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CHARACTERIZATION OF SILICON-CONTAINING FERRITIC/ MARTENSITIC STEEL AFTER EXPOSURE TO OXYGEN-CONTAINING FLOWING LEAD–BISMUTH EUTECTIC AT 450 AND 550°C

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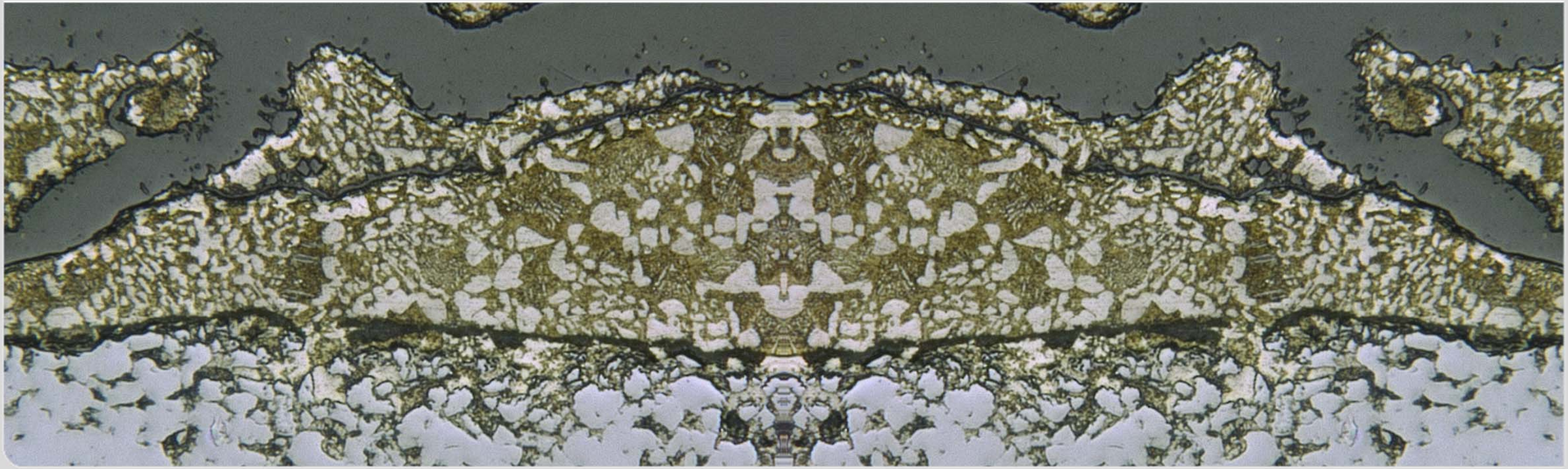


Background

- **Favourable properties of liquid metals**
  - High thermal conductivity and boiling point
  - Reasonably low dynamic viscosity
  - Some show minimum interaction with neutrons (e.g., sodium and lead)
  - Liquid heavy metals release neutrons under proton irradiation (e.g., mercury, lead and bismuth)
  - …

→ Efficient heat transfer medium/ coolant for thermal energy conversion

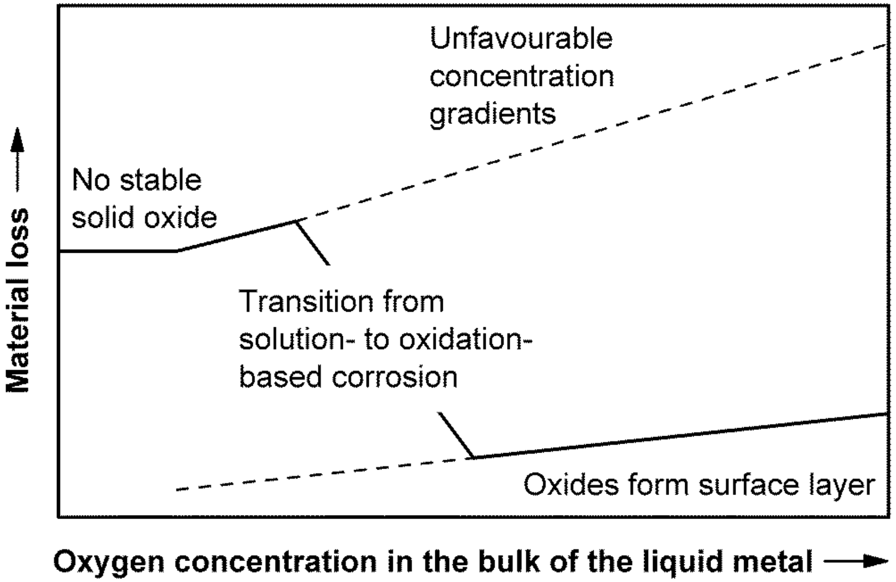
→ Essential for fast neutron reactors

→ Allows for burning sub-critical nuclear fuel in an accelerator driven system

- **Compatibility between liquid metals and steels?**
  - Major steel elements are soluble in liquid metals
  - Formation of intermetallic phases
  - Degradation of mechanical properties
  - Prominent issue for lead alloys, especially lead-bismuth eutectic (LBE)

Impact of oxygen solved on steel corrosion in liquid metals

- **“Absence” of oxygen**
  - Chemical oxygen potential too low for remarkable interactions with steel elements
  - Steel elements dissolve in the liquid metal
  - Absorption of liquid metal constituents by the steel
  - (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 <u>promote</u> 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

