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CORROSION IN STEEL T91 CAUSED BY FLOWING LEAD–BISMUTH EUTECTIC AT 400 °C AND 10^{-7} MASS% SOLVED OXYGEN

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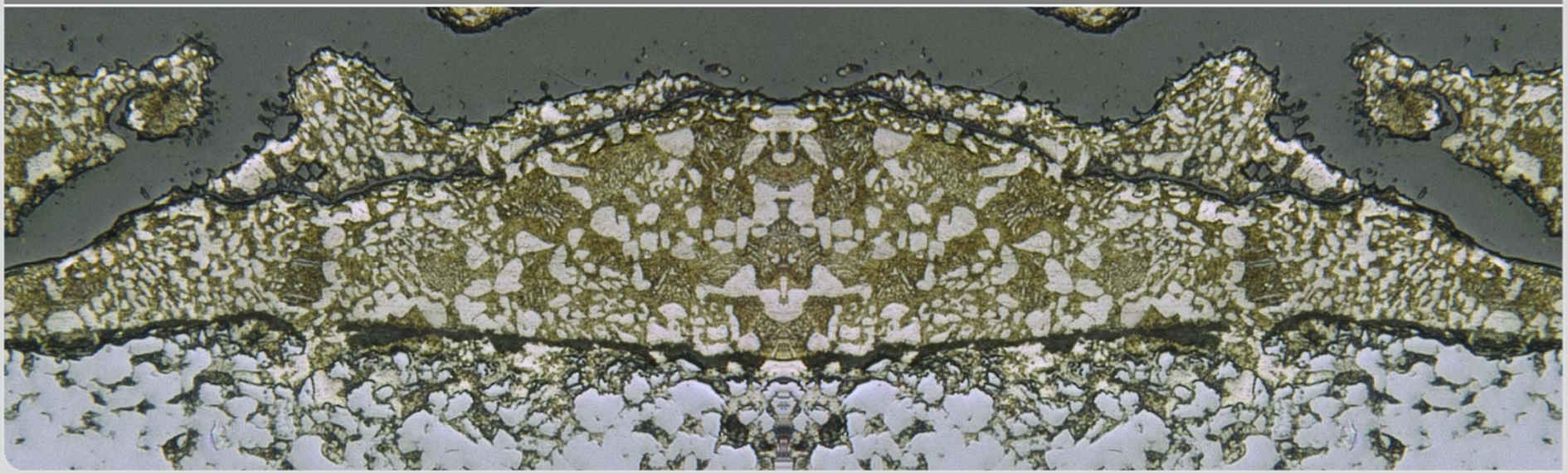


Background

- **Are liquid-metal coolants compatible with available steels under operating conditions?**
  - Steel elements are soluble in liquid metals
  - Formation of intermetallic phases
  - Degradation of mechanical properties
  - …

Prominent issues for lead–bismuth eutectic (LBE).

- **Pb or LBE: Not without specific means of corrosion protection!**
  - Ex-situ applied coatings
  - Stimulation of in-situ formation of protective surface layers (oxides, carbides, nitrides)
  - Modification of operating temperature
  - Possibly, all of the above

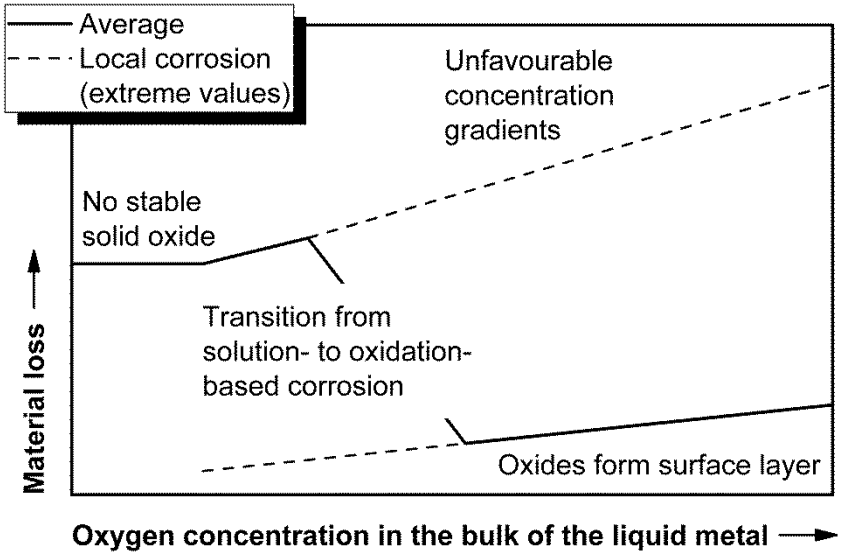
LBE:
Controlled oxygen addition so as to stabilize pre-formed oxides and promote in-situ oxidation.

