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Corrosion Aspects of Structural Materials in Presence of Heavy Liquid Metals (LBE) at 450–550°C and 10^{-6} mass% Dissolved Oxygen

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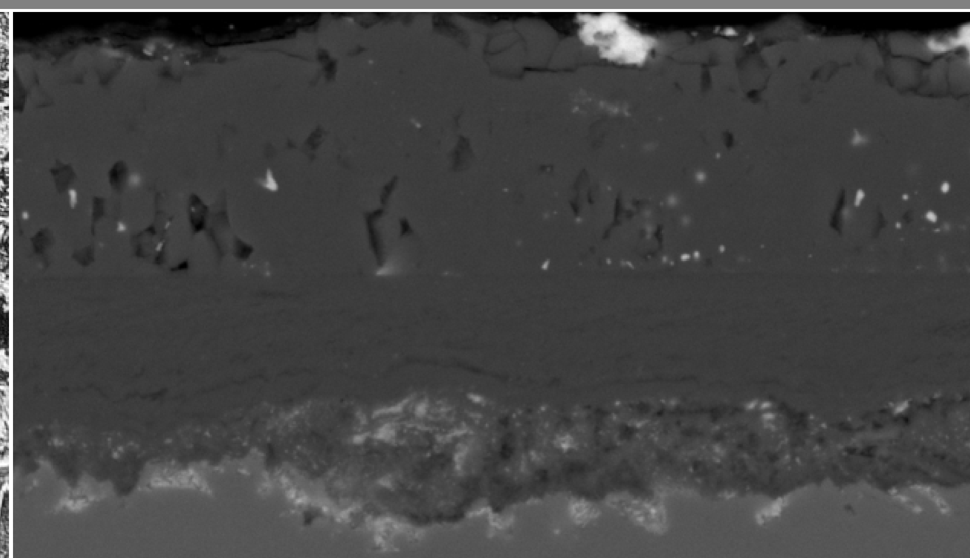
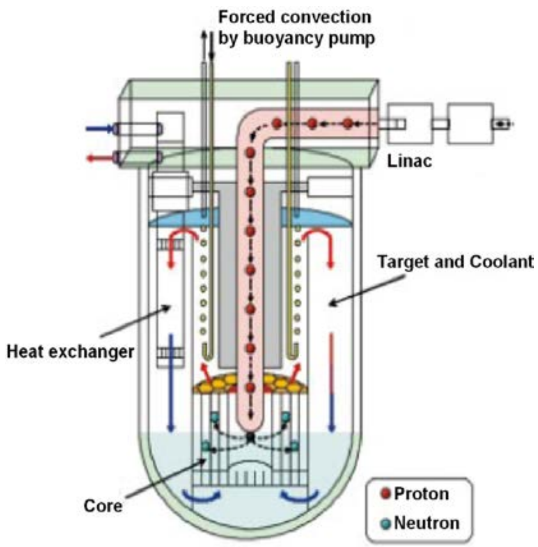


Lead-cooled Nuclear Reactors/Systems

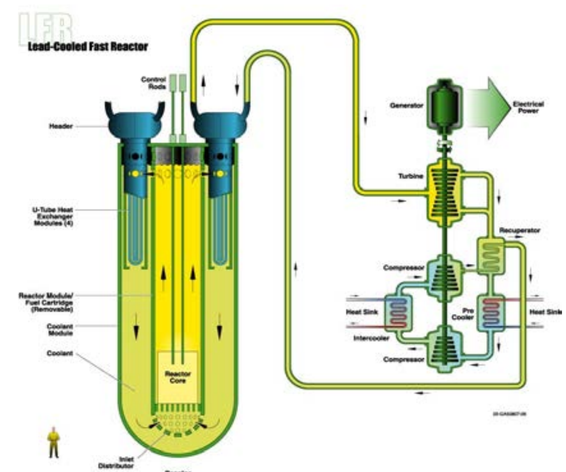


Accelerator Driven (Subcritical) System

- Transmutation of long-lived radioactive isotopes in nuclear waste
- Power generation
- Liquid lead (Pb) or lead-bismuth eutectic (LBE) as spallation target and primary coolant
- Maximum temperature, typically
  - 450 – 500°C for regular operation
  - Periodically 550°C (according to plant design)

Lead-Cooled Fast Reactor

- One of the concepts for the 4th generation of nuclear power plants (Gen IV)
- In the long-term, Pb as primary coolant at maximum ca. 800°C
- Short- to mid-term: Pb- or LBE-cooled at 450 – 550°C



Funding Sources for Nuclear Research at KIT

Project Partner/Collaborations:

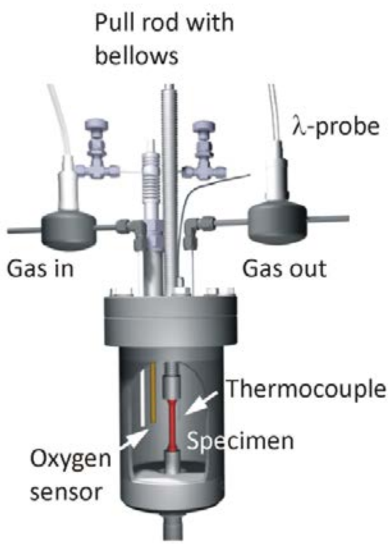
Fusion For Energy
EFDA
<u>EU-Programmes</u>
GETMAT
MATTER
SEARCH
MatISSE
IBRAE

Indira Gandhi Centre for Atomic Research

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

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

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



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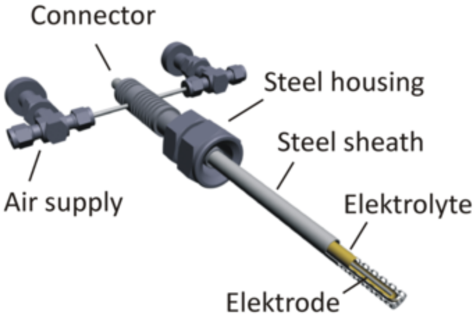
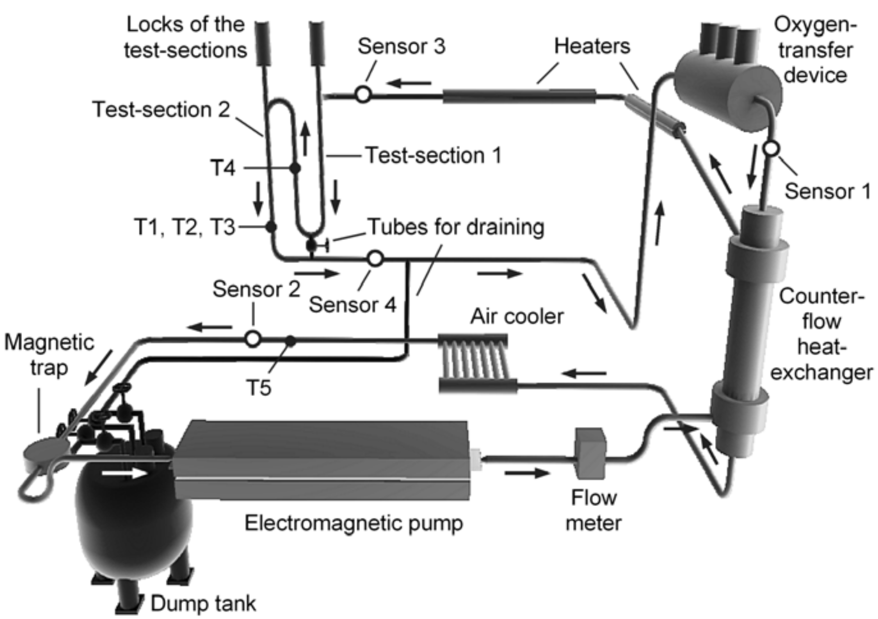


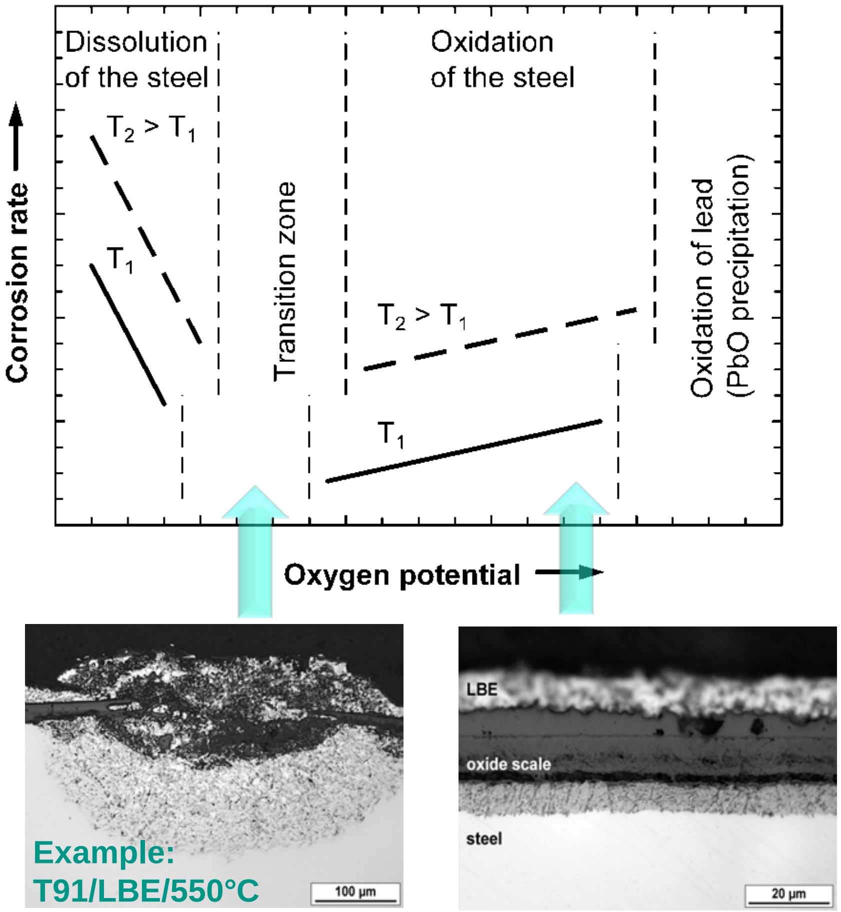
- Instruments and methods of oxygen control in Pb alloys
  - Via oxygen-containing gas
  - (gas/liquid oxygen transfer)
  - Oxygen sensors

CORRIDA: Corrosion-testing in dynamic lead alloys



- **Technical data**
  - Material: SS 316-Ti (DIN 1.4571)
  - Developed length: 36 m
  - Liquid metal: ~1000 kg LBE
  - Mass flow: 5.3 kg/s (steady state)
  - T_{max} = 550°C (test-sections, oxygen control-box)
  - T_{min} = 350–385°C depending on T_{max} at inlet of EM-pump
  - Oxygen control:
  - Gas with adjustable O_2-content introduced at T_{max}
- **Operating data**
  - Commissioning in July 2003
  - ca. 70,000 h of effective operation at Tmax = 450 to 550°C
  - Longest exposure time of specimens: 20,000 h

Impact of oxygen addition to Pb alloys on steel corrosion



- **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")

