Karlsruhe Institute of Technology

GEMMA – Generation IV Materials Maturity
Workshop on AFA steels
Karlsruhe, November 28th, 2018

Corrosion in aluminium-alloyed austenitc steel caused by static lead–bismuth eutectic:

Effect of dissolved oxygen concentration after exposure for 1000 h at 550 °C

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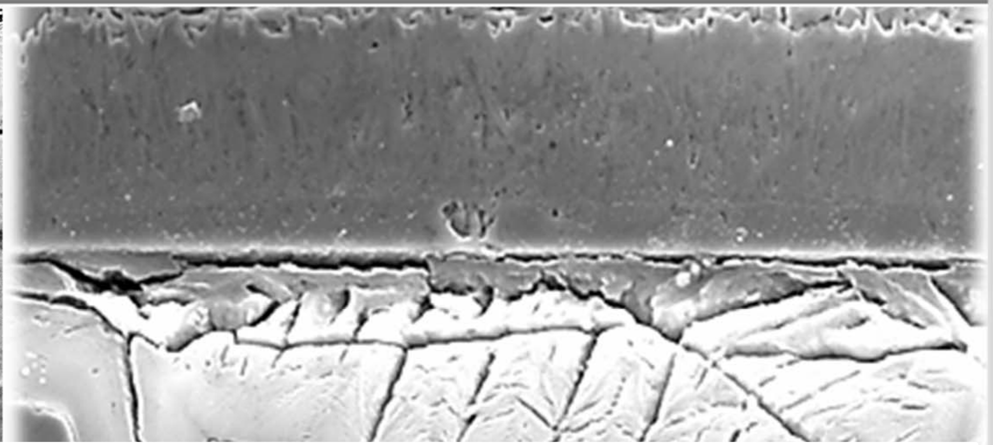
INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS (IAM-WPT)



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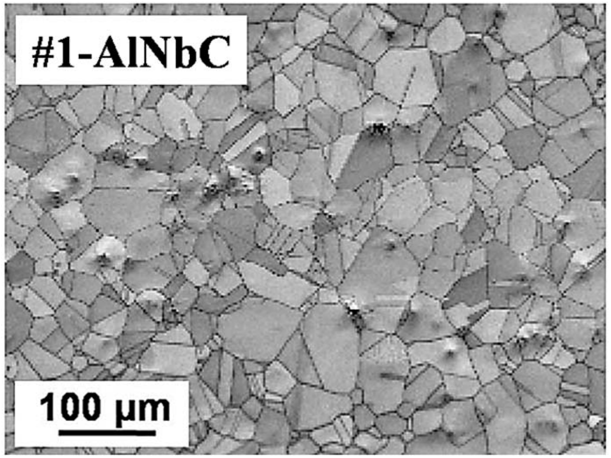
INVESTIGATED STEELS

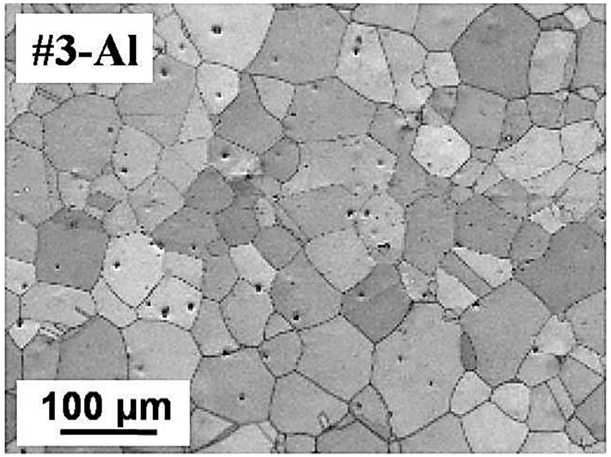
Produced at the University of Science and Technology Beijing, Beijing 100083, PR China

	Fe	Cr	Ni	Mo	Mn	Si	Al	Nb	C
# 1-AlNbC	Bal.	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	Bal.	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)

- Ingots prepared by vacuum induction melting.
- Forged to 37 mm thickness at 1230 °C.
- Hot rolled to 13 mm thickness with final rolling at 1000 °C.

