Development of Electrochemical Processes for Aluminum-based Coatings for Fusion Applications

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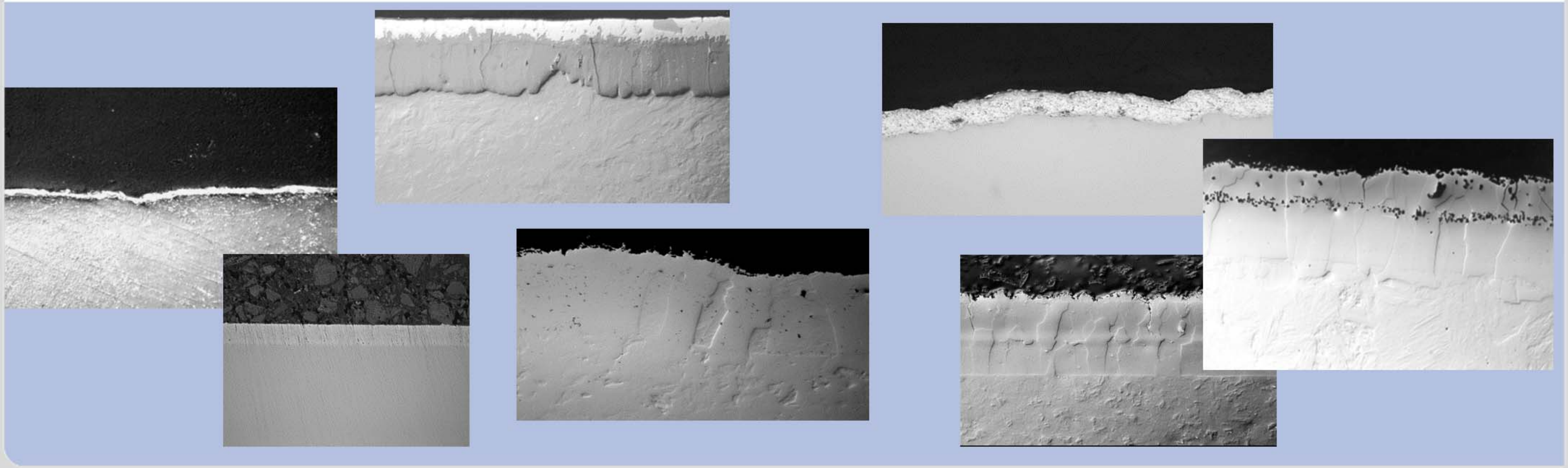

KIT – University of the State of Baden-Wuerttemberg and
National Research Center of the Helmholtz Association

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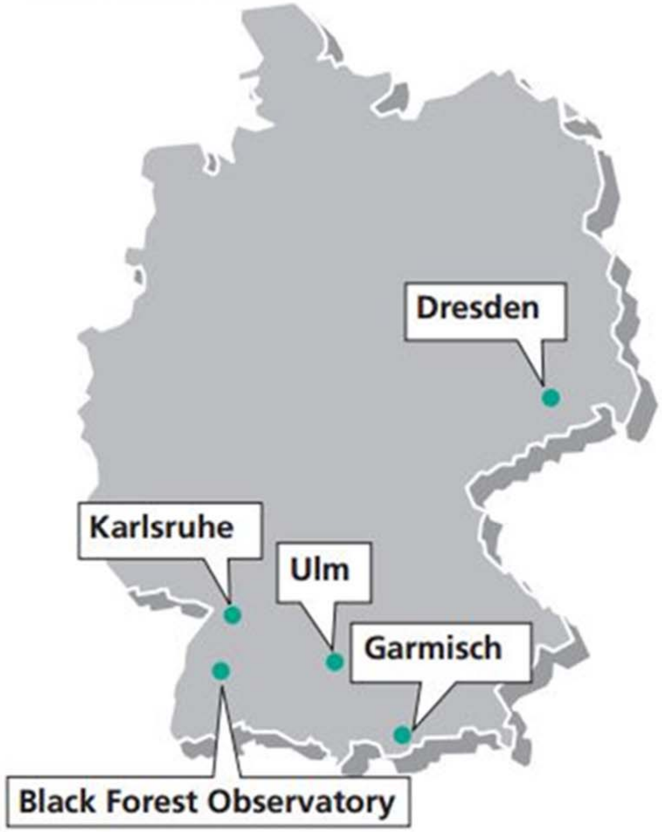
Introduction - Location of KIT, Germany

