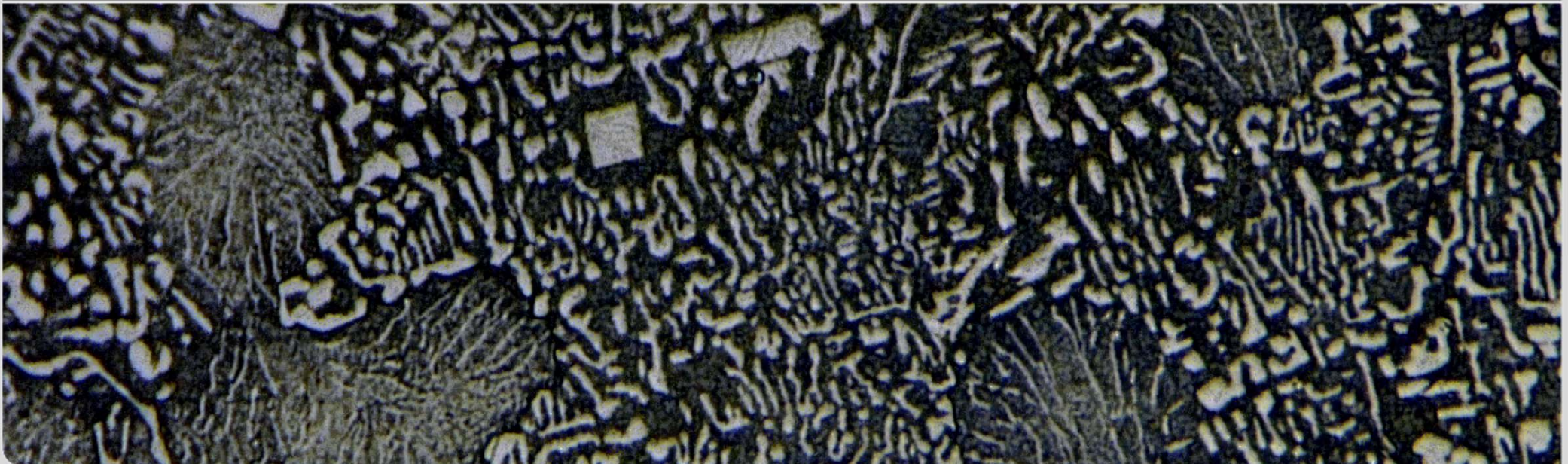


## Estimation of corrosion product formation in MYRRHA

Carsten Schroer, Alfons Weisenburger

Institute for Applied Materials – Material Process Technology (IAM-WPT), Corrosion Department  
Institute for Pulsed Power and Microwave Technology (IHM), Pulsed Power Technology Department



## ❑ 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

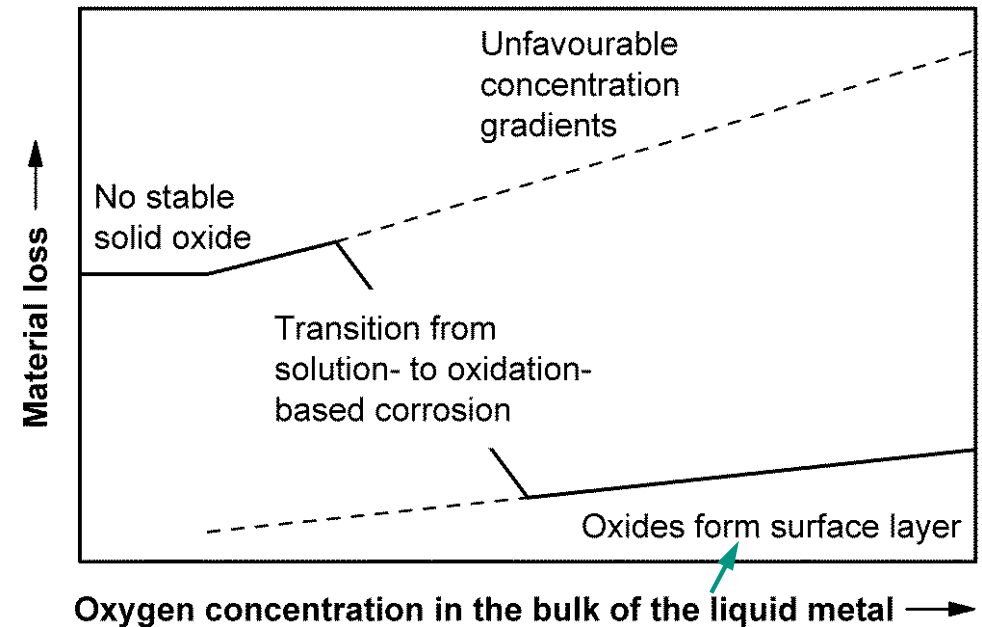
# MYRRHA reactor: Process medium and materials