Oxygen transfer from gas to flowing LBE at 550°C

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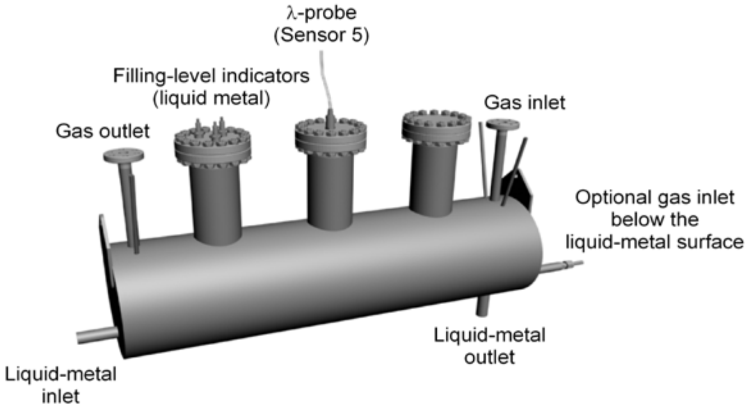
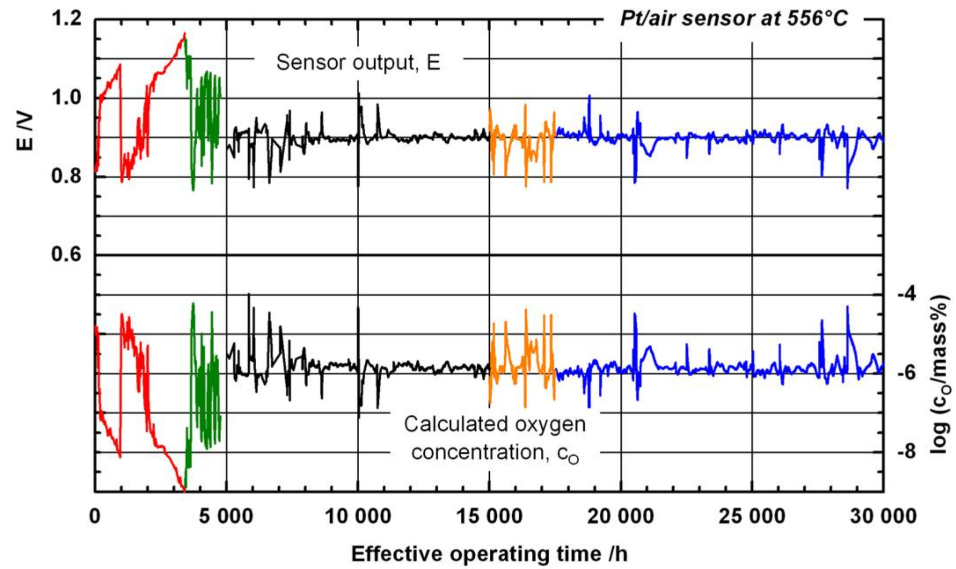
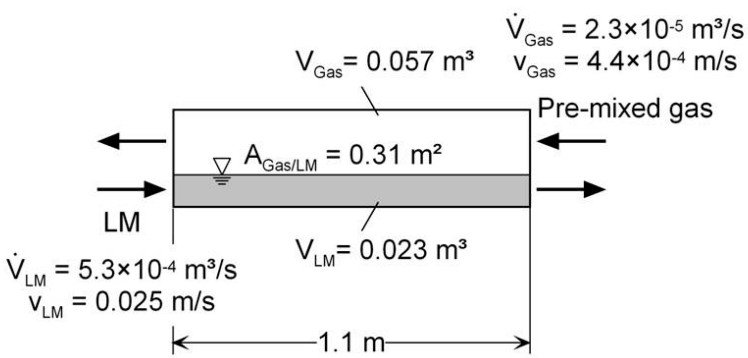
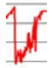
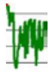








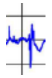
- Ar + Ar-5%H_2 (135:1) humidified at 4°C
- Gas flow: 500 cm³/min (referred to 25°C)



- Discontinous addition of air to humidified Ar-H_2

- Continous addition of 1-1.5 cm³/min air to humidified Ar-H_2

- 500 cm³/min dry Ar
- 1-1.5 ml/min air



- 500 cm³/min Ar humidified at 18°C
- 1-1.5 cm³/min air

FM steels tested in the CORRIDA loop

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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

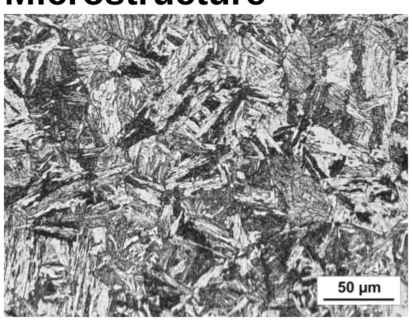
* Nominal composition
† In the form of yttria (Y_2O_3)

Nominally 9 mass% Cr

⇧ ⇧ Elements besides Cr that are likely to improve oxidation performance

Mainly ferritic: ODS-A, ODS-B

Microstructure

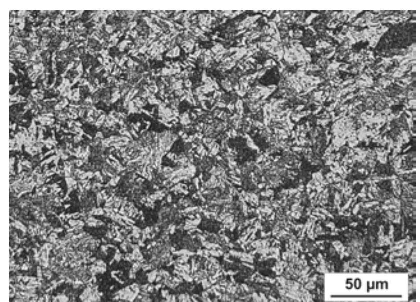


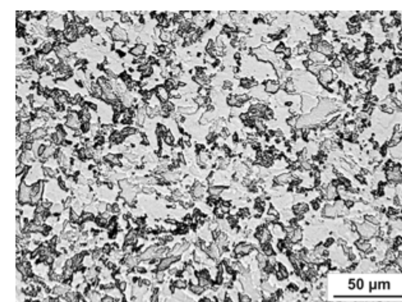
Fully martensitic:
E911, T91-A

T91-B

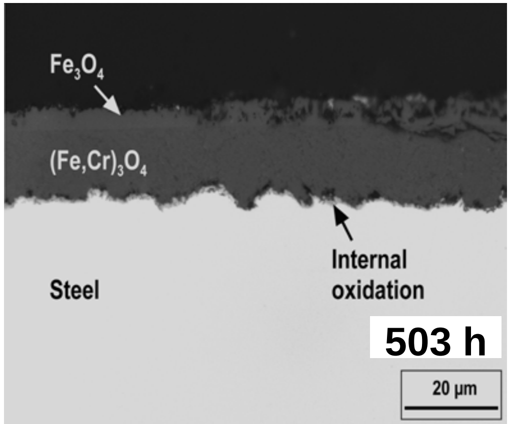
Grain Size

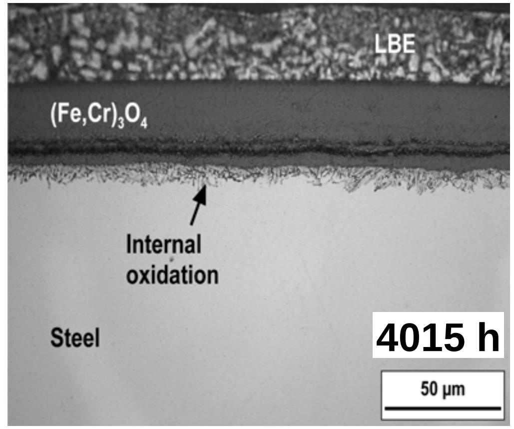
EUROFER

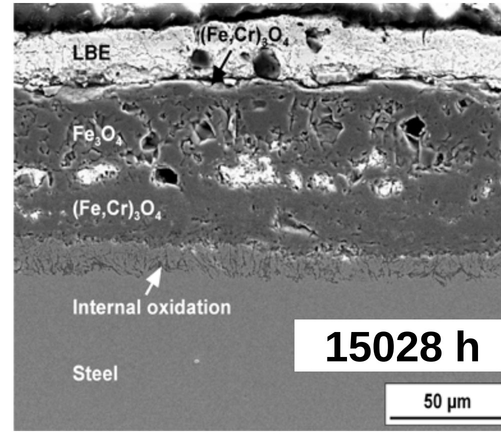




T91: Qualitative performance in oxygen-containing LBE at 550°C, v = 2 m/s and $c_O = 1.6\times10^{-6}$ mass% (I)



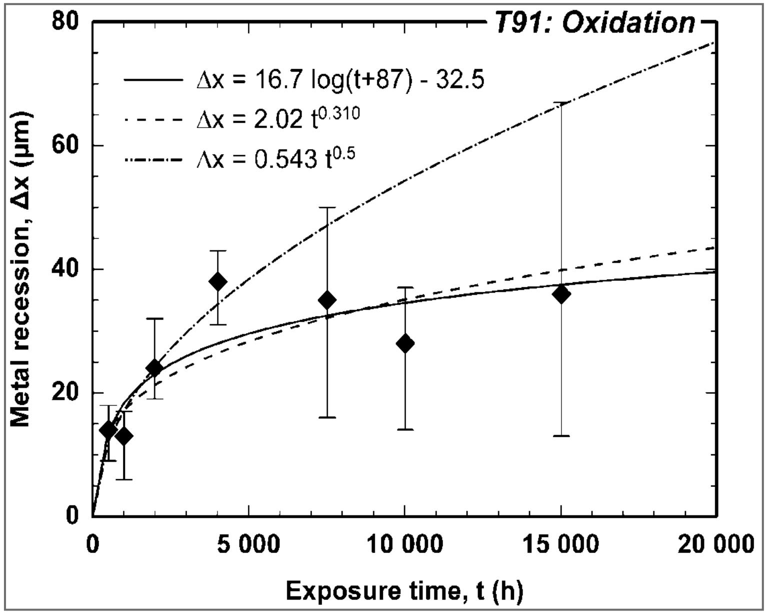




- Oxidation
- Oxide scale consists of
  - Magnetite (Fe_3O_4)
  - Cr-deficient spinel ($Fe(Fe_xCr_{1-x})_2O_4$)
  - Internal Oxidation Zone (IOZ)
- Magnetite is mostly missing, i. e., Fe is partially dissolved by the liquid metal (or eroded after Fe_3O_4 formation?)
- Inclusions of Pb and Bi inside the scale, espesially after long exposure times

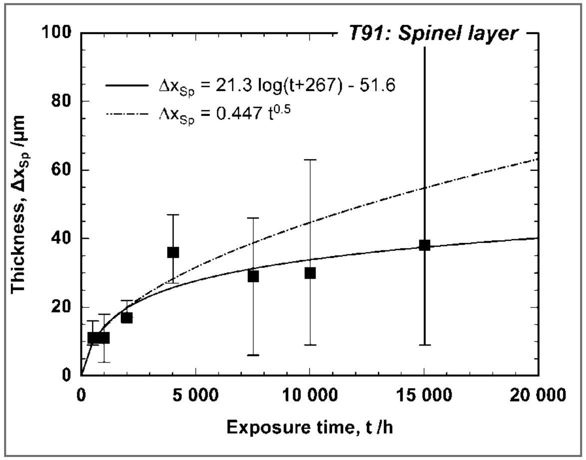
T91: Quantification of oxidation in oxygen-containing LBE at 550°C, v = 2 m/s and $c_O = 1.6\times10^{-6}$ mass% (II)

- **Metal recession (loss of cross-section)**
- **Compromises the structural integrity of plant components**
- **Determined from measurements in the LOM (generally six measurements per investigated cross-section)**
- **Includes internal oxidation**



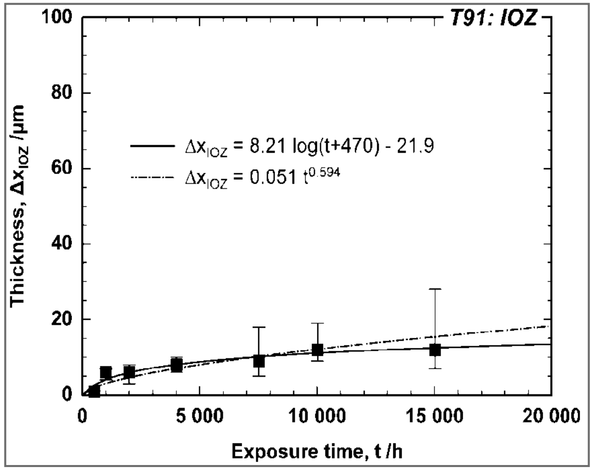
- **Local variation significantly increases with increasing exposure time**
- **Optimistic prediction: 50–70 µm after 100,000 h**
- **Worst-case: 100 µm after 4 years**