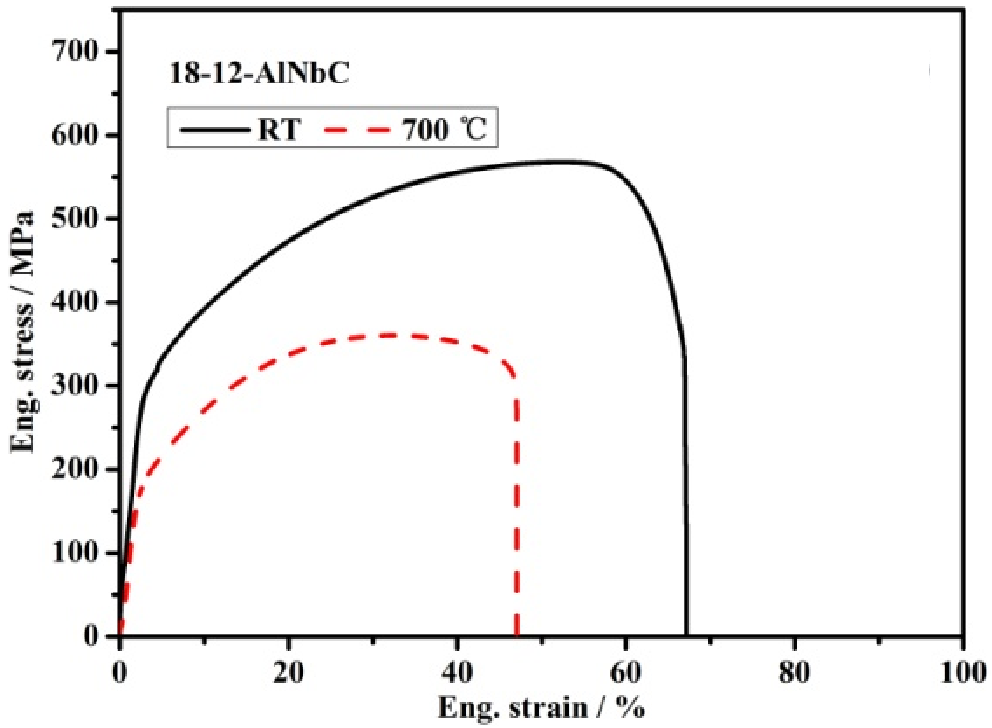


Fe–18Ni–12Cr–AlNbC



Fe–18Ni–12Cr–Al

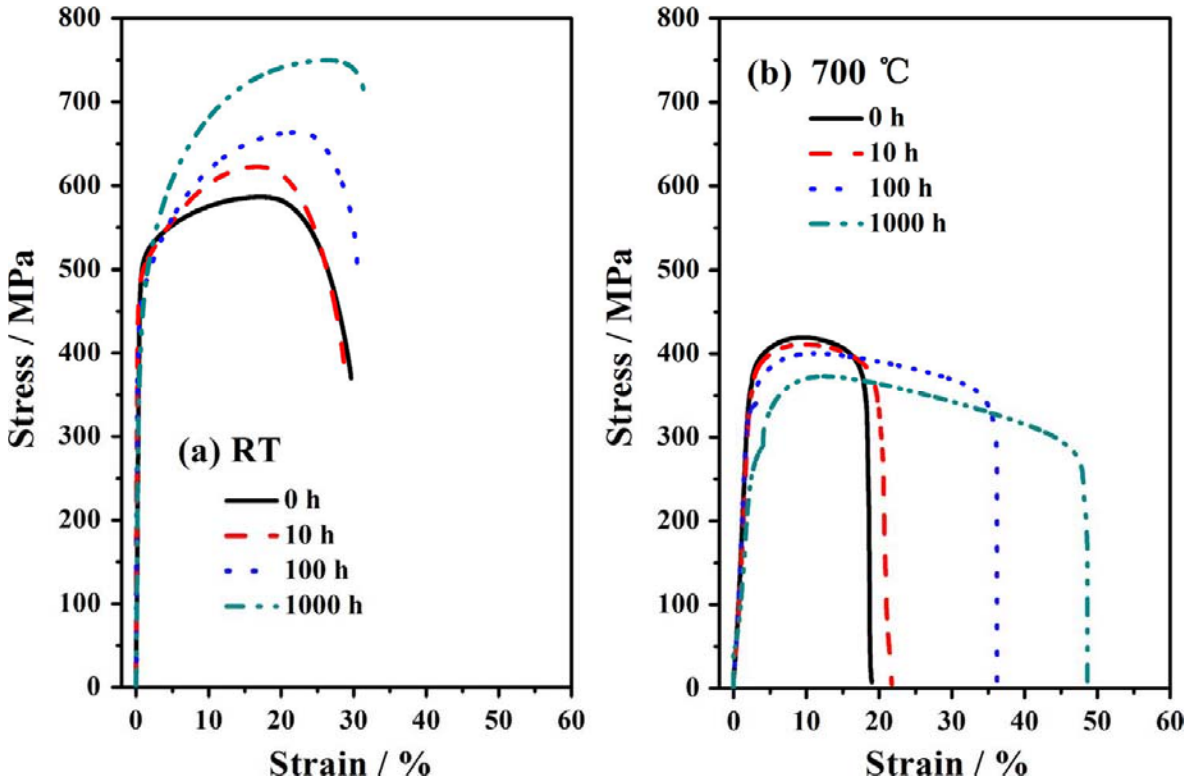
SOME CHARACTERISTICS OF Fe–18Ni–12Cr–AlNbC



Material as investigated in the corrosion study.

Results from tensile tests at room temperature and 700 °C on hot-rolled (1000 °C) material.

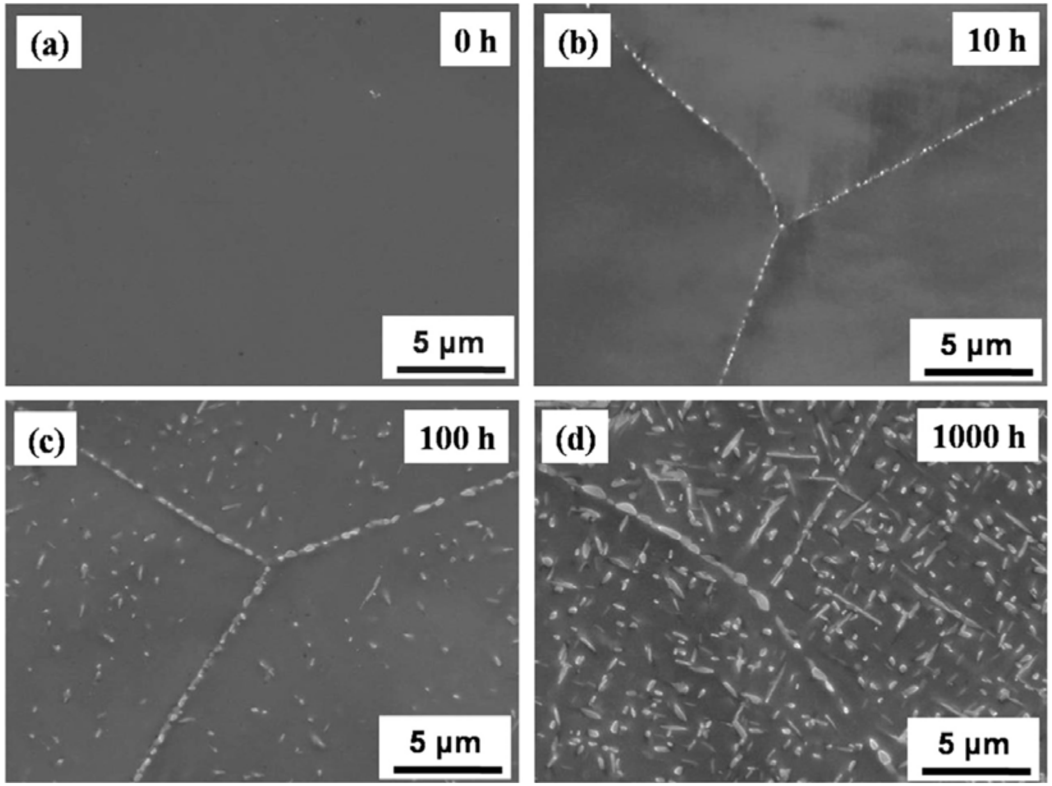
SOME CHARACTERISTICS OF Fe–18Ni–12Cr–AlNbC



Results from tensile tests at
(a) room temperature and
(b) 700 °C
on cold-rolled (10 % reduction in thickness) material
without and after ageing for up to 1000 h at 700 °C.

Wang et al., Mater. Sci. Eng., A 627 (2016) 23–31.

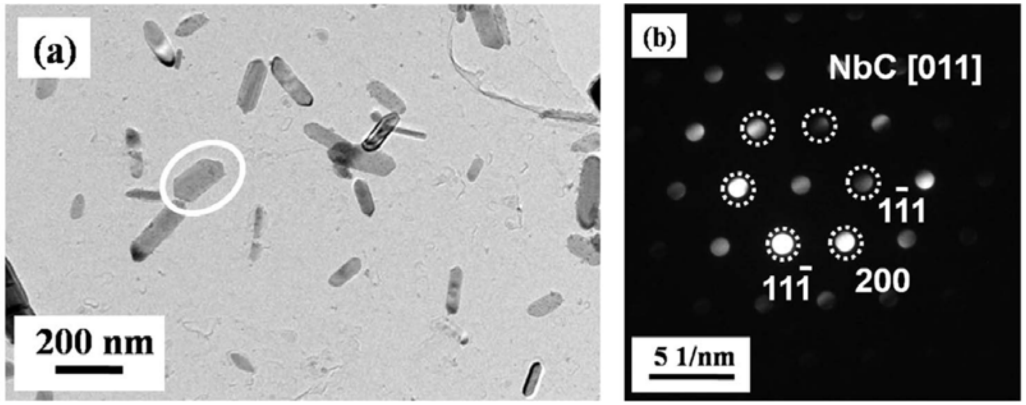
SOME CHARACTERISTICS OF Fe–18Ni–12Cr–AlNbC



Comparatively coarse (~100–1000 nm) precipitates forming in cold-rolled Fe–18Ni–12C–AlNbC at 700 °C are $(Fe,Cr)_2(Nb,Mo)$ Laves phase and NiAl.

Wang et al., Mater. Sci. Eng., A 627 (2016) 23–31.

SOME CHARACTERISTICS OF Fe–18Ni–12Cr–AlNbC

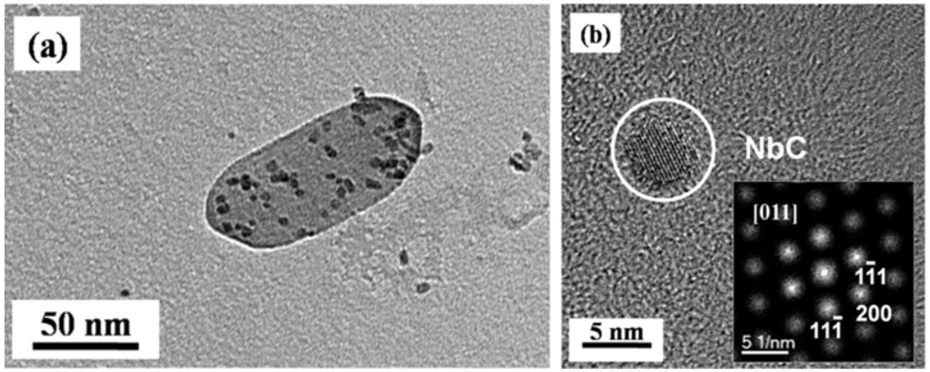


Nano beam diffraction pattern.

Fine precipitates inside the grains are plate-like (~10–100 nm) …

HR-TEM and electron diffraction pattern of selected area.