KIT-locations in Germany



Advanced processes for tritium permeation and corrosion barriers

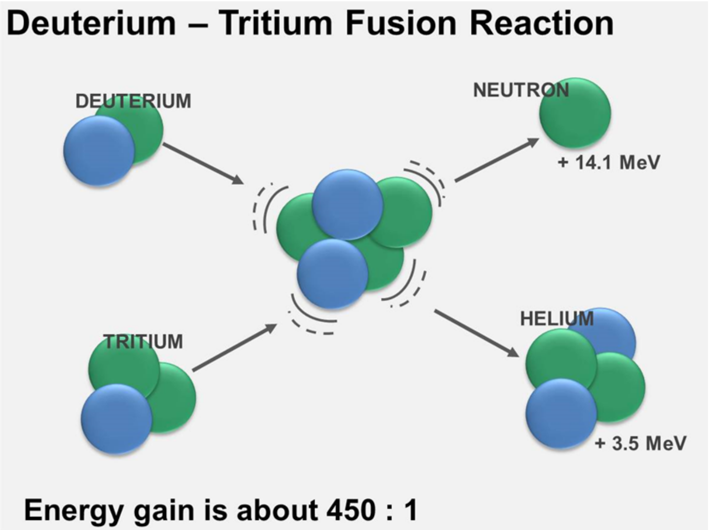
Outline

- Applications for Nuclear Fusion

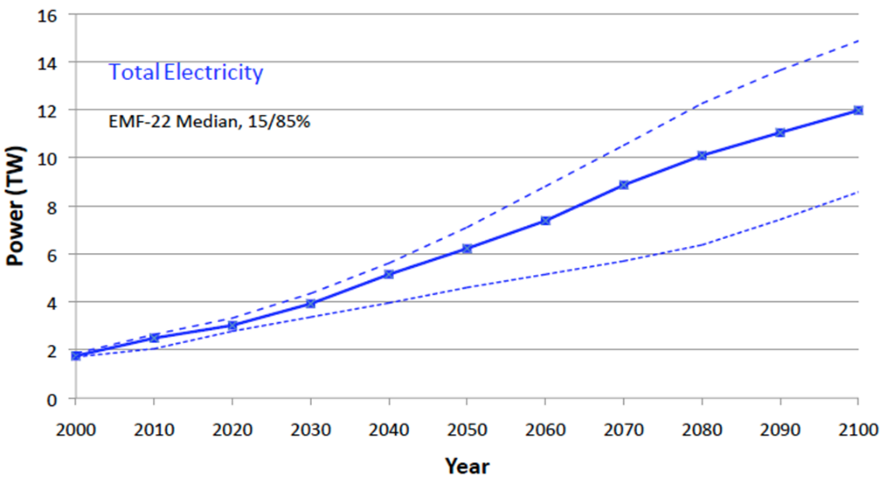
  T-permeation and/or anti-corrosion barriers for liquid breeder blanket concepts in ITER and future Fusion Power Reactors

  ► Why **Al-based** barriers?
- Overview of previous coating activities → Hot-dip-aluminization process
- New electrochemical Al coating processes
  - Al deposition from organic aprotic electrolytes (ECA)
  - Al deposition from ionic liquids + metal salt (ECX)
- Conclusions

Nuclear Fusion as an long-term Option for the Worldwide Energy Demand

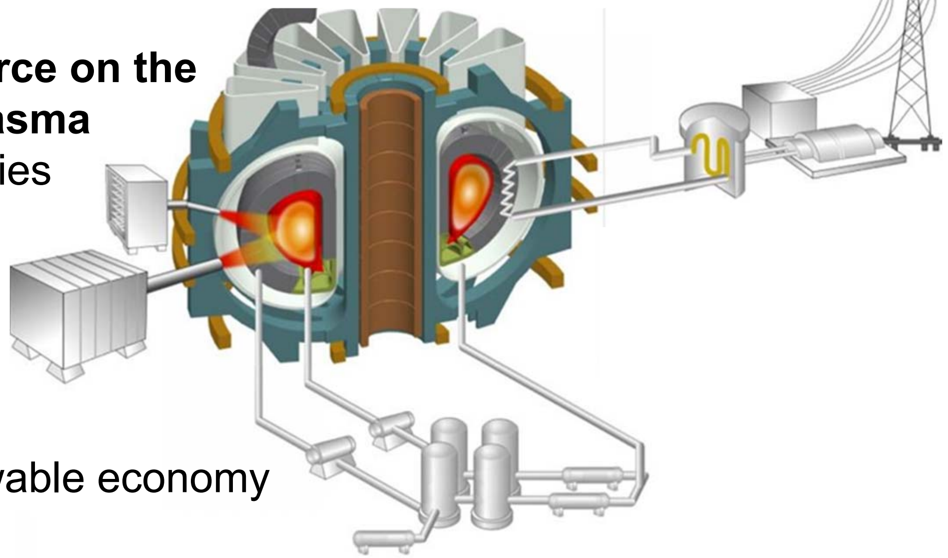


Worldwide energy demand is rising continuously



Development of a new primary energy source on the basis of a magnetically confined fusion plasma

- Favorable environmental and safety properties
- Unit size 2 – 5 GW_{th} / 1 – 2 GW_e
  - Size of present base load power plants
- Potential fusion applications
  - Base load for large cities
  - Energy intensive industries
  - High temperature process heat in a renewable economy



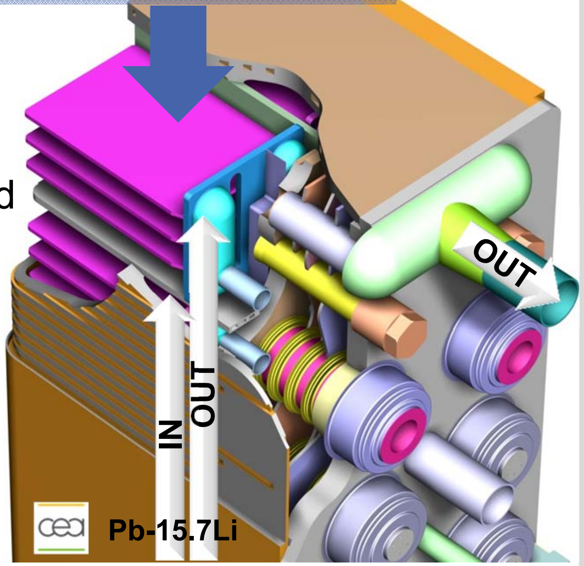
The He-PbLi blanket concept for ITER: Application of T-permeation and/or anti-corrosion barriers

