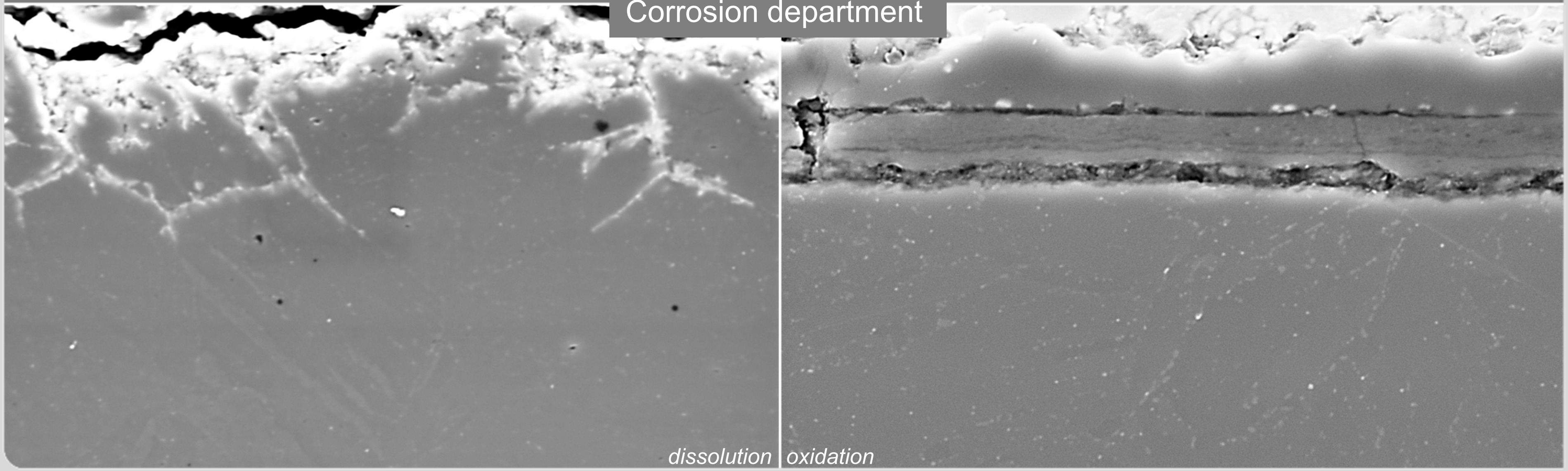
European Commission funded International Workshop
"Materials resistant to extreme conditions for future energy systems"
12-14 June 2017, Kyiv - Ukraine

CORROSION ISSUES IN STEELS CONTACTING Pb-Bi EUTECTIC AT HIGH TEMPERATURES – OVERVIEW OF KIT ACTIVITY

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

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

Corrosion department



Candidate liquid-metal media for Fusion and Fission reactors

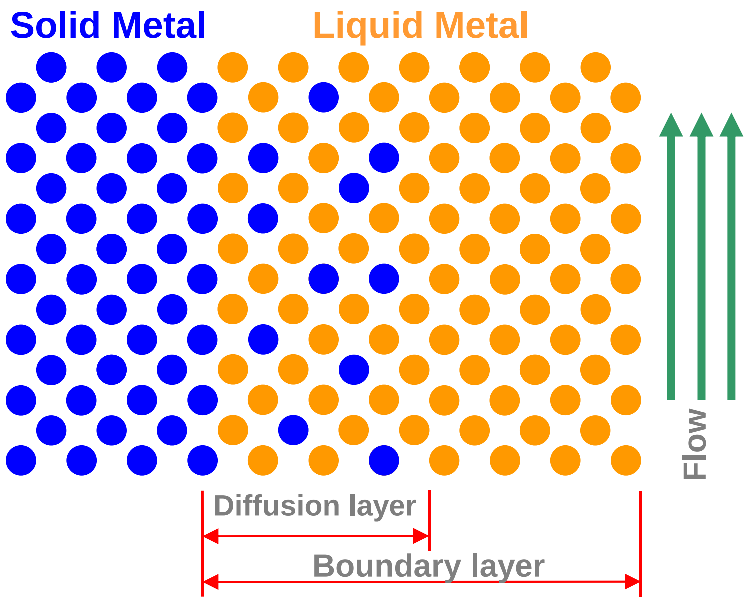
- ❑ Good nuclear and thermal-physical properties
- ❑ High thermal efficiency
- ❑ High boiling temperatures
- ❑ Wide range between melting and boiling temperatures
- ❑ Low vapor pressure
- ❑ High heat transfer coefficient

Liquid Metal	Advantages	Disadvantages
Li Tm = 180*C coolant and/or breeder	● Very low induced activity ● Low density (0.5316 g/cm^3) ● High tritium breeding ratio (TBR) ● Low tritium leakage ● Easiness of neutralization	● High chemical activity to air and water ● MHD pressure drop; ● Tritium recovery;
Pb-Li Tm = 235*C coolant and/or breeder	● Low chemical activity to air and water ● Sufficient TBR	● Tritium leakage; ● MHD pressure drop issue; ● Corrosion aggressiveness;
Pb Tm = 327*C Coolant Pb-Bi Tm = 123*C coolant and/or spallation target	● High spallation neutron yield ● Low γ-radioactivity induced in Pb and Pb-Bi ● Low neutron moderation and capture ● Chemical inertness with water ● Neutron multiplication	High corrosion aggressiveness ● Liquid Metal Embitterment (LME); ● Production of α-radioactive volatile 210Po from Bi and Pb – hazard for the environment

Interaction between solid and liquid metals

Dissolution - basic interaction phenomenon !

Weeks - 1962



- **Fail in bond among atoms in solid metal;**
- **Bonding of dissolved atom with atoms of liquid metal.**

Dissolution process is characterized by:

1. SOLUBILITY – saturation concentration of solid metal in liquid one;
2. CONSTANT of DISSOLUTION RATE.

Dissolution rate is expressed by Nernst equation:

$dC_v/dt = \alpha \cdot (S / V) \cdot (C_{sat} - C_v)$;

C_v – concentration of dissolved metal in liquid metal;

C_{sat} – saturation concentration of solid metal in liquid metal;

t – time;

α – constant of dissolution rate;

S - surface area of solid metal contacting with liquid metal (cm^2);

V - liquid metal volume (cm^3).

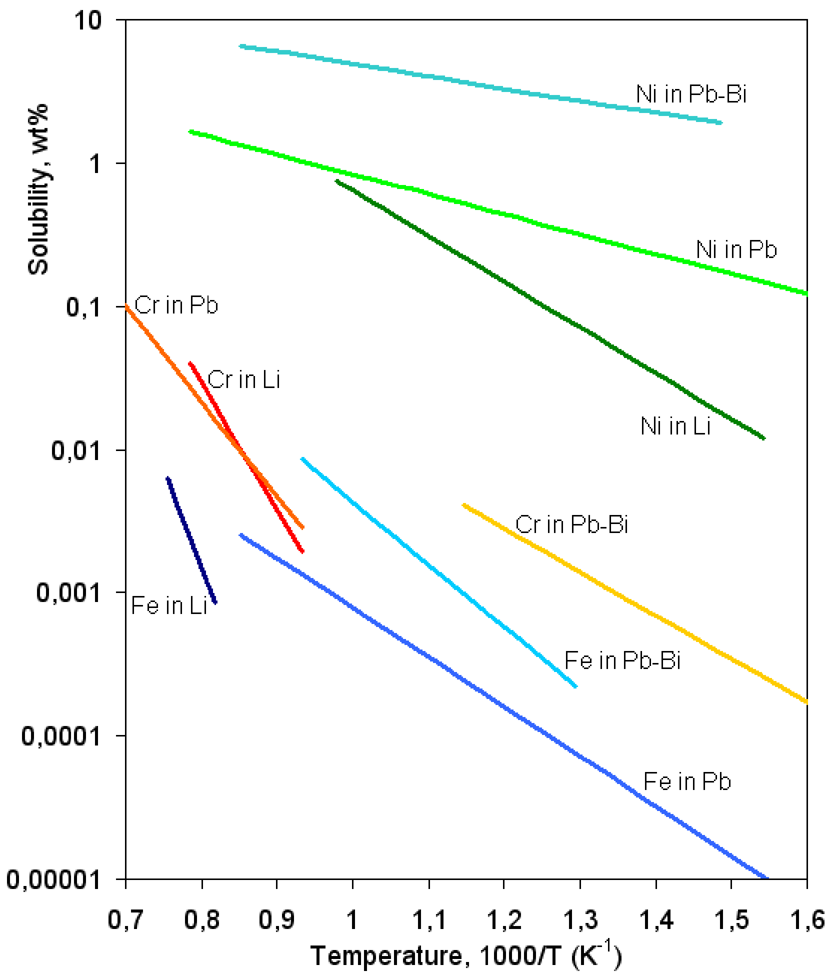
Kinetic equation of dissolution:

$C_v = C_{sat} \cdot [1\text{-}\exp(-(\alpha \cdot S/V) \cdot t)]$

Constant of dissolution rate:

$\alpha = \ln [C_{sat} / C_{sat} - C_v] \cdot V / S \cdot t$

Solubility of Fe, Cr and Ni as a pure metals in liquid Li, Pb and Pb-Bi



Temperature dependence of dissolution:

log C (wt.%) = A – B / T;

T – temperature (*K*);

A and B - constants

- The solubility of Fe, Cr and Ni in melts (corrosion aggressiveness of liquid metals) increases in the following sequence:
  Li → Pb → Pb-Bi.

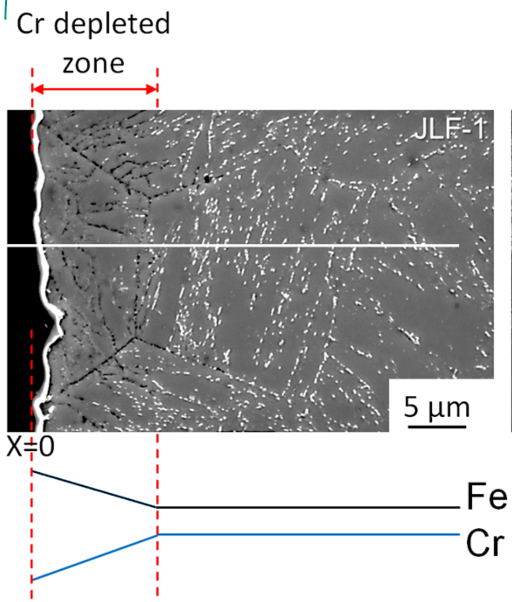
Lyublinski et al., JNM 224 (1995) 288;

http://www.nea.fr/html/science/reports/2007/nea6195-handbook.html.

