23rd International Conference on Nuclear Engineering
ICONE 23
May 17-21, 2015, Chiba, Japan

Karlsruhe Institute of Technology

Influence of cold work on solution-based corrosion attack on 1.4970 (15-15Ti) austenitic steel in static liquid lead-bismuth eutectic at 550°C and ≤ 10^{-8} mass % dissolved oxygen

Institute for Applied Materials – Applied Materials Physics (IAM-AWP), Corrosion Dep.

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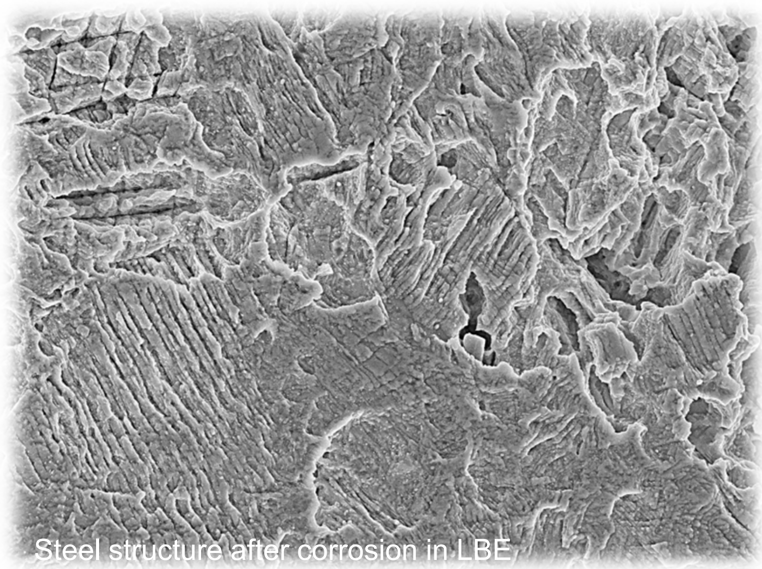

In-situ technology of doping of Pb or Pb-Bi melt by oxygen in order to form the protective oxide layer on the surface of steel

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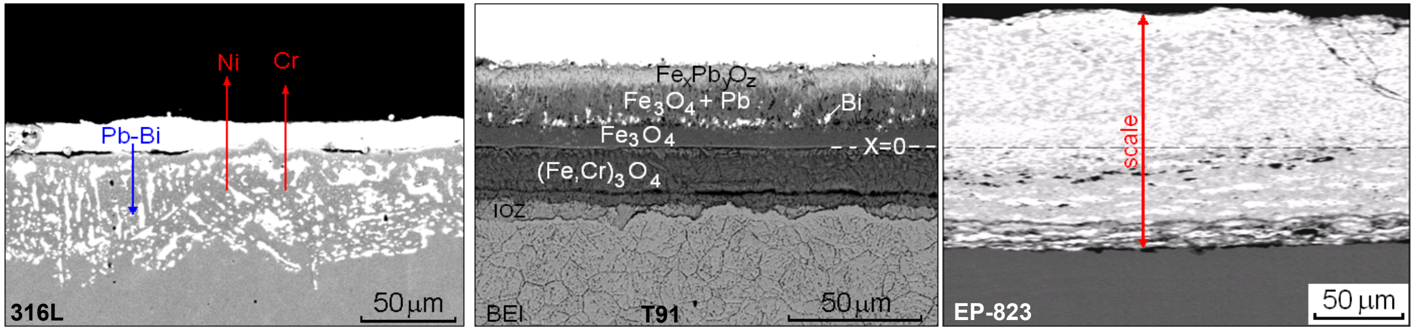
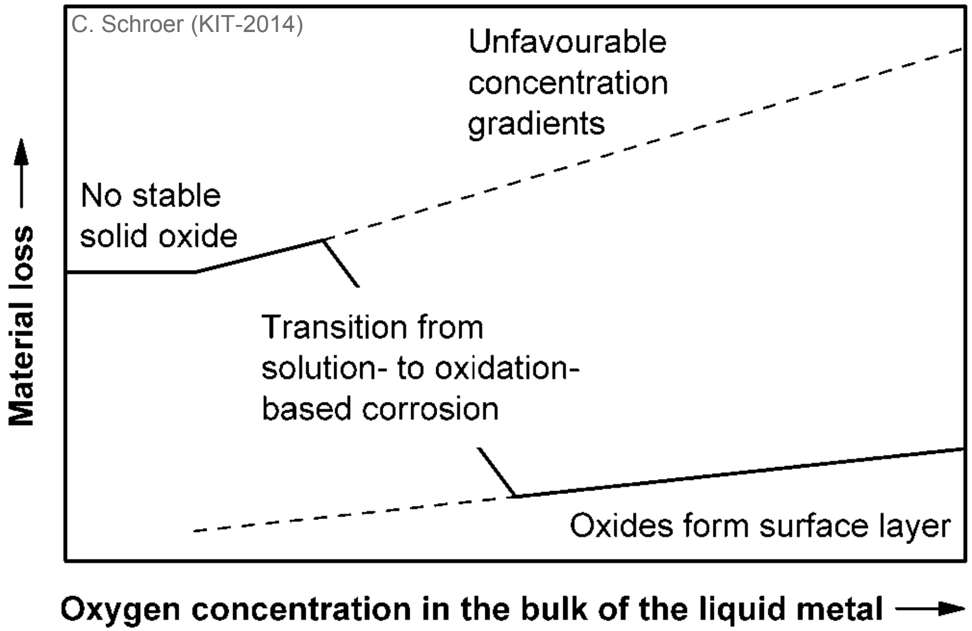
Dissolution **Oxidation** **Severe oxidation**





Scheme of corrosion loss and interaction modes of steels with Pb and Pb-Bi melts depending on the oxygen concentration in the liquid metal

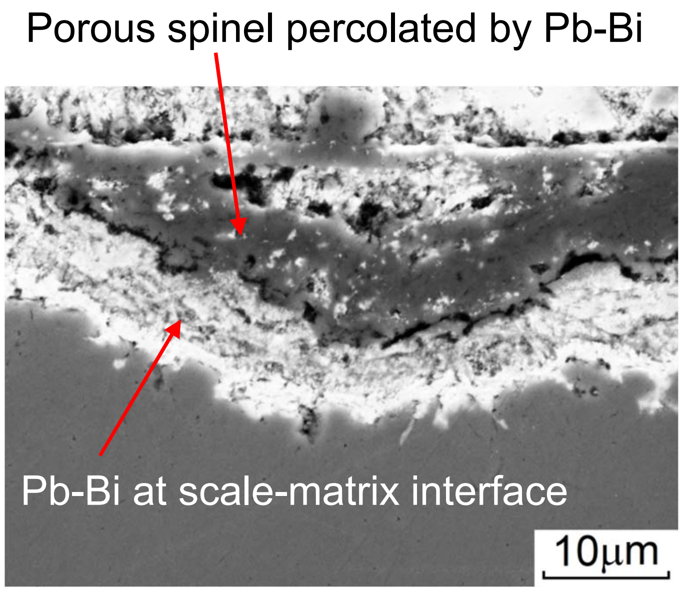
Main aim of Pb-Bi technology

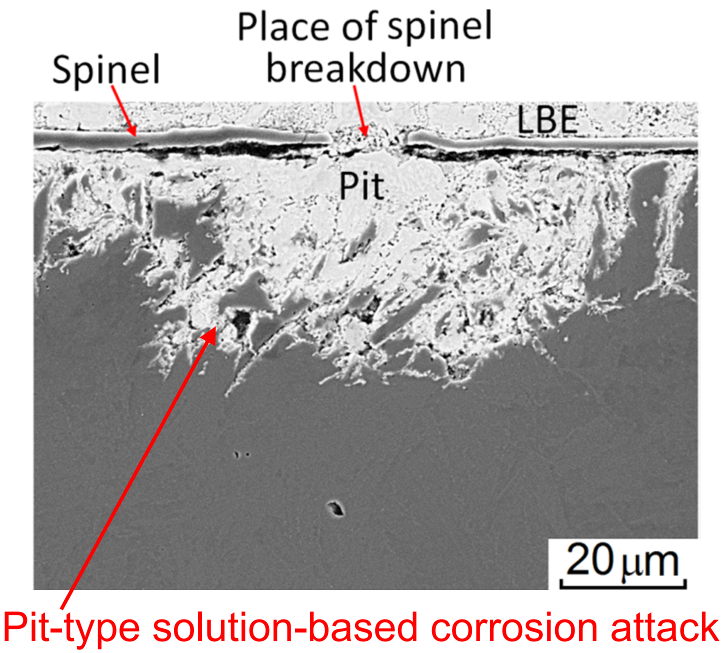
- To mitigate dissolution of steel constituents in Pb / Pb-Bi;
- To provide moderate oxidation of steels by continuous control and monitoring of concentration of oxygen in liquid metal;
- To avoid severe oxidation of steels and Pb (Bi).