Impact of oxygen solved on steel corrosion in liquid metals

- **“Absence” of oxygen**
  - Chemical oxygen potential too low for remarkable interactions with steel elements
  - Adsorption on the steel surface, absorption of liquid metal constituents by the steel
  - Steel elements dissolve in the liquid metal
  - (Formation of intermetallic phases)

- **Low-oxygen conditions**
  - Solid oxides of steel elements are stable
  - Amount of oxides formed too small for a continuous surface layer
  - Concentration gradients that promote solution of steel elements may develop in the liquid metal

- **High-oxygen conditions**
  - Solid oxides of steel elements form a continuous surface layer
  - Solution of steel elements still possible, but only after diffusion through solid oxide



→ Transition from solution-based to oxidation-based corrosion with increasing oxygen concentration.

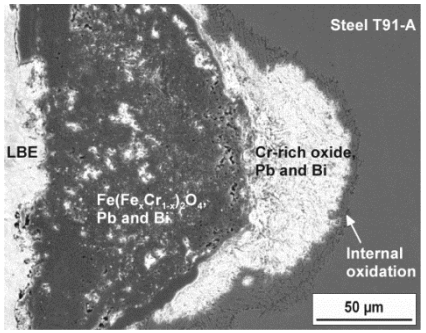
→ **Continuous oxide layer is the goal of deliberate oxygen addition (Pb, LBE).**

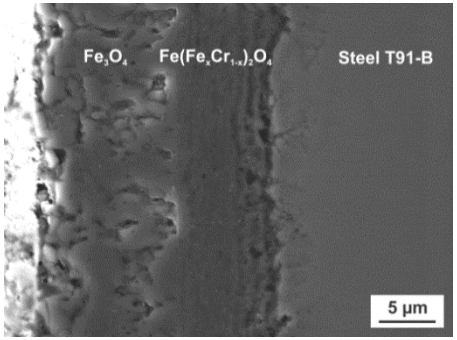
→ Locally low-oxygen conditions even when oxygen concentration in the bulk of the liquid metal is high.

Observed modes of steel corrosion

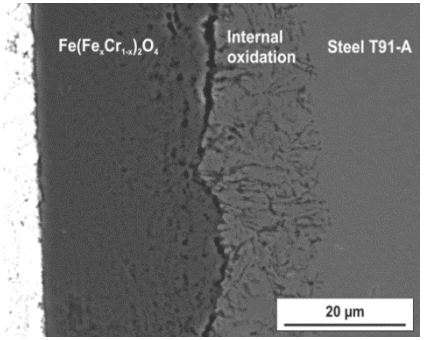
in oxygen-containing LBE (or Pb), on the example of Steel T91 (9Cr-1Mo)

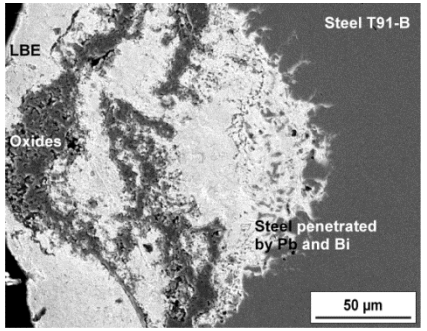
- **Protective scaling**
  - Cr- (Si-)rich oxide
  - No remarkable steel consumption
  - Short-term phenomenon for T91
- **Accelerated oxdiation**
  - Fe oxide (Fe_3O_4), Fe-based mixed oxide ($Fe[Fe,Cr]_2O_4$), Cr-rich internal oxides
  - Clearly measurable oxidation, but not necessarily intolerable steel consumption or oxide scale thickness
  - Typically follows protective scaling in the case of T91
- **Solution-based corrosion**
  - Steel elements first transfer to the liquid metal; subsequent processes may include oxidation
  - In the case of T91, usually after failure of the oxide scale resulting from accelerated oxidation
  - Outcome depends on various factors





