SEARCH/MAXSIMA International Workshop

October 7 –10, 2014

Karlsruhe Institute of Technology (KIT), Germany

Estimation of corrosion product formation in MYRRHA

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Corrosion-related issues
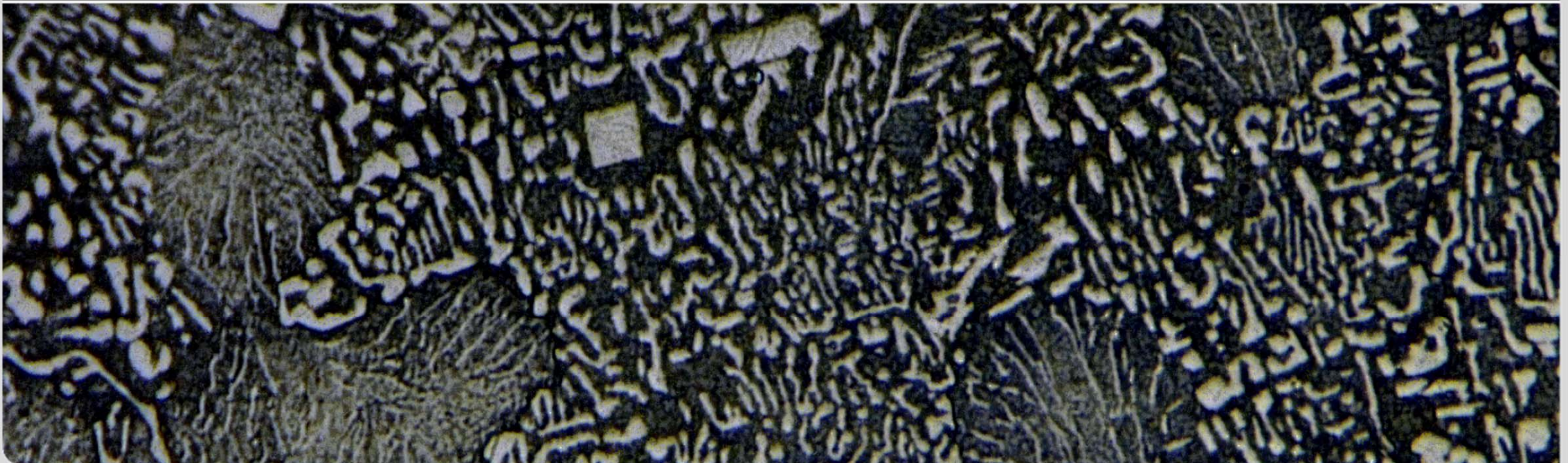
❑ Materials

- Thinning of the material cross-section
- Altered near-surface material properties
- Impaired properties of functional surfaces
- Overall change of geometric dimensions, e.g., material plus solid corrosion scale

❑ Corrosive medium

- Depletion in corrosive agents
- Contamination with corrosion products
- Contaminant diffusion and convective transport
- Subsequent chemical reactions
- Re-precipitation of absorbed elements
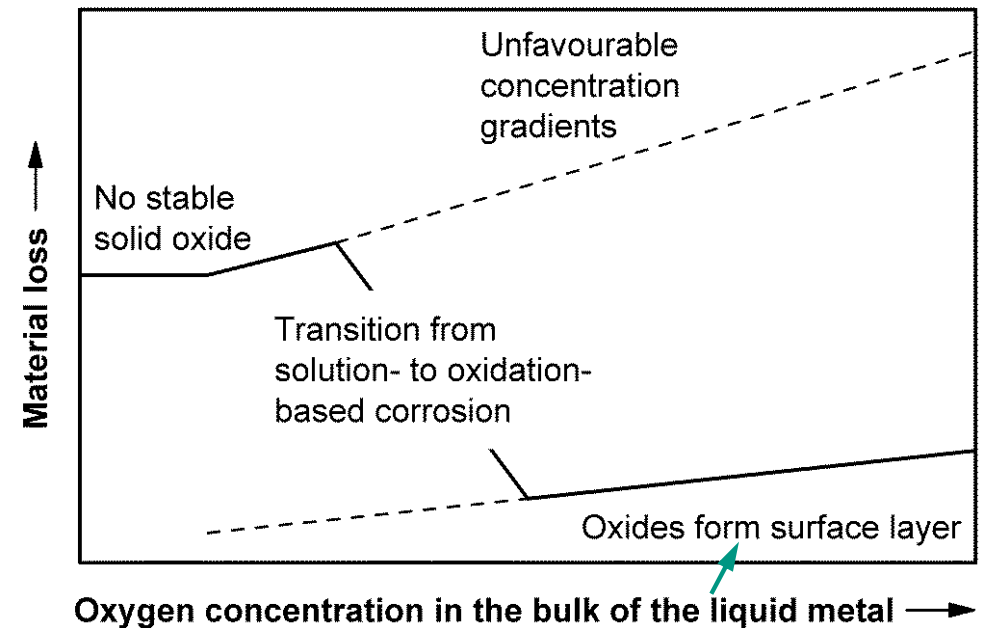- Deposition of solid matter