T91: Quantification of oxidation in oxygen-containing LBE at 550°C, v = 2 m/s and $c_O = 1.6\times10^{-6}$ mass% (III)

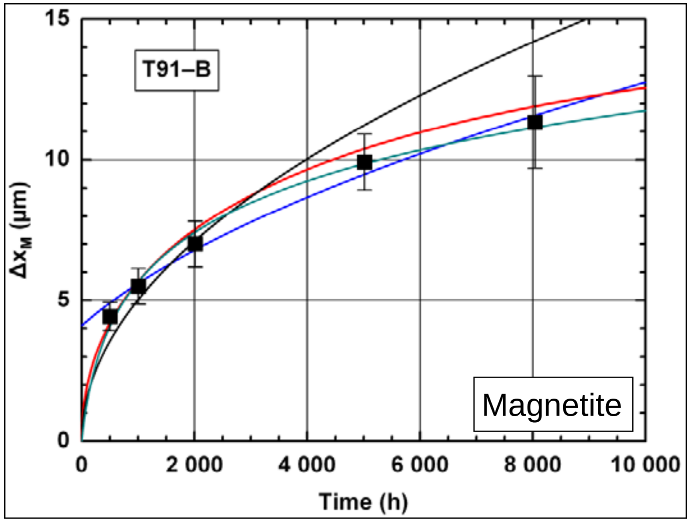


- Thickness of different layers of the oxide scale
- May affect heat transfer in the case of thermally-loaded plant components
- Generally twelve measurements per investigated cross-section
- Thickness of spinel layer significantly varies locally with increasing exposure time
- Average thickness of the spinel layer is in the order of the metal recession

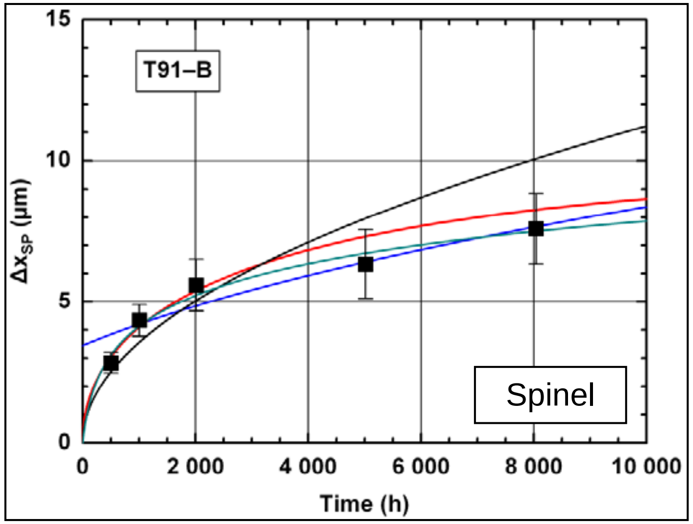
Fe flux into the LBE can be estimated from the spinel layer thickness



Kinetics of oxide-scale growth for T91-B at 450°C, 2 m/s and 10^{-6} mass% oxygen (I)

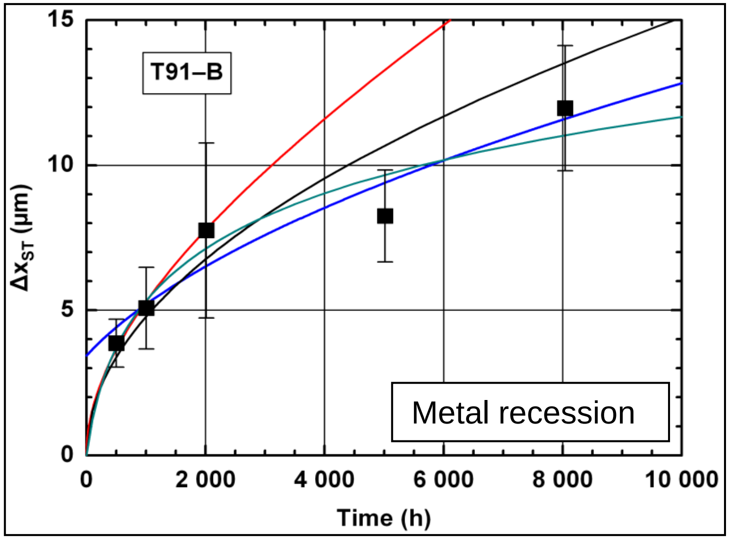


Parabolic:	$\Delta x^2 = k_2 t$
Parabolic after faster initial kinetics:	$\Delta x^2 = k_2 t + C_2$
Logarithmic:	$\Delta x = k_{log} \log (t + t_0) + C_{log}$
Paralinear:	$\frac{d\Delta x}{dt} = \frac{k_p}{d\Delta x} + k_1$



- **Local internal oxidation was not considered**
- Thickness of the oxide layers slightly lower (by ~20%) for T91-A

Data extrapolation for T91 at 450°C, 2 m/s and 10^{-6} mass% oxygen (II)

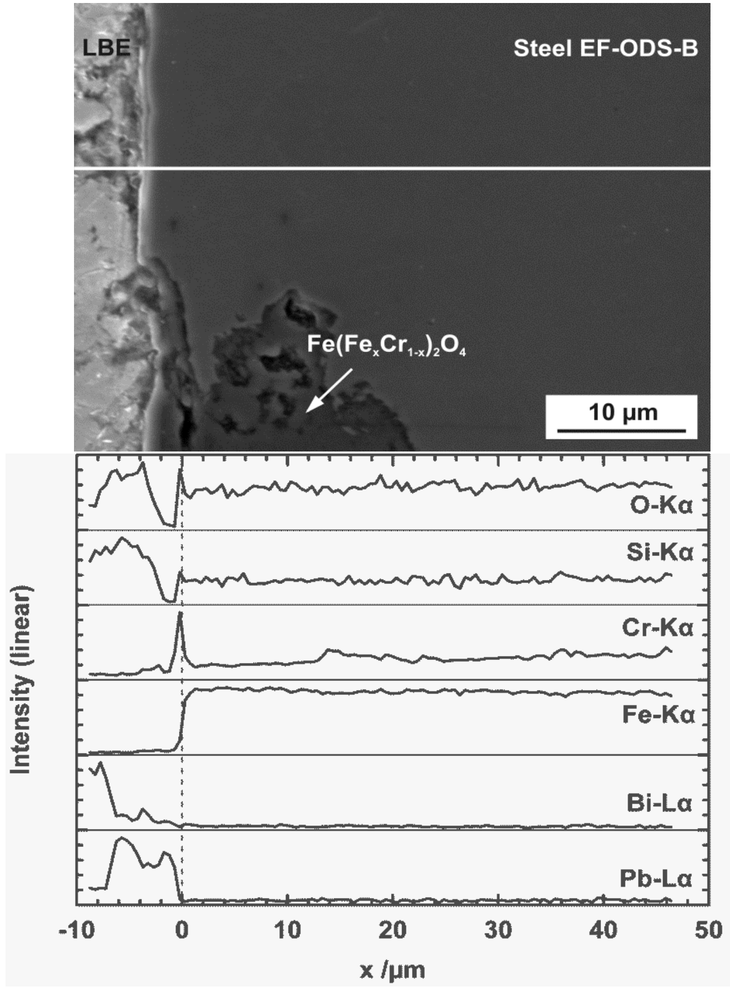


Parabolic:	$\Delta x^2 = k_2 t$
Parabolic after faster kinetics:	$\Delta x^2 = k_2 t + C_2$
Paralinear model of oxide scale growth	
Logarithmic:	$\Delta x = k_{log} (t + t_0) + C_{log}$

Exposure time (years)	1	5	10
T91-A → Upper limit of Cr content specified for T9			
Δx_M (µm)	10	13 – 22	13 – 31
Δx_{SP} (µm)	7	8 – 14	8 – 20
Δx_{ST} (µm)	9	20	28
T91-B → Lower limit of Cr content specified for T91			
Δx_M (µm)	12	15 – 26	15 – 36
Δx_{SP} (µm)	8	10 – 16	10 – 23
Δx_{ST} (µm)	12	26	37

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

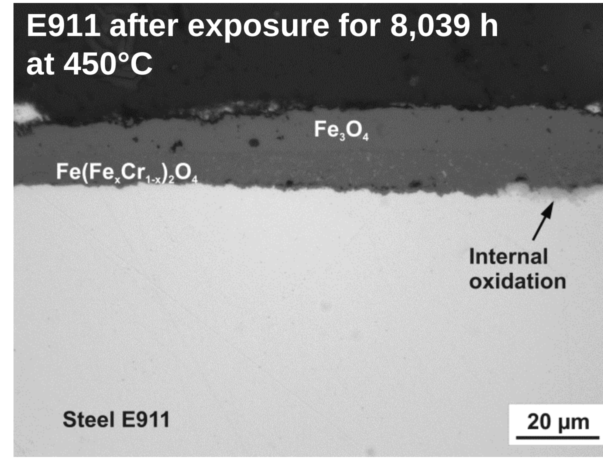
- Formation of a thin Cr-rich oxide scale
  - Probably chromia (Cr_2O_3)
  - Negligible scale growth or metal recession
- Either a local or short-term phenomena at 9% Cr
  - Rarely observed for E911 at 450°C
  - Remnants found in considerably thicker oxide scale on T91 at 550°C
  - Thin scale forms more 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

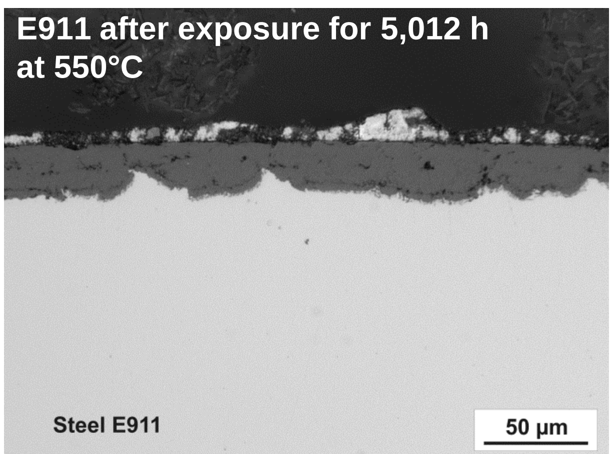


EF-ODS-B after exposure for 20,039 h at 550°C

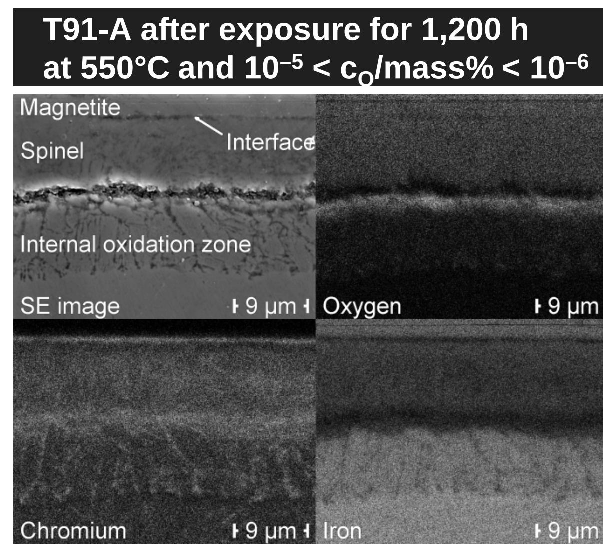
Oxidation of F/M steels in flowing LBE at 450–550°C: Accelerated oxidation