450 °C/ 10^{-6}% O/ 2 m/s





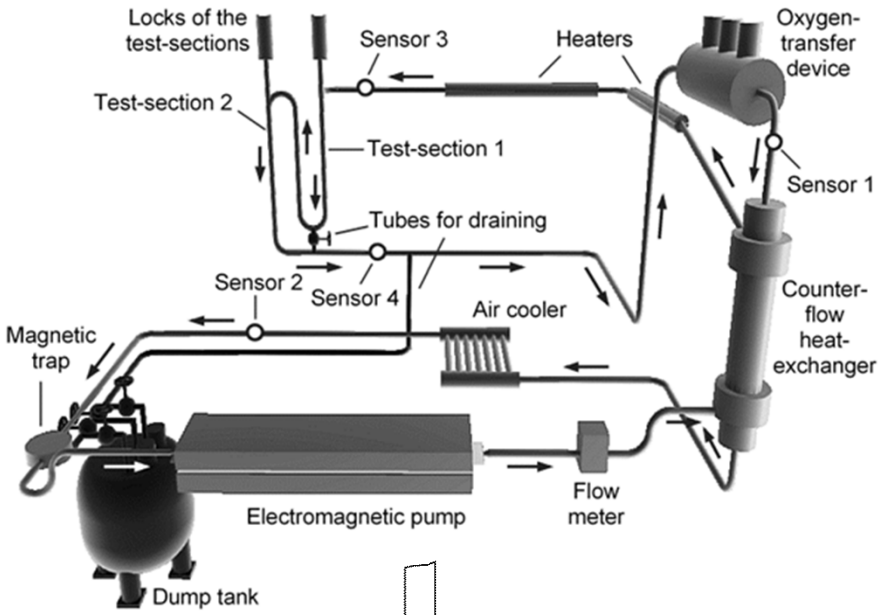
550°C / 10^{-6}% O/ 2 m/s

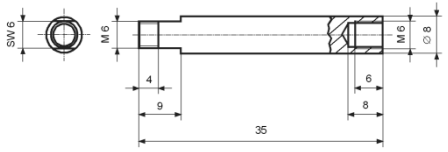
Institute for Applied Materials –
Applied Materials Physics (IAM-AWP)
Corrosion Department

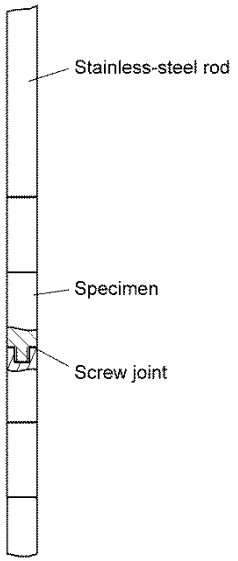
Testing of steels in the CORRIDA loop

in flowing LBE at 2 m/s (5.3 kg/s)

- **Experimental details**
  - Simultaneous exposure of various steel grades (ferritic-martensitic, austenitic)
  - 550 °C maximum possible temperature; 10^{-7} mass% minimum oxygen solved in the LBE
  - Oxygen chemical potential controlled via oxygen-containing gas; monitored using electrochemical sensors
  - Ø8 mm cylindrical specimens
  - Organized in packages of samples with same scheduled exposure time
  - Intermittent removal/ cooling in the case of specimens with longer exposure times