❑ Plant operation

- Reduced efficiency of plant components
- Risk of premature material failure
- Short- and long-range secondary effects, e.g., plugging of narrow sections
- Contribution to the emission of pollutants

MYRRHA reactor: Process medium and materials

- ☐ **Process medium**

  - ▪ Lead-bismuth eutectic (LBE)

  - ▪ Addition of oxygen so as to favour oxidation over solution of material elements

  - ▪ Oxygen activity or concentration required is material- and temperature-dependent

- ☐ **Materials**

  - ▪ Austenitic steels:
    316L for the main structural components,
    15-15Ti in the core

  - ▪ 9Cr ferritic/martensitic steels:
    T91 for parts of the core support and spallation target assembly

- ➡️ **Under MYRRHA-relevant conditions, the same steel may show different corrosion modes in oxygen-containing LBE!**

Goal of deliberate oxygen addition

Objectives and approaches

- ❑ **Estimation of corrosion product formation in respect of**

  - Solution of steel elements by the LBE ➡ **May re-precipitate and contribute to floating solid oxides or plugging**

  - Oxygen consumption, i.e., depletion if oxygen is not replaced ➡ **Input for dimensioning appropriate oxygen-transfer devices**

  - Uptake/precipitation of solid oxides ➡ **Contributes to deposition of solid matter; input for dimensioning filters or other to remove floating oxides**

- ❑ **Work performed**

  - Analysis of availability of required corrosion data: mechanisms, rate laws, activation energies, incubation times, surface area affected by local processes ➡ **Available data is incomplete, requiring a number of assumptions and simplifications!**
  - Simplified spread sheet calculations for design operating conditions of MYRRHA, separately for the corrosion modes to be considered
  - Specific calculations for reactor start-up and first power cycles

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MYRRHA design data used

Design operating parameters

Material	Temperature (°C)	Surface area (m²)	Oxygen conc. (mass%)	Average flow velocity (m/s)
316L	400	120	$\sim 10^{-7}$	To be specified
	350	419 (360)		
	310	125		
	270	1697 (1596)		
15-15Ti	410	194	$\sim 10^{-7}$	To be specified
	270	1150		
T91	450	4	$\sim 10^{-7}$	To be specified
	350	(59)		
	270	1 (102)		

	Duration (days)	Temperature (°C)
Start-up	180	270°C
1st Power cycle	90	Components at design operating temperature; temperature transients
Downtime	90	270°C
2nd Power cycle	90	As above

Early operating stages

Oxidation of 9Cr ferritic/martensitic and austenitic steels in oxygen-containing LBE

❏ **Protective scaling**
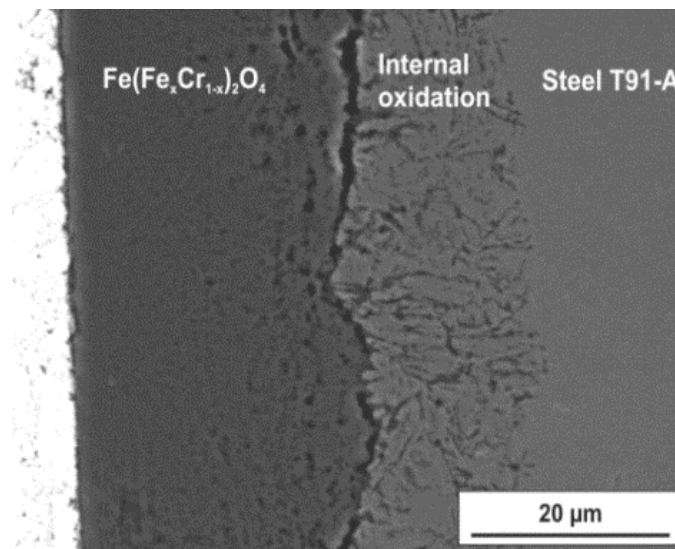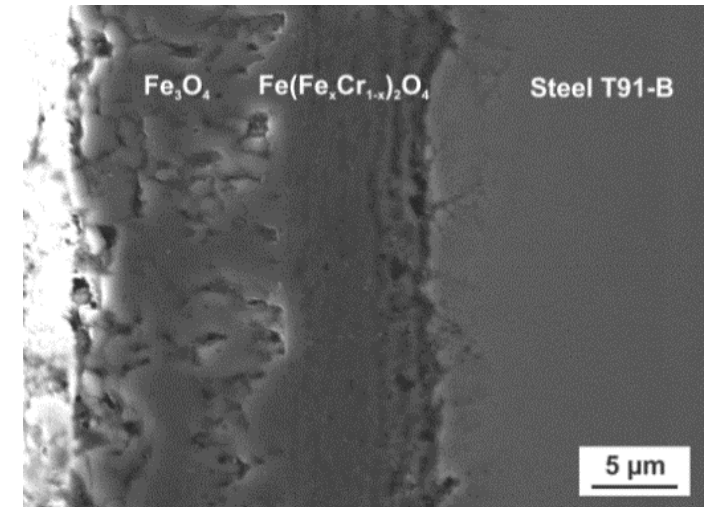
- Thin Cr- (Si-) rich oxide scale (thickness ~1 µm or less)
- Precursors of this scale are likely to be present already on the original material
- Local degradation gives way to faster corrosion processes
- Dominant oxidation process for Type 316 steels and 15-15Ti, especially at $T \leq 450°C$ and $c_O \leq 10^{-6}$ mass%
- Release of steel elements is likely to be negligible
- Oxygen consumption mainly confined to the initial formation of this scale

