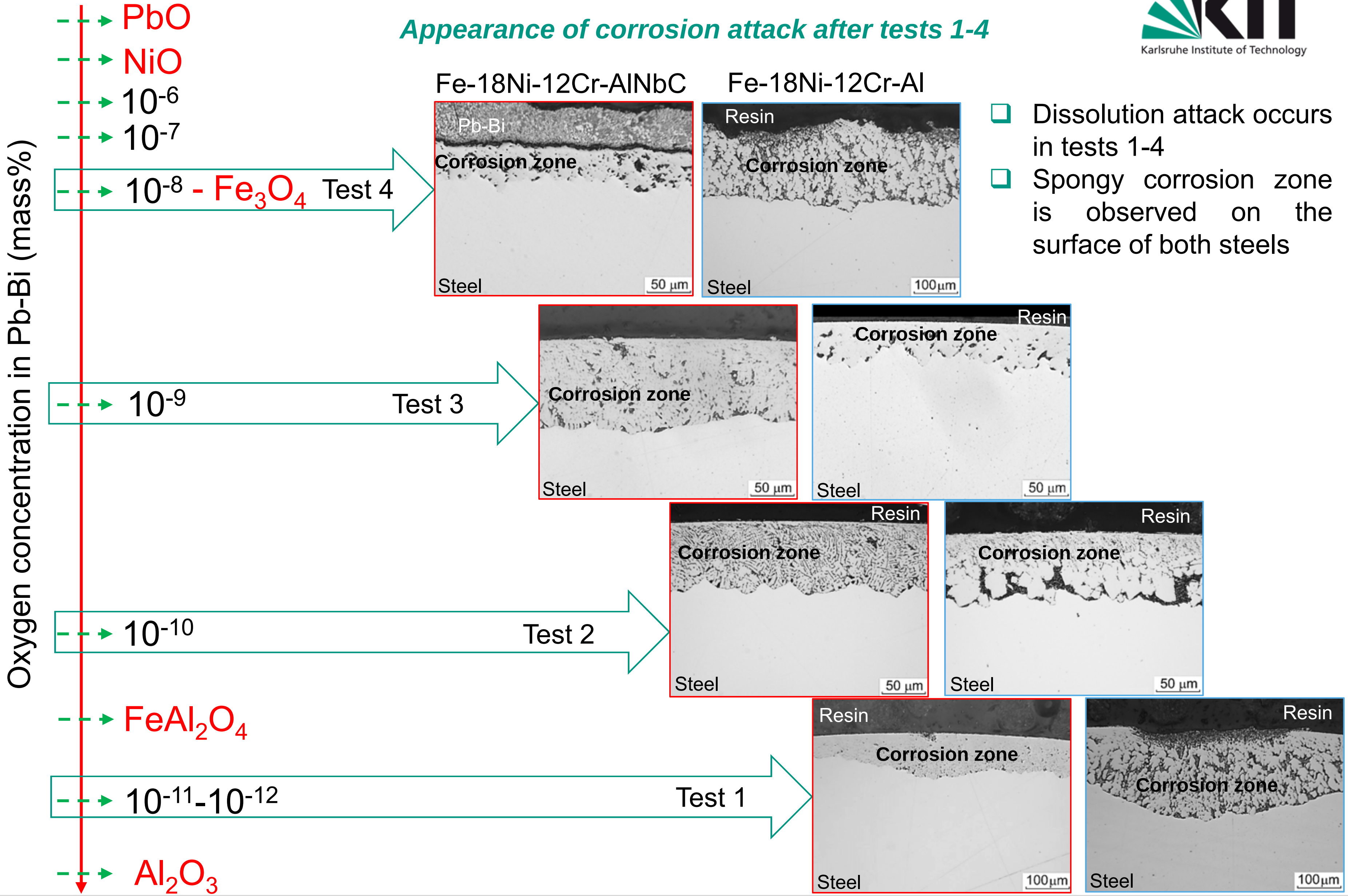
Recalculation of sensor output into the oxygen concentration:

$$log(CO_{Pb-Bi}) = -3.2837 + \frac{6949.8}{T} - 10080\frac{E}{T}$$



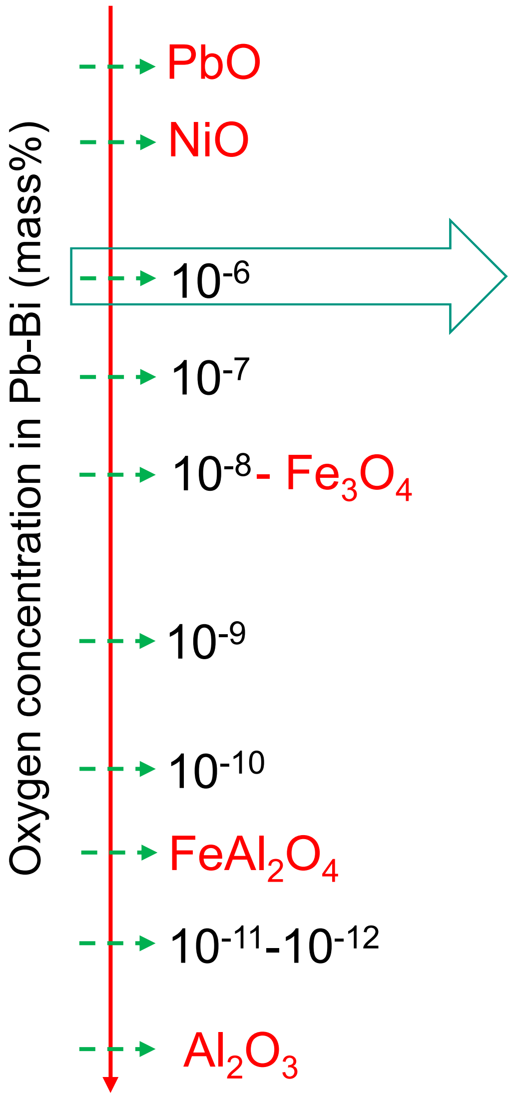
RESULTS OF CORROSION TESTS #1-4

Appearance of corrosion attack after tests 1-4



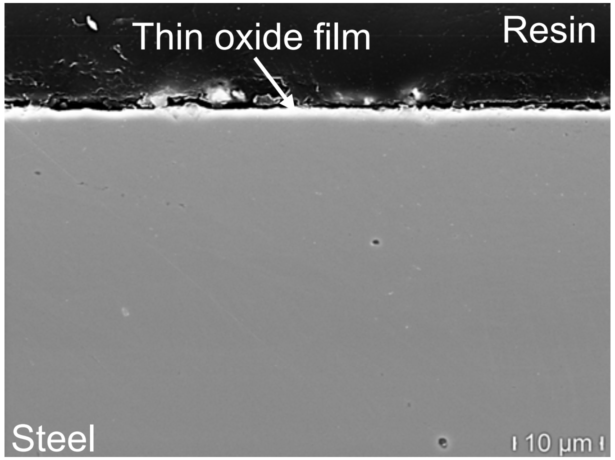
- Dissolution attack occurs in tests 1-4
- Spongy corrosion zone is observed on the surface of both steels

CORROSION TEST 5



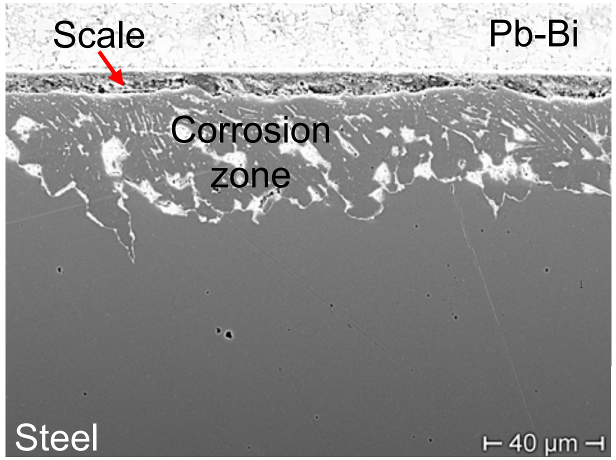
General corrosion appearances on AFA steels

