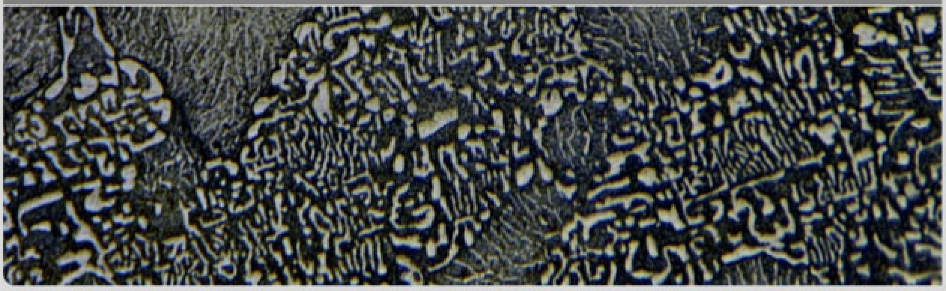
Karlsruhe Institute of Technology

Corrosion chemistry of Heavy Liquid Metals for Fusion and Nuclear Applications

INSTITUTE FOR APPLIED MATERIALS – MATERIAL PROCESS TECHNOLOGY | CORROSION DEPARTMENT



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Outline

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1) Application of heavy liquid metals for Fusion and Nuclear energy production
2) Corrosion testing and corrosion modeling of EUROFER steel in flowing Pb-15.7Li for fusion application
3) Development of advanced processes for Al-based anti-corrosion and T-permeation barriers for HLM environments
4) Non-metal chemistry of heavy liquid metal corrosion of iron-based structural materials
5) Conclusions

Application of Heavy Liquid Metals for Fusion and Nuclear Energy Production

The use of eutectic Pb-15.7Li alloy for the European HCLL blanket concept

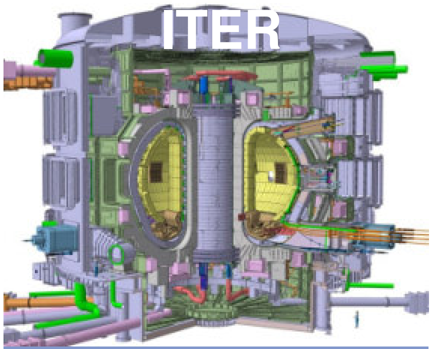
Thermo-nuclear power reactor

D + T ⇒ n (14.1 MeV) + He (3.52 MeV)

Tritium is generated from Li

^{6}Li + n ⇒ T + He + 4.8 MeV
^{7}Li + n ⇒ T + He + n' - 2.87 MeV

Eutectic Pb-15.7Li
0.65 mass% Li, T_m = 235°C



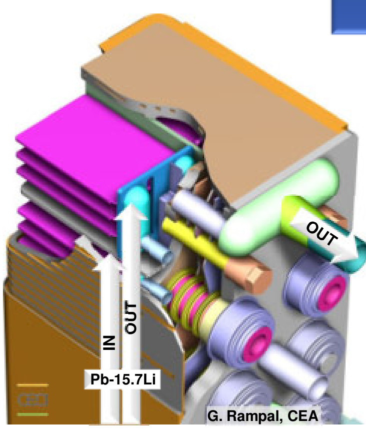
HCLL = Helium-Cooled Lithium-Lead

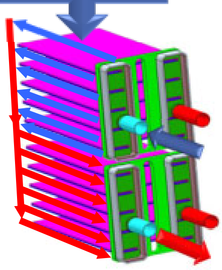
The HCLL (He-PbLi) TBM (and DEMO) Blanket

DEMO HCLL MAIN FEATURES
2m x 2m modules
RAFM steel (e.g. EUROFER)
He (8 MPa, 300-500°C)
Liquid Pb-15.7Li (eutectic) as breeder and multiplier
PbLi slowly re-circulating (10/50 rec/day)
90% ^{6}Li in PbLi Pb-Li velocities in breeding unit ~ 1 cm/s range
TBR = ≤1.15 with 550mm Breeder radial depth
Lifetime 7.5 MWy/m²

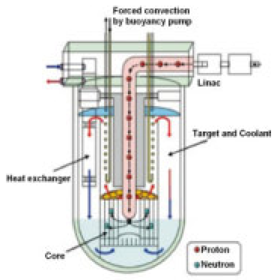
Corrosion of cooling and stiffening plates and permeation of tritium from PbLi into He gas