## □ 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



**Goal of deliberate oxygen addition**

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

# Objectives and approaches

## □ Estimation of corrosion product formation in respect of

- Solution of steel elements by the LBE
- Oxygen consumption, i.e., depletion if oxygen is not replaced
- Uptake/precipitation of solid oxides

→ **May re-precipitate and contribute to floating solid oxides or plugging**

→ **Input for dimensioning appropriate oxygen-transfer devices**

→ **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
- 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

→ **Available data is incomplete, requiring a number of assumptions and simplifications!**

# MYRRHA design data used

## Design operating parameters

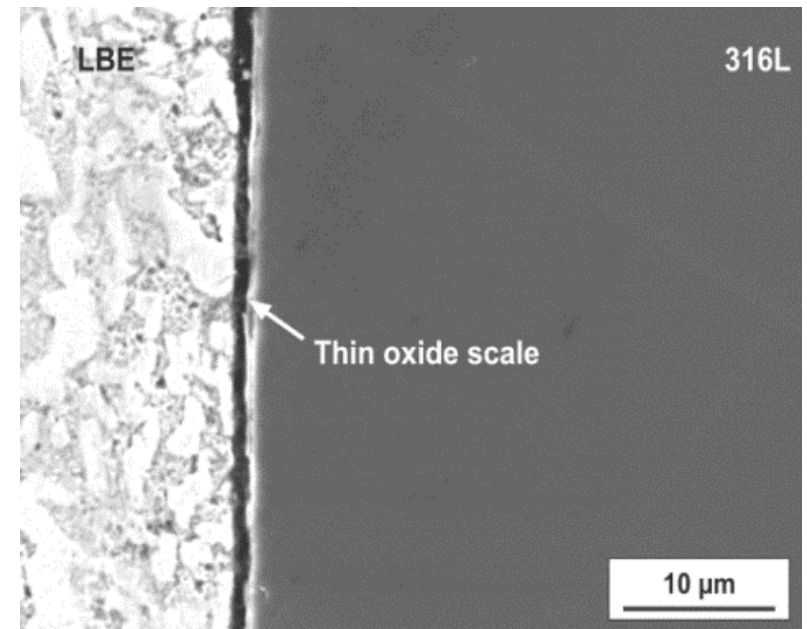
Material	Temperature (°C)	Surface area (m <sup>2</sup> )	Oxygen conc. (mass%)	Average flow velocity (m/s)
316L	400	120	~10 <sup>-7</sup>	To be specified
	350	419 (360)		
	310	125		
	270	1697 (1596)		
15-15Ti	410	194	~10 <sup>-7</sup>	To be specified
	270	1150		
T91	450	4	~10 <sup>-7</sup>	To be specified
	350	(59)		
	270	1 (102)		