Fe-18Ni-12Cr-AlNbC



Slight oxidation is observed on 80% of surface)

Fe-18Ni-12Cr-Al



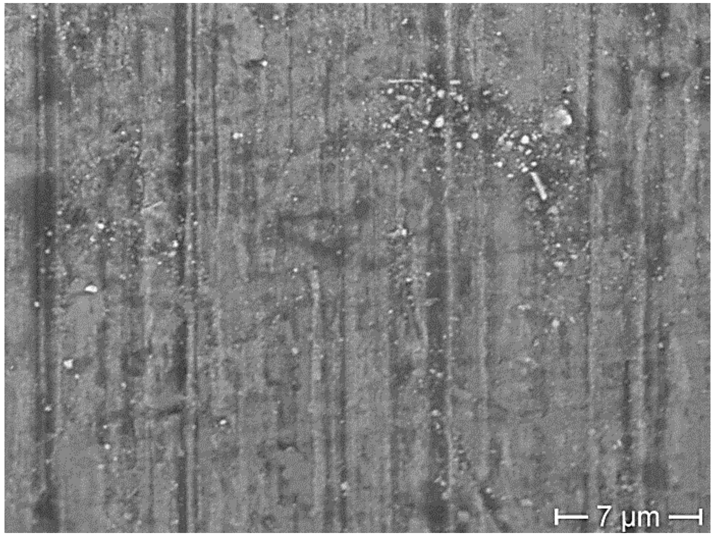
Dissolution + oxidation

- Slight oxidation reflects the general corrosion trend in the case of Fe-18Ni-12Cr-AlNbC steel
- Dissolution attack in combination with oxidation reflects the general corrosion trend on Fe-18Ni-12Cr-Al steel

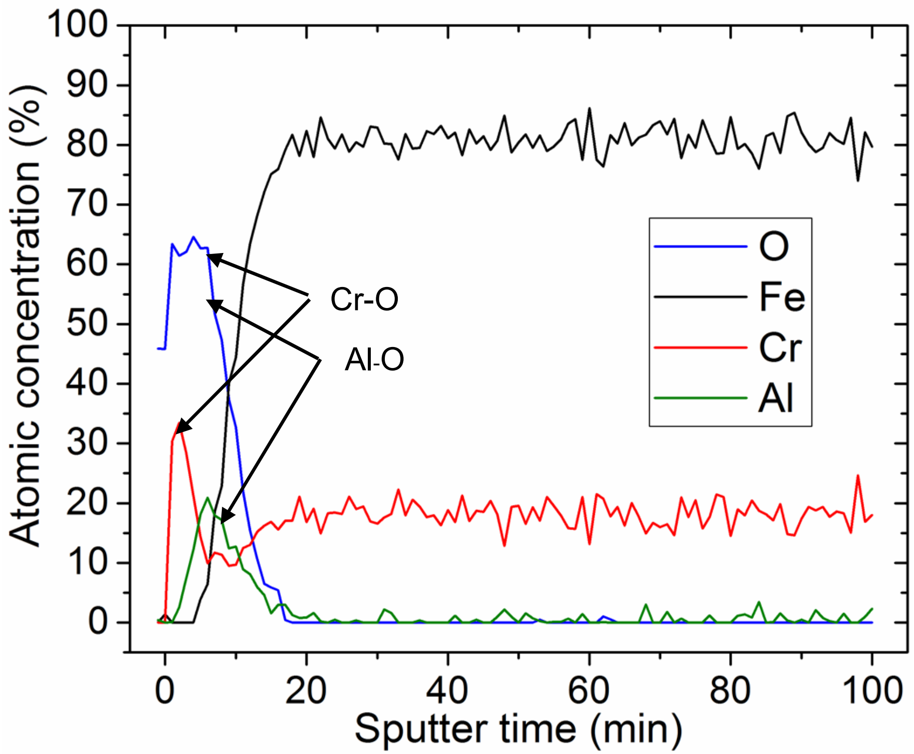
CORROSION TEST 5

Characterization of general corrosion appearance (80%) on Fe-18Ni-12Cr-AlNbC steel