PbLi flow velocity ~ 1 cm/s





Lead-cooled Nuclear Reactors/Systems

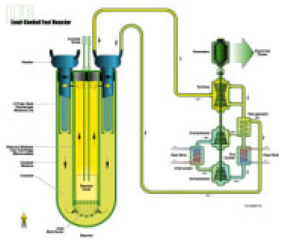


Accelerator Driven (Subcritical) System

- 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

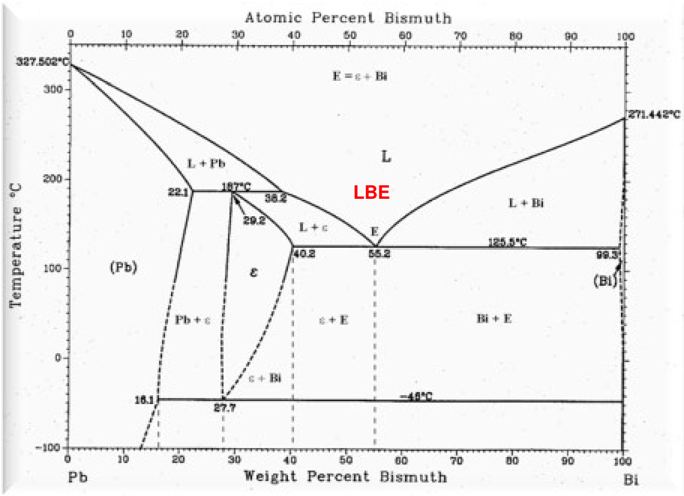
- One of the concepts for the 4th generation of nuclear power plants (Gen IV)
- In the long-term, Pb as primary coolant at maximum ca. 800°C
- Short- to mid-term: Pb- or LBE-cooled at 600 – 650°C



Some Specific Properties of (Heavy) Liquid Metals

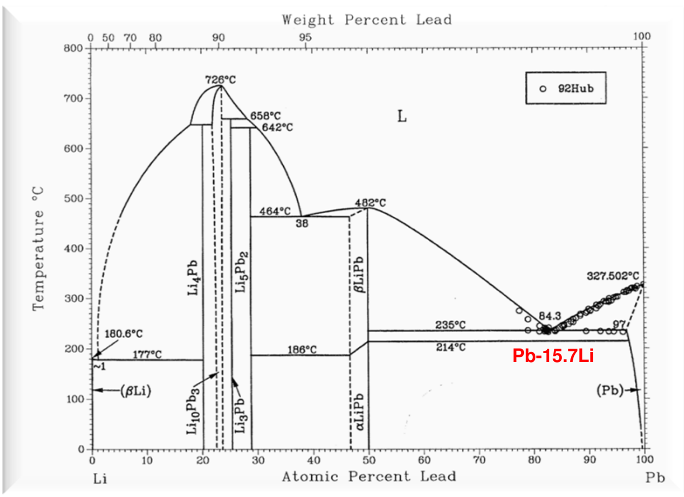
		UNIT	$Pb^{45}Bi^{55}$	LITHIUM	WATER
Melting Point at 0.1 MPa		[°C]	125	180.5	0
Boiling Point at 0.1 MPa		[°C]	2516	1317	100
			300°C	**300°C**	**25°C**
Density	ρ	[kg/m³]	10325	505	1000
Heat Capacity	c_p	[J/(kgK)]	146.33	4279	4180
Kinematic Viscosity	ν	$[m2/s] \cdot 10^{-7}$	1.754	9	9.1
Heat Conductivity	λ	[W/(m K)]	12.68	29.2	0.6
Electric Conductivity	σ_{el}	$[A/(V m)] \cdot 10^{5}$	8.428	33.5	$2 \cdot 10^{-4}$ (tap)
Thermal Expansion Coefficient	α	$[K^{-1}] \cdot 10^{-3}$	6.7	43.6	6
Surface Tension	σ	$[N/m] \cdot 10^{-3}$	410	421	52 (tap)

Phase Diagram Lead – Bismuth (Pb-Bi)



LBE = Lead-Bismuth Eutectic

Phase Diagram Lead – Lithium (Pb-Li)