- 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



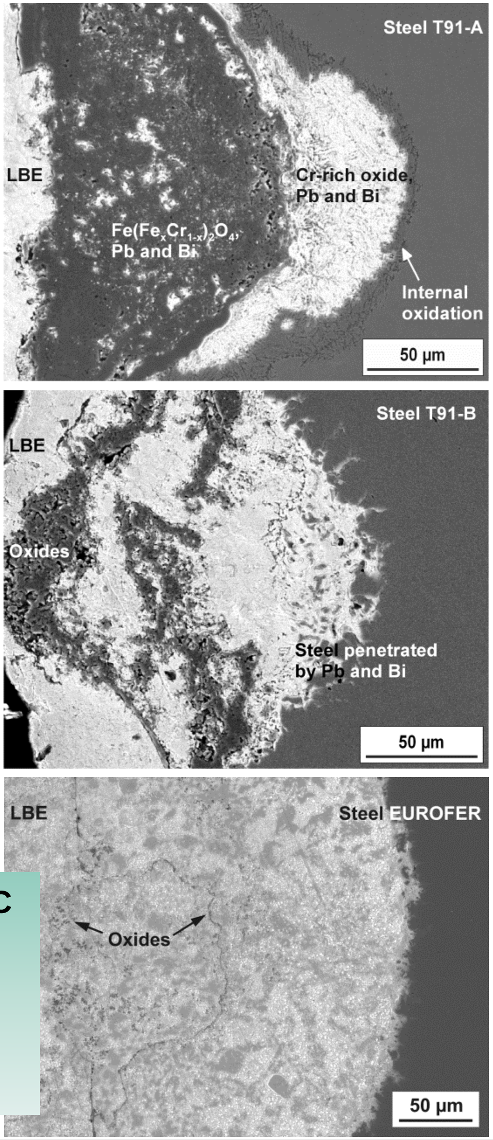


- Likely to start where the thin protective scale did not form or lost integrity
  - Cr enrichment at Fe_3O_4 / $Fe(Fe_xCr_{1-x})_2O_4$ interface
  - Oxide filled pits or irregular scale thickness where growing pits abutted on to each other



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

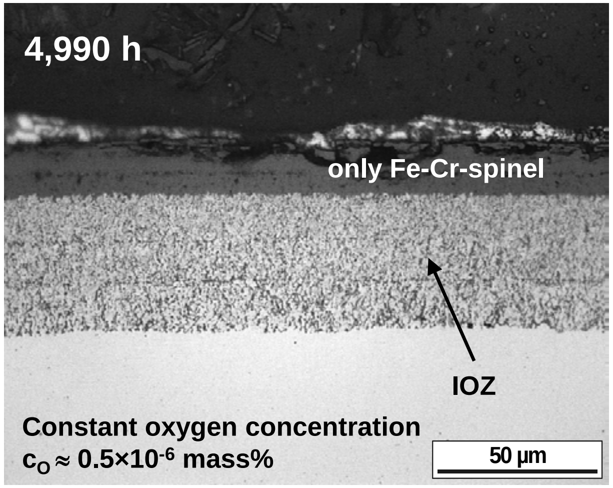
- After accumulation of LBE underneath the oxide scale
  - May occur for both the thin and thicker scale
  - Different outcome depending on oxide scale composition or structure
  - Observed only once at 450°C, for E911 after 8039 h
  - Occurred more frequently at 550°C than at 450°C
  - EUROFER seems 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

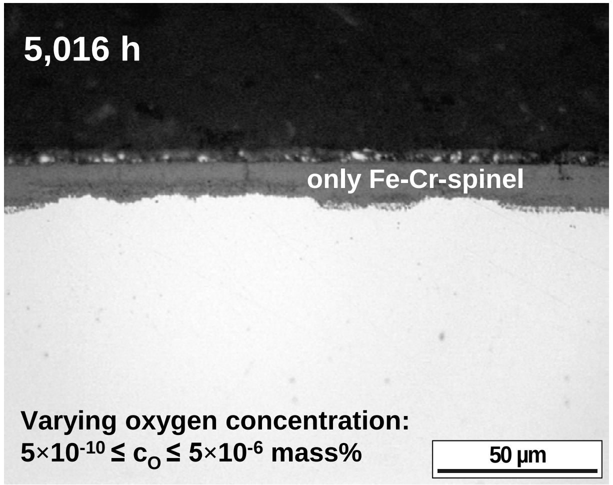


After exposure at 550°C for

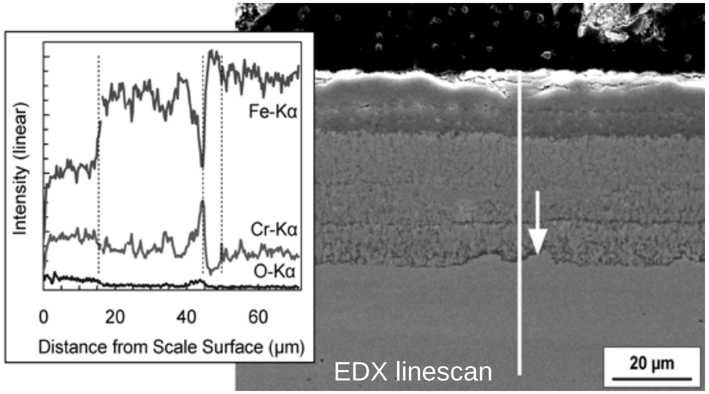
(top)	**15,028 h**
(middle)	**7518 h**
(bottom)	**3000 h**

Corrosion of martensitic 9%Cr-ODS steel at 550°C: Influence of varying oxygen concentration

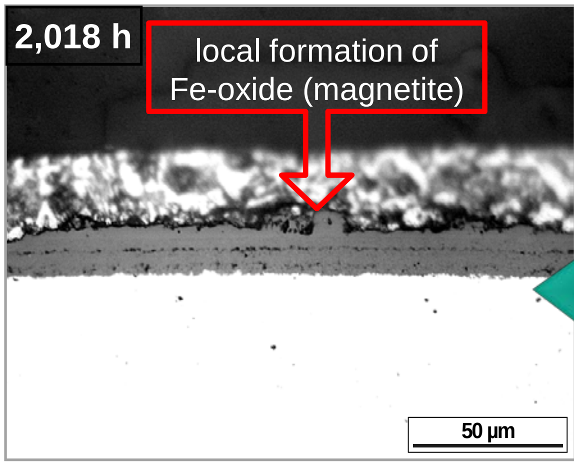




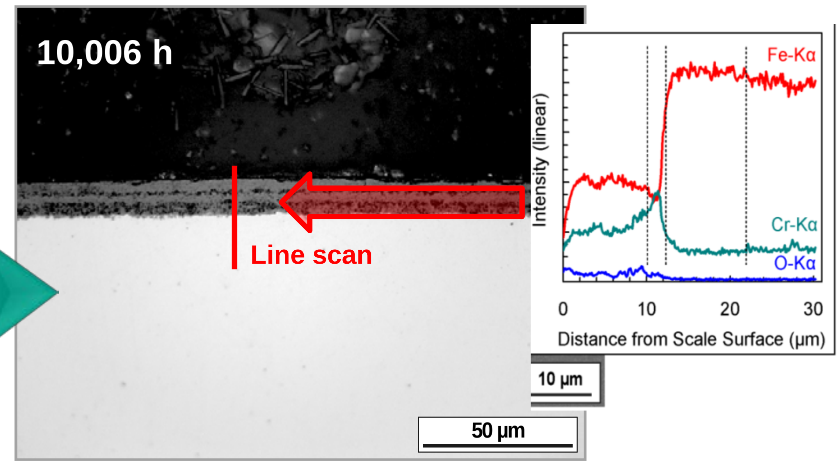
- Comparatively thin spinel scale (12µm)
- Significantly less internal oxidation
- Cr-enrichment in oxide at metal/scale interface



Corrosion of martensitic 9%Cr-ODS steel at 550°C
Time dependence of oxidation under varying oxygen concentrations



Cr-enrichment in oxide scale at metal/scale interface



Oxygen:
$5\times10^{-9} \leq c_O \leq 5\times10^{-6}$ mass%

- Spinel scale (11 µm); local formation of Fe-oxide
- Little internal oxidation in comparison to scale formed at $c_O \approx 0.5\times10^{-6}$ mass%

Oxygen:
$5\times10^{-10} \leq c_O \leq 5\times10^{-6}$ mass%;
$c_O \approx 0.5\times10^{-6}$ mass% during the last 4,990 h

- Comparatively thin spinel scale (11 µm) and little internal oxidation

Varying (mostly "low-oxygen") conditions during the first half of the exposure dominates the oxidation behavior

Corrosion of type 316-Ti austenitic steels in oxygen-containing LBE (1)

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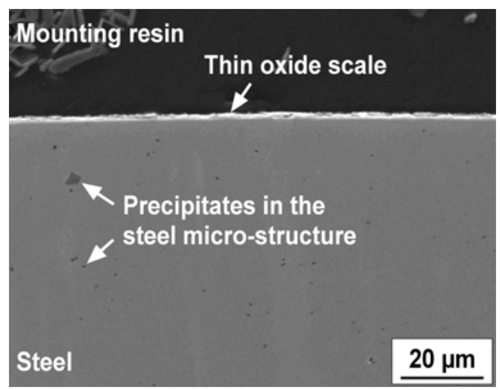
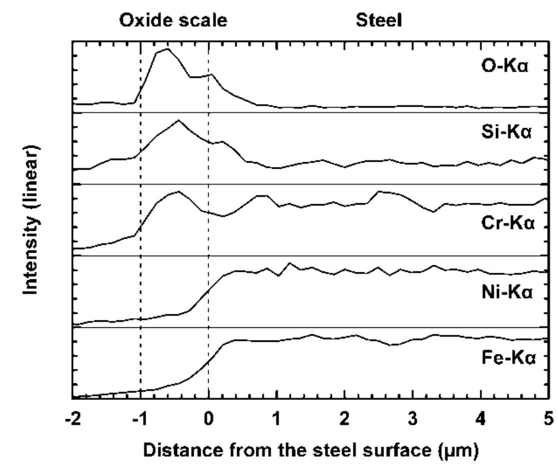
- **Protective scaling**
  - Thin oxide scale (< 1 µm) consisting of Cr- or Si-rich oxide layers
  - Might have evolved from thin films already existing on the steel surface before exposure
  - Similar to the scale formed by pre-oxidation in dry gas (Ar)
  - Locally long-lasting phenomenon on specimens exposed at 450/550°C, 10^{-6} mass% O in the test-sections of the loop
  - Not observed on tube samples taken from the hot leg of the loop; effect of long exposure time and variying c_O (?)