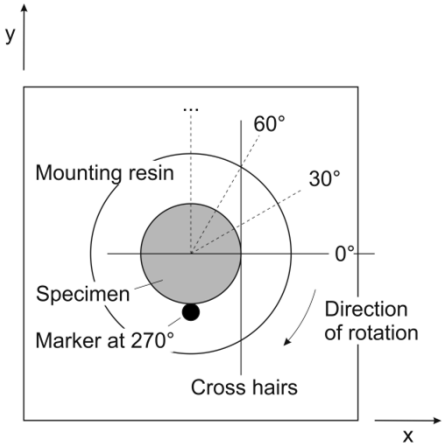




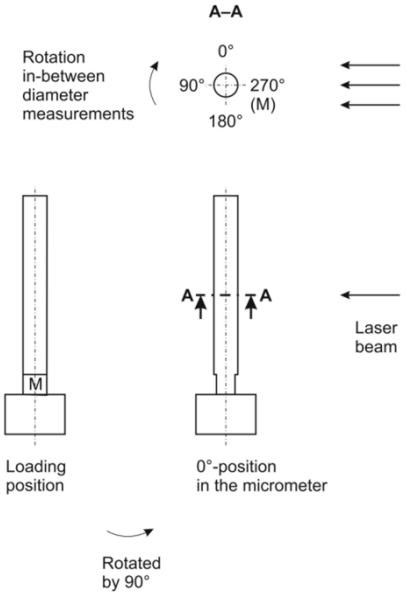


Quantification of corrosion

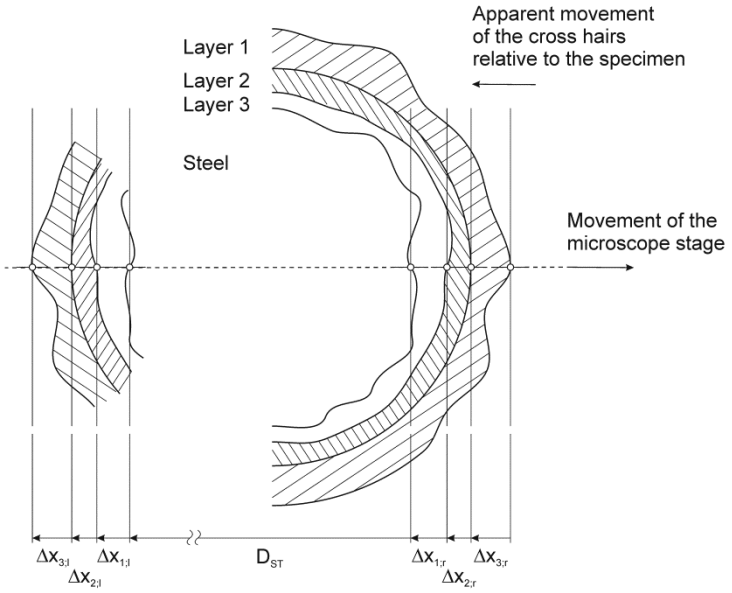
- **Goal of quantification**
  - Material loss, average of general corrosion and maximum of local corrosion
  - Thickness of adherent (oxide) scale
  - Overall change in dimensions, including the scale
  - Frequency of occurrence of different corrosion modes
  - Amount of metals transferred to the liquid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



- **Metallographic method (cylindrical specimens)**
  - Initial diameter from measurement in a laser micrometer (0.1 µm resolution)



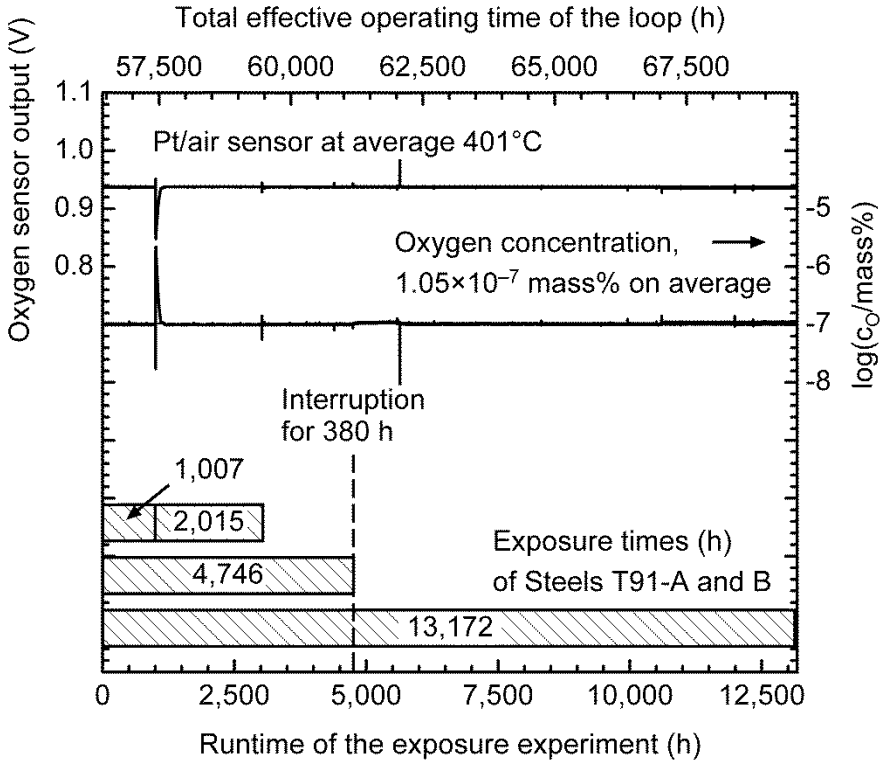
- Diameter of unaffected material and thickness of corrosion scales determined in a microscope (LOM) at minimum ×500 magnification, with 1 µm resolution
- Identification of corrosion modes
- Occurrence of different corrosion modes on opposing sides of the re-measured diameter is considered in the evaluation



