Corrosion Kinetics of Steel T91 in Flowing Oxygen-Containing Lead-Bismuth Eutectic at 450° and 550° C

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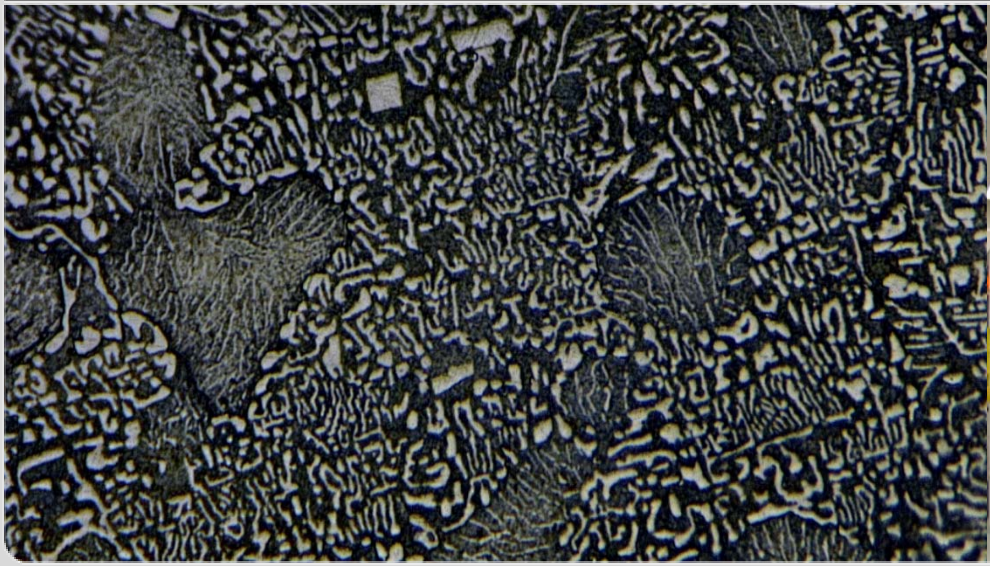
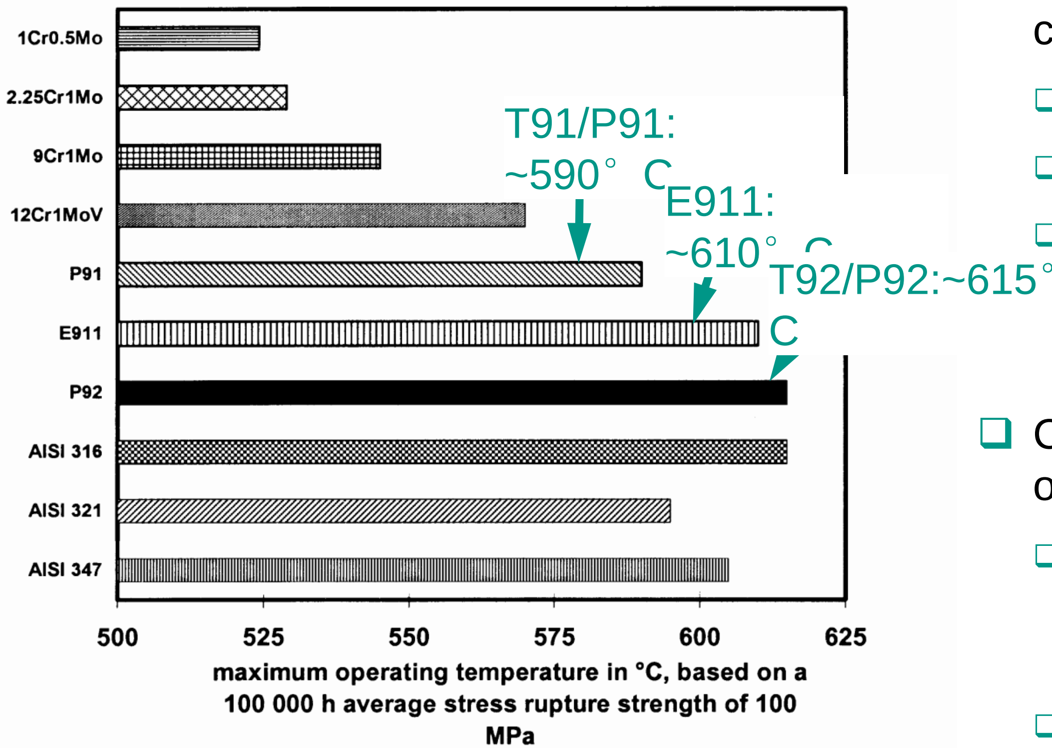


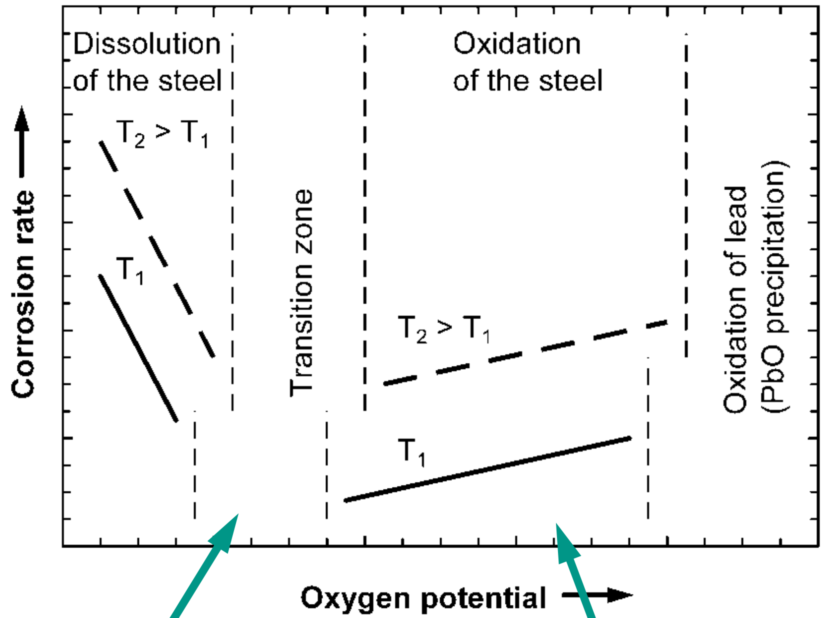
Creep strength-enhanced ferritic steels (CSEF)

