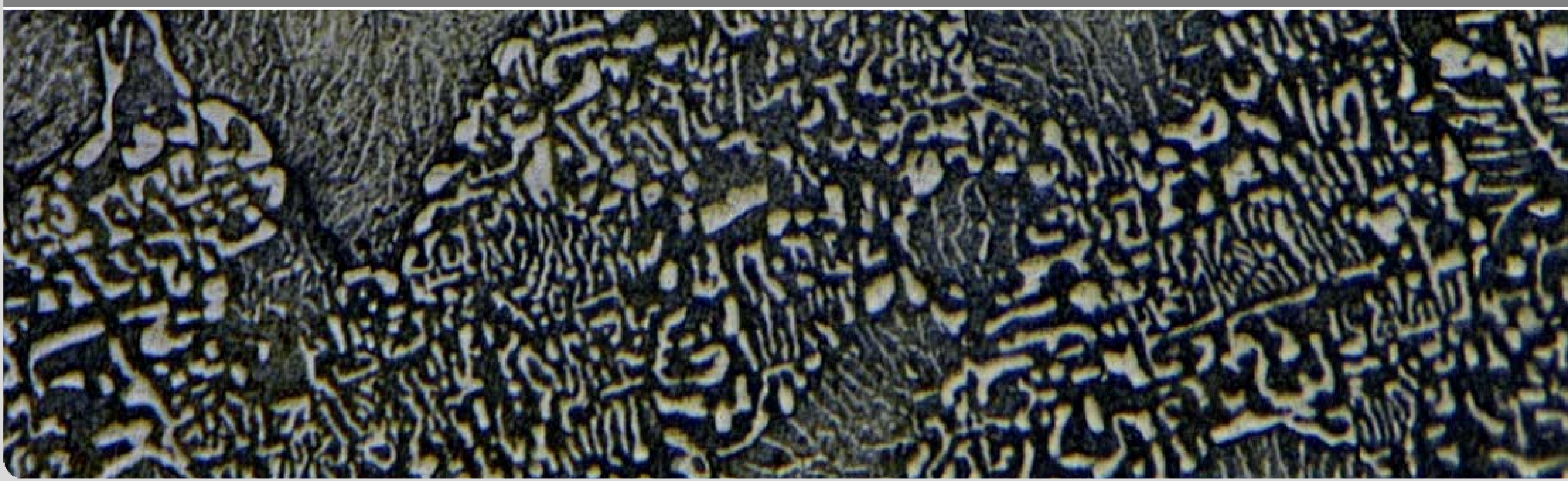
Karlsruhe Institute of Technology

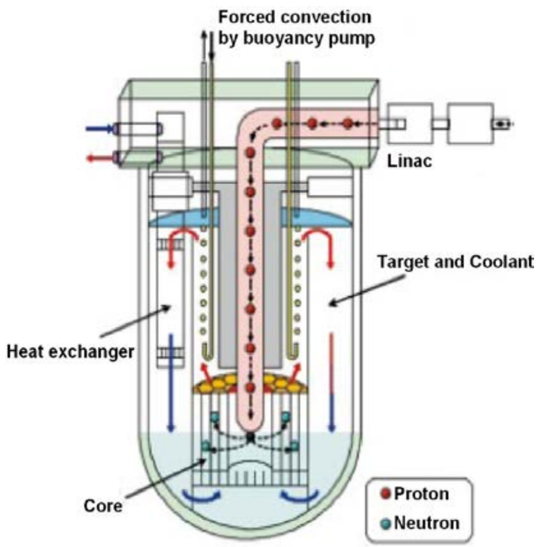
Development of Oxygen Sensors for Monitoring Oxygen Levels in Heavy Liquid Metal Systems

Jürgen Konys

INSTITUTE FOR APPLIED MATERIALS – MATERIAL PROCESS TECHNOLOGY (IAM-WPT)



Lead-cooled Nuclear Reactors/Systems

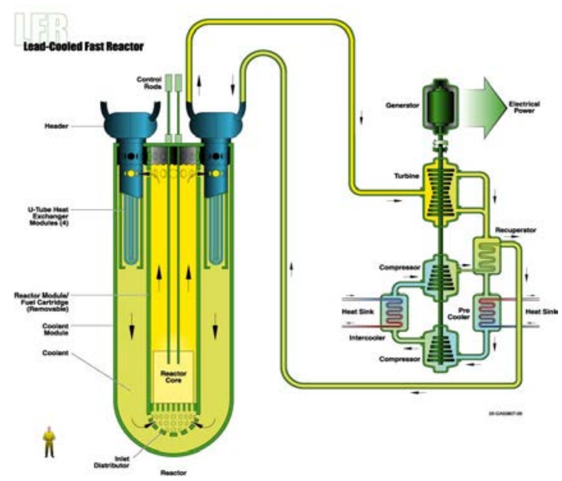


Accelerator Driven (Subcritical) System

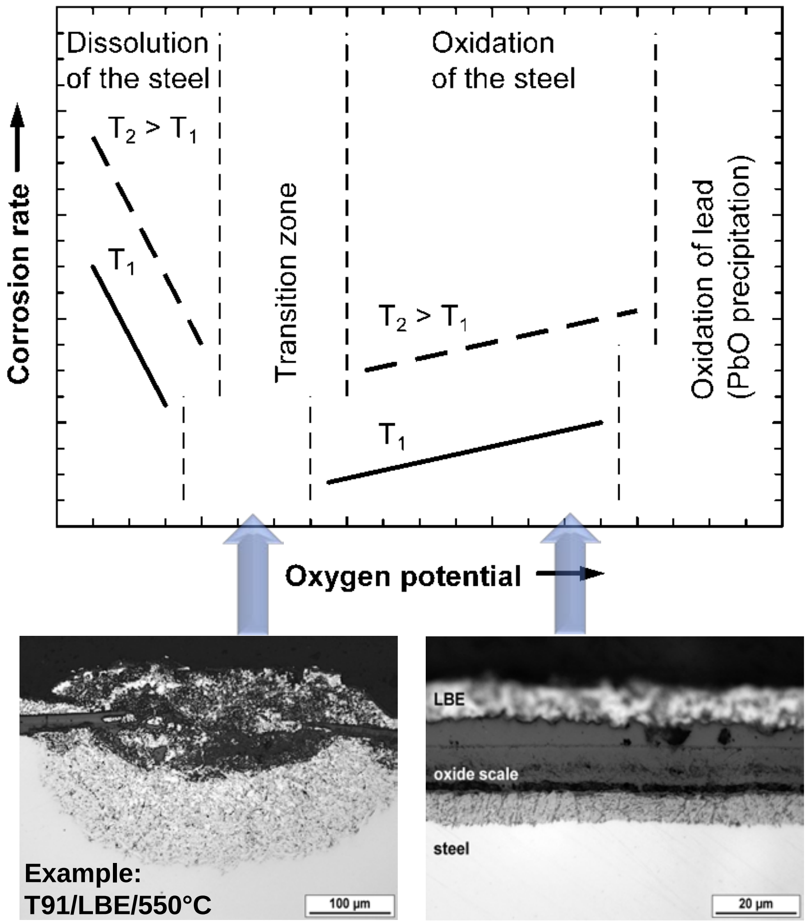
- Transmutation of long-lived radioactive isotopes in nuclear waste
- Power generation
- Liquid lead (Pb) or lead-bismuth eutectic (LBE) as spallation target and primary coolant
- Maximum temperature, typically
- 450 – 500°C for regular operation
- Periodically 550°C (according to plant design)

