Karlsruhe Institute of Technology

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Effect of oxygen concentration in static Pb-Bi eutectic on corrosion behavior of aluminum-alloyed austenitic steels at 550 °C for 1000 h

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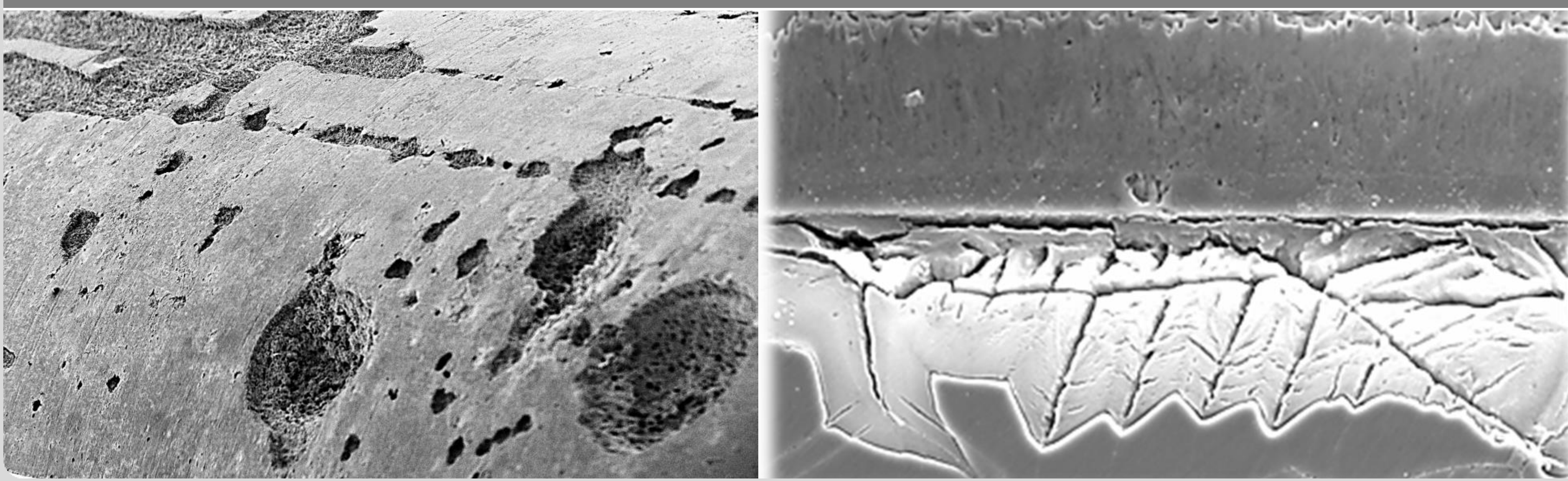
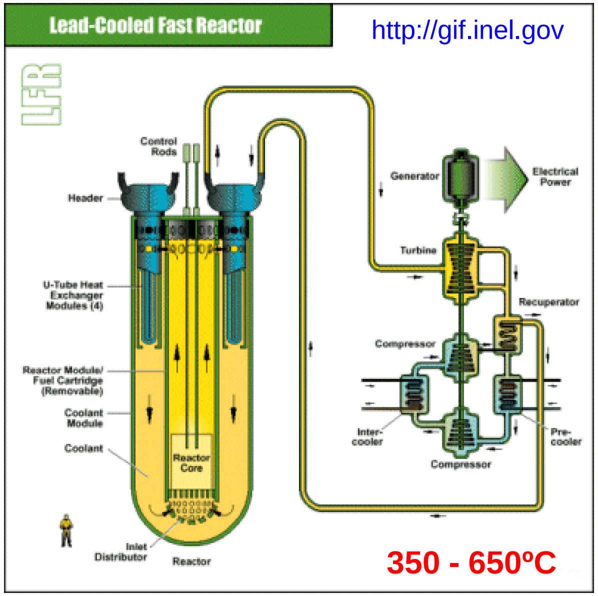
INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS (IAM-WPT)

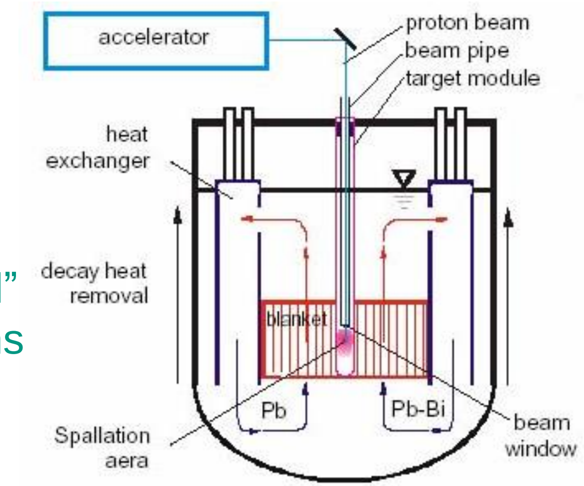


LIQUID-METALS AS A FUNCTIONAL MEDIA FOR NOVEL REACTORS

GENERATION IV



Accelerator Driven System

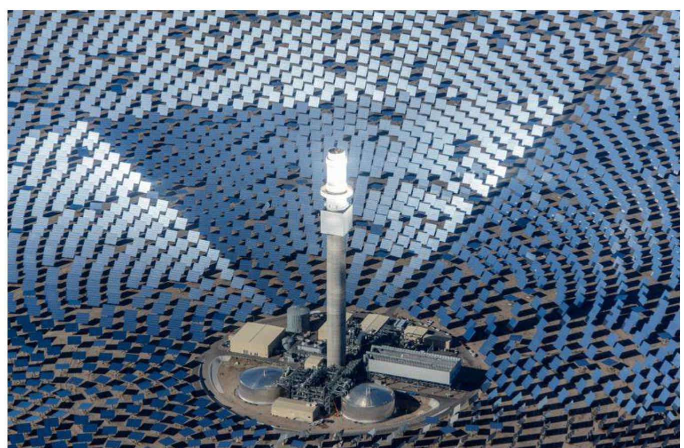


http://nucleartimes.jrc.nl

Accelerator Driven System

System “liquid metal / solid metal” – a common area of investigations

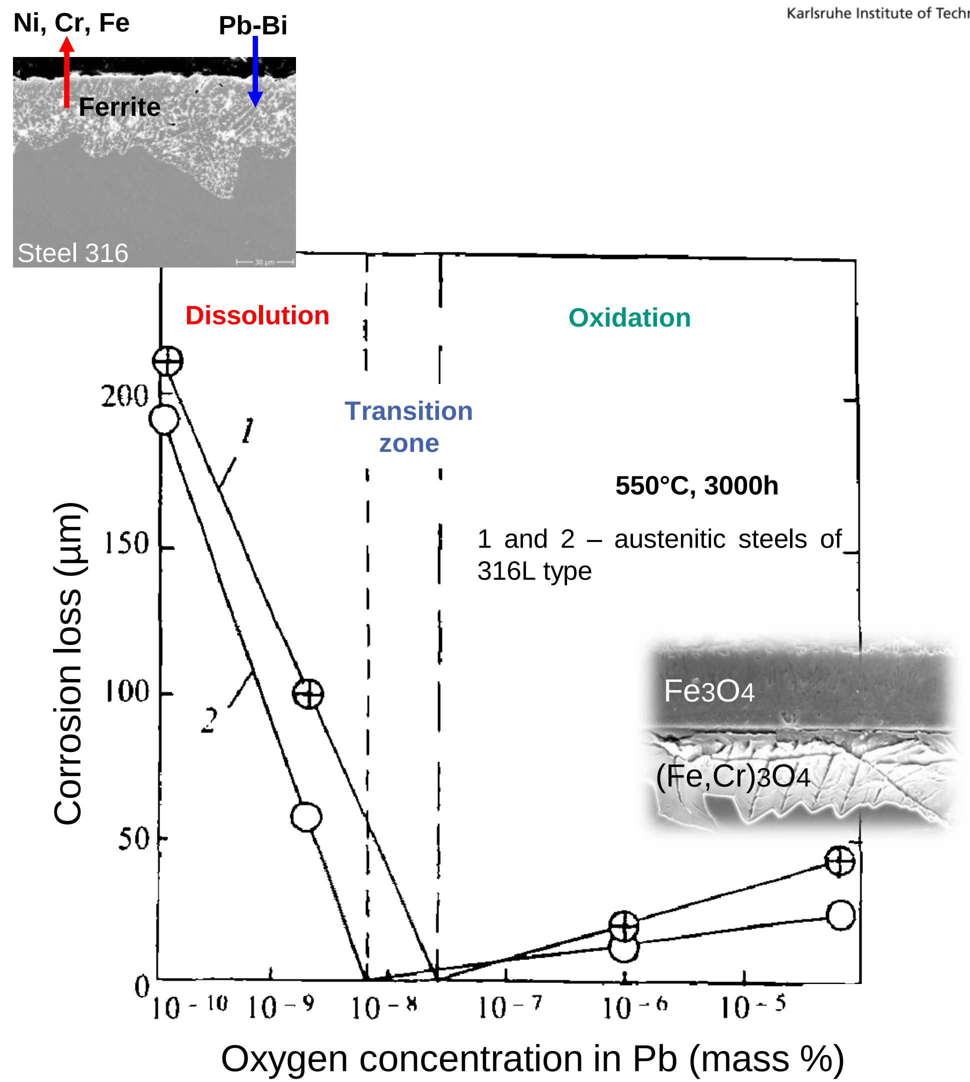
Concentrating Solar Power



SYSTEM “LIQUID Pb-Bi EUTECTIC / STEEL”

Main corrosion modes

1. **Dissolution**
   - Leaching of Ni, Cr and Fe
2. **Oxidation**
   - Formation of Fe-based scale



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

OXIDATION OF STEELS IN Pb-Bi EUTECTIC

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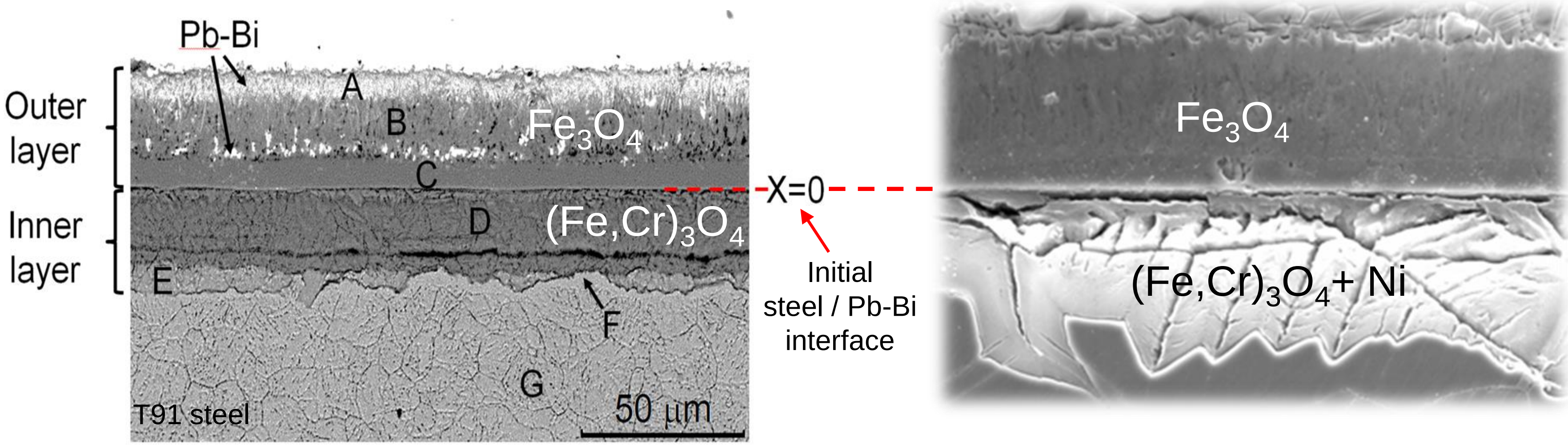
Ferritic / martensitic steels　　　　Austenitic steels