Corrosion testing and corrosion modeling of EUROFER steel in flowing Pb-15.7Li

Introduction

Reduced activation ferritic-martensitic steels, e.g. EUROFER, are considered as structural materials for TBMs in ITER

EUROFER is in direct contact with the liquid breeder Pb-15.7Li in the HCLL blanket concept

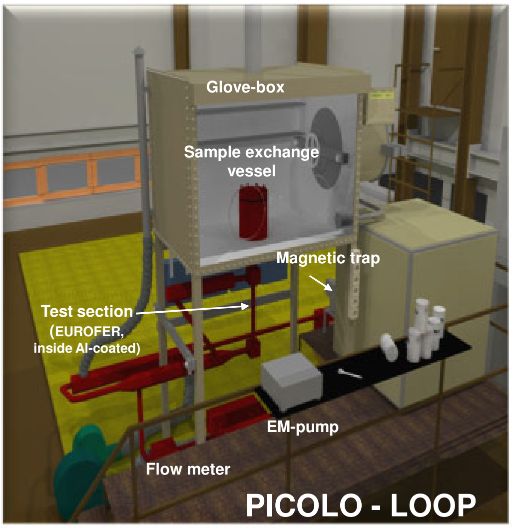
For the design of PbLi-operated TBMs and for future blankets in DEMO, a reliable and safe long-term operation must be guaranteed

This means for R&D respectively for experimental data evaluation:

- Long-term corrosion data at relevant conditions (T, v) must be available
- The precipitation behavior of Fe-(Cr) particles in PbLi must be understood
- .... and the development of modeling tool has to be carried out

Pb-15.7Li corrosion testing in PICOLO loop

PICOLO is a major loop for Pb-15.7 Li corrosion testing in frame of TBM consortium



Parameters of Pb-15.7Li Loop PICOLO

Test temperature: 480-550°C

T_{max} in test section: 550°C
T_{low} at EM-pump: 350°C

Pb-15.7Li volume: 20 litres

Flow velocity range: 0.01 - 1 m/s
Test velocity up to 2007: 0.22 m/s

Loop materials:
Cold legs: 18 12 CrNi steel
Hot legs: 10 % Cr steel

Total loop operation:
at 480°C > 125,000 h
at 550°C > 15,000 h

Test conditions since 2008

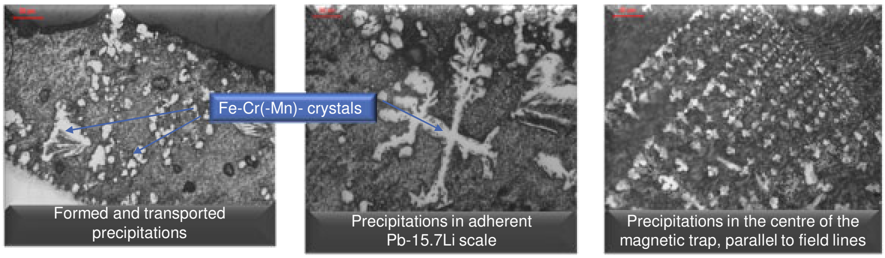
Pb-15.7Li velocity 0.1 m/s

Compromise to laminar/turbulent flow regimes, data for modeling and TBM requirements

Experience from corrosion testing in PICOLO loop

Precipitation and transport behavior of corrosion products

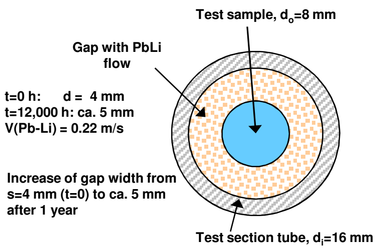
- Only rudimentarily data on transportation effects of corrosion products and their precipitation behavior are available.
- Only some small sections of PICOLO loop are analysed.
- But high risk was detected for loop blockages due to precipitations.
- New testing campaigns are extended to smaller flow rates towards mixed and laminar conditions with more TBM relevance.

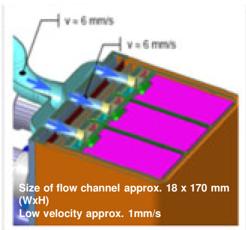


TBM test conditions concerning corrosion

Figures of merit for TBM/DEMO derived from PICOLO tests and modeling by MATLIM

Geometry of test section Picolo	Geometry of TBM





The flow in pipes is laminar up to a Reynolds number of ca. 2,300 and it becomes fully turbulent at a Reynolds number of e.g. 10,000.