BASIS of Pb-Bi technology

- Pb and Pb-Bi dissolve and transport the oxygen;
- Components of steels (Si, Cr, Fe…) have high affinity to oxygen than Pb or Bi.

Motivation of work





- Oxide layers tend to degrade with time resulting in penetration of liquid metal to the unprotected steel surface;
- Solution-based corrosion attack usually initiates preferentially instead of re-passivation;
- Composition and microstructure of steel become dominant factors for further propagation of solution-based attack into bulk of material;
- Effect of steel composition on the corrosion rate is well understood, i.e., the higher steel is alloyed by high-soluble elements (Ni, Cr, Mn, Al etc.) the more severe is the solution-based attack;
- Effect of the structural state of the material has not yet been elucidated in detail.

Effect of structural state of steels on the corrosion response to Pb and Pb-Bi melt – literature review

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- Most of the works concerning effect of material structure on the corrosion resistance of steels in Pb-Bi are focused on the effect of cold working;
- Results are contradictory describing **positive** and **negative** effect of cold work simultaneously!

- Johnson et al. [JNM 328 (2004) 88-96]: cold-rolled austenitic steel 316L forms a protective chromium oxide layer in non-isothermal oxygen-controlled (30 - 50 ppb) LBE at 550°C for, 3000 h while an annealed sample, forms a thicker, less protective oxide, consisting of outer iron oxide and inner spinel;
- Soler et al. [EUROCOR 2005]: better oxidation resistance of AISI 304L steel is a result of surface state of samples caused by cold working;
- Rivai et al. [JNM 431 (2012) 97-104]: 20% of cold working limits dissolution attack on JPCA steel (15-15 Ti) in flowing LBE containing ~ 10^{-8}-10^{-9} mass% O at 450°C. Fe-Cr oxide layer was formed on the surface of 20% cold-worked sample while it does not formed on the surface of annealed sample. However, *in-situ* formed iron-chromium oxide layer did not protect steel surface perfectly resulting in development of local corrosion damages.

- Kurata [JNM 448 (2014) 239-249]: the higher level of cold working the deeper ferritization zone (corrosion attack) on austenitic JPCA and 316 steels, tested in static LBE with ≤ 10^{-8} mass% O;
- Kurata [JNM 448 (2014) 239-249]: cold working accelerates oxidation of austenitic steels at 550 °C for 1000 h in liquid LBE with ~10^{-5} wt.%;
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- Tsisar et al. [JNM 454 (2014) 332–342]: importance of structural state of solid metal on the corrosion response of austenitic steels to flowing LBE with 10^{-7} mass% O is underlined. However the difference in the composition among the austenitic steels tested with respect to high soluble element as Ni (10-15 mass%) did not allow us to make a clear conclusion.

Aim of the present work is to reinvestigate the effect of cold work on the corrosion resistance of austenitic steels in Pb-Bi eutectic.

Tested material: austenitic steel 1.4970 (15-15Ti)

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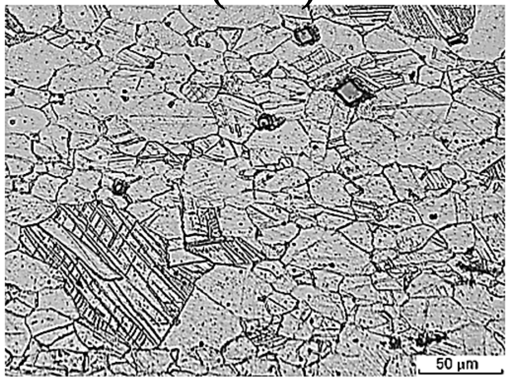
(Fe – Bal.)

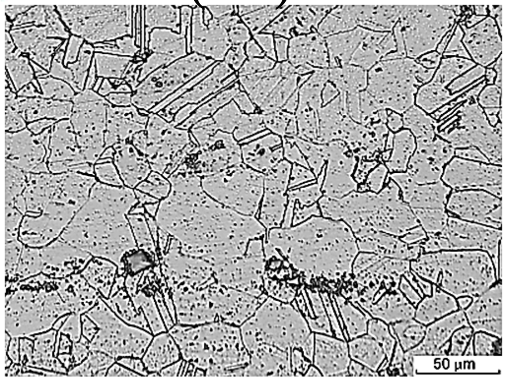
Austenitic steel	Cr	Ni	Mo	Mn	Si	Cu	V	W	Al	Ti	C	N	P	S	B
1.4970	15.95	15.4	1.2	1.49	0.52	0.026	0.036	< 0.005	0.023	0.44	0.1	0.009	< 0.01	0.0036	< 0.01

Cold Worked (CW)

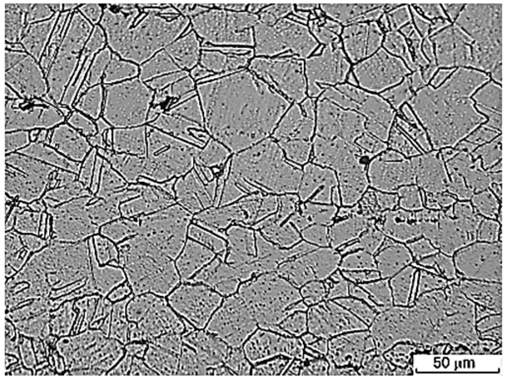
As-received (AR) → Solution annealed (SA) → 20% CW → 40%CW



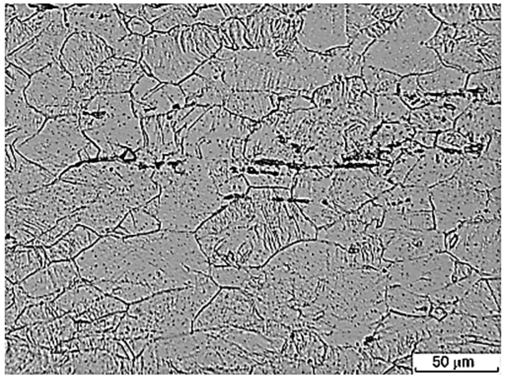
- HV_{30} = 253;
- Grain size ranged from 15 to 70 µm;
- Intersecting deformation twins and slips.



- Solution annealed at 1100ºC for 30 min;
- HV_{30} = 130;
- Grain size averaged 40 µm;
- Annealing twins.