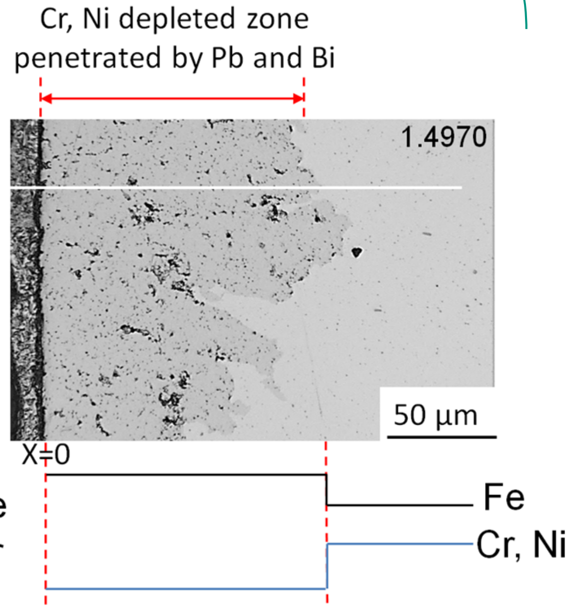
Solution-based corrosion modes

Leaching of steel constituents by liquid metal

Selective leaching

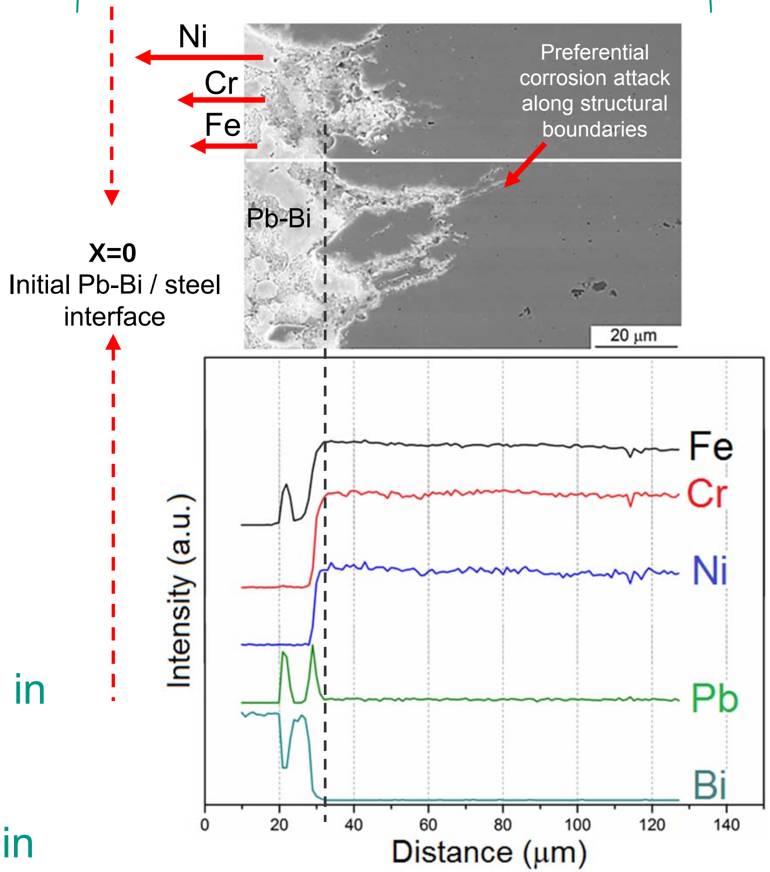


(a)



(b)

Non-selective leaching



(c)

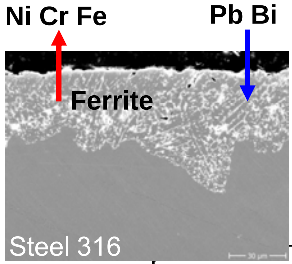
(a) Solution-based attack is controlled by the Cr diffusion in the near surface layer of steel;

(b, c) Solution-based attack is controlled by the diffusion in boundary layer of liquid metal.

Liquid metal corrosion - background

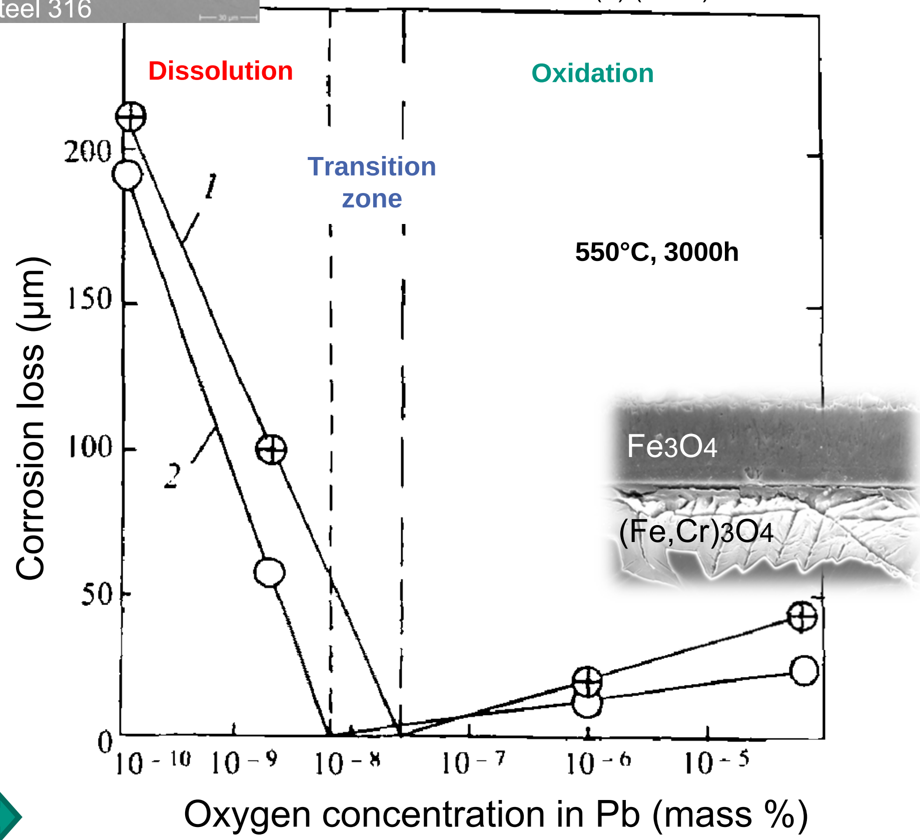
Issue !

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



Earlier findings !

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

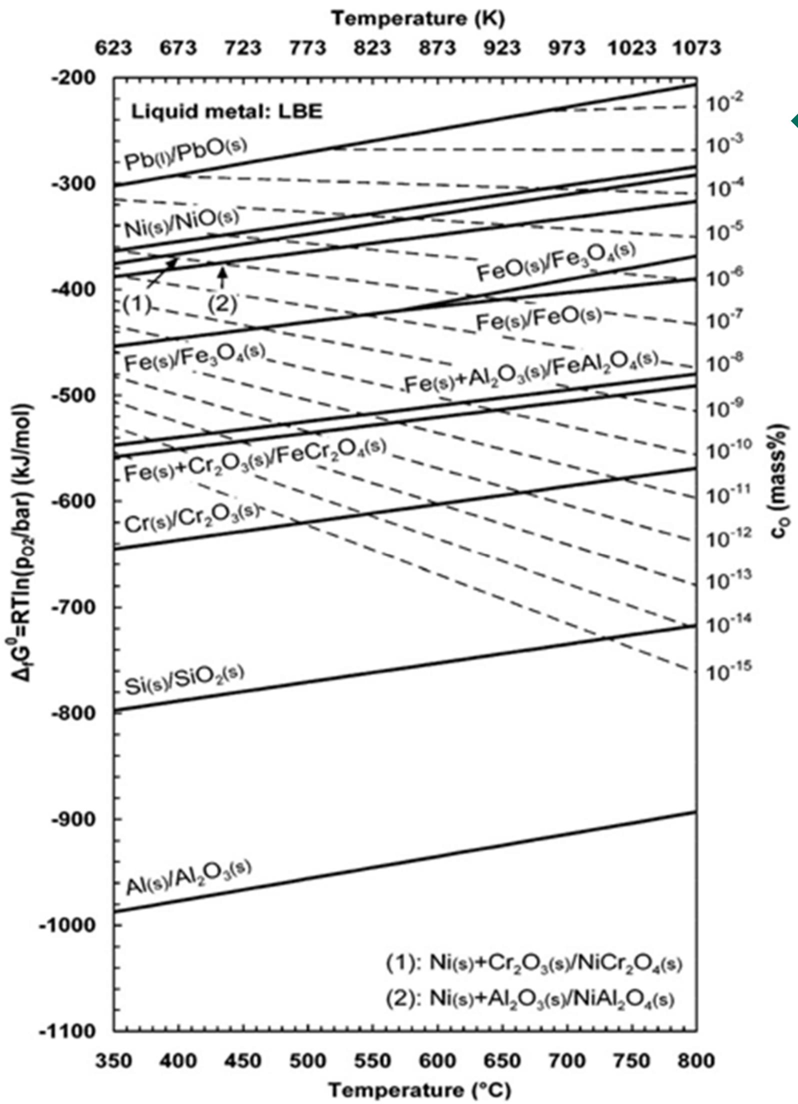


1 and 2 – austenitic steels of 316L type

Solution !?