Hydraulic diameter Picolo	Hydraulic diameter TBM
d_{hyd} = 4A/U = d – d0 = 2s d_{hyd} = 0.8 cm	dhyd = 4A/U = 4 (WxH) /2 (W+H) dhyd = 3.25 cm

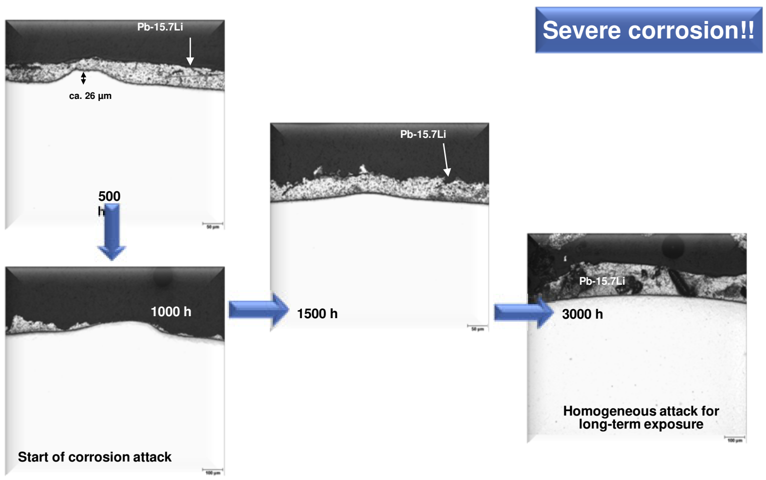
TBM Test Conditions Concerning Corrosion

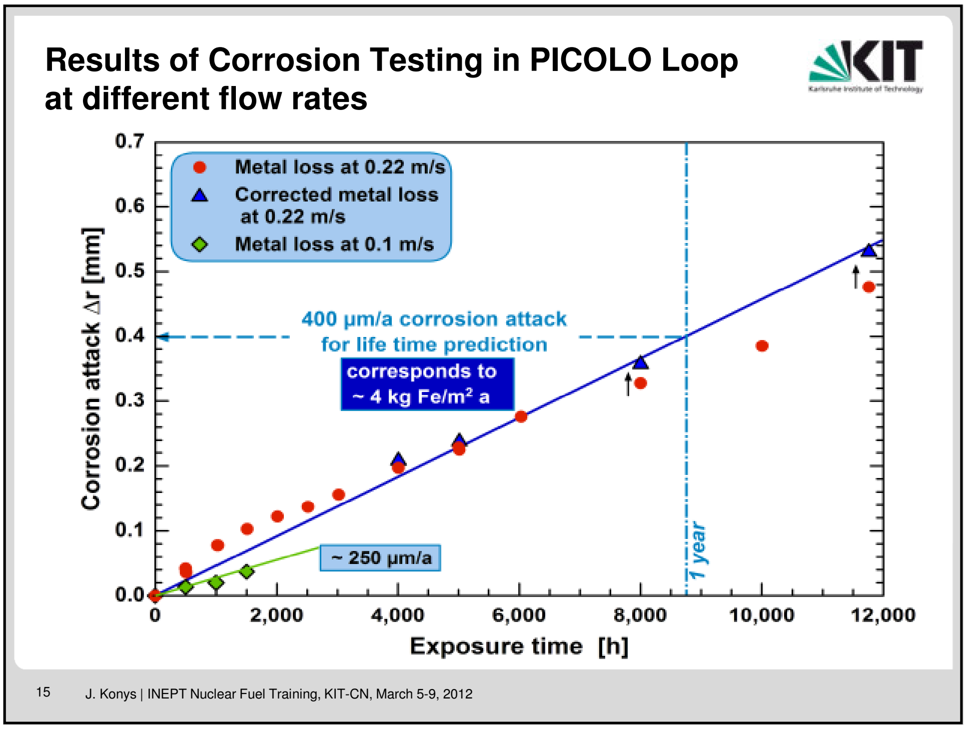
Envisaged Reynolds number for TBM Re = some 100 in accordance with MHD calculations of L. Bühler, KIT