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

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

## □ Protective scaling

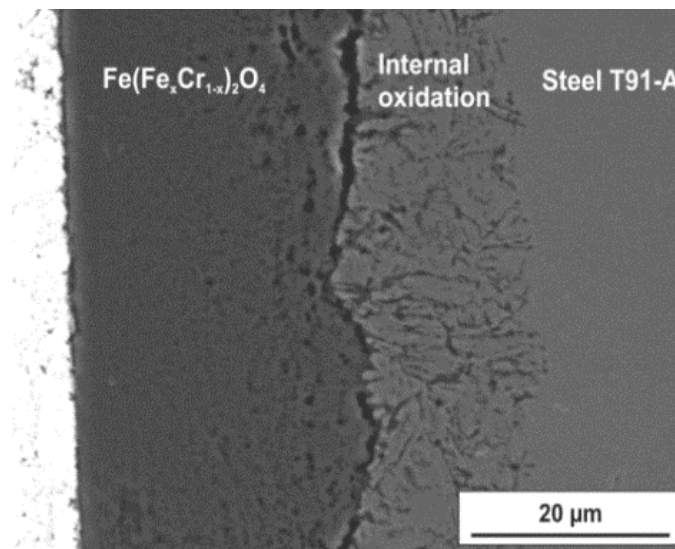
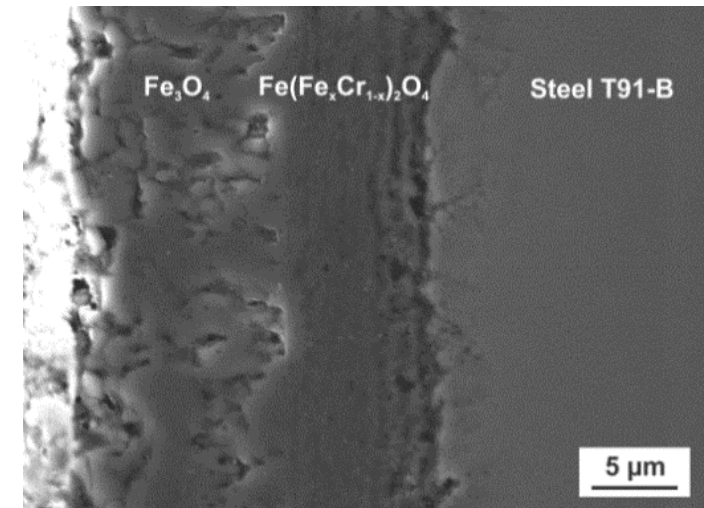
- Thin Cr- (Si-) rich oxide scale (thickness  $\sim 1 \mu\text{m}$  or less)
- Precursors of this scale are likely to be present already on the original material
- Local degradation gives way to faster corrosion processes
- Dominant oxidation process for Type 316 steels and 15-15Ti, especially at  $T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