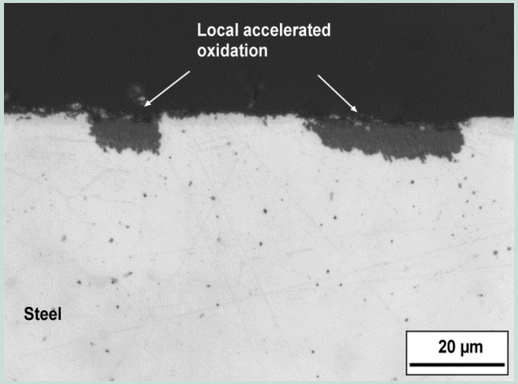


SS 316-Ti specimen in the test-section of the loop after exposure for 3495 h to oxygen-containing flowing LBE at 550°C and cO ≈ 10–6 mass%

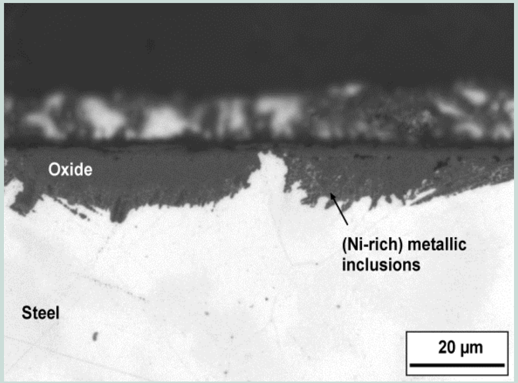
Corrosion of type 316-Ti austenitic steels in oxygen-containing LBE (2)

- **Accelerated oxidation**
  - Starts locally where the thin oxide scale lost integrity or did not form
  - Formation of $Fe(Fe_xCr_{1-x})_2O_4$, Fe_3O_4 and an internal oxidation zone; the latter two depending on oxygen content, temperature (or flow velocity)
  - The thicker scale spreads on the steel surface with time and becomes partially continuous
  - Varying c_O (mostly lower than 10^{-6} mass%) seems to promote accelerated oxidation

SS 316-Ti specimens in the test-sections of the loop:



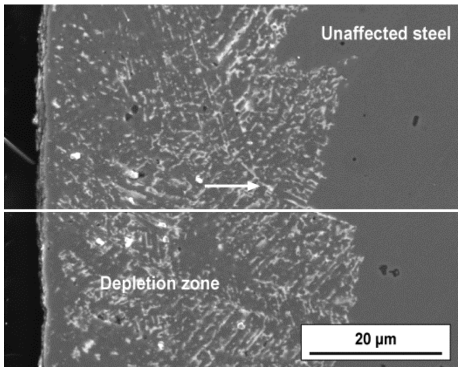
After exposure for 3495 h at 550°C and $c_O \approx 10^{-6}$ mass%

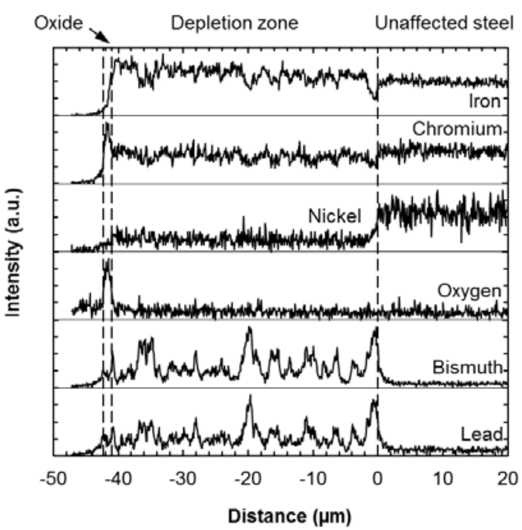


After exposure for 10,006 h at 550°C and variying c_O

Corrosion of type 316-Ti austenitic steels in oxygen-containing LBE (3)

SS 316-Ti after exposure for 5012 h at 550°C and $c_O \approx 10^{-6}$ mass%

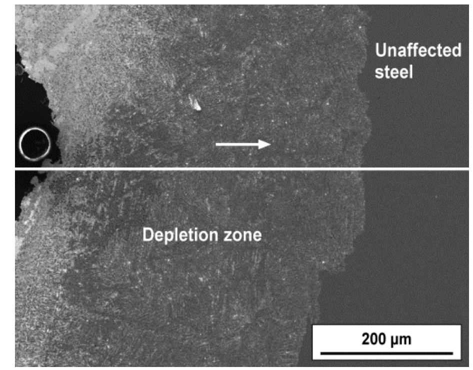


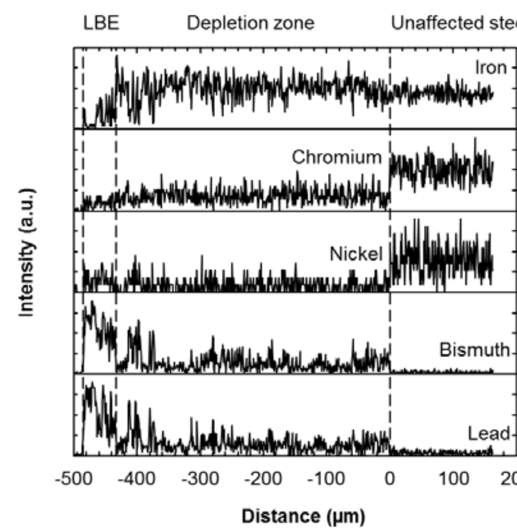


Selective leaching (Ni, Cr)

- Starts locally with preferential dissolution of Ni and penetration of Pb and Bi into the depletion zone
- Phase transition from austenite into ferrite resulting from Ni depletion
- Dissolution of Cr after oxygen depletion in the liquid metal penetrating the steel (critical penetration depth)
- In general, insignificant amounts of Cr oxide inside or on the surface of the depletion zone
- Removal of loosened steel grains bythe liquid-metal flow in a later stage of severe selective leaching

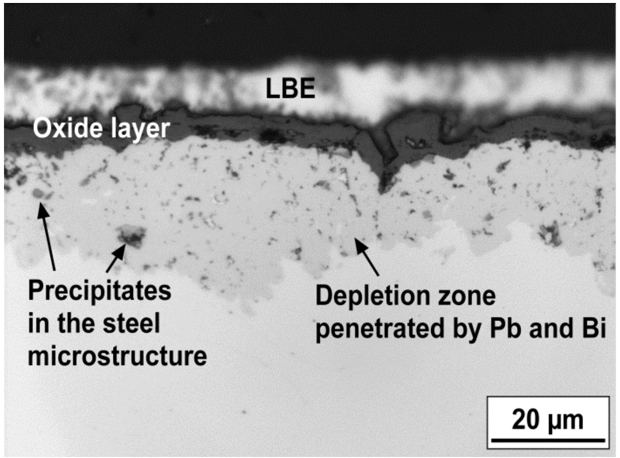
SS 316-Ti after exposure for 5012 h at 550°C and $c_O \approx 10^{-6}$ mass%



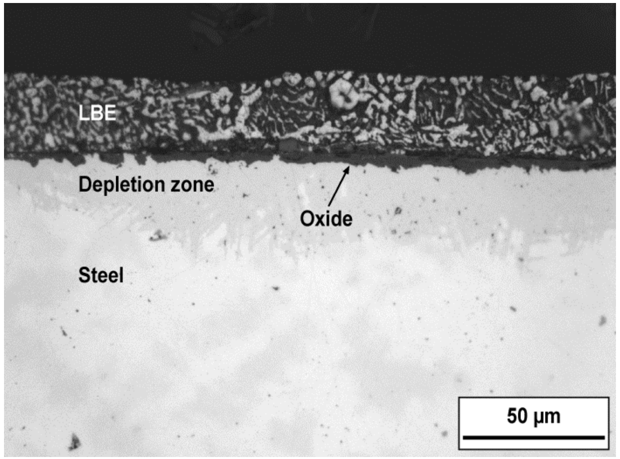


Corrosion of type 316-Ti austenitic steels in oxygen-containing LBE (4)

- **"Mixed mode"**
  - Depletion zone penetrated by Pb and Bi underneath an oxide scale
  - Oxide is Cr-rich in comparison to the Fe $(Fe_xCr_{1-x})_2O_4$ layer formed by accelerated oxidation
  - Result of the transition from selective leaching to oxidation (?)
  - Formation of Cr-rich oxide scale can stop selective leaching (?)



Tube sample taken from the CORRIDA loop after exposure for ~23,000 h to flowing oxygen-containing LBE at 550°C

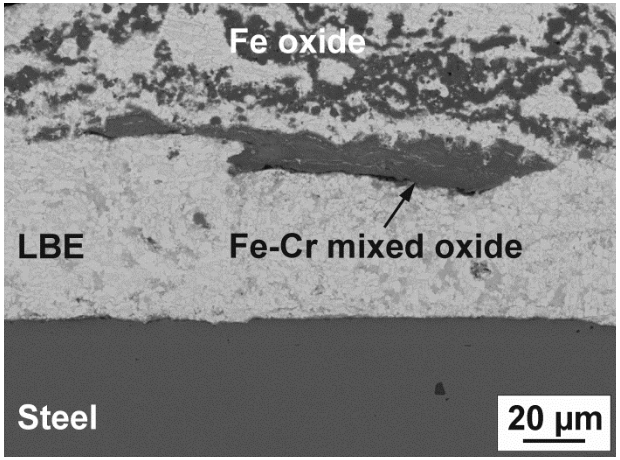


- Typical scale observed for some of the tube samples from the CORRIDA loop

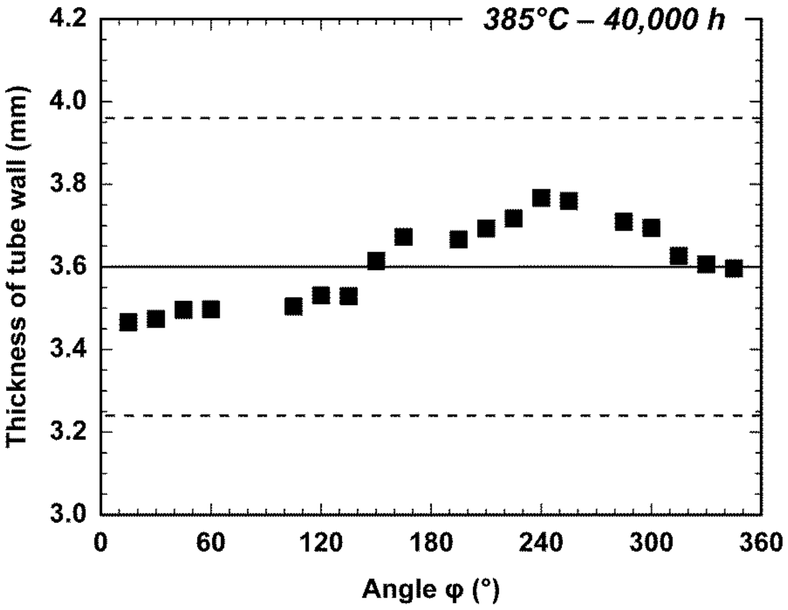
SS 316-Ti specimen exposed in the test sections after 3495 h at 550°C and $c_O \approx 10^{-6}$ mass%

Performance of the tubing of the CORRIDA loop

- **Sample T5 after 40,000 h at 385°C**
  - Position after the cooler, before magnetic trap
  - No significant change in wall thickness after the long-term exposure
  - Oxide deposits in adherent solidified LBE, but only in some distance from the tube wall
  - Neither deposits nor significant amounts of oxide on the surface



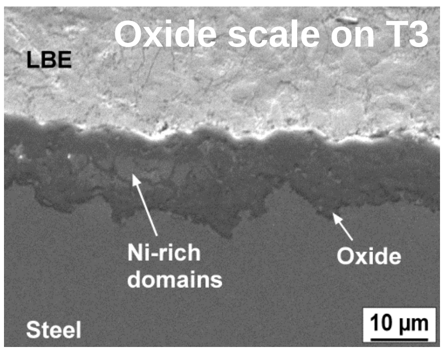
Electron-optical micrograph (BSE)