Effects of Si in steels

on the performance in oxygen-containing LBE (or Pb)

- ❑ **Likely to enrich in surface oxides**
  - Reduced growth rate of oxides
  - Minimum oxygen potential required is above the threshold for SiO_2(s) stability
  - Beneficial effect at high rather than low temperature

Birks, Meier: Introduction to High Temperature Oxidation of Metals

- ❑ **Austenitic steel with 4.8 mass% Si**
  - Prevention of solution-based corrosion in nominally oxygen-saturated static LBE at 550°C for 3000 h
  - Si-enriched protective oxide

Kurata, Futakawa, J. Nucl. Mater. 325 (2004) 217–222

- ❑ **9Cr steel with 1.5 mass% Si or Type 316 steel with 2.4 mass% Si**
  - Remarkable decrease in oxide scale thickness at 550°C/10^{-5} mass% oxygen in static LBE
  - Si-effect not noticeable at 550°C/ 10^{-8} mass% oxygen

Kurata, J. Nucl. Mater. 437 (2013) 401–408

- ❑ **10Cr–2Si steel in flowing LBE at 550°C, 10^{-8} or 10^{-6} mass% solved oxygen**
  - Oxide scales tend to crack and detach
  - But thin Cr- or Cr- and Si-rich oxide layer still adheres to the surface

Kondo, Takahashi, J. Nucl. Mater. 356 (2006) 203–212

12Cr–2Si steel EP-823

Russian candidate material for LBE/Pb-cooled reactors

- ❑ **Flowing LBE at 470°C/ 10^{-6} mass% O**
  - Overall thinner oxide scales in comparison to 9Cr steels (Optifer IV, T91)
  - Si-enrichment in the inner part of the scale
  - Less oxidation resistant than 1.4970 in 3000 h test

Barbier, Rusanov, J. Nucl. Mater. 296 (2001) 231–236

- ❑ **Static LBE, nominally oxygen saturated**
  - Prominent internal oxidation after about 5000 h at 490°C

Lambrinou et al., J. Nucl. Mater. 450 (2014) 244–255

  - Mechanical instability of inner part of the oxide scale formed during 1500 h at 550°C, as revealed by cracking in nano-indentation tests

Van den Bosch et al., J. Nucl. Mater. 429 (2012) 105–112

- ❑ **Static Pb, nominally oxygen saturated**
  - Apparently, periodic detachment and re-formation of the surface oxide at 550°C (specific for the experimental procedure?)
  - After 3000 h at 550°C, higher material loss due to oxidation than observed for similar steel with less Si

Tsisar, Yeliseyeva, Mater. High Temp. 24 (2007) 93–101

  - At 650°C, porous multi-layer oxide with a remarkable growth rate of 5 µm/h

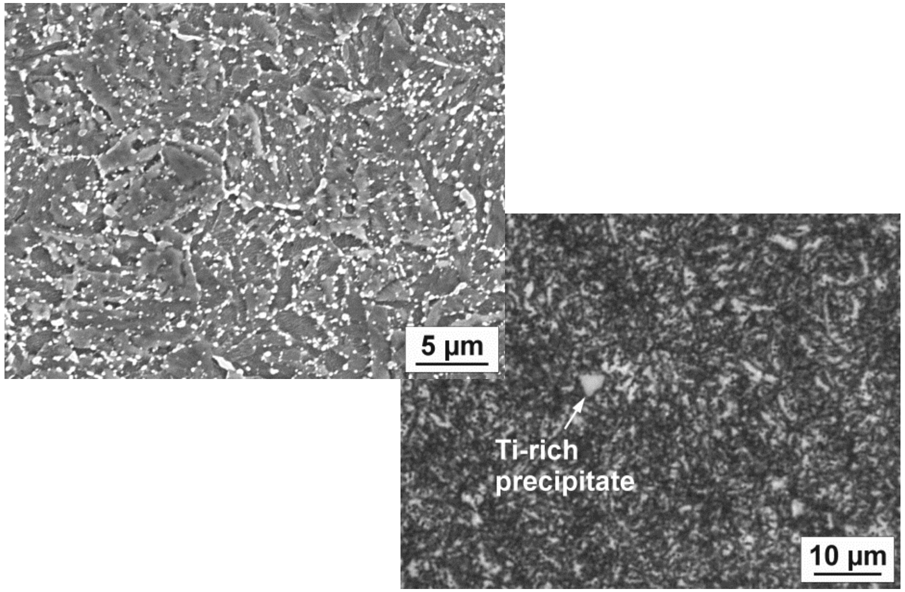
Eliseeva, Tsisar, Mater. Sci. 43 (2007) 230–237