Surface morphology



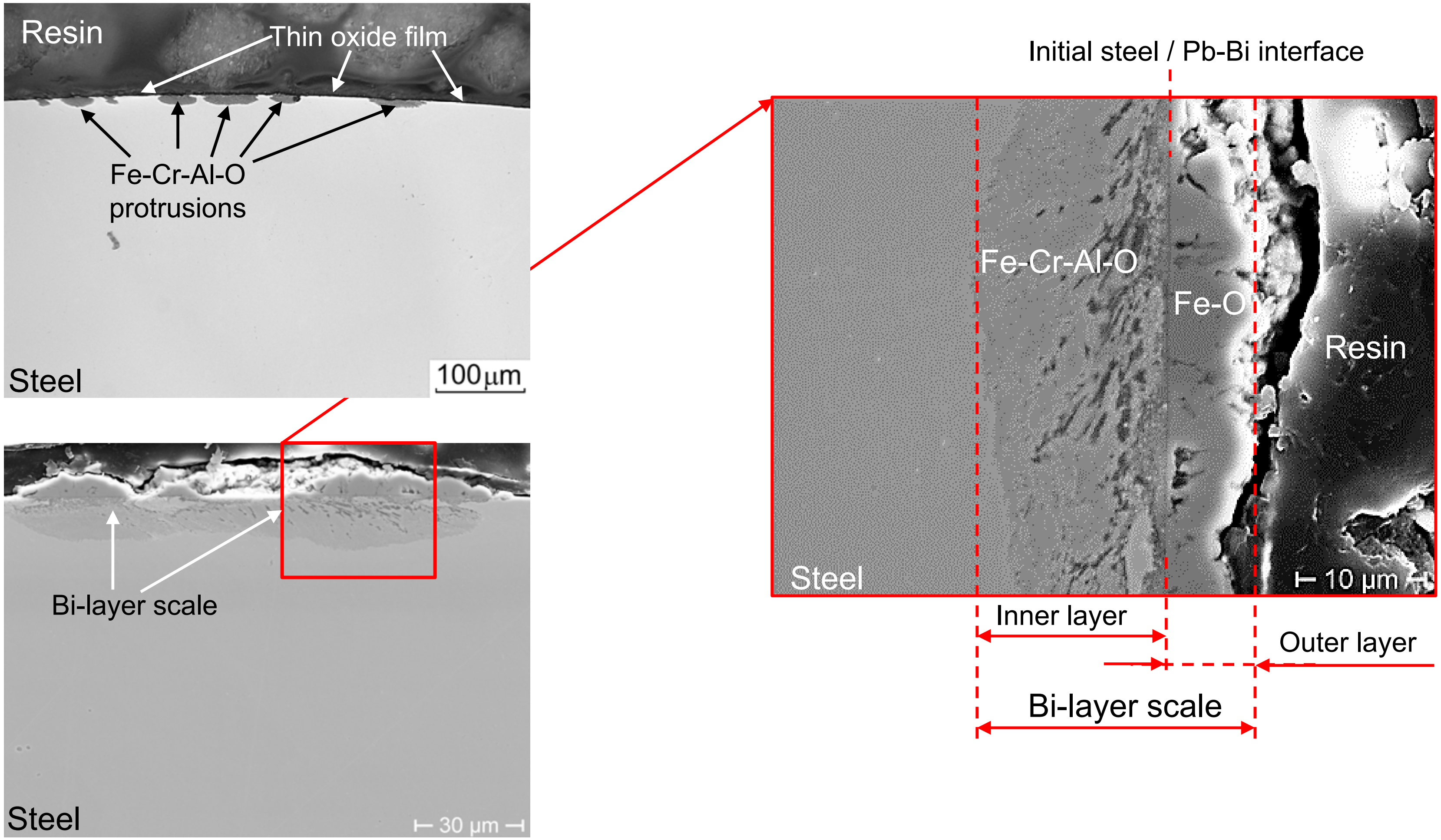
Auger sputter depth profile from surface