- Deuterium (D) is highly available, e.g. in sea water
- Tritium (T) is naturally “not really“ available, but
  - produced in CANDU reactors by (n, γ) reaction on deuterium
  - **and bred by nuclear reactions from Lithium**

    ^{6}Li (8%) + n → T + He + 4.8 MeV → enrichment is needed

    ^{7}Li (92%) + n → T + He - 2.87 MeV
- Worldwide, many fusion reactor concepts are designed to use lithium in different chemical form
  - as solid breeder (ceramic), e.g. Li_4SiO_4, Li_2O
  - **as liquid metal, e.g. pure Li or Pb-15.7Li (T_m = 235°C)**

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



EUROFER	8.82	0.47	0.20	1.09	0.13	--	0.11	0.02
(wt.-%)	Cr	Mn	V	W	Ta	Mo	C	Ni

→ **Barriers are required!**

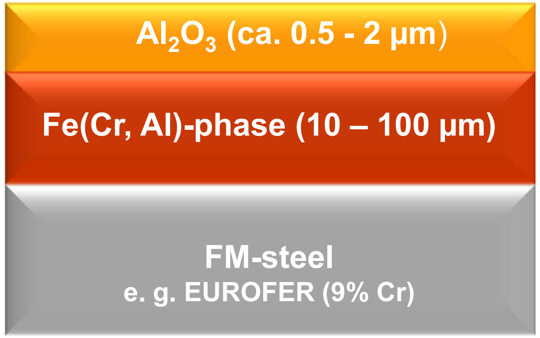
Why do we need Tritium Permeation Barriers for “(European) Liquid Breeder Concepts”?

Safety and cost: Its to reduce the tritium release from the PbLi (where its formed) into the coolant significantly (water for WCLL and helium for HCLL blanket concept)
→ limit for ITER 1gT/a

Investigated barrier systems

Type of coatings	Thickness	Agency / Country	Year reported
$FeAl+Al_2O_3$ ECA, ECX	150-180 µm 20-70 µm	KIT, (HDA) & CEA, (CVD) KIT, China, etc.	Feb-Sep ’04 > 2009
$FeAl+Al_2O_3$	100 µm	JRC, Ispra, Italy (VPS)	1998
Er_2O_3, Al_2O_3, $W+Al_2O_3$	1 µm 1 + 0.5 µm	IPP, Germany (PVD)	Aug 2007
$(Cr_2O_3+SiO_2)+$ $CrPO_4$	80-200 µm	JAERI, Japan (CDC)	Nov 2007
W	10-120 µm	KIT, Germany (EC) & CRPP, Switzerland (EC, PVD, PS)	June 2007

Structure and technical requirements for an Al-based T-permeation and/or corrosion barrier



Al_2O_3 (ca. 0.5 - 2 µm)

Fe(Cr, Al)-phase (10 – 100 µm)

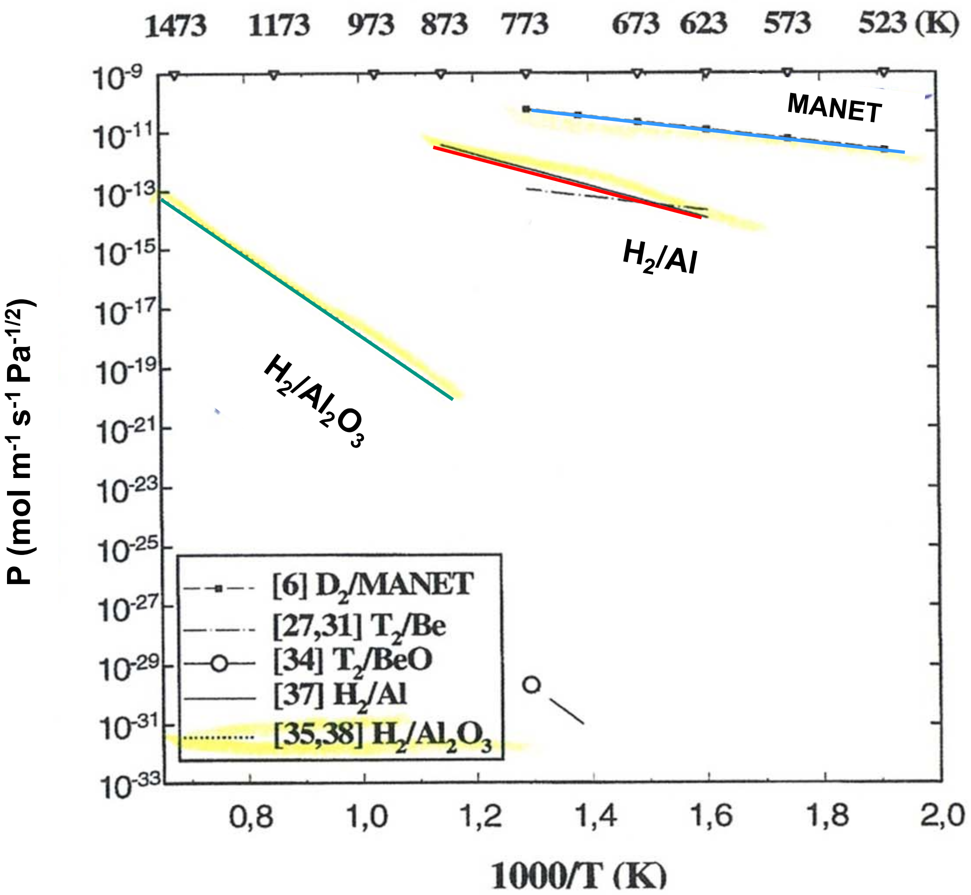
FM-steel
e. g. EUROFER (9% Cr)