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

## □ Accelerated oxidation

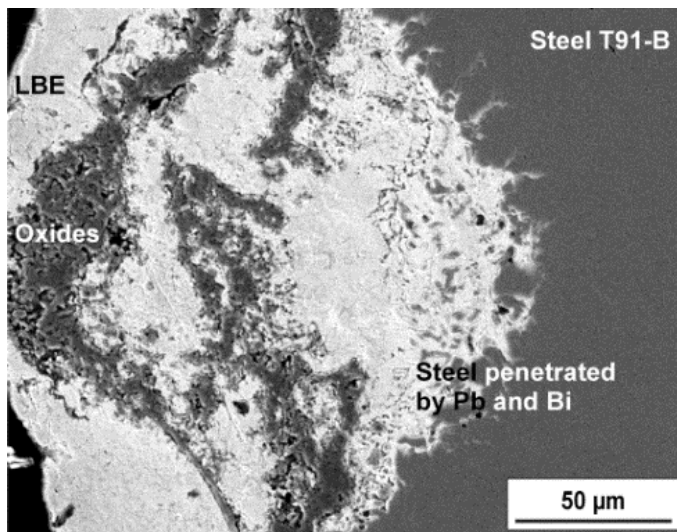
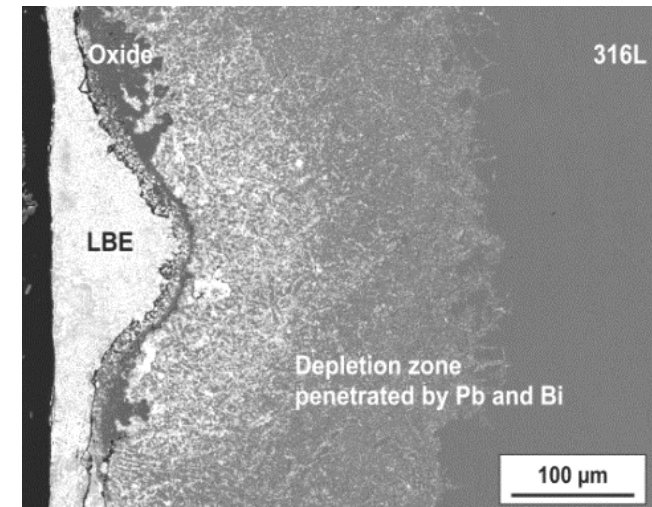
- Typical for and, finally, the general corrosion process of 9Cr steels, after failure of the thin Cr-rich scale
- Less frequent occurrence on austenitic steels, especially at  $T \leq 450^\circ\text{C}$  and  $c_{\text{O}} \leq 10^{-6}$  mass%
- Comparatively thick scales generally consisting of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}(\text{Fe}_x\text{Cr}_{1-x})_2\text{O}_4$  and an internal oxidation zone
- Release of Fe to the LBE at the oxide scale surface
- Oxygen consumption due to continuous growth of oxides



# 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



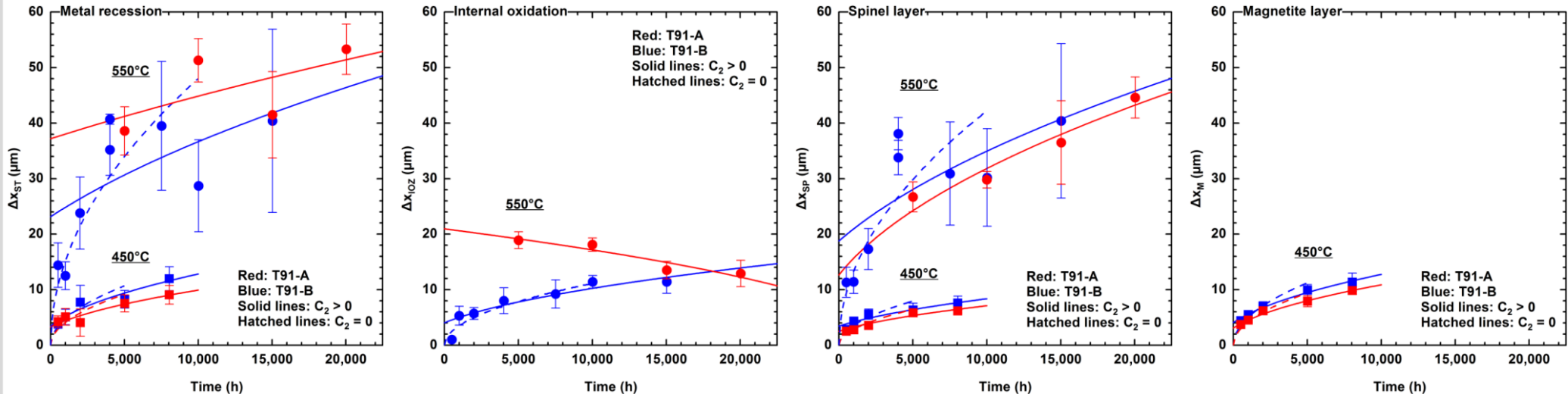
## □ 9Cr ferritic/martensitic steel

- 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<sup>-6</sup>% dissolved oxygen