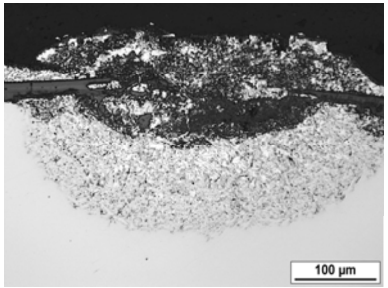


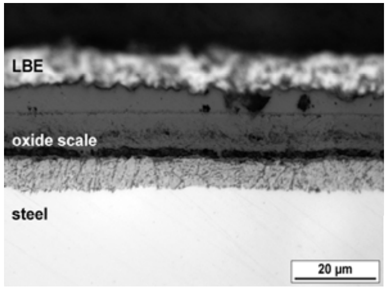
Maximum temperature for 100,000 h stress rupture strength $\sigma_{RS/100,000\ h}$ = 100 MPa according to Ennis and Czyrska-Filemonowicz (Sādhanā 28[3-4], 2003, 709-730)

- Favourable properties of CSEF in comparison to austenitic steels
  - High thermal conductivity
  - Moderate thermal expansion
  - Higher allowable irradiation dose
- Criteria for service in an ADS with Pb or LBE target
  - Compatibility with thermo-mechanical loads under regular and exceptional operating conditions
  - **Resistance against liquid-metal corrosion**
  - Long-term stability of mechanical properties under extensive neutron and proton irradiation

Impact of oxygen dissolved in liquid Pb-alloys on steel corrosion







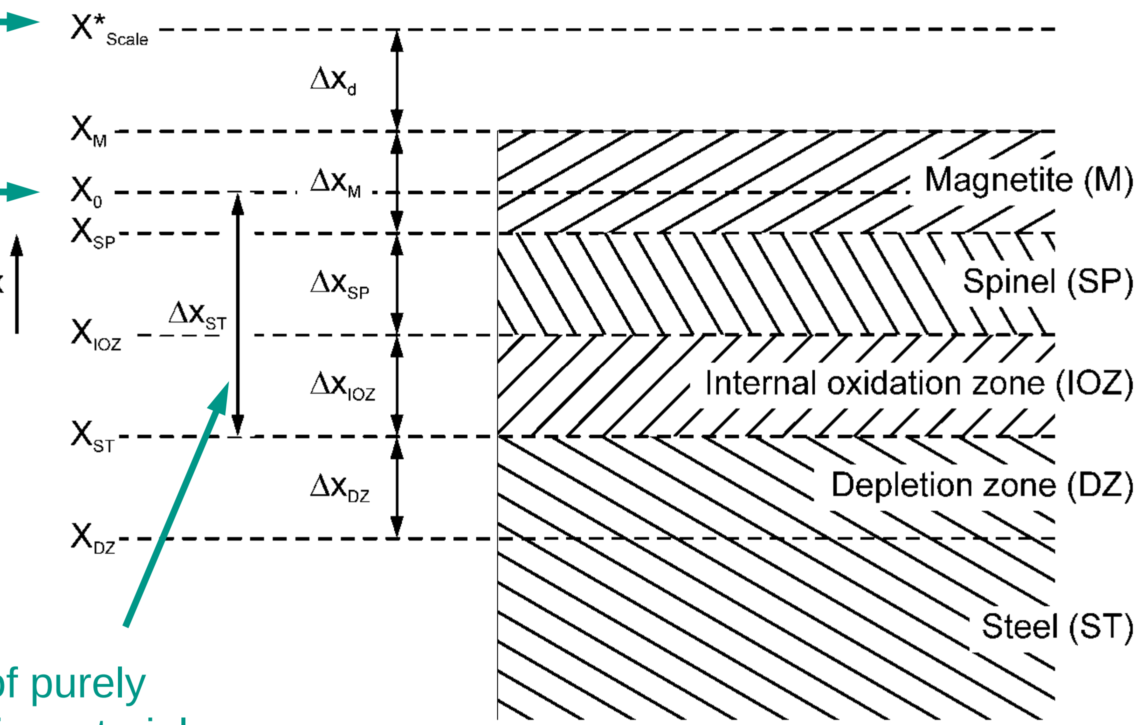
Example:
T91/LBE/550° C

- Stimulation of the oxidation of steel constituents
  - Formation of an oxide scale on the steel surface
  - Spatial separation of the steel from the liquid metal
  - Reduced dissolution rate
- Steel constituents must be less noble than the constituents of the liquid metal
  - Applicable to pure Pb and LBE
  - Not applicable to Pb17Li and Na

Generalized corrosion scale on basically Fe-Cr alloys

Scale surface w/o dissolution

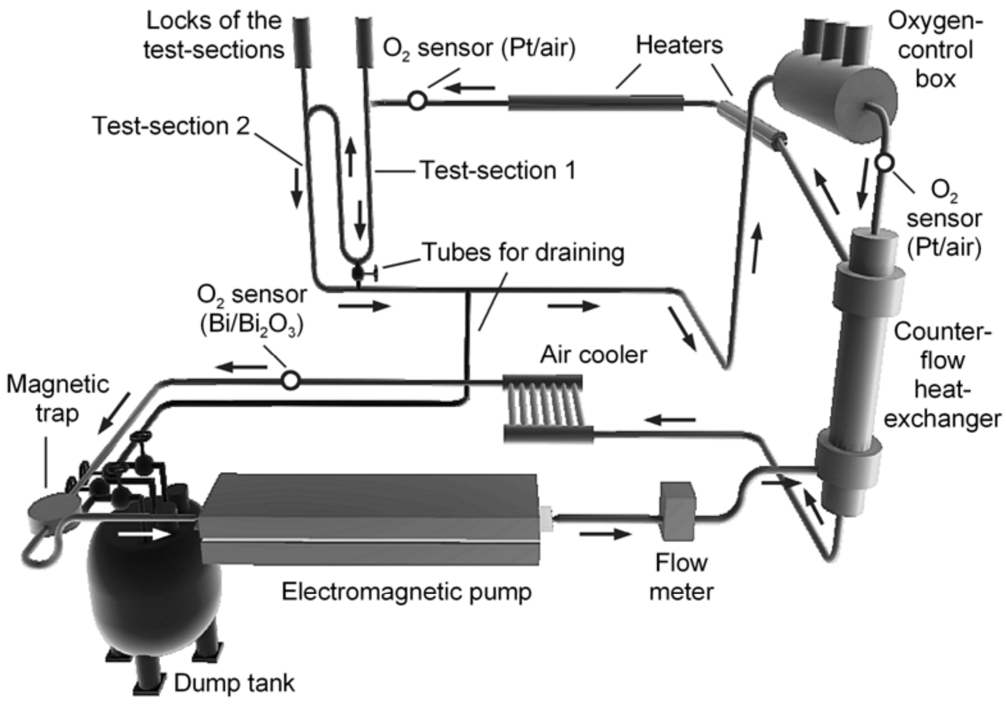
Initial position of steel surface



Loss of purely metallic material (metal recession)