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

Thermodynamic basis for *in-situ* addition of oxygen into liquid Pb-Bi eutectic



Free energy of formation of oxides (solid lines) and Pb-Bi[O] solutions (dashed lines)

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

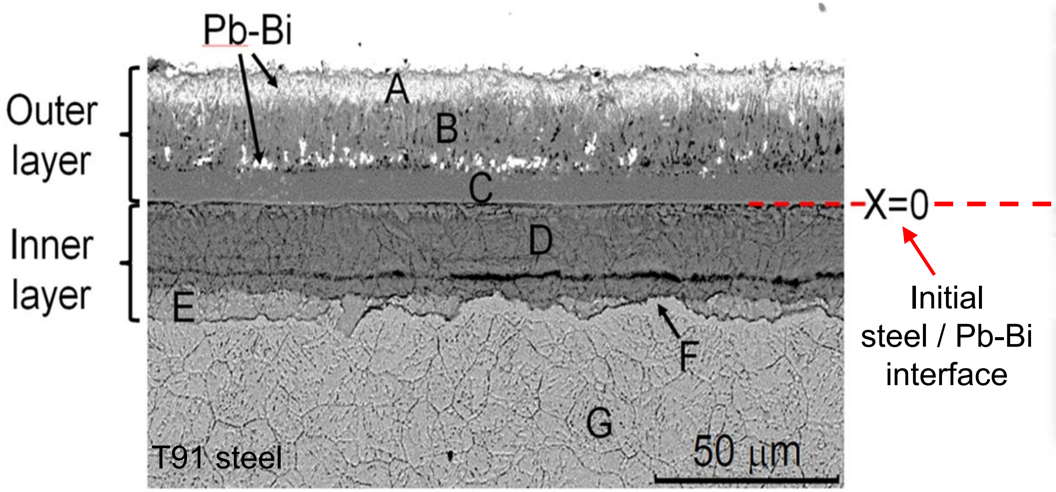
Oxidation of steel surface instead of dissolution of steel constituents by liquid metal

European Commission funded International Workshop "Materials resistant to extreme conditions for future energy systems“, 12-14 June 2017, Kyiv - Ukraine

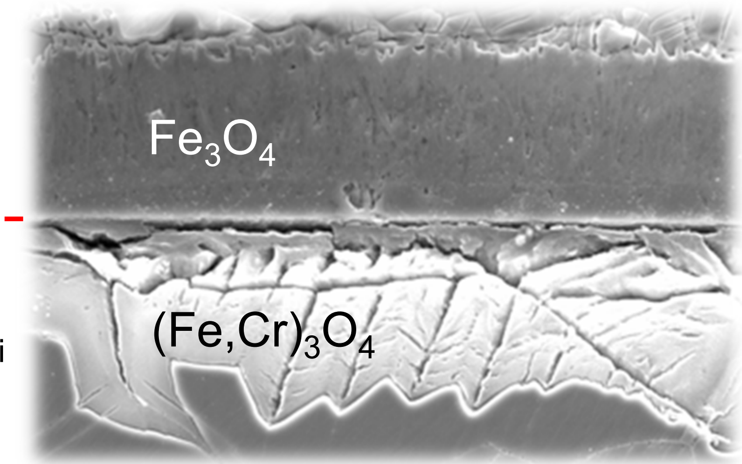
Oxidation of steels in Pb, Pb-Bi melts

Karlsruhe Institute of Technology

Ferritic/martensitic steels



Austenitic steels

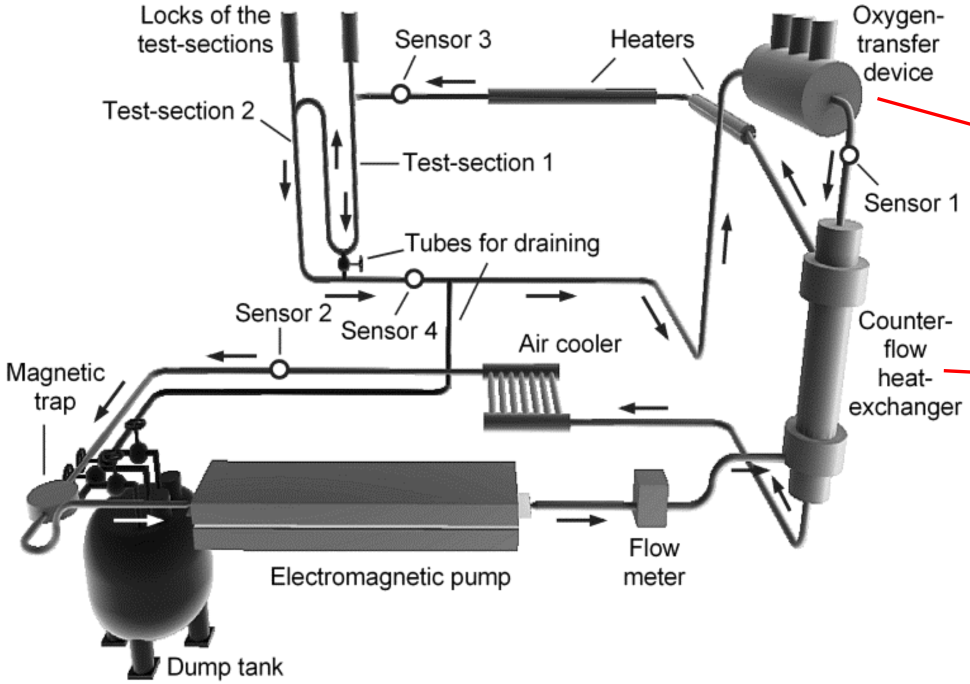


- Bi-layer scale, with outer Fe_3O_4 (magnetite spinel) and inner $Fe(Fe,Cr)_2O_4$ spinel-type oxide layers, typically forms on the surface of steels in contact with oxygen-containing Pb and Pb-Bi melts
- Growth of scale is governed by the outward diffusion of iron cations
- Inward growth of Fe-Cr spinel 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).

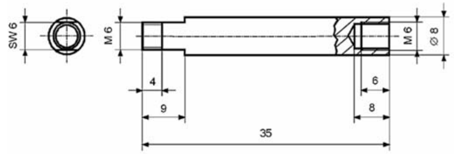
Activity towards successful application of liquid metal technologies

- **Principal understanding of corrosion phenomena** taking place in the steel / Heavy Liquid Metals system does not free from the experimental determination of the optimal temperature – oxygen concentration range.
- **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.
- **The reliable quantitative data on corrosion loss** based on the long-run tests performed **in liquid metals with controlled oxygen concentration** are still very scarce up to date.

CORRosion In Dynamic lead Alloys
CORRIDA Pb-Bi eutectic liquid-metal loop



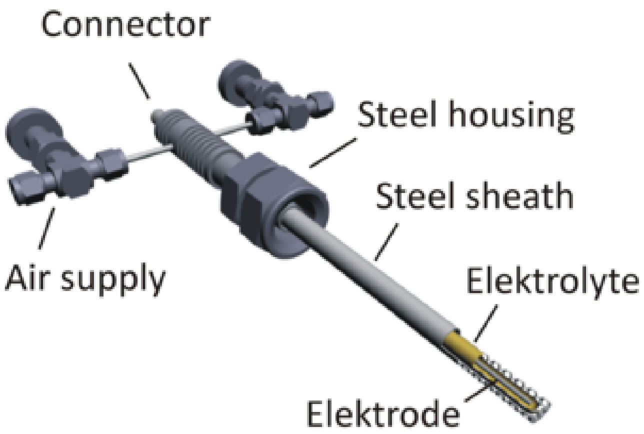
The CORRIDA facility – a forced-convection loop made of austenitic stainless steel (1.4571) designed to expose material (steel) specimens to flowing (2 m/s) Pb-Bi eutectic (~1000 kg) <u>with controlled oxygen concentration</u>.