TEM on carbon replica.



… and spherical NbC (~5 nm).

Wang et al., Mater. Sci. Eng., A 627 (2016) 23–31.

EXPECTATION OF AFA STEELS AS CONCERNING CORROSION CAUSED BY LIQUID LEAD OR LEAD ALLOYS

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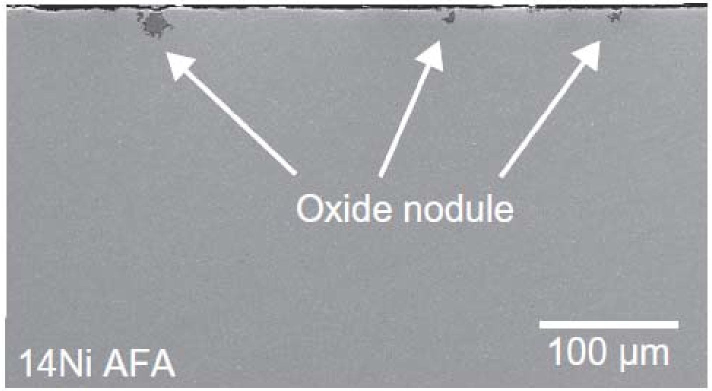
- Aluminium contributes to the formation of a protective oxide layer that impedes the solution of the material in the liquid metal.
- Oxygen addition to the liquid metal required in order to prevent critical oxygen depletion at the oxide/ liquid metal interface.
- Goal:
  Lower oxygen concentration in the bulk of the liquid metal required
  or higher liquid metal temperature allowed
  so that the protective oxide will not fail
  (in comparison to classic austenitic steels).

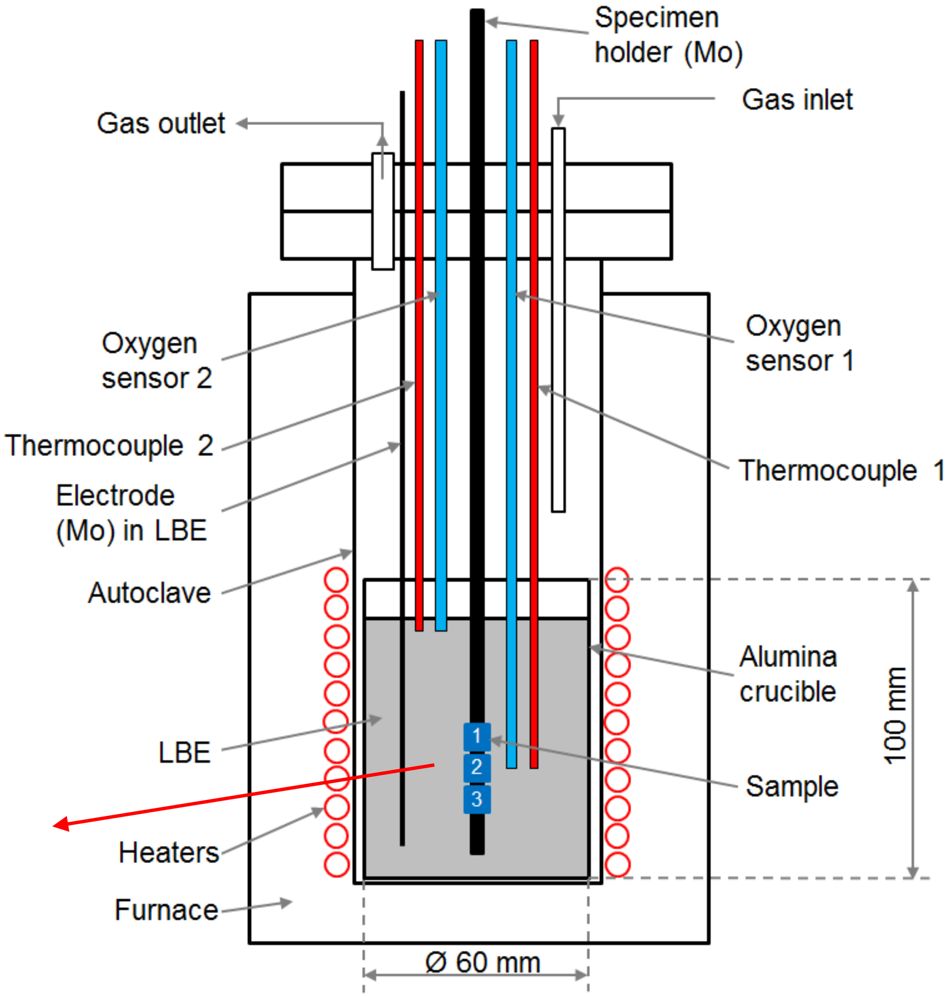
Fe–14Ni–14Cr–2.5Al–1.6Mn–2.5Mo–0.9Nb after exposure to static liquid lead at 550 °C and 10^{-7} % dissolved oxygen:
Thin oxide layer with insignificant oxide nodules after one year of exposure!



Ejenstam & Szakálos, J. Nucl. Mater. 461 (2015) 164–170.

→ Promising performance of similar material in liquid lead.
Performance in lead–bismuth eutectic?

APPARATUS FOR CORROSION TESTS IN STATIC LIQUID METALS WITH CONTROLLED OXYGEN CONTENT

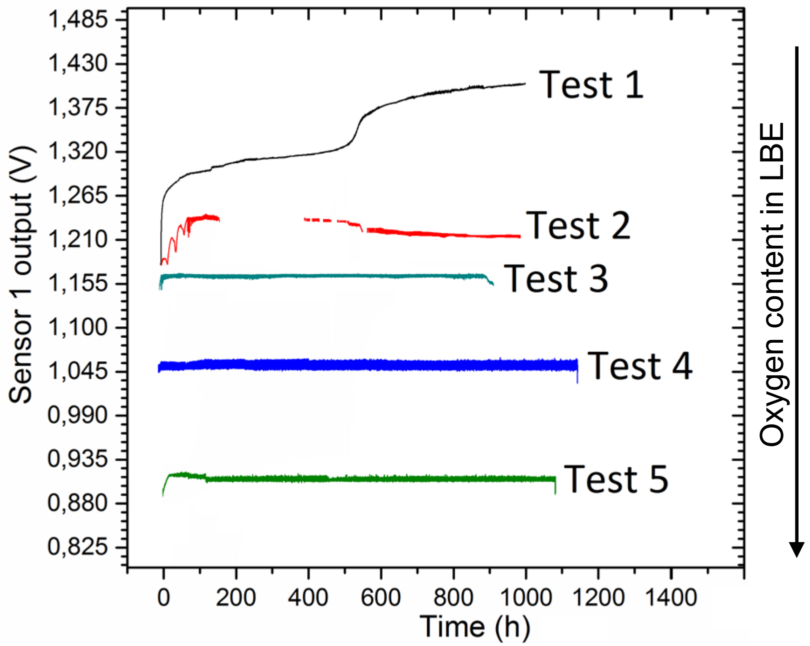


Normally, Ø8 mm cylindrical samples with variable length.

- ~200 ml liquid metal (Pb, Pb–Bi, Sn).
- Operating temperature up to 750 ºC.
- Ar–5 % H_2, Ar, air or mixtures of these introduced above the liquid metal.
- Two Pt/ air oxygen sensors.
- Automated variation of gas composition in response to the measured oxygen content.