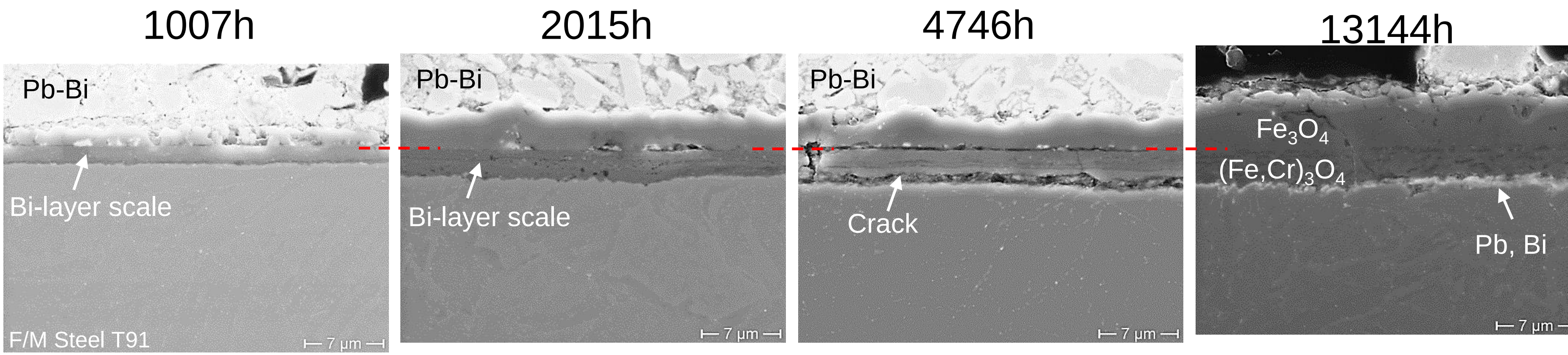
Composition of bi-layer scale

- ❑ X=0 – initial steel / HLM interface
- ❑ Outer layer – Fe_3O_4
  - A + B – sub-layers with loose columnar structure containing Pb and Bi
  - C – sub-layer with compact equiaxed structure
- ❑ Inner layer
  - D – $Fe(Fe,Cr)_2O_4$ spinel
  - E – inner oxidation zone (Fe + Cr_2O_3)
  - F – Cr-depleted zone
- ❑ Steel T91 – G

- ❑ Bi-layer scale, with outer Fe_3O_4 (magnetite spinel) and inner $Fe(Fe,Cr)_2O_4$ spinel-type oxide layers, typically forms on the surface of steels in contact with oxygen-containing Pb and Pb-Bi melts
- ❑ Growth of scale is governed by the outward diffusion of iron cations
- ❑ Inward growth of Fe-Cr spinel at the oxide/steel interface could be accessed from the ***dissociative growth theory***: vacancies generated by outward diffusion of iron cations precipitate at the oxide/steel interface forming cavities (pores) into which the oxide dissociates with evaporating oxygen providing further oxidation of steel (S. Mrowec, Corrosion Science 7 (1967) 563-578).

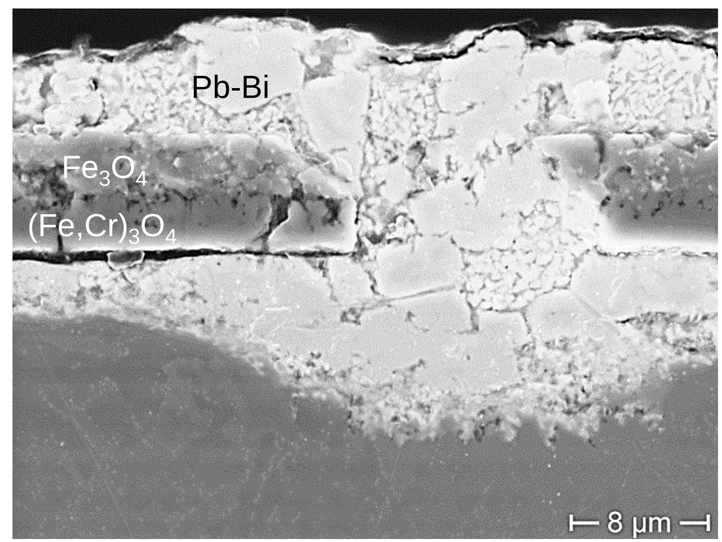
EXAMPLE OF SCALE EVOLUTION WITH TIME

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



- - - - Initial steel / liquid Pb-Bi interface

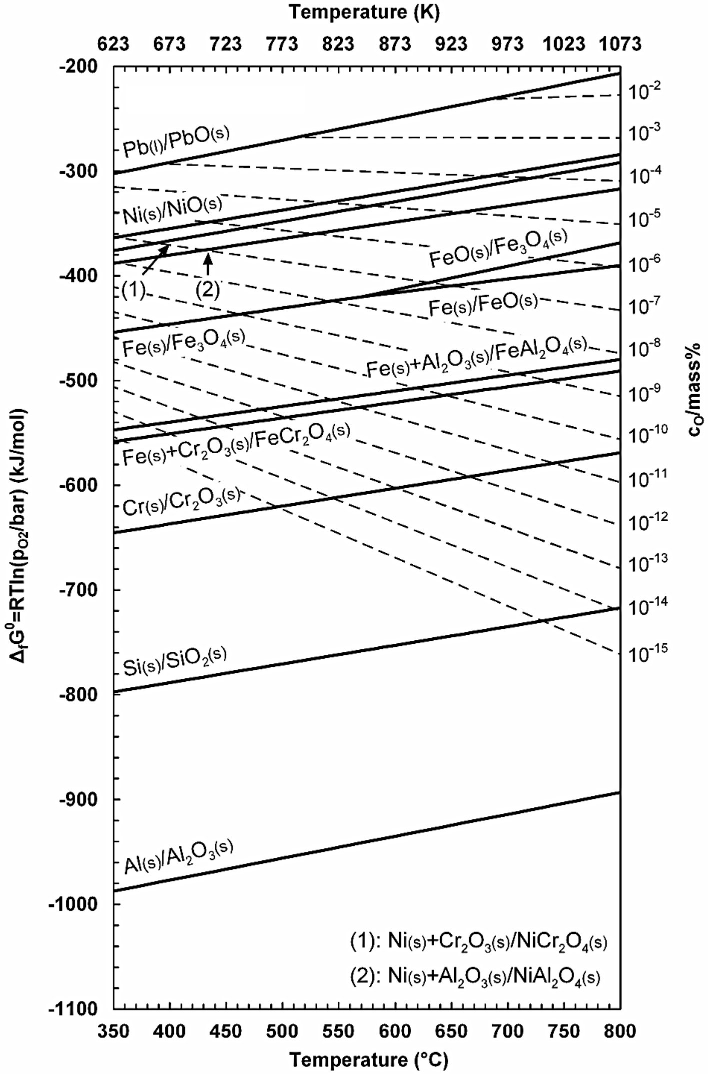
Dissolution attack as a result of scale failure



- Degradation of scale with time results in initiation of local dissolution attack
- Re-healing of scale does not take place
- The long-term viability of protective scale on the surface of steels facing Pb melts is one of the main task for successful application of oxygen-controlled Pb melts

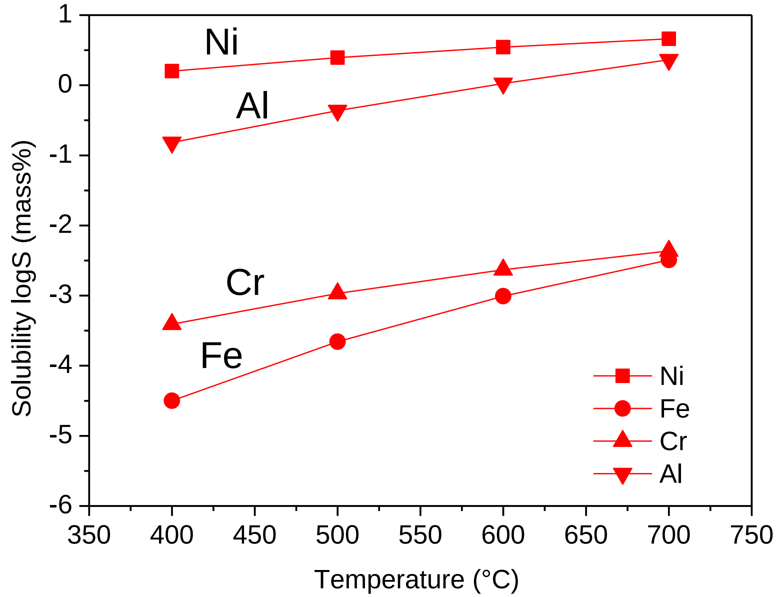
EFFECT OF ALLOYING ON CORROSION

Effect of alloying on oxidation



- Transfer from Fe-based bi-layer scale to single layer oxide films based on Cr, Si, Al is highly desirable

Effect of alloying on dissolution



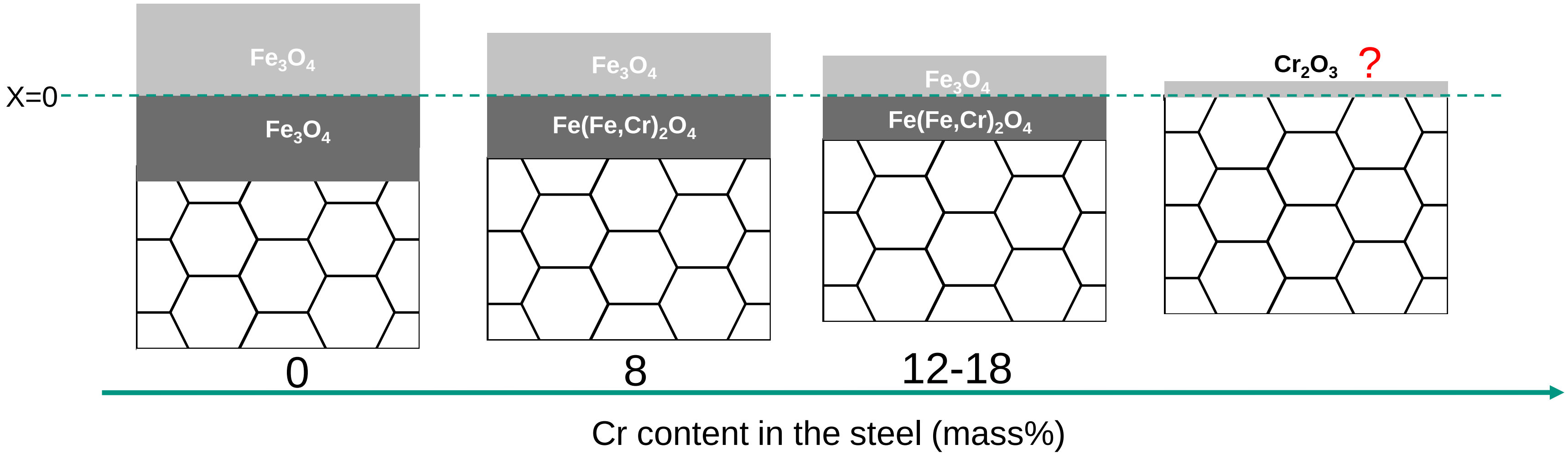
Solubility of pure metals in LBE as a function of temperature

