Karlsruhe Institute of Technology

Compatibility of Ferritic/Martensitic Steels with Flowing Lead-Bismuth Eutectic at 450–550°C and 10^{-6} mass% Dissolved Oxygen

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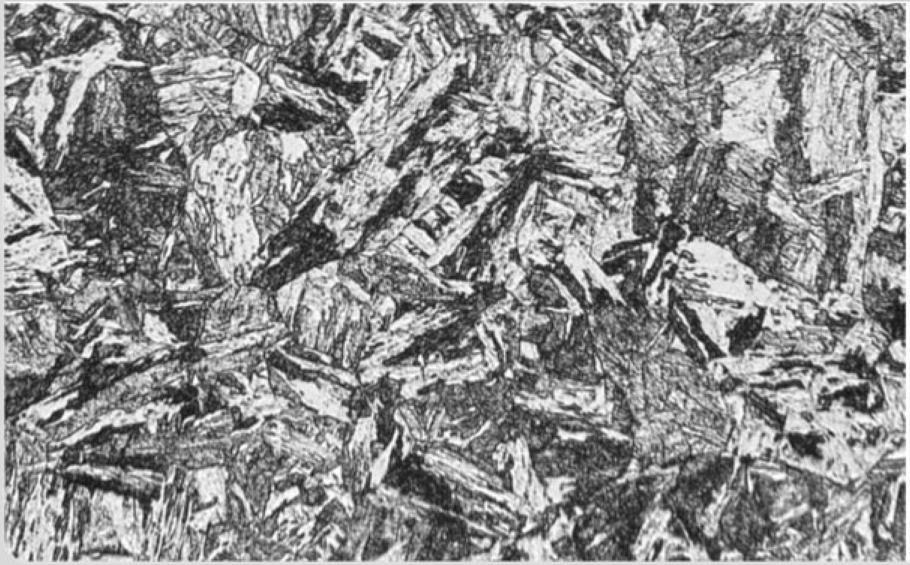
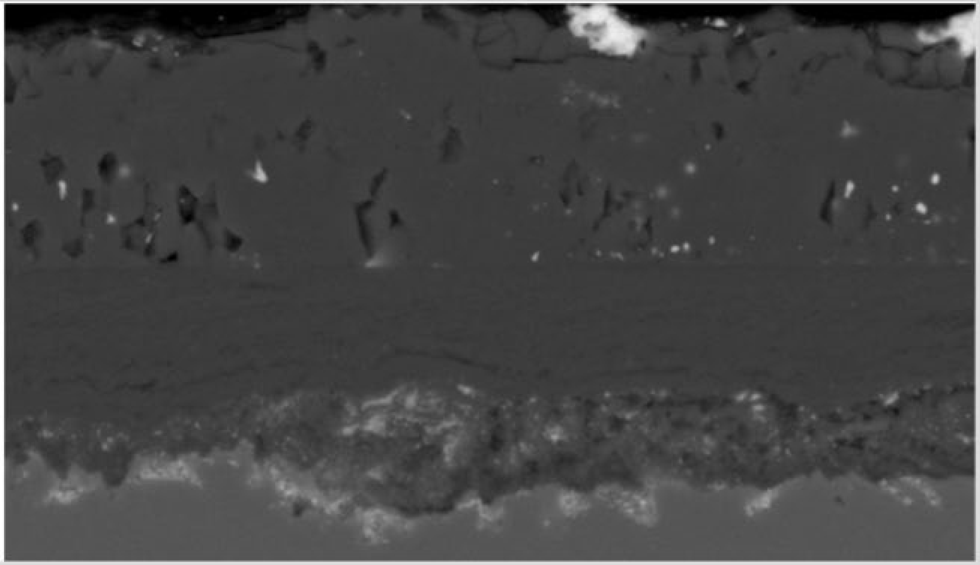
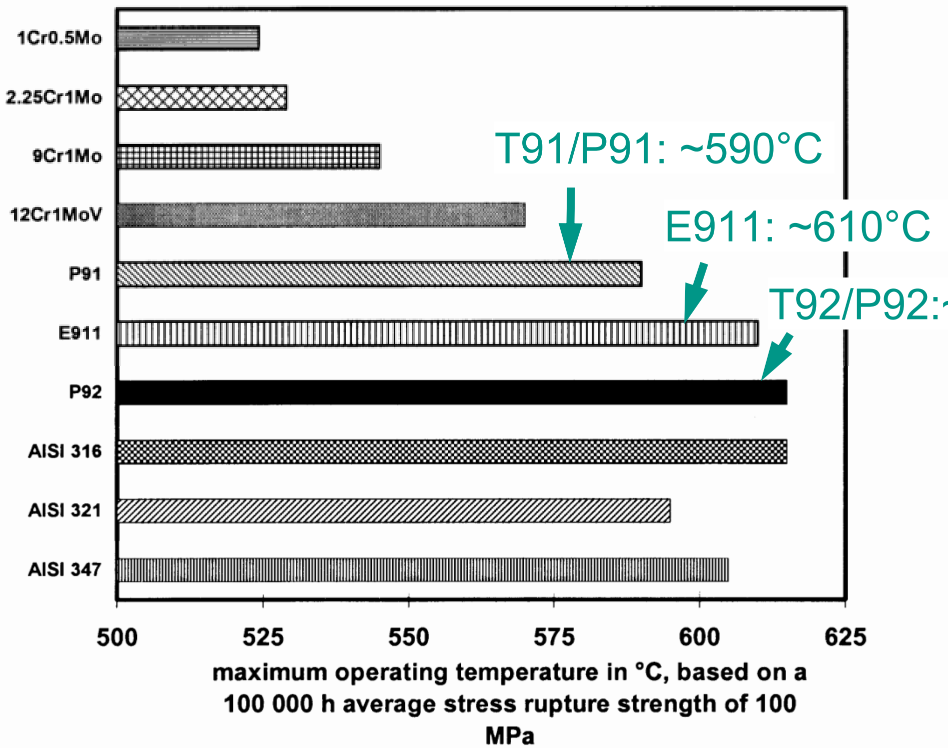