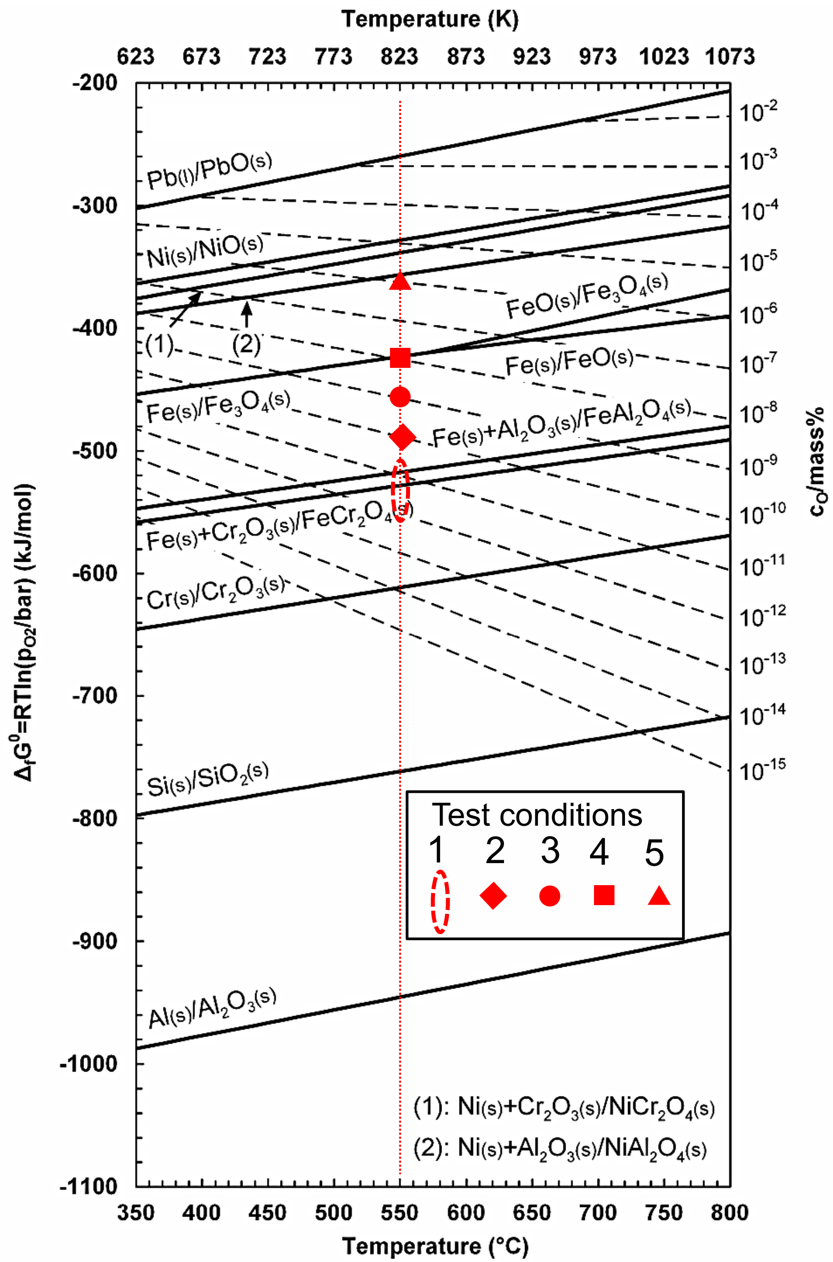
CONDITIONS OF CORROSION TESTS

- Constant parameters of the tests:
  - Volume of Pb–Bi eutectic: 2 kg
  - Ratio of Pb–Bi volume to surface of samples: ~25 cm^2/ cm^3
  - **Temperature: 550°C**
  - **Exposure time: ~1000 h**
- **Varying oxygen concentration** in Pb-Bi eutectic:
  - Test 1: 10^{-11} -10^{-12} % (by mass)
  - Test 2: 10^{-10} %
  - Test 3: 10^{-9} %
  - Test 4: 10^{-8} %
  - Test 5: 10^{-6} %



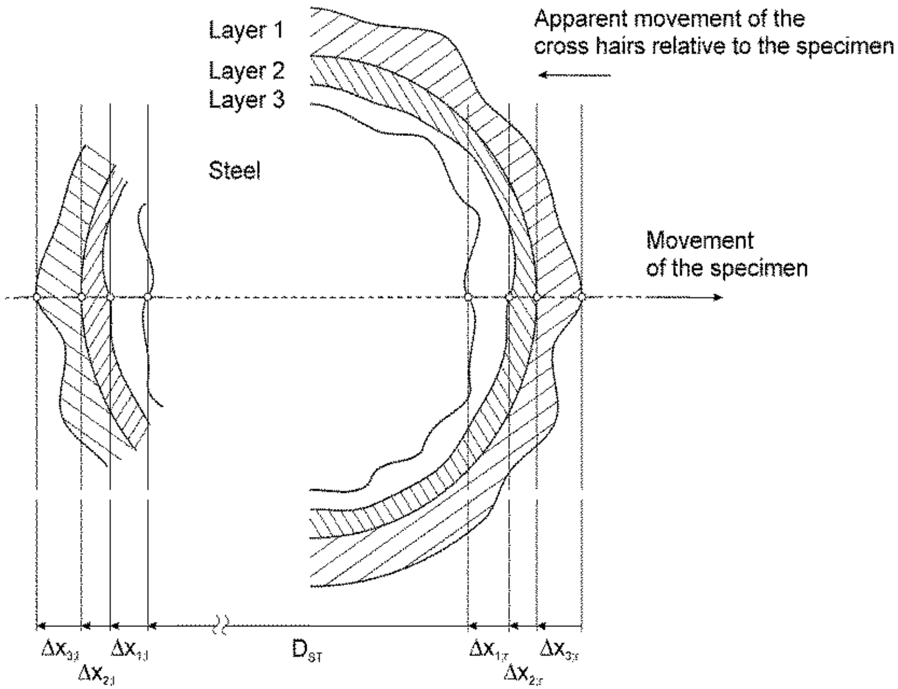
Conversion of sensor output into the oxygen concentration:

$$log(C_{O\,in\,Pb-Bi}) = -3.2837 + \frac{6949.8}{T} - 10080\frac{E}{T}$$



QUANTIFICATION OF CORROSION LOSS WITH METALLOGRAPHIC METHOD

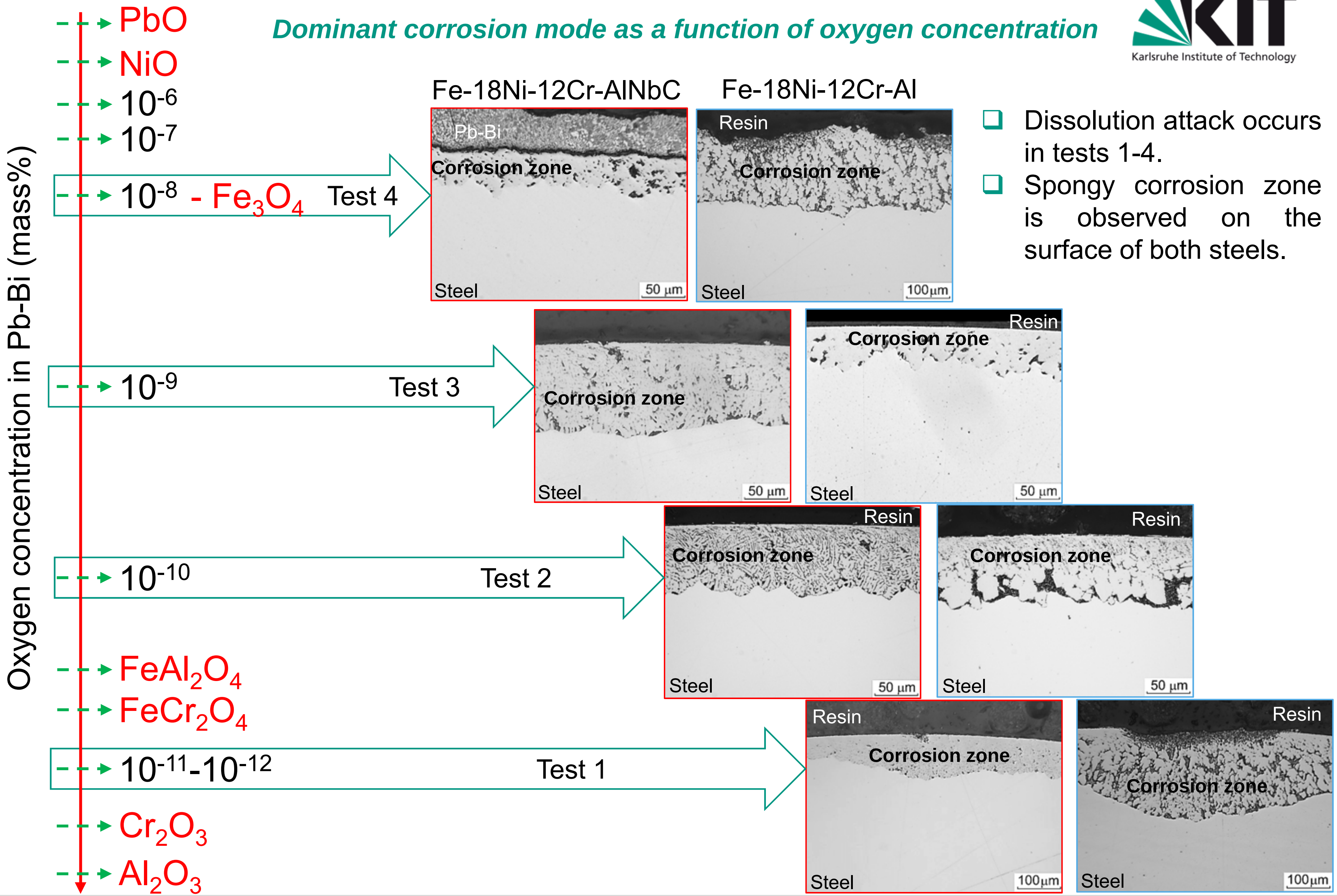
- **Initial diameter D_0**
  - Measurement in the laser micrometer.
  - Average of four measurements close to the cross section evaluated after the test.
- **Thinning or recession of sound steel**
  - From diameter of sound material after exposure, D_{ST}, and initial diameter D_0.
  - Normally, $\Delta x_{ST} = 0.5\ (D_0 - D_{ST})$.
  - 12 diameter measurements, uniformly distributed.
- **Scale thickness**
  - Separately for distinguishable layers.
  - Two for each diameter.
- **Percentage of surface area affected by different corrosion modes**
  - From count of affected sites and total number of evaluated sites (uniformly distributed).