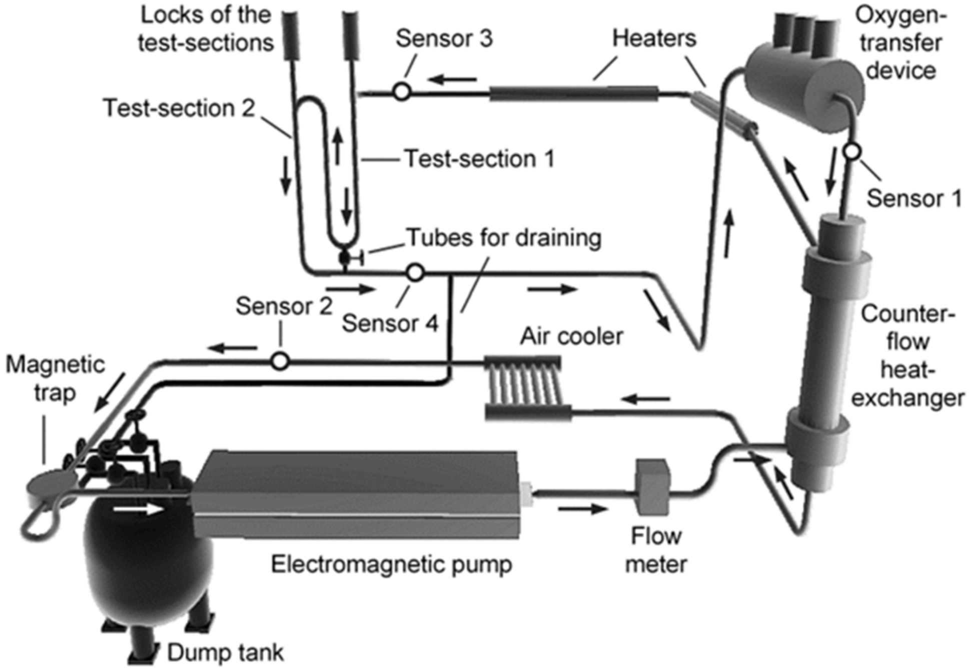
- ❑ **Solution-based corrosion not reported for any of these conditions**

Tests on Si-containing steel in the CORRIDA loop

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

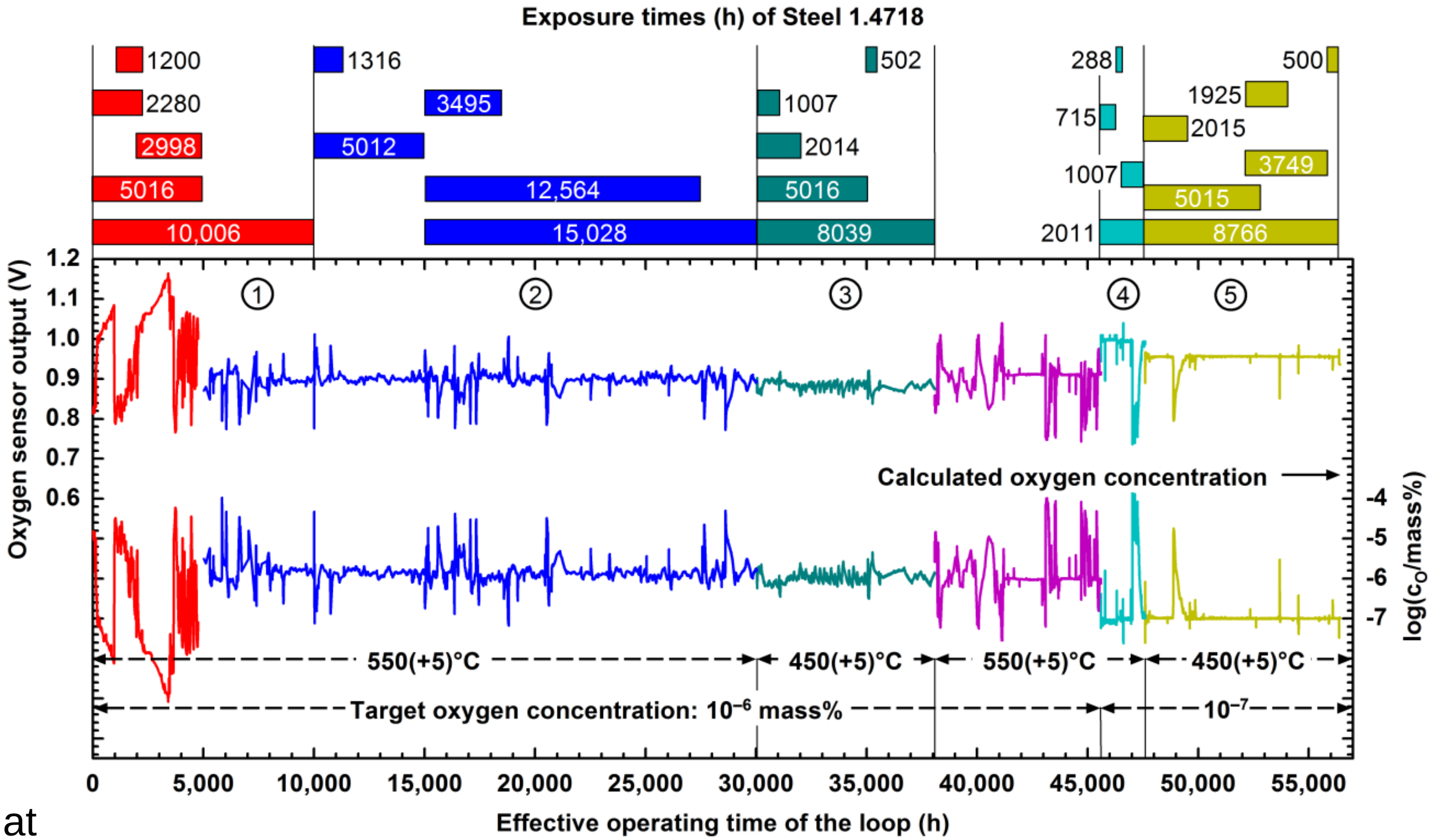
- ❑ **Material: 1.4718 (X45CrSi9-3)**
  - Heat-resistant steel typically used for exhaust valves in combustion engines
  - Martensitic structure in the quenched and tempered state
  - Cr-rich (carbide) precipitates, some Ti-rich precipitates