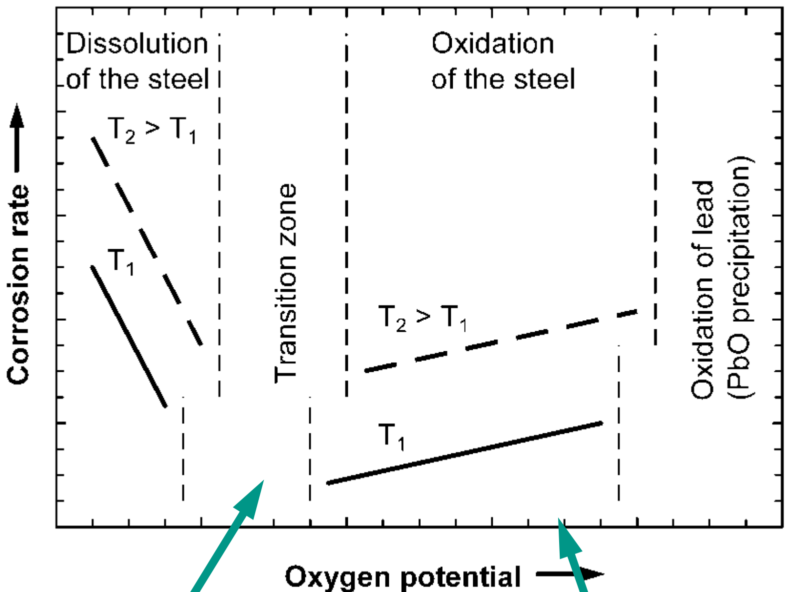
Ferritic/martensitic (FM) steels for nuclear power plants

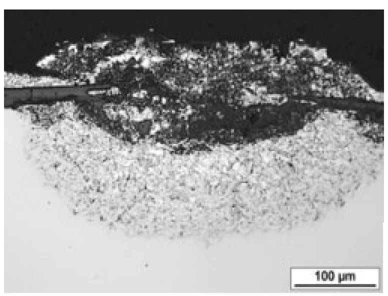


Maximum temperature for 100,000 h stress rupture strength $\sigma_{RS/100,000\ h}$ = 100 MPa according to Ennis and Czyrska-Filemonowicz (Sādhanā 28[3-4], 2003, 709-730)

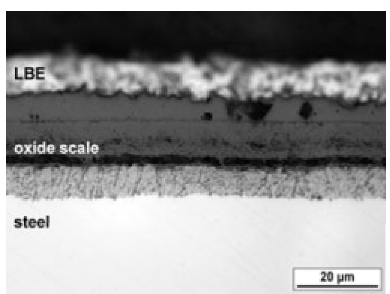
- High-temperature creep strength
  - Comparable to austenitic steel
  - Or likely to be superior (ODS)
- Other favourable properties in comparison to austenitic materials
  - High thermal conductivity
  - Moderate thermal expansion
  - Higher allowable irradiation dose
  - Likely to be less prone to dissolution or embrittlement in liquid metal (important for SFR, LFR, ADS)
- Sufficient long-term resistance against degradation needs to be demonstrated for
  - Thermal ageing
  - Irradiation
  - **Corrosion,** i.e., coolant/steel interactions in nuclear reactors

Impact of oxygen addition to Pb alloys on steel corrosion





Example:
T91/LBE/550°C

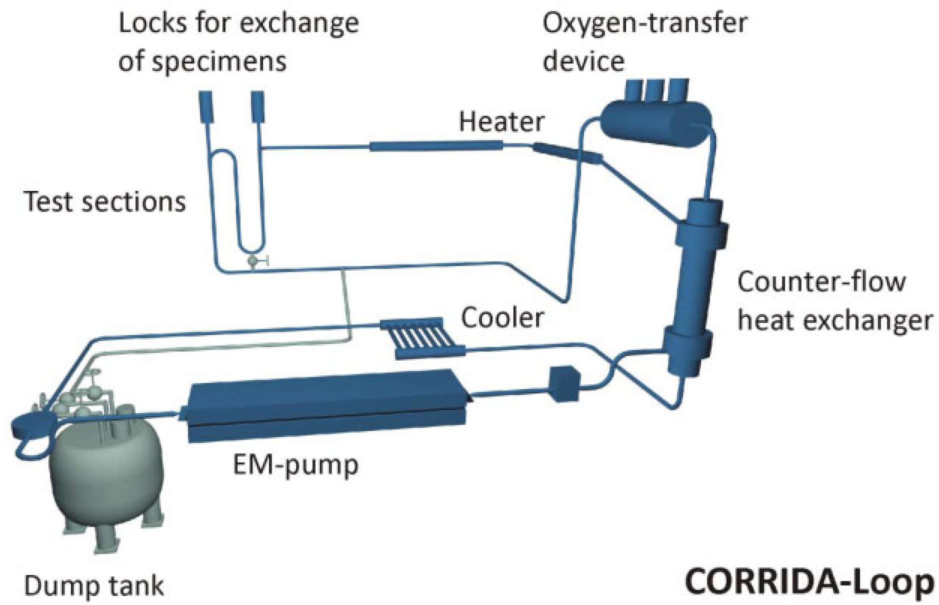


- Stimulation of the oxidation of steel constituents
  - Formation of an oxide scale on the steel surface
  - Spatial separation of the steel from liquid metal
  - Reduced dissolution rate or risk of embrittlement
- Steel constituents must be less noble than the constituents of the liquid metal
  - Applicable to Pb, lead-bismuth
  - Not applicable to lead-lithium (Pb17Li) or Na
- However, thick oxide scales impair heat-transfer across the steel surface
  - Practical limit of oxygen addition