Separate measurement of maximum corrosion depth if not contained in the systematic assessment.

RESULTS OF CORROSION TESTS 1-4

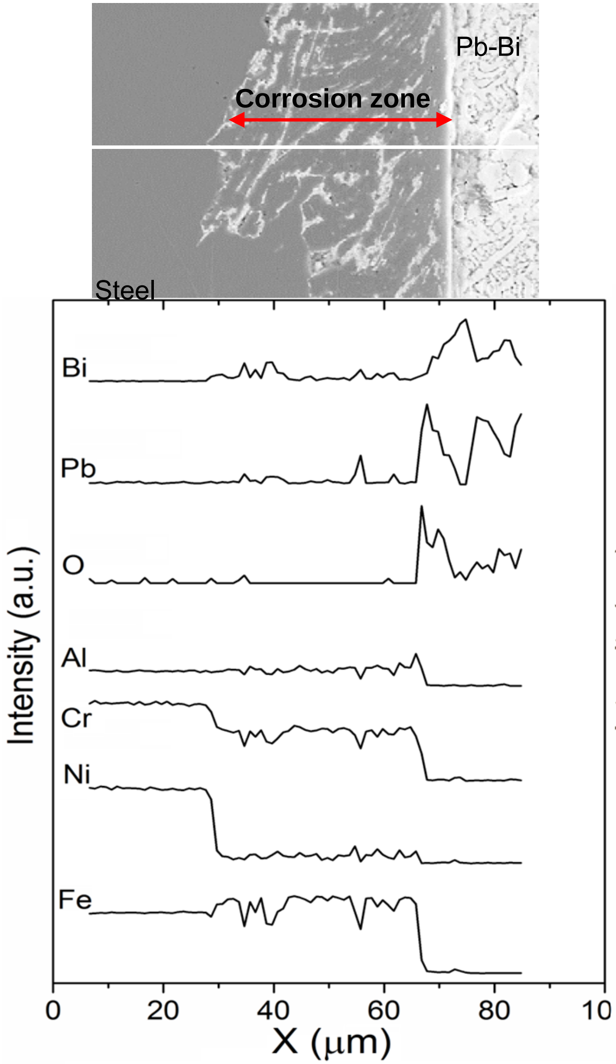
Dominant corrosion mode as a function of oxygen concentration



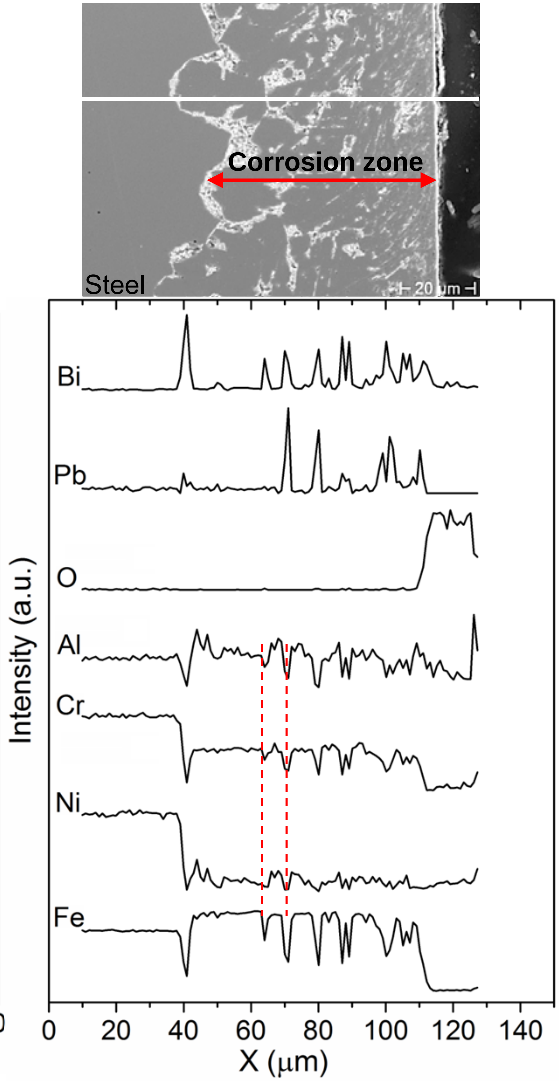
- Dissolution attack occurs in tests 1-4.
- Spongy corrosion zone is observed on the surface of both steels.

MORPHOLOGY AND COMPOSITION OF CORROSION ZONES: TEST 2, 10^{-10} % OXYGEN

Fe-18Ni-12Cr-AlNbC



Fe-18Ni-12Cr-Al



- Corrosion zone is ferrite formed along with substantial depletion in Ni and Cr.
- Penetration of Pb and Bi.
- Indications of nickel aluminide in the ferrite domain, ternary Ni–Al oxide unlikely to be stable.