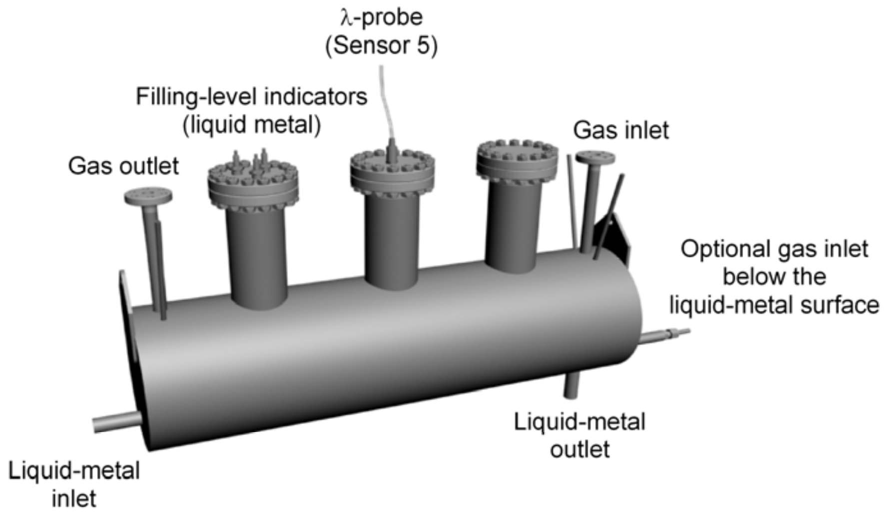
C

Gas/liquid oxygen-control system

Pt/air oxygen sensor



Oxygen-transfer device

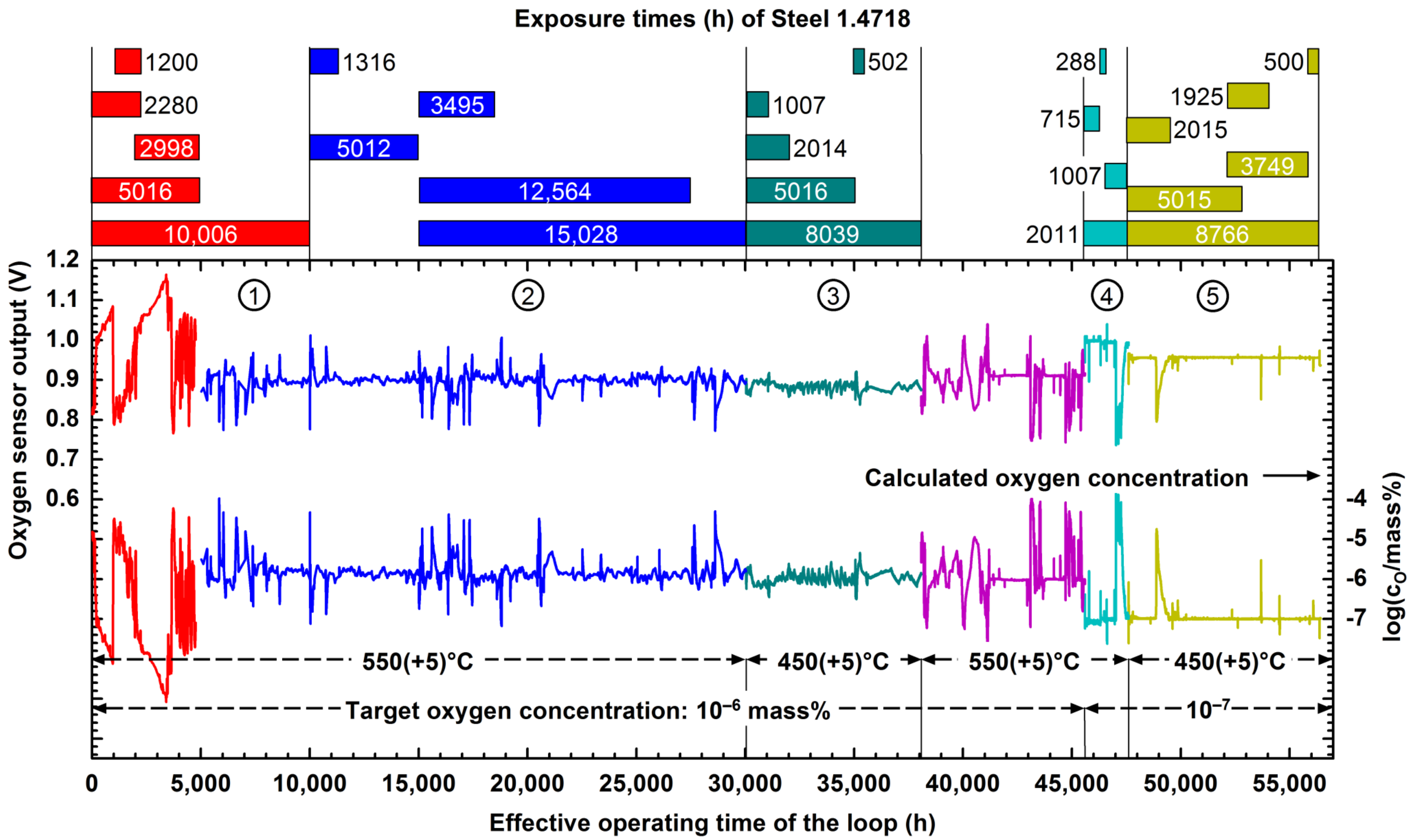


- Transformation of a difference in the chemical potential of oxygen into a difference in the electrochemical potential of electrons
- Transmission to a voltmeter and indication as electric voltage
- Calculation of the unknown oxygen potential from the known potential at the reference electrode: $log(CO_{Pb-Bi}) = -3.2837 + \frac{6949.8}{T} - 10080\frac{E}{T}$
- Conversion to partial pressure, concentration of dissolved oxygen, etc.

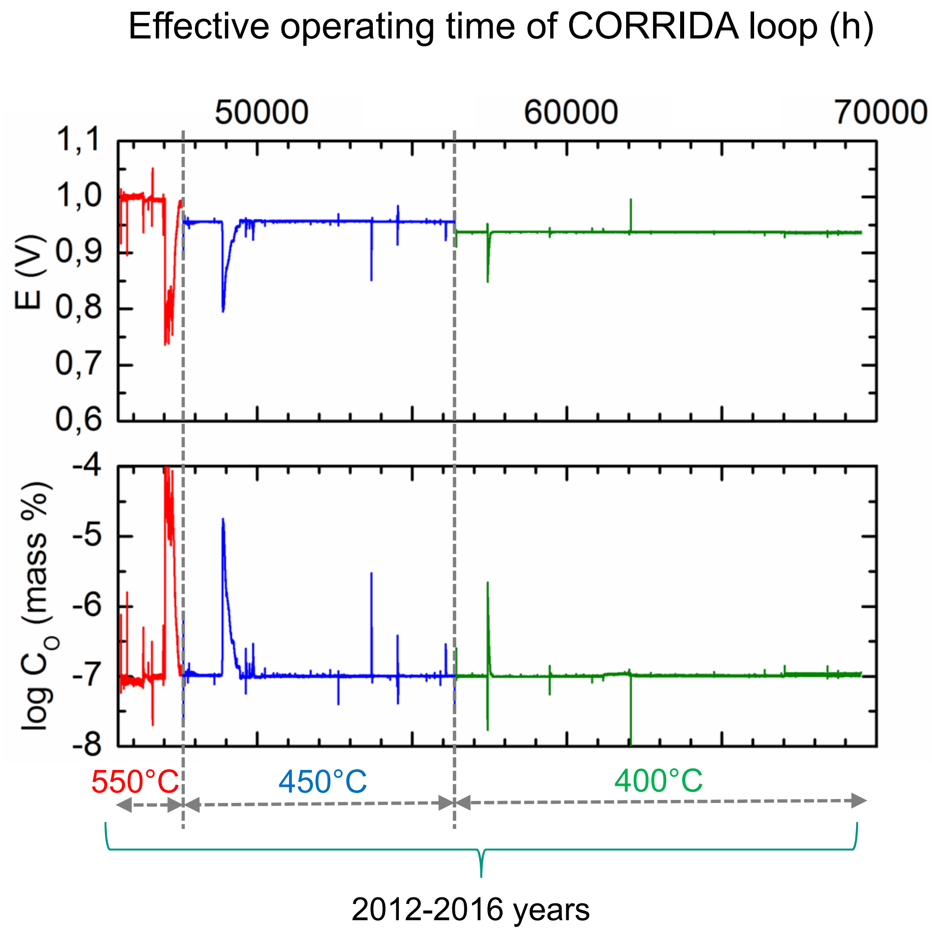
- Ar-carrier gas with automated air addition
- Optional humidification of the gas
- Ar-H_2 for removal oxygen from the liquid Pb-Bi

Measured oxygen potential/concentration as a function of operating time

Karlsruhe Institute of Technology



Conditions of corrosion tests performed for period from 2012 to 2016 years



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

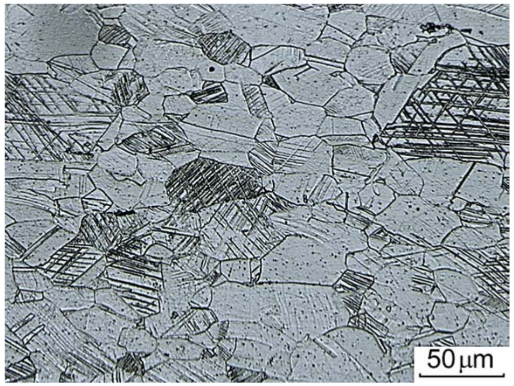
- **T = 400°C**

  t = 1007; 2015; 4746; 13194 h

Austenitic steels tested in the CORRIDA loop

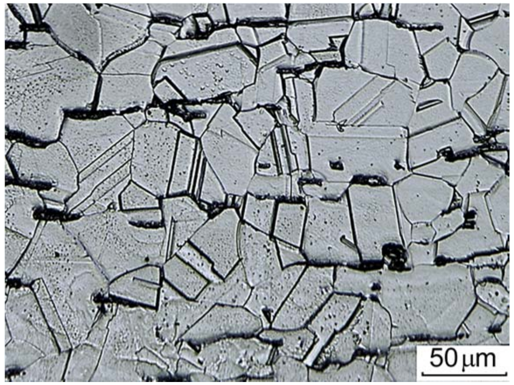
(Fe – Bal.)	Cr	Ni	Mo	Mn	Si	Cu	V	W	Al	Ti	C	N	P	S	B
316L	16.73	9.97	2.05	1.81	0.67	0.23	0.07	0.02	0.018	-	0.019	0.029	0.032	0.0035	-
1.4970	15.95	15.4	1.2	1.49	0.52	0.026	0.036	< 0.005	0.023	0.44	0.1	0.009	< 0.01	0.0036	< 0.01
1.4571	17.50	12	2.0	2.0	1.0	-	-	-	-	0.70	0.08	-	0.045	0.015	-

1.4970 (15-15Ti)



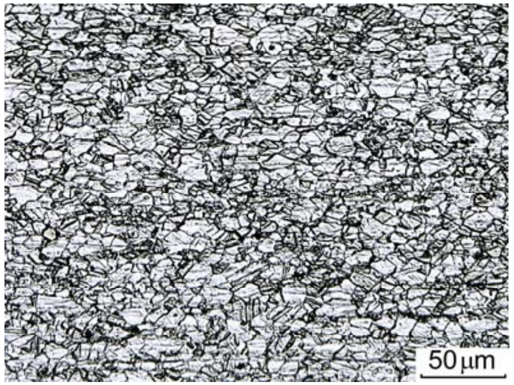
- HV_{30} = 253;
- Grain size ranged from 20 to 65 μm;
- Intersecting deformation twins.