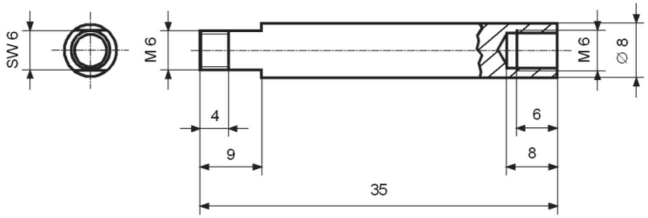
- Quantifiable by metallographic measurements
- Initial specimen geometry must be known for quantification of Δx_{ST} and Δx_d

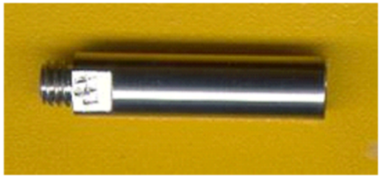
CORRIDA: Corrosion-testing in dynamic lead alloys

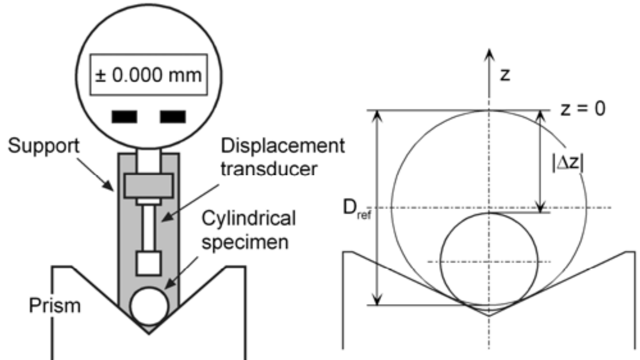


- ***Technical data***
  - Material: 17-12 Cr-Ni steel (1.4571)
  - Developed length: 36 m
  - Liquid metal: ~1000 kg LBE
  - Mass flow: 5.3 kg/s (steady state)
  - T_{max} = 550° C (test-sections, oxygen control-box)
  - T_{min} = 350–385° C depending on T_{max} at inlet of EM-pump
  - Oxygen control:
    Gas with adjustable O_2-content introduced at T_{max}
- ***Operating data***
  - Commissioning in July 2003
  - 30,000 h of effective operation at T_{max} = 550° C reached in February 2008
  - Longest exposure time of specimens: 20,000 h
  - Another 8000 h of operation at T_{max} = 450° C reached in June 2009

Specimens for exposure in the CORRIDA loop







$$D(\Delta z) = D_{ref} + \frac{2\sin\frac{\theta}{2}}{1+\sin\frac{\theta}{2}}\Delta z$$

θ: Opening angle of the prism

- ***Standard specimen***
  - Basic geometry: Ø8 × 35 mm
  - Maximum 18 specimens joined via screw-threads and introduced into the test-section (vertical tube)
  - v = 2 m/s in the gap between specimens and tube wall for standard specimen geometry and liquid-metal mass-flow

- ***Preparation***
  - Surface finish by turning
  - Determination of the initial diameter
  - Degreasing with acetone

- ***Post-test analyses***
  - Metallography on cross-sections in the light-optical microscope (LOM) and SEM/EDX
  - Determination of remaining metal diameter and scale thickness in the LOM

Long-term corrosion studies in flowing oxygen-containing LBE conducted at KIT

Karlsruhe Institute of Technology

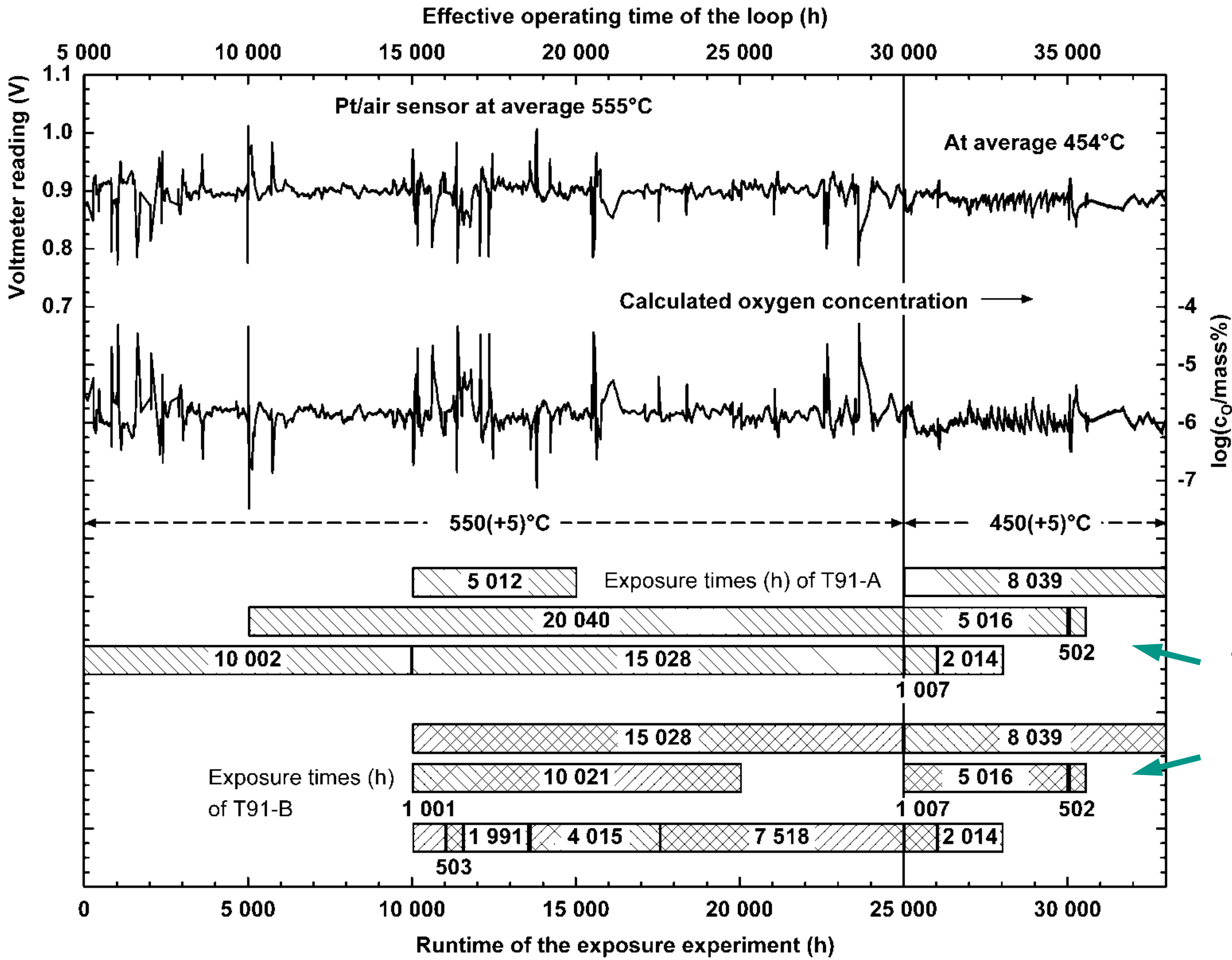
Temperature	Flow velocity	Nominal oxygen concentration	Maximum Exposure times	Tested materials
550 (+5)° C	2 (±0.2) m/s	10^{-6} mass%	~ 20,000 h	CSEF (T91, E911, EUROFER), ODS steels, Type 316SS, surface alloyed steels (Al), ...
450 (+5)° C	2 (±0.2) m/s	10^{-6} mass%	~ 8000 h	CSEF (T91, E911), pure Fe, Type 316SS, ...