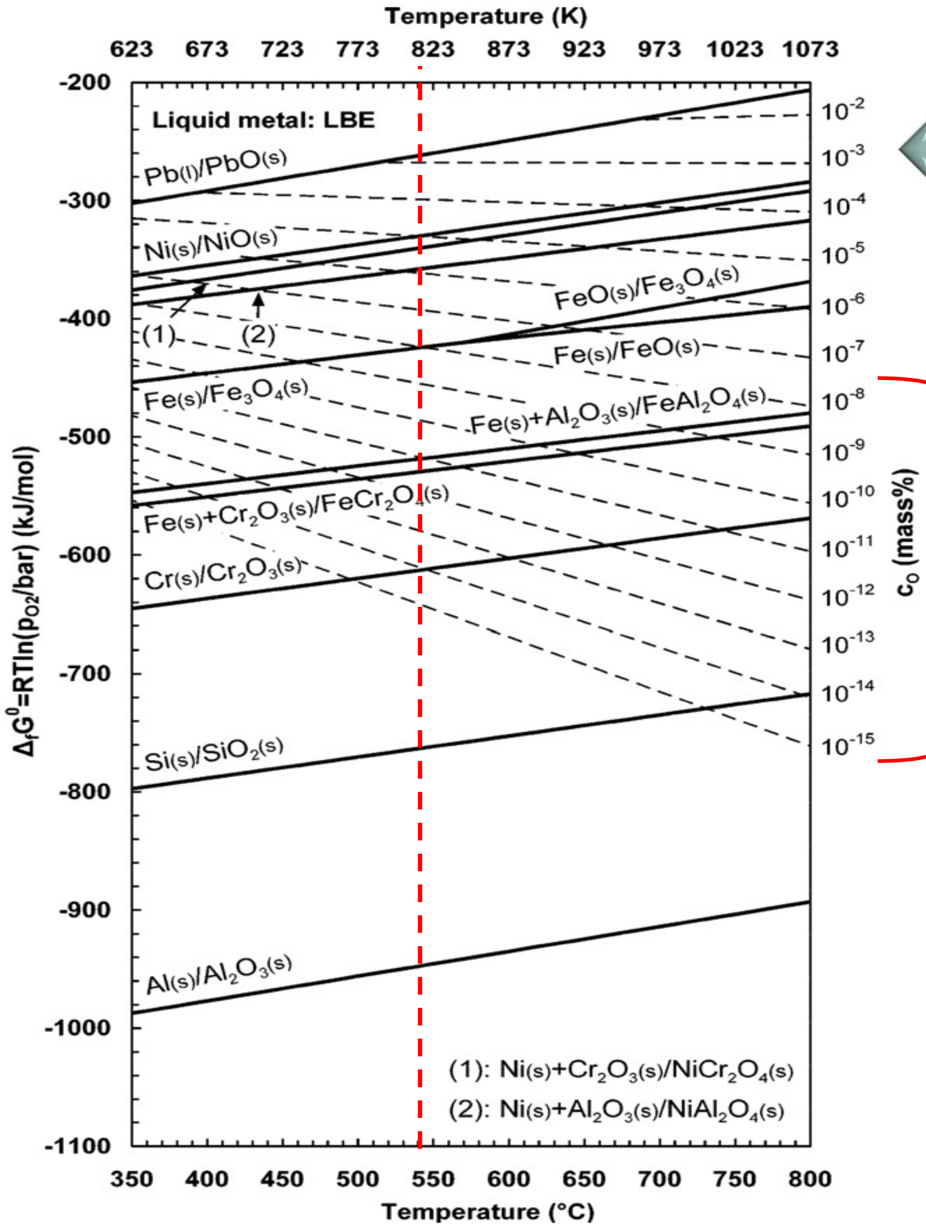


- HV_{30} = 245;
- Grain size ~ 40 µm;
- Annealing twins and deformation twins and slips.



- HV_{30} = 300;
- Grain size ~ 40 µm;
- Deformation twins and slips.

Thermodynamic considerations on corrosion test

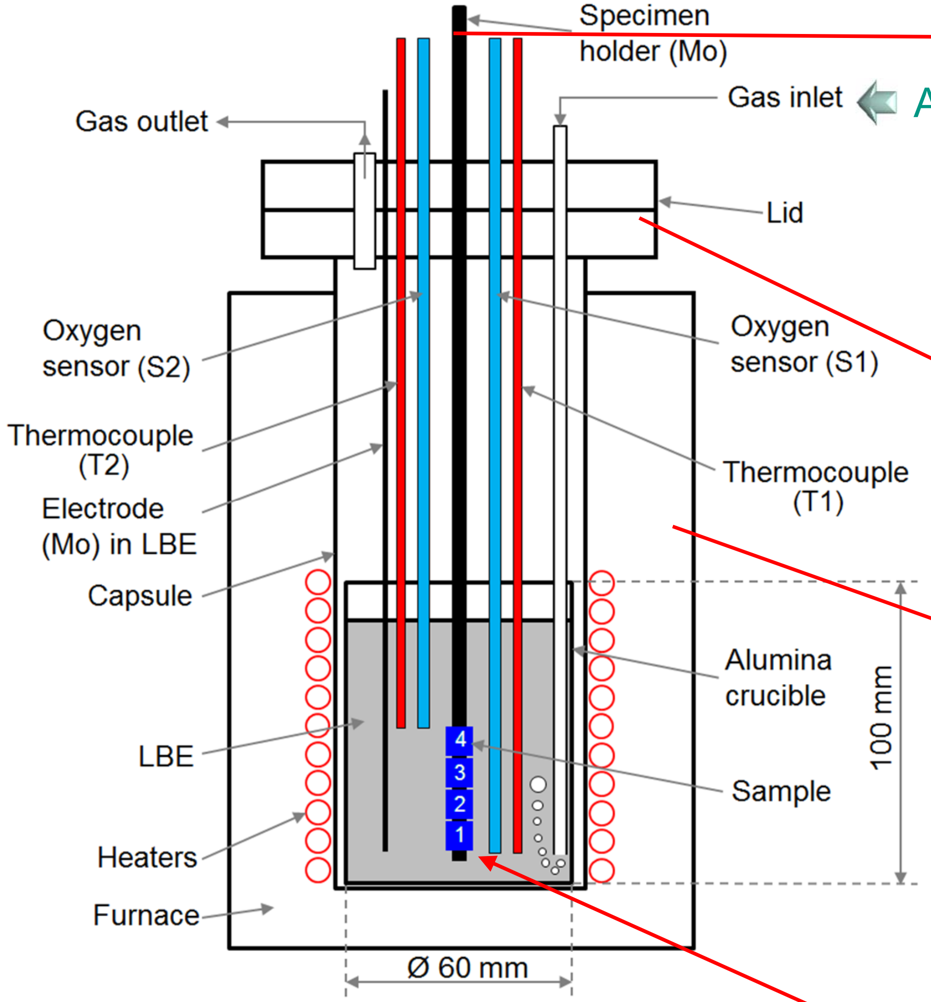


Gibbs free energy of formation of oxides (solid lines) and oxygen solutions in Pb-Bi (dashed lines)
[C. Schroer et al., NED 2012]

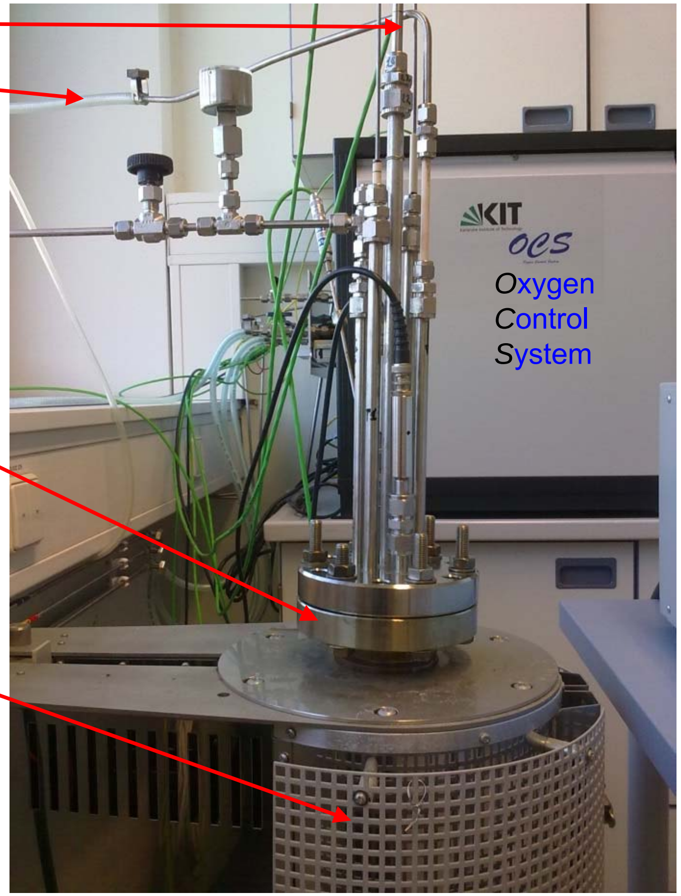
Target concentration of oxygen in LBE at 550ºC should be ≤10^{-8}mass%O in order to provide preferential dissolution of steel constituents.