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

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

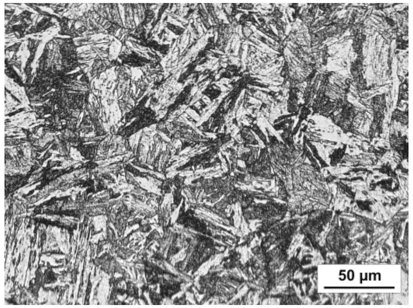
*nominal composition

Nominally 9 mass% Cr

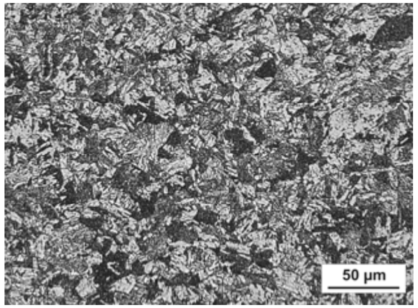
Element besides Cr that improves oxidation resistance

Martensitic microstructure of F/M steels

E911, T91-A, T91-B, P92



Grain size



EUROFER

Corrosion response of austenitic steels

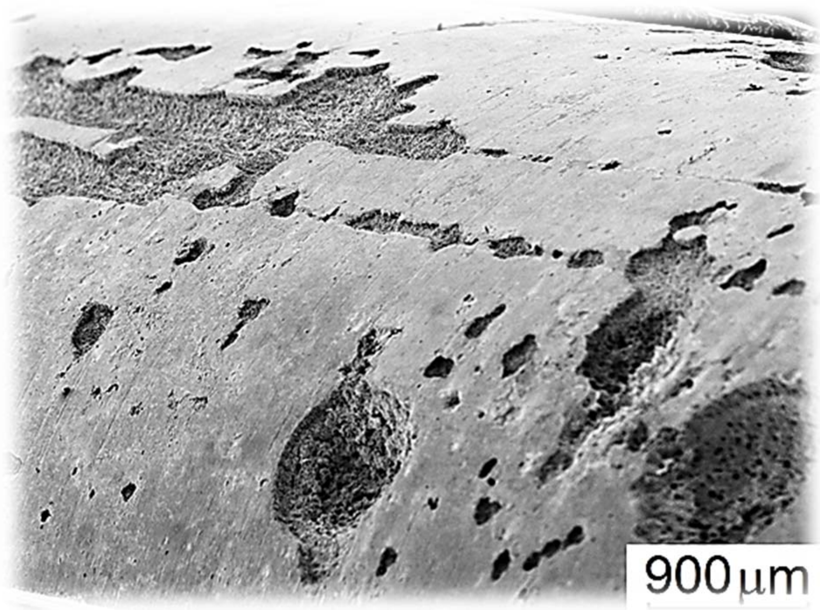
Flowing Pb-Bi (2 m/s), 10^{-7} mass% O, 400-550°C

Karlsruhe Institute of Technology

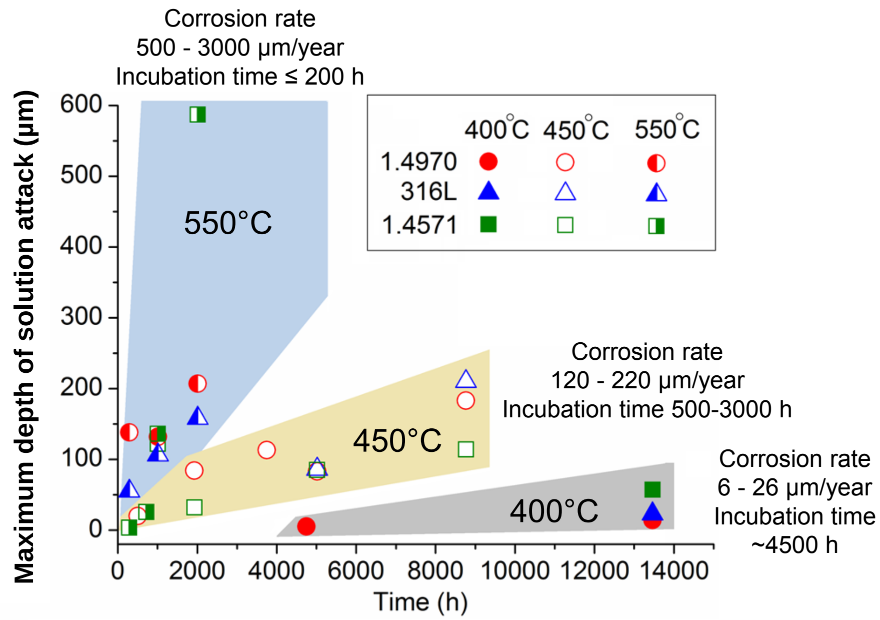
0 h 2000 h

➔ Oxidation + Local pit-type solution-based attack

Local solution-based corrosion attack



Time-temperature dependence of local attack

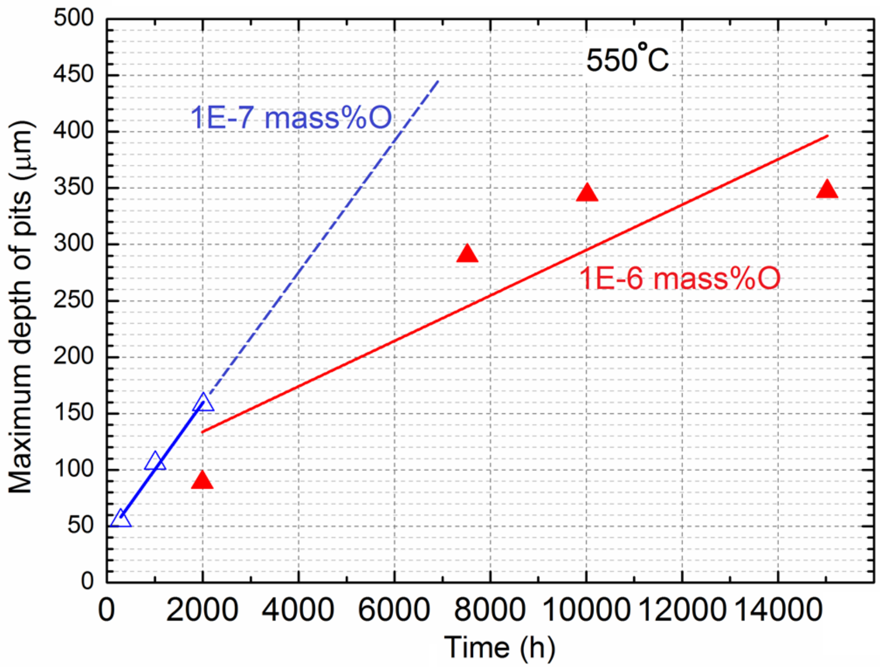


- 10% of wall thinning for cladding tube - corrosion criterion suggested for “steel / sodium” system;
- Corrosion limit for 450 µm thick cladding tube made of 1.4970 steel is 45 µm;
- 550 and 450°C could not be a working temperatures in Pb-Bi with 10^{-7} mass% O;
- At 400°C, corrosion limit for 1.4970 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.

Local corrosion depending on oxygen concentration in the Pb-Bi eutectic

Karlsruhe Institute of Technology

Austenitic steel 316L

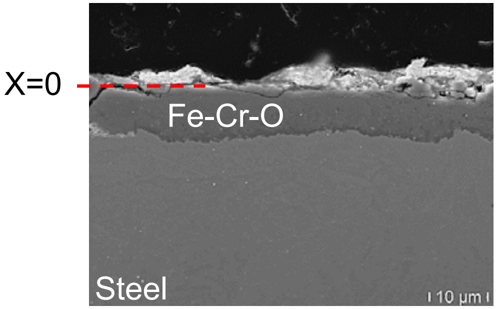


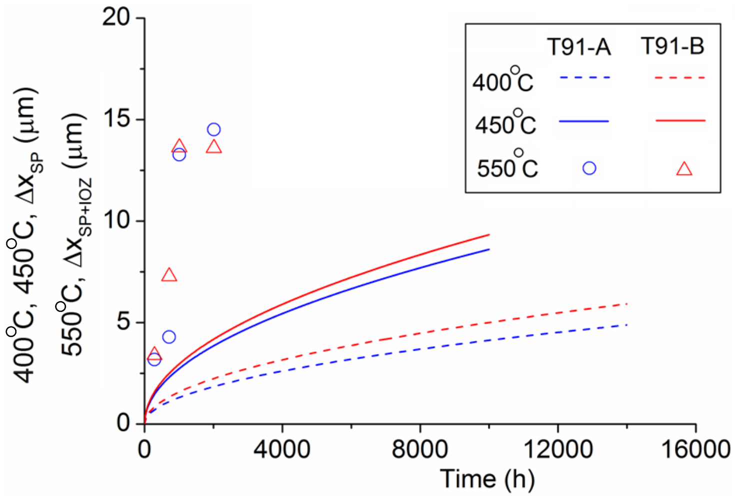
- Local corrosion rate (linear law) increases with decreasing oxygen concentration at constant T = 550°C:
  - 270 µm/year for 10^{-6} mass%O
  - 560 µm/year for 10^{-7} mass%O
- Incubation time for initiation of dissolution attack decreases with decreasing oxygen concentration in Pb-Bi eutectic:
  - ≤ 300 h for 10^{-7} mass%O
  - ≤ 2000h for 10^{-6} mass%O

Corrosion loss on 9%Cr F/M steels in

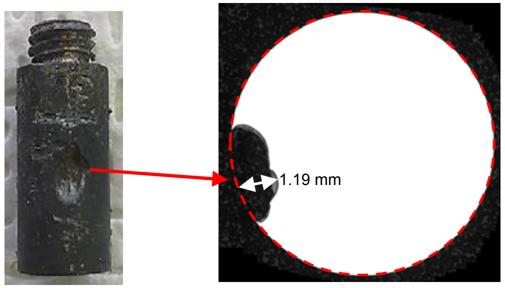
Flowing Pb-Bi (2 m/s), 10^{-7} mass% O, 400-550°C

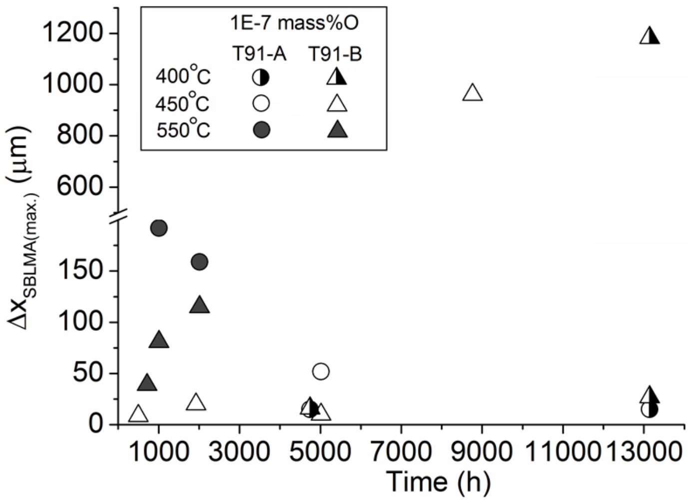
General corrosion trend: oxidation





Local corrosion trend: solution-based leaching of steel constituents (Fe, Cr)

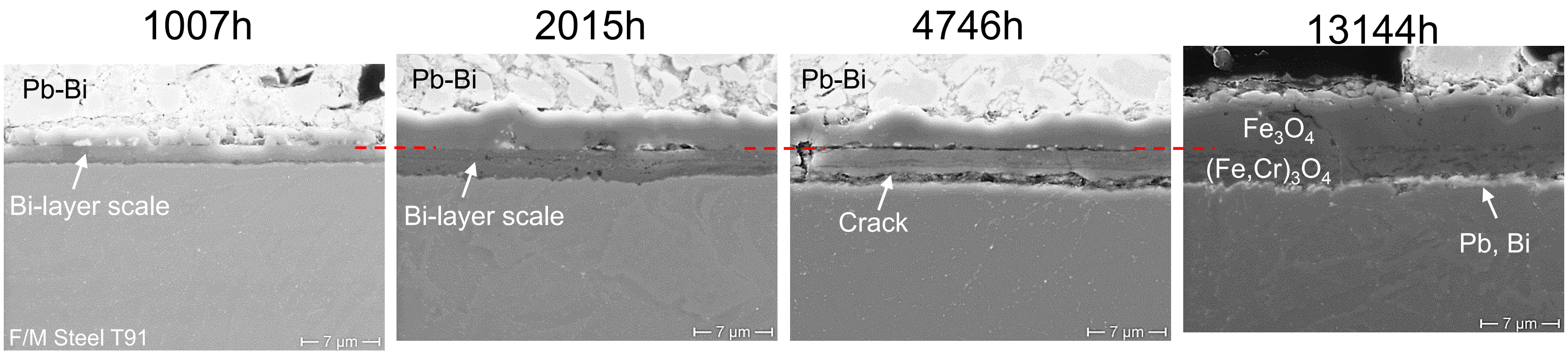




- ❑ In comparison to 450 or 550°C the impact of oxidation is significantly reduced at 400 °C;
- ❑ Severe local dissolution attack, as a result of scale failure, occurs.