- Relevant to
  - Lead-cooled fast reactor (LFR)
  - Accelerator driven system ("Actinide Burner")

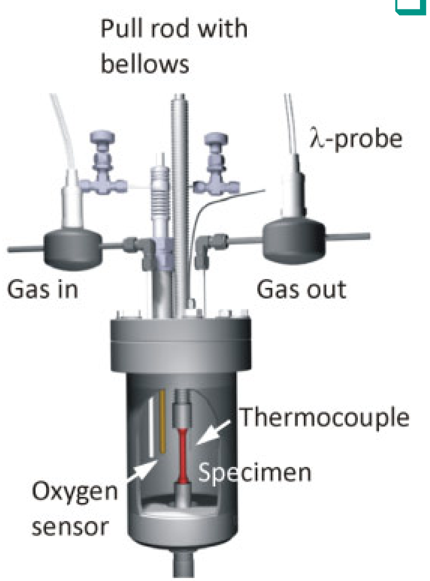
Activities at KIT/IAM-WPT related to ADS and LFR

- Long-term corrosion in oxygen-containing lead-bismuth eutectic (LBE)
  - At a flow velocity of 2 m/s
  - T = 450–550°C
  - $c_O = 10^{-7}–10^{-6}$ mass%

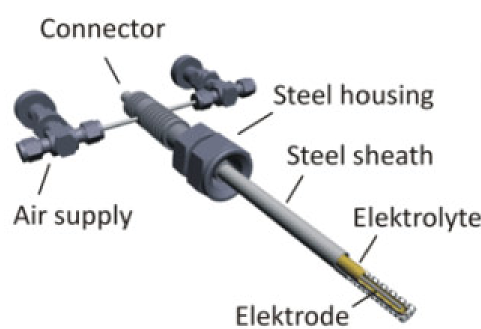


CORRIDA-Loop

- Creep-to-rupture in oxygen-containing Pb alloys
  - Static Pb or LBE
  - T = 450–650°C
  - $c_O = 10^{-7}–10^{-6}$ mass%



CRISLA



- Instruments and methods of oxygen control in Pb alloys
  - Via oxygen-containing gas (gas/liquid oxygen transfer)
  - Oxygen sensors

FM steels tested in the CORRIDA loop

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

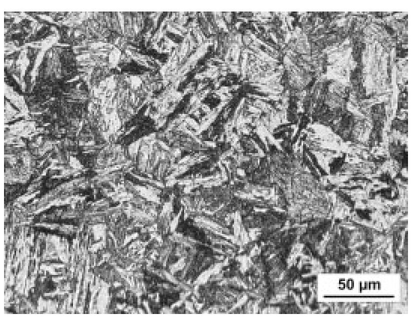
	Cr	Mo	W	V	Nb	Ta	Y	Mn	Ni	Si	C
T91-A	9.44	0.850	<0.003	0.196	0.072	n.a.	n.a.	0.588	0.100	0.272	0.075
T91-B	8.99	0.89	0.01	0.21	0.06	n.a.	n.a.	0.38	0.11	0.22	0.1025
E911*	8.50–9.50	0.90–1.10	0.90–1.10	0.18–0.25	0.060–0.100	–	–	0.30–0.60	0.10–0.40	0.10–0.50	0.09–0.13
EUROFER	8.82	<0.0010	1.09	0.20	n.a.	0.13	n.a.	0.47	0.020	0.040	0.11
EF-ODS-A	9.40	0.0040	1.10	0.185	n.a.	0.08	0.297†	0.418	0.0670	0.115	0.072
EF-ODS-B	8.92	0.0037	1.11	0.185	n.a.	0.078	0.192†	0.408	0.0544	0.111	0.067

* Nominal composition
† In the form of yttria (Y_2O_3)