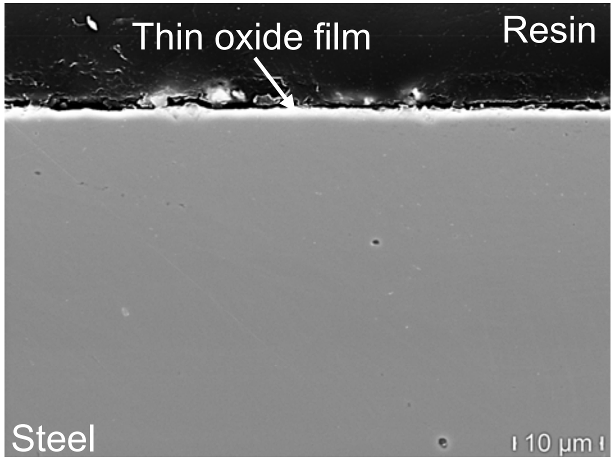
CORROSION TEST 5

Oxygen concentration in Pb-Bi (mass%)

- PbO
- NiO
- $NiCr_2O_4$
- $NiAl_2O_4$
- 10^{-6}
- 10^{-7}
- 10^{-8} - Fe_3O_4
- 10^{-9}
- 10^{-10}
- $FeAl_2O_4$
- $FeCr_2O_4$
- 10^{-11}-10^{-12}
- Cr_2O_3
- Al_2O_3

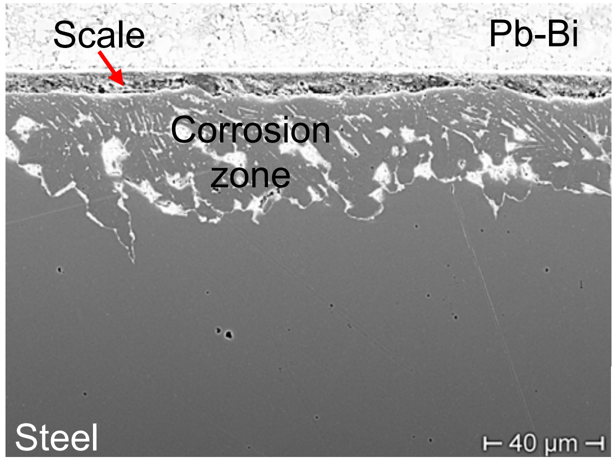
General corrosion appearances on AFA steels

Fe-18Ni-12Cr-AlNbC



Thin oxide film
80 % of the surface

Fe-18Ni-12Cr-Al



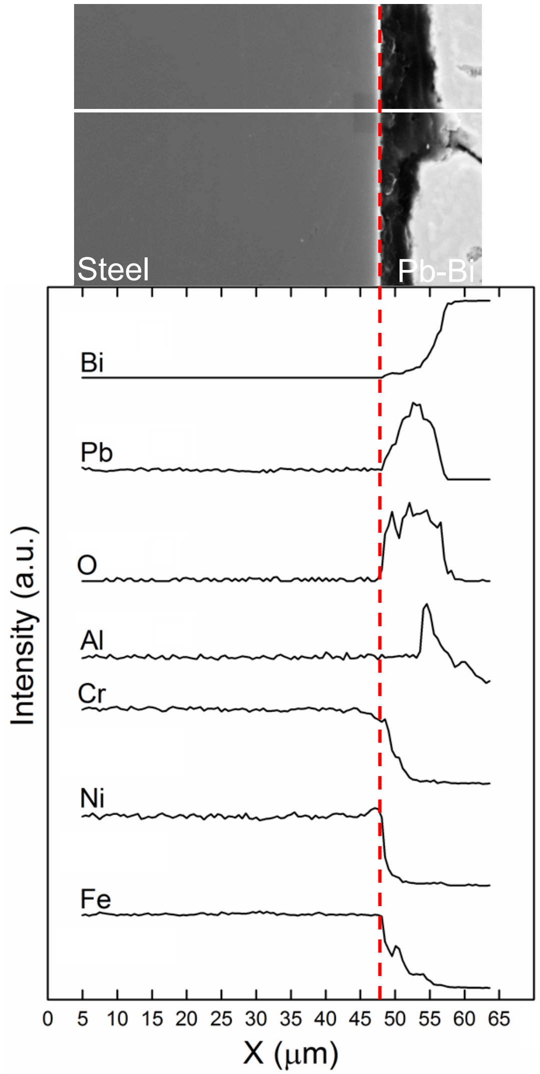
Dissolution
underneath thick oxide scale

- 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.

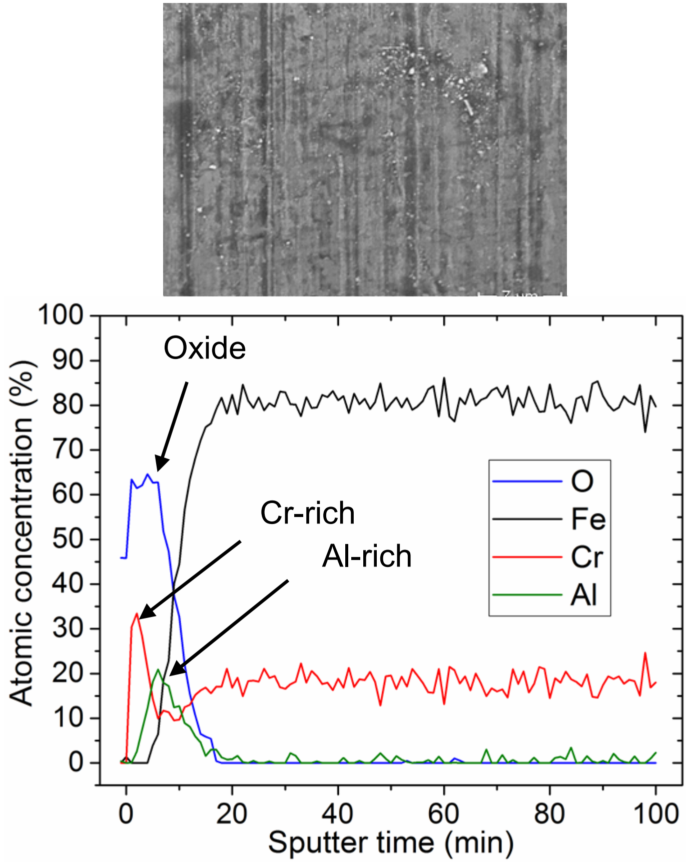
CORROSION TEST 5

General corrosion (80 % of the surface) in Fe-18Ni-12Cr-AlNbC

SEM/EDX line scan



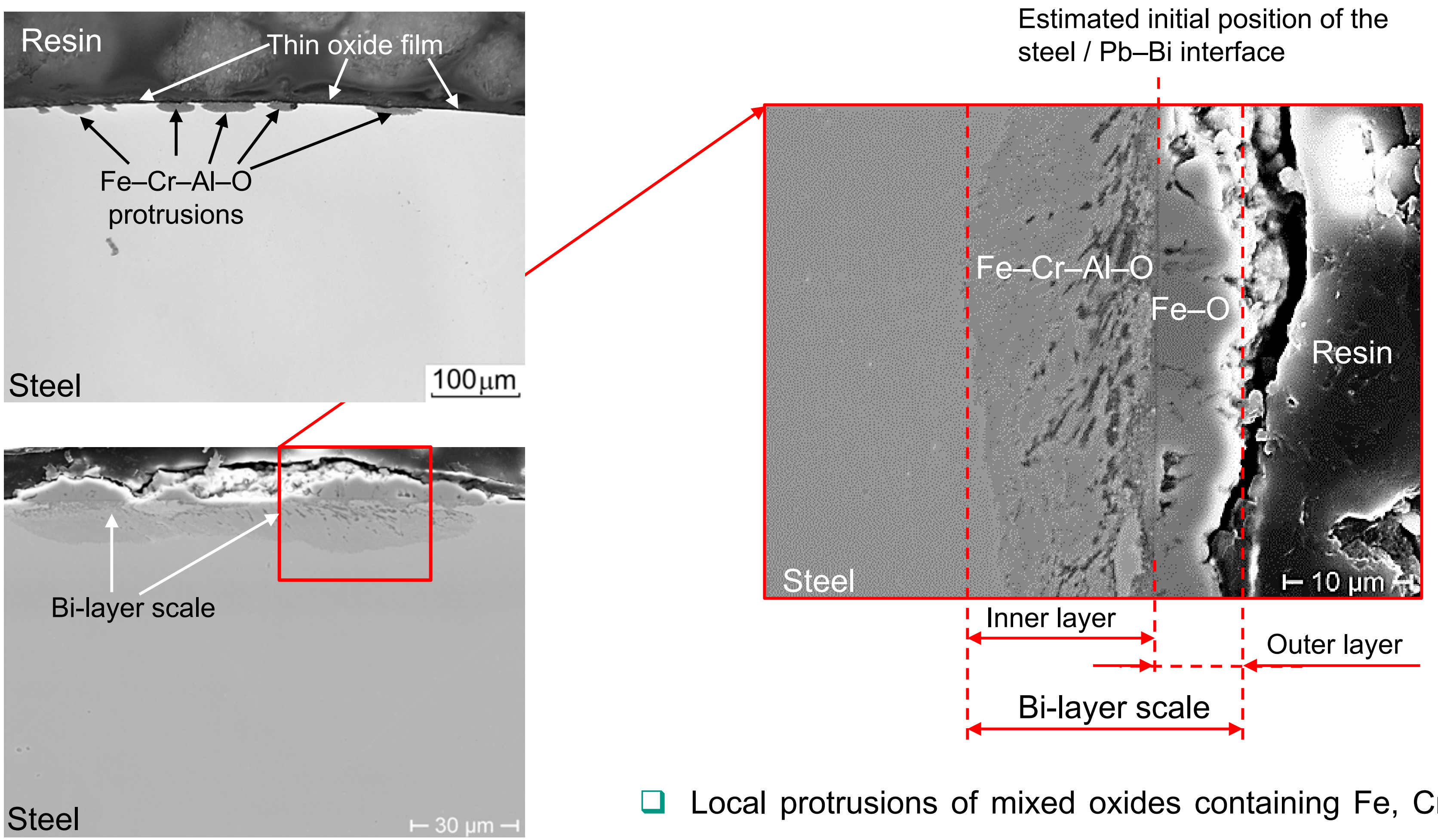
Auger sputter depth profile from surface