- Cr/Al-rich oxide film (on 80% of surface appearance) is formed on steel surface indicating synergetic effect of Cr and Al on the formation of oxide layer

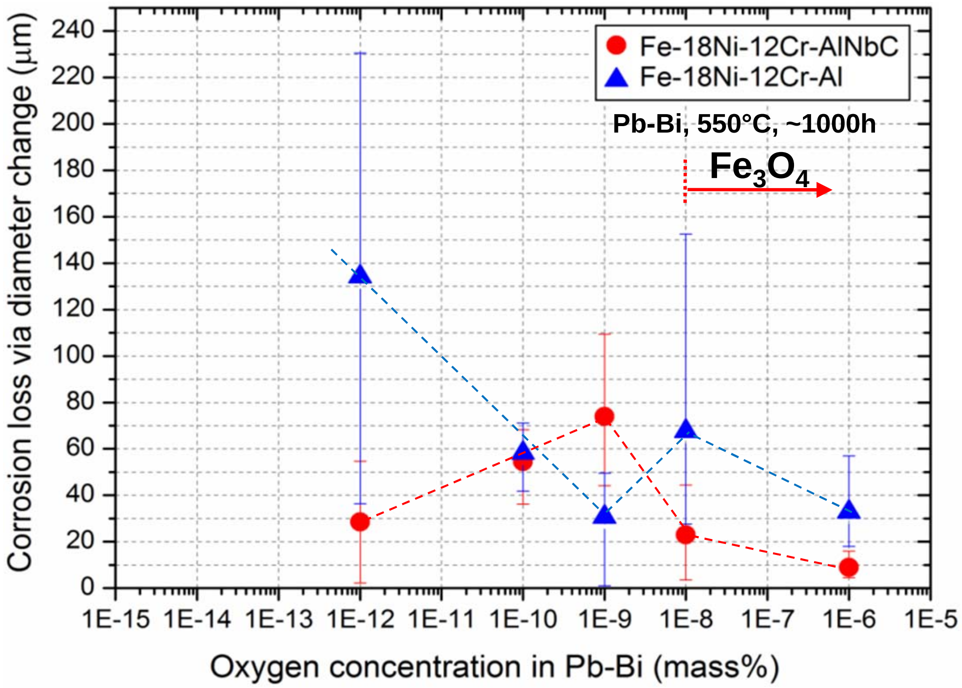
CORROSION TEST 5

Characterization of local corrosion appearances (20%) on Fe-18Ni-12Cr-AlNbC steel



- ❑ Local protrusions of bi-layer magnetite scale or inner Fe-Cr-Al-O spinel are observed
- ❑ Local accelerated oxidation is observed on 20% of surface