Next exposure experiments:

550° C	2 m/s	10^{-7} mass%
450° C	2 m/s	10^{-7} mass%
350° C	2 m/s	10^{-7} mass%

Additionally, P92 and 15-15 CrNiTi (1.4970)

Times of exposure at 550° and 450° C of T91, and actual oxygen potential (concentration) in the course of the experiments



Two sample materials (T91-A and B) from different suppliers

Composition (in mass%) and final heat treatment of T91 samples

T91-A

Fe	Cr	Mo	Mn	Si	V	Cu	Ni	Nb	Co
bal.	9.44	0.850	0.588	0.272	0.196	0.0980	0.100	0.072	0.0156
C	N	P	S	Al	Zn	Sn	Ti	W	As
0.075	n.a.	0.018	0.006	0.007	0.0043	0.004	0.0010	<0.003	n.a.

Heat treatment of 100×100×40 mm sample:

(1) 2 h at 1050° C; furnace-cooling down to 350° C, followed by air-cooling

(2) 4 h at 750° C; furnace cooling

T91-A:
Higher Cr content and longer heat treatment in comparison to T91-B

T91-B

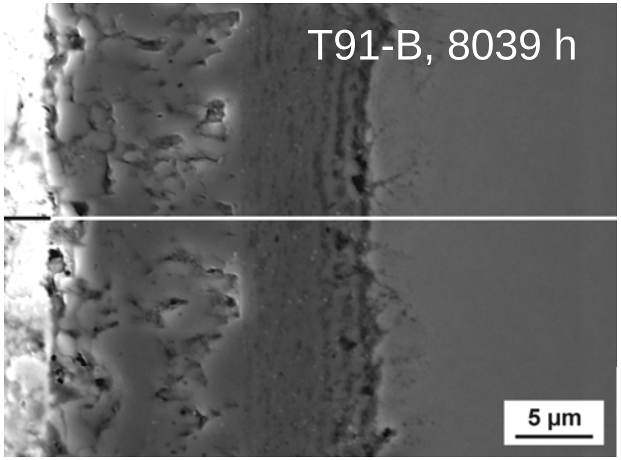
Fe	Cr	Mo	Mn	Si	V	Cu	Ni	Nb	Co
bal.	8.99	0.89	0.38	0.22	0.21	0.06	0.11	0.06	n.a.
C	N	P	S	Al	Zn	Sn	Ti	W	As
0.1025	0.0442	0.021	0.0004	0.0146	n.a.	0.004	0.034	0.01	0.008

Final heat treatment of hot-rolled 15 mm thick plate:

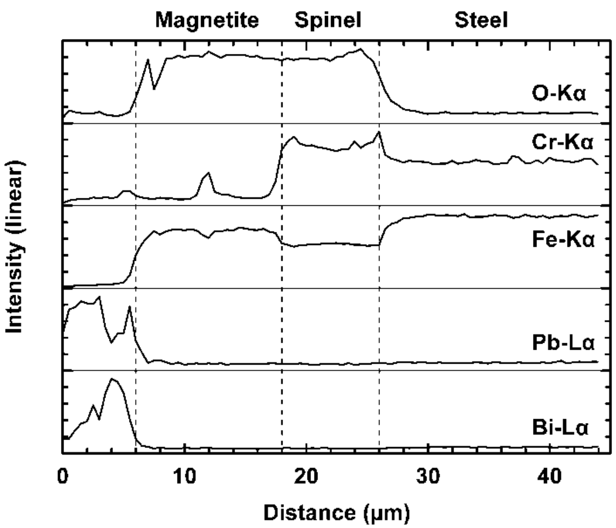
(1) 15 min at 1050° C; water cooling

(2) 45 min at 750° C; air cooling

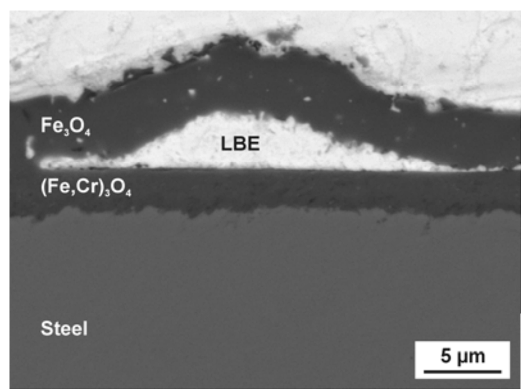
Oxide scale on T91 at 450° C, 2 m/s and 10^{-6} mass% oxygen



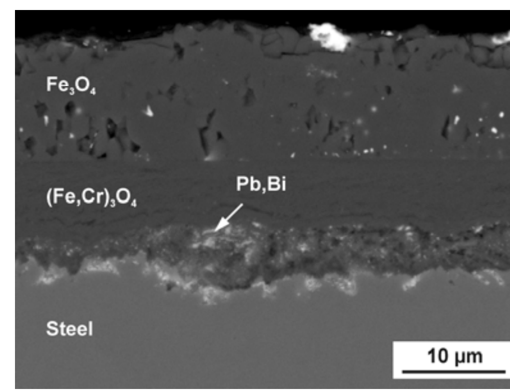
- Bi-layer scale (magnetite, spinel)
- Slight internal oxidation along steel-grain boundaries, no important IOZ
- Local Cr-enrichment inside the magnetite layer has not been observed in all EDX linescans



- Occasionally, accumulation of Pb and Bi in the scale (with insignificant impact on corrosion damage)