Temperature/ oxygen concentration so far investigated

in the CORRIDA loop (flowing LBE)

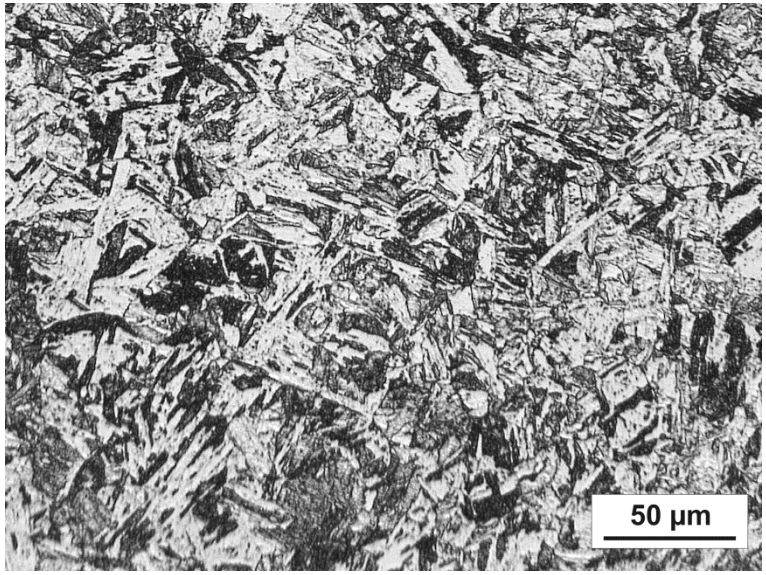
T (°C)	ΔT (°C)	Nominal c_O (mass%)	v (m/s)	Maximum t (h)
550 (+5)	~ 165	10^{-6}	2 (±0.2)	~ 20,000
450 (+5)	~ 100	10^{-6}	2 (±0.2)	~ 8000
550 (+5)	~ 165	10^{-7}	2 (±0.2)	~ 2000
450 (+5)	~ 100	10^{-7}	2 (±0.2)	~ 8800
400 (+6)	~ 110	10^{-7}	2 (±0.2)	~ 13,000