- Alloying elements in steels which might improve oxidation resistance are typically highly soluble in HLM

EFFECT OF ALLOYING ON OXIDATION IN Pb MELTS

Cr-alloyed steels

Effect of Cr content on scale composition, morphology and thickness

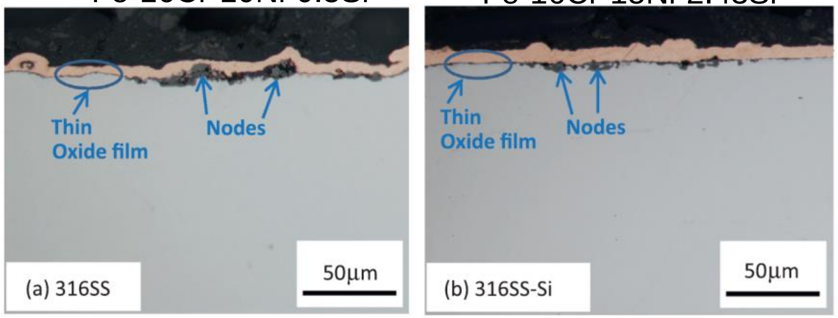


- Conditions: T≤570°C, $C[O]_{HLM}$>Fe_3O_4
- Thickness of bi-layer scale decreases with increasing Cr content in the material
- Formation of single-layer Cr-rich oxide film is a short-time period (incubation)

Silicon alloyed steels

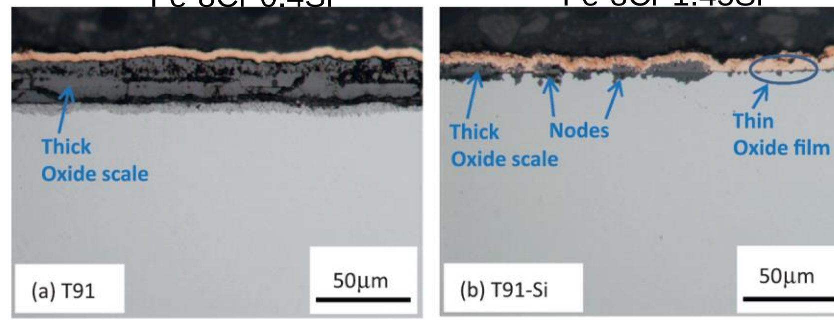
Silicon-alloyed austenitic steels

Fe-16Cr-10Ni-0.5Si   Fe-16Cr-15Ni-2.43Si



Silicon-alloyed F/M steels

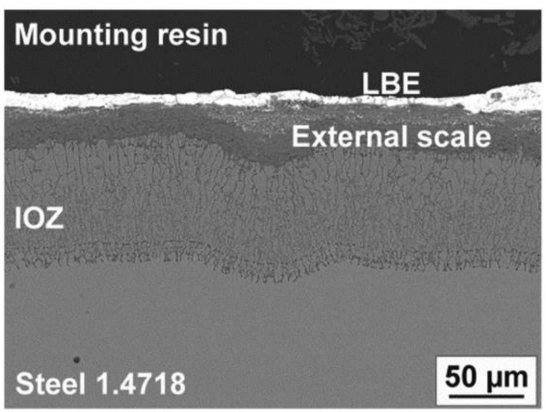
Fe-8Cr-0.4Si   Fe-8Cr-1.45Si



Yuji Kurata / Journal of Nuclear Materials 437 (2013) 401–408

- Static Pb-Bi at 550°C with 10^{-5} mass%O, ~1300h
- The Si addition reduces the scale thickness under the high oxygen condition
- The Si addition has no significant effect under the low oxygen condition (10^{-8} mass%O)

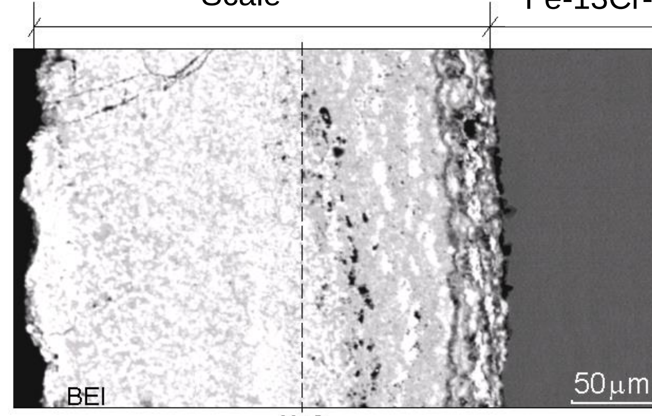
Fe-9Cr-3Si



- Flowing LBE, 550°C, 10^{-6} mass%O, 15028 h
- Intensive development of IOZ after long-term exposure

C. Schroer et al. / Journal of Nuclear Materials 469 (2016) 162–176

Fe-13Cr-3Si

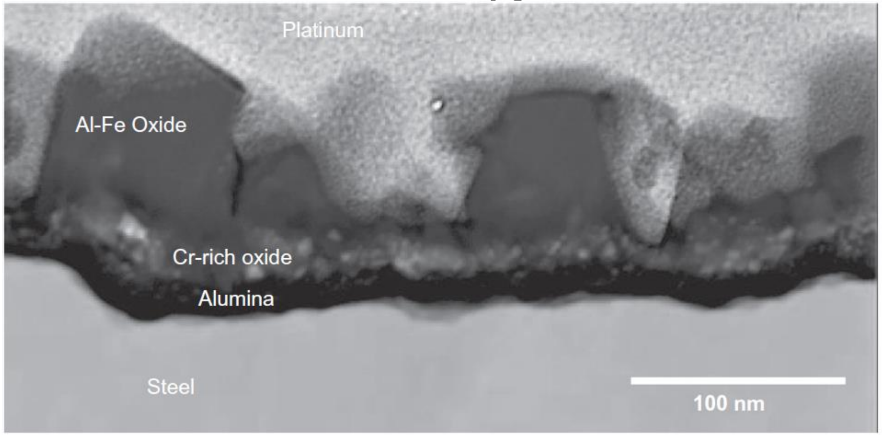


- Static Pb, 650°C, 10^{-3} mass%O, 50 h
- Extreme oxidation with formation of non-protective thick scale totally penetrated by Pb

V. Tsisar / PhD (2005)

Aluminum-alloyed F/M steels

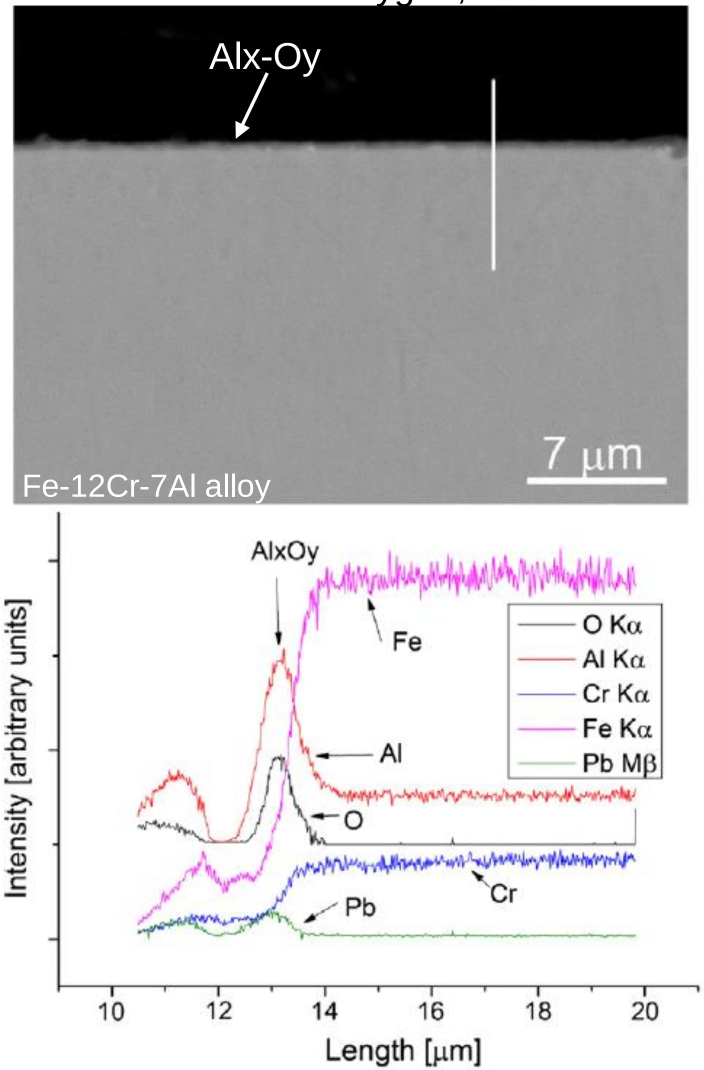
Static Pb, Fe-10Cr-6Al-RE alloy, 550 °C, 10^{-7} wt.% oxygen, 10000h



J. Ejenstam, P. Szakálos /Journal of Nuclear Materials 443 (2013) 161–170

- Thin Al-rich oxide layer, formed at the metal–oxide interface, prevented Pb penetration into the bulk steel at least up to 10000 h
- Synergetic effect of Cr and Al is important for formation of protective oxide film
- Preliminary results shows a potential for using Al-alloyed steels at higher temperatures (>550 °C)
- Tests in dynamic HLM are necessary to investigate viability of alumina films and it self-healing abilities

Static Pb, Fe-12Cr-7Al alloy, 600 °C, 10^{-6} wt.% oxygen, 1830h



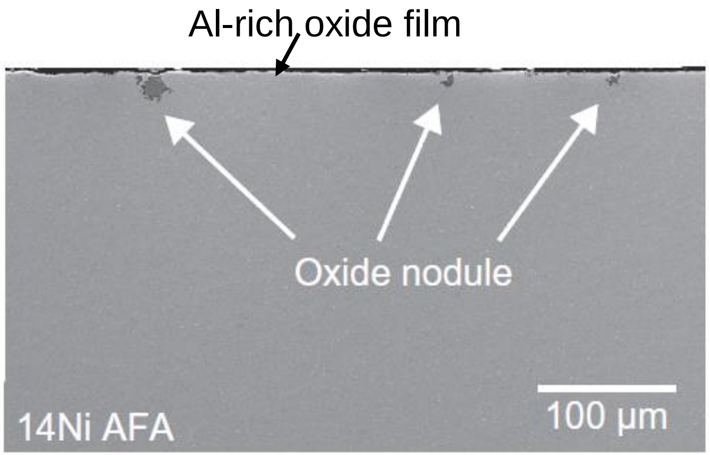
A. Weisenburger et al. / Journal of Nuclear Materials 437 (2013) 282–292

Aluminum-alloyed austenitic steels

- 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-14Cr-14Ni-2.5Al-1.6Mn-2.5Mo-0.9Nb

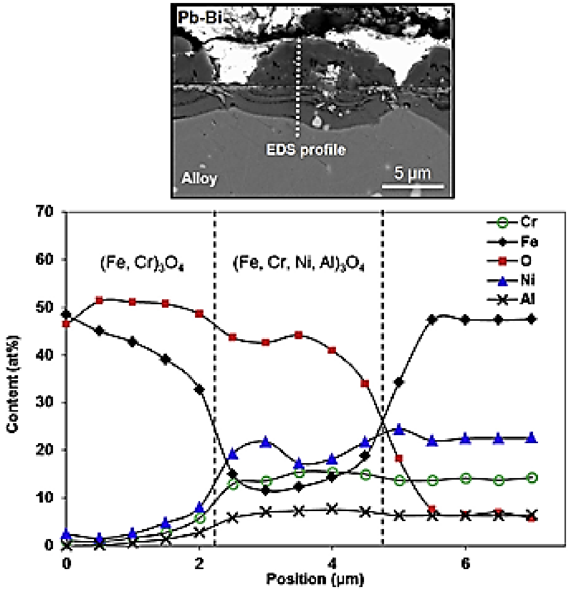
Static Pb, 550°C, 10^{-7} wt.% oxygen, one year