- ❑ **Experimental**
  - Ø8 mm specimens exposed in the loop simultaneously to other steels
  - At 450°C and 550°C; oxygen solved in the LBE controlled via oxygen-containing gas
  - Interruption and intermittent cooling especially for long-term exposures

Exposure conditions of evaluated specimens



1: Five specimens exposed for between 1200 and 10,006 h at 550°C and varying c_O.

2: Five specimens exposed for between 1316 and 15,028 h at 550°C and c_O around 10^{-6} mass%.

3: Five specimens exposed for between 502 and 8039 h at 450°C and c_O around 10^{-6} mass%.

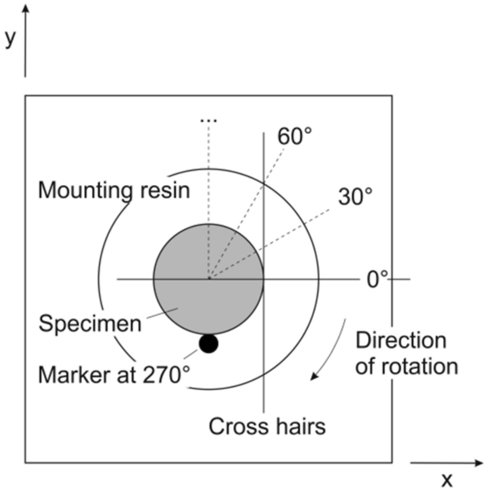
4: Four specimens exposed for between 288 and 2011 h at 550°C and c_O around 10^{-7} mass%; c_O higher (~10^{-4} mass%) in the final stage of exposure for 1007 and 2011 h.

5: Six specimens exposed for between 500 and 8766 h at 450°C and c_O around 10^{-7} mass%; c_O peaked at ~10^{-5} mass% in the final stage of exposure for 2015 h or during the first half of exposure for 5015 and 8766 h.

Quantification of corrosion

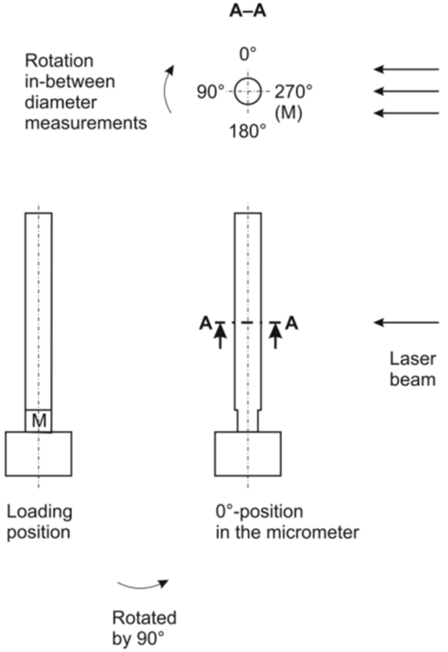
❑ Goal of quantification

- 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

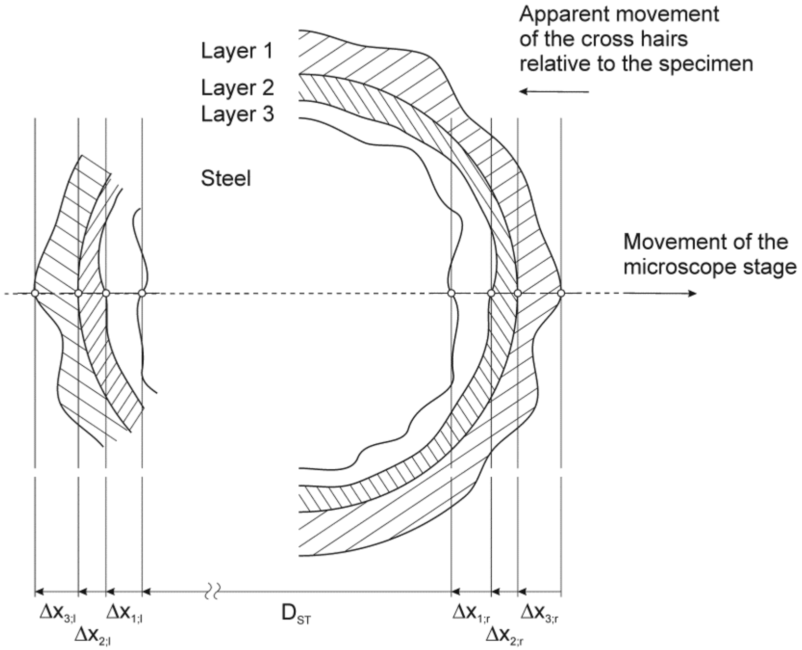


❑ Metallographic method (cylindrical specimens)