LBE

316L

Thin oxide scale

10 µm

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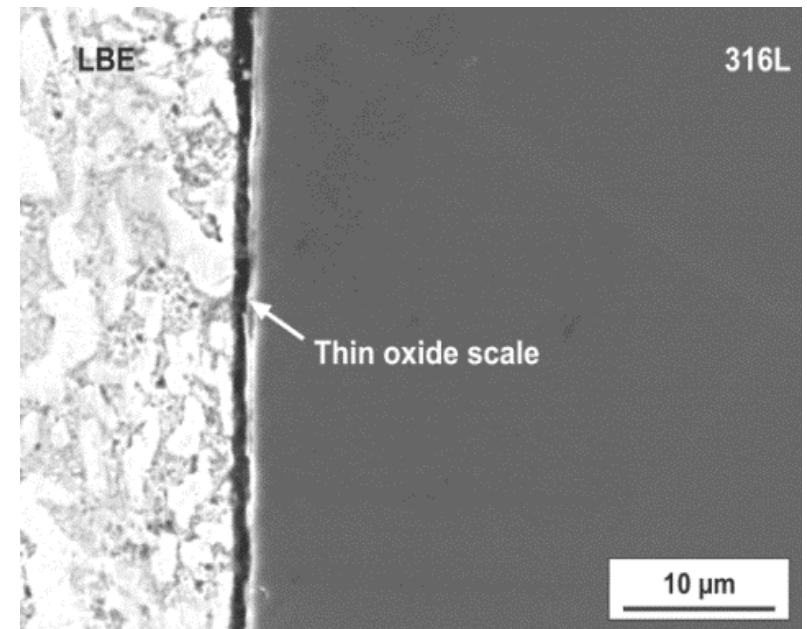
Oxidation of 9Cr ferritic/martensitic and austenitic steels in oxygen-containing LBE
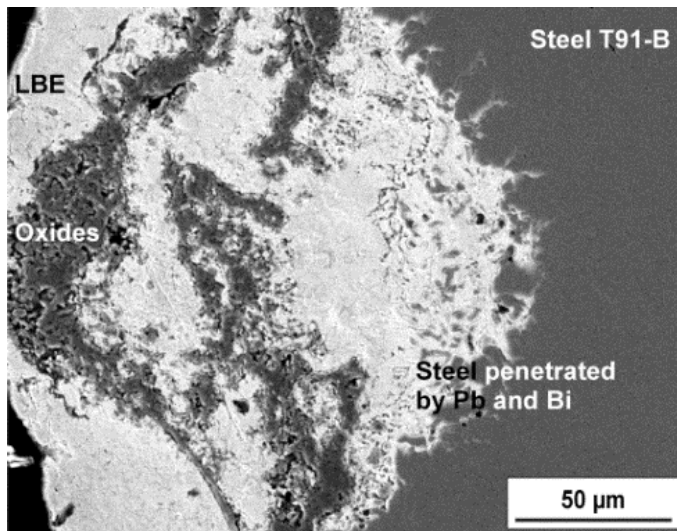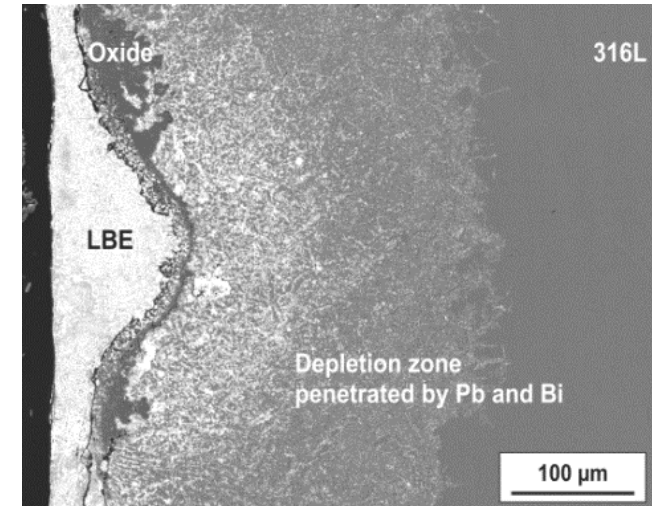
- ❑ **Accelerated oxidation**
  - ▪ Typical for and, finally, the general corrosion process of 9Cr steels, after failure of the thin Cr-rich scale
  - ▪ Less frequent occurrence on austenitic steels, especially at $T \leq 450°C$ and $c_O \leq 10^{-6}$ mass%
  - ▪ Comparatively thick scales generally consisting of Fe_3O_4, $Fe(Fe_xCr_{1-x})_2O_4$ and an internal oxidation zone
  - ▪ Release of Fe to the LBE at the oxide scale surface
  - ▪ Oxygen consumption due to continuous growth of oxides

