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Effect of structural state of austenitic steel 15-15 Ti on initiation and propagation of solution-based corrosion attack in flowing liquid Pb-Bi eutectic at 400 and 500 °C

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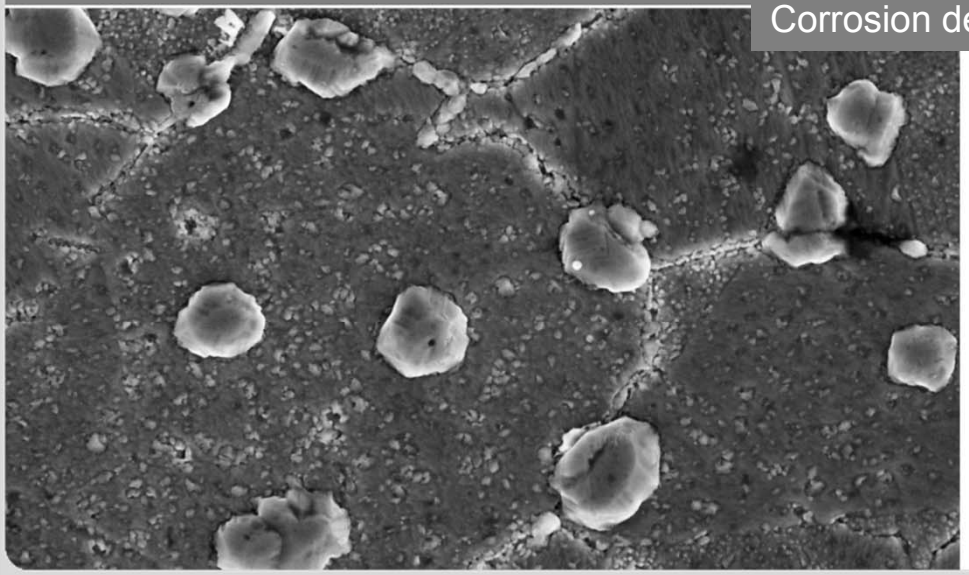
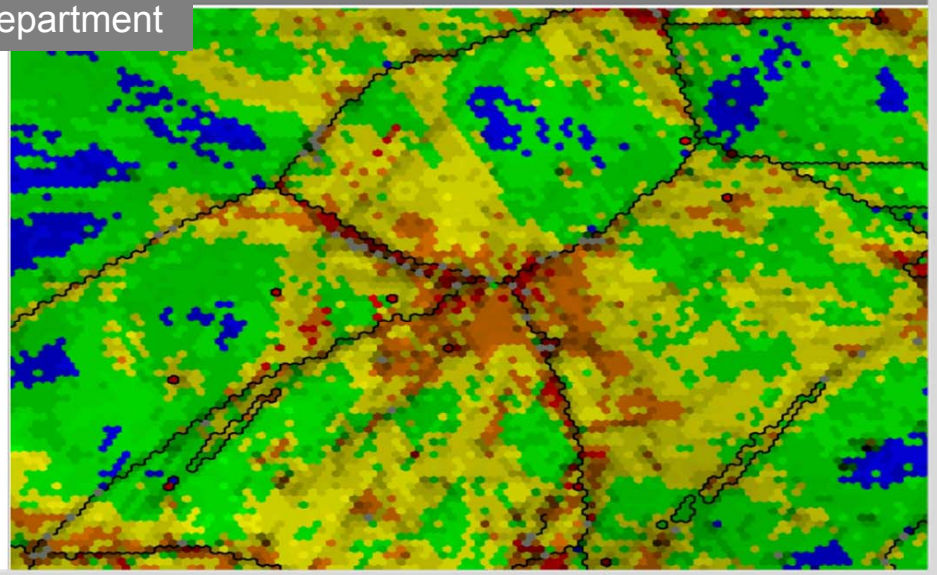
Corrosion department





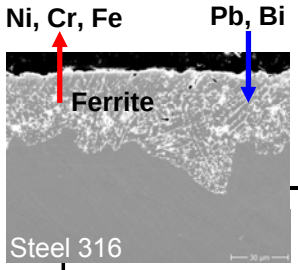
Corrosion modes of steels in Pb and Pb-Bi melts

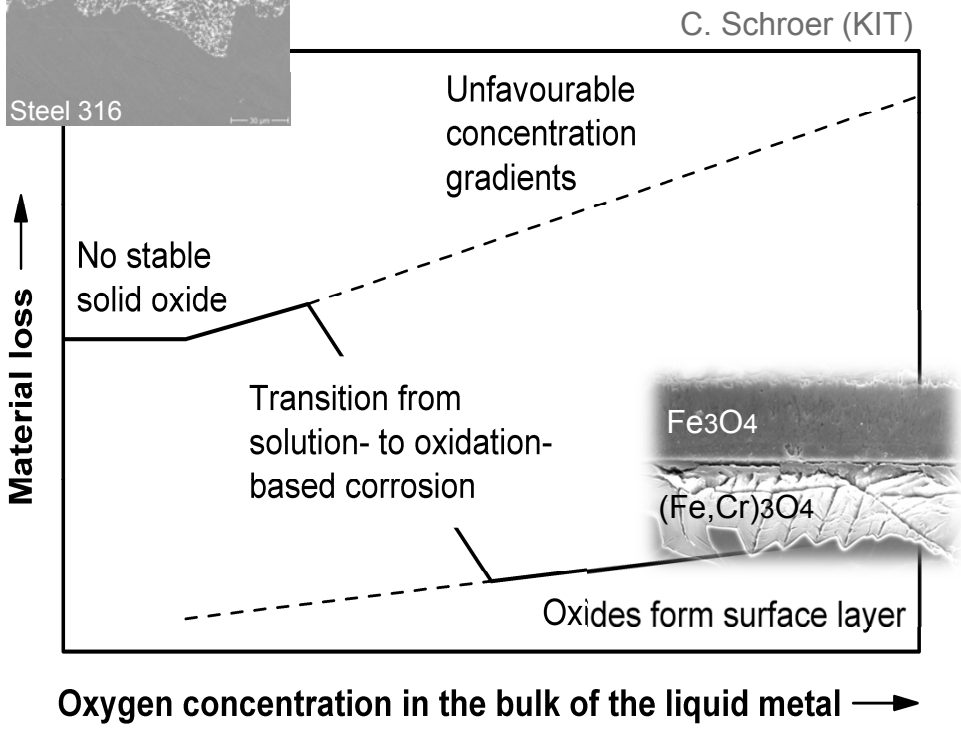
Issue !

- **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 corrosion zone

Solution !?