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



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")

Components of an oxygen control system

Sensors for on-line monitoring

Electrochemical oxygen monitoring

- Solid electrolyte on the basis of yttria-stabilized zirconia (YSZ)
- Metal/metal-oxide or Pt/gas reference electrode

Issues to be addressed (in general)

- Compatibility with the use in Pb alloys (YSZ/steel joint)
- Accuracy
- Long-term reliability

Licensing for nuclear application

- Structural stability of the YSZ product used
- Risk of contamination in case of electrolyte cracking

Oxygen-transfer device(s)

“Classic“ mass transfer across the interface between oxygen source/sink and the liquid metal

Type	**Oxygen source**	**Oxygen sink**
Solid-liquid	PbO	(less noble metals)
Gas-liquid	Ar, H_2O, air	Ar-H_2

Long-term experience from operating experimental facilities for testing materials (steels) in oxygen-containing Pb alloys exists

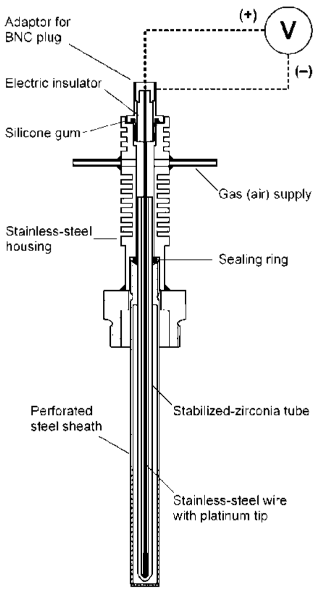
Electrochemical oxygen sensors for liquid lead alloys

Karlsruhe Institute of Technology

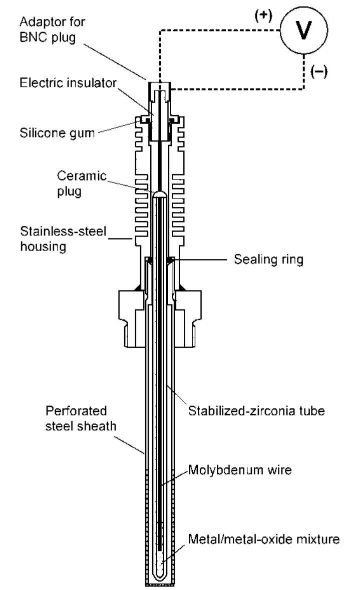
Basic components	Sensor output
▪ Solid electrolyte ▪ Yttria stabilized zirconia (YSZ) ▪ Tubes with 4.5–4.8 mole% Y_2O_3 ▪ "Thimble" with 3 mole% Y_2O_3	▪ Voltmeter reading, E ▪ Measure of the chemical potential of oxygen in the liquid metal ▪ May in general depend on the specific combination of the sensor with a high-impedance voltmeter
▪ Reference electrode ▪ Metal/metal-oxide like Bi/Bi_2O_3 and In/In_2O_3 with Mo wire as electric lead ▪ Pt/air using steel wire with platinised tip as electric lead	▪ Ideal sensor/voltmeter system ▪ Ideal zero-current potential: $E^* = \frac{(\mu_{O_2;Ref} - \mu_{O_2})}{4F}$
▪ Second (working) electrode ▪ The liquid Pb alloy ▪ Auxiliary wire or the steel housing of the sensor serves as part of the electric lead	▪ Calculated oxygen concentration, c_O: $\log(c_O / \mathrm{mass\%}) = C_1 + \frac{C_2}{T/K} - 10{,}080 \frac{E^*/V}{T/K}$ ▪ C1 and C2 are constants specific for the reference electrode

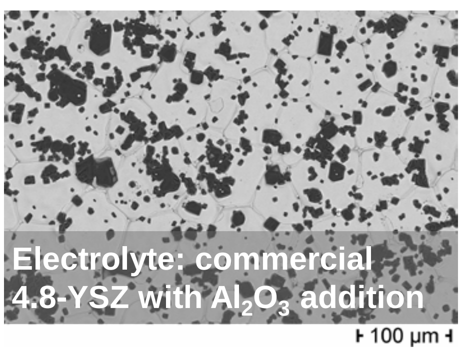
Oxygen sensors developed at KIT

Karlsruhe Institute of Technology

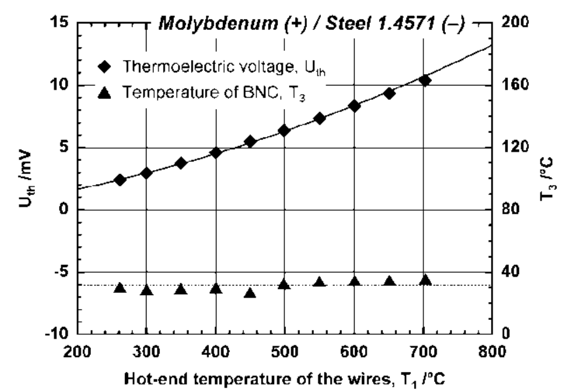


- Long electrolyte tube (Ø 6×255 mm)
- Polymer sealing ring in sufficient distance from the liquid metal
- Cooling fins for reducing the thermal load on the sealing ring
- Steel sheath for protecting the electrolyte from shear forces, serving as electric lead on the liquid-metal side
- Reference electrodes
  - (Steel)Pt/air
  - (Mo)Bi/Bi_2O_3





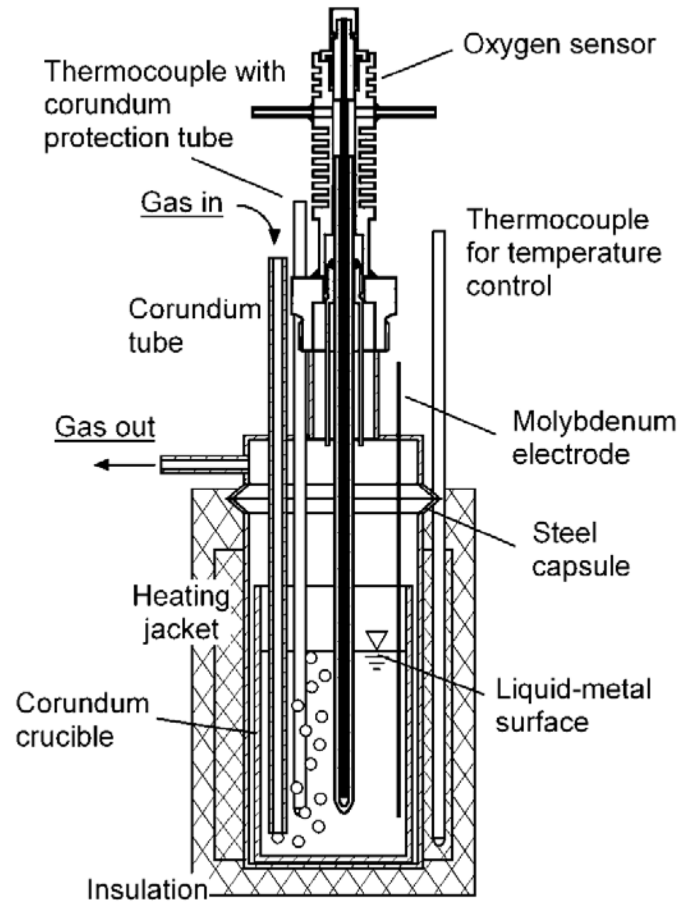
U_{th} :
~3 mV at 300°C
~11 mV at 700°C (Mo/stainless steel)