Schematic structure

Requirements for a tritium permeation barrier

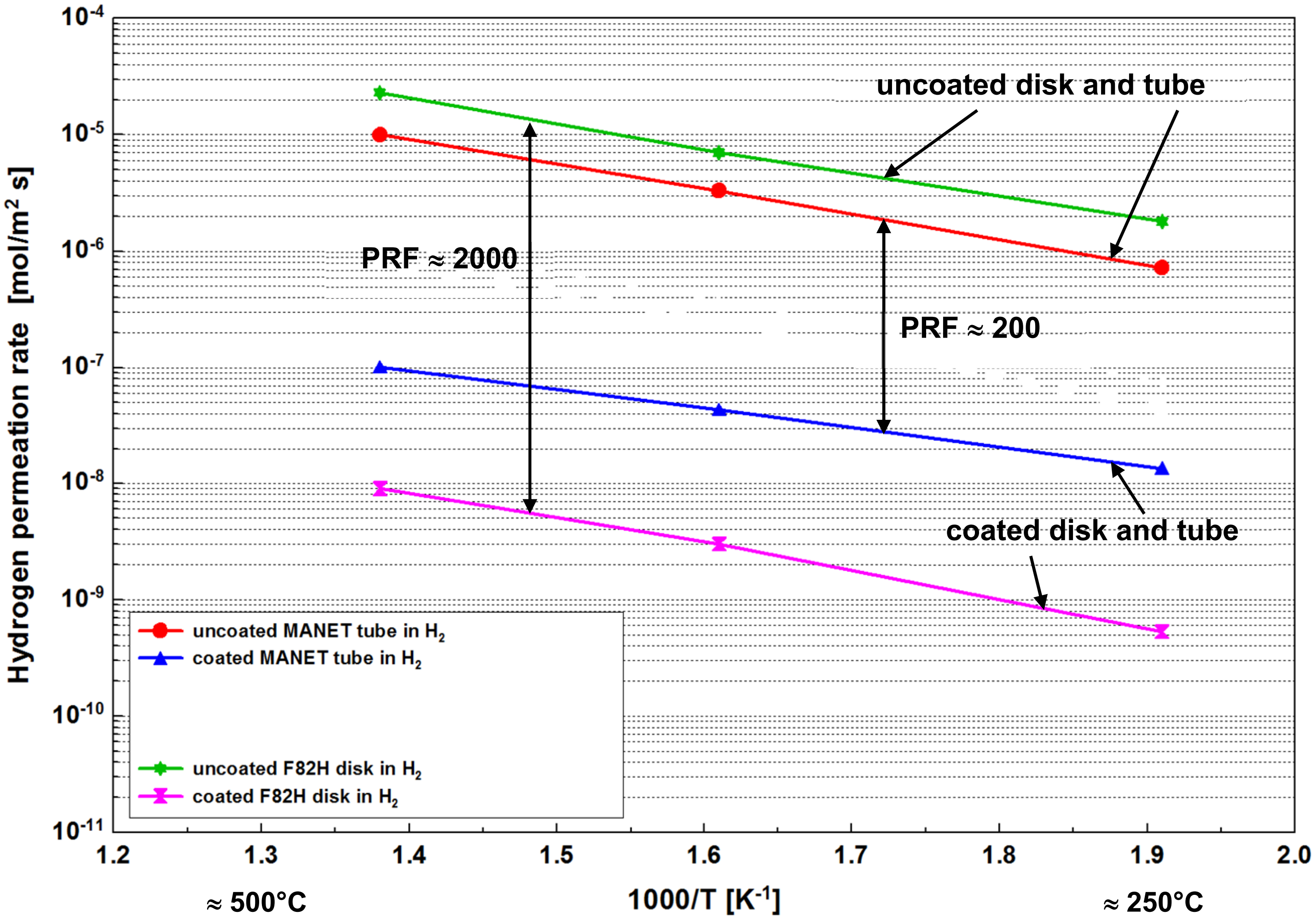
- **Reduction of T-permeation by a factor of <100 in Pb-15.7Li (1000 in gas phase)**
- Self-healing of (mechanically) damaged layer must be thermodynamically possible in Pb-15.7Li (re-oxidizing)
- Long-term corrosion resistant in Pb-15.7Li up to ca. 550°C
- High content of low activation elements
- No negative influence on mechanical properties of the steel due to the coating process
- The coating process must be of industrial relevance

Permeation data of different barriers on FM-steel

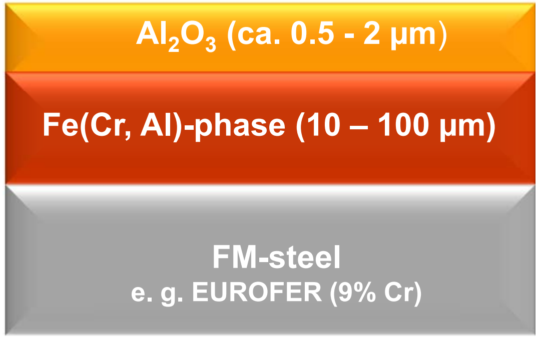


Taken from: *E. Serra et al. / Journal of Nuclear Materials 255 (1998) 105–115*

Permeation data of Al-coated FM-steels in H_2



Structure and technical requirements for an Al-based T-permeation and/or corrosion barrier