Apparatus for static corrosion tests in liquid metals

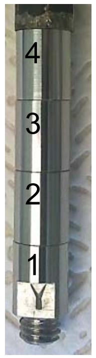
Scheme



Photo



Assembly of cylindrical specimens (Ø8×10 mm)



Test conditions:

- Pb-Bi eutectic (~2kg) – fresh for each test;
- 550ºC;
- Ar+5%H_2 gas mixture bubbling through the liquid LBE with a rate of 30 ml/min.

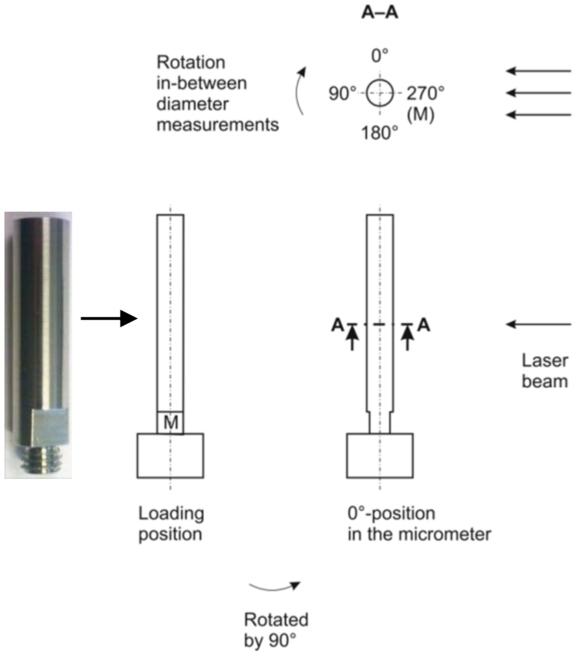
Quantification of corrosion loss

❑ Goal of quantification

- Material loss, average of general corrosion and maximum of local corrosion
- Thickness of adherent (oxide) scale
- Overall change in dimensions, including the scale
- Amount of metals transferred to the liquid metal

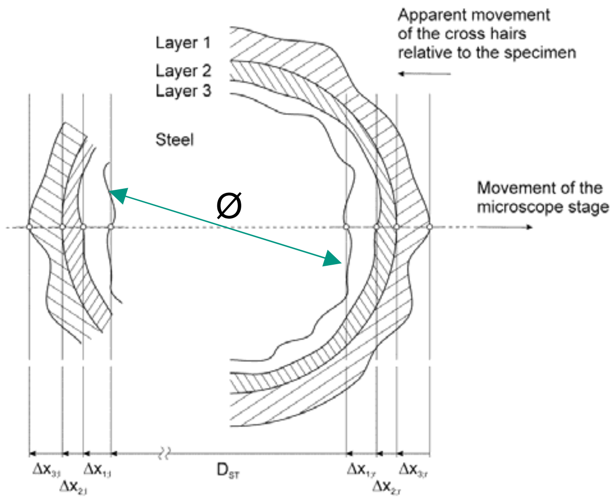
❑ Metallographic method (cylindrical specimens)

Initial parameters - Ø



- Measurement of initial diameter in a laser micrometer with 0.1 µm resolution
- Diameter of unaffected material (12th measurements with rotation angle 15°) and thickness of corrosion zones determined in a microscope (LOM) with 1 µm resolution
- Occurrence of different corrosion modes on opposing sides of the re-measured diameter is considered in the evaluation (% of surface circumference)

Post-test examination



Transverse circular cross-section

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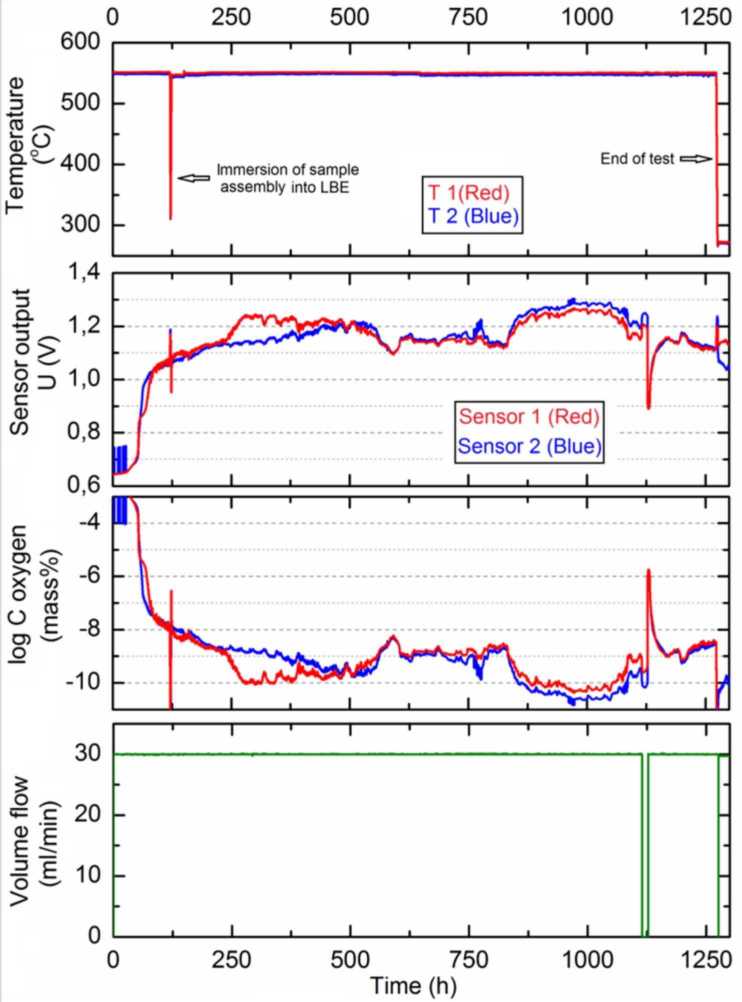
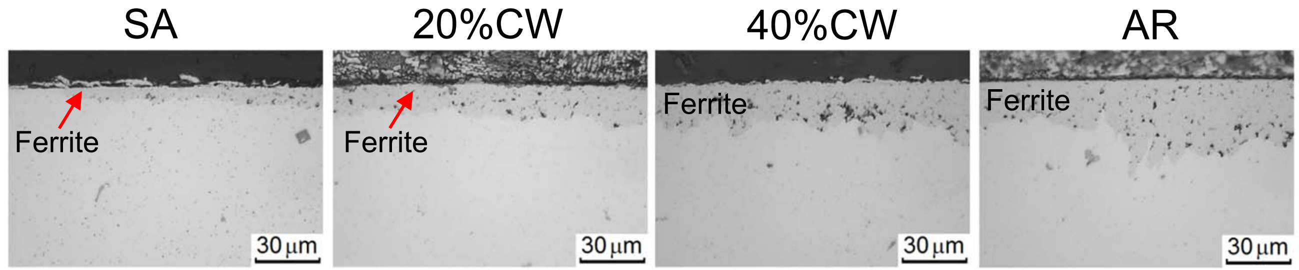
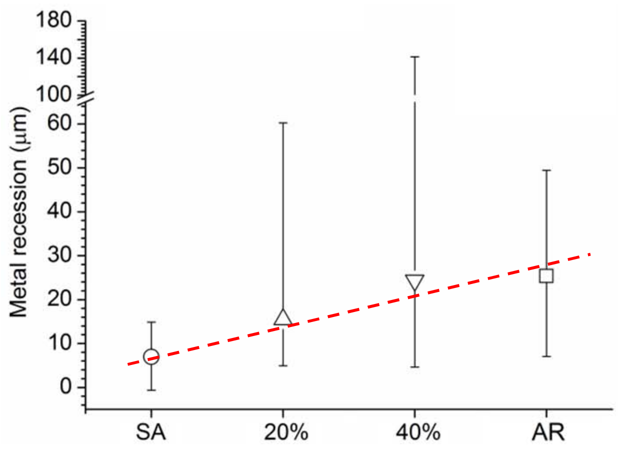
Corrosion test 1: 550°C, ~10^{-9}-5×10^{-11} mass%O, 1100 h