Testing of the sensor accuracy

Adjusting known oxygen potentials in LBE
Pb/PbO (oxygen saturation)
Co/CoO
Fe/Fe-oxide equilibria
Fe and Co added in the form of powder
Stabilization of these potentials using gases with varying oxygen partial pressure
Ar
Ar + air
Ar + H_2
Temperature range: 350–700°C
Digital multimeter with high impedance >1GW

Sensors were tested without metallic sheath (Mo electrode as auxiliary electric lead), so as to minimize unintentional contamination of the LBE with metals.

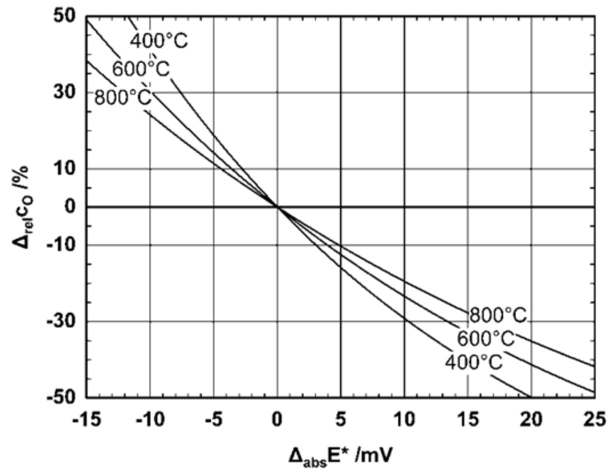


Aspects of sensor accuracy

Systematic errors

$$E = (\{1 - t_e\} E^* + U_{th}) \frac{R_V}{R_V + R_E + \Sigma R_j}$$

- Non-ideal performance of the electrolyte
  - Electron conductivity reduces E* by a factor $(1 - t_e)$ with $t_e < 1$
  - $t_e < 10^{-4}$ for 8-YSZ and 10-YSZ (at < 800°C)
- Thermoelectric voltage, Uth
  - Resulting from the use of different materials for the electric leads of reference and working electrode
  - Uth = 4–11 mV at 350–700°C for Mo(+)/austenitic steel(–)
- Ratio of the electric resistance of the electrolyte (R_E) and the internal resistance of the voltmeter (R_V)
  - R_V > 1 GW generally sufficient for accurate measurements in liquid metals

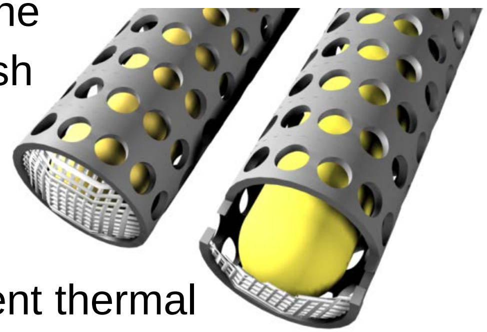


Required accuracy

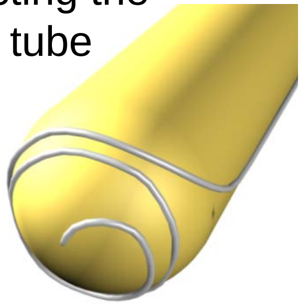
- From experience:
  - Fluctuations of c_O by half an order of magnitude may significantly influence the oxidation mechanism of F/M steels
  - – 57 mV < $\Delta_{abs}E^*$ < +25 mV (at 550°C)
- Estimation of allowable DabsE*:
  - ± 25 mV at 550°C for reliable detection of such fluctuations
  - Allowable DabsE* decreases with decreasing temperature
- ± 5 mV required for ± 10% error of c_O

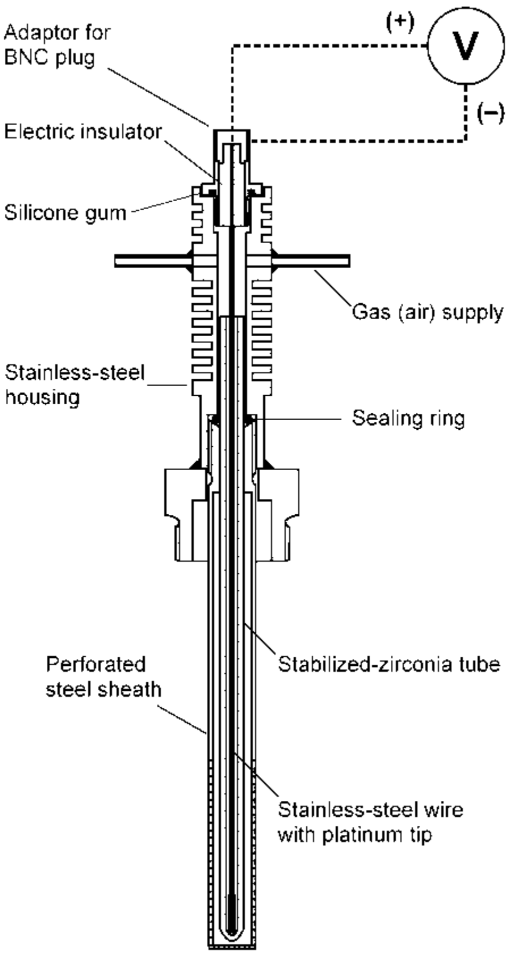
Testing of sensor accuracy in flowing gases
Configuration of the working electrode

- **Metallic sheath (austenitic steel) with Pt mesh**
  - Electric contact by pressing the
  - electrolyte against the Pt mesh
  - The contact with the mesh is
  - established at the highest testing temperature
  - Disadvantages are the different thermal expansion of YSZ tube and steel sheath (rupture of the mesh during cooling) and oxidation of the steel sheath at high temperature