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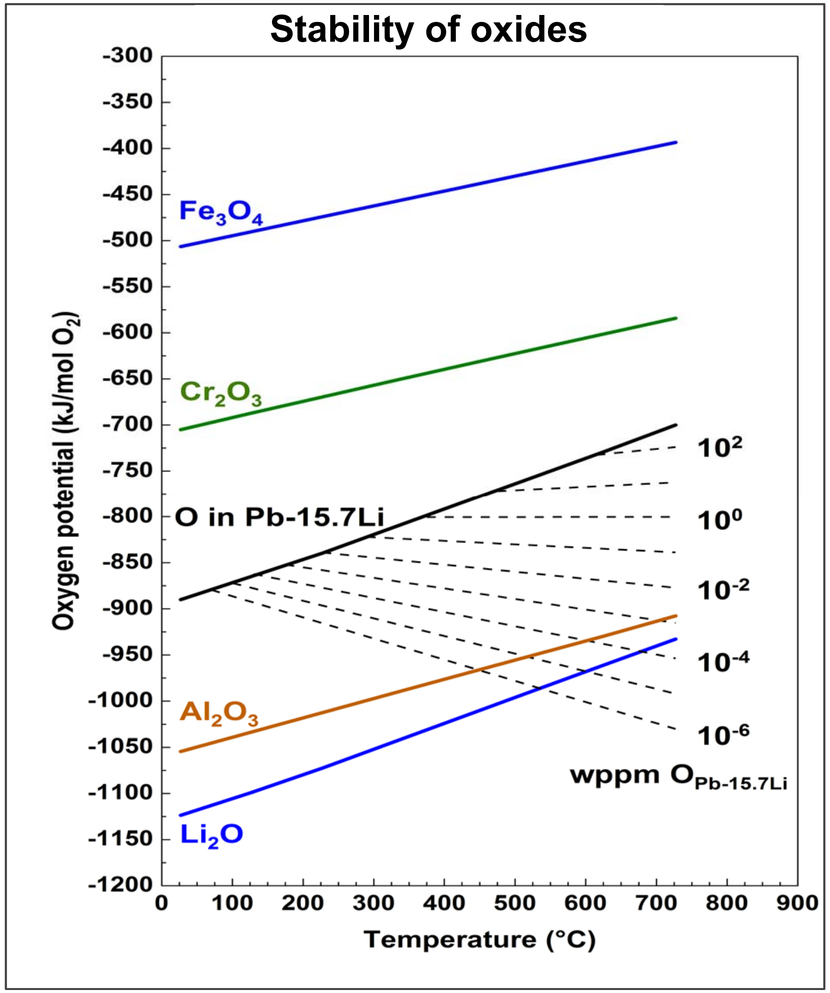
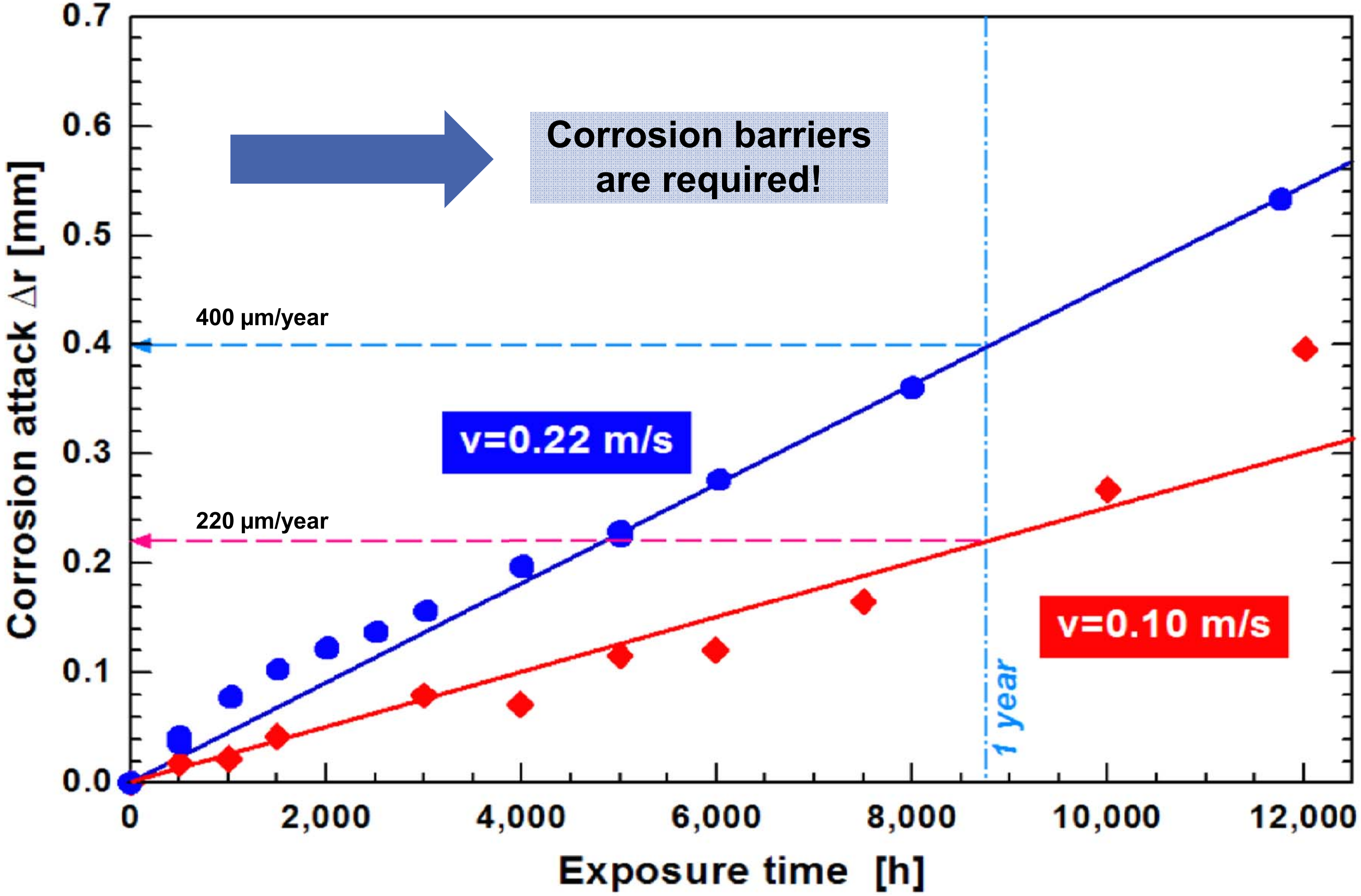
Thermodynamics of Al/Al_2O_3-based T-permeation barriers