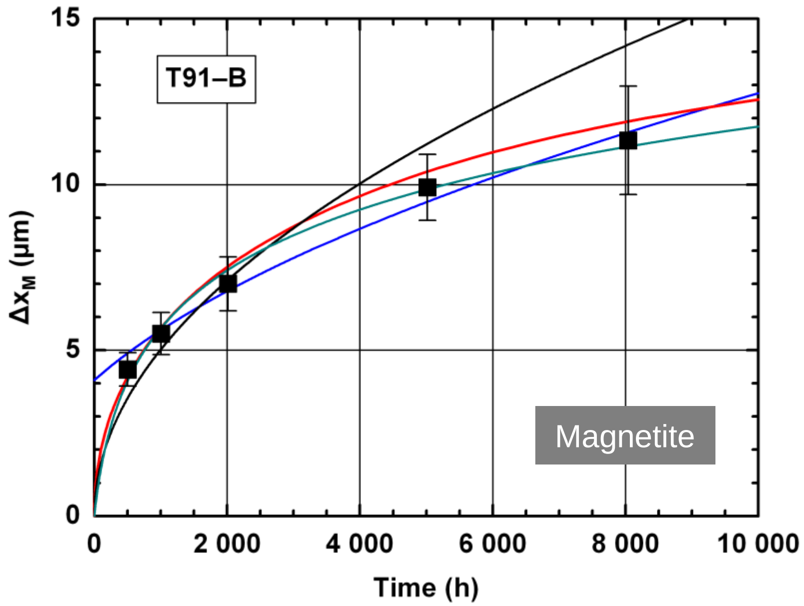


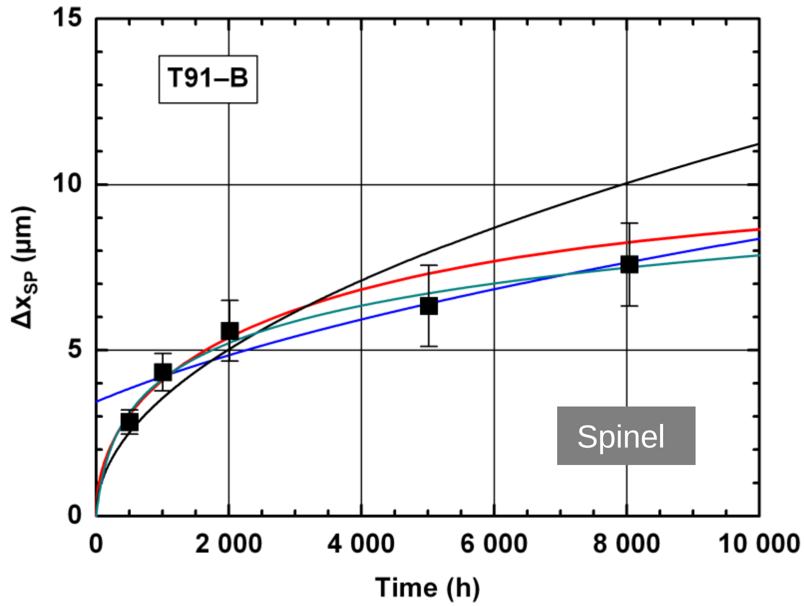
T91-B, 502 h



T91-A, 8039 h

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





Parabolic: $\Delta x^2 = k_2 t$

Parabolic after faster initial kinetics: $\Delta x^2 = k_2 t + C_2$

Logarithmic:

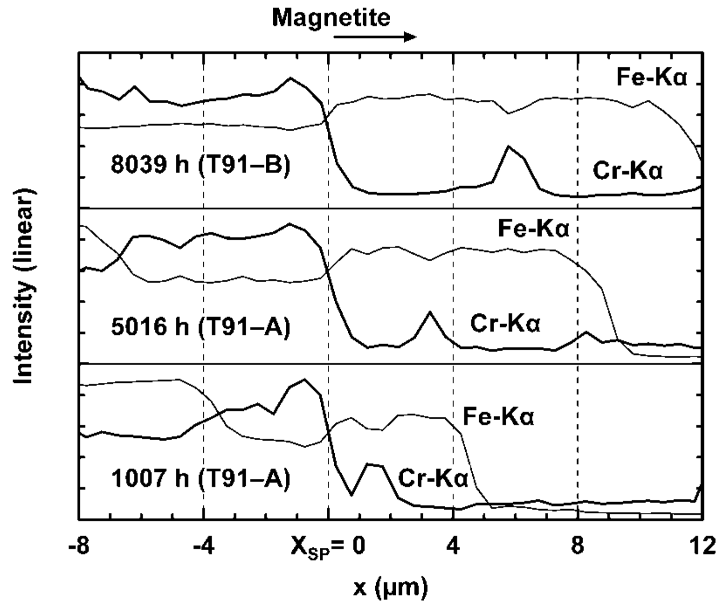
$$\Delta x = k_{log} \log(t + t_0) + C_{log}$$

Paralinear: $\frac{d\Delta x}{dt} = \frac{k_p}{2\Delta x} + k_1$

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

Implications from paralinear model of oxide-scale growth

- Paralinear kinetics of spinel growth with rate constants $k_{p;SP}$ (parabolic part) and $k_{l;SP}$ (linear part) means
  - Movement of the magnetite/spinel interface (with position X_{SP}) from X_0 towards the instantaneous position of the steel surface (X_{ST})
    $\rightarrow$ $-(X_0 - X_{SP}) = k_{l;SP}\, t$
  - Transformation of spinel into magnetite at this interface
  - Local enrichment of Cr inside the magnetite layer indicates incomplete spinel transformation



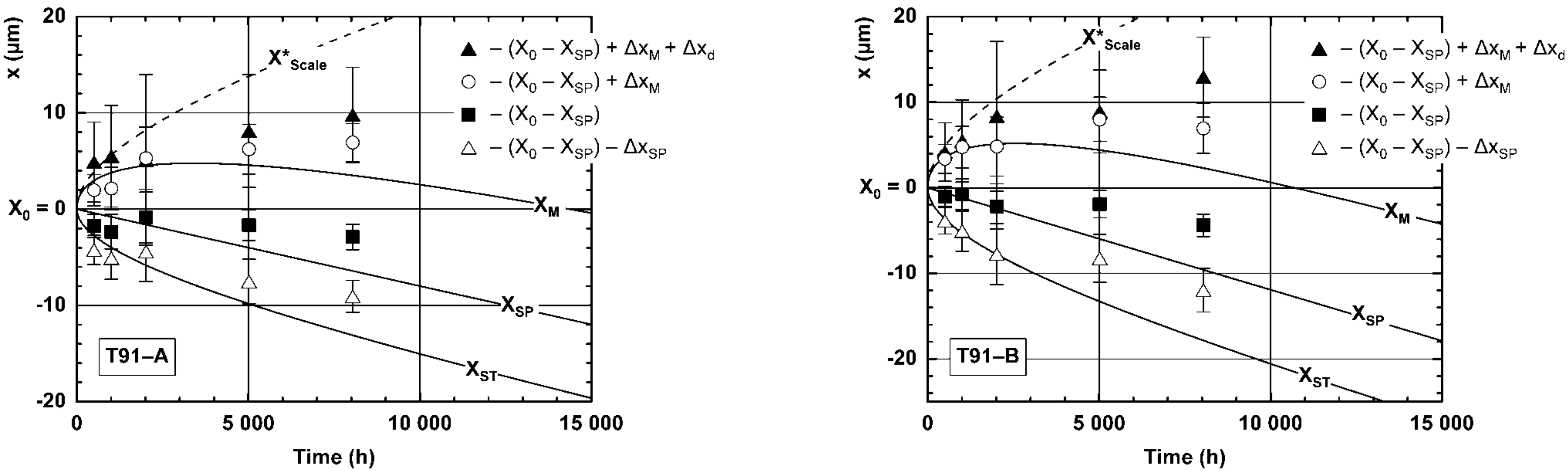
- Metal recession:

$$-(X_0 - X_{ST}) = -\Delta x_{ST} = k_{l;SP}\, t - \Delta x_{SP}$$

- Dissolved part of the oxide scale (magnetite layer):