Nominally 9 mass% Cr

Elements besides Cr that are likely to improve oxidation performance

Microstructure

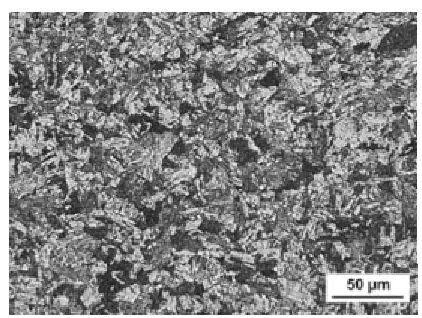


Fully martensitic: E911, T91-A

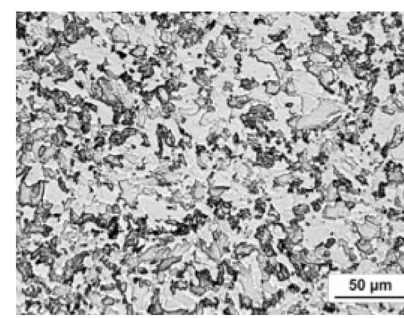
T91-B

Grain size

EUROFER



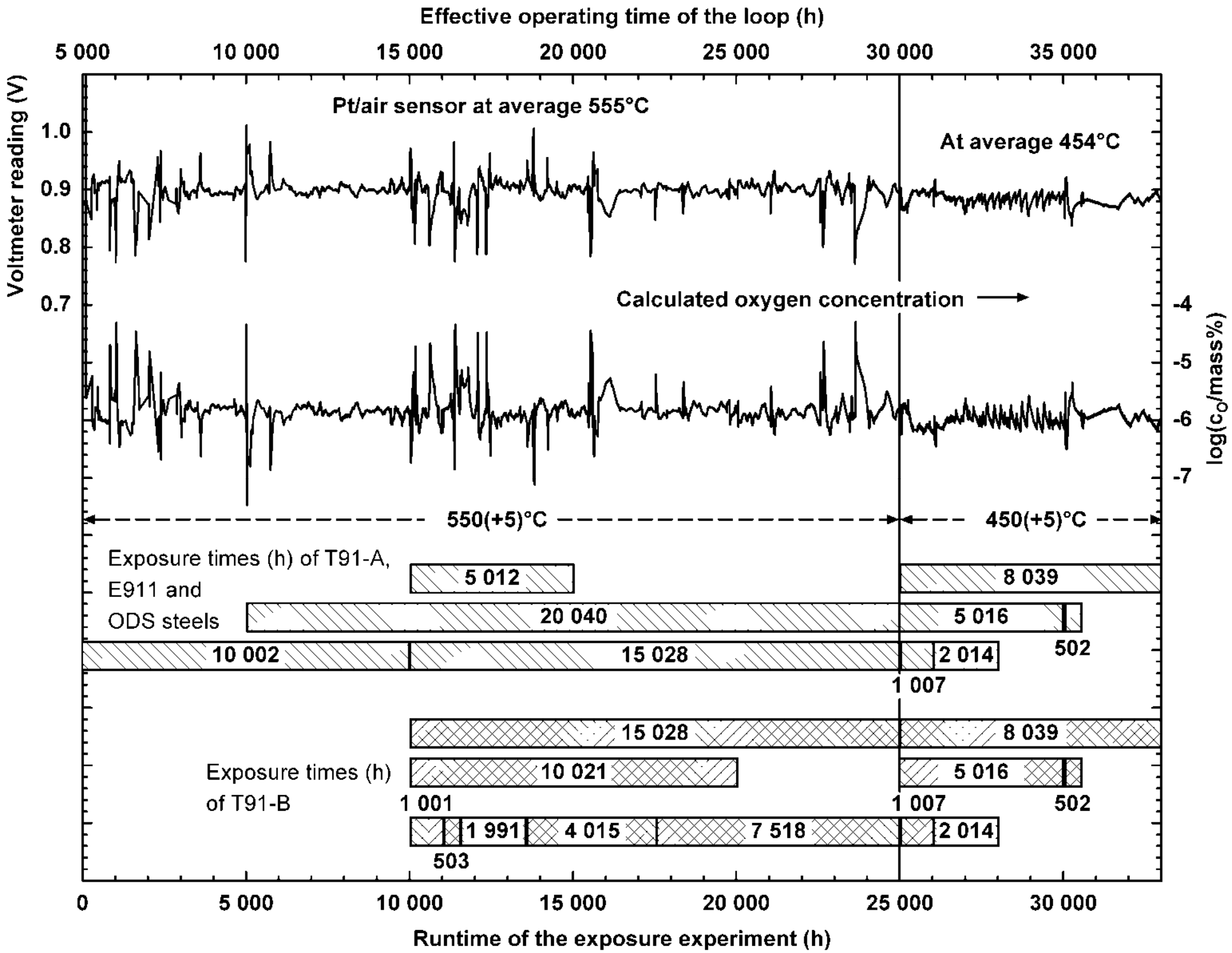
Mainly ferritic: ODS-A, ODS-B



Exposure to flowing LBE (1)

T91-A, T91-B, E911, EF-ODS-A, EF-ODS-B

- T = 450(+5)°C,
  c_O = 1.1×10^{-6} mass%,
  v = 2(+/–0.2) m/s,
  t ≤ 8000 h
- T = 550(+5)°C,
  c_O = 1.4×10^{-6} mass%,
  v = 2(+/–0.2) m/s,
  t ≤ 20,000 h,
  except for T91-B
- T91-B:
  T = 550(+5)°C,
  c_O = 1.6×10^{-6} mass%,
  v = 2(+/–0.2) m/s,
  t ≤ 15,000 h