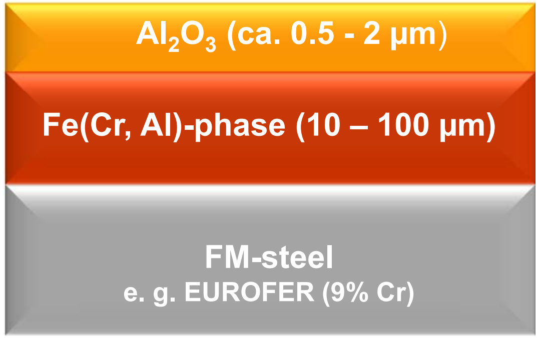


Corrosion attack of bare EUROFER steel in Pb-15.7Li at 550°C as a function of flow velocity



Corrosion barriers are required!

Structure and technical requirements for an Al-based T-permeation and/or corrosion barrier



Al_2O_3 (ca. 0.5 - 2 µm)

Fe(Cr, Al)-phase (10 – 100 µm)

FM-steel
e. g. EUROFER (9% Cr)

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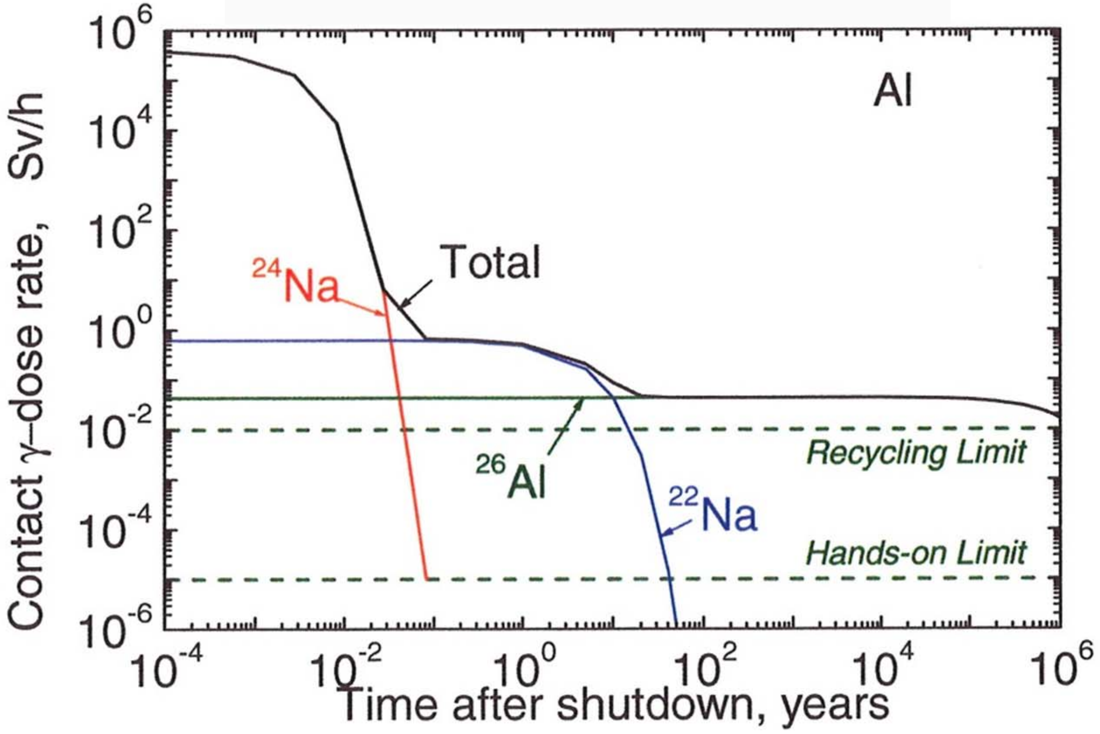
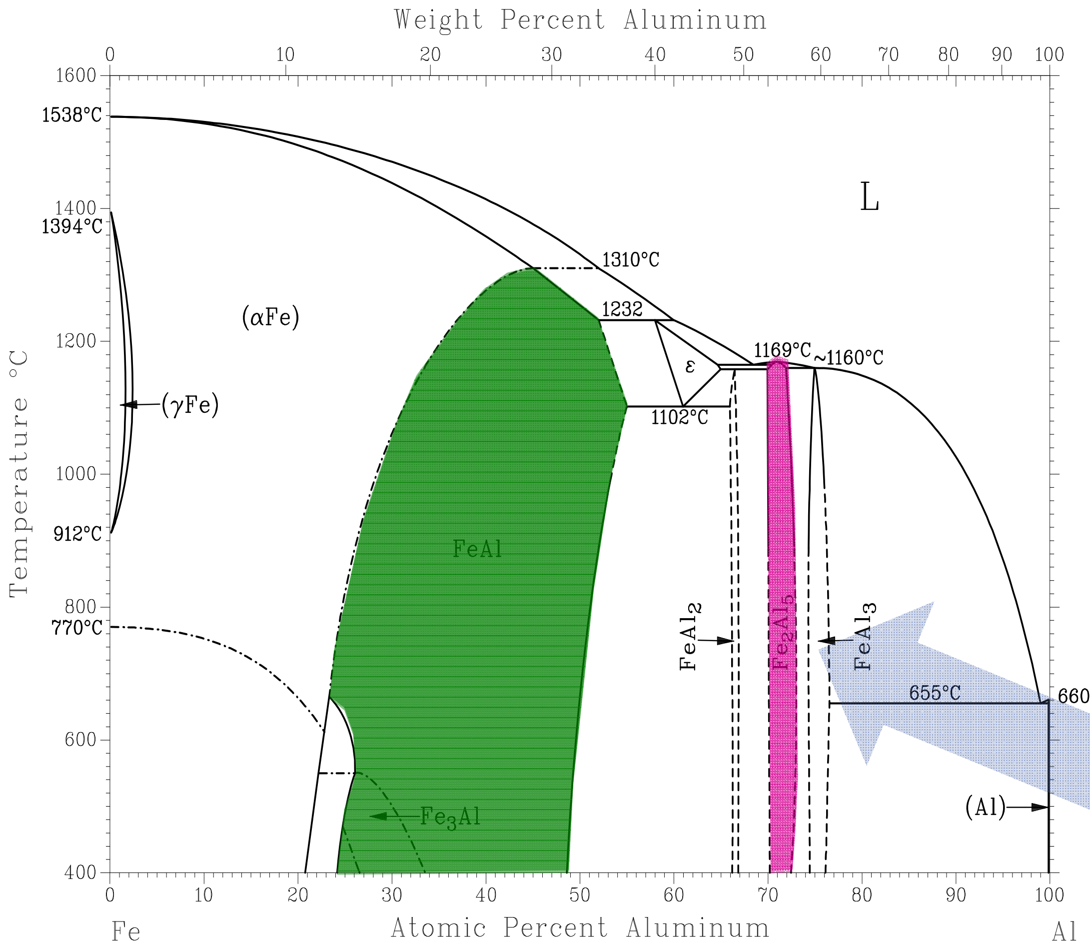
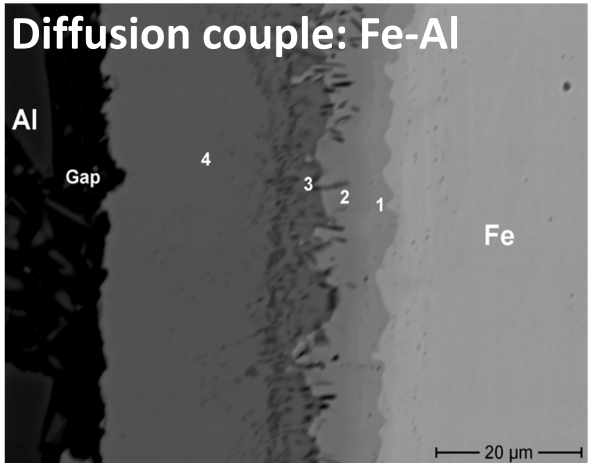
Activation of Al for Al-based barriers in a "fusion irradiation environment"

Aluminium irradiation for 2 years



Al-based coatings: The Fe-Al phase diagram to understand the complexity of intermetallics