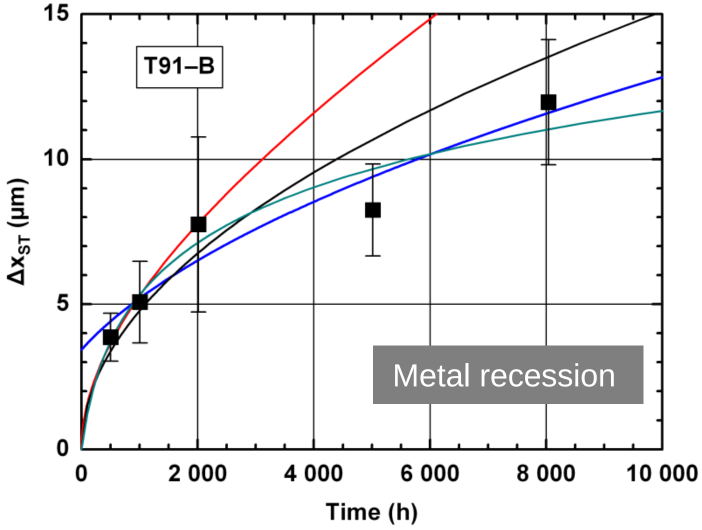
$$\Delta x_d = -(k_{l;SP} + k_{l;M})\, t$$

Simulation on the basis of paralinear model of oxide-scale growth



- Discrepancies between model and experimental data mainly result from inaccurate prediction of the movement of the magnetite/spinel interface (X_{SP})
- Kinetics of this movement is apparently slower than linear, possibly parabolic with respect to the part of the spinel layer transformed into magnetite
- Δx_d (X^*_{Scale}) depends on oxide porosity which was not taken into account

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



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Parabolic after faster initial kinetics: $\Delta x^2 = k_2 t + C_2$

Paralinear model of oxide scale growth

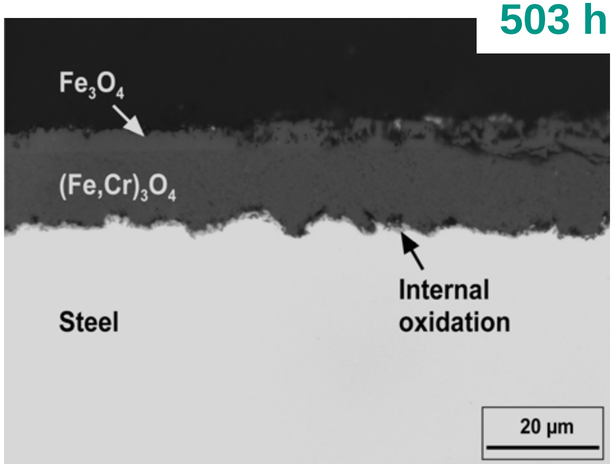
Logarithmic:

$$\Delta x = k_{log} \log(t + t_0) + C_{log}$$

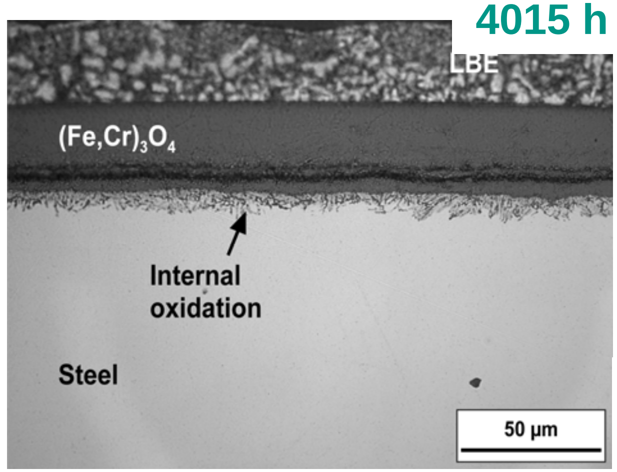
	Exposure time (years)		
	1	5	10
T91-A → Upper limit of Cr content specified for T91			
Δx_M (µm)	10	13–22	13–31
Δx_{SP} (µm)	7	8–14	8–20
Δx_{ST} (µm)	9	20	28
T91-B → Lower limit of Cr content specified for T91			
Δx_M (µm)	12	15–26	15–36
Δx_{SP} (µm)	8	10–16	10–23
Δx_{ST} (µm)	12	26	37

Oxide scale on T91 at 550°C, 2 m/s and 10^{-6} mass% oxygen

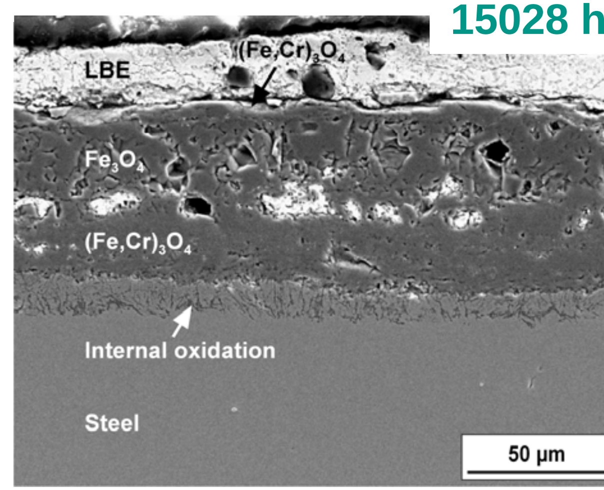
503 h



4015 h



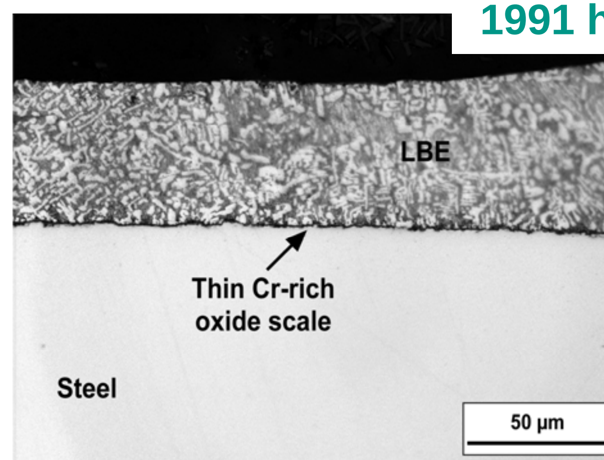
15028 h



- ***Structure***
  - In general, spinel layer and 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, especially after long exposure times