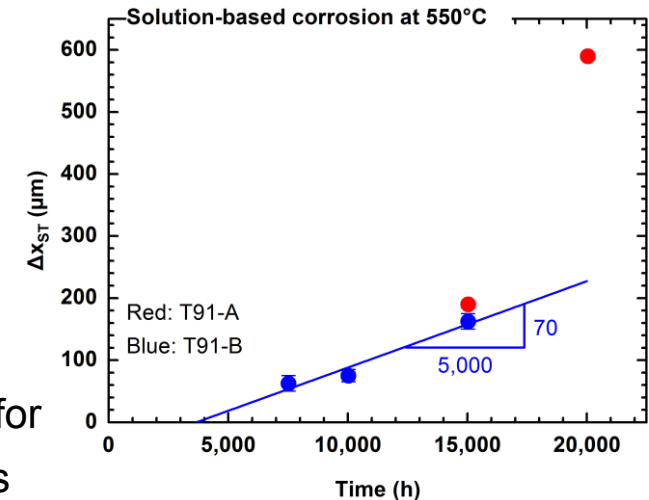
## Accelerated oxidation



- 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

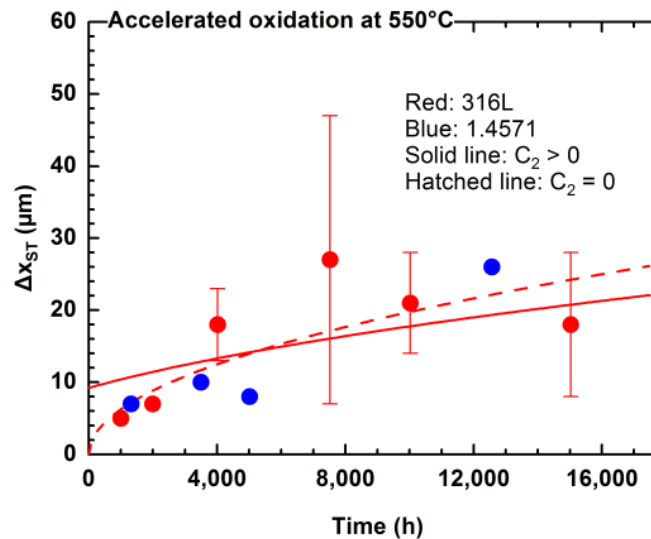
- Significantly increased material loss
- Comparatively small database for kinetic analysis
- Underlying corrosion mechanisms may differ for the particular data points