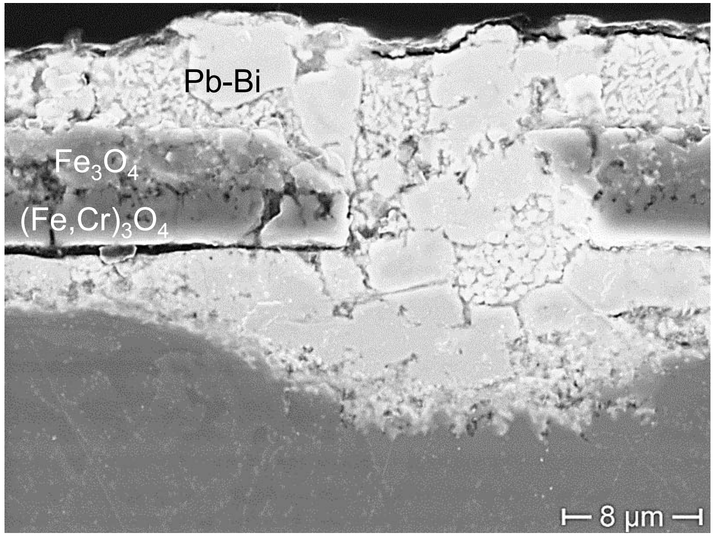
Example of oxide scale evolution with time

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



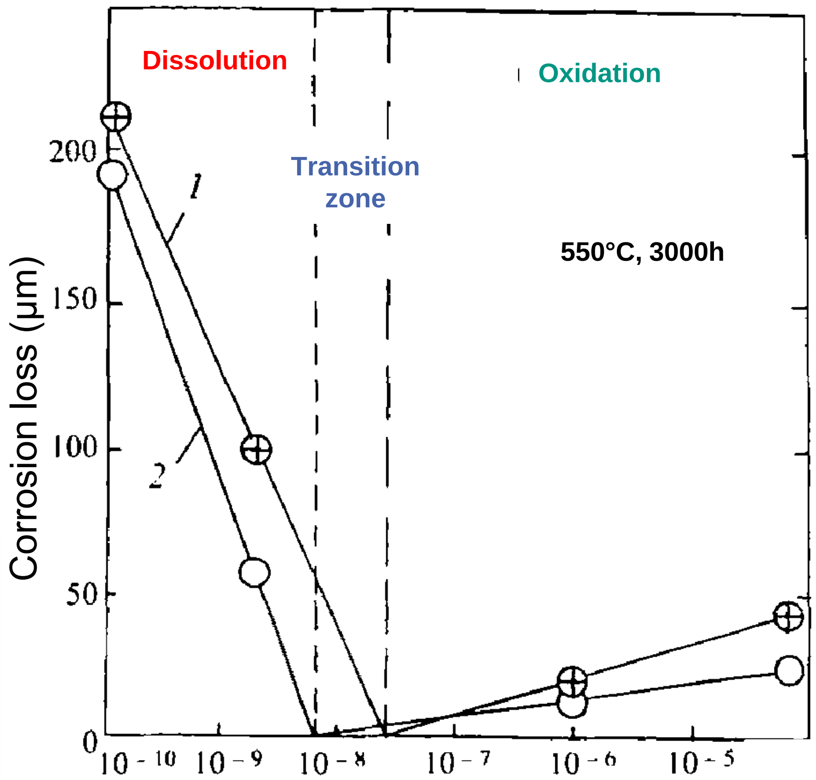
- General corrosion trend is oxidation
- Degradation of scale with time results in initiation of dissolution attack
- **Re-healing of scale does not take place !**

 European Commission funded International Workshop "Materials resistant to extreme conditions for future energy systems“, 12-14 June 2017, Kyiv - Ukraine

Comparison of earlier findings and today's vision !

Earlier findings !

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

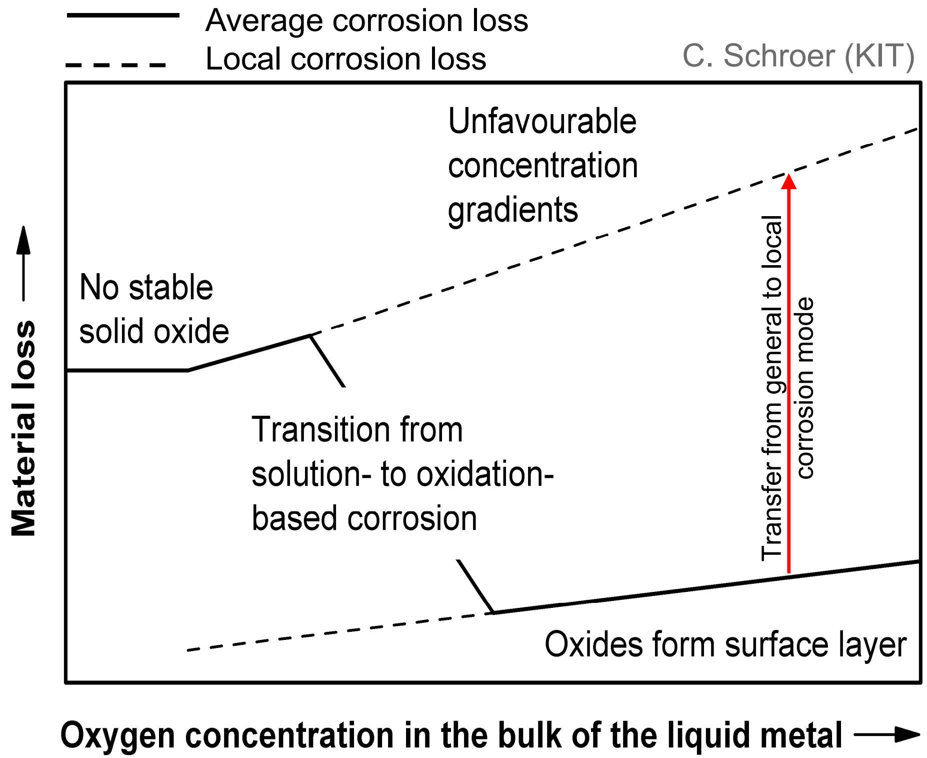


Oxygen concentration in Pb (mass %)

1 and 2 – austenitic steels of 316L type

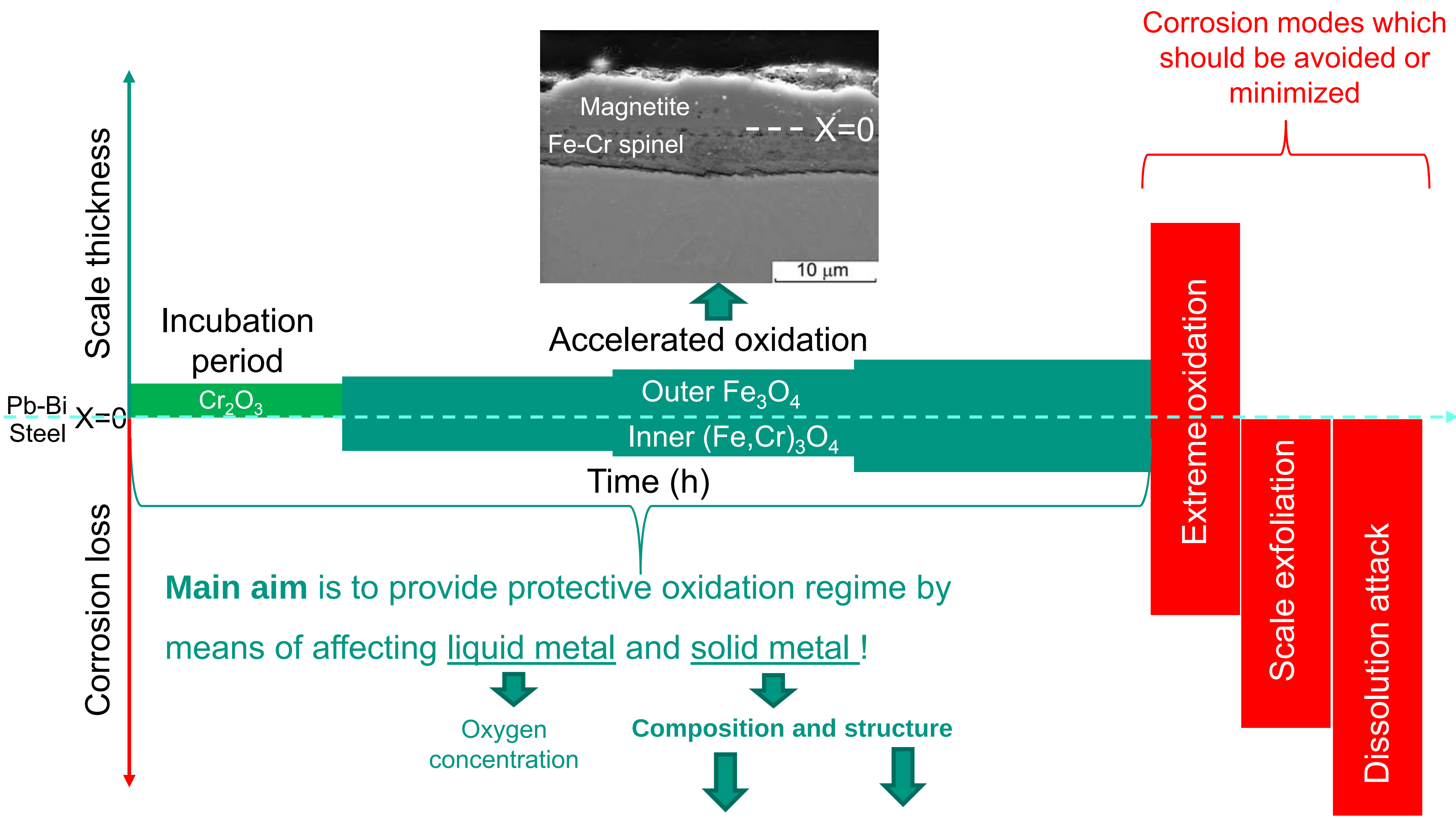
- In general correct
- In particular - too idealistic !