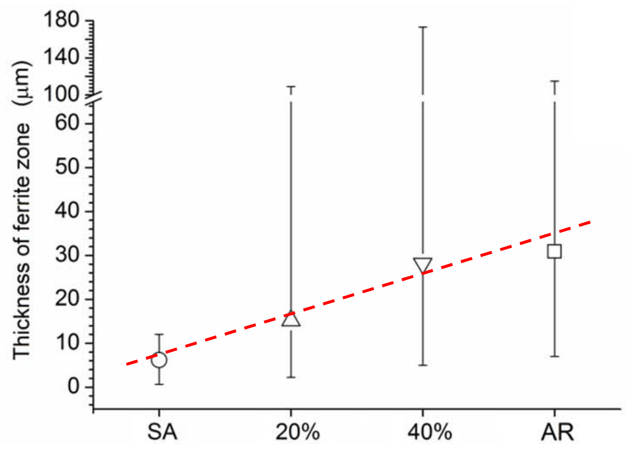
Experimental parameters of test 1





- Ferrite layer (Ni and Cr depleted and percolated by Pb and Bi) is formed;
- Corrosion loss increases with increasing cold working level of steel.

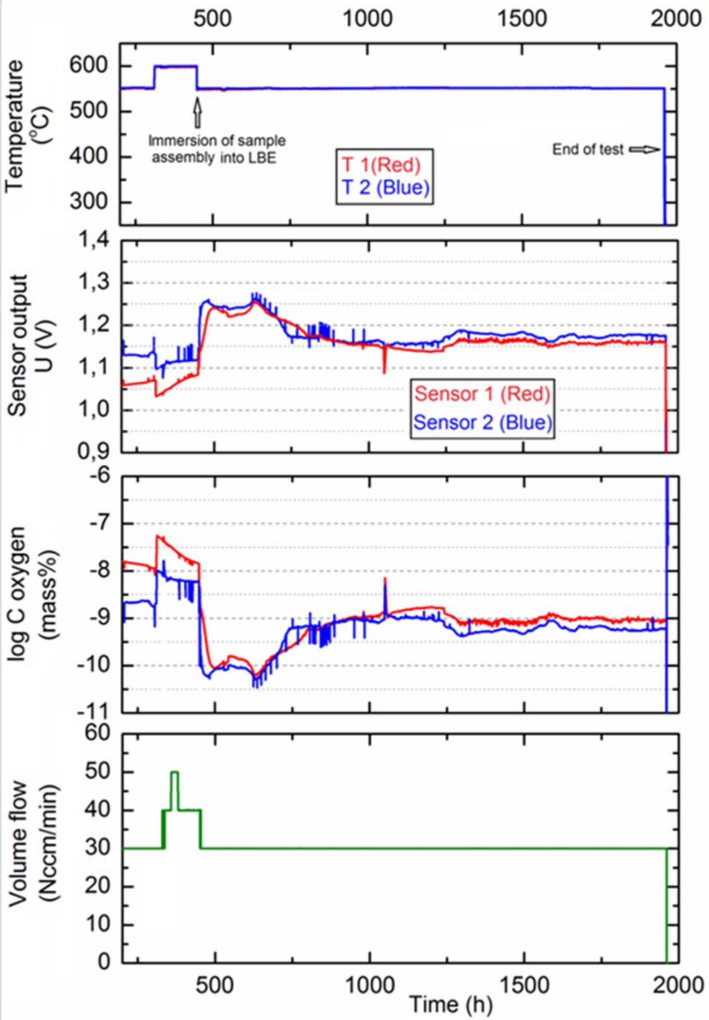




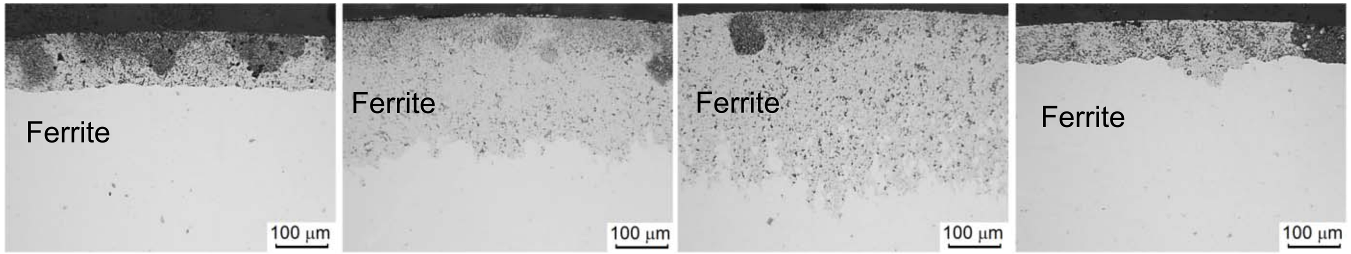
log Co(mass%)=-3.2837+6949.8/T(K)-10.080×E(V)/T(K)

Corrosion test 2: 550°C, ~10^{-9}-5×10^{-11} mass%O, 1500 h

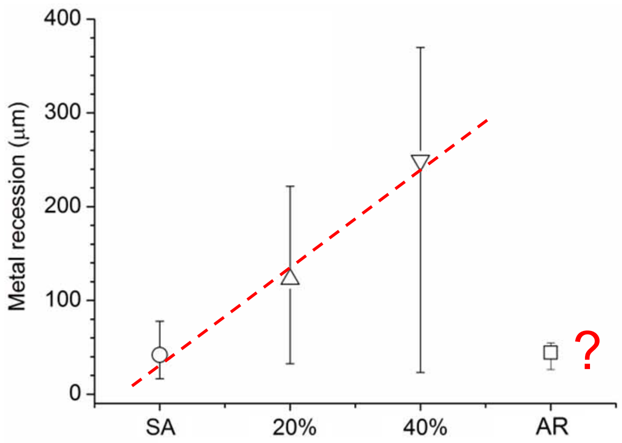
Experimental parameters of test 2

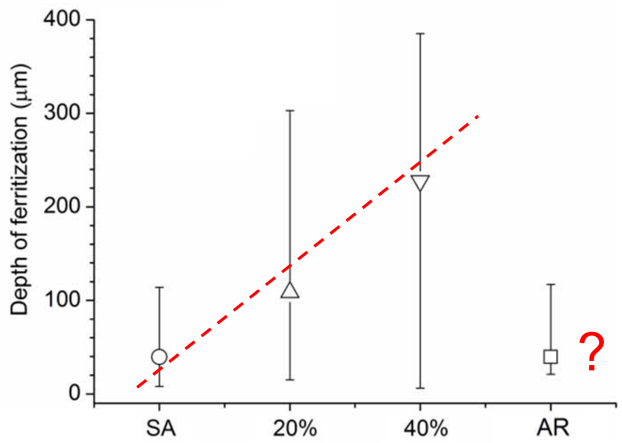


SA | 20%CW | 40%CW | AR



- ❑ Uniform ferrite layer is formed on solution annealed (SA) sample;
- ❑ Highly non-uniform in thickness ferrite layers are formed on cold worked (CW) samples;
- ❑ Corrosion loss increases in order SA → 20%CW → 40%CW.
- ❑ AR sample showed comparable smaller corrosion loss (?).