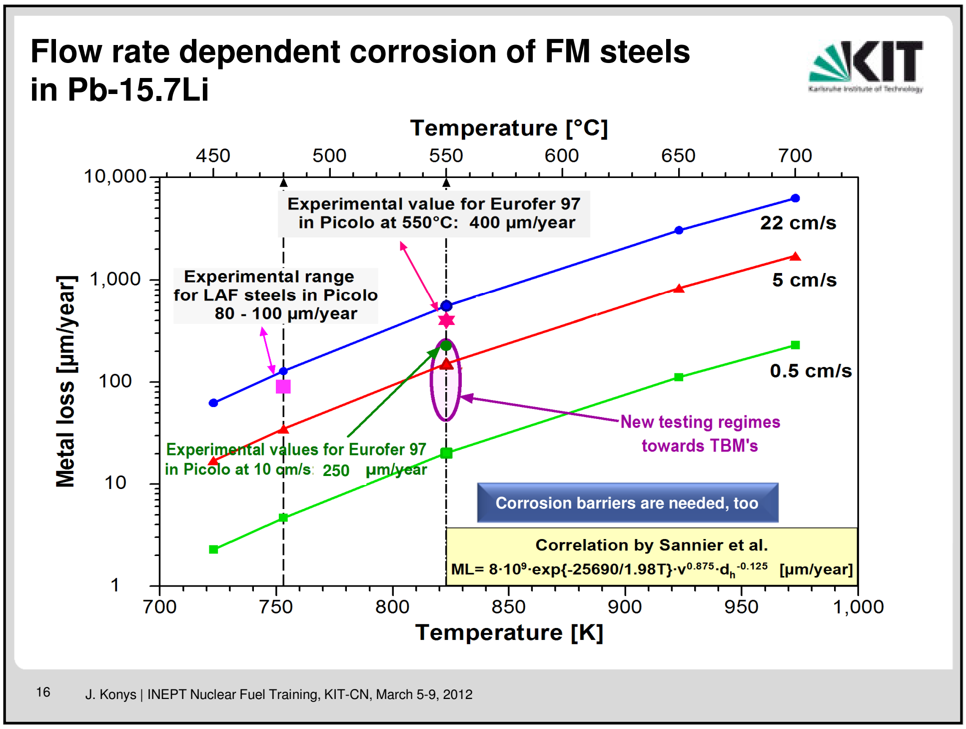
	PICOLO 22 cm/s	PICOLO 10 cm/s	PICOLO 1 cm/s	TBM 0.1 cm/s
Reynolds $Re = u_{fl}\, d_{hyd} / \nu_{fl}$	22 * 0.8 / 0.105 * 10^{-2} = (17.6 /10.5) *10^4 = 16,800	10 * 0.8 / 0.105 * 10^{-2} = (8 /10.5) *10^4 = 7,620	1 * 0.8 / 0.105 * 10^{-2} = (0.8 /10.5) *10^4 = 762	0.1 * 3.25 / 0.105 * 10^{-2} = 0.325/10.5 * 10^4 = 310 100<Re<1000
	turbulent	Main part turbulent	laminar	laminar
Schmidt $Sc = \nu_{fl} / D$	0.105 * 10^{-2} / 1,185 * 10^{-6} = 860	= 860	= 860	= 860
Sherwood number for laminar flow in Picolo is assumed to be 3.66 “Inlet” corrections have to consider the Graetz number : G = Re Pr d / l				

Results of Corrosion Testing in PICOLO Loop EUROFER Steel Exposed to Pb-15.7Li;

v = 0.1 m/s, 550°C




Results of Corrosion Testing in PICOLO Loop at different flow rates
Metal loss at 0.22 m/s
Corrected metal loss at 0.22 m/s
Metal loss at 0.1 m/s
400 µm/a corrosion attack for life time prediction
corresponds to ~ 4 kg Fe/m² a
~ 250 µm/a
1 year
Corrosion attack Δr [mm]
Exposure time [h]
15
J. Konys | INEPT Nuclear Fuel Training, KIT-CN, March 5-9, 2012