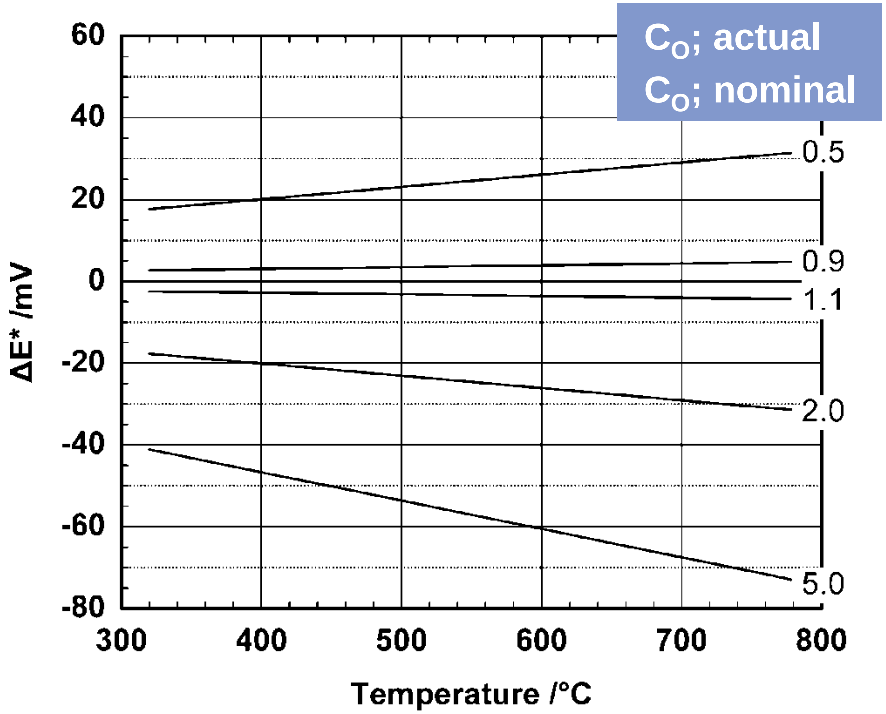


- **Pt wire fixed with Pt paste**
  - Allows for producing different thermoelectric voltages using different materials (wires) for connecting the Pt wire at the closed end of the electrolyte tube with the sensor housing
  - Electric contact with the electrolyte may degrade during thermal cycling
  - Comparatively small area of electric contact gives rise to high electrolyte resistance





Sensor accuracy required for efficient oxygen control in HLMs



Experience

- Half an order of magnitude in oxygen concentration can significantly change oxidation mechanisms for F/M steels
- Reproducibility under service conditions better than +20 mV/-45 mV at 400°C and +30 mV/ -65 mV at 700°C is needed

Minimum requirement

- Better than ± 20 mV at 400°C; ± 30 mV at 700°C
- Range of actual c_O from 0.5 to 2 c_O;nominal

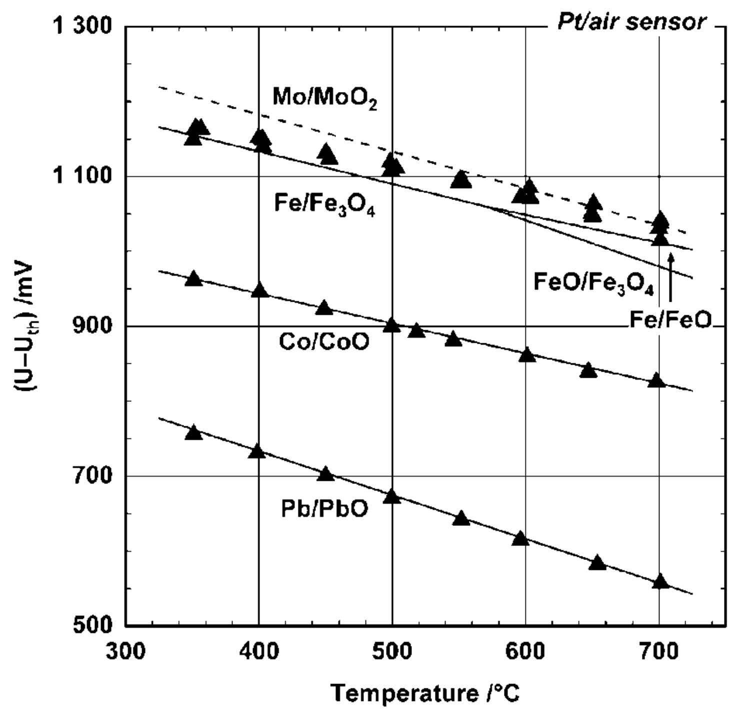
Practical limit

- ± 5 mV, corresponding to ± 10% in c_O, resulting from uncertainty in thermodynamic data used for calculating reference potentials

Pt/air sensor and voltmeter with R_V > 1GΩ

Karlsruhe Institute of Technology

Accuracy of measurement resulting from comparison with metal/metal-oxide equilibria adjusted in LBE



Fe oxide equilibria

- Stepwise cooling or heating
- Ar-15% H_2 bubbling continuously through the LBE (5 ml/min) or quasi-stagnant
- Oxygen potentials move from Fe-oxide to Mo/MoO_2 equilibrium with temperature variation (Mo comes from wire submerged in the LBE)

Co/CoO

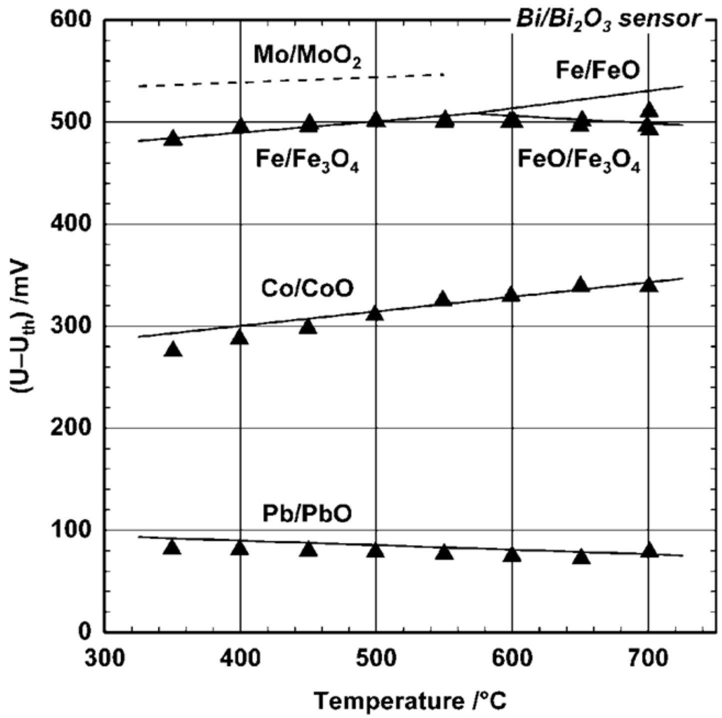
- Stepwise cooling
- Ar 5.0 bubbling continuously through the LBE (5 ml/min)
- Periodically addition of air (5 ml/min) at 700 and 650°C
- Maximum deviation from theoretical prediction < 6 mV

Pb/PbO

- Stepwise cooling
- Ar 5.0 bubbling continuously through the LBE (5 ml/min)
- Maximum deviation from theoretical prediction < 4 mV

Bi/Bi_2O_3 sensor and voltmeter with $R_V > 1G\Omega$

Accuracy of measurement resulting from comparison with metal/metal-oxide equilibria adjusted in LBE



Fe oxide equilibria

- Stepwise cooling or heating
- Ar-15% H_2 mostly quasi-stagnant
- Maximum deviation from theoretical prediction < 8 mV