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



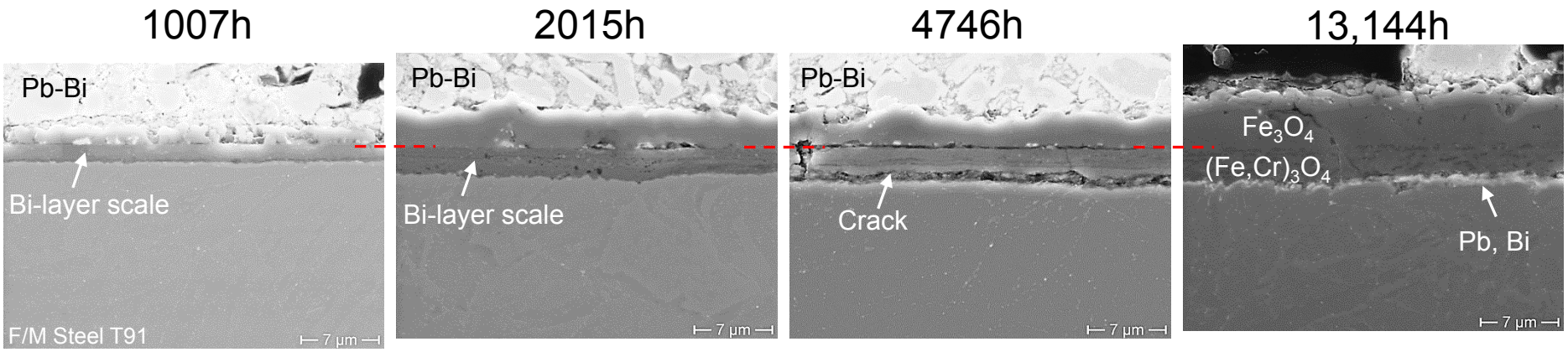


Main aim is to provide protective oxidation regime by means of affecting liquid metal and solid metal !

- **Control of oxygen concentration in liquid metal**
- **Composition and structure**

Example of scale evolution on steel surface with time

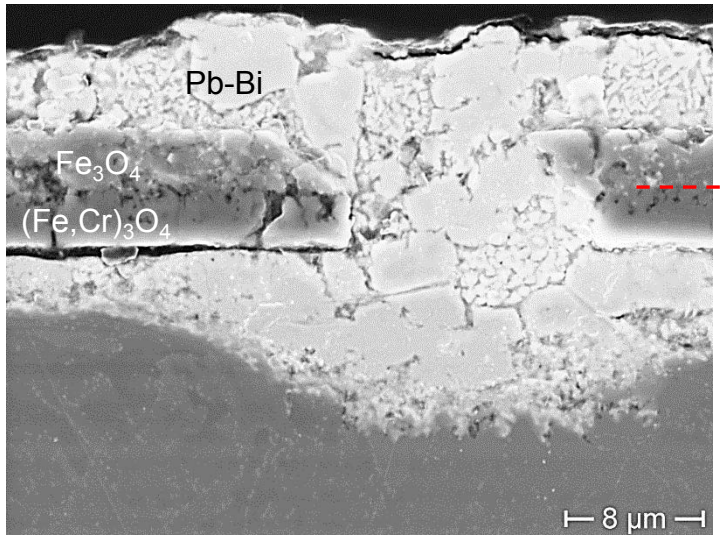
Flowing Pb-Bi (2 m/s), 10^{-7} mass%O, 400°C



Initial steel / liquid Pb-Bi interface

- Bi-layer scale grows on steel surface with time
- Local failure of scale with time results in initiation of dissolution attack
- **Re-healing of scale does not take place !**
- Composition and microstructure of steel become dominant factors for further propagation of solution-based attack into bulk of material.

Dissolution attack as a result of local scale failure

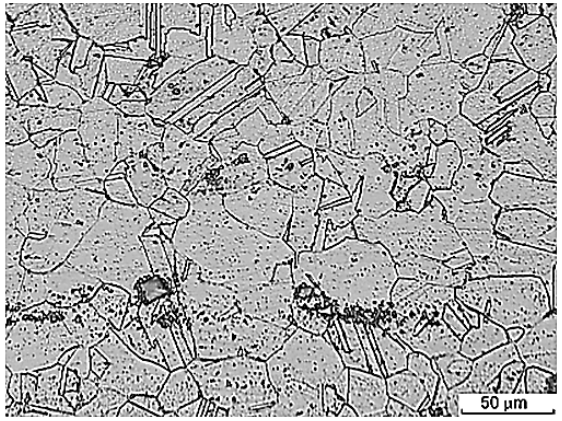


Test material - austenitic steel 1.4970 (15-15Ti)

(Fe – Bal.)	Cr	Ni	Mo	Mn	Si	Cu	V	W	Al	Ti	C	N	P	S	B
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

Structural state of steel:

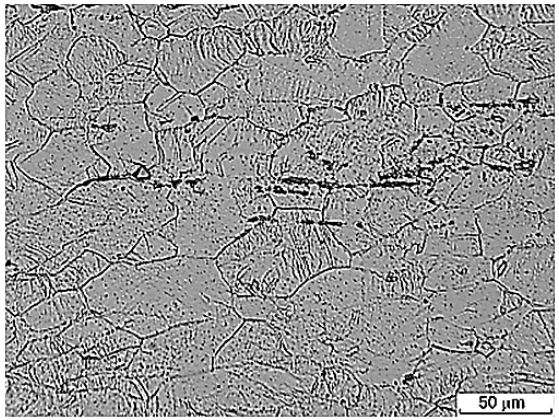
- Solution annealed (1100°C, 30 min)



- HV_{30} = 130
- Annealing twins

- HV_{30} = 300
- Deformation twins and slips

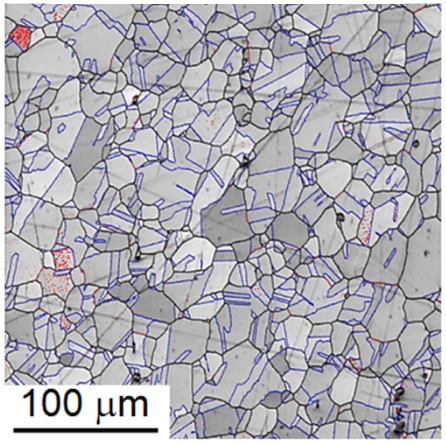
- 40% cold-work



Scanning Electron Microscopy based Electron Back Scatter Diffraction (SEM-EBSD) / Orientation-Imaging Microscopy (OIM).

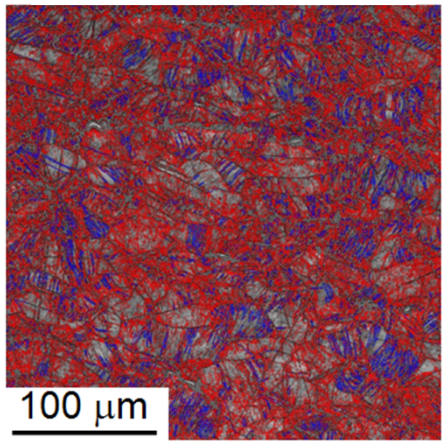
Grain-boundary character distribution in 1.4970 steel (Fe-15Ni-15Cr)

Solution annealed



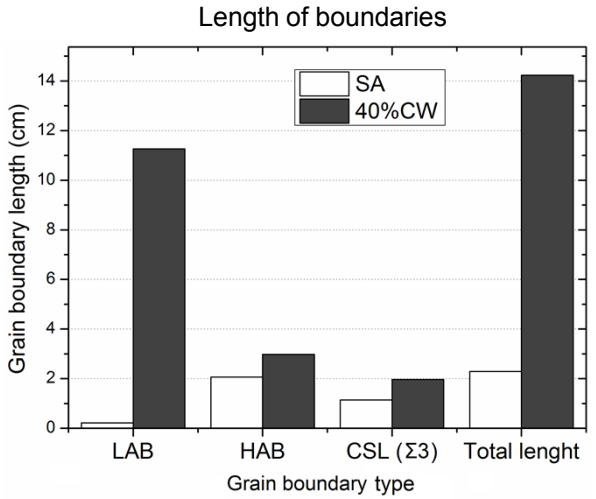
(a)