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

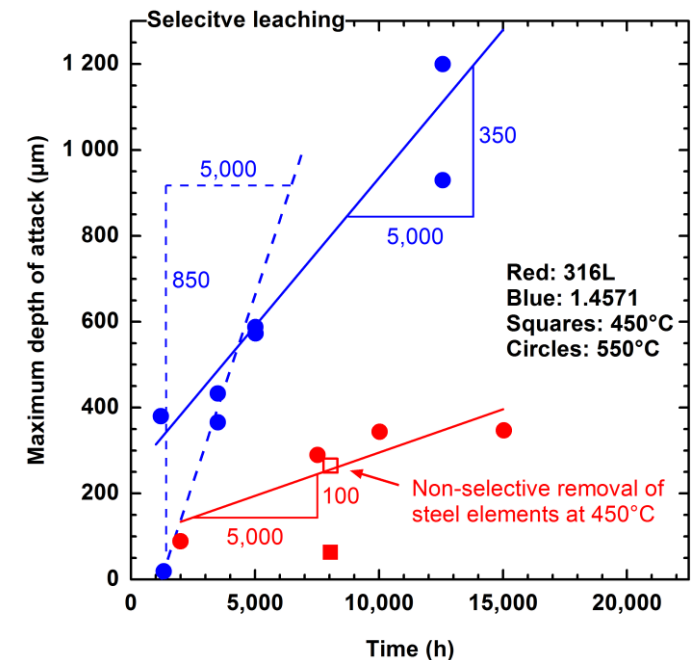
## Accelerated oxidation

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



## 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



## □ Protective scaling

- Neglected

## □ Procedure:

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

## □ 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  $\text{Fe}(\text{Fe}_x\text{Cr}_{1-x})_2\text{O}_4$  (SP) and  $\text{Fe}_3\text{O}_4$  (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:  
 $k_{2,\text{ST}} = 0.023$ ;  $k_{2,\text{SP}} = 0.013$ ;  $k_{2,\text{M}} = 0.025 \mu\text{m}^2/\text{h}$
  - Activation energy 160 kJ/mol considered for start-up, downtime or transient temperature during power cycle

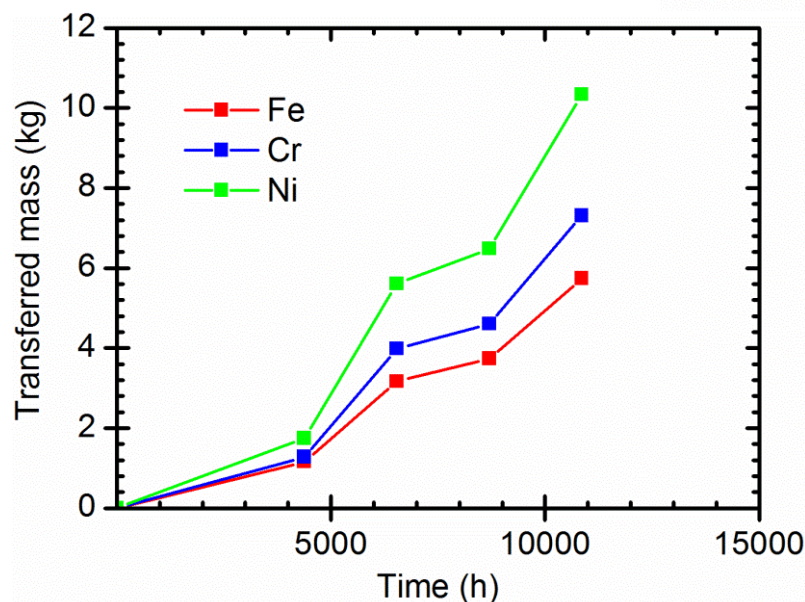
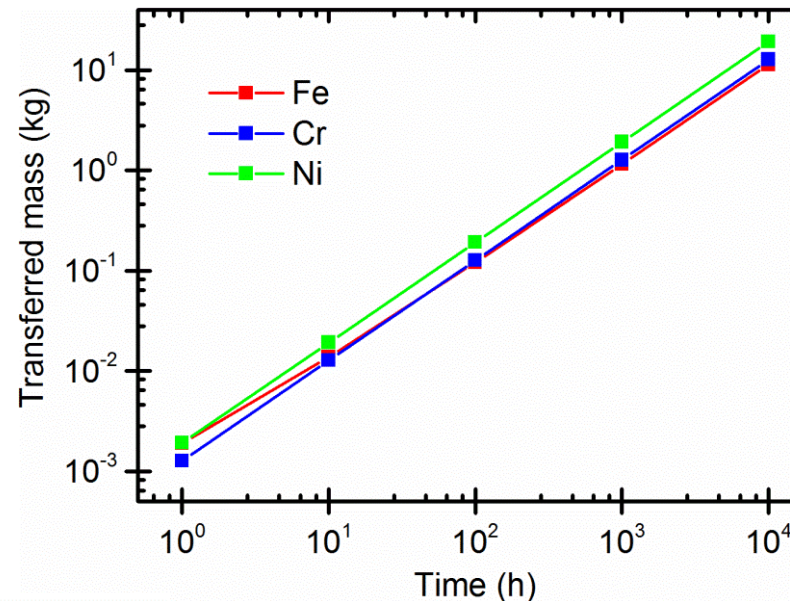
## □ Solution-based corrosion