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Solution-based corrosion in oxygen-containing LBE

- **Type 316 steels, 15-15Ti**
  - Selective leaching of Ni and Cr
  - Formation of a ferritic depletion zone that is penetrated by the liquid metal
  - Occasionally oxide (precipitated) on the surface, but transfer of removed elements to the LBE dominates
 - Starts locally from failure of the thin Cr-scale

- **9Cr ferritic/martensitic steel**
  - Probably starts from penetration of LBE into the oxide scale formed during accelerated oxidation
  - Steel elements may be selectively (Cr) or generally removed, depending on local conditions
  - Predominance of steel element release over accumulation in oxides not always clear

Quantitative results from experiments in the CORRIDA loop: T91 in LBE at 450–550°C, 2 m/s and 10^{-6}% dissolved oxygen
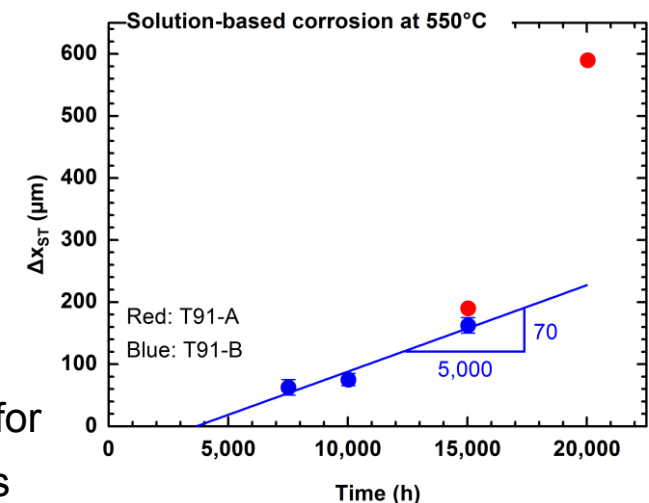
☐ **Accelerated oxidation**
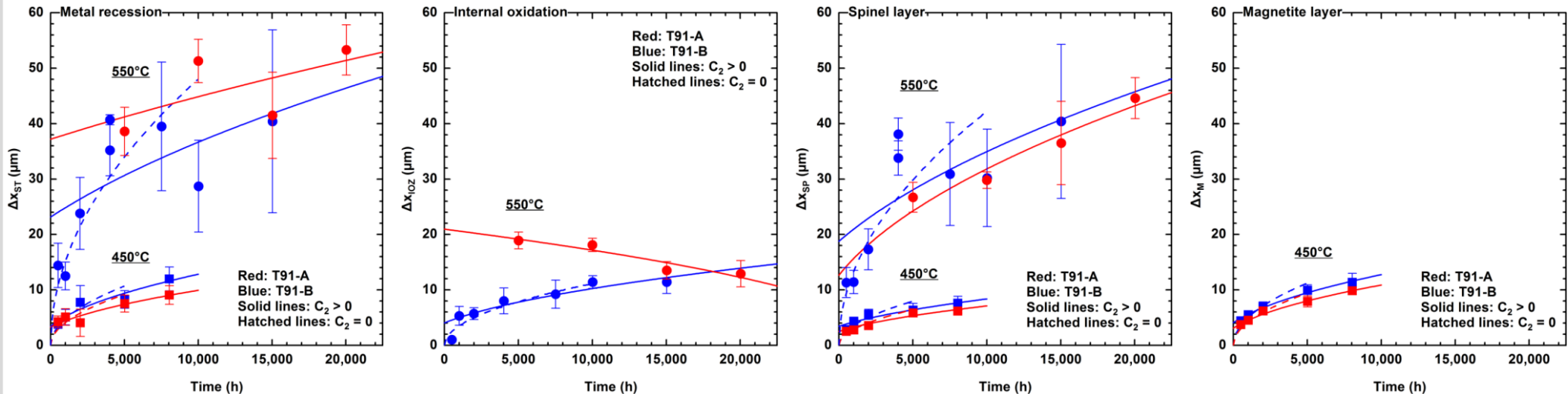
- Thickness of magnetite approximates the overall increase in specimen radius
- Dissolved Fe from balancing the mass consumed and present in oxides
- Extrapolation of data naturally depends strongly on the type of rate law assumed