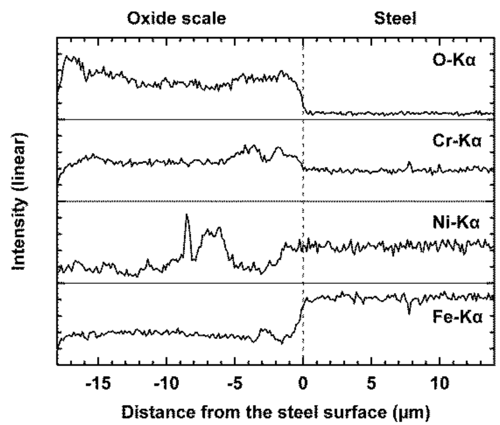


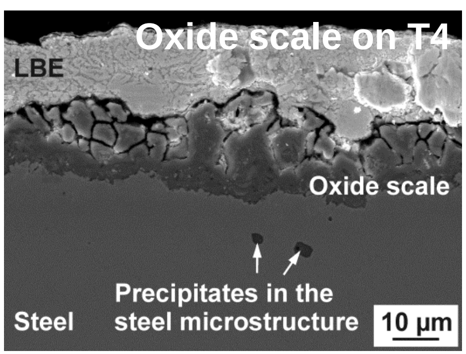
Results from measuring the residual wall thickness in the microscope

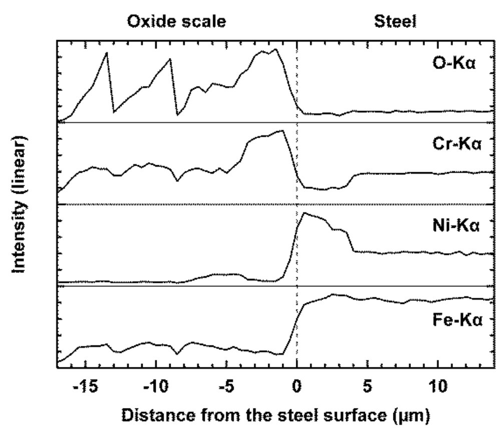
Performance of the tubing of the CORRIDA loop

- **Corrosion scales formed in the hot leg (550°C)**
  - T3 (6000 h) and T4 (40,000 h) mainly show oxidation; T3 was not pre-oxidised
  - T1 (23,000 h) and T2 (29,000 h) show significant selective leaching

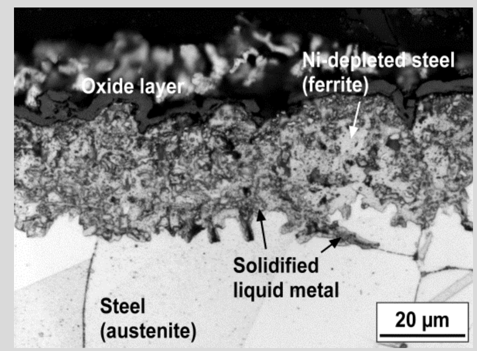


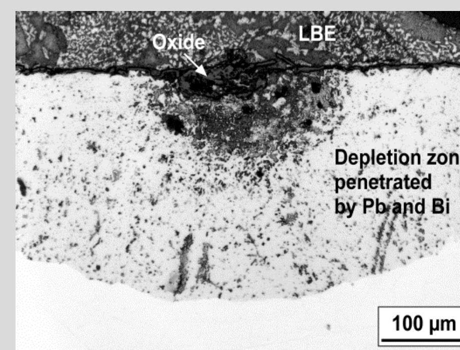






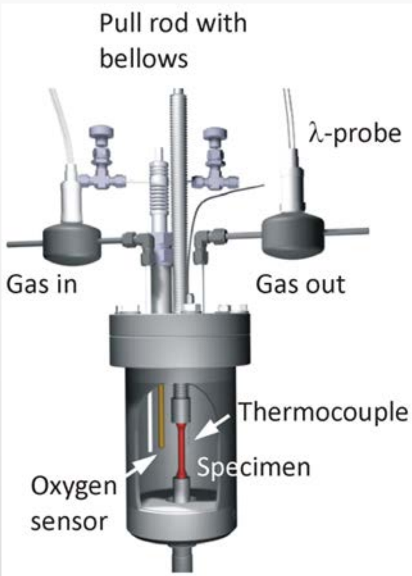
Corrosion scales typically observed on T1 and T2





Creep-to-Rupture tests in stagnant, oxygen-controlled liquid Pb at 650°C

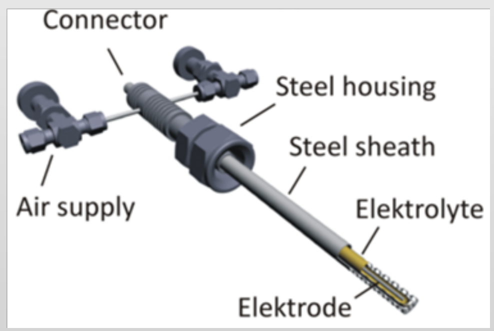
CRISLA-capsule



Facility with infrastructure:

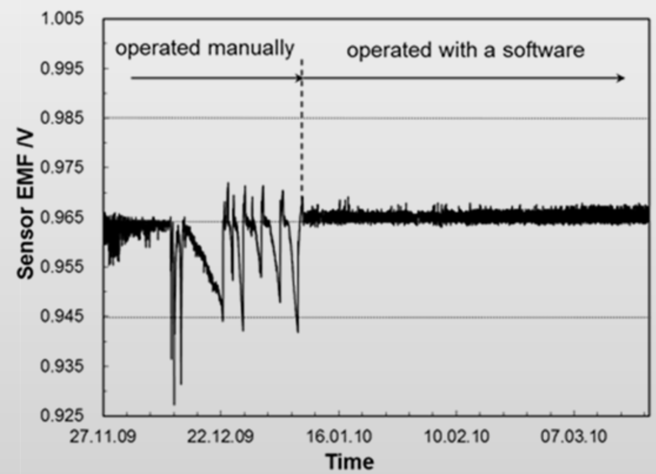
- 5 capsules for stagnant Pb with volume of 900 ml. Oxygen control periphery for each capsule.
- 3 capsules for stagnant air with volume of 230 ml

Pt/air oxygen sensor



Gas supply:

- Ar (continuous) – 96-99 ml/min
- Ar/H_2 (continuous) – 3 ml/min
- synthetic air (pulsed) – 1ml/min if E≥965 mV



- stagnant Pb or LBE
- T = 450–650°C
- $c_O = 10^{-7}–10^{-6}$ mass.-%

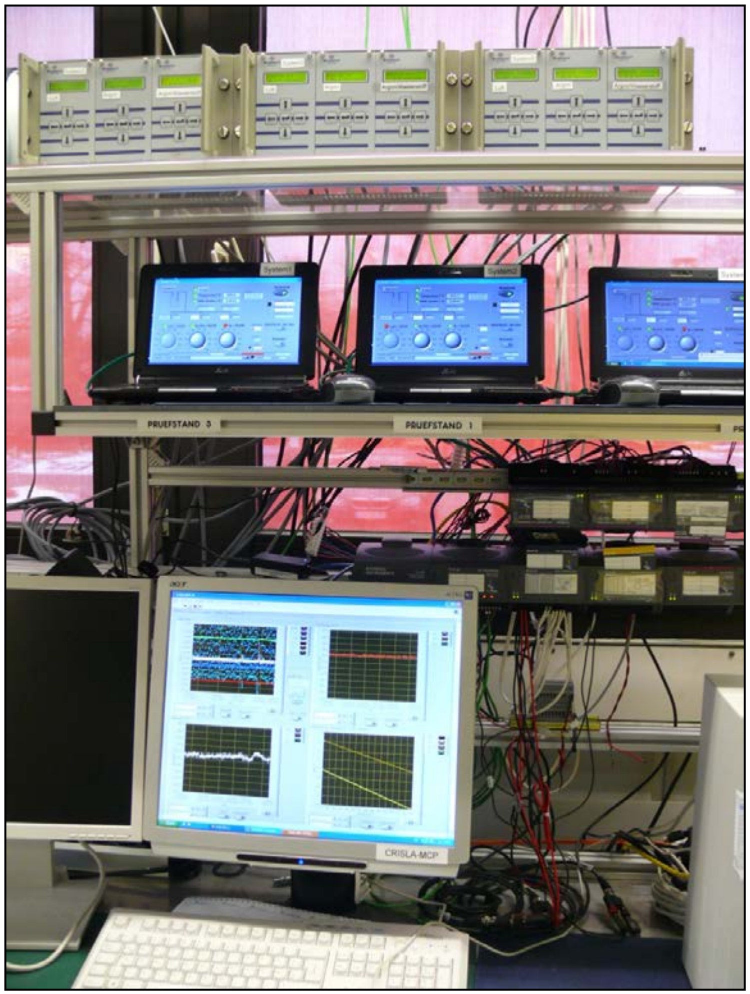
- through oxygen contained gas (gas/liquid oxygen-transfer)

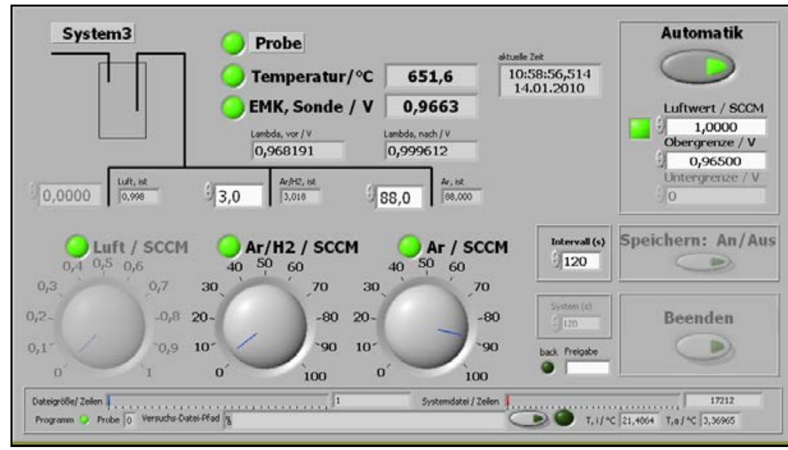
- E: 965±20 mV → 965±2 mV

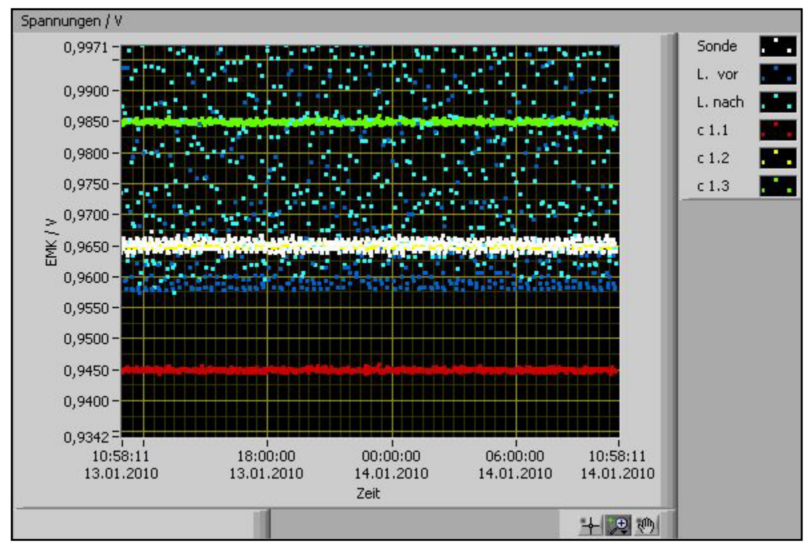
CRISLA Facility for Creep-Rupture Tests in Lead