- 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;  $k_1 = 0.017 \mu\text{m}/\text{h}$  (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

- **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 ( $\text{Cr}_2\text{O}_3$ ) scale
- An equivalent mass of  $0.5 \mu\text{m}$  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  $\text{Fe}(\text{Fe}_x\text{Cr}_{1-x})_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  (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

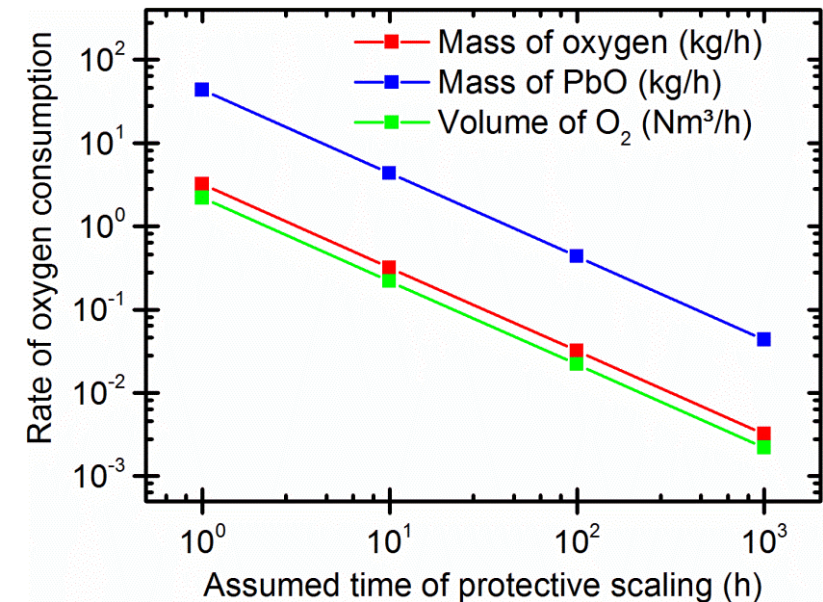


**After typical corrosion processes have established**

# Results on oxygen consumption for design operating conditions

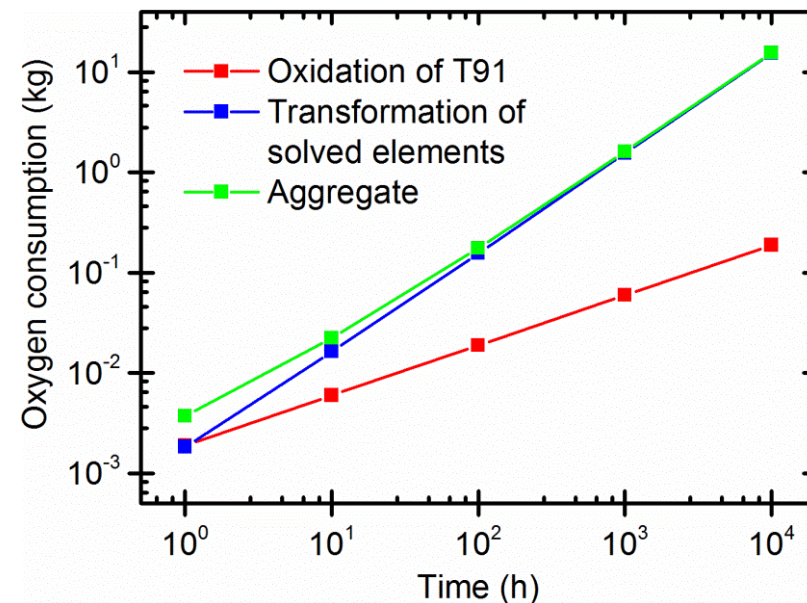
## □ Protective scaling

- 3.2 kg of oxygen being consumed when formation of 0.5  $\mu\text{m}$  thick scale is assumed
- Corresponds to 43.5 kg or 2.2  $\text{Nm}^3$  of PbO and gaseous  $\text{O}_2$ , 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