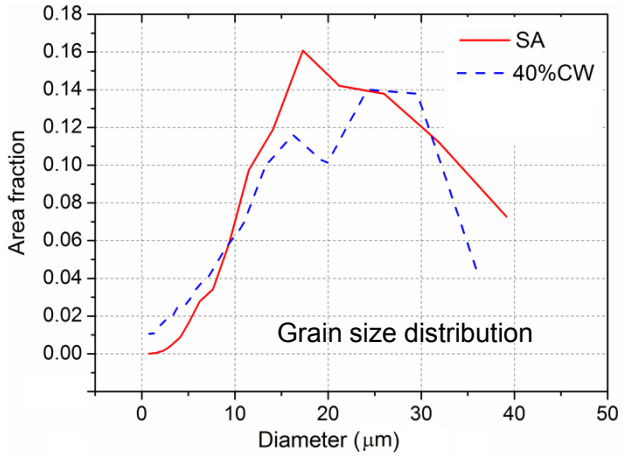
After 40% cold work



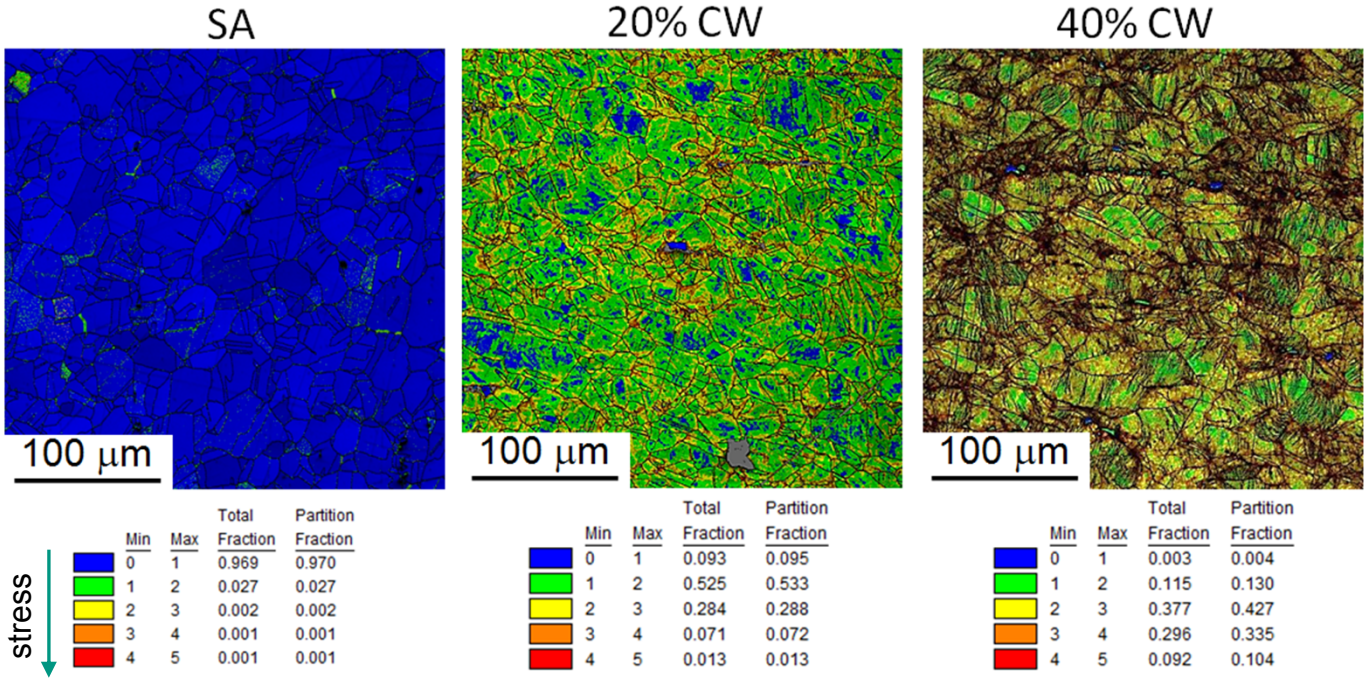
(b)

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

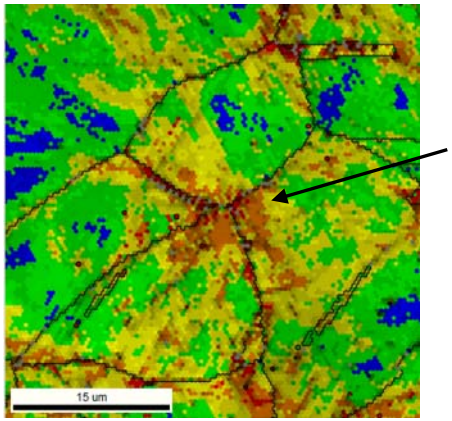




Accumulation of stresses in steel depending on the level of cold-work

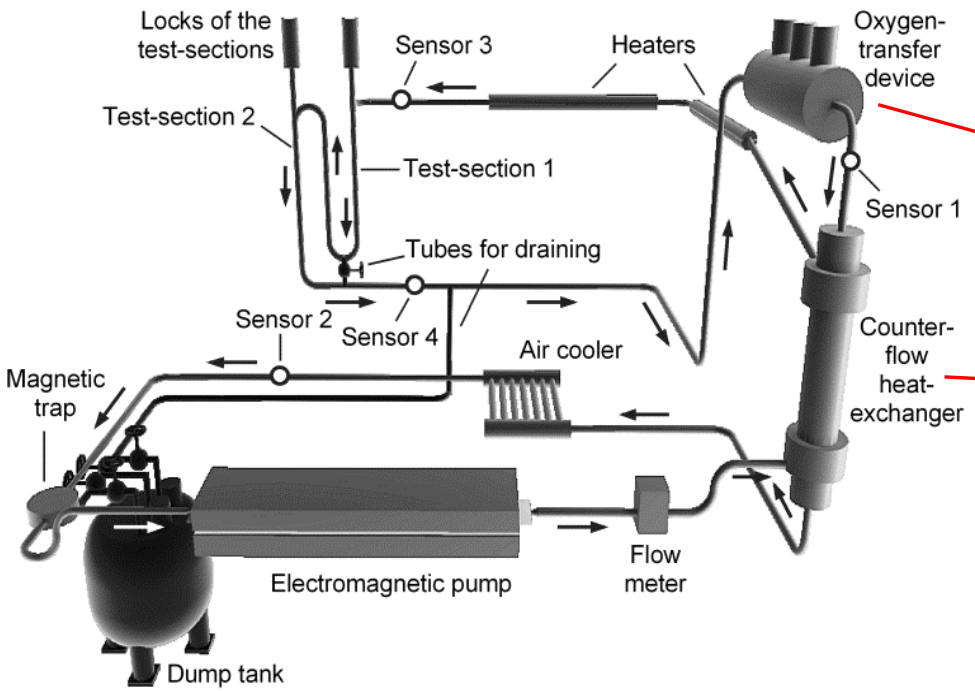


- Fraction of structure in stressed state increases with increasing level of deformation.