Today`s vision !



- 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 !!!

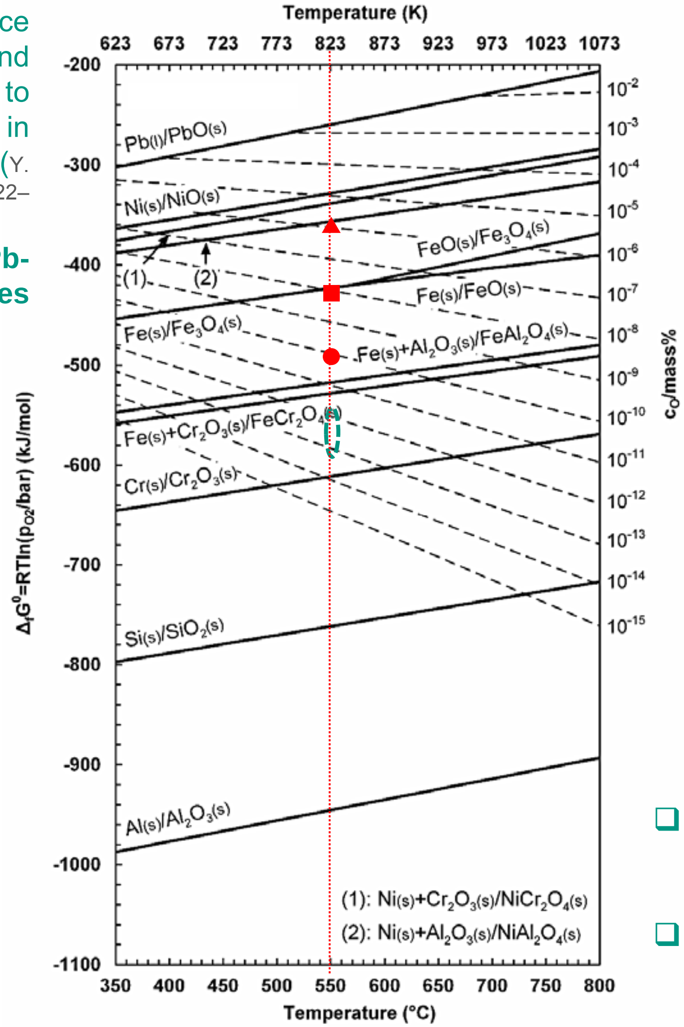
Developing of the scale on the surface of steels contacting Pb and Pb-Bi



ALUMINUM-ALLOYED AUSTENITIC STEELS

- Improvement of oxidation resistance by means of formation of protective oxide films on the base of elements with higher affinity to oxygen (Al, Cr, Si) than Fe – one of the ways towards development of liquid-metal technologies;
- 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**.

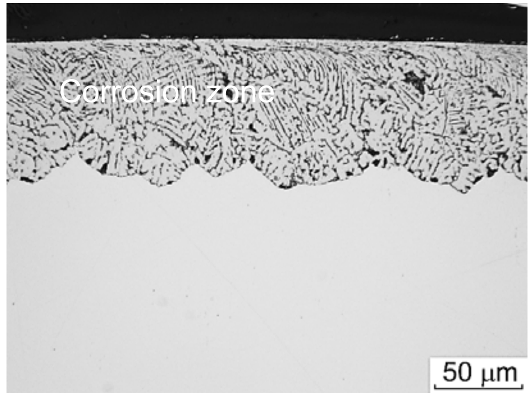
Element	Fe-18Ni-12Cr-Al-Nb-C ICP-OES
C	0.0086
Al	**2.32**
Si	0.401
Ti	0.0568
V	0.0048
Cr	**11.7**
Mn	0.0887
Fe	64.4
Ni	**18.0**
Cu	0.0031
Nb	0.577
Mo	1.99
W	0.0031



Test conditions

Tests in progress

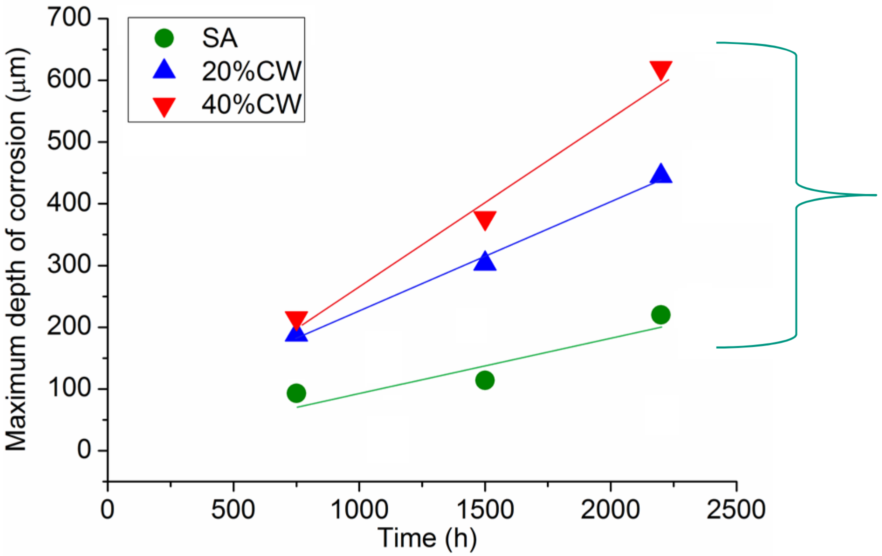
Corrosion response of Fe-18Ni-12Cr-Al-Nb-C steel to oxygen-pure Pb-Bi



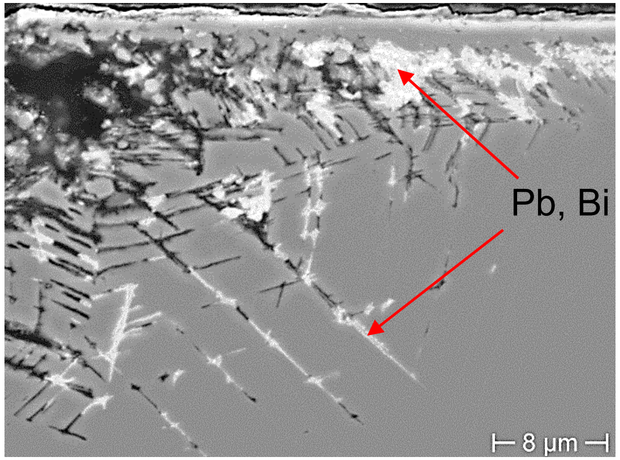
- Protective Al_2O_3 layer is not formed *in-situ* on AFA steel in Pb-Bi eutectic with 10^{-12} mass%O;
- Spongy ferrite corrosion layer penetrated by Pb and Bi is observed.

Correlation between initial structure and solution-based corrosion attack

Maximum depth of corrosion attack



Corrosion appearance



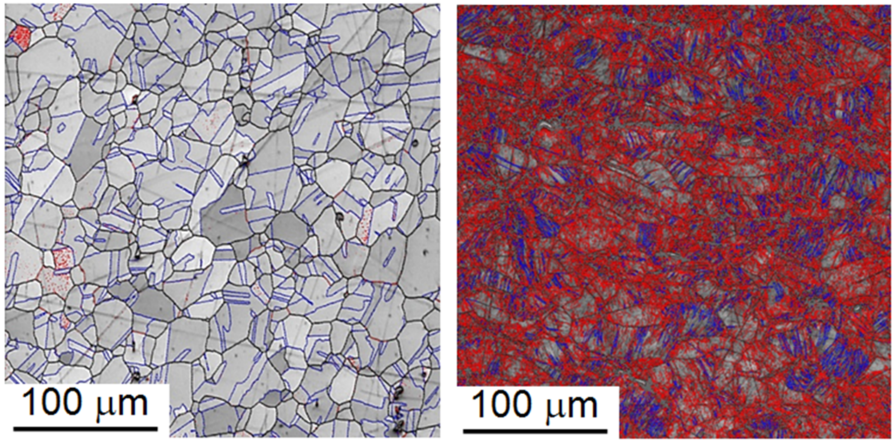
- Corrosion rate via dissolution increases with increasing of cold-work level in steel
- Pre-existing active diffusion paths (grain or sub-grain boundaries and deformation slips and twins etc.) are preferential pathways for solution-based attack via selective leaching of Ni and Cr and subsequent penetration of Pb and Bi into steel matrix

Effect of structural state of steels on the corrosion response to liquid metals

Scanning **E**lectron **M**icroscopy based **E**lectron **B**ack **S**catter **D**iffraction (**SEM-EBSD**) / **O**rientation-**I**maging **M**icroscopy (**OIM**).