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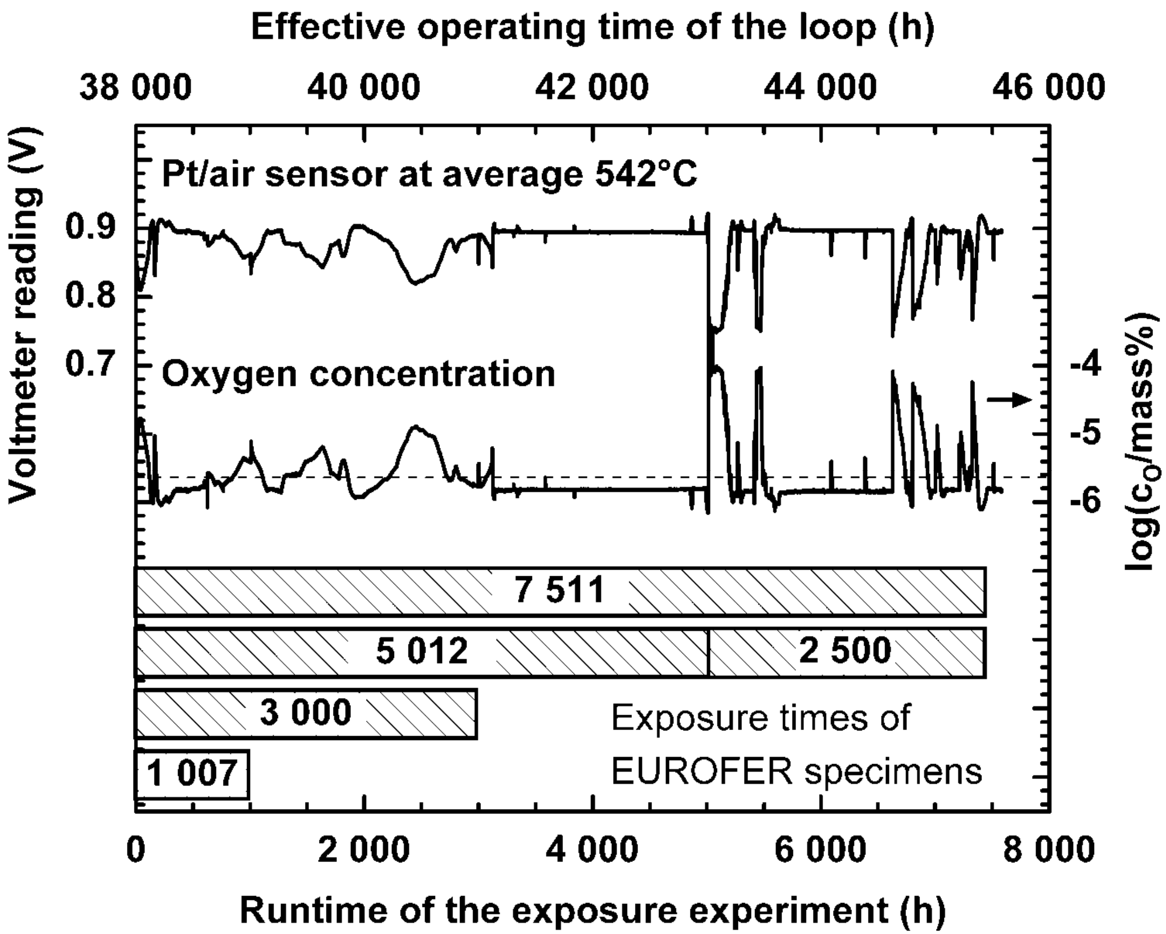
Exposure to flowing LBE (2)

EUROFER

- T = 550(+5)°C,
  c_O = 1.3–2.3×10^{-6} mass%,
  v = 1.8(+/–0.5) m/s,
  t ≤ 7500 h



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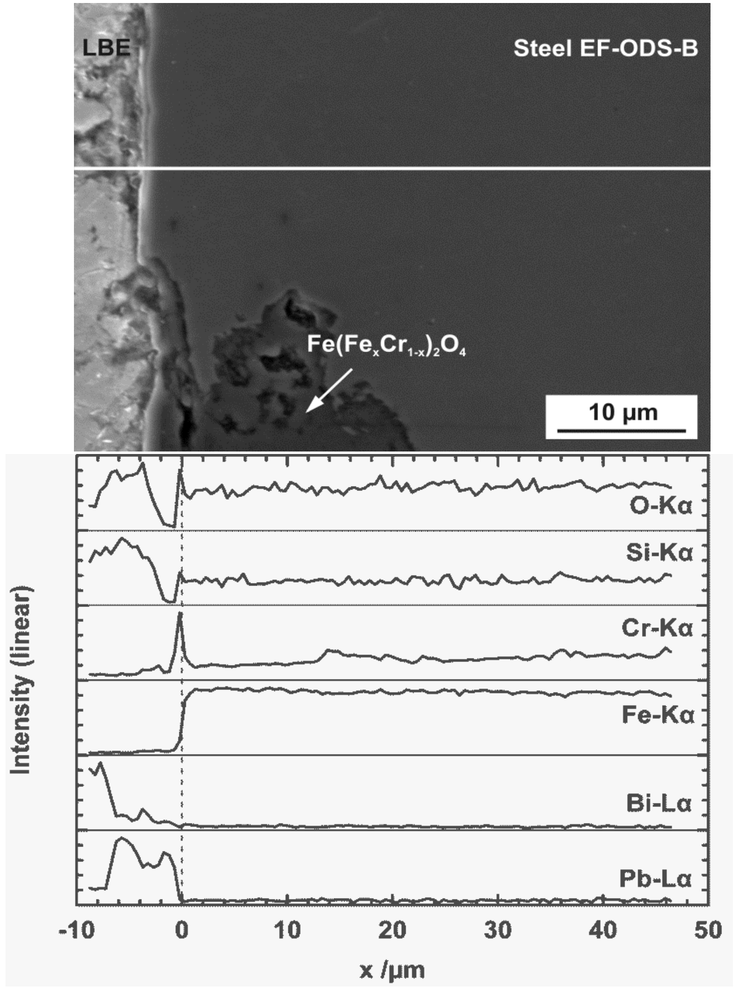
Oxidation of F/M steels in flowing LBE at 450–550°C: Protective scaling