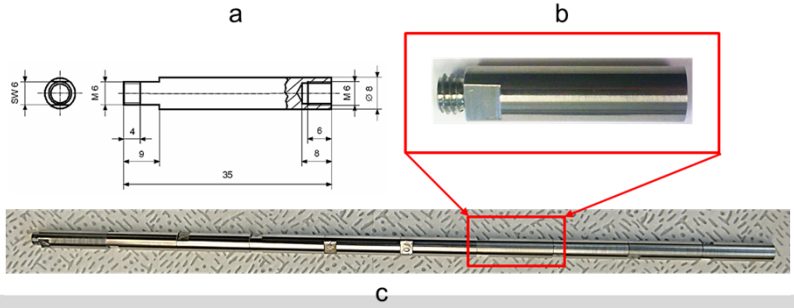


- Stresses accumulates near structural boundaries.

CORRosion **I**n **D**ynamic lead **A**lloys
CORRIDA Pb-Bi eutectic liquid-metal loop

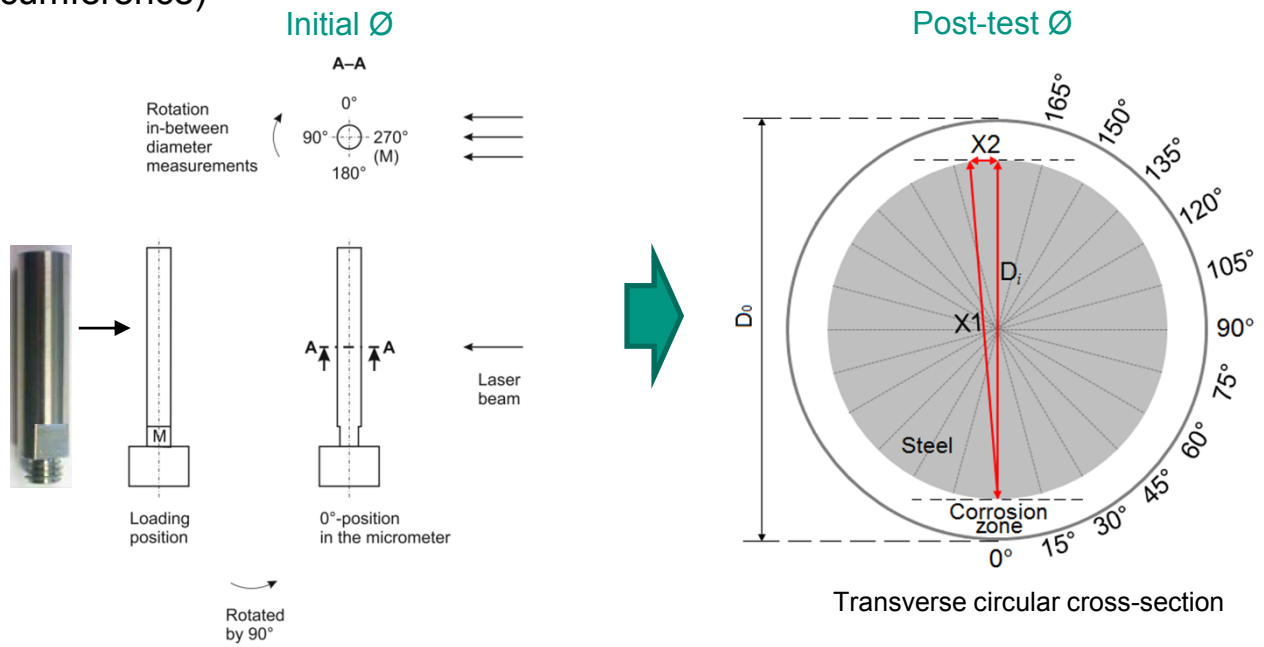


The CORRIDA facility – a forced-convection loop made of austenitic stainless steel (1.4571) designed to expose material (steel) specimens to flowing (2 m/s) Pb-Bi eutectic (~1000 kg) with controlled oxygen concentration.



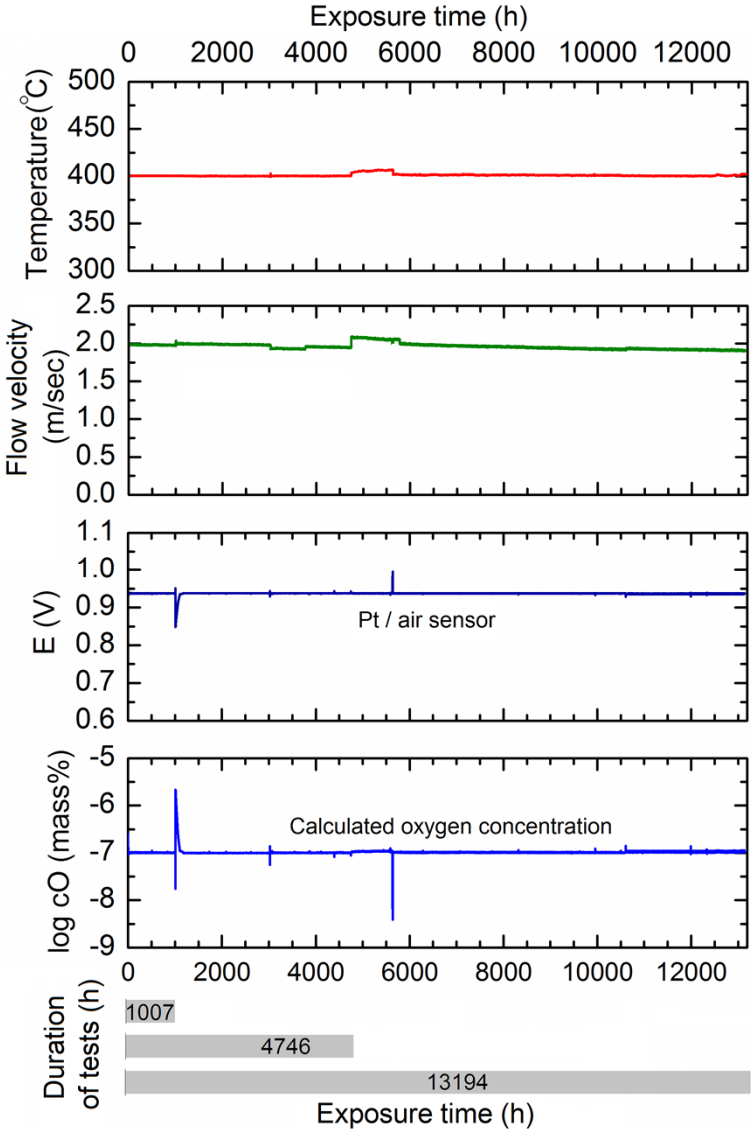
Quantification of corrosion loss

- **Goal of quantification**
  - Material loss: average and maximum of local corrosion
  - Thickness of adherent (oxide) scale
- **Metallographic method for cylindrical specimens**
  - Measurement of initial diameter in a laser micrometer with 0.1 µm resolution
  - Measurement of post-test diameter of unaffected material (12th measurements with rotation angle 15°)
  - Measurement of thickness of corrosion zones in a microscope (LOM) with 1 µm resolution
  - Occurrence of different corrosion modes on opposing sides of the re-measured diameter (% of surface circumference)