Co/CoO

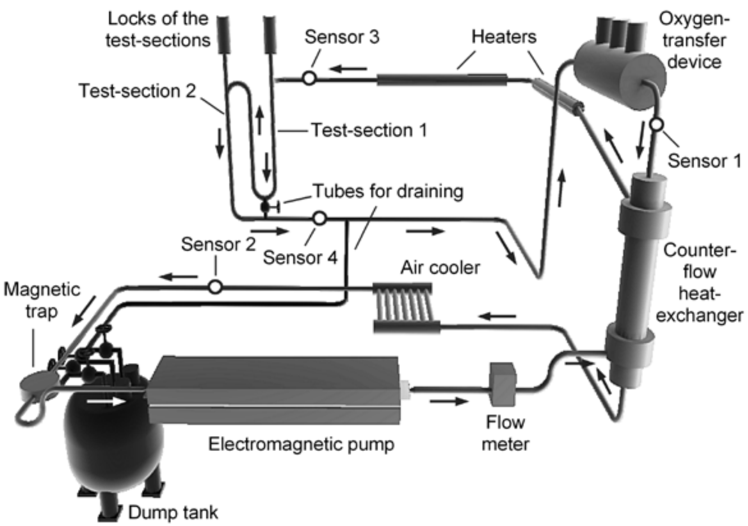
- Stepwise cooling
- Ar 5.0 bubbling continuously through the LBE (5 ml/min)
- Maximum deviation from theoretical prediction < 15 mV

Pb/PbO

- Stepwise cooling
- Ar 5.0 bubbling continuously through the LBE (5 ml/min)
- Maximum deviation from theoretical prediction < 8 mV

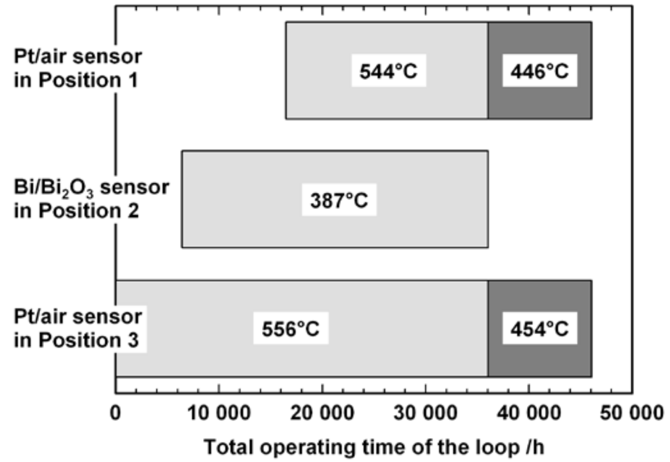
Long-term performance of oxygen sensors in the LBE loop CORRIDA

- Criterion for proper operation ("plausibility")
  - Comparison of the output of all operating sensors on the basis of the calculated c_O
  - In consideration of possible oxygen consumption and expected accuracy of the sensors



CORRIDA loop for materials testing in flowing oxygen-containing LBE

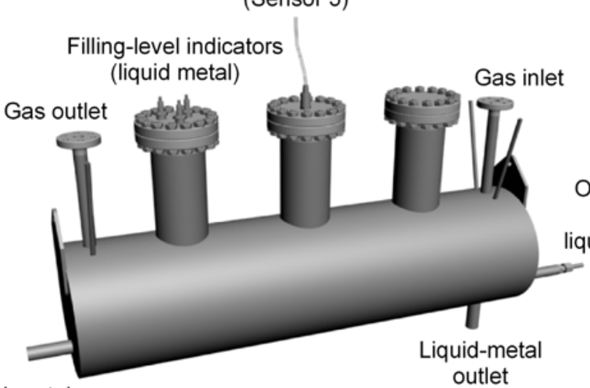
Longest operating times

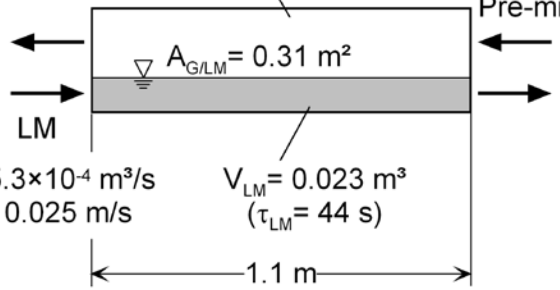


- Observed types of malfunction
  - Cracking of the electrolyte
  - Drifting of the sensor output to higher voltage, corresponding to lower c_O (several orders of magnitude!) → Fouling of the electrolyte surface?
  - Pt/air sensors are less prone to cracking and did not show drifting of the output

Oxygen-transfer device of the CORRIDA loop

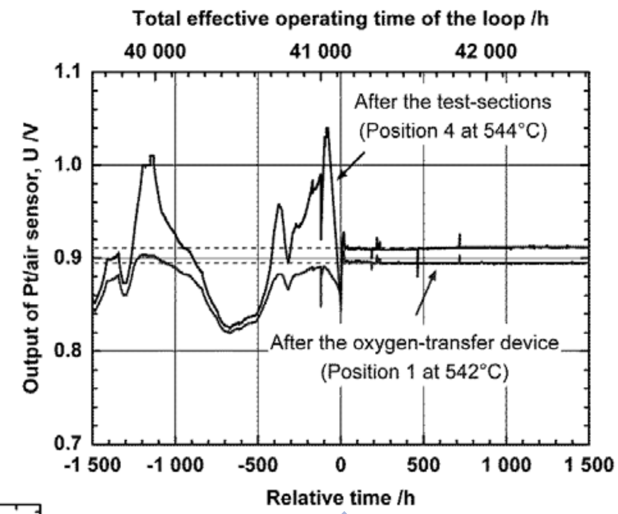
- **Gas/liquid**
  - Transfer across a plane liquid-metal surface
  - 5.3 kg/s LBE
  - ~500 cm³/min gas (referred to 25°C)
  - λ-probe for monitoring p_{O_2} in the gas-space
- **Gas mixture optimized for maintaining c_O=10^{-6} mass% at 550°C**
  - 500 cm³/min Ar humidified at 18°C (p_{H_2O} = 0.02 bar)
  - Continuous addition of 1–1.5 cm³/min ai (manually adjusted)
- **Gas mixture used for maintaining c_O=10^{-6} mass% at 450°C**
  - 500 cm³/min Ar humidified at 18°C (p_{H_2O} = 0.02 bar)
  - Discontinuous addition of 0.5 cm³/min air(manually adjusted)