- Formation of a thin Cr-rich oxide scale
  - Probably chromia (Cr_2O_3)
  - Negligible scale growth or metal recession
- Either a local or short-term phenomena at 9% Cr
  - Rarely observed for E911 at 450°C
  - Remnants found in considerably thicker oxide scale on T91 at 550°C
  - ✘ Thin scale forms more frequently or is more persistent for EF-ODS at 450°C and especially at 550°C
  - ✘ Protected domains present on EUROFER at 550°C after longest exposure time (7500 h)
- Fine-grained microstructure is likely to be decisive rather than slightly different Cr content



EF-ODS-B after exposure for 20,039 h at 550°C

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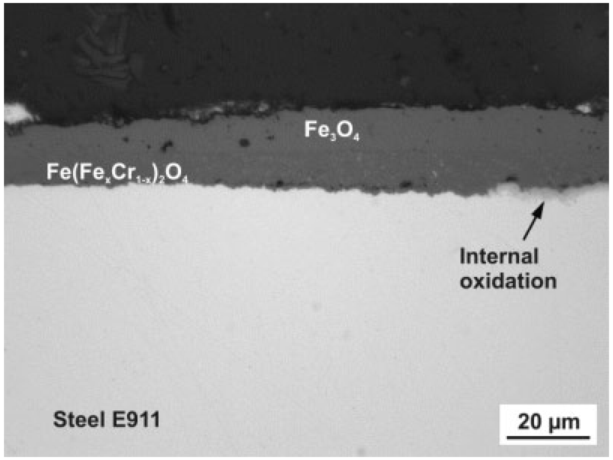
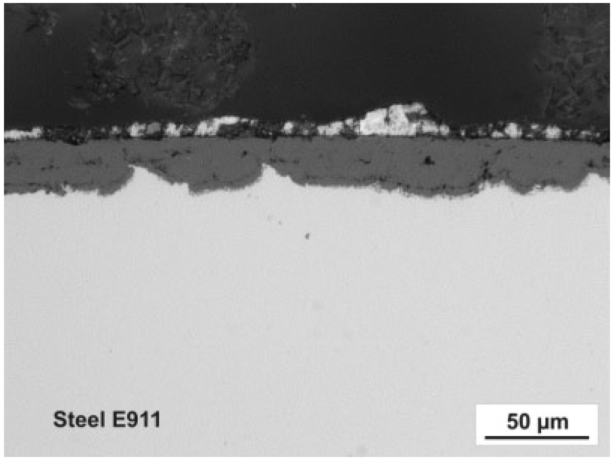
Oxidation of F/M steels in flowing LBE at 450–550°C: Accelerated oxidation

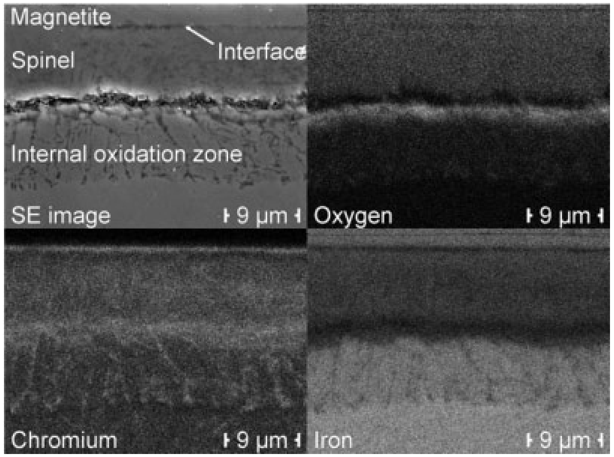
- The formed scale typically consists of three layers:
  - Magnetite (Fe_3O_4) at the interface with the LBE
  - Cr-deficient spinel, i.e., $Fe(Fe_xCr_{1-x})_2O_4$
  - Internal oxidation zone (IOZ)
- Magnetite is usually missing at 550°C/10^{-6} mass% O
  - Fe dissolution instead of magnetite formation
- Internal oxidation is negligible at 450°C/10^{-6} mass% O, except for EF-ODS
- Likely to start where the thin protective scale did not form or lost integrity
  - Cr enrichment at Fe_3O_4 / $Fe(Fe_xCr_{1-x})_2O_4$ interface
  - Oxide filled pits or irregular scale thickness where growing pits abutted onto each other



E911 after exposure for 8039 h at 450°C



E911 after exposure for 5012 h at 550°C



T91-A after exposure for 1200 h at 550°C and $10^{-5} < c_O$/mass% $< 10^{-6}$

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Oxidation of F/M steels in flowing LBE at 450–550°C: Direct liquid-metal attack