Transverse circular cross-section

Conditions of corrosion test at 400 °C



- T = 400°C
- Flow velocity 2 m/s
- Target oxygen concentration 10^{-7} mass%

Evolution of steel surface with time depending on the structural state of steel

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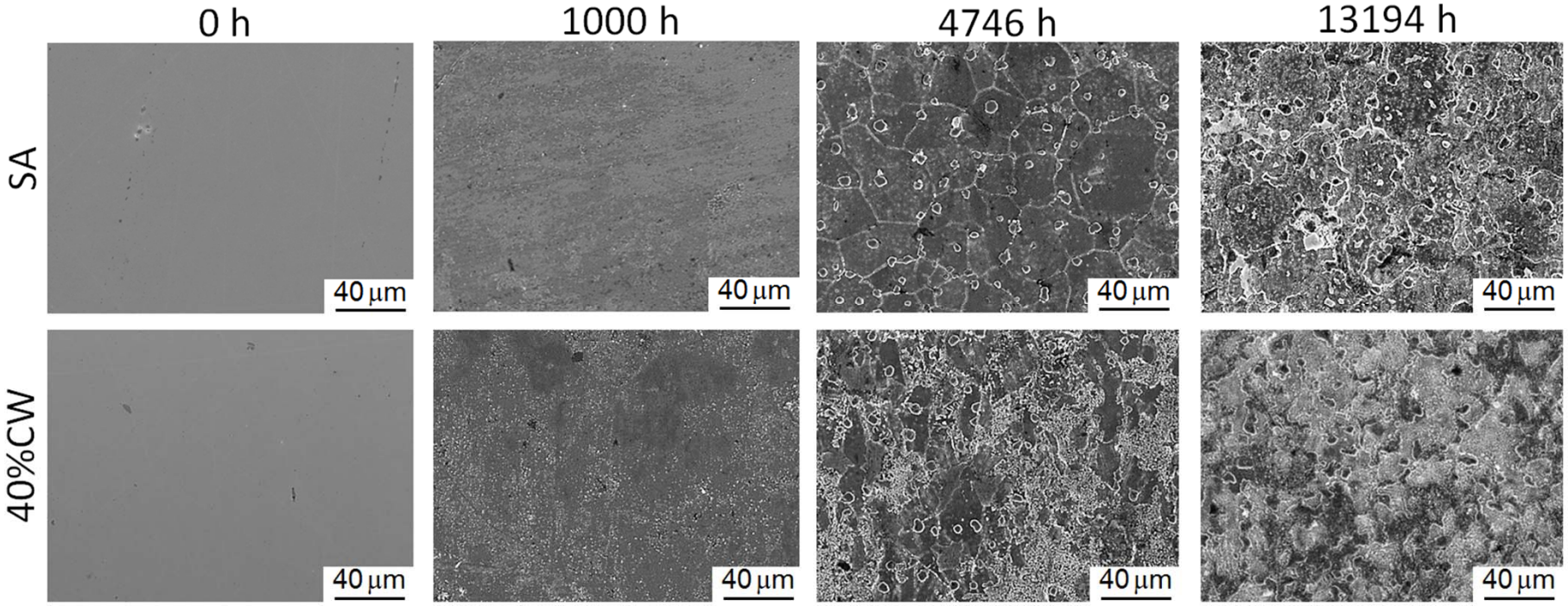
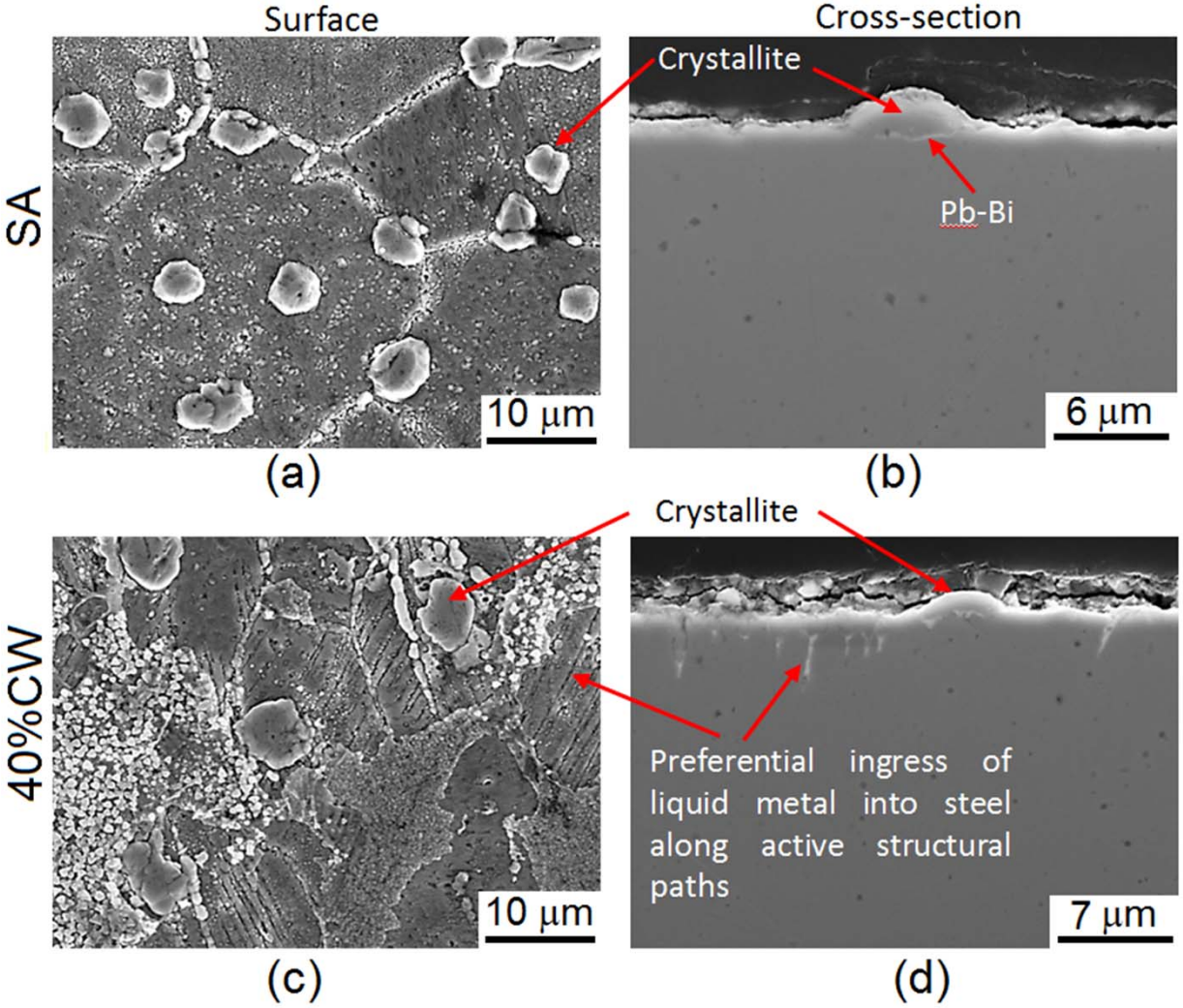
400 °C



- Initial smooth surface, obtained by mirror-polishing, markedly changes with time indicating development of the corrosion process

Detailed analyses of surface and cross section depending on structural state of steel

Samples tested for 4746 h



Solution-annealed state:

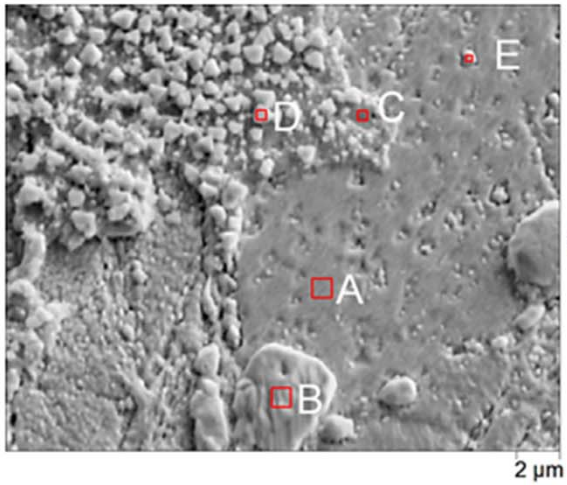
- Developing of grain boundary structure;
- Fe-based crystallites (3-5 µm in diameter) populate boundaries and body of the grains are d by of about;
- Interface between crystallites and matrix is decorated by a of Pb-Bi band.