- 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



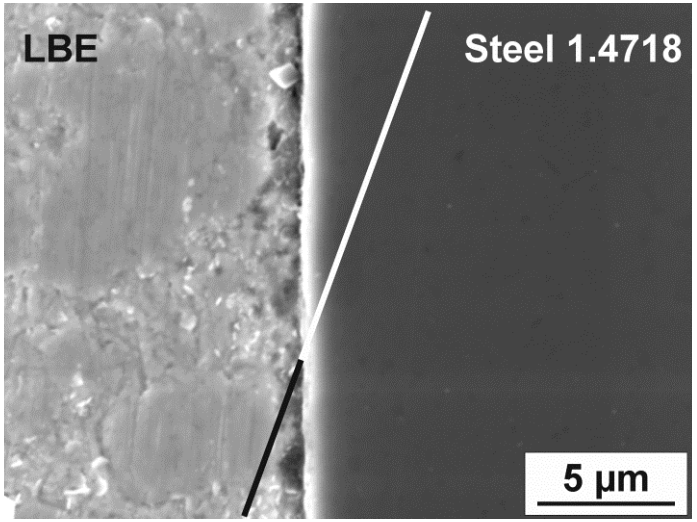
Oxidation in oxygen-containing LBE (1)

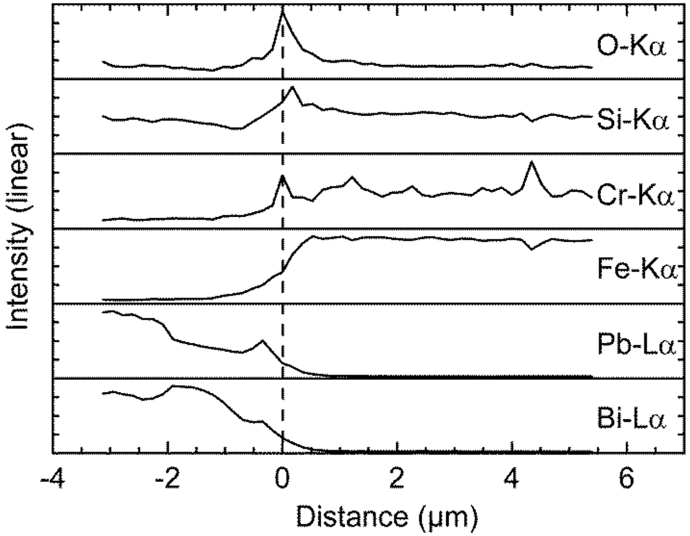
of 9Cr–3Si ferritic/martensitic steel

- ☐ **Protective scaling**
  - Thin Cr- and Si-rich oxide scale (thickness ~1 µm or less)
  - Insignificant growth in thickness with increasing exposure time
  - Negligible release of Fe or other steel elements to the liquid metal

  - Dominant in terms of surface area affected at
    450°C and 10^{-6} mass% O,
    450°C and 10^{-7} mass% O and
    550°C and high c_O
    between $>10^{-6}$ mass% and saturation

8039 h at 450°C/10^{-6} mass% O

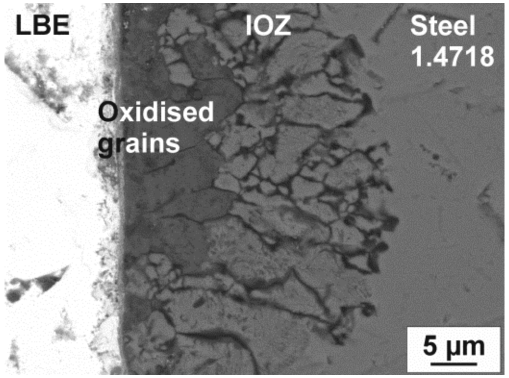




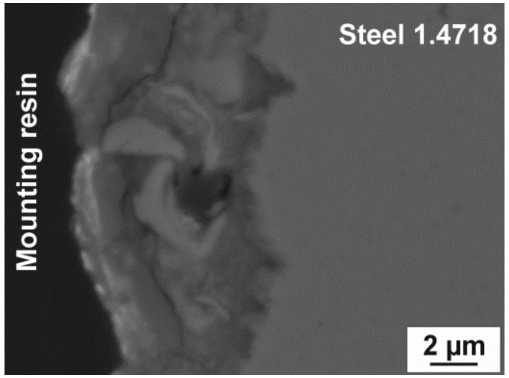
Oxidation in oxygen-containing LBE (2)

of 9Cr–3Si ferritic/martensitic steel

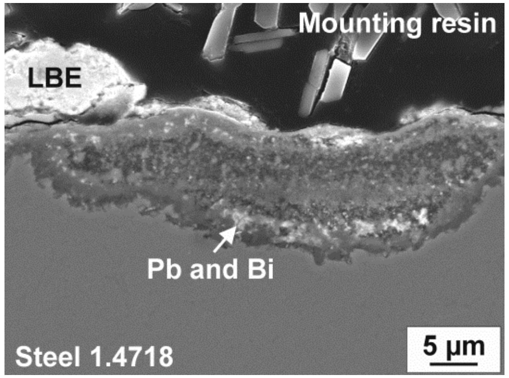
- **Accelerated oxidation**
  - Primarily internal oxidation at 550°C
  - Transition to external oxide formation initiated by complete oxidation of steel grains
  - Inward-growing conglomerate of Si-, Cr- and Fe–Cr oxides
  - External oxides dominate at 450°C, but distinction from internal oxidation not always clear (slight attack)
  - Outward growing Fe oxide in exceptional cases, e.g., at 450°C/10^{-6} mass% O