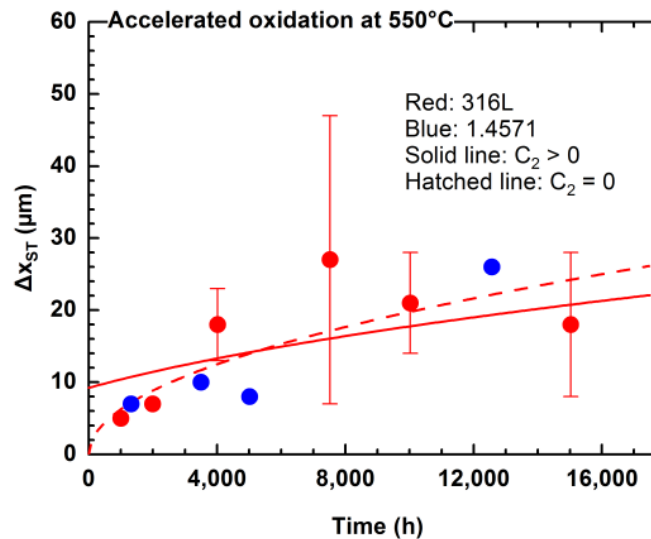☐ **Solution-based corrosion**

- Significantly increased material loss
- Comparatively small database for kinetic analysis
- Underlying corrosion mechanisms may differ for the particular data points

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Quantitative results from experiments in the CORRIDA loop: Type 316 in LBE at 450–550°C, 2 m/s and 10^{-6}% dissolved oxygen

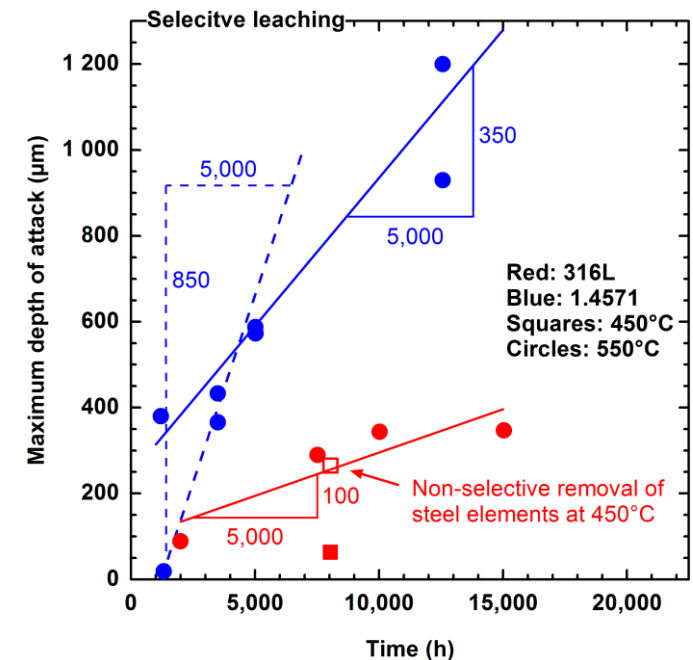❑ **Accelerated oxidation**

- Observed locally at 550°C
- In parts continuous scale after long exposure time
- Not observed at 450°C

Red: 316L
Blue: 1.4571
Solid line: $C_2 > 0$
Hatched line: $C_2 = 0$

❑ **Solution-based corrosion**

- Only few sites on investigated specimens may be affected
- Mostly selective leaching of Ni and Cr
- But also general dissolution of all steel elements at 450°C
- Incubation time decreases from around 5000 h at 450°C to 1000 h at 550°C

Red: 316L
Blue: 1.4571
Squares: 450°C
Circles: 550°C

Non-selective removal of steel elements at 450°C

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Estimation of steel element transfer

❑ **Procedure:**
- Calculate material- and area-specific transfer of metals at relevant temperatures after given time
- Multiply by associated surface area in the reactor