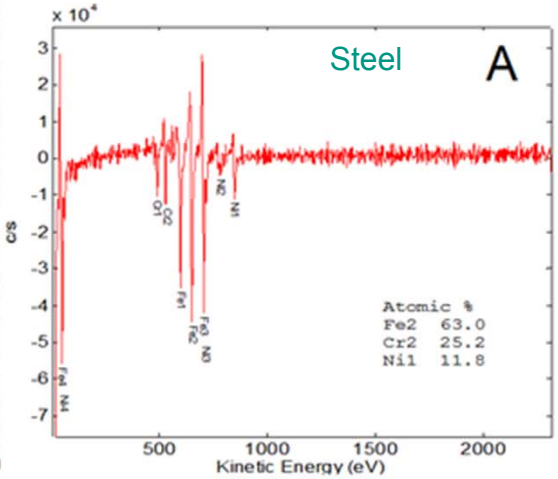
Cold-worked state:

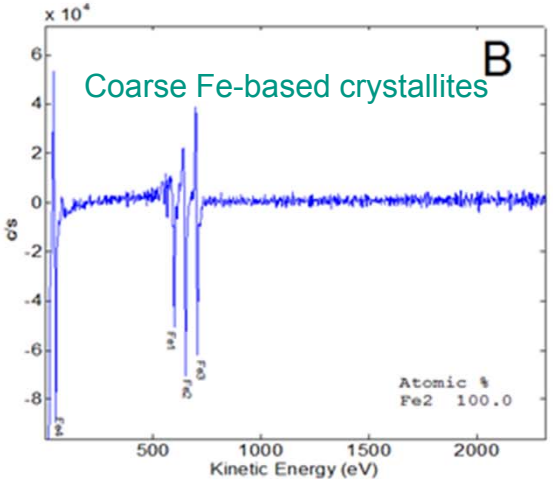
- Developing of grain boundary structure;
- Fe-based crystallites;
- Ingress of liquid metal into steel matrix along active structural paths up to depth of about 7 µm;
- Non-continuous thin film populated by fine crystallites

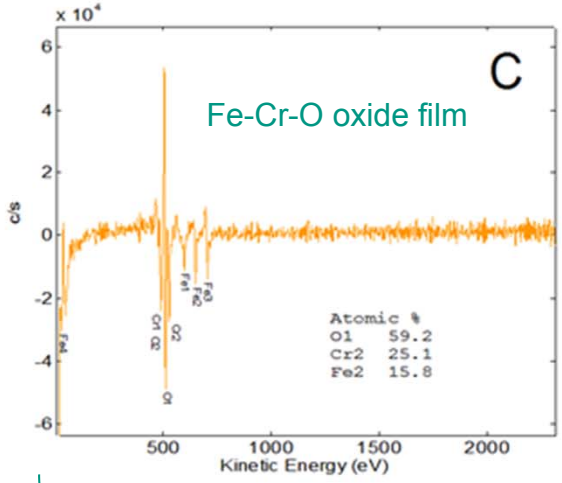
Surface morphology and corresponding Auger spectra

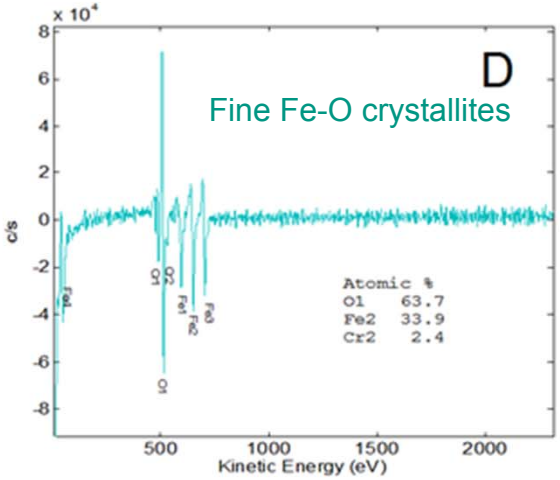
Sample in 40%CW state exposed at 400 °C to flowing Pb-Bi eutectic (~ 2 m/sec) with 10^{-7} mass % dissolved oxygen for 4746 h.