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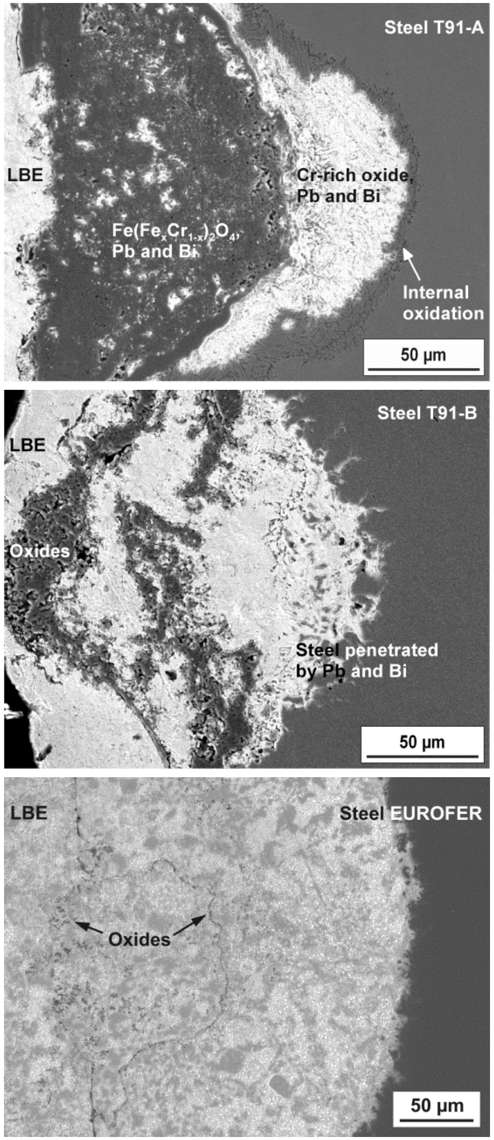
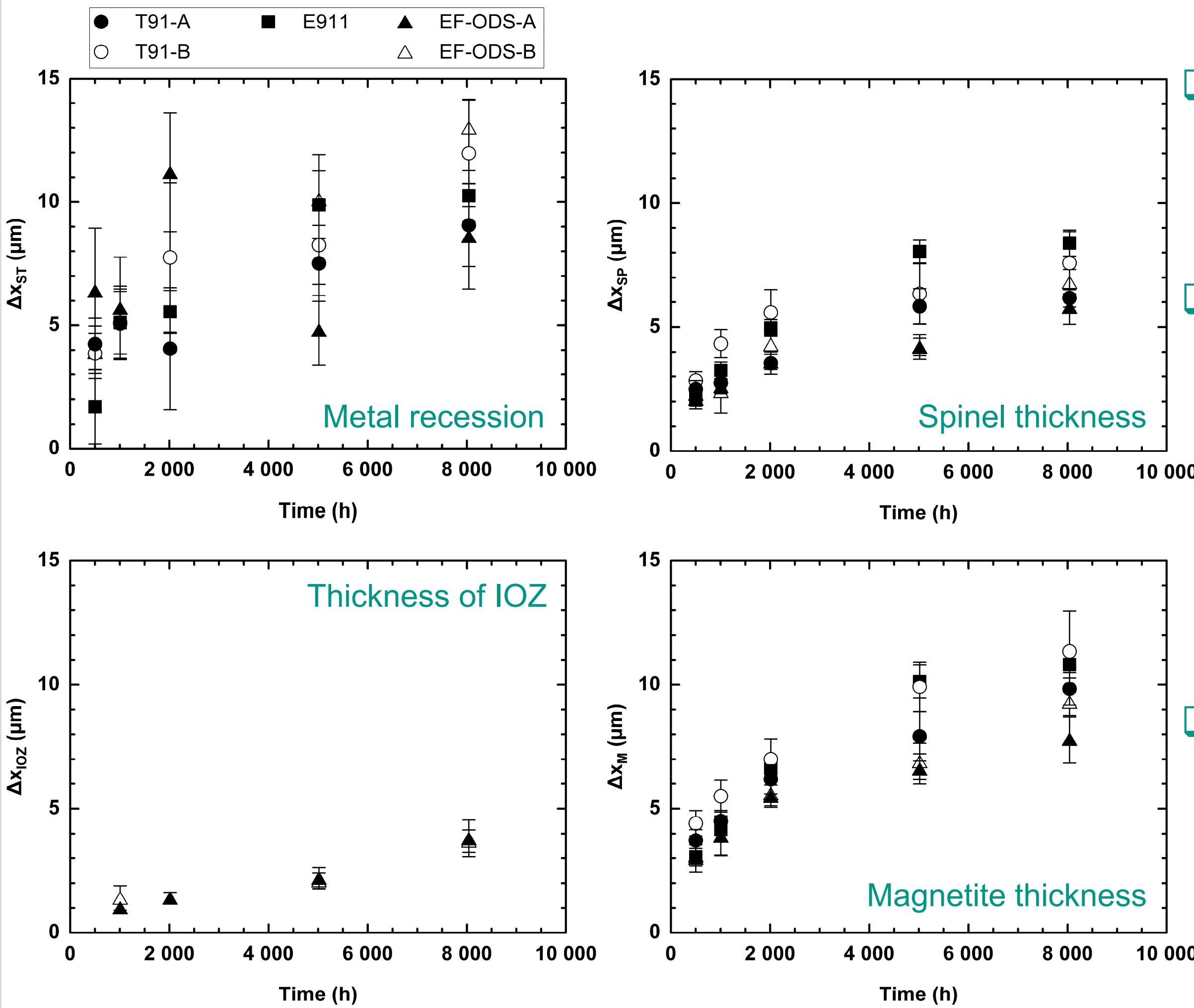
- After accumulation of LBE underneath the oxide scale
  - May occur for both the thin and thicker scale
  - Different outcome depending on oxide scale composition or structure
  - Observed only once at 450°C, for E911 after 8039 h
  - Occurred more frequently at 550°C than at 450°C
  - EUROFER seems to be especially prone to direct liquid-metal attack at 550°C (under certain conditions)
- Substantial local loss of material
  - E911: ~125 µm after 8000 h at 450°C
  - EUROFER: ~200 µm after 3000 h at 550°C
  - T91- A, -B: ~200 and 150–175 µm, respectively, after 15,000 h at 550°C
  - EF-ODS-B: ~60 µm after 15,000 h at 550°C
  - Depends not only on the corrosion rate but also on incubation time
- Potentially initiated by, e.g.,
  - Open porosity of the oxide scale
  - Local scale detachment
  - Cracking of the scale