Grain-boundary character distribution in 1.4970 steel (Fe-15Ni-15Cr)

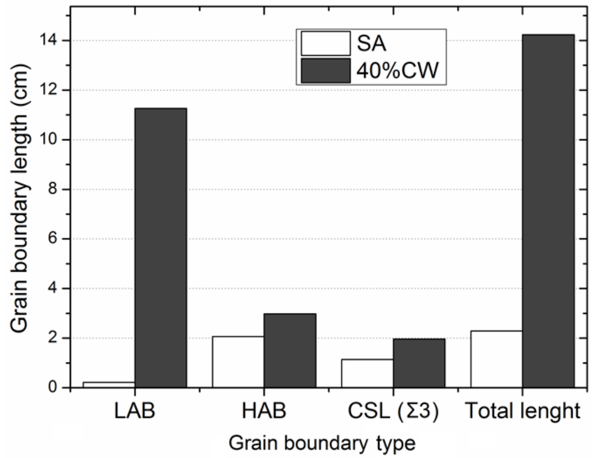
Solution annealed | After 40% cold work

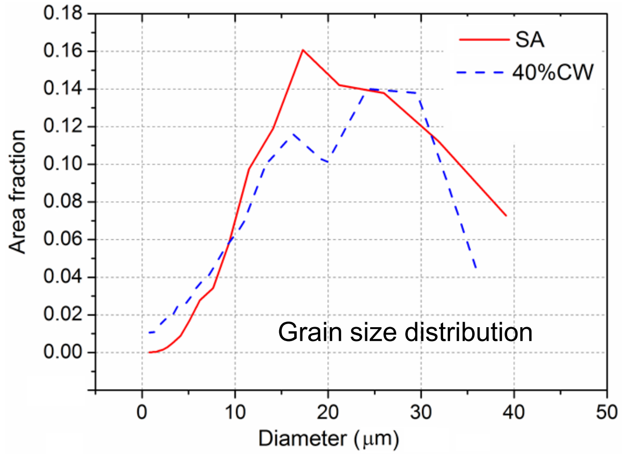


(a) (b)

- ❑ Black lines - High-Angle Boundaries (HAB ≤ 15°);
- ❑ Red lines - Low-Angle Boundaries (LAB ≤ 15°);
- ❑ Blue lines - Special Coincidence Site Lattice Boundaries (Σ3).

Length of boundaries



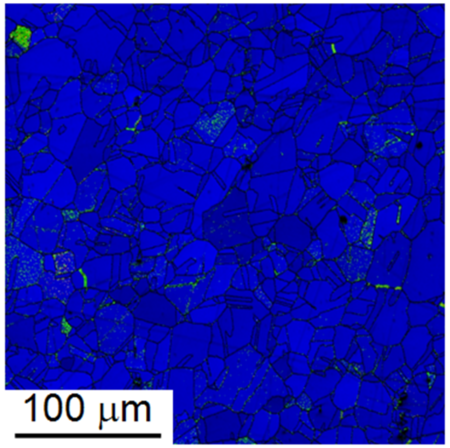


European Commission funded International Workshop "Materials resistant to extreme conditions for future energy systems“, 12-14 June 2017, Kyiv - Ukraine

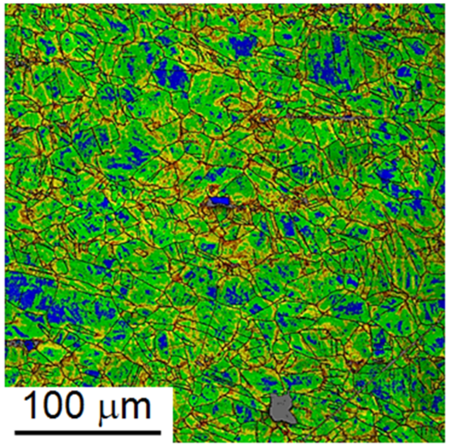
Accumulation of stresses in steel depending on the level of cold-work

Karlsruhe Institute of Technology

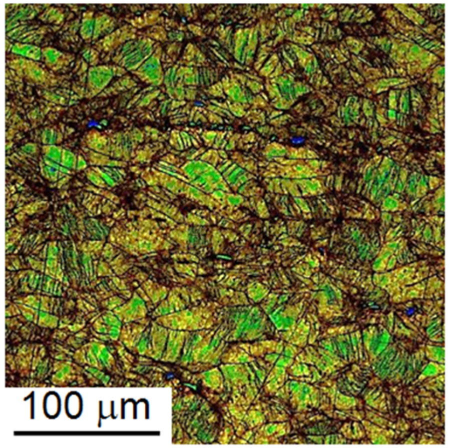
SA



20% CW



40% CW



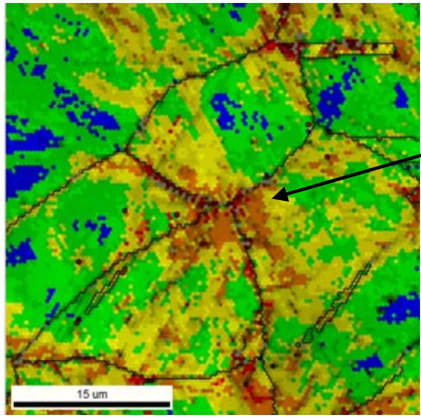
stress

	Min	Max	Total Fraction	Partition Fraction
blue	0	1	0.969	0.970
green	1	2	0.027	0.027
yellow	2	3	0.002	0.002
orange	3	4	0.001	0.001
red	4	5	0.001	0.001

	Min	Max	Total Fraction	Partition Fraction
blue	0	1	0.093	0.095
green	1	2	0.525	0.533
yellow	2	3	0.284	0.288
orange	3	4	0.071	0.072
red	4	5	0.013	0.013

	Min	Max	Total Fraction	Partition Fraction
blue	0	1	0.003	0.004
green	1	2	0.115	0.130
yellow	2	3	0.377	0.427
orange	3	4	0.296	0.335
red	4	5	0.092	0.104

- ❑ Fraction of structure in stressed state increases with increasing level of deformation.



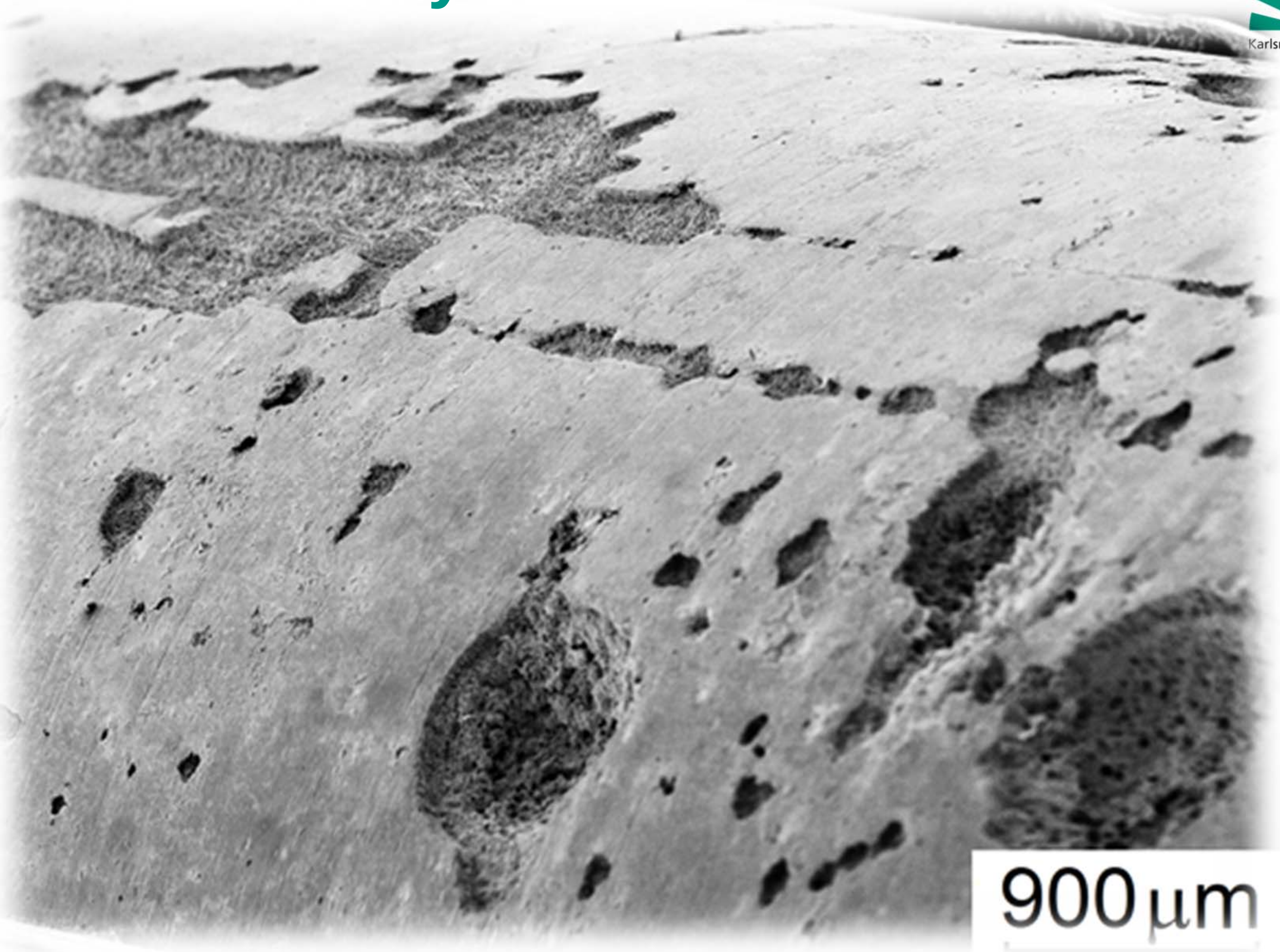
- ❑ Stresses accumulates near structural boundaries.

- ❑ The larger fraction of stressed structural boundaries in steel the higher corrosion rate via dissolution

SUMMARY

- ❑ Corrosion phenomena in steel / liquid Pb-Bi are understandable in general
- ❑ Application of oxygen-control system, allowing precise control of oxygen activity in Pb melts, is aimed to form protective oxide scale on the steel surface and mitigate corrosion via dissolution of steel constituents
- ❑ Reliable experimental data on corrosion of candidate steels are still scarce:
  - Oxidation of candidate steels depending on the oxygen concentration and temperature;
  - Dissolution of candidate steels depending on the oxygen concentration and temperature;
- ❑ Large number of required experimental data on corrosion stimulates collaboration among scientific groups around the world !

Thank you for attention !!!



Example of severe corrosion attack on austenitic steel in Pb-Bi

Victory would go to those who could best operate at higher temperatures !