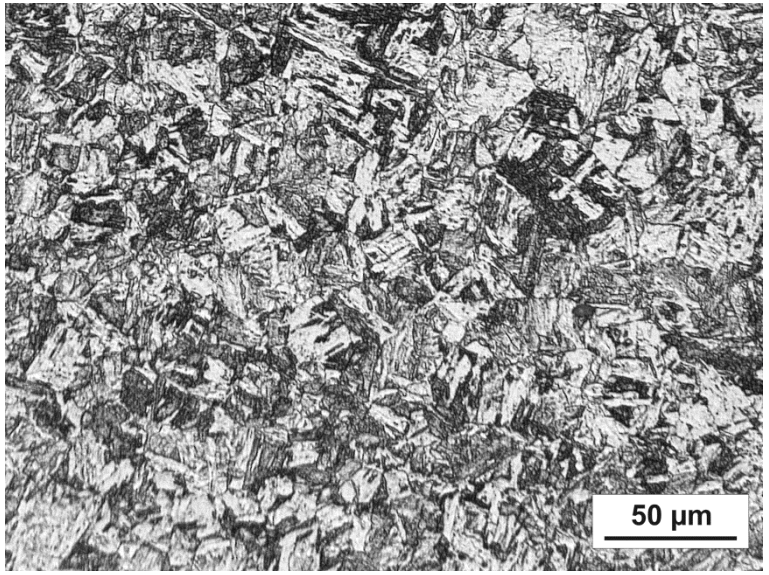
Heats of T91 tested in the CORRIDA loop

	Cr	Mo	W	V	Nb	Ta	Y	Mn	Ni	Si	C
T91-A	9.44	0.850	<0.003	0.196	0.072	n.a.	n.a.	0.588	0.100	0.272	0.075
T91-B	8.99	0.89	0.01	0.21	0.06	n.a.	n.a.	0.38	0.11	0.22	0.1025

Concentration (in mass%) of alloying elements other than Fe



T91-A

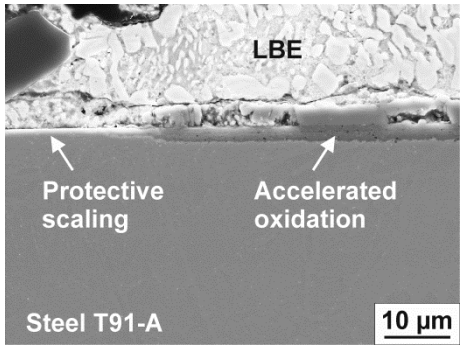


T91-B

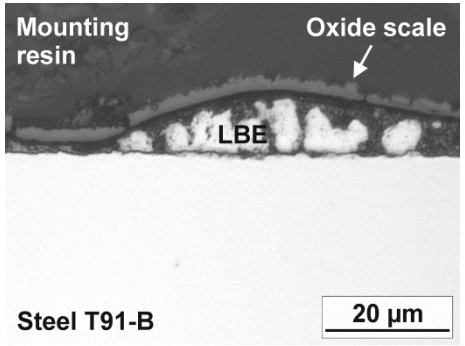
Oxidation of T91 at 400 °C/ 10^{-7}% oxygen

in flowing LBE (2m/s)

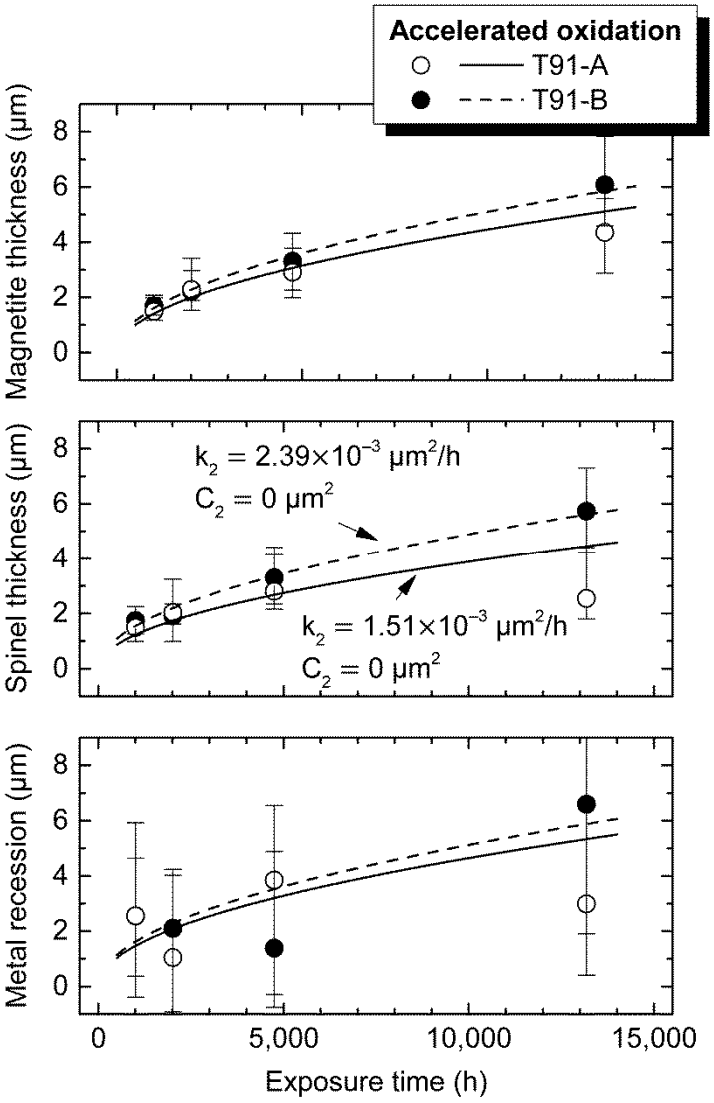
- **Protective scaling is rarely observed**
  - Primarily found on T91-A
- **Accelerated oxidation is the general corrosion process**
  - Bi-layer scale of Fe_3O_4 and $Fe(Fe,Cr)_2O_4$
  - This scale tends to buckle and detach
  - Quite often only fragments of scale found
  - Fair correspondence to parabolic rate law $(\Delta x)^2 = k_2\, t + C_2$ with $C_2 = 0$ µm²