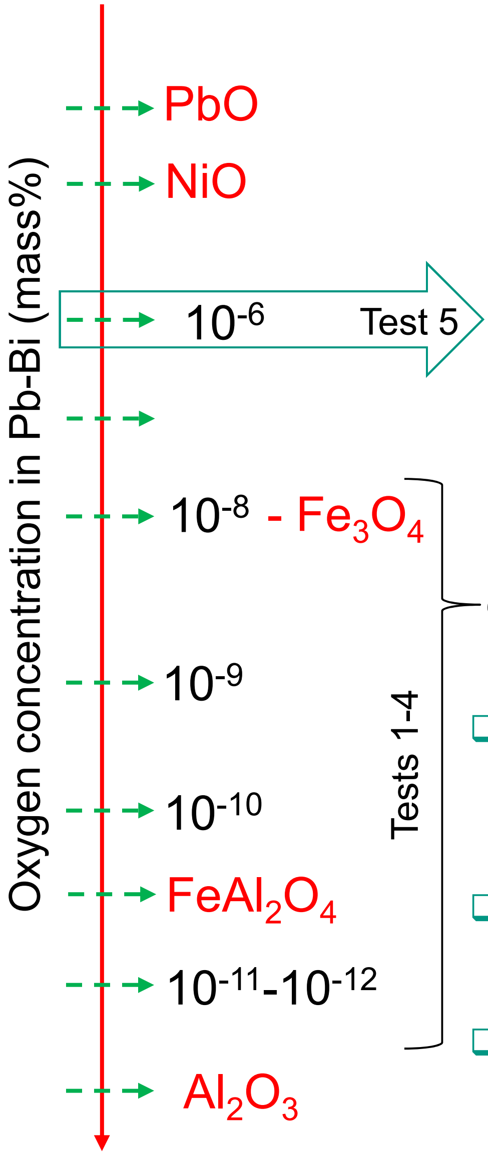
QUANTIFICATION OF CORROSION LOSS



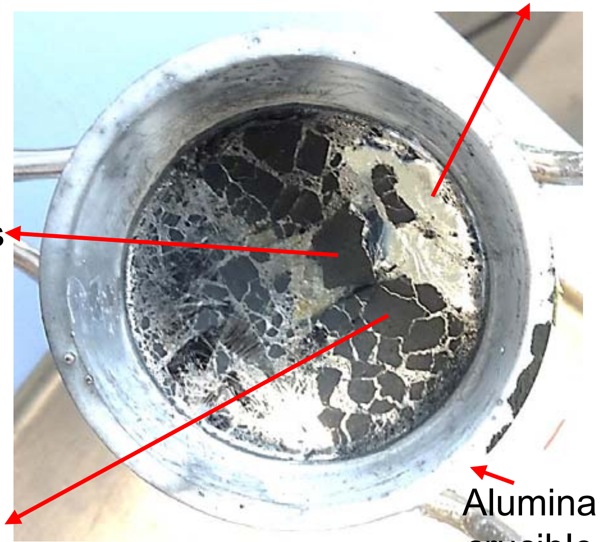
- With increase in oxygen concentration in Pb the corrosion mode changes from dissolution to oxidation resulting in substantial decreasing in corrosion loss
- Change in corrosion loss with increase in concentration is not straight-proportional

CHEMICAL COMPOSITION OF LIQUID METAL AFTER TESTS

Karlsruhe Institute of Technology



Surface of the Pb-Bi bath with floating oxides



- Oxygen from the gas phase reacts with dissolved constituents of steel and forms floating oxides on the surface of liquid metal bath
- Cr-based oxides are forming on the surface of LBE when concentration of oxygen in Pb-Bi is ≤ than necessary for the stability of magnetite
- Fe-based oxides are formed on the surface of LBE when concentration of oxygen in Pb-Bi is > than necessary for the stability of magnetite

Composition of LBE after test 5

	mass%
Al	< 0.00001
Cr	< 0.00001
Fe	< 0.00001
Ni	0.00432 (±0.00001)

Saturation concentration At 550°C (mass%)	
Al	-
Cr	0.0016
Fe	0.00048
Ni	3.2

Composition of LBE after test 1

	mass%
Al	< 0.00005
Cr	0.00019 (±0.00002)
Fe	0.00023 (±0.00007)
Ni	0.00230 (±0.00004)

SUMMARY on corrosion of aluminium-alloyed austenitic steels in HLM

Karlsruhe Institute of Technology

- The effect of oxygen concentration in static Pb-Bi eutectic at 550°C on the corrosion behavior of Fe-18Ni-12Cr-2.3Al and Fe-18Ni-12Cr-2.9Al-Nb-C austenitic steels is investigated for about 1000 h
- The oxidation potential of the liquid metal, similar to the conventional austenitic steels not-alloyed by Al, should be higher than required for the thermodynamic stability of magnetite (Fe_3O_4) in order to promote oxidation of AFA steels in Pb-Bi eutectic
- The more complex alloying in Fe-18Ni-12Cr-2.9Al-Nb-C steel seems favors the formation of more protective oxide film
- Single layer of Al_20_3 is not formed while the multi-layer oxides are detected: Cr/Al-O in Pb-Bi and Fe/Cr/Al-O in Pb
- **Long-term tests under the flowing conditions are necessary to investigate the viability of thin Fe/Cr/Al-based oxide film**

Thank you for attention !!!