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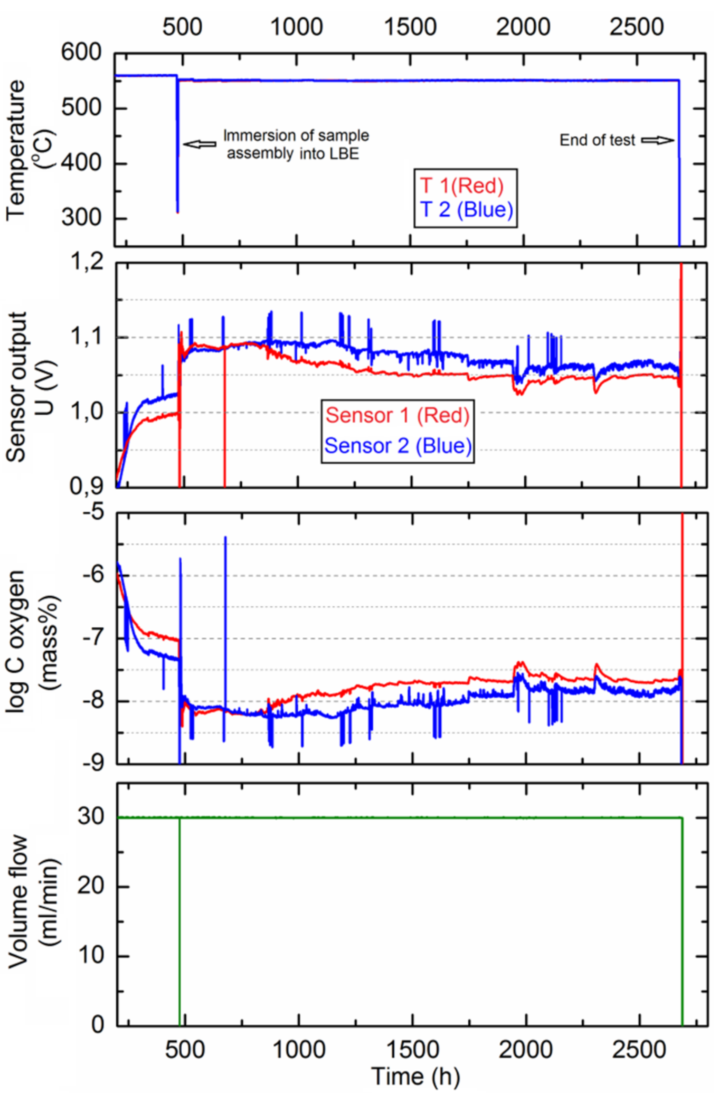
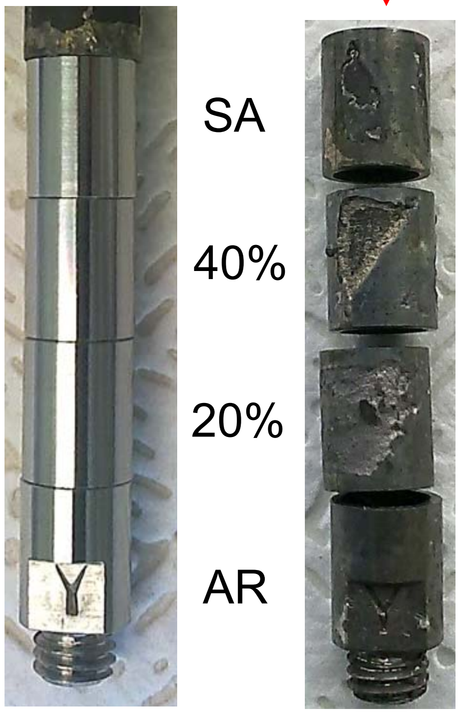
Corrosion test 3: 550°C, ~10^{-8} mass%O, 2200 h

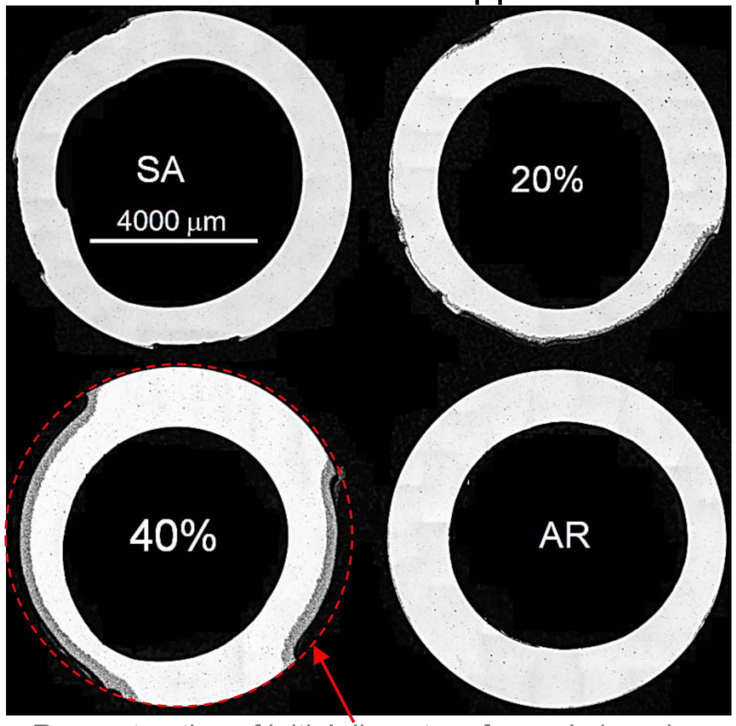
Experimental parameters of test 3



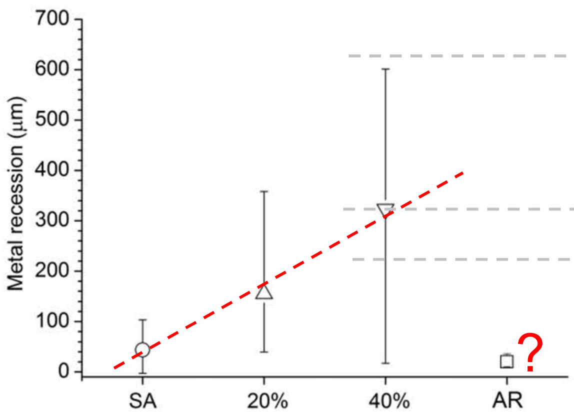
General view of sample assembly before and after test