After 2015 h



After 1007 h

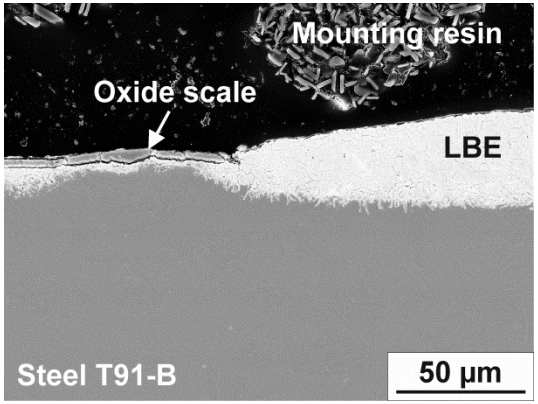


- Metal recession derived from spinel ($Fe[Fe,Cr]_2O_4$) thickness probably more reliable than direct measurement

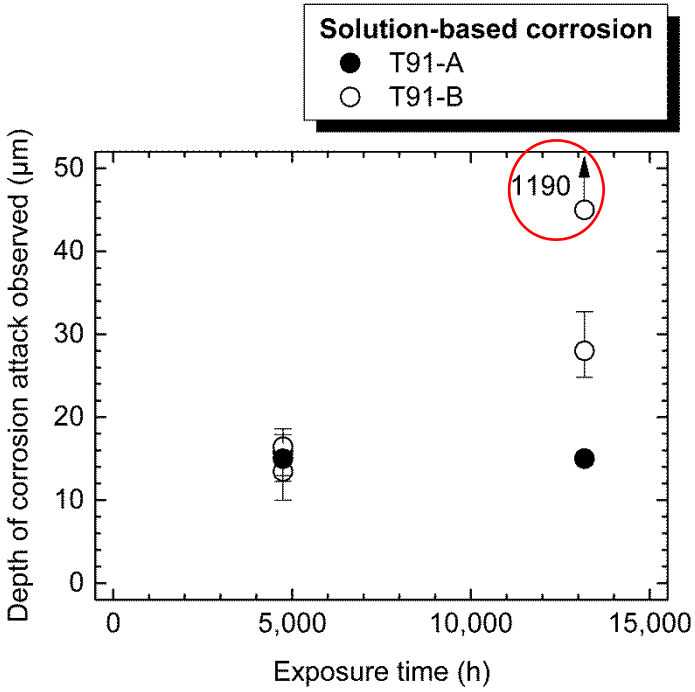
Solution-based corrosion on T91 at 400 °C/ 10^{-7}% oxygen

in flowing LBE (2m/s)

- **Only few spots on respective specimens affected**
  - First observed after exposure for 4746 h (both T91-A and -B)
  - Occurs less frequently on T91-A
  - Insignificant oxide formation during the course of solution-based corrosion (apparently only remnants of failed oxide scale present)
  - Non-selective removal of steel elements
  - Slight preference for features of the microstructure, grain boundaries or other