Flow rate dependent corrosion of FM steels in Pb-15.7Li
Temperature [°C]
Experimental value for Eurofer 97 in Picolo at 550°C: 400 µm/year
Experimental range for LAF steels in Picolo 80 - 100 µm/year
22 cm/s
5 cm/s
0.5 cm/s
New testing regimes towards TBM's
Experimental values for Eurofer 97 in Picolo at 10 cm/s: 250 µm/year
Corrosion barriers are needed, too
Correlation by Sannier et al.
ML= 8·10⁹·exp{-25690/1.98T}·v^0.875·d_h^-0.125 [µm/year]
Metal loss [µm/year]
Temperature [K]
16
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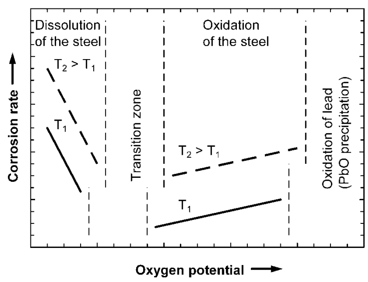
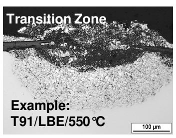
Corrosion and Chemistry of Metallic Materials in Heavy Liquid (Lead) alloys

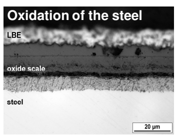
Typical corrosion mechanisms

- Dissolution of alloying elements into the heavy liquid metal (W<<Fe, Cr<Ni)
  - ➡ **predominant corrosion mechanism in Pb-15.7Li**
- Mass transport of structural materials in the liquid lead alloys due to temperature gradients ⇒ dissolution in hot areas and precipitation in colder regions (heat exchanger, cooler, pumps etc.) ⇒ blocking of pipes
- Exchange of non-metals (O, N, C, H) between structural materials and liquid metals:
  - ➡ **in lead and LBE, it's mainly oxygen which affects the chemical stability by in-situ formed "protective" oxide scales**
- Erosion of structural materials in dynamic (fast flowing) systems
- Liquid metal embrittlement at low temperatures (with and without irradiation)

Impact of oxygen dissolved in liquid lead and LBE on steel corrosion for Nuclear applications



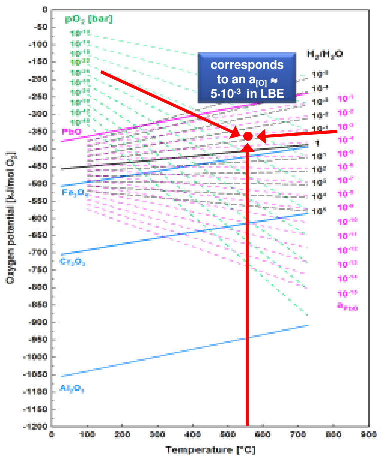




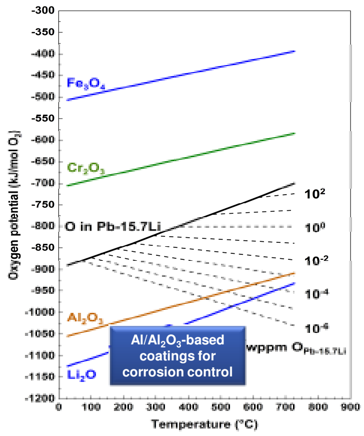
- Stimulation of the oxidation of steel constituents
  - Formation of an oxide scale on the steel surface
  - Separation of the steel from the liquid metal
  - Hence, reduced dissolution rate
- Steel elements must be less noble than the liquid metal
  - Applicable to Pb, lead-bismuth (LBE)
  - Not applicable to lead-lithium (Pb-15.7Li)
- Relevant to
  - Lead-cooled fast reactor (LFR)
  - Accelerator driven system (ADS)

Oxygen Potentials of Metal/Metal-oxides, relevant for the Stability of Structural Materials in

Pb, LBE



Pb-15.7 Li



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

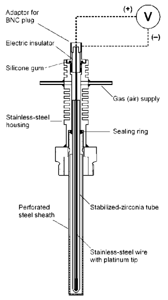
Oxygen-transfer device(s)

“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

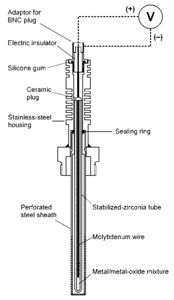
Long-term experience from operating experimental facilities for testing materials (steels) in oxygen-containing Pb alloys exists