Karlsruhe Institute of Technology

PC-supported control system for oxygen content: user defined settings



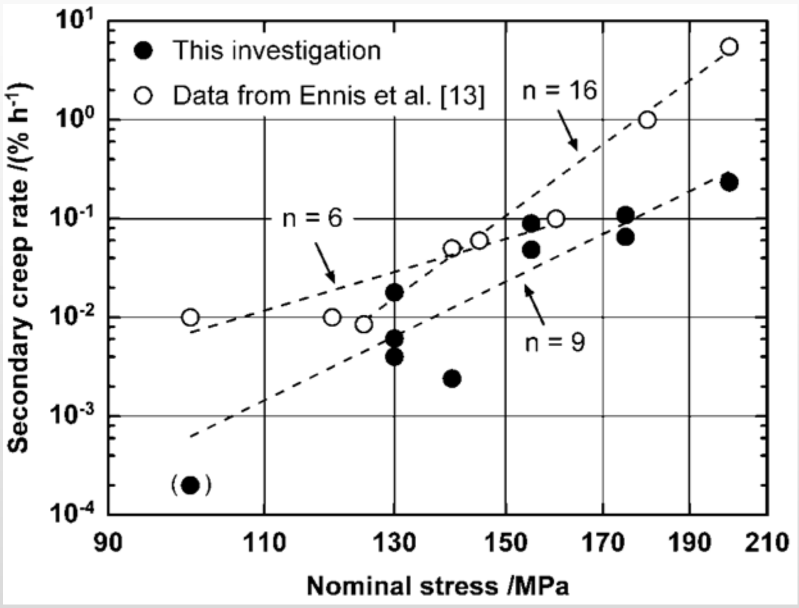


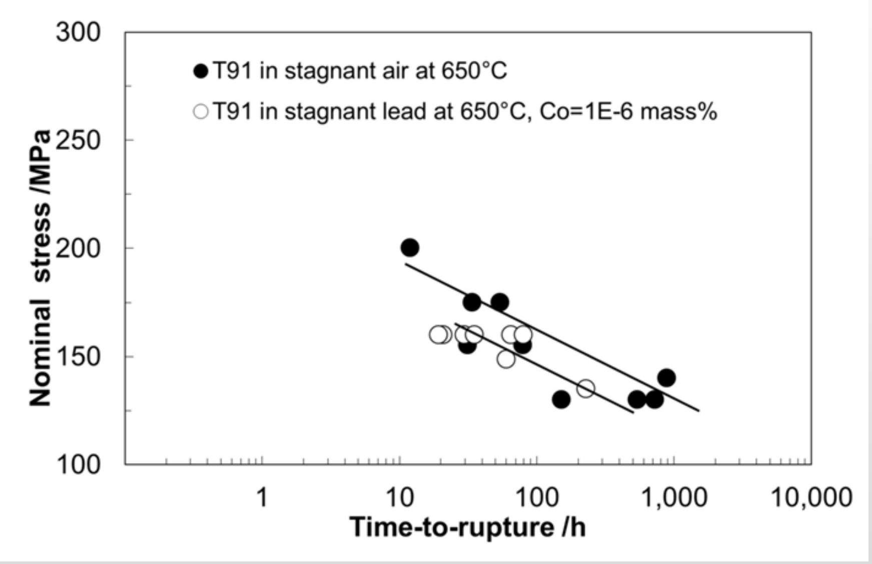


Creep strength of T91 in air and lead at 650°C

Karlsruhe Institute of Technology

Experimental and literature data for T91 in air





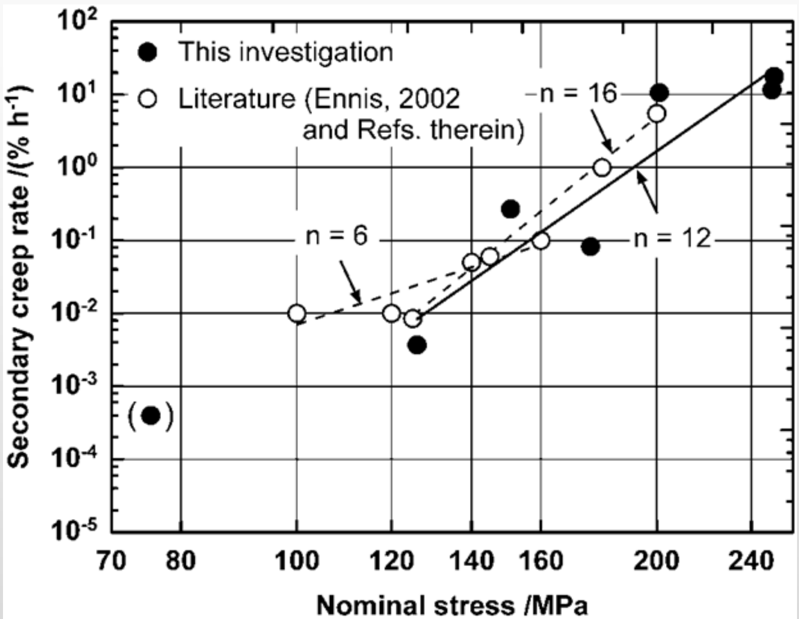
Stress exponent n in Northon law:

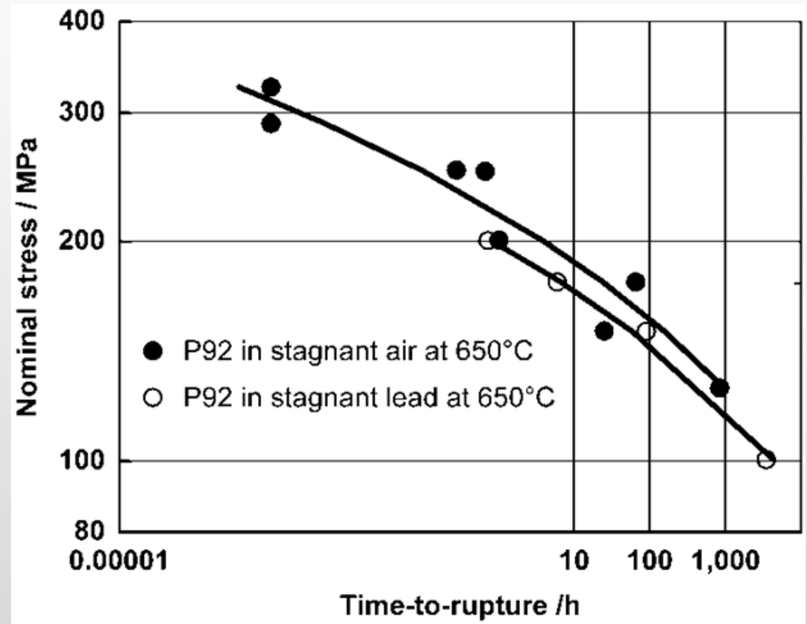
$$\dot{\varepsilon}_s = k\sigma^n$$

- No great difference in creep strength of T91 tested in both environments

Creep strength of P92 in air and lead at 650°C

Experimental and literature data for P92 in air



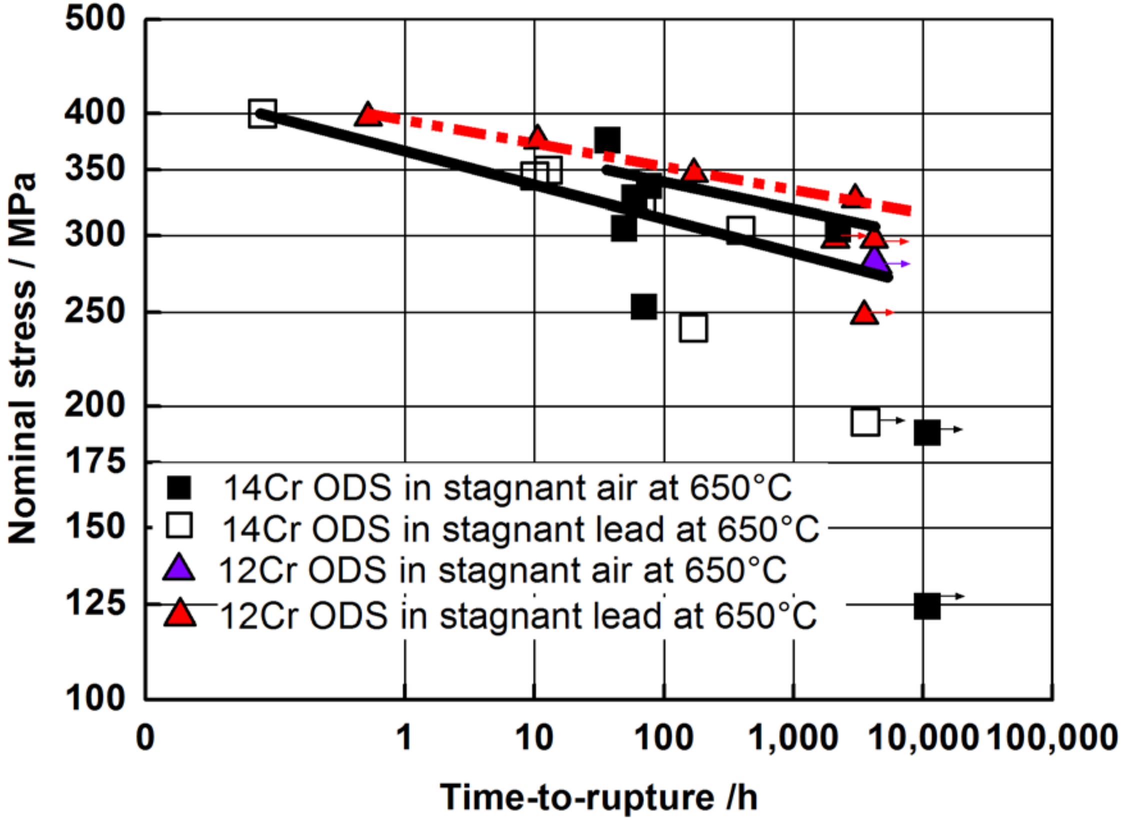


Stress exponent n in Northon law:

$$\dot{\varepsilon}_S = k\sigma^n$$

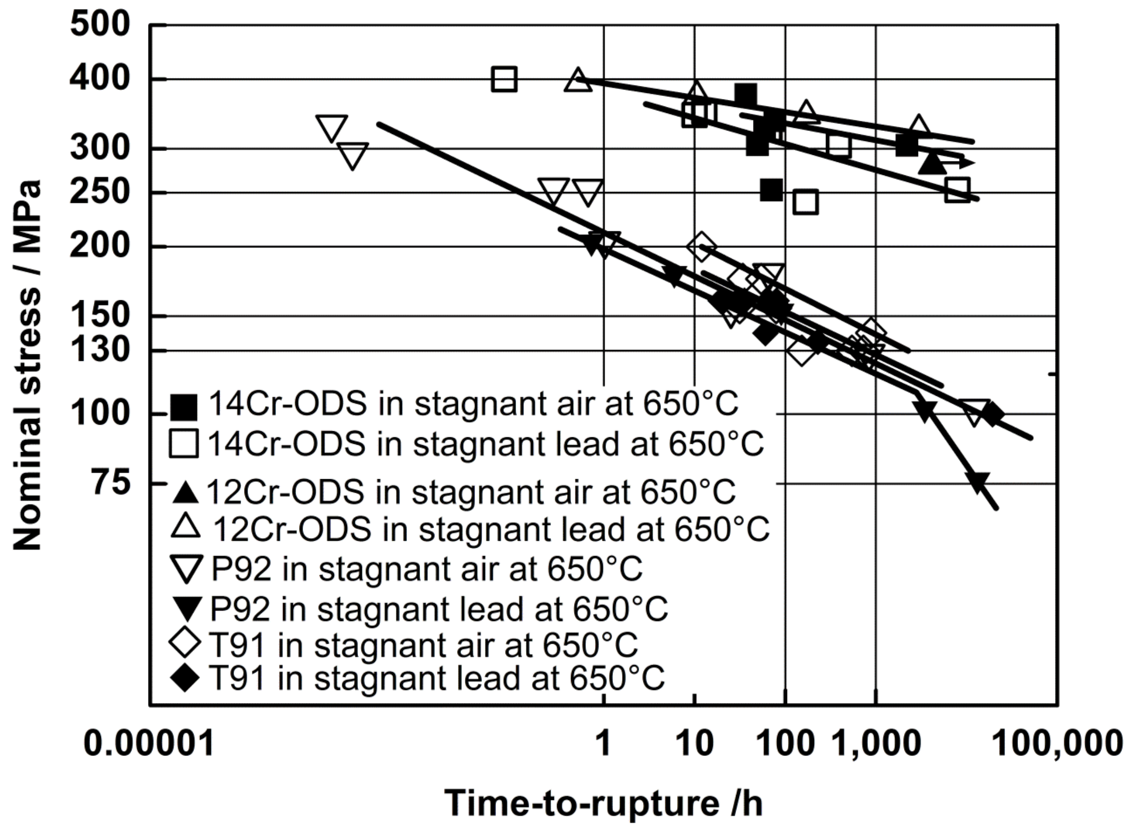
- Creep strength exhibited in Pb is on the low scattering range limit of that obtained in air