J. Ejenstam, P. Szakálos.
Journal of Nuclear Materials 461 (2015) 164–170

Fe-14Cr-25Ni-3.5Al-2Mn-2Mo-2.5Nb

Static Pb-Bi, at 520°C, $10^{-9} \leq [O] \leq 5x10^{-4}$, 1850 h



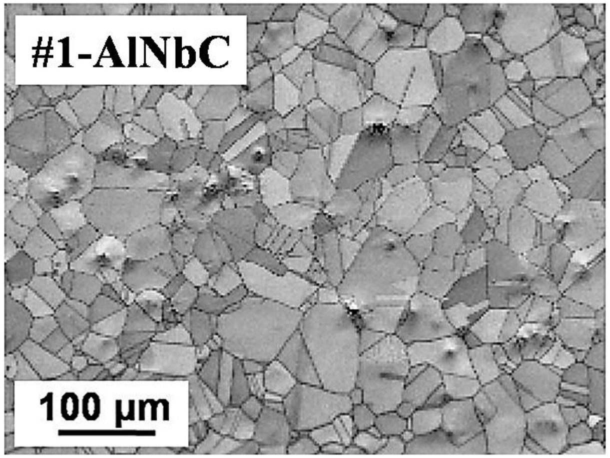
M. Roy, L. Martinelli, K. Ginestar et al.,
Journal of Nuclear Materials 468 (2016) 153-163

- Thin (<100 nm) protective Al-rich oxide film was formed on the14Ni AFA alloy after one year indicating that this alloy is a potential candidate for use in Pb-cooled reactors
- Tests in flowing oxygen-controlled HLM are of interest to show the long-term viability of protective oxide film on the alloy surface
- Bi-layer magnetite scale formed on the AFA alloy shows that there is no substantial gain in using this alloy in comparison with conventional austenitic steels not-alloyed by Al

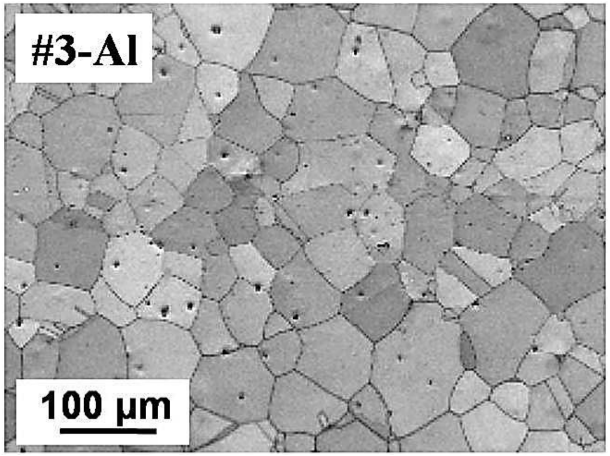
CHEMICAL COMPOSITION AND STRUCTURE OF AUSTENITIC STEELS ALLOYED BY ALUMINUM

(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

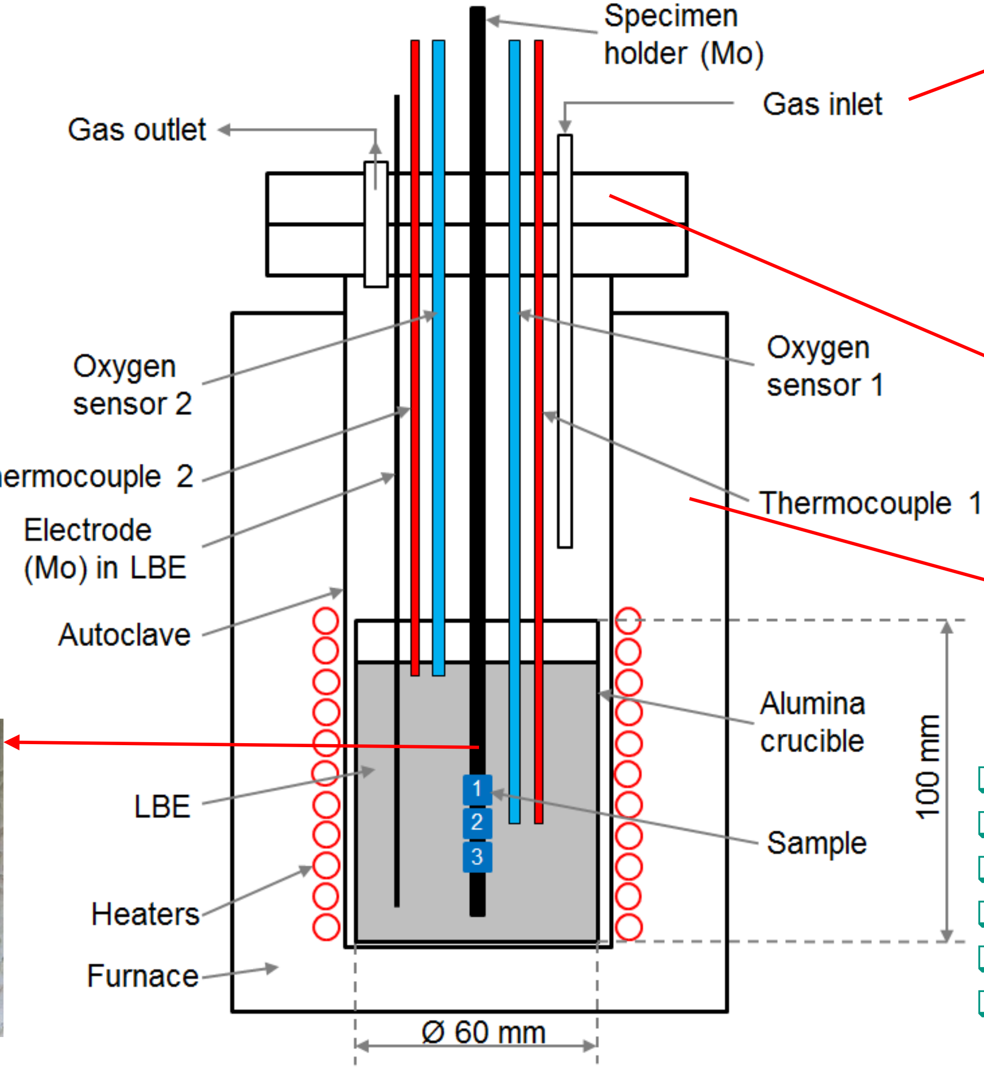


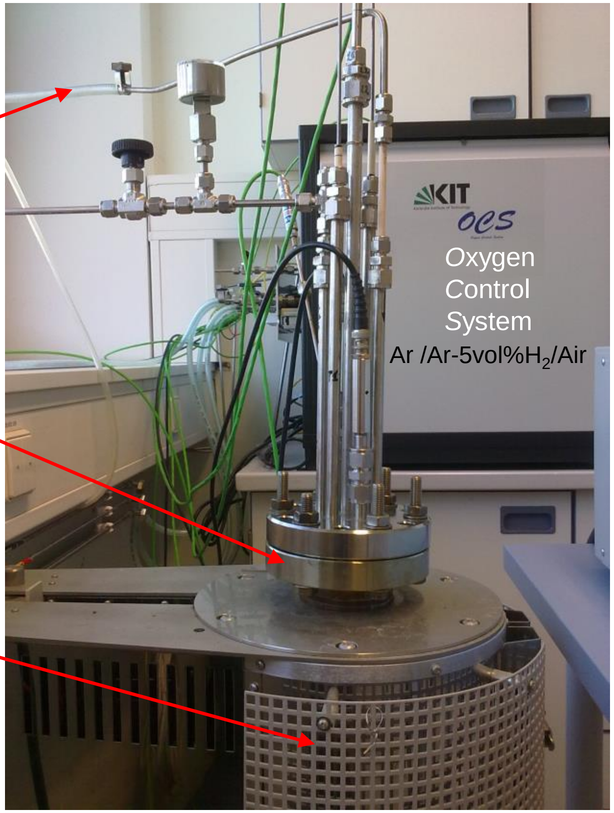
Fe-18Ni-12Cr-Al



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

APPARATUS FOR STATIC CORROSION TESTS IN HEAVY LIQUID METALS

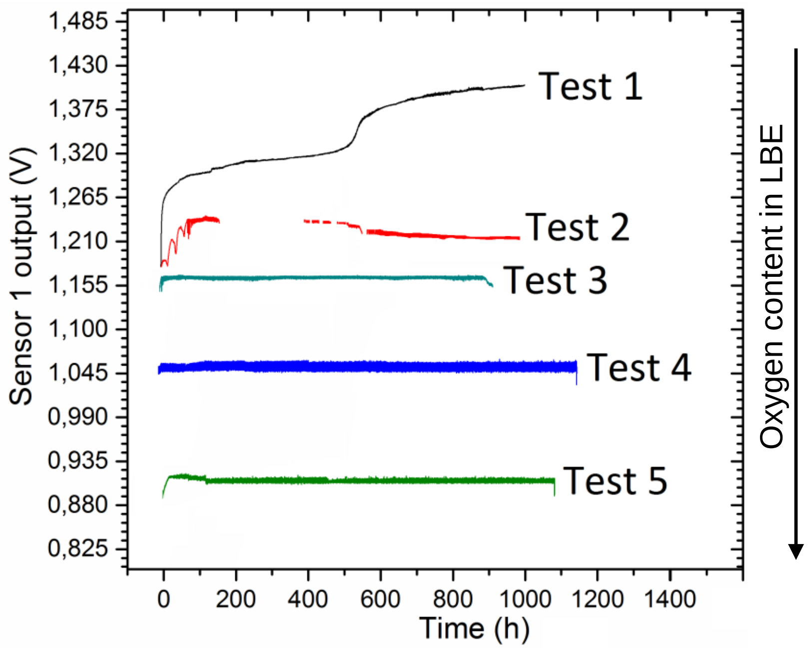




- ~2kg HLM (Pb, Pb-Bi, Sn)
- Working temperature up to 700ºC
- Ar+5%H2 / Ar / Air gas mixture above melt
- Two Pt/Air oxygen sensors
- Oxygen control system
- Cylindrical samples (Ø8x10 mm)