15,028 h at 550°C/10^{-6} mass% O



3749 h

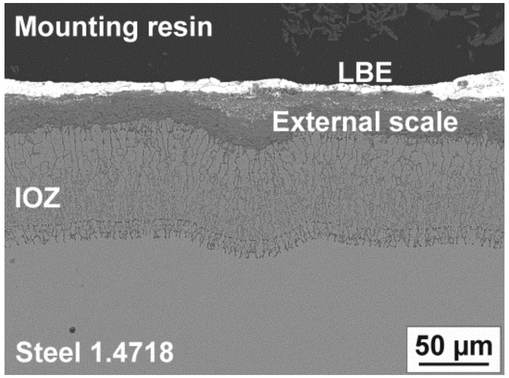


8766 h
at 450°C/10^{-6} mass% O

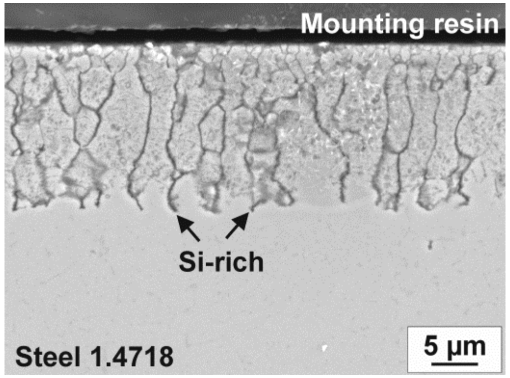
Specific features of accelerated oxidation

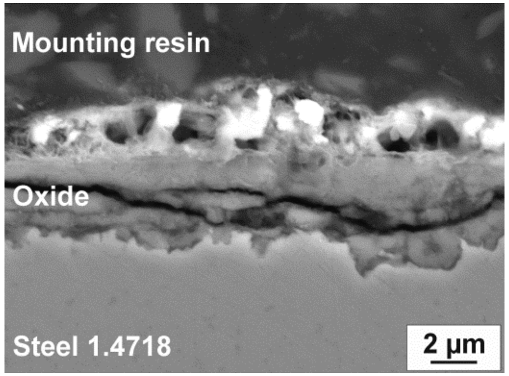
of 9Cr–3Si ferritic/martensitic steel

- **Internal oxidation at 550°C/10^{-6} mass% O**
  - Substantial internal oxidation zone after exposure for 1316, 5012 or 15,028 h
  - Elongated steel grains in the internal oxidation zone (IOZ) and Cr depletion of the steel
  - IOZ with equiaxed steel grains after exposure for 3495 and 12,564 h that is comparatively thin, causing less loss of steel
- **Cracking, detachment, spalling of oxide scales**
  - Especially observed at 550°C and 10^{-6} mass% or varying c_O
  - Compressive stress from inward-growing oxide?
  - Detachment of steel grains completely engulfed by oxides (thin IOZ)?

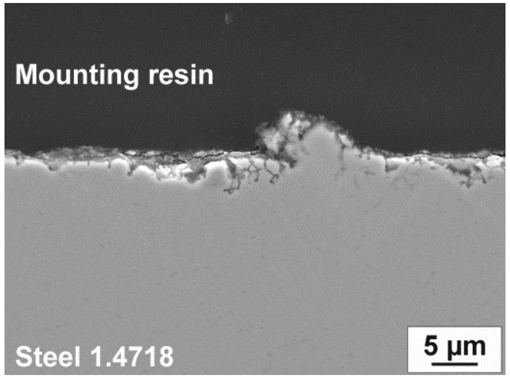


15,028 h
at 550°C/10^{-6} mass% O





2280 h
at 550°C/varying c_O

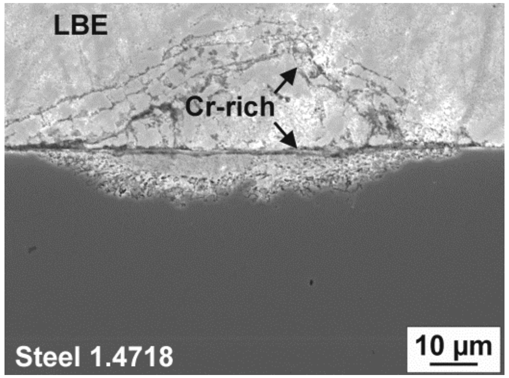


3495 h
at 550°C/10^{-6} mass% O

Solution-based corrosion in oxygen-containing LBE

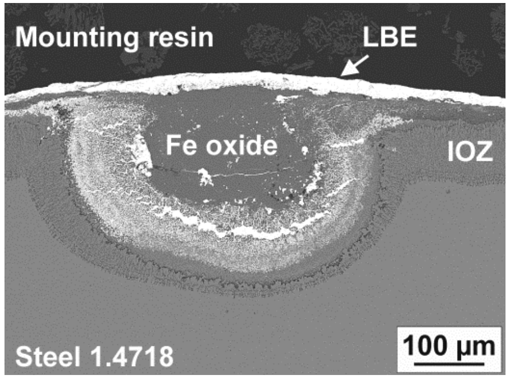
in 9Cr–3Si ferritic/martensitic steel

- **At 450°C/10^{-7} mass% O**
  - Leaching of Cr and re-precipitation as oxide
  - Depth of attack in the order of accelerated oxidation