After 4746 h

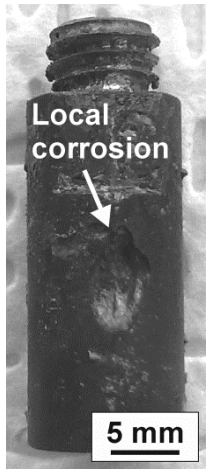


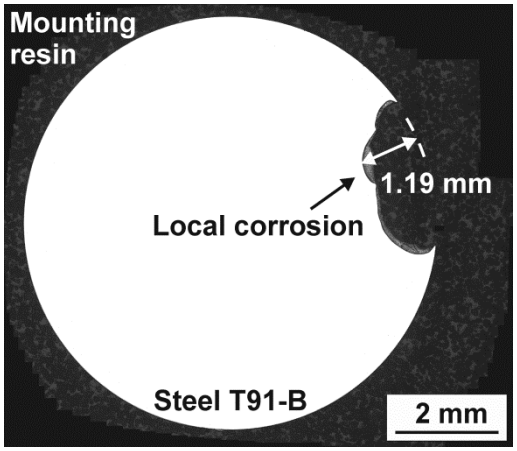
- Exceptionally severe local corrosion in one spot on T91-B after 13,172 h

Solution-based corrosion on T91 at 400 °C/ 10^{-7}% oxygen

in flowing LBE (2m/s)

- **Exceptionally severe local corrosion**
  - Most likely, not only earlier incubation but also faster progress
  - Occurs on specimen exposed in the upper part of the test-section (removed/ re-introduced during specimen exchanges, resided closer to the inlet, …)
  - Qualitatively similar observations on specimens from previous experimental runs





T91-B after exposure for 13,172 h and subsequent cleaning from adherent LBE

Comparison with observations for T91 at higher temperature

in flowing LBE (2m/s, 10^{-7}% solved oxygen)

- **Protective scaling**
  - Less frequent than at 450 °C
  - No data for 550 °C/ 10^{-7}% solved oxygen

  → Loss in Cr mobility in the steel at 400 °C
- **Accelerated oxidation**
  - Magnetite, in general, present in the scale at 400 °C / 10^{-7}% solved oxygen, but absent at 450 and 550 °C

    → Reduced simultaneous Fe solution
  - Around 5 µm metal recession after 13,000 h at 400 °C; same material consumption already after 4000 and 300 h at 450 and 550 °C, respectively

    → Less thermal activation
  - Less clear gain in terms of thinner oxide scale, especially in comparison to 450 °C

    → Presence of magnetite
- **Regular solution-based corrosion**
  - Incubation after about 2000–4500 h as compared to 500–5000 h at 450°C and <300 h at 550°C
  - 20–40 µm depth of corrosion observed after 13,000 h not significantly different from findings at 450 °C, but clearly less than at 550 °C (e.g. 200 µm after 1000 h for T91-A)

  → ?
  - But: Apparently no clear gain from reducing temperature from 450 to 400 °C!
- **Exceptional solution-based corrosion**
  - 1.2 mm depth after 13,000 h not significantly different from findings at 450 °C (1 mm after 9000 h for T91-B)

See the paper in the conference proceedings for references.

Conclusions

- **Compatibility of T91 and LBE at 400 °C, 10^{-7}% solved oxygen and 2 m/s flow velocity?**
  - Yes, if regular behaviour can be assumed and 20–40 µm local material loss after 13,000 h are tolerable.
  - Probably not, if exceptional solution-based corrosion cannot be excluded.

- **Expected benefit from reducing operating temperature from, e.g., 450 to 400 °C?**
  - Clearly less material loss from accelerated oxidation.
  - No clear benefit with respect to local solution-based corrosion.

Acknowledgements

The construction and operation of the CORRIDA loop was financially supported by the Nuclear Waste Management, Safety and Radiation Research Program (NUSAFE) of KIT. The experimental run at 400 °C and 10^{-7} mass% solved oxygen was part of the MATTER project that received funding from the EURATOM 7th Framework Program (Grant Agreement No. 269706).

Thank you for your attention!