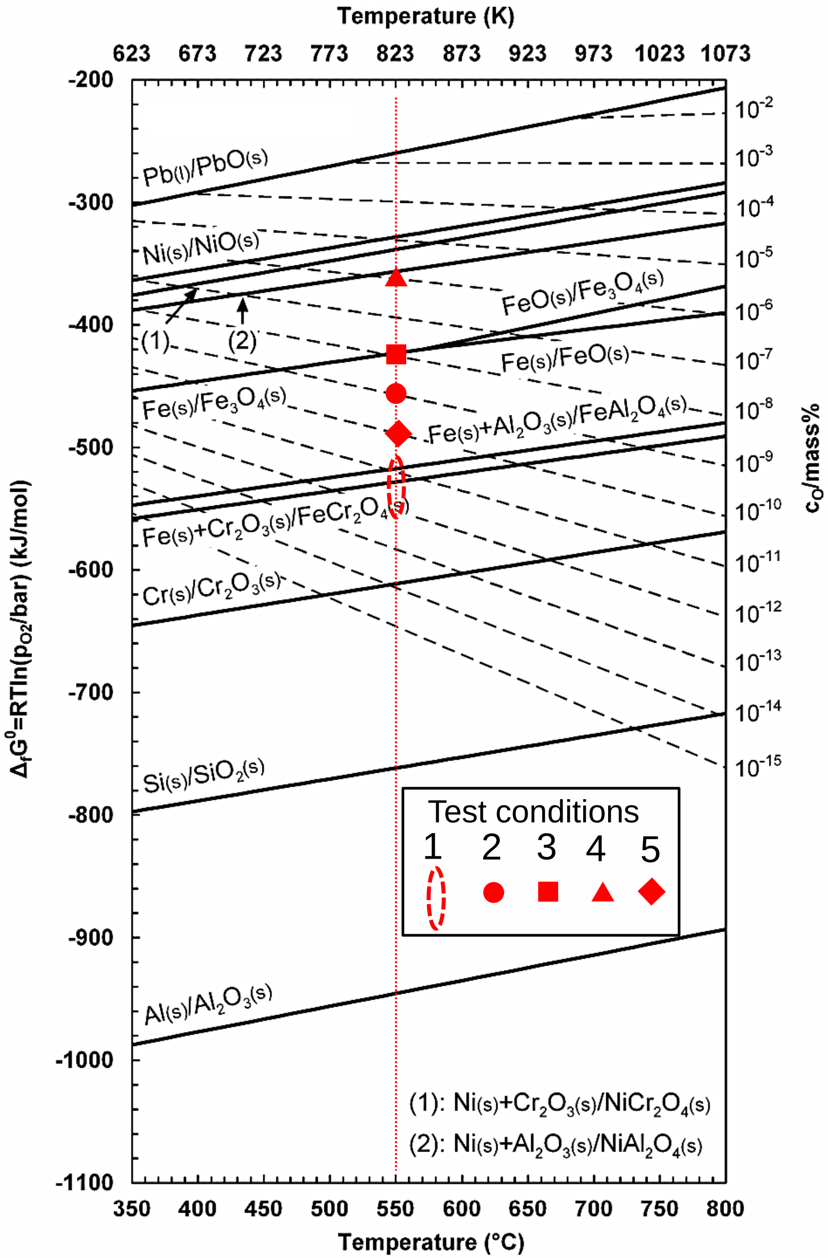
CONDITIONS OF CORROSION TESTS

- Constant:
  - 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

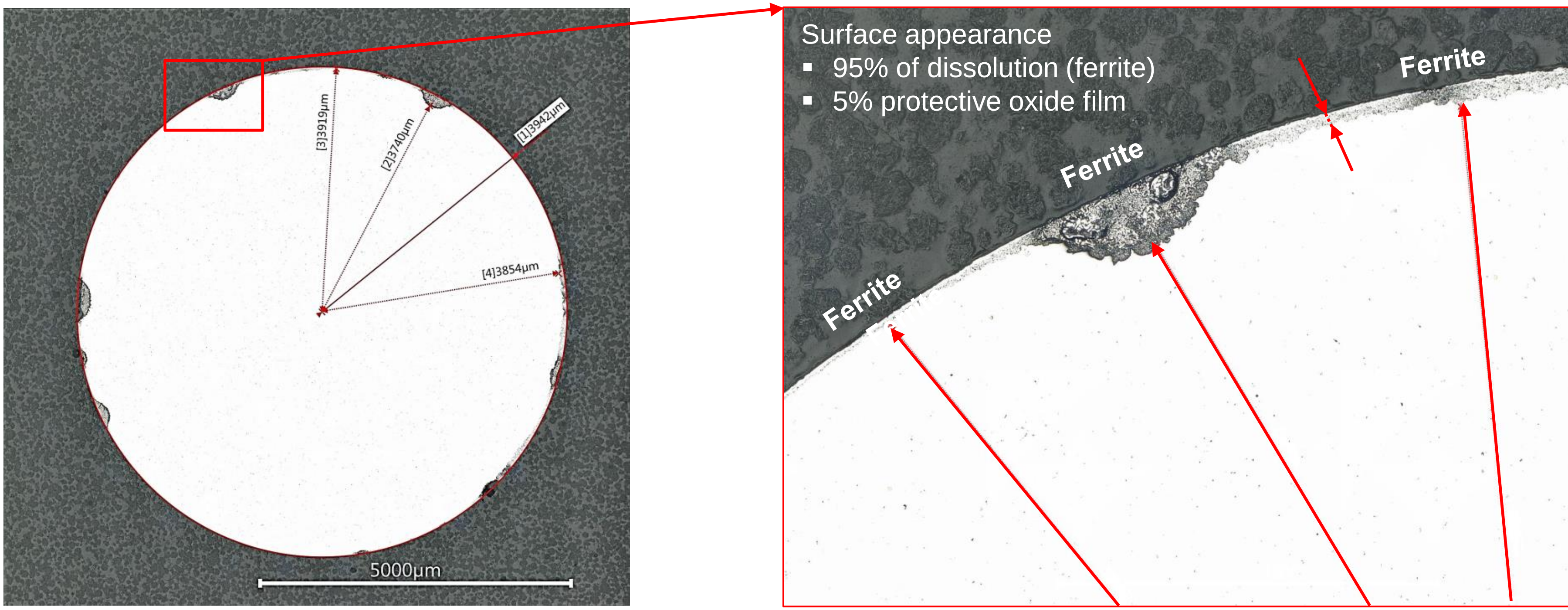


Recalculation of sensor output into the oxygen concentration:

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



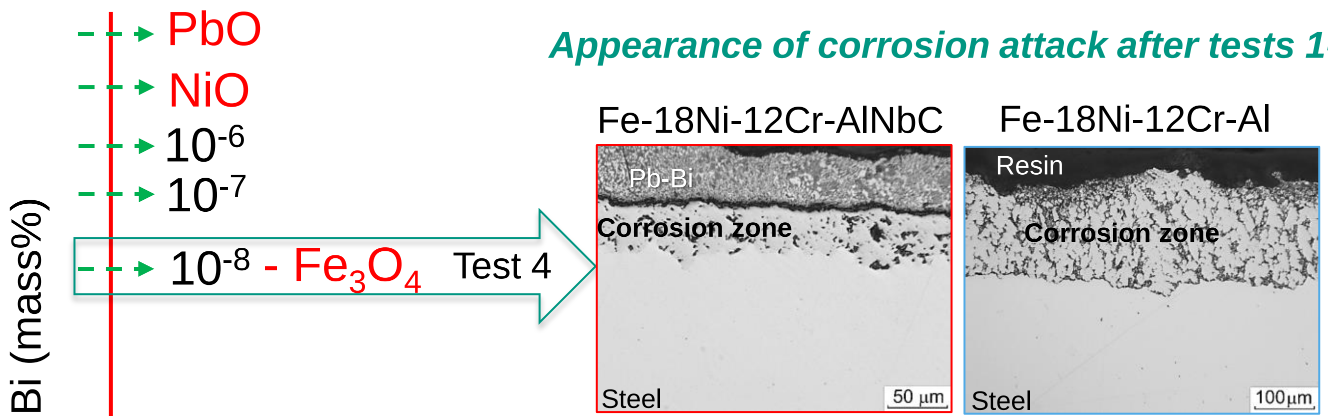
POST-TEST QUANTIFICATION OF CORROSION LOSS USING METALLOGRAPHIC METHOD FOR CYLINDRICAL SPECIMENS

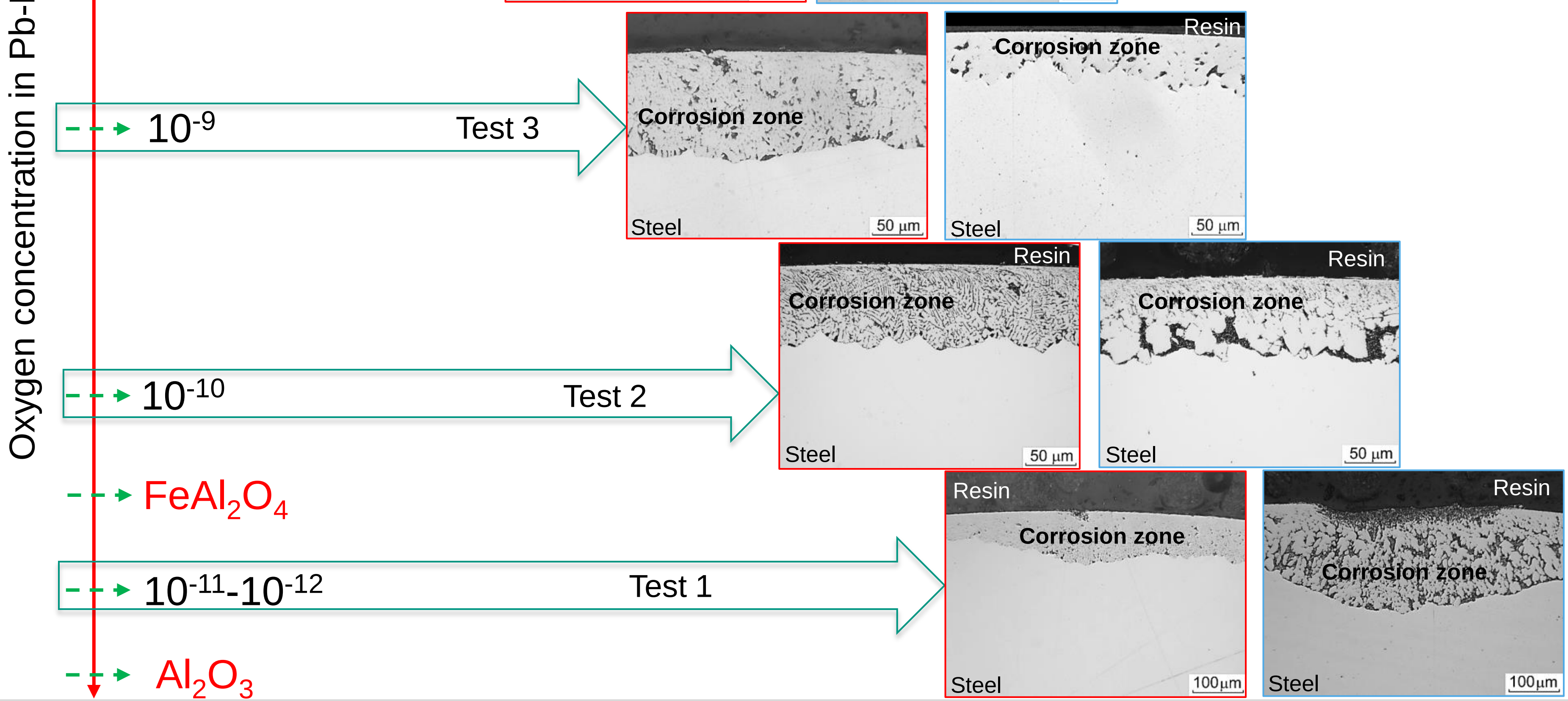


1. Measurement of initial diameter in a laser micrometer (0.1 µm resolution)
2. Measurement of post-test diameter (12th measurements with rotation angle 15°) or radius of unaffected material on cross-section
3. Measurement of thickness of corrosion zones (1 µm resolution)
4. % of occurrence of different corrosion modes
5. Extra measurements for determination of maximum depth of corrosion attack