- Cr- and Al-rich oxide film, indicating synergetic effect of Cr and Al on the formation of oxide layer.

CORROSION TEST 5

Local corrosion (20 % of the surface) in Fe-18Ni-12Cr-AlNbC

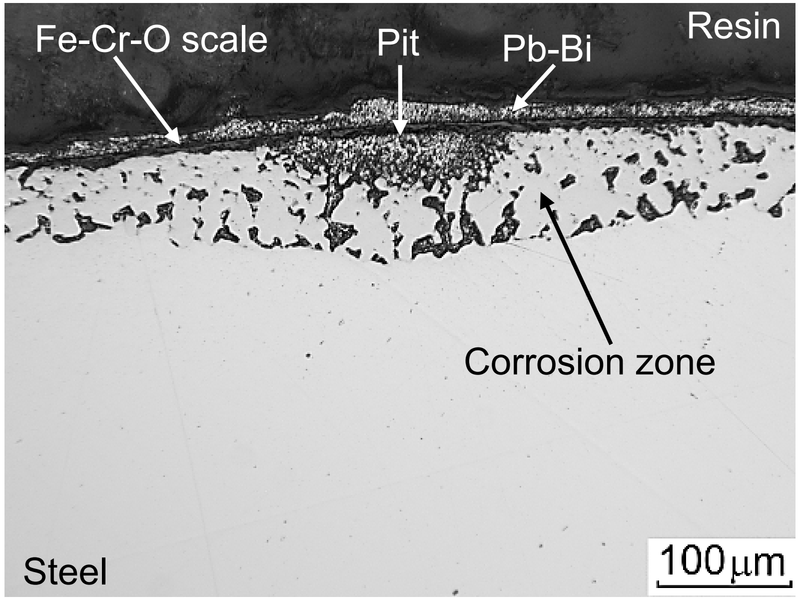


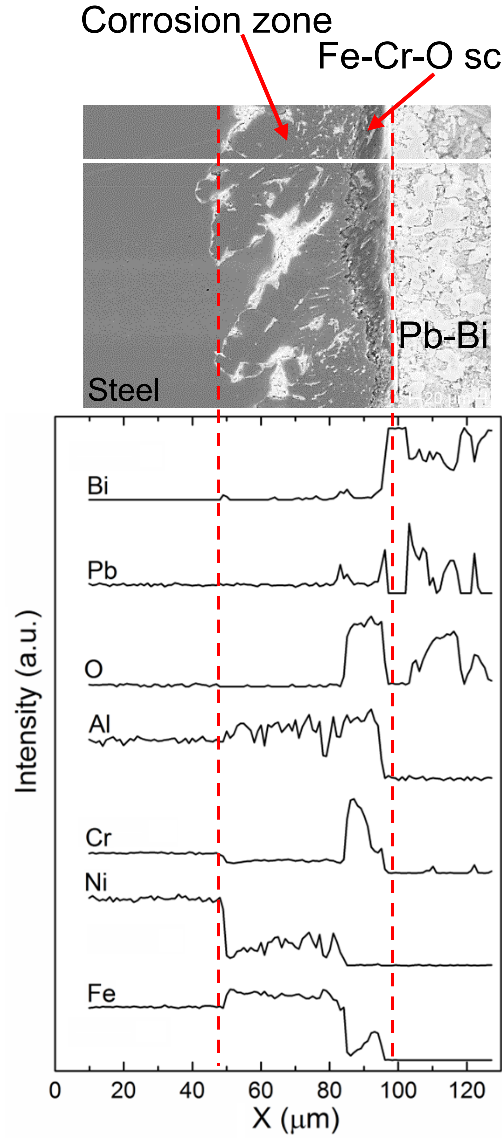
- Local protrusions of mixed oxides containing Fe, Cr and Al, possibly plus metallic component.
- With or without magnetite at the interface with Pb–Bi.

CORROSION TEST 5

Corrosion in Fe-18Ni-12Cr-Al

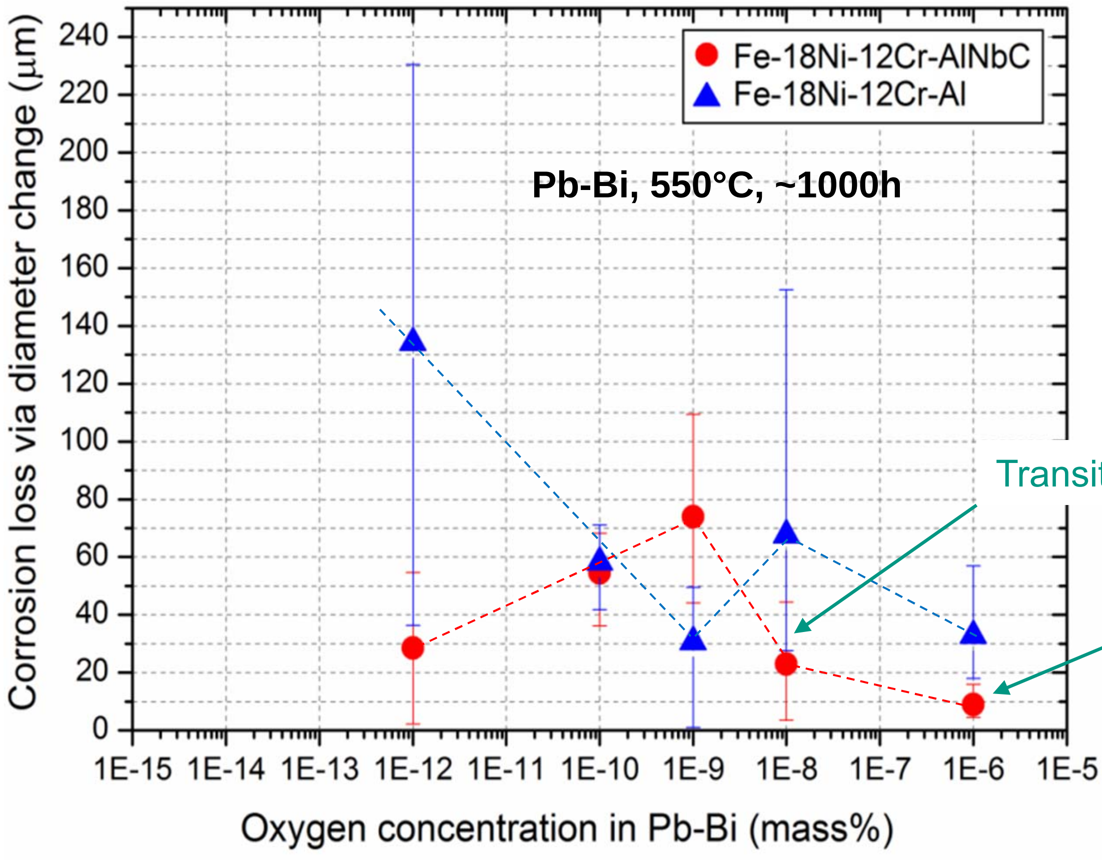
Dissolution + Oxidation





- Pure dissolution (ferrite layer – 35 % of the surface) and dissolution in combination with oxidation (40 % of the surface).
- Thin oxide film on 20 % of surface.
- Thick oxide scale (~4-8 μm) on 5 % of surface.