- ***Exceptional behaviour (oxidation)***

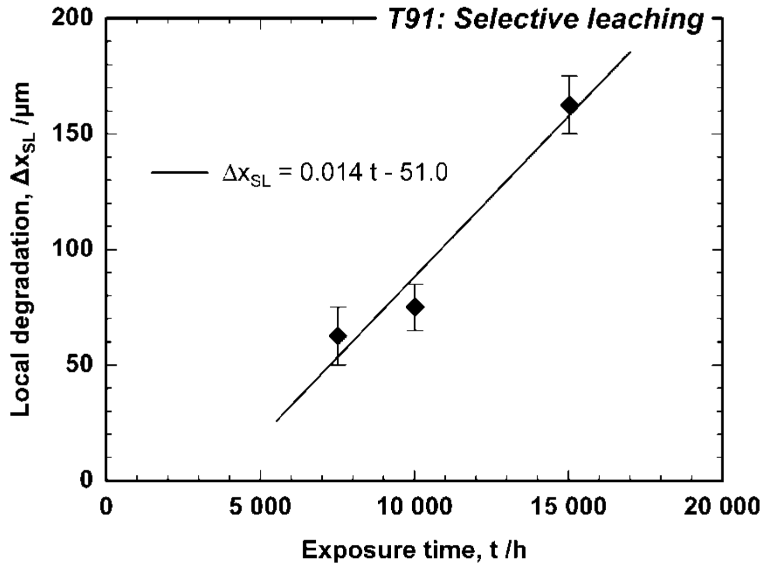
1991 h



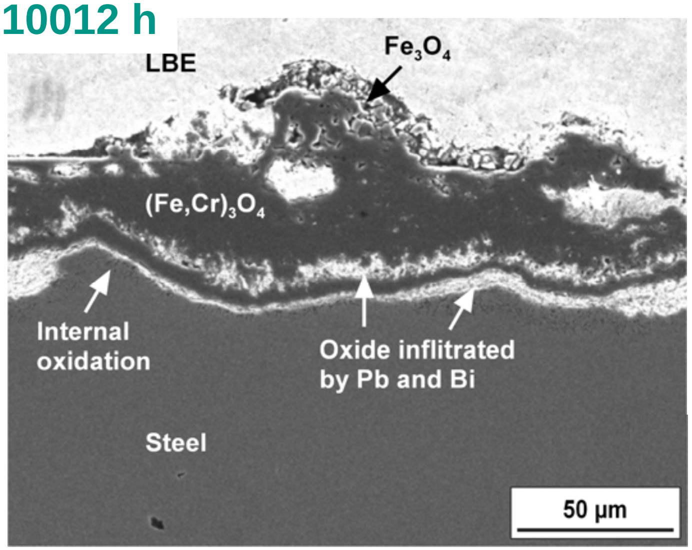
Local selective leaching

Maximum local damage observed for T91-B

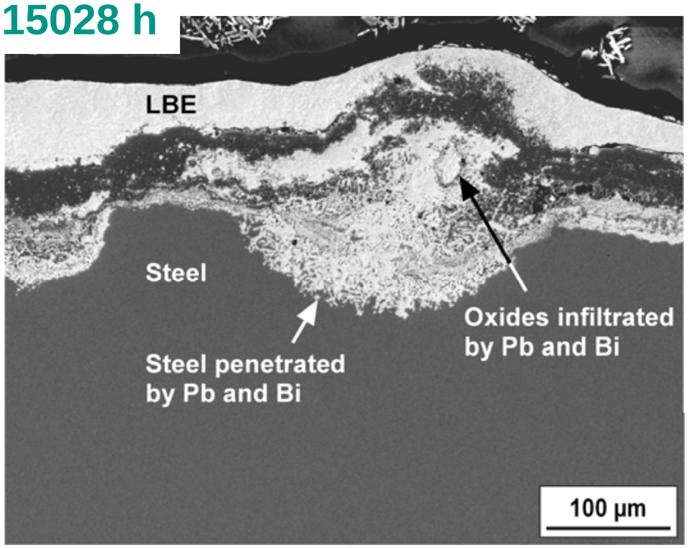
- **_Selective leaching of Cr at 550 ° C_**
  - Pb and Bi penetrate the scale at the steel/scale interface
  - Local acceleration of mass (Fe) transfer as a result of liquid-state diffusion
  - Depletion of oxygen in the liquid metal beneath the scale promotes preferential dissolution of Cr