RESULTS OF CORROSION TESTS #1-4

Appearance of corrosion attack after tests 1-4

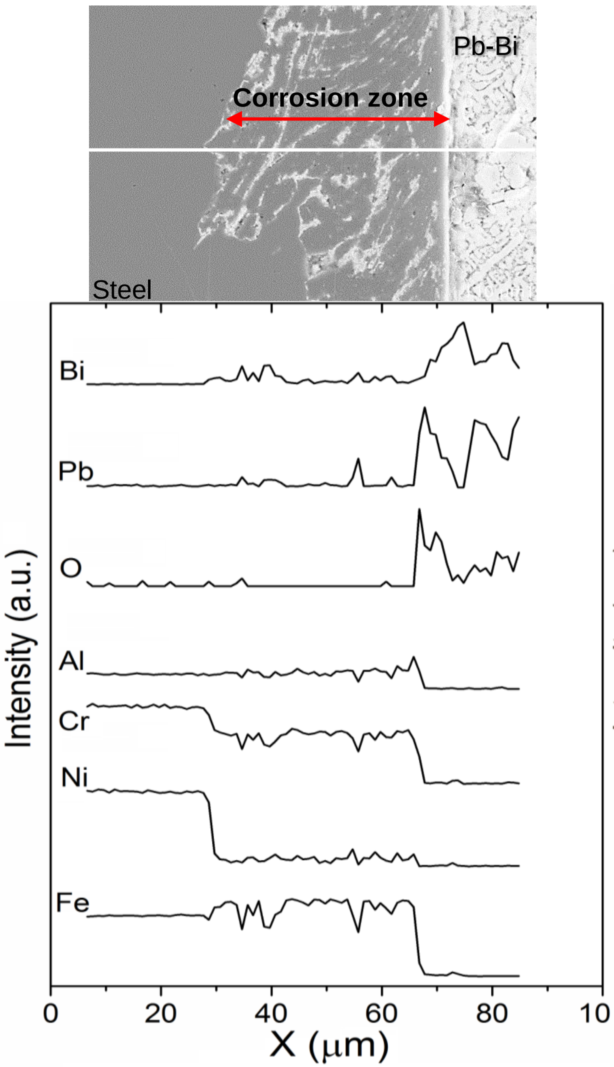




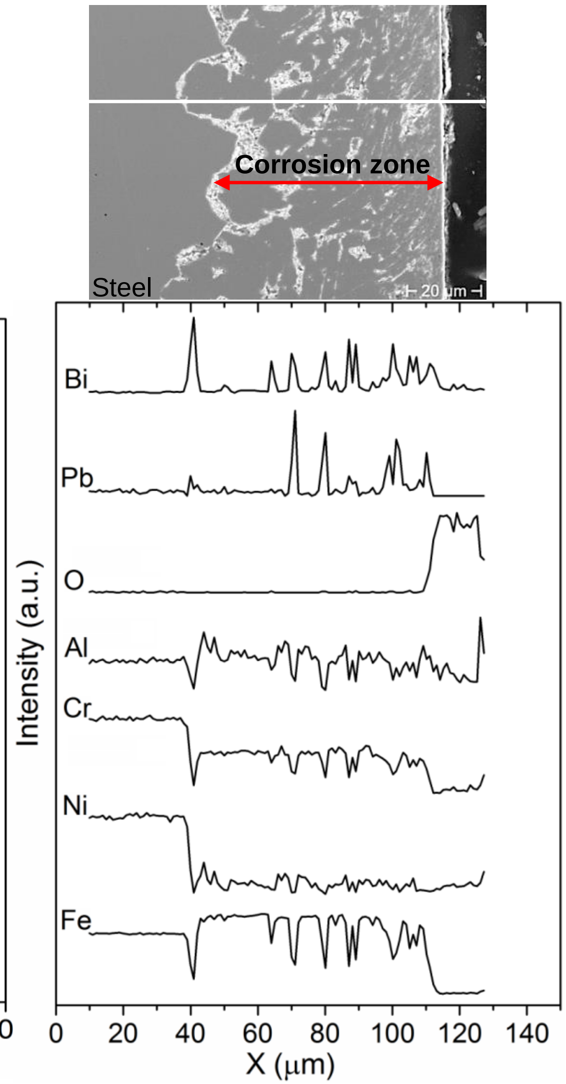
- Dissolution attack occurs in tests 1-4
- Spongy corrosion zone is observed on the surface of both steels

MORPHOLOGY AND COMPOSITION OF CORROSION ZONES

Fe-18Ni-12Cr-AlNbC

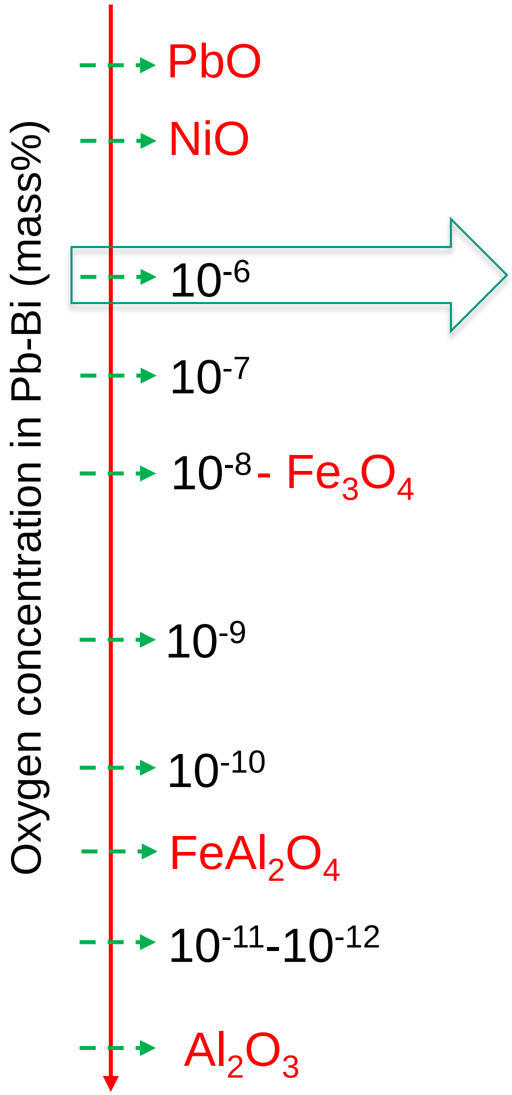


Fe-18Ni-12Cr-Al



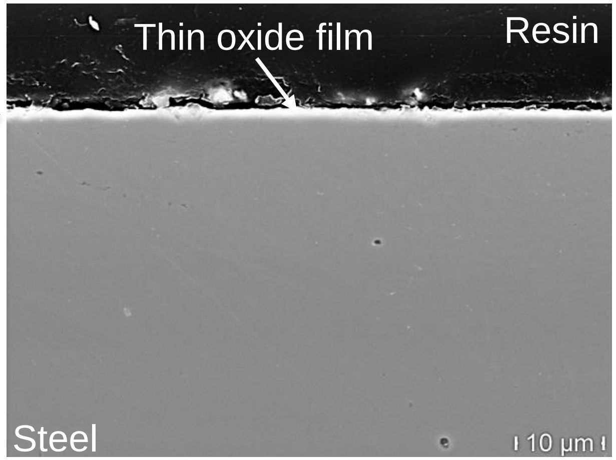
- Spongy corrosion zone is a ferrite layer depleted substantially in Ni and Cr, in comparison with initial steel composition, and penetrated by Pb and Bi

CORROSION TEST 5



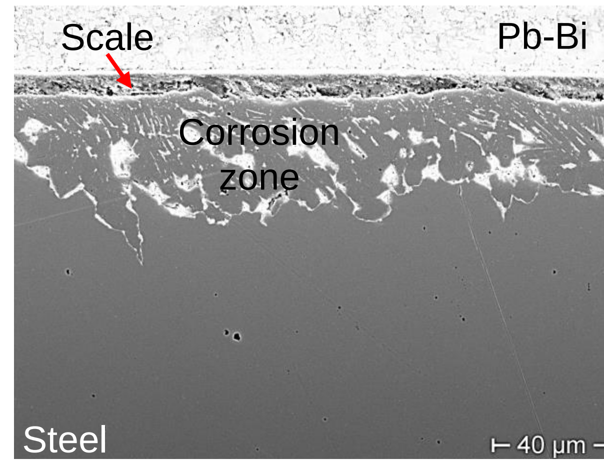
General corrosion appearances on AFA steels

Fe-18Ni-12Cr-AlNbC



Slight oxidation is observed on 79% of surface)

Fe-18Ni-12Cr-Al



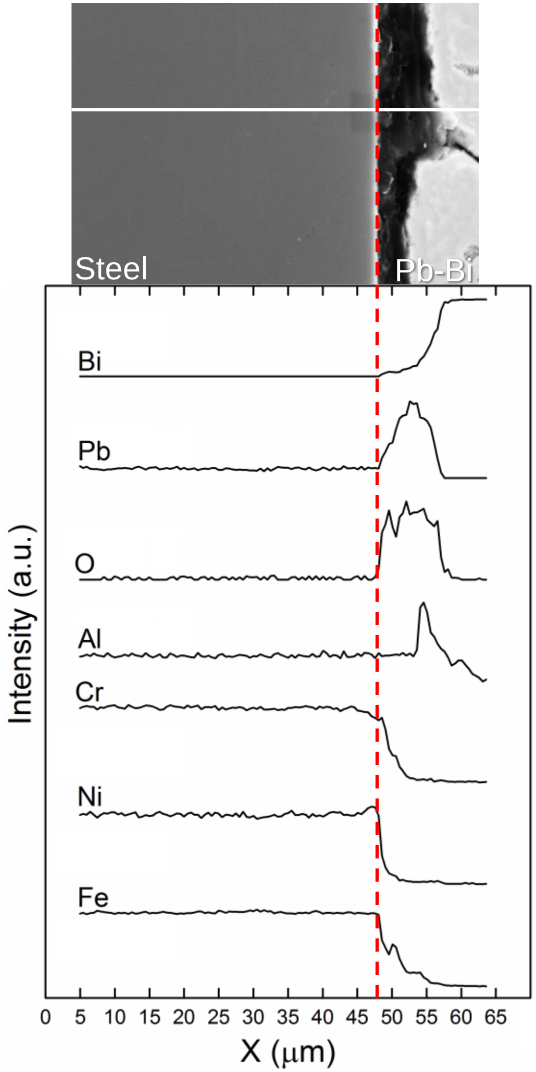
Dissolution + oxidation

- 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

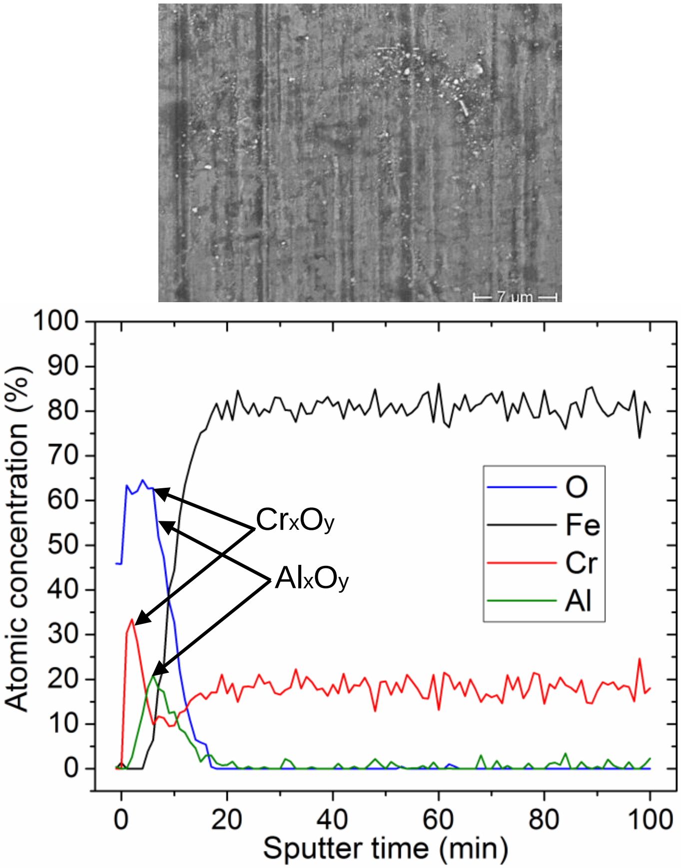
CORROSION TEST 5

Characterization of general corrosion appearance (79%) on Fe-18Ni-12Cr-AlNbC steel