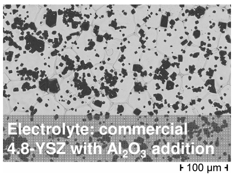
Oxygen sensors developed at KIT

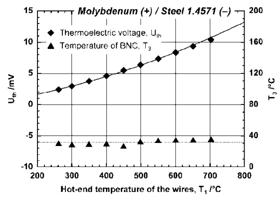


- Long electrolyte tube (Ø 6×255 mm)
- Polymer sealing ring in sufficient distance from the liquid metal
- Cooling fins for reducing the thermal load on the sealing ring
- Steel sheath for protecting the electrolyte from shear forces, serving as electric lead on the liquid-metal side
- Reference electrodes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

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

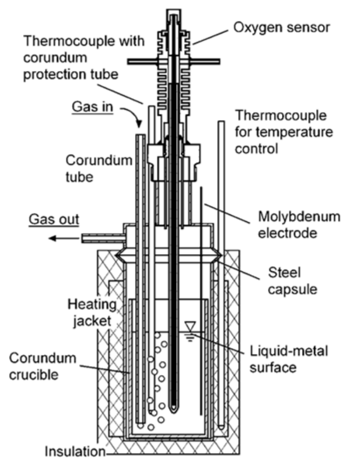




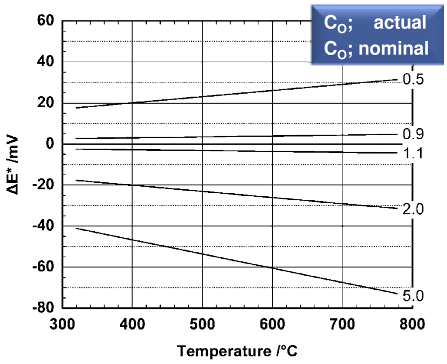


Testing of the sensor accuracy

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℃
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.



Sensor accuracy required for efficient oxygen control



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℃ and +30 mV/ -65 mV at 700℃ is needed

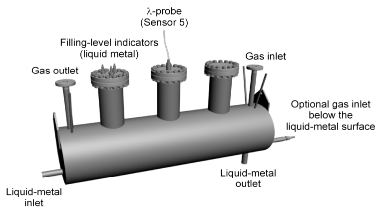
Minimum requirement:

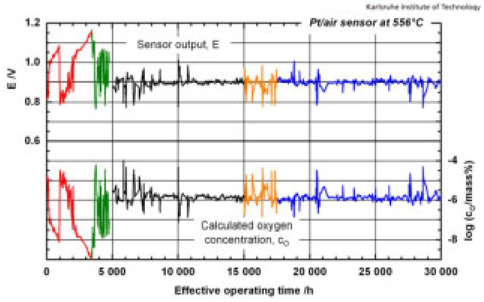
- Better than ± 20 mV at 400°C; ± 30 mV at 700°C
- Range of actual c_O from 0.5 to 2 $c_{O;nominal}$

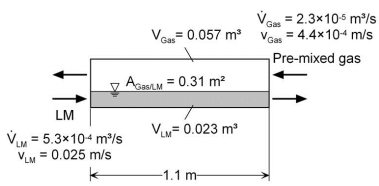
Practical limit:

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

Oxygen transfer from gas to flowing LBE at 550℃







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

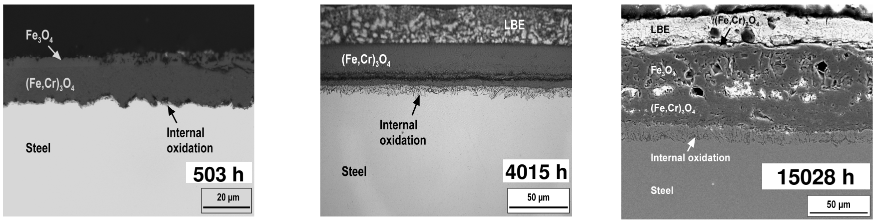
- Discontinous addition of air to humidified Ar-H_2

- 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

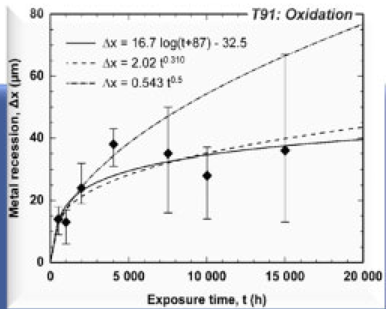
- 500 cm³/min Ar humidified at 18℃
- 1-1.5 cm³/min air