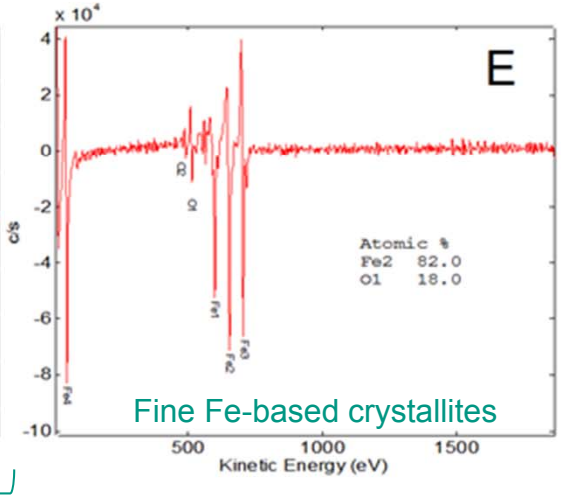






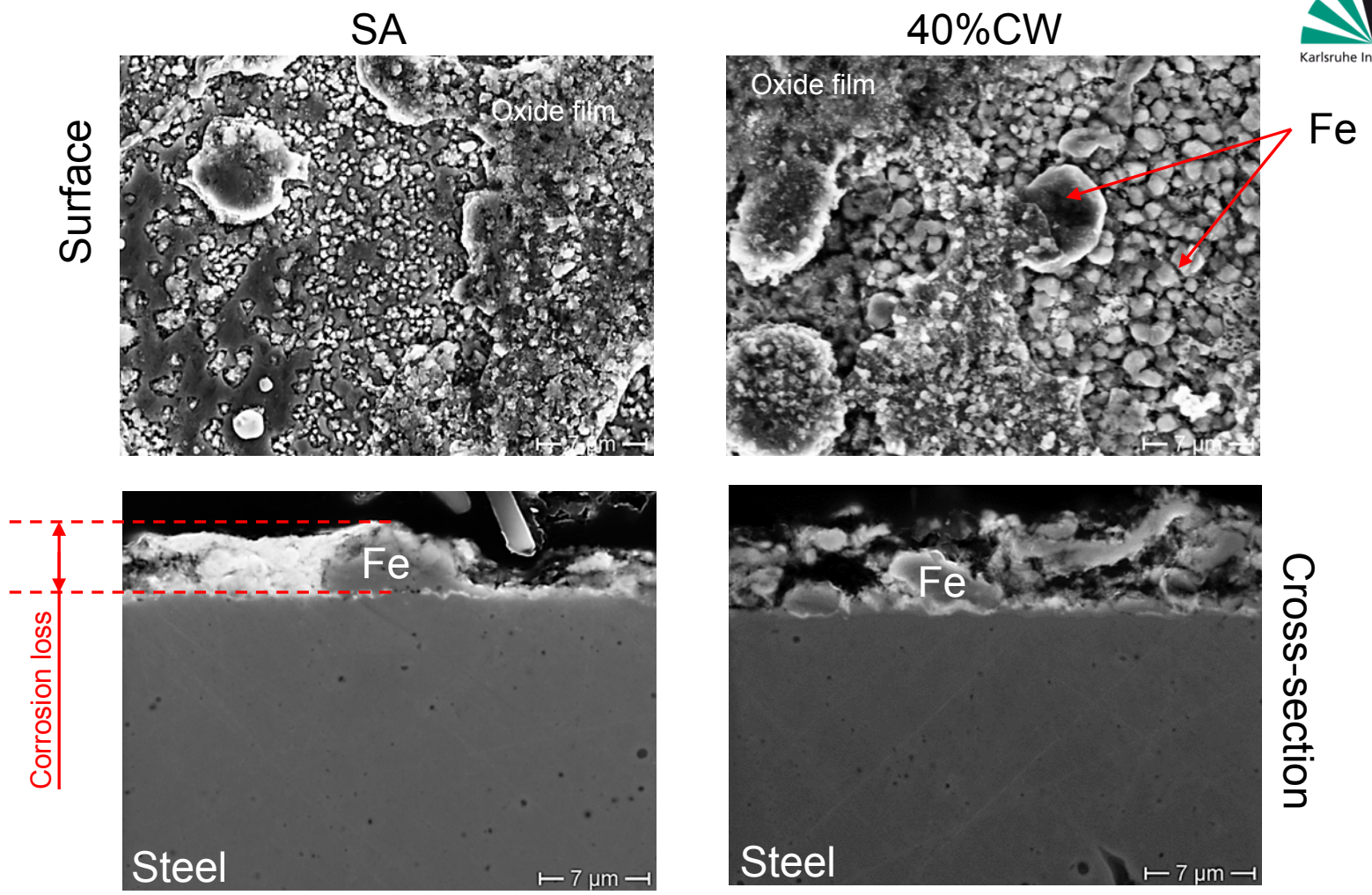






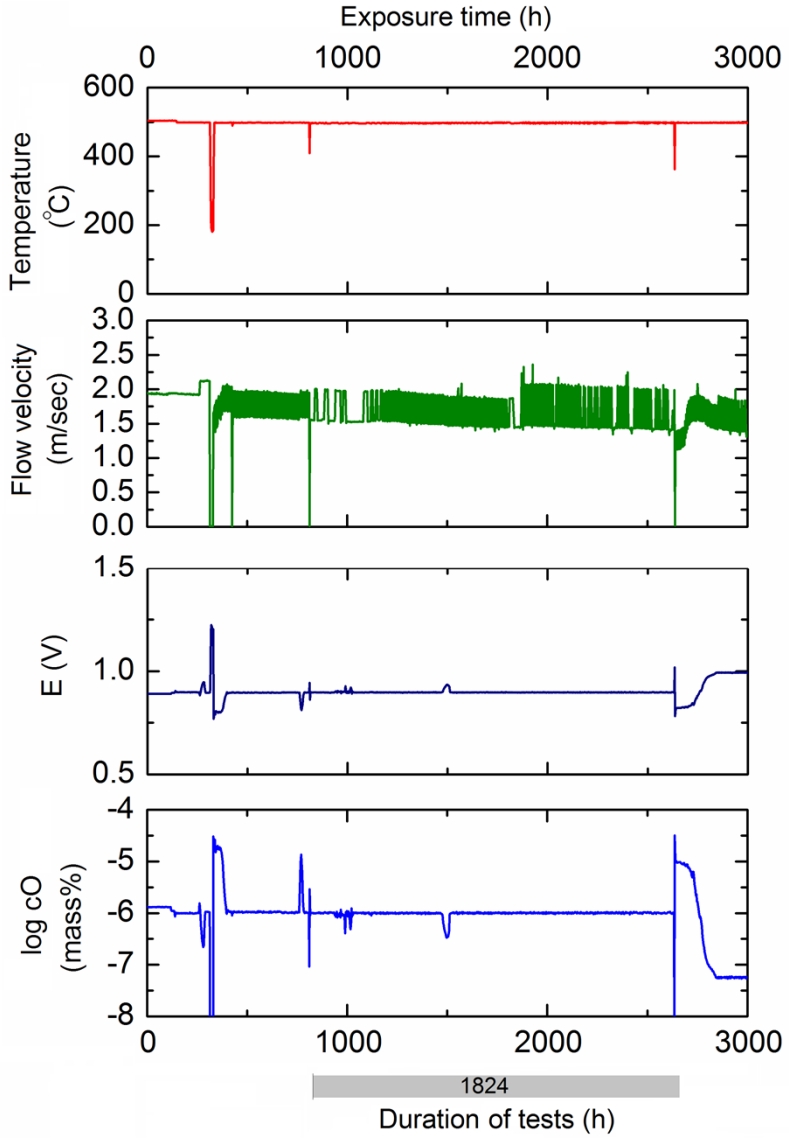
D+C = Bi-layer scale: outer magnetite + inner spinel