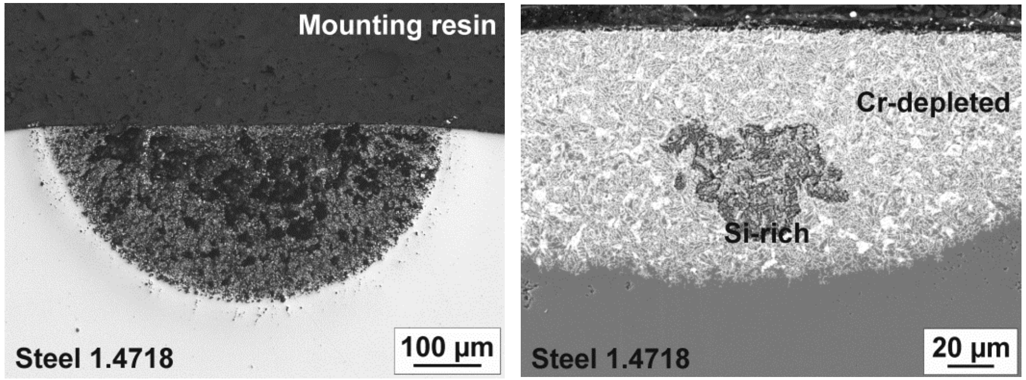


- Not observed at
  - 450°C/10^{-6} mass% O after up to 8039 h
  - 550°C/10^{-7} mass% O after up to 2011 h

- **At 550°C/10^{-6} mass% O**
  - Singular event observed after 15,028 h
  - Prominent participation of oxidation



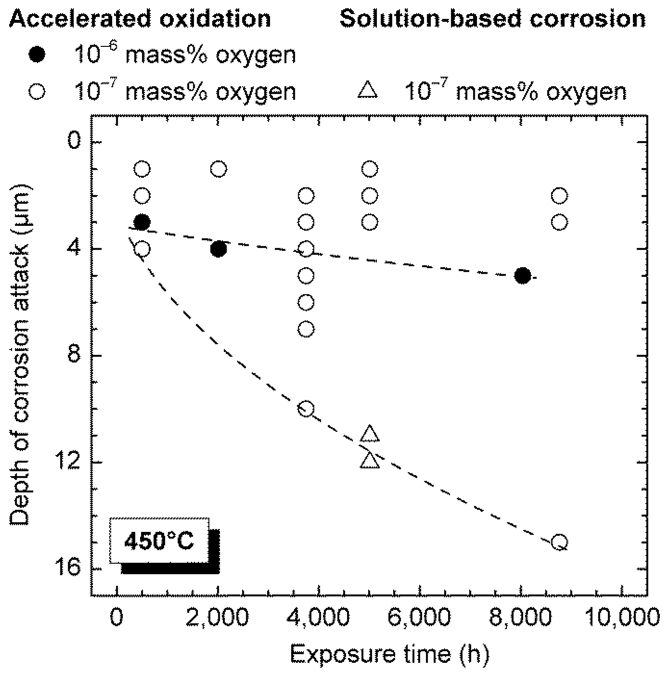
- **At 550°C/varying c_O, between >10^{-6} mass% and saturation**
  - Leaching of Cr and penetration of LBE
  - Comparatively frequent occurrence and high material loss after 1200 h



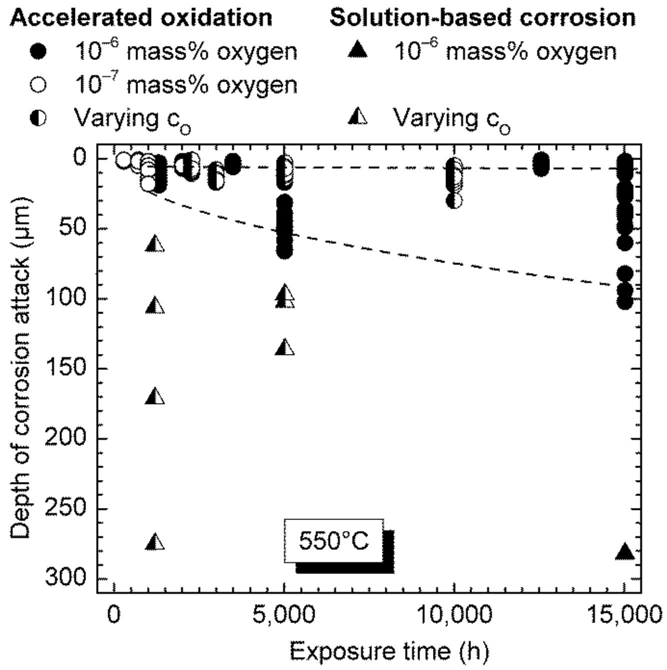
Depth of attack in 9Cr-3Si steel

determined from local corrosion scale thickness or depth of corrosion pits

- **450°C**
  - Local material loss is not particularly severe
  - Overall better performance of 1.4718 at 10^{-6} in comparison to 10^{-7} mass% O solved in LBE