❑ **Protective scaling**
- Neglected

❑ **Accelerated oxidation**
- Neglected for 316L and 15-15Ti
- T91:
  - Only release of Fe into the LBE considered
  - Mass of Fe in consumed steel (ST) balanced with mass of Fe accumulated in $Fe(Fe_xCr_{1-x})_2O_4$ (SP) and Fe_3O_4 (M)
  - Parabolic rate laws of steel recession and scale thicknesses as observed in flowing LBE at 450°C, 10^{-6} mass% O and 2 m/s: $k_{2,ST}$= 0.023; $k_{2,SP}$= 0.013; $k_{2,M}$= 0.025 µm²/h
 - Activation energy 160 kJ/mol considered for start-up, downtime or transient temperature during power cycle

❑ **Solution-based corrosion**
- Not considered for T91 due to the lack of appropriate mechanism and kinetic data (not justified at low oxygen concentration?)
- Selective leaching of 316L, 15-15Ti:
  - Linear kinetics in terms of maximum depth of attack as observed for 316L at 500°C, $<10^{-8}$ mass% O, static LBE; k_1= 0.017 µm/h (Yamaki et al., 2011)
  - Activation energy 75 kJ/mol (Yamaki et al., 2011)
  - Complete solution of Ni, 50 and 10% of available Cr and Fe, resp.

Results on transferred mass of steel elements

- ❑ **Regular operation starting at t= 0**
  - ▪ Remarkable influence of Fe release due to accelerated oxidation of T91 components confined to the first 10 h
  - ▪ Average transfer rates in the order of 1–2 g/h for each Fe, Cr and Ni
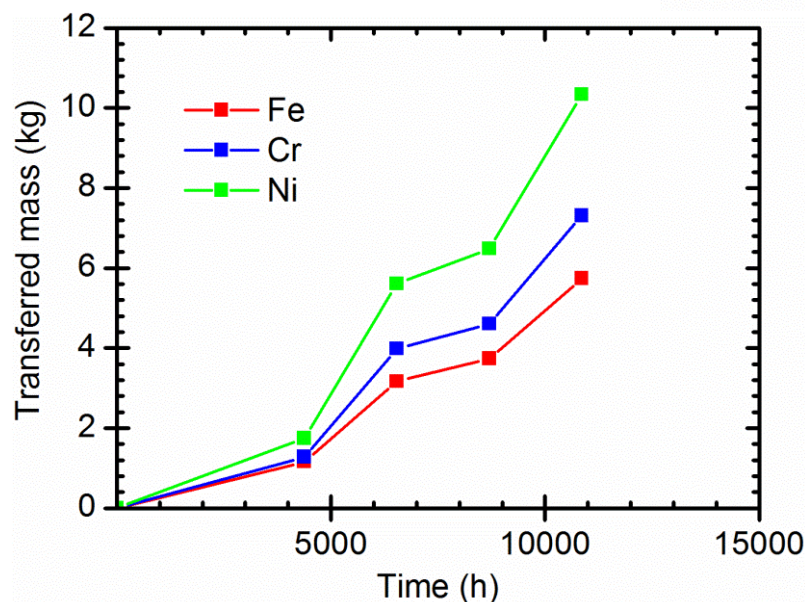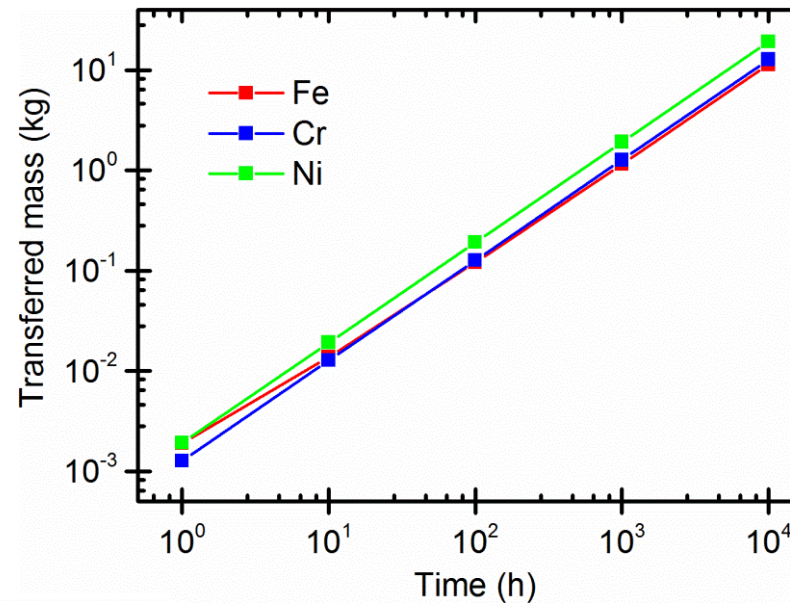
- ❑ **Start-up operation and first two power cycles**
  - ▪ Transfer of 0.2–0.4 g/h of each Fe, Cr, and Ni during start-up at 270°C
  - ▪ Fe release due to accelerated oxidation of T91 components negligible for power cycles and intermittent downtime at 270°C
  - ▪ Power cycle: 1–2 g/h of each Fe, Cr and Ni released into the LBE from austenitic steels