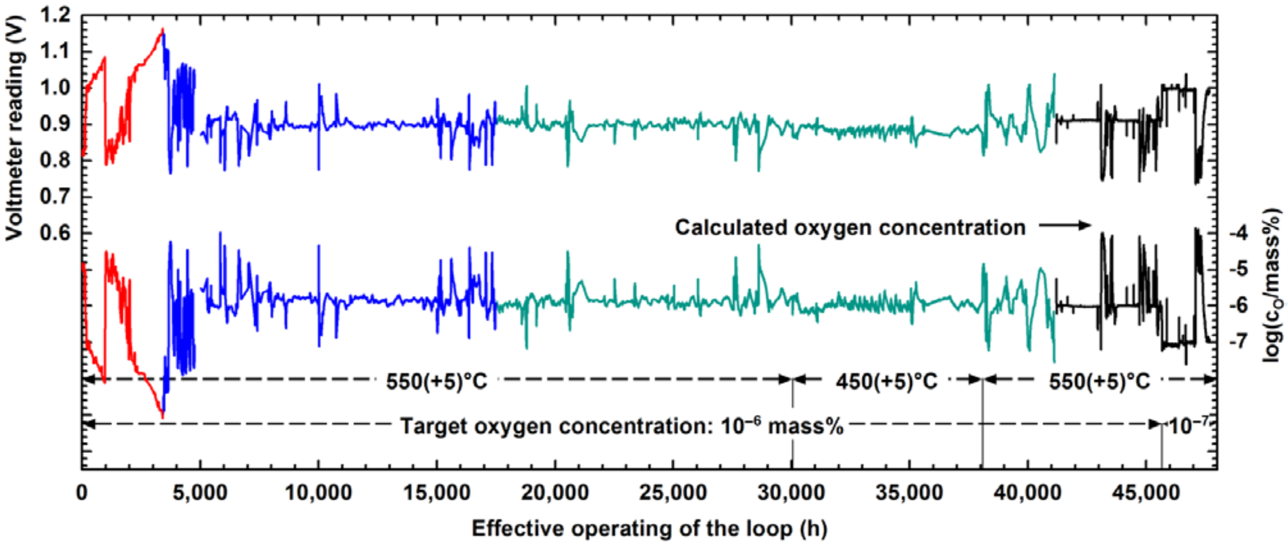




Performance of the oxygen-control system

- **Gas composition/control strategy**
  - Ar-H_2-H_2O corresponding to equilibrium at target oxygen concentration
  - Ar-H_2-H_2O, Ar-H_2O or Ar with varying air addition
  - Optimized manual air addition to Ar-H_2O
  - After implementation of automatic air addition to Ar or Ar-H_2



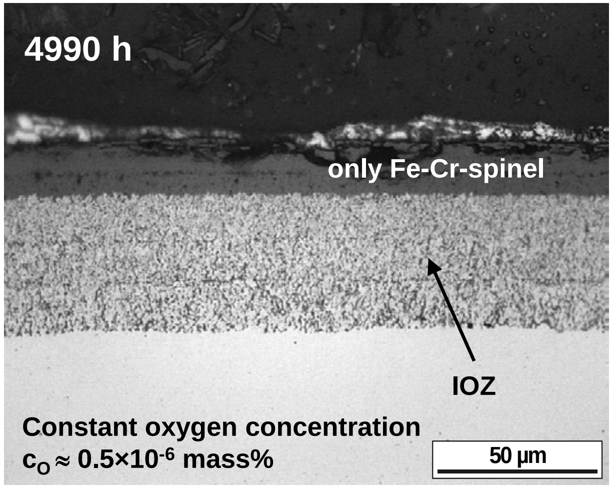


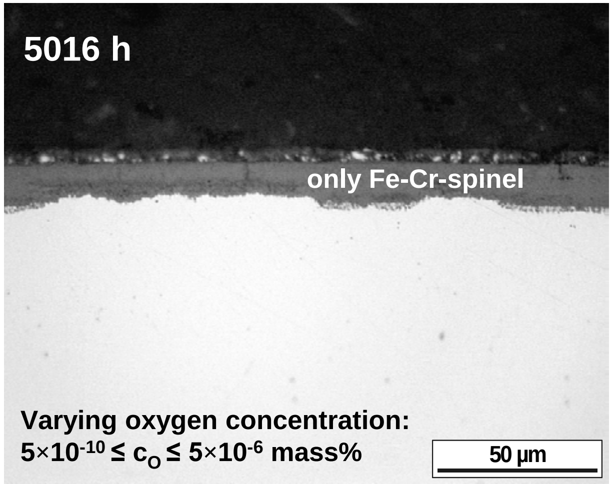
Before and after automatic air addition has been implemented

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

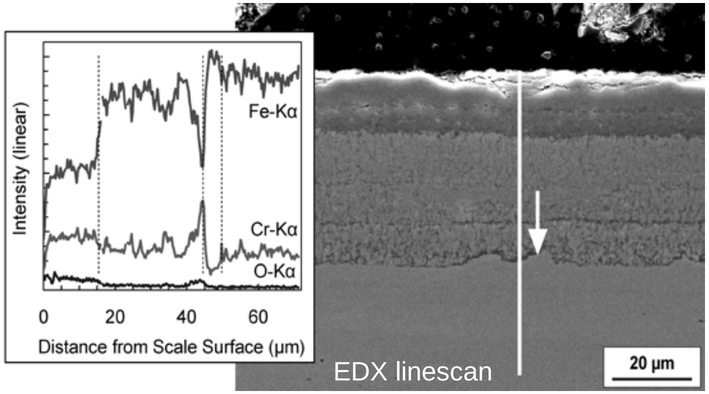
Temperature	Flow velocity	Nominal oxygen concentration	Maximum exposure times	Tested materials
550 (+5)°C	2 (±0.2) m/s	10^{-6} mass%	~ 20,000 h	CSEF (T91, E911, EUROFER), ODS steels, Type 316 SS, surface alloyed steels (Al), ...
450 (+5)°C	2 (±0.2) m/s	10^{-6} mass%	~ 8000 h	CSEF (T91, E911), pure Fe, Type 316SS, ...
Current 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 (DIN 1.4970)				

Corrosion of martensitic ODS steel in LBE at 550°C
Influence of varying oxygen concentration



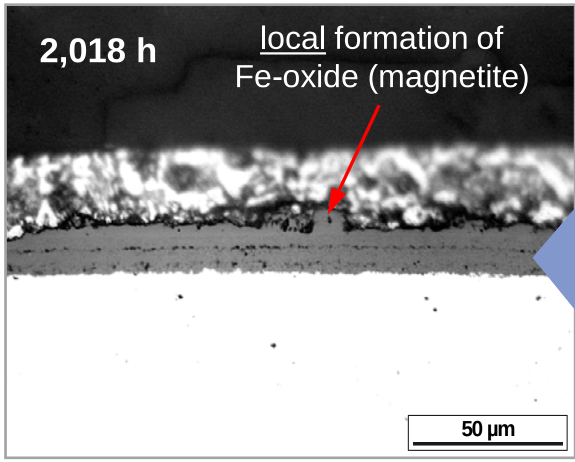


- **Comparatively thin spinel scale (12µm)**
- **Significantly less internal oxidation**
- **Cr-enrichment in oxide at metal/scale interface**