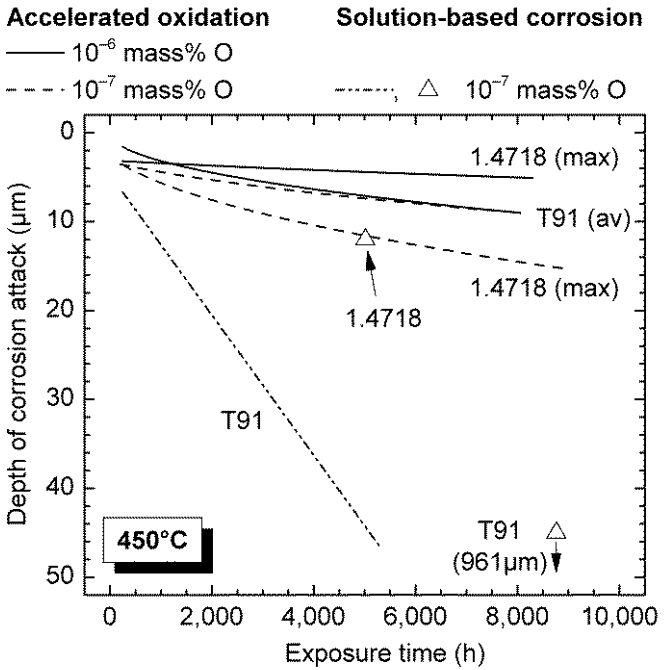


- **550°C**
  - Considerable depth of attack where solution-based corrosion occurs
  - Maximum loss of material due to accelerated oxidation when the thick IOZ forms
  - Quantitatively, no clear difference between accelerated oxidation at 10^{-7} and 10^{-6} mass% oxygen
  - High c_O seems especially detrimental for the performance of 1.4718 (following from exposure for 1200 h to varying c_O, between 10^{-6} mass% and oxygen saturation)



Comparison of 9Cr-3Si and T91

in terms of depth of corrosion attack



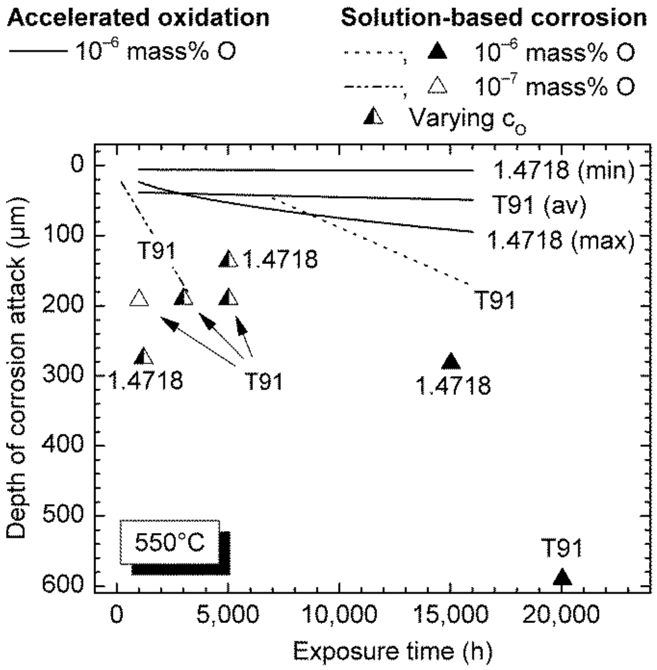
With data for T91 from Schroer et al., J. Nucl. Mater. 356 (2006) 189–197, Nucl. Eng. Des. 280 (2014) 661–672 and Tsisar et al., submitted for publication to Corros. Sci.

☐ 450°C

- Advantages of 1.4718 as to accelerated oxidation especially at 10^{-6} mass% oxygen solved in LBE
- Higher resistance of 1.4718 against local solution-based corrosion at 10^{-7} mass% oxygen

☐ 550°C

- Advantages of 1.4718 as to solution-based corrosion at 10^{-7} mass% oxygen (initial ~2000 h)
- Not so clear at 10^{-6} mass% oxygen, in view of singular events of solution-based corrosion (after >10,000 h)
- Comparatively week performance of 1.4718 at higher c_O
- Relative ranking of the steels in respect of accelerated oxidation depends on the type of IOZ that forms (10^{-6} mass% oxygen)



Conclusions

from exposure of 9Cr–3Si steel in the CORRIDA loop

- **Performance of the Si-containing steel as to corrosion in oxygen-containing flowing LBE is advantageous not in any case:**
  - Clearly favourable performance at 450°C/ 10^{-6} mass% solved oxygen, both in terms of depth of corrosion attack and frequency of occurrence of noticeable corrosion
  - Applies also to 10^{-7} mass% oxygen at 450 and 550°C, but primarily in respect of solution-based corrosion
  - No clear advantage at 550°C/10^{-6} mass% oxygen, in view of internal oxidation as well as singular events of solution-based corrosion
  - 550°C and c_O varying between >10^{-6} mass% and oxygen saturation seem especially detrimental conditions as to solution-based corrosion in the Si-containing steel

Acknowledgements

The construction and operation of the CORRIDA loop was financially supported by the Nuclear Waste Management, Safety and Radiation Research Programme (NUSAFE) of KIT.

Thank you for your attention!