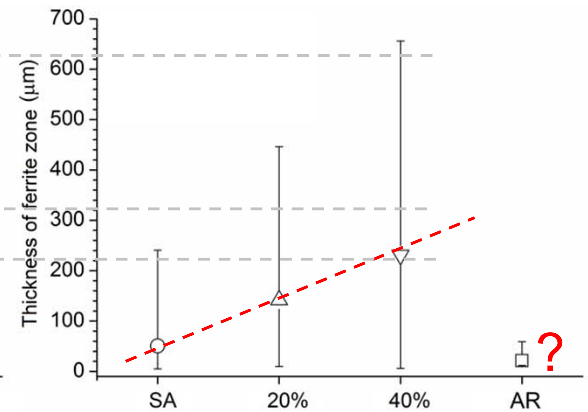


Total cross-section appearance



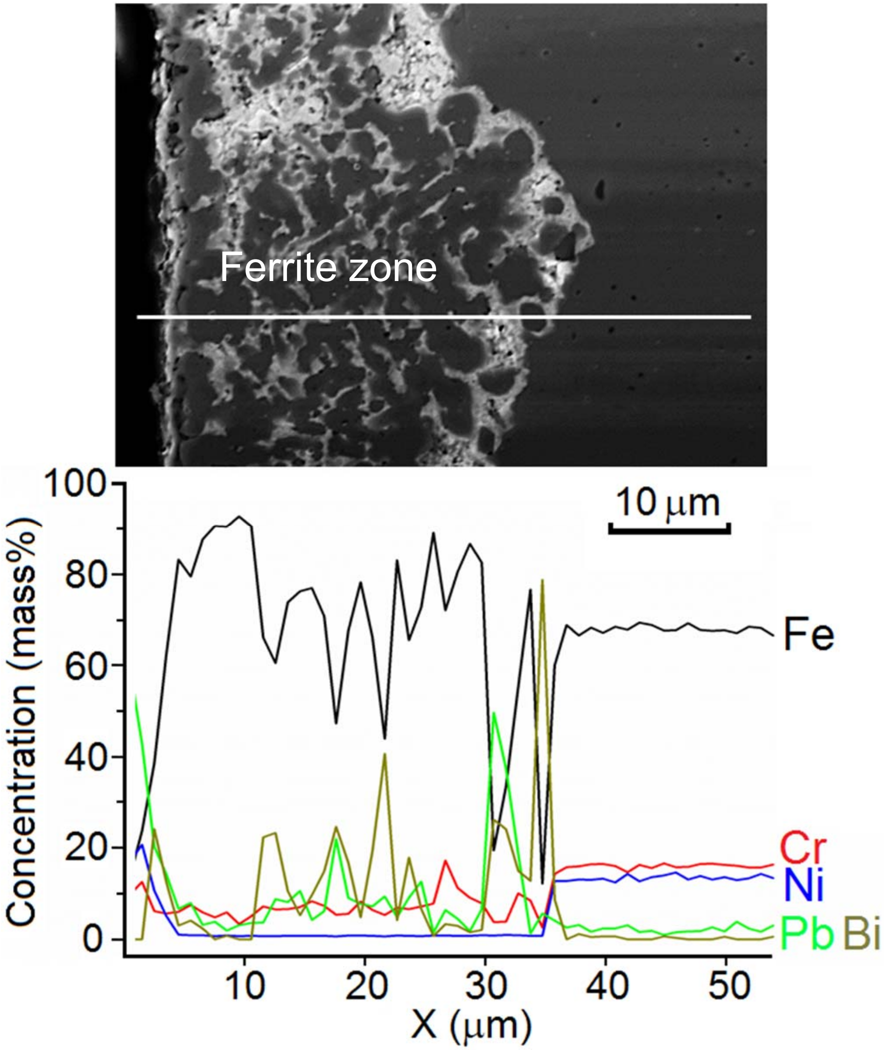
Reconstruction of initial diameter of sample in order to determine maximum corrosion depth





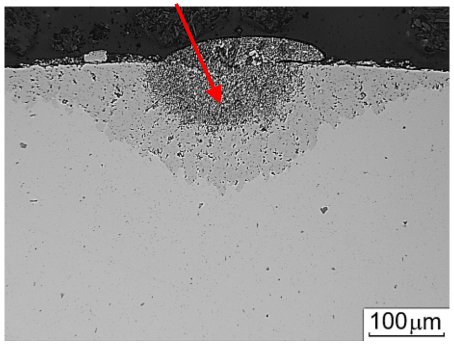
Generalization of the obtained results:

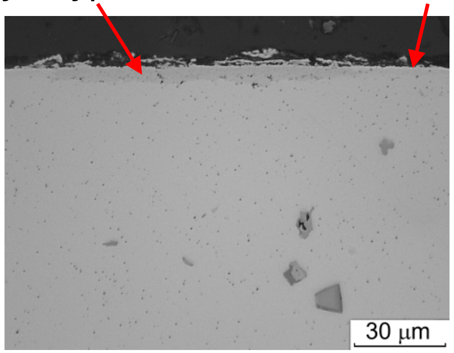
Phenomena observed



- Austenitic steel 1.4970 (15-15-Ti) underwent in general the solution-based attack: formation of ferrite zone depleted in Ni and Cr and percolated by Pb and Bi;
- Irregularity of corrosion attack increases with increasing level of deformation;
- Cold worked material reveals pit-type attack while solution annealed showed more regular layer type attack;
- Rare areas showed protective scaling surface of which decreases with increase in deformation level and exposure time;

Pit-type attack *Layer-type attack* *Protective scaling*





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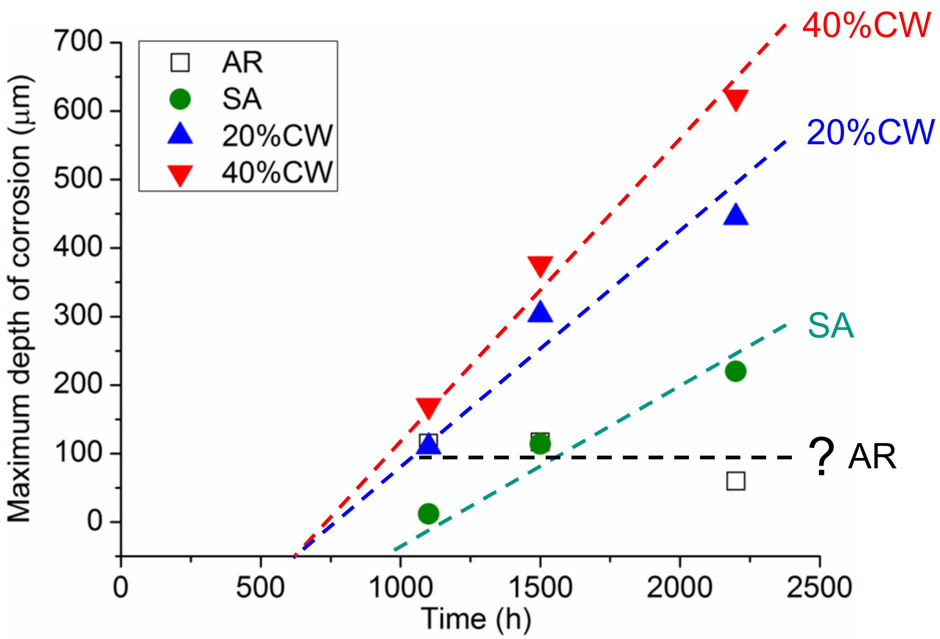
Generalization of the obtained results:

Corrosion kinetics



Linear corrosion rate equation:

40%CW - - - - - - $y = 0.4021x - 254.35$

20%CW - - - - - - $y = 0.2931x - 182.9$

SA - - - - - - $y = 0.1848x - 180.41$

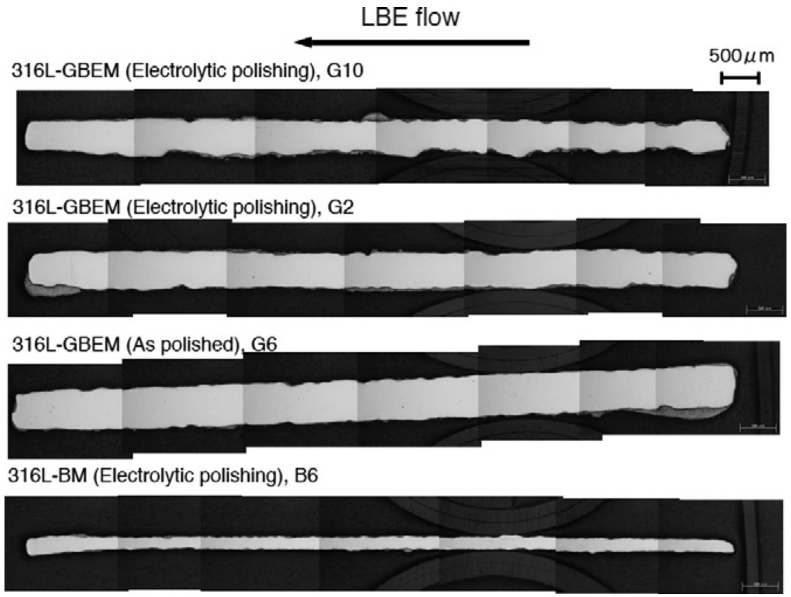
- ❑ Incubation time for initiation of solution-based attack is about 600 h for cold worked steels and 1000 h for solution annealed;
- ❑ Steepness of kinetic curves and corresponding linear corrosion rate increases in the following sequence: Solution Annealed → 20%CW → 40%CW;
- ❑ As-received material does not follow expected dependence !?!?