SEM/EDX line scan



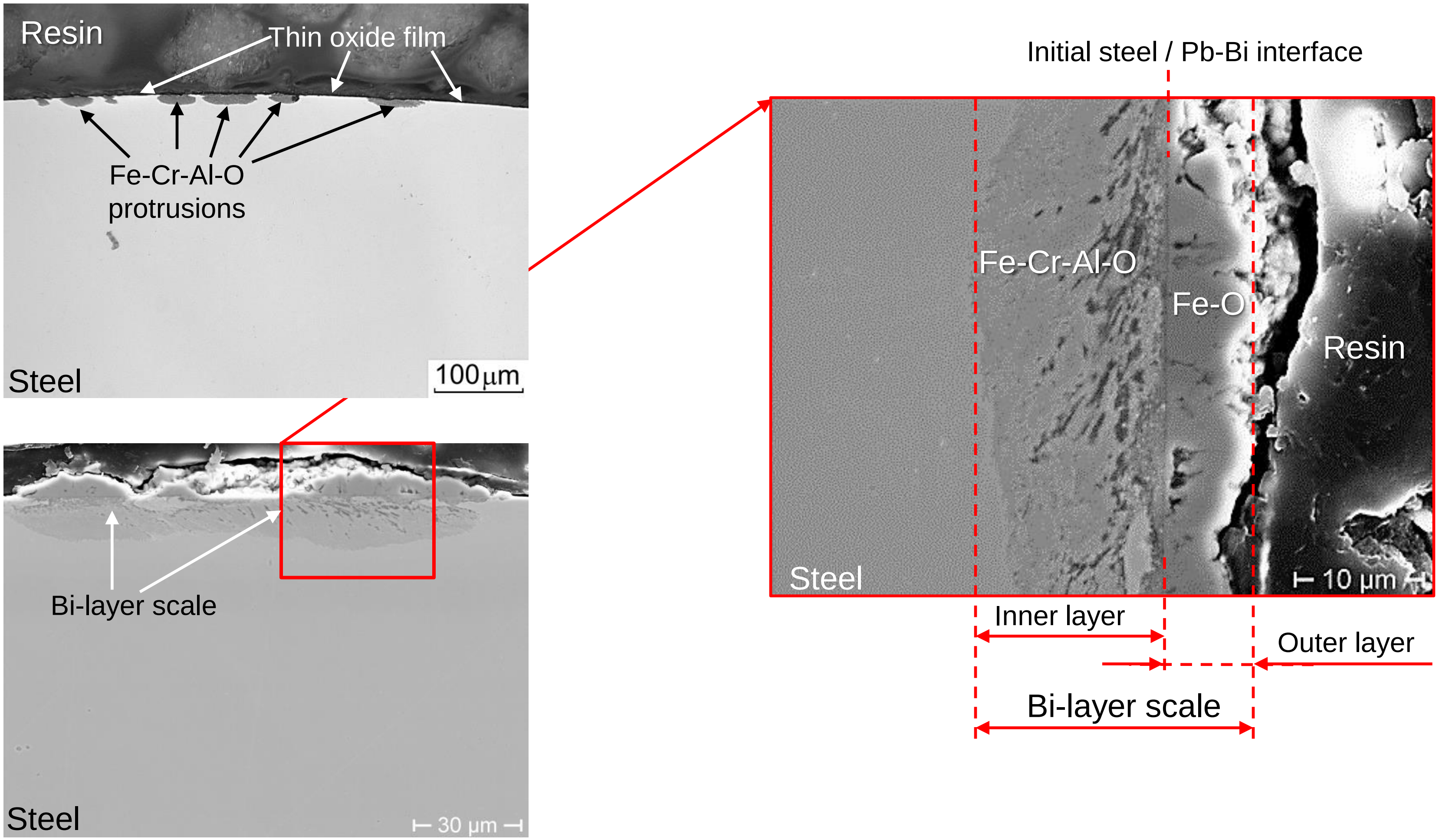
Auger sputter depth profile from surface



- Cr/Al-rich oxide film (on 79% 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 (21%) on Fe-18Ni-12Cr-AlNbC steel

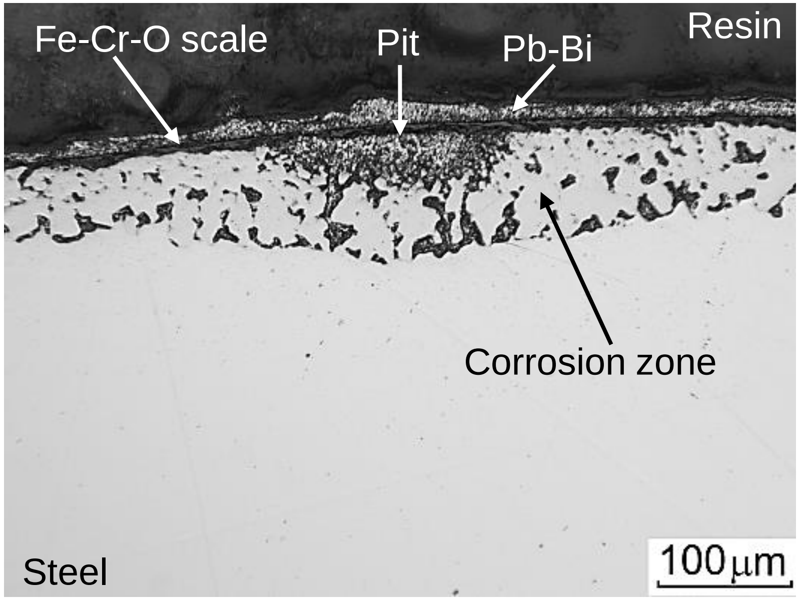


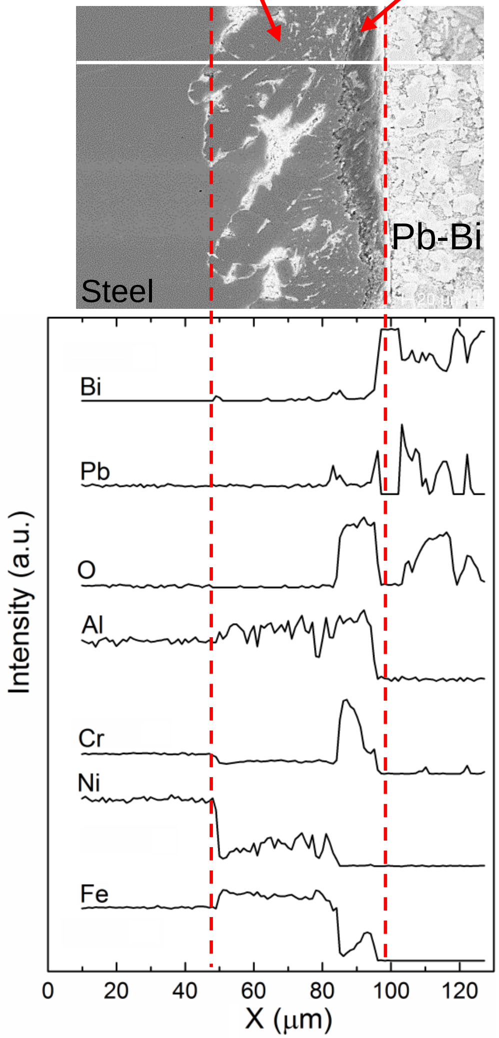
- Local protrusions of bi-layer magnetite scale or inner Fe-Cr-Al-O spinel are observed
- Local accelerated oxidation is observed on 21% of surface

CORROSION TEST 5

Characterization of general corrosion appearance on Fe-18Ni-12Cr-Al steel

Dissolution + Oxidation





- Pure dissolution attack (ferrite layer – on 33% of surface) and dissolution in combination with oxidation (42% of surface) reflects the general corrosion trend on Fe-18Ni-12Cr-Al steel
- Oxidation with formation of thin oxide film is detected on 21 % of surface
- Oxidation with formation of comparable thick Fe-Cr-Al-O spinel scale (~4-8 μm) is detected on 4 % of surface

CHEMICAL COMPOSITION OF LIQUID METAL AFTER TESTS

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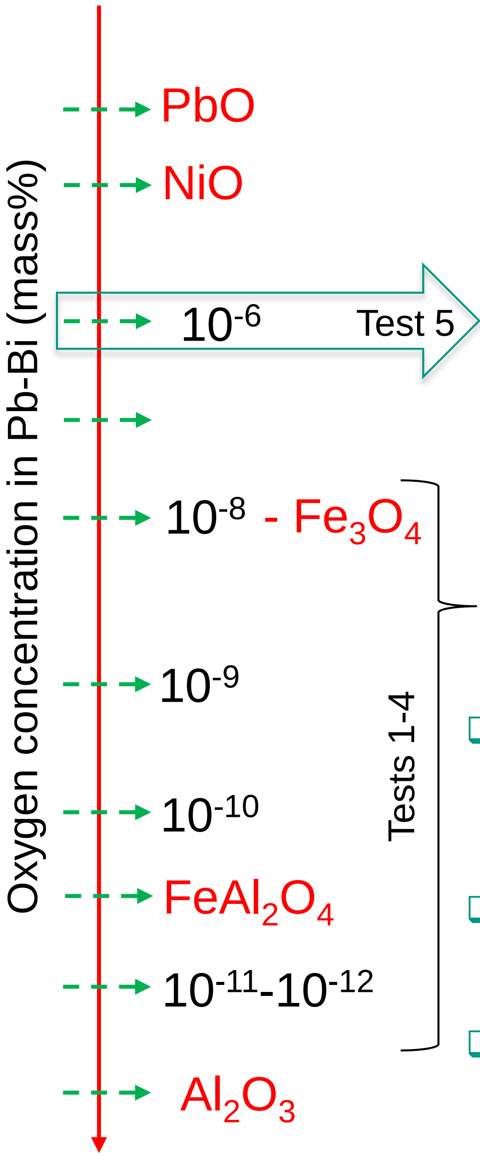
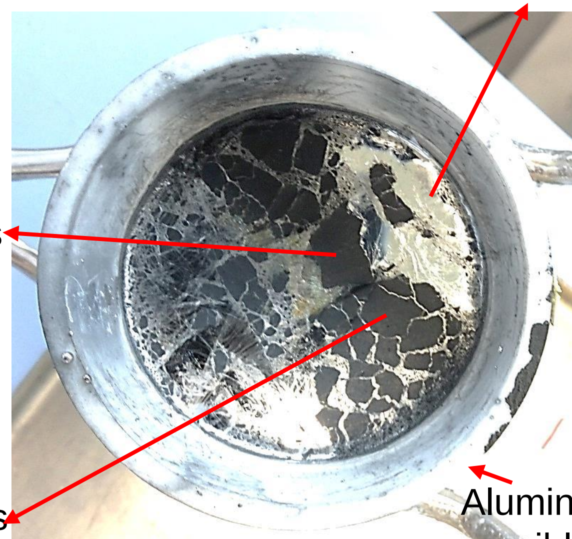