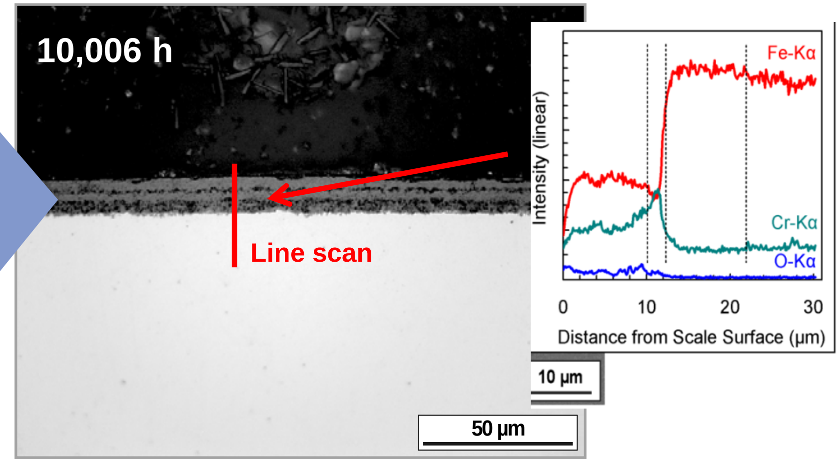


Corrosion of martensitic ODS steel in LBE at 550°C Time dependence of oxidation under varying oxygen concentrations

Karlsruhe Institute of Technology



Cr-enrichment in oxide scale at metal/scale interface



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

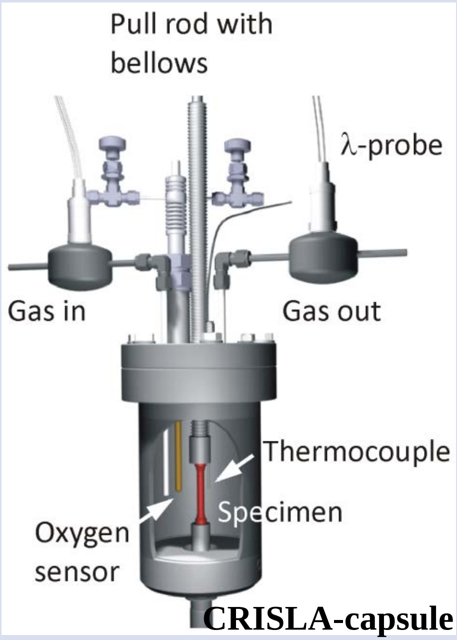
- Spinel scale (11 µm); local formation of Fe-oxide
- Little internal oxidation in comparison to scale formed at $c_O \approx 0.5\times10^{-6}$ mass%

Oxygen:
$5\times10^{-10} \leq c_O \leq 5\times10^{-6}$ mass%;
$c_O \approx 0.5\times10^{-6}$ mass% during the last 4990 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

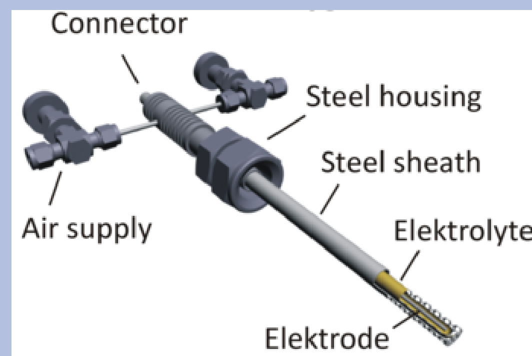
Creep-to-Rupture tests in stagnant, oxygen-controlled liquid Pb at 650°C



CRISLA-capsule

Facility with infrastructure:

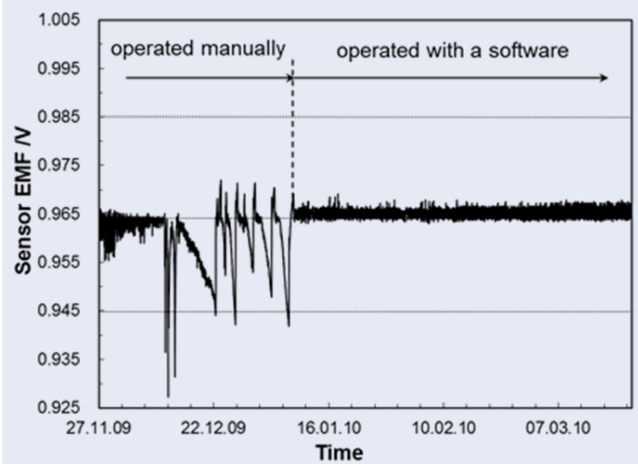
- 5 capsules for stagnant Pb with volume of 900 ml. Oxygen control periphery for each capsule.
- 3 capsules for stagnant air with volume of 230 ml



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.-%

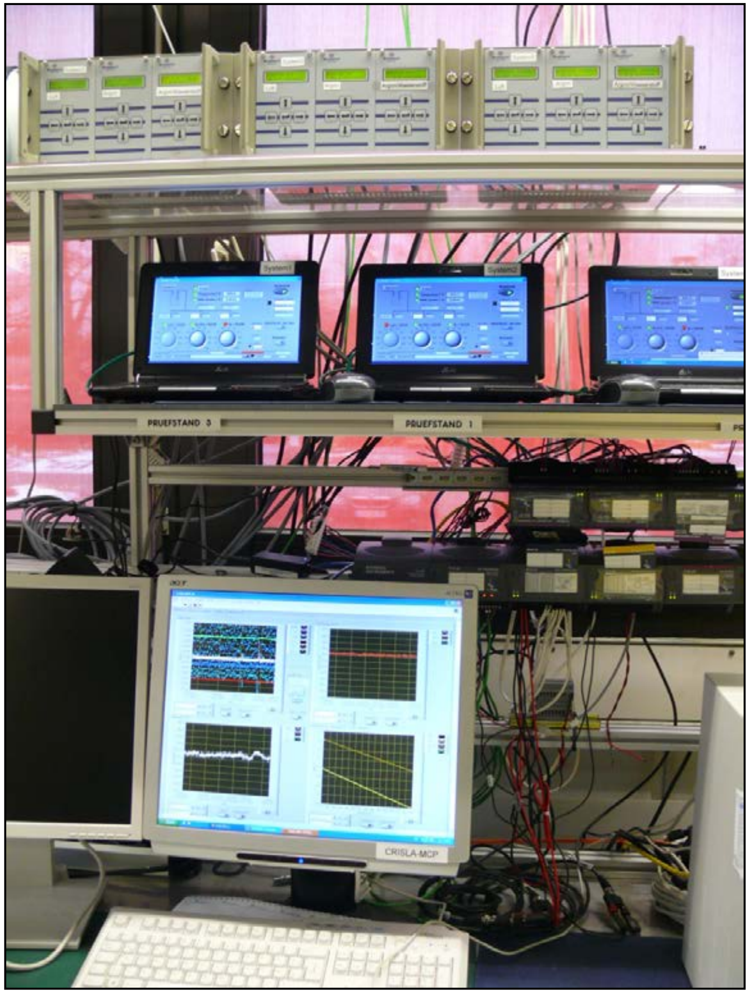
- through oxygen contained gas (gas/liquid oxygen-transfer)