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Estimation of oxygen consumption

| Procedure: | ▪ Calculate material- and area-specific oxygen consumption at relevant temperatures after given time |
| | ▪ Multiply by associated surface area in the reactor |

❑ **Protective scaling**

- All steels/component surfaces initially form a thin chromia (Cr_2O_3) scale
- An equivalent mass of 0.5 μm scale thickness has to form, irrespective of the actual operating temperature
- Instantaneously – in 1 h – 10 h – 100 h …

⬇

Initial demand for oxygen replacement

❑ **Accelerated oxidation of T91**

- Formation of adherent $Fe(Fe_xCr_{1-x})_2O_4$ and Fe_3O_4 (M) under design operating conditions
- Same assumptions in regard of the oxidation process as for steel element transfer

❑ **From solved steel elements**

- Steel elements released into the LBE may oxidise somewhere in the reactor

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After typical corrosion processes have established

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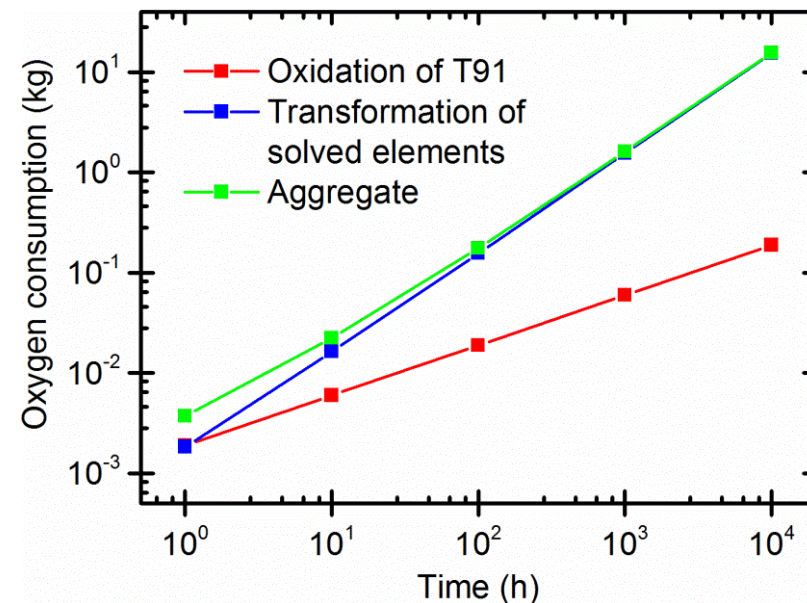
Results on oxygen consumption for design operating conditions

❑ **Protective scaling**

- 3.2 kg of oxygen being consumed when formation of 0.5 µm thick scale is assumed

- Corresponds to 43.5 kg or 2.2 Ncm³ of PbO and gaseous O_2, respectively

- 3.2–32 g/h average rate of oxygen consumption if the scales form in 10–100 h

- Initial oxygen concentration in LBE may be higher than required, i.e., only partial replacement of consumed oxygen needed
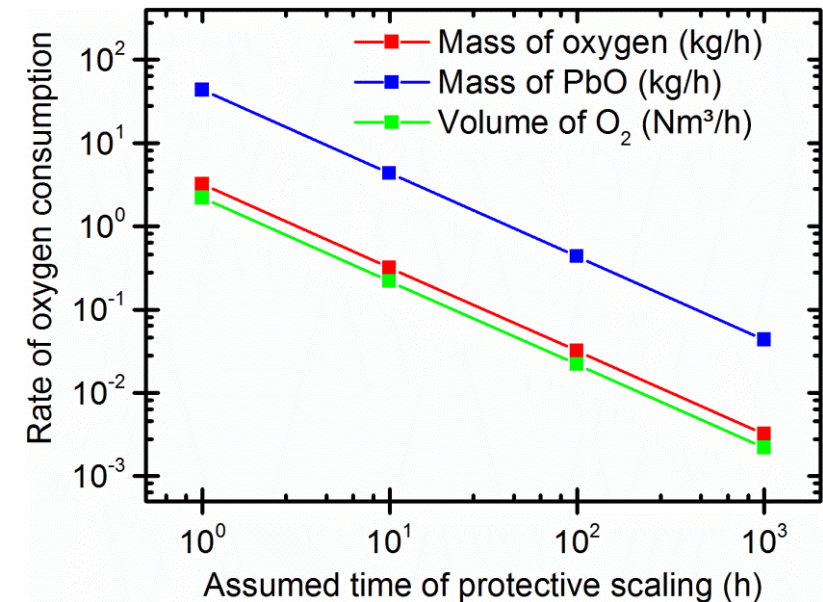
❑ **Subsequent corrosion processes**