Surface of the Pb-Bi bath with floating oxides



- 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

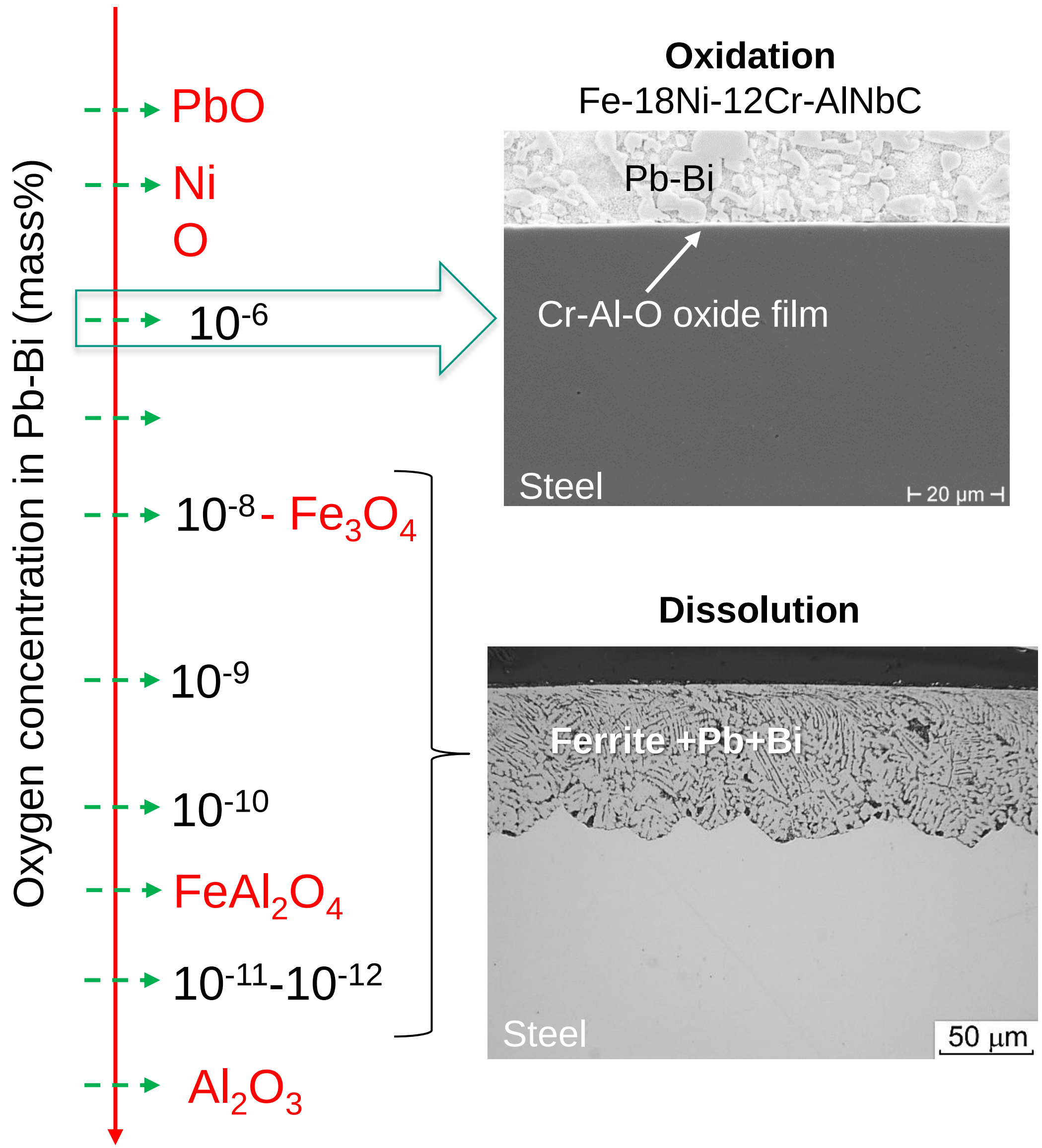
	mass%
Al	< 0.00001
Cr	< 0.00001
Fe	< 0.00001
Ni	0.00432 (±0.00001)

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)

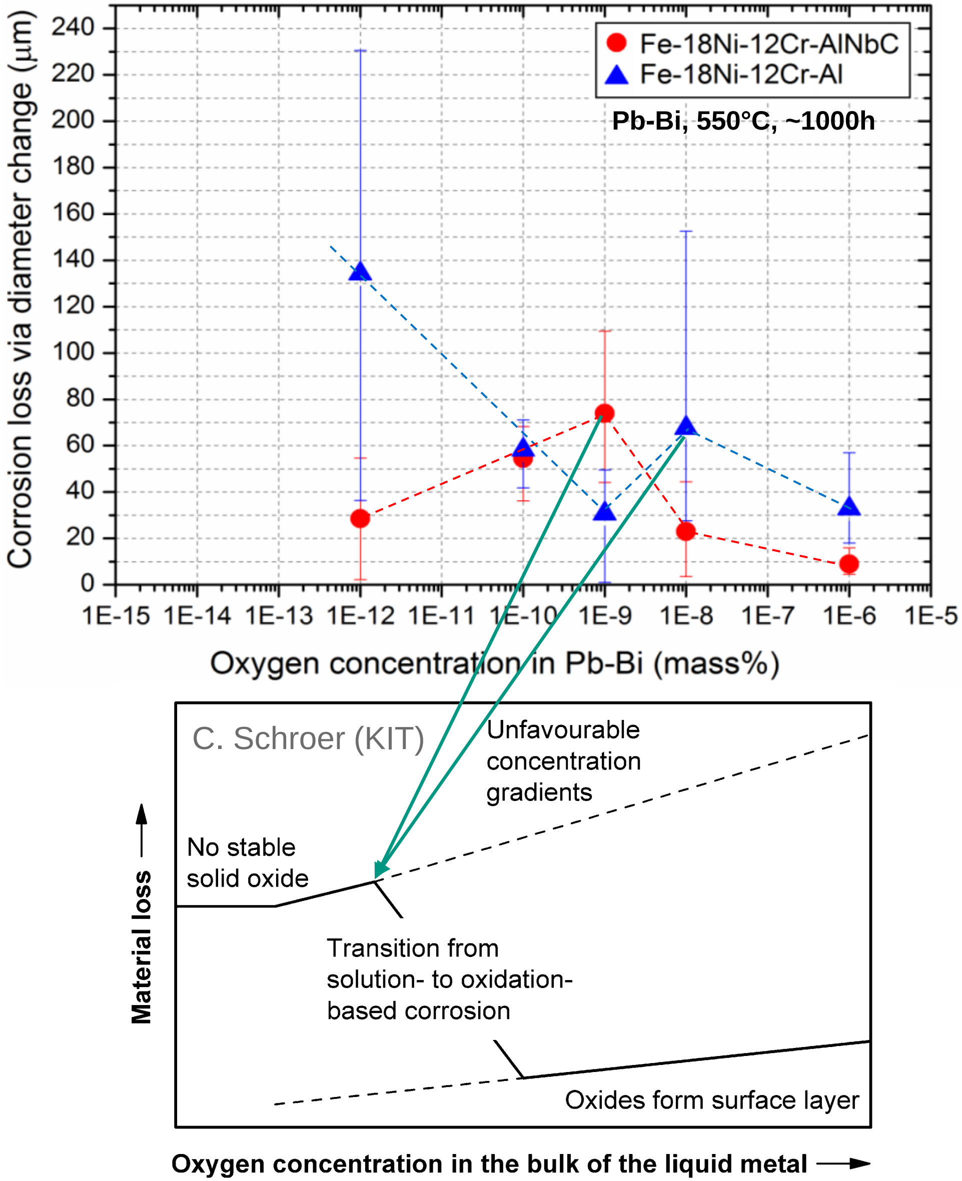
GENERALIZATION OF THE EXPERIMENTAL RESULTS



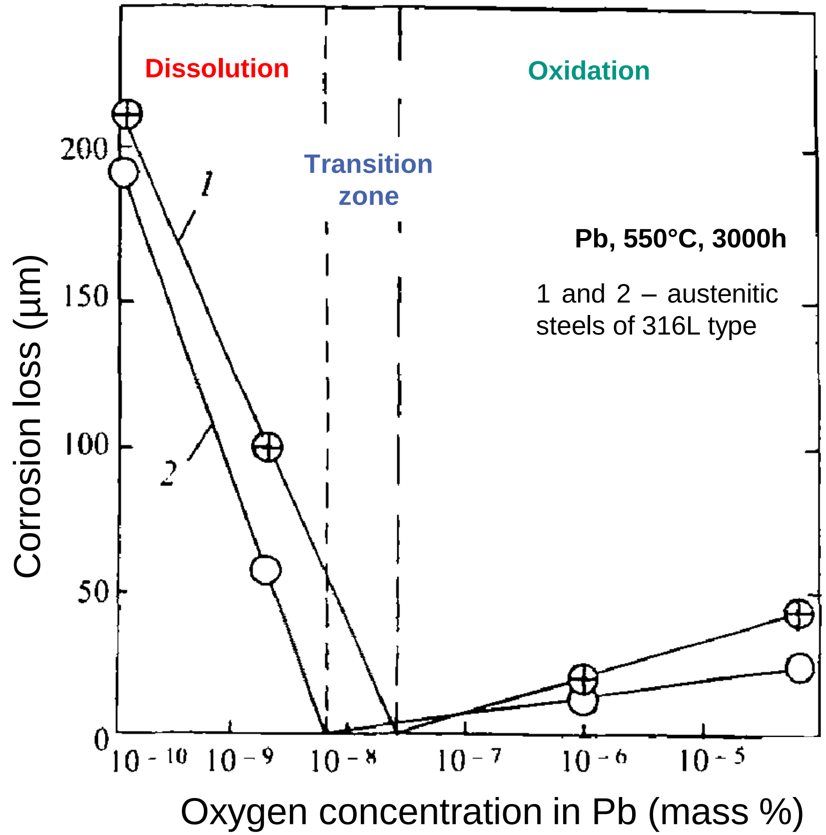
- Dissolution attack occurs when concentration of oxygen in Pb-Bi is ≤10^{-8} mass%O
- Cr-Al-O oxide film is formed *in-situ* on the surface of Fe-18Ni-12Cr-AlNbC steel in Pb-Bi with 10^{-6} mass% dissolved oxygen while Fe-18Ni-12Cr-Al shows dissolution and oxidation simultaneously resulting in larger corrosion loss

QUANTIFICATION OF CORROSION LOSS

This work



Earlier literature data



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

- Increase in corrosion loss in transition zone ($C_{O[Pb-Bi]} \leq Fe_3O_4$) is observed in comparison with lower oxygen concentrations in LBE

SUMMARY

- 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
- When oxygen concentration in the Pb-Bi is controlled at 10^{-12}-5×10^{-11}, 10^{-10}, 10^{-9} and 10^{-8} mass %, both steels underwent solution-based attack resulted in formation of spongy ferrite layer penetrated by Pb and Bi
- In Pb-Bi with 10^{-6} mass % O:
  - Fe-18Ni-12Cr-2.90Al-Nb-C steel shows general slight oxidation (~79%) with the formation of very thin Cr-Al-based oxide film and local enhanced oxidation (21%) resulted in the formation of Fe-Cr-O spinel or bi-layer scale corresponding to the material loss of about 10 µm
  - In contrast, the thicker Fe-Cr-Al-O spinel with ferrite zone beneath is observed on the Fe-18Ni-12Cr-2.30Al steel (~79%) resulting in average material loss of about 33 µm
  - The more complex alloying in Fe-18Ni-12Cr-2.9Al-Nb-C steel seems favors the formation of more protective oxide film
- 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
- Long-term tests under the flowing conditions are necessary to investigate the viability of thin Cr-Al-based oxide film

Thank you for attention !!!