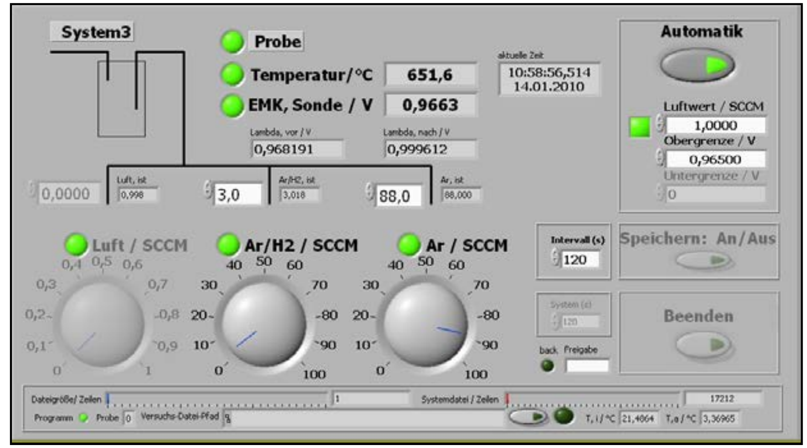
- E:965±20 mV → 965±2 mV

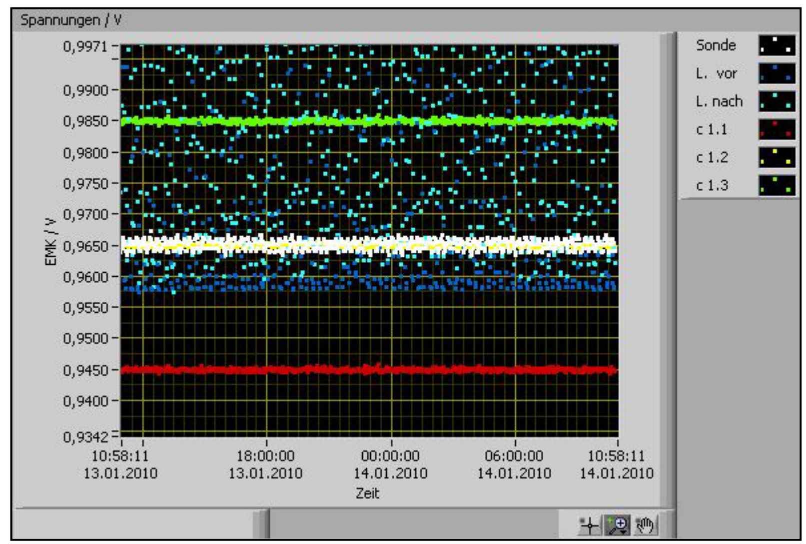
CRISLA Facility for Creep-Rupture Tests in Lead

Karlsruhe Institute of Technology

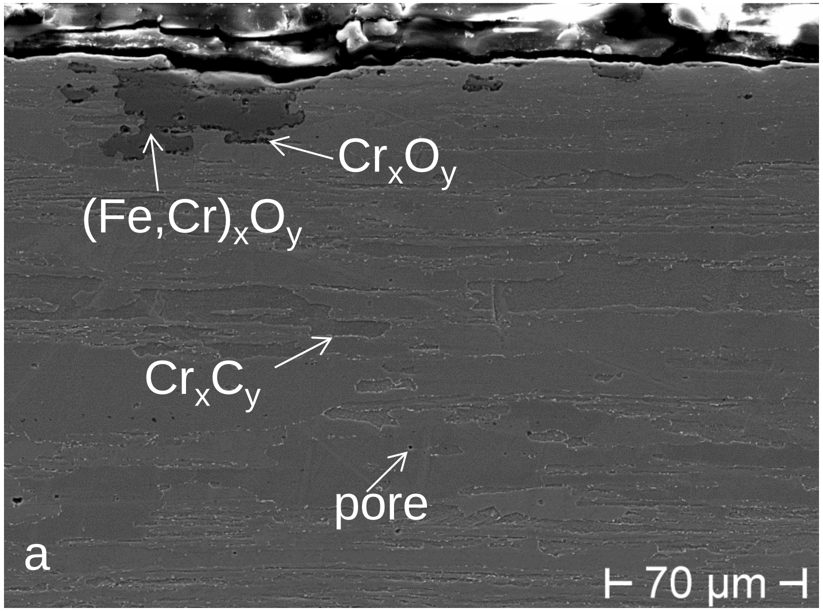
PC-supported control system for oxygen content: user defined settings

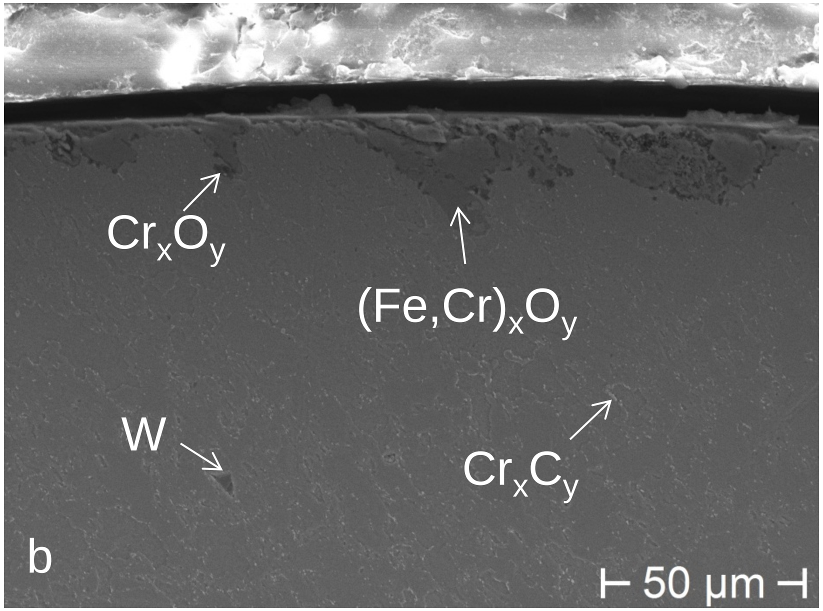






12Cr-ODS steels after creep-to-rupture tests





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**

Conclusions

	Electrochemical oxygen sensors	Gas/liquid oxygen-transfer
General conclusions	▪ Accuracy of the observed oxygen potential sufficient for characterizing the conditions in the liquid metal ▪ Correction of thermoelectric voltages is recommended ▪ Absolute accuracy of the calculated c_O is not assessed by the experimental testing method	▪ Feasibility on the laboratory scale has been proven (e. g. operation of the LBE-loop CORRIDA)
Experimental facilities (Materials testing, thermo-hydraulic experiments, etc.)	▪ Reliable sensors with promising service time (30,000–45,000 h) are available ▪ Sensors with Pt/air reference electrode are less prone to failure (in comparison to Bi/Bi2O3)	▪ Appropriate pO2in is much higher than the threshold for PbO formation ▪ Dispersion in the transfer-device however prevents PbO formation ▪ Available mass of oxygen limits the flux across the gas/liquid interface
Industrial-scale plants	▪ Design with higher structural stability of the electrolyte is required ▪ Risk of contamination of the environment determines the choice of the reference electrode	▪ Reasonable size of the transfer-device will require much higher flux than in experimental facilities ▪ Experimental investigation of the kinetic limit is needed

Acknowledgements

With distinguished contributions from Carsten Schroer, Alexandre Skrypnik and Olaf Wedemeyer

Funding by the EURATOM 7th Framework Programme was gratefully acknowledged.