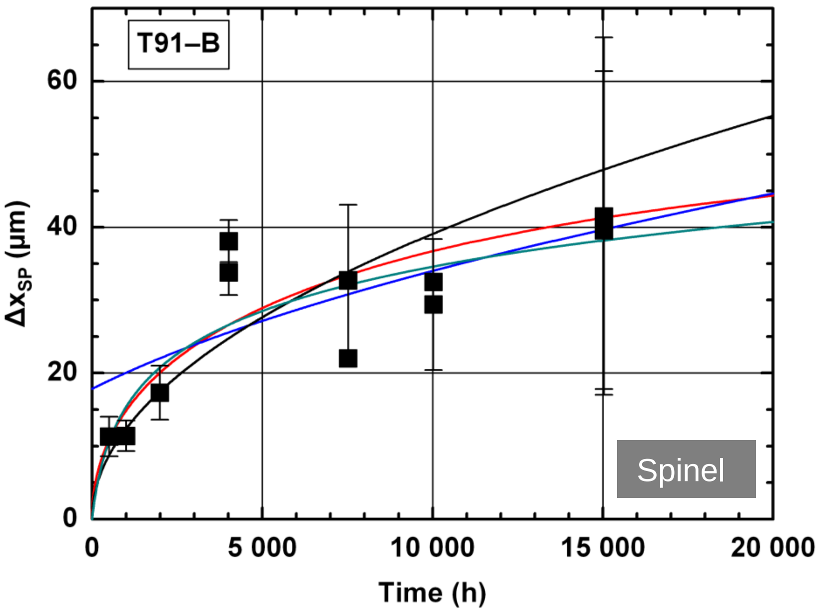
10012 h

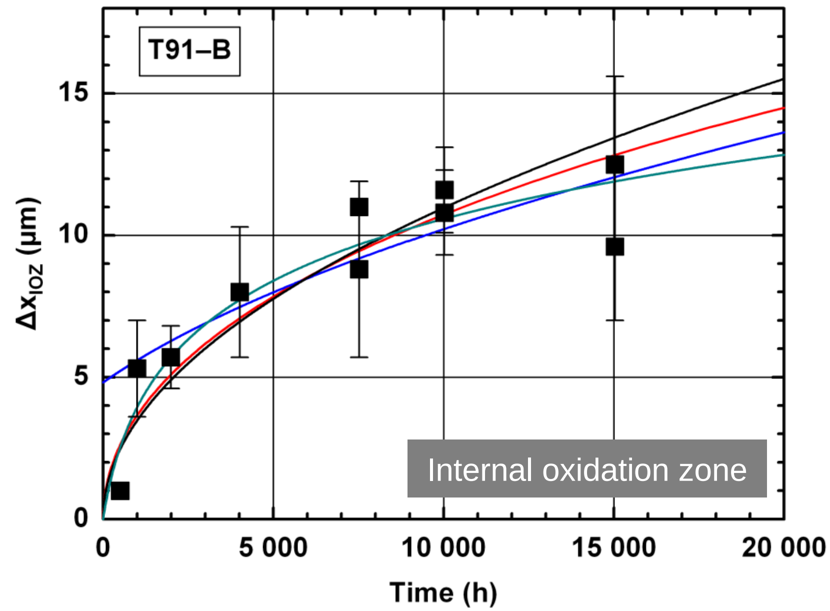


15028 h



Kinetics of oxide-scale growth for T91-B at 550° C, 2 m/s and 10^{-6} mass% oxygen





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Parabolic after faster initial kinetics: $\Delta x^2 = k_2 t + C_2$

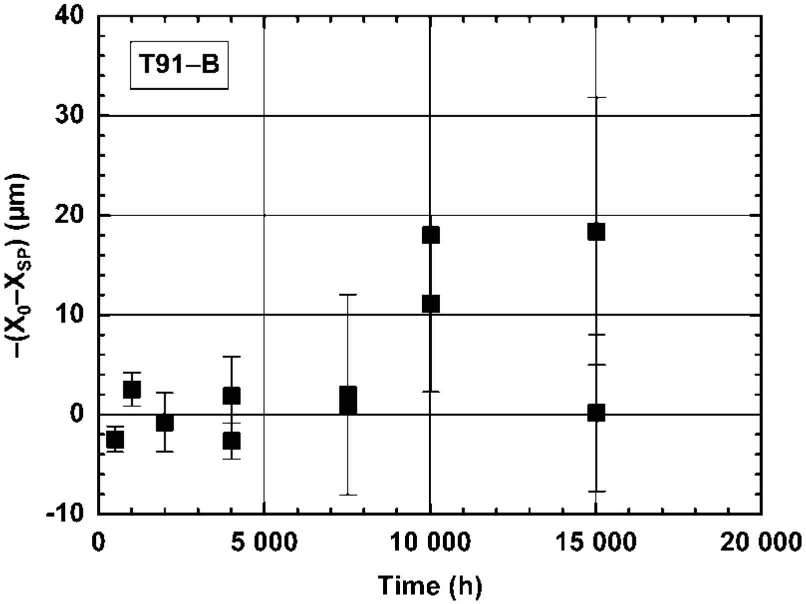
Logarithmic:

$$\Delta x = k_{log} \log(t + t_0) + C_{log}$$

Paralinear: $\frac{d\Delta x}{dt} = \frac{k_p}{2\Delta x} + k_1$

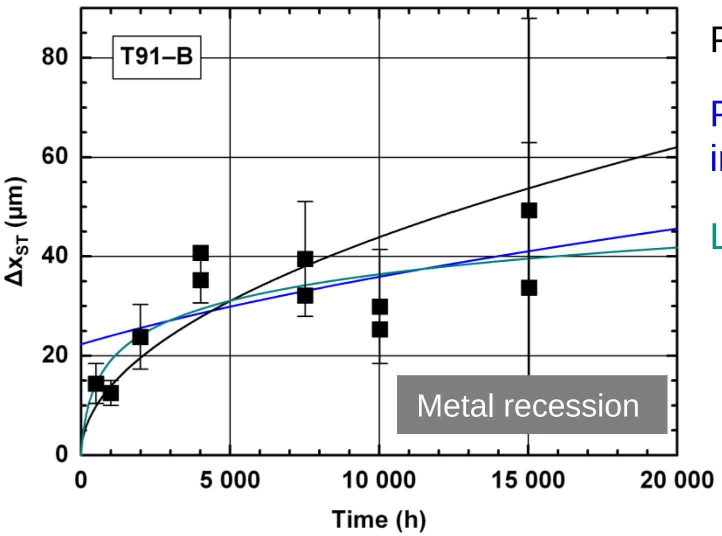
- Large scatter of the data in comparison to 450° C, especially for long exposure times
- Similar results for T91-A and T91-B

Movement of spinel surface (= oxide-scale surface) at 550° C, 2 m/s and 10^{-6} mass% oxygen



- ***Results of metallographic measurements***
  - Direction of movement not evident (no movement) up to 7500 h
  - Indication of growth of the spinel layer above the initial steel surface (in position X_0) rather than spinel dissolution for >7500 h
  - Further analyses needed for finding the most appropriate kinetic model for spinel growth

Data extrapolation for T91 at 550° C, 2 m/s and 10^{-6} mass% oxygen



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Parabolic after faster initial kinetics: $\Delta x^2 = k_2 t + C_2$

Logarithmic:

$$\Delta x = k_{log} \log(t + t_0) + C_{log}$$

Only regular oxidation, selective leaching not considered.

	Exposure time (years) 5	10
T91-A		
Δx_{SP} (µm)	62–67	87–95
Δx_{ST} (µm)	64–93	83–131
T91-B		
Δx_{SP} (µm)	63–82	88–116
Δx_{ST} (µm)	63–92	86–130

Extrapolated using the parabolic models with $C_2 = 0$ and > 0, respectively.

Conclusions on the performance of T91 in flowing (2 m/s) oxygen-containing (10^{-6} mass%) LBE

	At 450° C	At 550° C
Formation of thin protective oxide scale	• Not observed for t ⩾ 500 h	• Minor aspect of short-term behaviour
Typical scaling behaviour of Fe-Cr alloys	• Magnetite, spinel and slight internal oxidation • Paralinear models describe the growth of the magnetite and spinel layer fairly well • Improved model for the implied transformation at the magnetite/ spinel interface required • 30–40 µm metal-recession and 20–60 µm scale-thickness expected after 10 years	• In general, spinel layer and IOZ • Magnetite mostly missing • Large scatter of experimental data makes analysis of the kinetics difficult • 80–130 µm metal-recession, 90–120 µm scale-thickness (without IOZ) expected after 10 years
Selective leaching (of Cr)	• Local accumulation of Pb and Bi inside the scale and at the scale/steel interface • Slight Cr-depletion of the steel (for t ⩽ 8000 h)	• Expected local damage ~ 10-times higher than for pure oxidation • Minimum for optimized steel micro-structure?

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