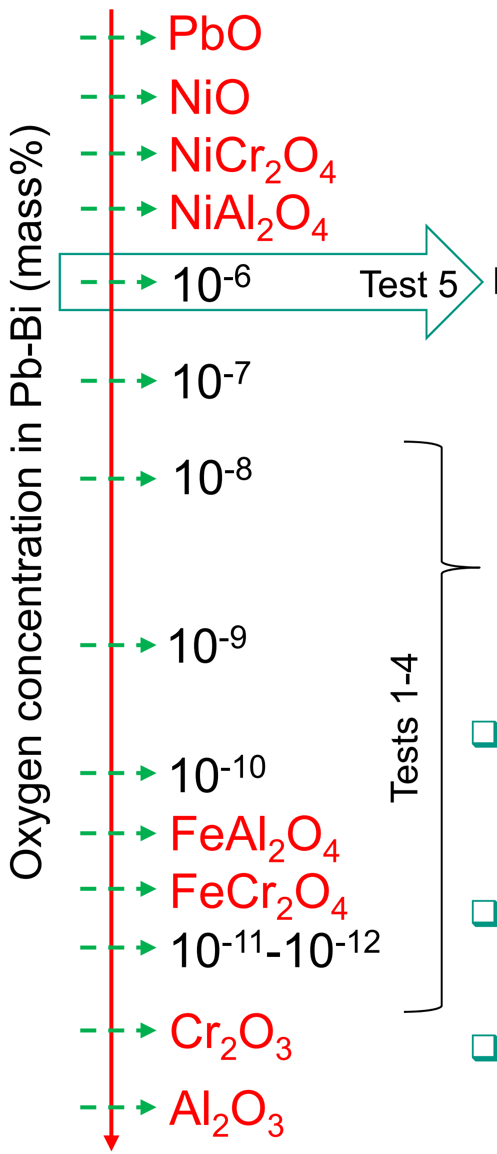
QUANTIFICATION OF CORROSION LOSS



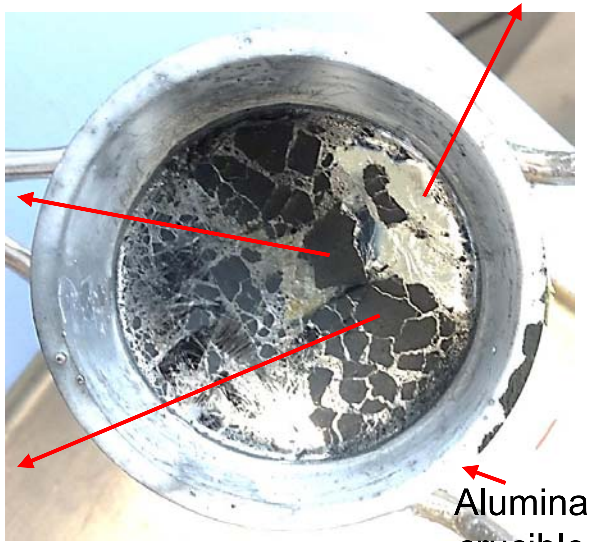
Transition to oxidation

Oxidation

CHEMICAL COMPOSITION OF LIQUID METAL AFTER TESTS



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

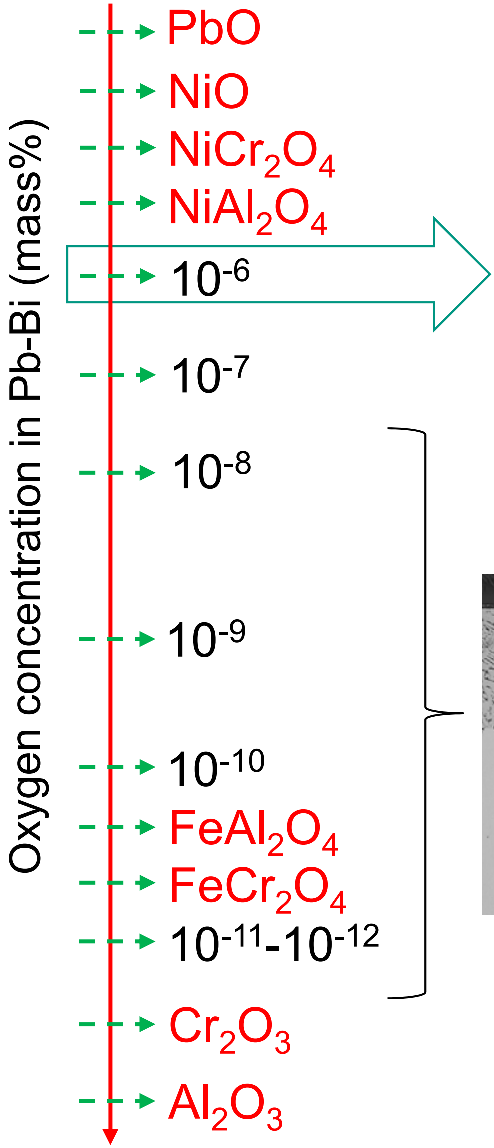
	mass%
Al	< 0.00001
Cr	< 0.00001
Fe	< 0.00001
Ni	0.00432 (±0.00001)

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

Composition of LBE after test 1

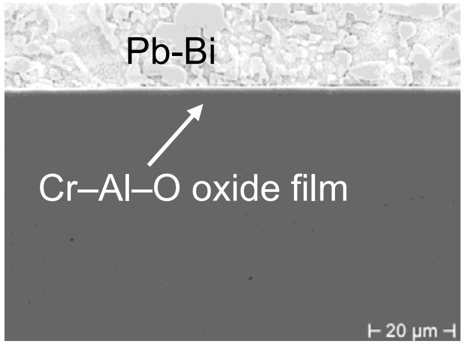
	mass%
Al	< 0.00005
Cr	0.00019 (±0.00002)
Fe	0.00023 (±0.00007)
Ni	0.00230 (±0.00004)

18 Ni–12 Cr AFA STEELS AFTER EXPOSED FOR 1000 h TO STATIC LEAD–BISMUTH EUTECTIC AT 550 °C

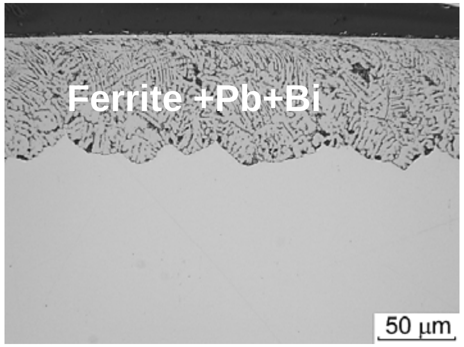


Oxidation

Fe–18Ni–12Cr–AlNbC



Dissolution



- Thin Cr-Al-O oxide film dominates at 10^{-6} % dissolved oxygen, but only for Fe–18Ni–12Cr–AlNbC.
- Acceleration of oxidation where this film has failed/ did not form.
- Fe–18Ni–12Cr-Al shows dissolution at 10^{-6} % oxygen, along with oxidation.

- Dissolution at $\leq 10^{-8}$ % oxygen for both steels investigated.

Dissolved oxygen concentration that favours oxidation over dissolution at 550 °C is similar as for classic austenitic steels (Type 316).

Look for advantages of Fe–18Ni–12Cr–AlNbC with respect to long-term performance at 10^{-6} % dissolved oxygen or at higher LBE temperature.