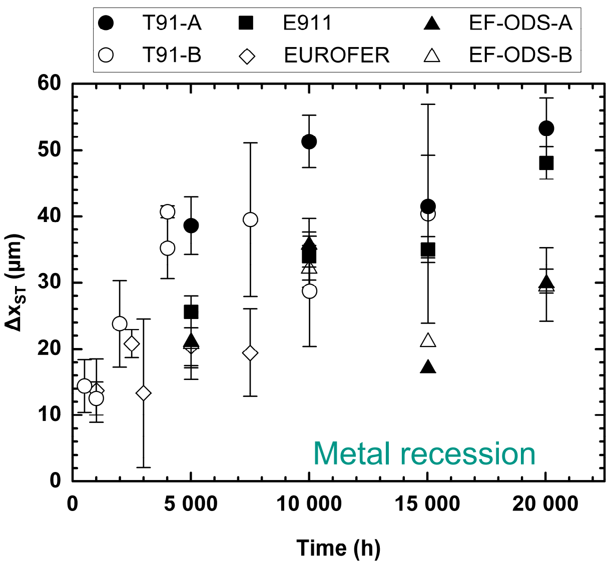
After exposure at 550°C for
(top) 15,028 h
(middle) 7518 h
(bottom) 3000 h

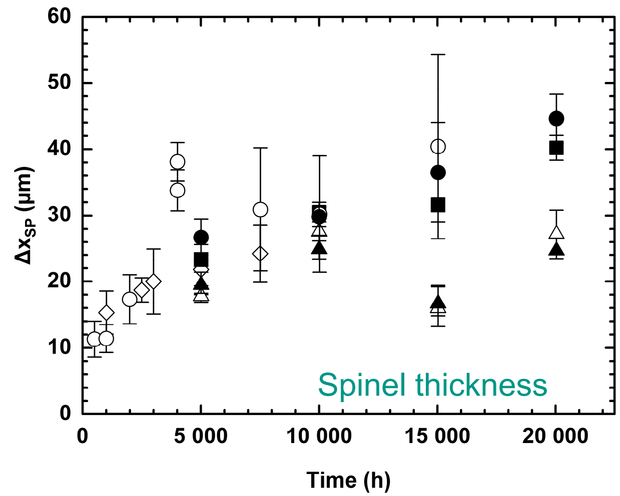
Quantification of accelerated oxidation in flowing LBE: At 450°C, 10^{-6} mass% O, 2 m/s

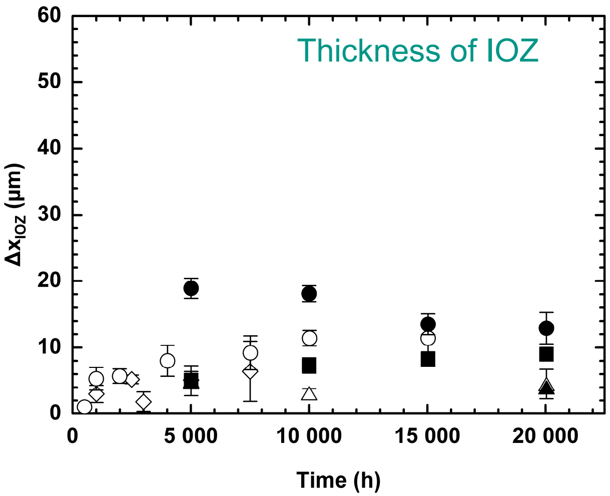


- Results from measurements in the microscope
  - Comparatively large scatter in the data for metal recession
- Data indicates slower-than-parabolic oxidation kinetics for metal recession, magnetite and spinel growth
  - Rate laws were derived on the basis of the general power law
    $\Delta x^n = k_n t + C_n$
- Corrosion rate decreases with increasing Cr content for same type of steel
  - T91-A/T91-B
  - EF-ODS-A/EF-ODS-B

Quantification of accelerated oxidation in flowing LBE: At 550°C, 10^{-6} mass% O, 2 m/s







- Increase in corrosion rate by factor 2–3 in comparison to 450°C
  - Absolute difference between materials increases
  - Scatter in the data increases
- Data indicates slower-than-parabolic oxidation kinetics for metal recession and spinel growth
  - Scatter and missing data for <5000 h aggravates the analysis of the kinetics
- EUROFER and especially EF-ODS perform slightly better than T91 or E911
  - Mainly an effect of fine-grained microstructure

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Summary

- F/M steels with 9%Cr show three stages of oxidation in flowing LBE at 450–550°C, 10^{-6} mass% dissolved oxygen, 2 m/s
  - Protective scaling – short term or local phenomenon
  - Accelerated oxidation – the general degradation mechanism
  - Direct liquid-metal attack – locally, after accumulation of liquid metal underneath the oxide scale
- Fine-grained microstructure rather than (slightly) higher Cr content promotes protective scaling
- Average rate of accelerated oxidation is lower
  - For higher Cr-content at 450°C
  - For fine-grained materials at 550°C
- Observed kinetics of accelerated oxidation is slower than parabolic
  - Corrosion rate increases by factor 2–3 for increase in temperature from 450 and 550°C
- Liquid metal attack shows
  - Different outcome depending on the actually formed oxide scale
  - High local material loss in comparison to accelerated oxidation, e.g., increase by factor 10 for EUROFER at 550°C and E911 at 450°C, by factor 3–5 for T91 and EF-ODS at 550°C

Acknowledgements

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