T91: Qualitative performance in oxygen-containing LBE at 550°C, v = 2 m/s and $c_O = 1.6 \times 10^{-6}$ mass% (I)



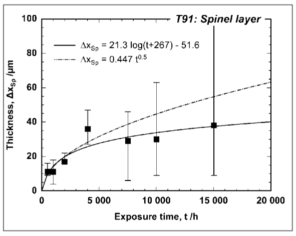
- Oxidation
- Oxide scale generally consists of
  - Magnetite (Fe_3O_4)
  - Cr-deficient spinel ($Fe(Fe_xCr_{1-x})_2O_4$)
  - Internal Oxidation Zone (IOZ)
- Magnetite is mostly missing, i. e., Fe is partially dissolved by the liquid metal (or eroded after Fe_3O_4 formation?)
- Inclusions of Pb and Bi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

T91: Quantification of oxidation in oxygen-containing LBE at 550°C, v = 2 m/s and $c_O = 1.6 \times 10^{-6}$ mass% (II)



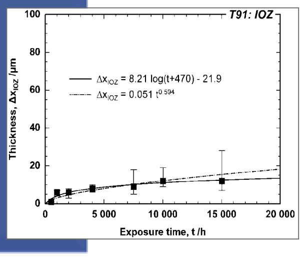
- Metal recession (loss of cross-section)
- Compromises the structural integrity of plant components
- Determined from measurements in the LOM (generally six measurements per investigated cross-section)
- Includes internal oxidation
- Local variation significantly increases with increasing exposure time
- 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)

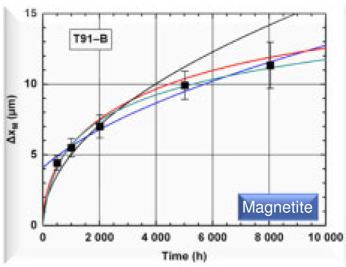


- Thickness of different layers of the oxide scale
- May affect heat transfer in the case of thermally-loaded plant components
- Generally twelve measurements per investigated cross-section
- Thickness of spinel layer significantly varies locally with increasing exposure time
- Average thickness of the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

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

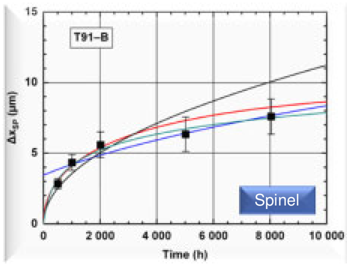


Kinetics of oxide-scale growth for T91-B at 450°C, 2 m/s and 10^{-6} mass% oxygen (I)

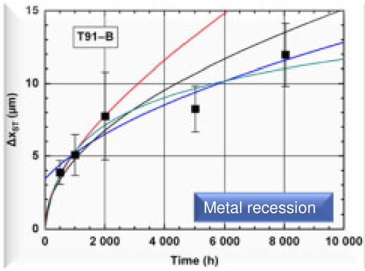


Parabolic:	$\Delta x^2 = k_2 t$
Parabolic after faster initial kinetics:	$\Delta x^2 = k_2 t + C_2$
Logarithmic:	$\Delta x = k_{log} \log (t + t_0) + C_{log}$
Paralinear:	$\frac{d\Delta x}{dt} = \frac{k_p}{d\Delta x} + k_1$

- 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

Conclusions

- Heavy liquid metals (HLMs) are very appropriate coolants/targets for Nuclear (ADS, LFR) and Fusion (blanket) applications. Worldwide R&D has been established to buildup databases for compatibility issues of potential reference materials. A realization of first large demonstration plants within a time scale of about 25 years seems to be reasonable.
- The chemistry of materials corrosion issues in HLMs, i.e. the influence of oxygen as the major non-metal, is well characterized and understood.
- The accuracy of developed oxygen sensors, as part of required oxygen control systems, is reliable enough for evaluating the chemistry of HLMs. The feasibility on laboratory scale has been successfully proven.
- Further progress in the development of new materials with sufficient stable oxide layer formation for long-term operation and up-scaling of oxygen control processes is still required.