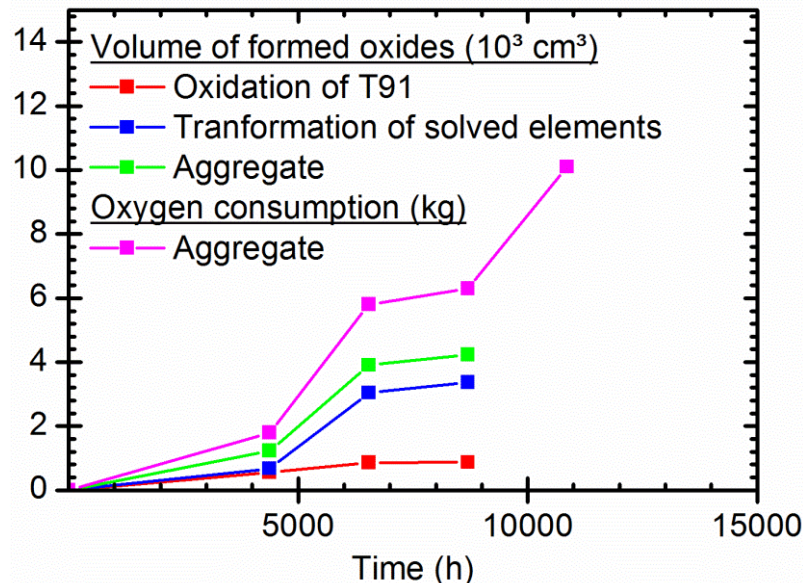
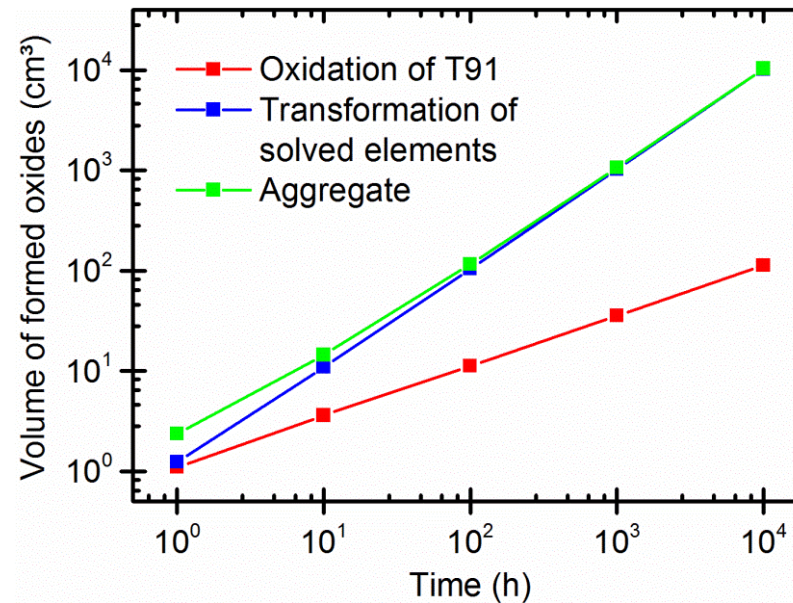
- Solid oxides on T91 surfaces initially contribute by 50% to the over all oxygen consumption
- Oxidation of previously solved steel elements dominates oxygen consumption in the long run
- Oxygen consumption rate averages 2–3 g/h



# 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 cm<sup>3</sup>/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 cm<sup>3</sup>/h oxide formation estimated for the first power cycle
- Associated oxygen consumption of 1.8 g/h

## □ 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 cm<sup>3</sup>/h of produced solid oxides are to be removed by filters or other
- Oxide particle size and distribution not yet investigated in detail



*Thank you  
for your attention!*