- Solid oxides on T91 surfaces initially contribute by 50% to the over all oxygen consumption

- Oxidation of previously solved steel elements dominates oxygen consumption in the long run

- Oxygen consumption rate averages 2–3 g/h

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Amount of formed oxides

- **Design operating conditions**
  - Estimation without protective scaling
  - Qualitative same results as for oxygen consumption in regard of accelerated oxidation (T91) and transformation of solved elements
  - Average formation rate in the order of 1–2 cm³/h
  - Oxides formed on steel surfaces are immobile as long as they do not detach
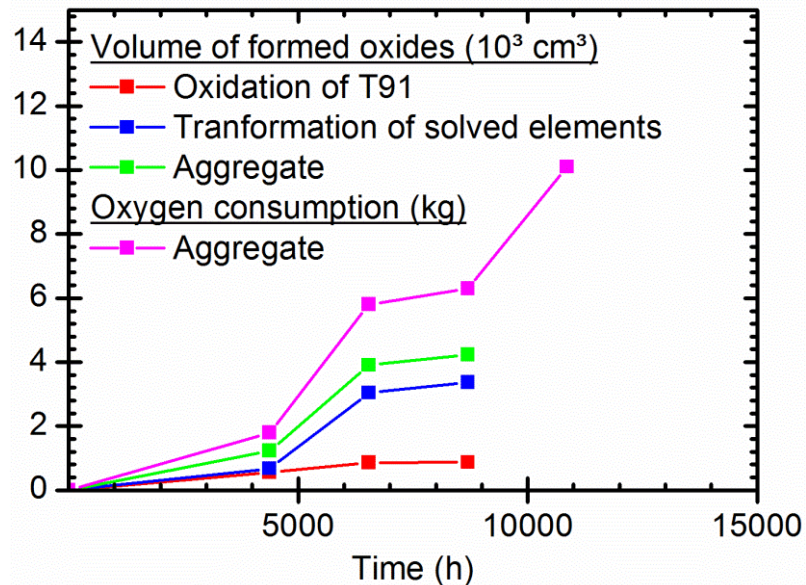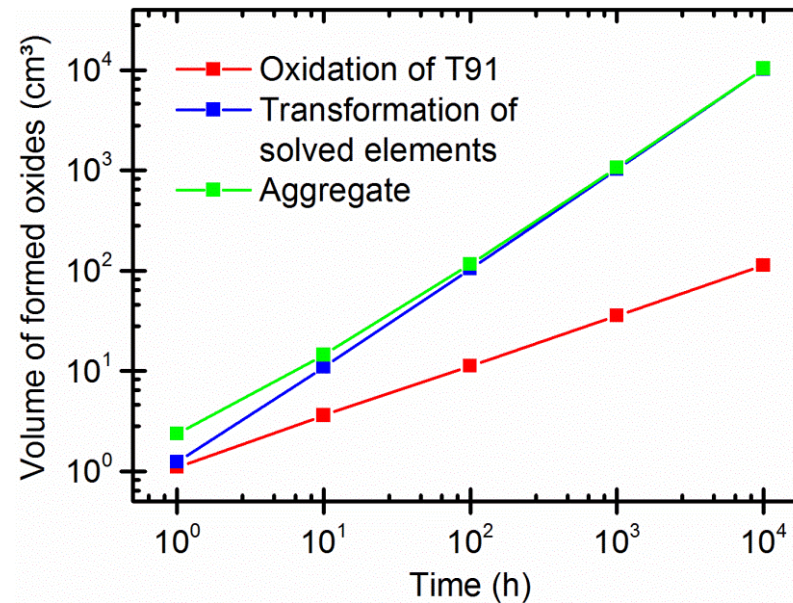
- **Start-up operation and first power cycles**
  - Average 1.25 cm³/h oxide formation estimated for the first power cycle
  - Associated oxygen consumption of 1.8 g/h

Summary and conclusions

- **In regard of the method of estimating corrosion products**
  - Simplified procedure
  - Gives estimates of the order of magnitude
  - Overall conservative, because most detrimental corrosion was assumed especially for austenitic steels (selective leaching)
  - More sophisticated estimating procedures useful only after existing gaps in the available quantitative corrosion data were closed

- **Implications for "chemistry control"**
  - 2–3 g/h oxygen needs to be replaced using an oxygen-transfer device, possibly except for the very initial stage (for protective scaling of steels)
  - Initially higher than required oxygen concentration in the LBE may partially compensate for increased consumption (up to 30 g/h?)
  - 1–2 cm³/h of produced solid oxides are to be removed by filters or other
  - Oxide particle size and distribution not yet investigated in detail

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Thank you
for your attention!

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