Possible explanation

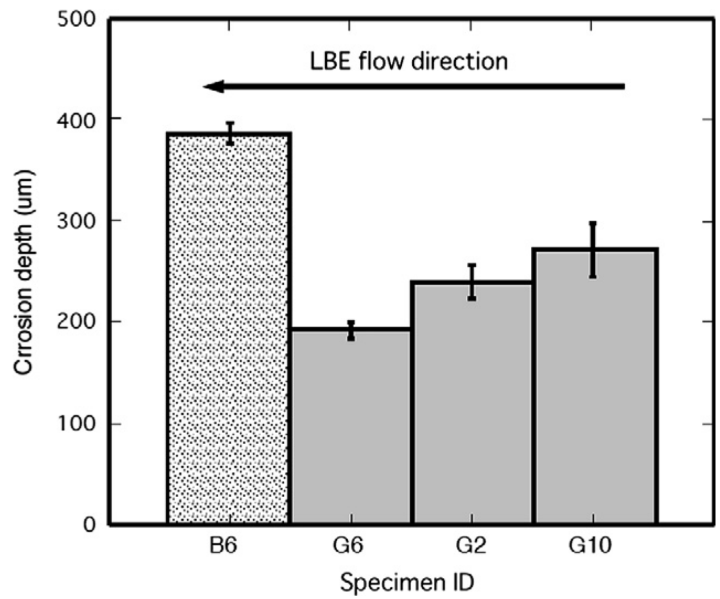
Possible explanation of exceptional behavior of as-received material based on the results published by Saito et al.

[Journal of Nuclear Materials 431 (2012) 91–96].

- Solution annealed 316L steel underwent more severe corrosion attack in flowing LBE (5 L/min, 450°C, 10^{-8}–10^{-9} wt.%.O) in comparison with material after grain-boundary engineering (GBEM: 3% pre-straining by cold rolling and subsequent annealing).
- The frequency of low-energy coincidence site lattice (CSL) boundaries is 86% in GBEM.
- Due to Grain-Boundary Engineering the dissolution attack is suppressed by interrupting the continuity of grain boundaries.



The macro photographs of cross-sections after corrosion test.



Corrosion depth/one side of the specimens.

Further plan - electron backscatter diffraction (EBSD) for as-received material !

Effect of structural state of steels on the corrosion response to Pb and Pb-Bi melt – literature review.

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- Most of the works concerning effect of material structure on the corrosion resistance of steels in Pb-Bi are focused on the effect of cold working;
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Positive:

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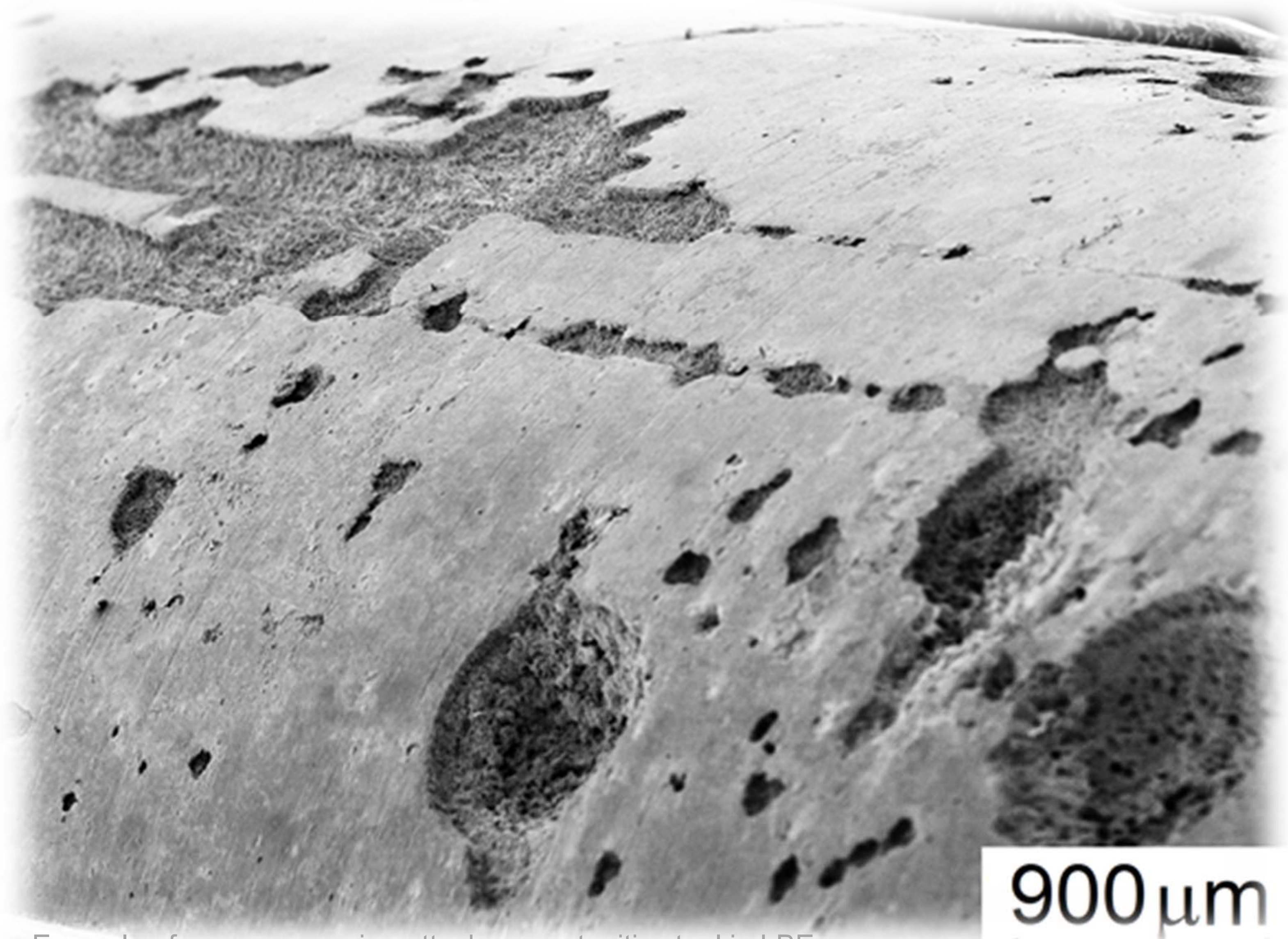
- **Present work: The higher deformation level of 1.4970 austenitic steel the deeper solution-based corrosion attack !!!**

SUMMARY

- Deformation generates dislocations in the crystal structure and as a result, the number density of structural defects (easy-diffusion pathways) increases;
- The higher deformation level the higher density of easy-diffusion pathways → the more intensive diffusion processes at constant temperature → as a result, leaching of steel constituents by liquid metal intensifies;
- Cold working impairs corrosion resistance of structural materials in LBE providing that the dissolution corrosion mode dominates !

Thank you for attention !!!



Example of severe corrosion attack on austenitic steel in LBE