Corrosion appearance after 13,194 h



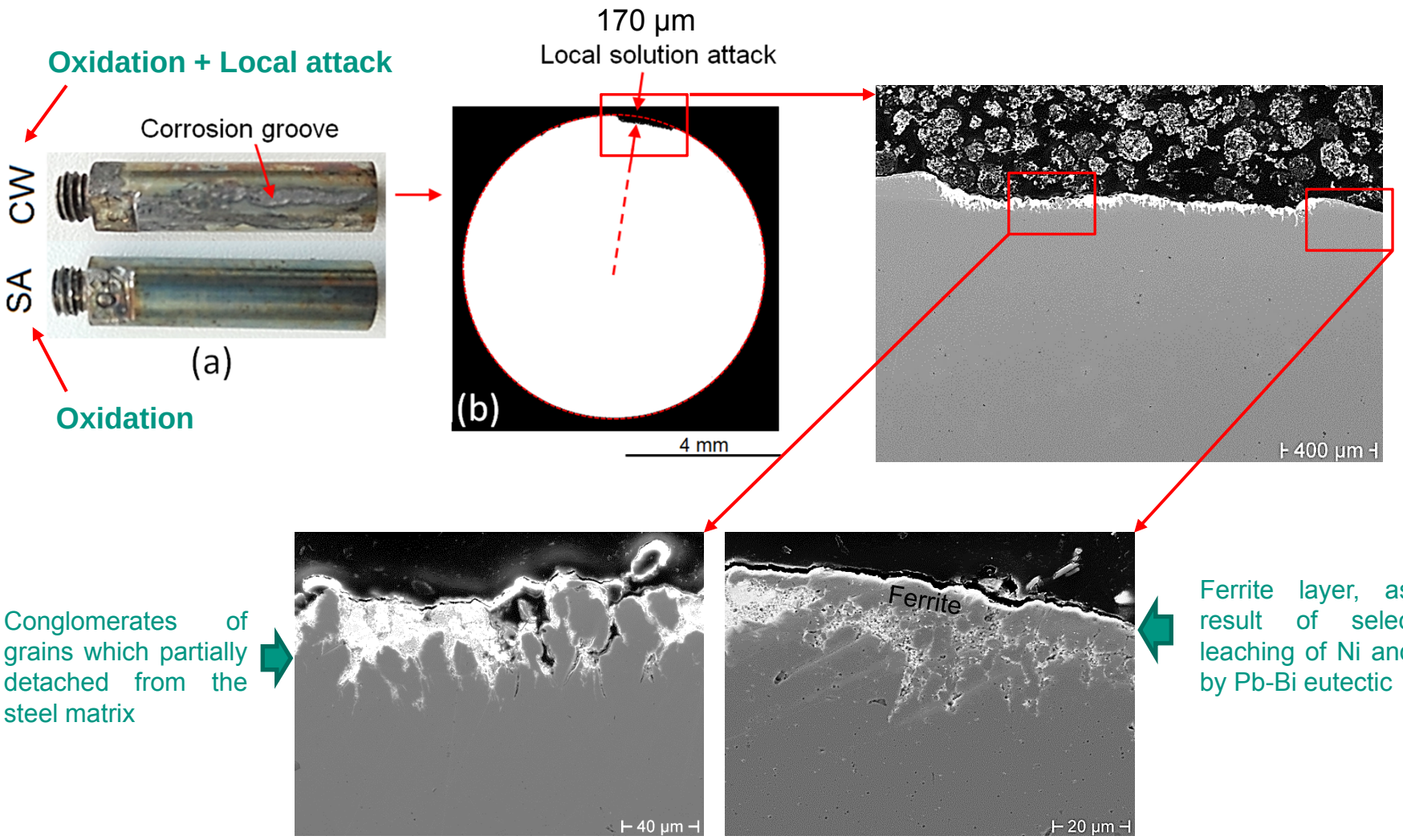
- Surface fraction of Fe-based crystallites substantially increases indicating progress in developing of the solution-based corrosion attack with time;
- Oxide film is covering surface of steel in both structural states irregularly in spite of the high oxidation potential of the Pb-Bi eutectic containing 10^{-7} mass% dissolved oxygen at 400 °C.

Conditions of corrosion tests at 500 °C



- T = 500°C
- Flow velocity 1.5-2 m/s
- Target oxygen concentration 10^{-6} mass%
- 2000 h

Corrosion response of steel at 500 °C after 2000 h



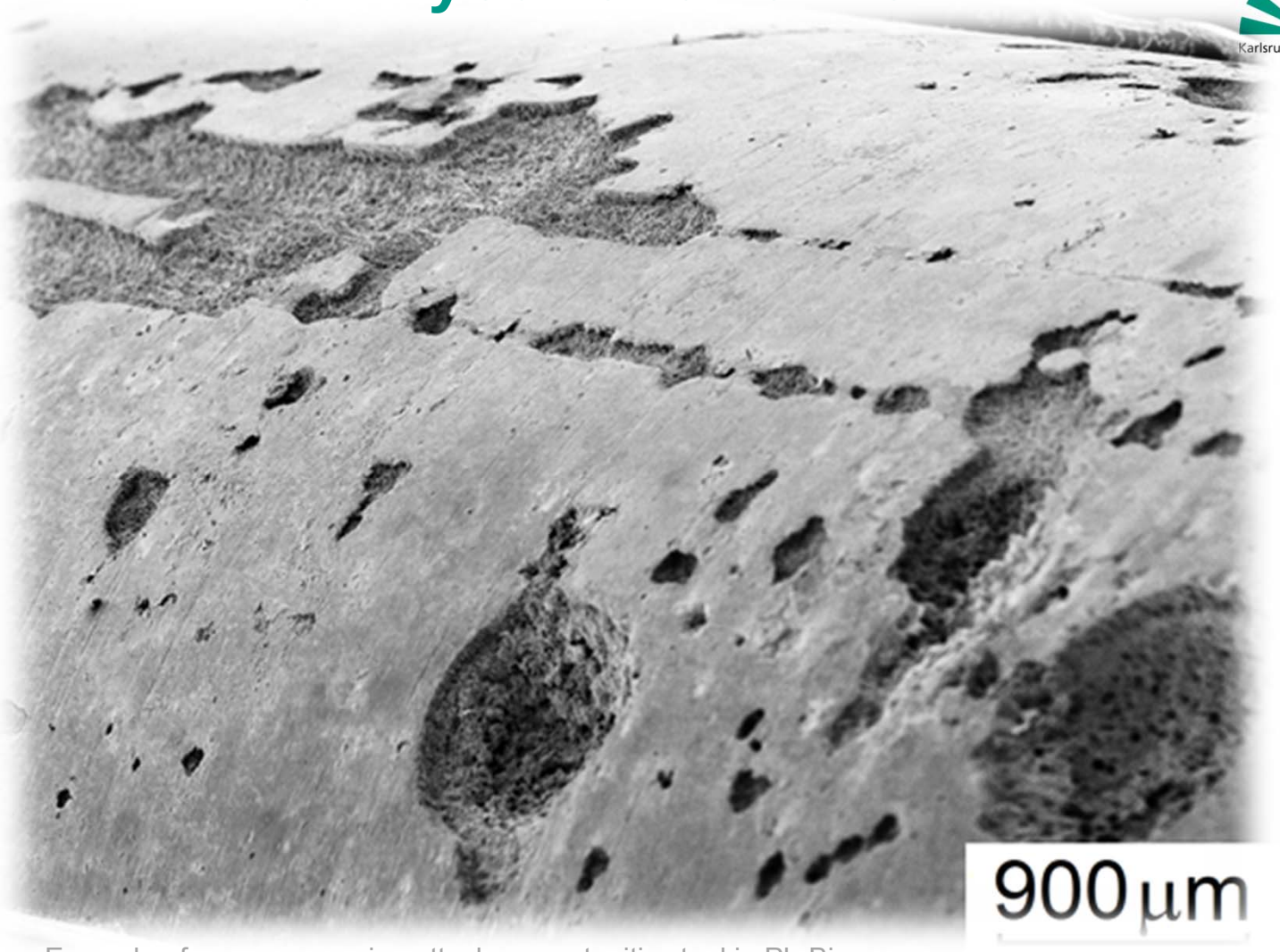
Conglomerates of grains which partially detached from the steel matrix

Ferrite layer, as a result of selective leaching of Ni and Cr by Pb-Bi eutectic

SUMMARY

- Structure of 1.4970 austenitic steel in solution annealed and 40% cold-worked states was analyzed using Scanning Electron Microscopy based Electron Back Scatter Diffraction (SEM-EBSD) / Orientation-Imaging Microscopy (OIM). After 40% cold work the total length of boundaries increases about seven times in comparison with solution-annealed state, mainly due to low-angle boundaries. Deformed steel showed substantial stored stresses.
- After the test in flowing Pb-Bi at 400 °C, corrosion losses via oxidation or solution are minor even after ~13,000 h exposure. Steel in both structural states suffered from slight but clearly preferential solution-based corrosion attack along grain and sub-grain boundaries. Cross-section examinations on cold-worked material revealed spike-like liquid-metal ingress into the steel bulk along deformation bands to the depth about 7 µm.
- After the test at 500 °C, samples in both structural states showed general protective scaling (Cr-based oxide film). Severe solution-based attack of about 170 µm in depth was observed exclusively on steel in the cold-worked state.
- 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.

Thank you for attention !!!



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