Creep strength of 14Cr-1W and 12Cr-2W ODS steels in stagnant lead ($c_o=10^{-6}$ mass%) and air at 650°C



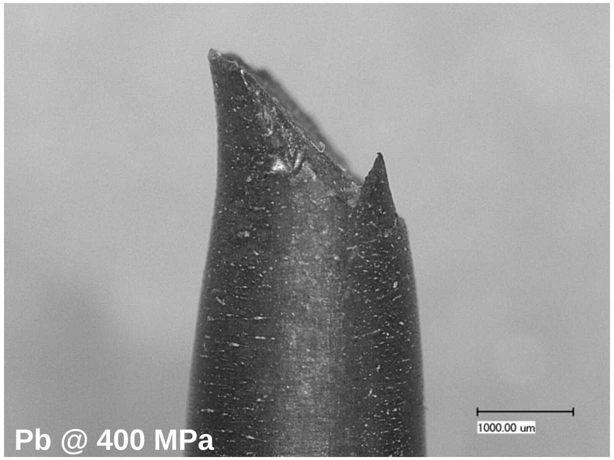
The 12-Cr ODS steel exhibits a slightly higher creep strength in stagnant Pb than the 14Cr-ODS steel

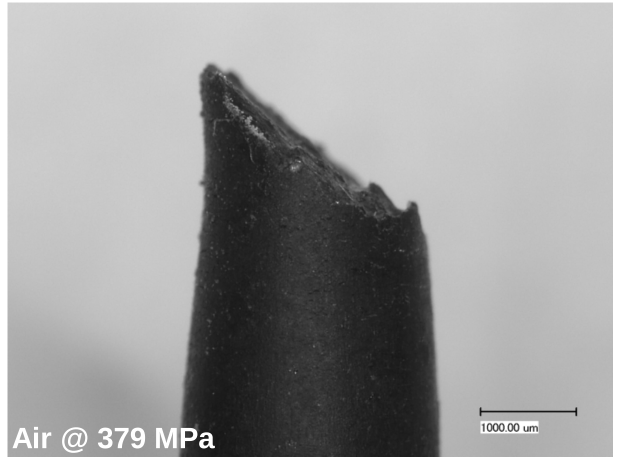
ODS steels against f/m steels T91 and P92, tested in air and lead at 650°C

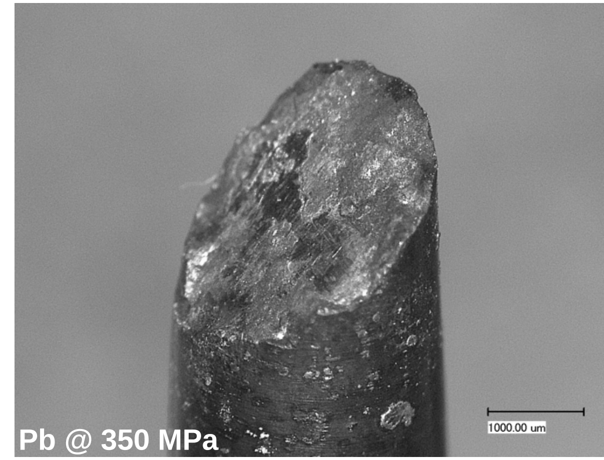


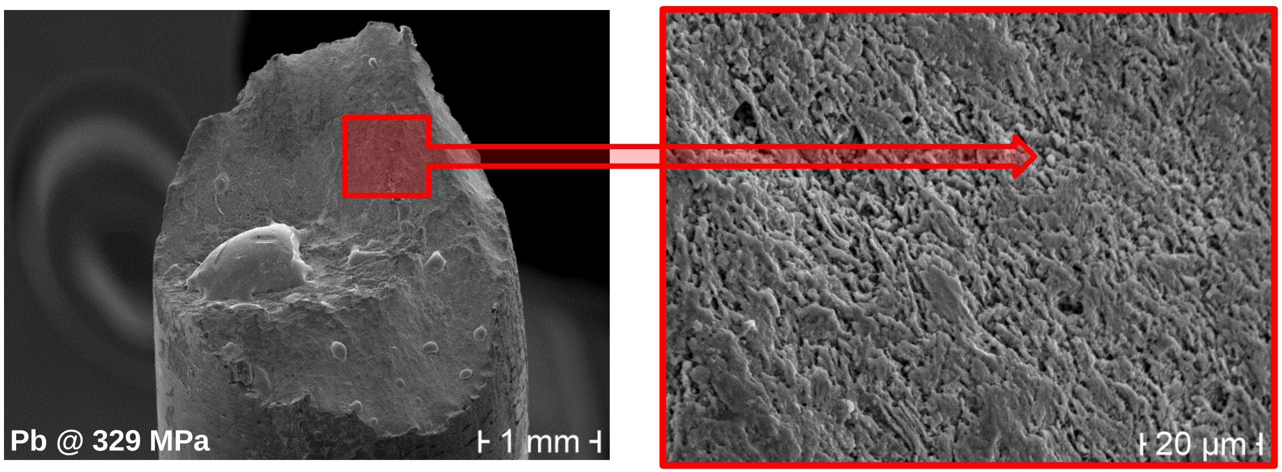
Creep-rupture strength of 12Cr- and 14Cr-ODS steels is factor 2.5 higher then the f/m steels until t_R=10,000 h and show no LME in contrast to P92 tested in Pb.

12Cr-ODS steels after creep-to-rupture tests



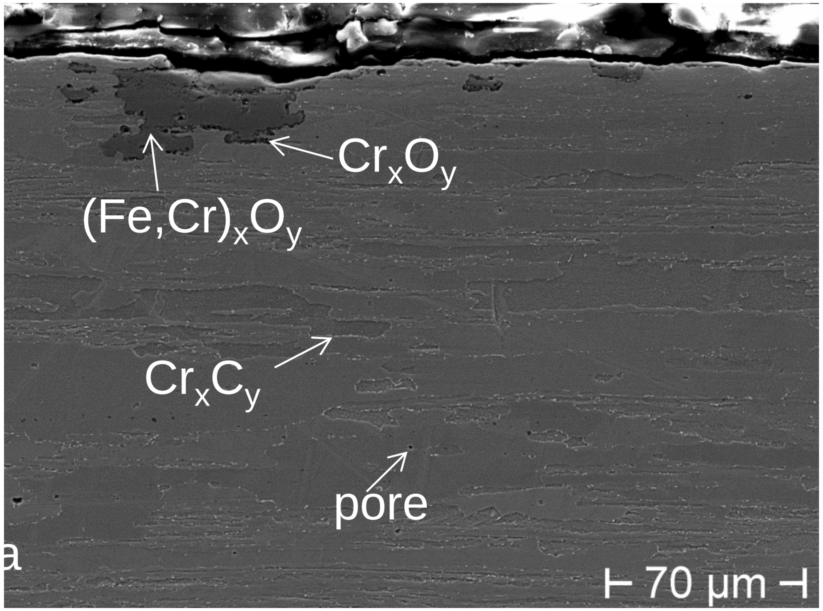


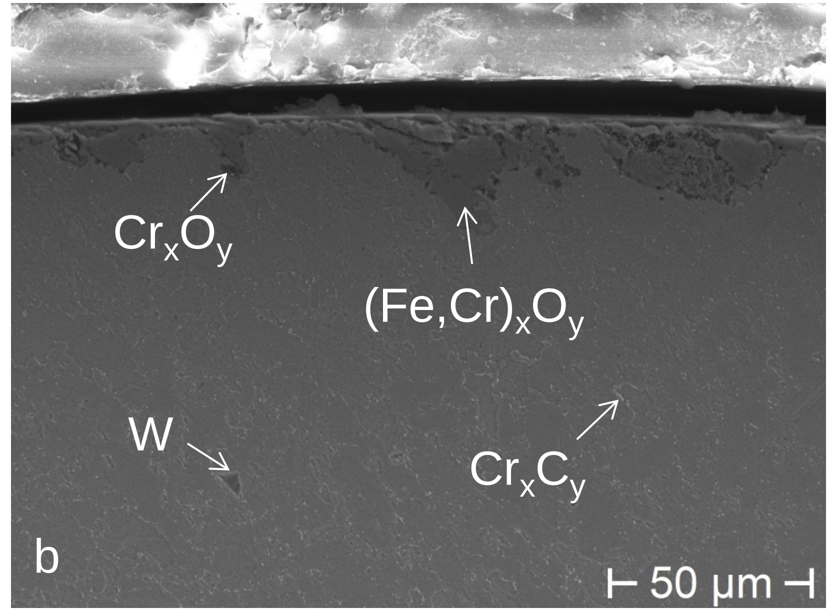




Shear fracture which is characteristic for ductile mode is proved by εc;R and Z
The higher stress, the higher $\varepsilon_{c;R}$ and Z were determined

12Cr-ODS steels after creep-to-rupture tests





Longitudinal (a) and perpendicular (b) cross-sections of the steel ruptured after t_R=2,982 h in Pb at 329 MPa

- **Oxide scale is irregular and contains Fe, Cr and O. The thickness is up to 30 µm.**
- **Until 2,982h exposure to Pb, no dissolution of the steel was observed**

Summary

- Heavy liquid metals (HLMs) are very appropriate coolants/targets for Nuclear (ADS, LFR) applications. Worldwide R&D has been established to buildup databases for compatibility issues of potential structural materials.
- F/M steels with 9%Cr show three stages of interaction with flowing LBE at450-550°C, 10^{-6} mass% dissolved oxygen, 2 m/s
  - Protective scaling – short term or local phenomenon
  - Oxidation – the general degradation mechanism
  - Direct liquid-metal attack – locally, after accumulation of liquid metal underneath the oxide scale
- Average rate of oxidation is lower
  - For higher Cr-content at 450°C
  - For fine-grained materials at 550°C
- Observed kinetics of oxidation is slower than parabolic
  - Corrosion rate increases by factor 2–3 for increase in temperaturefrom 450 and 550°C
- Liquid metal attack shows
  - High local material loss in comparison to oxidation, e.g., increase by factor by factor 3–5 for T91 and 9%Cr-ODS at 550°C

Acknowledgements

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