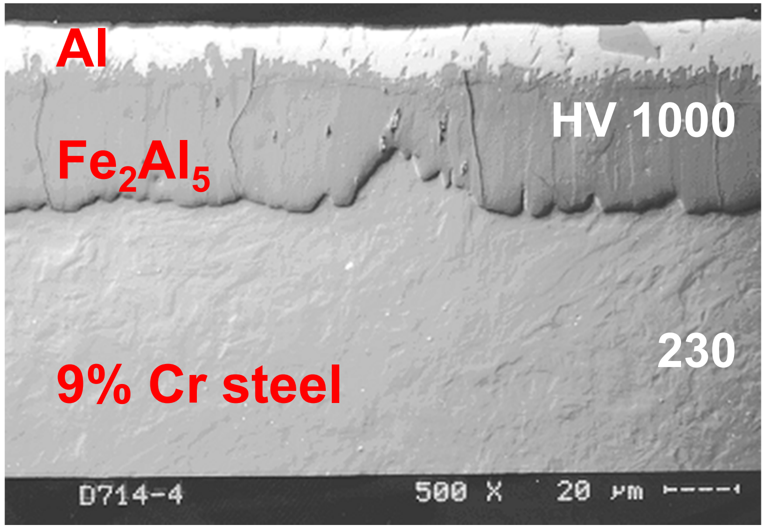

Diffusion couple: Fe-Al

1: Fe_3Al
2: FeAl
3: $FeAl_2$
4: Fe_2Al_5

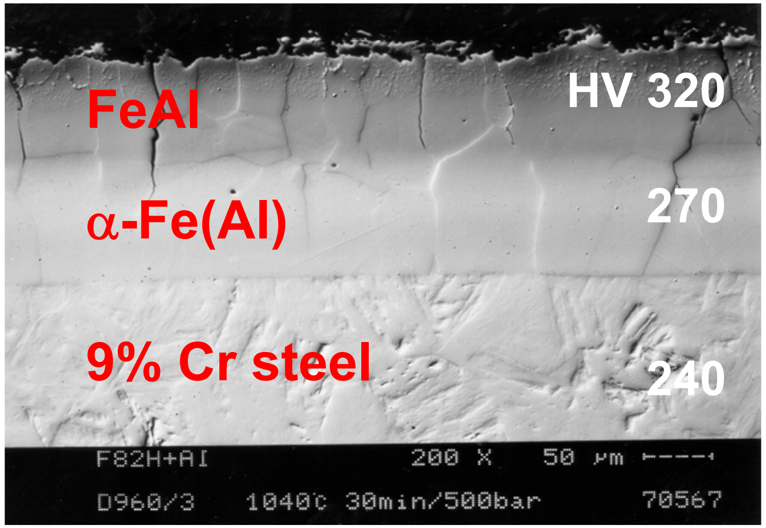
Brittle phases

Hot-Dip aluminizing process parameters for hot dipping are: T_{dip} = 700°C, dipping time of 30 s in Ar-5%H_2 atmosphere

Microstructure of hot dipped surface



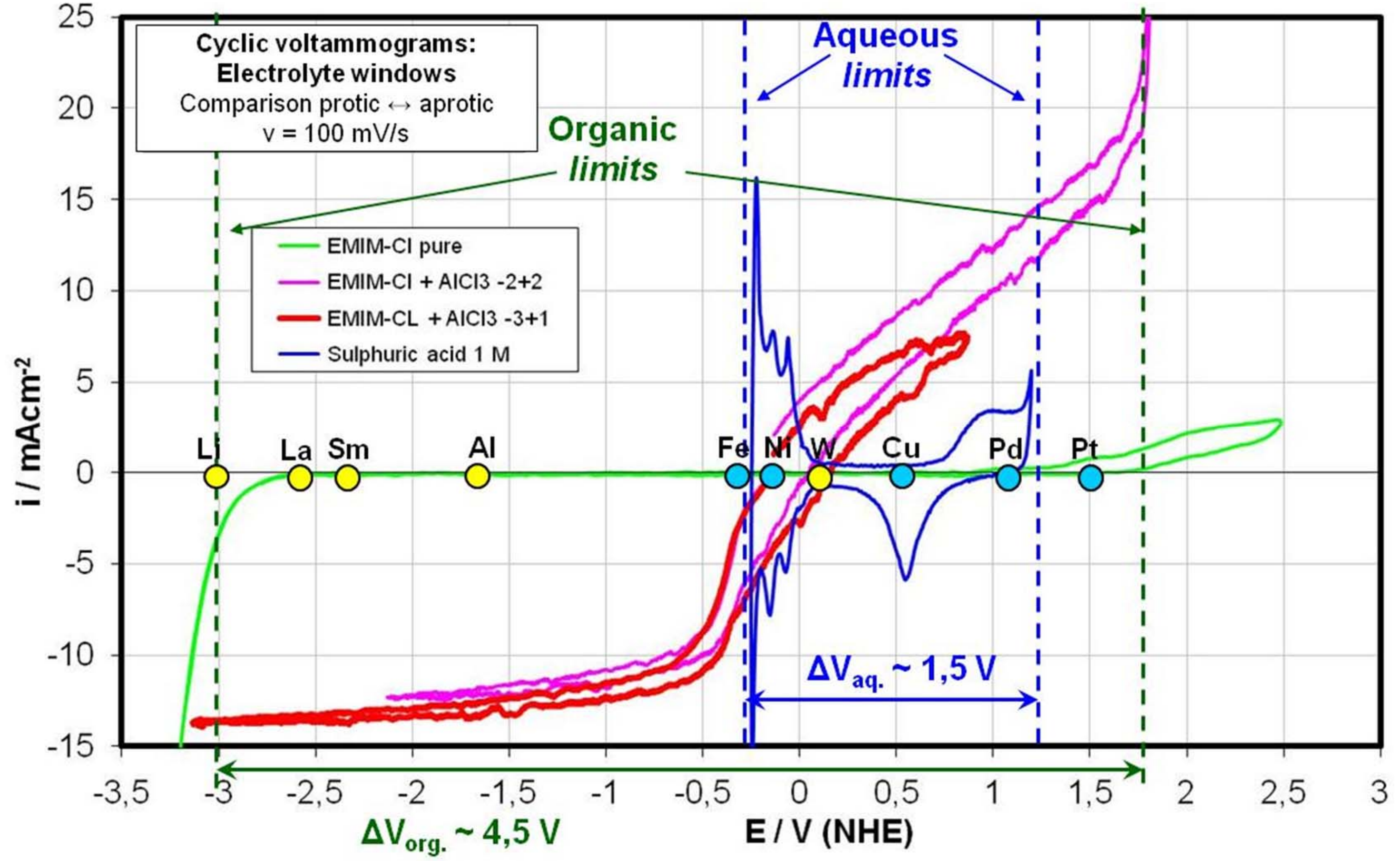
Microstructure after heat treatment



The alloyed surface layer consists of brittle Fe_2Al_5, covered by solidified Al

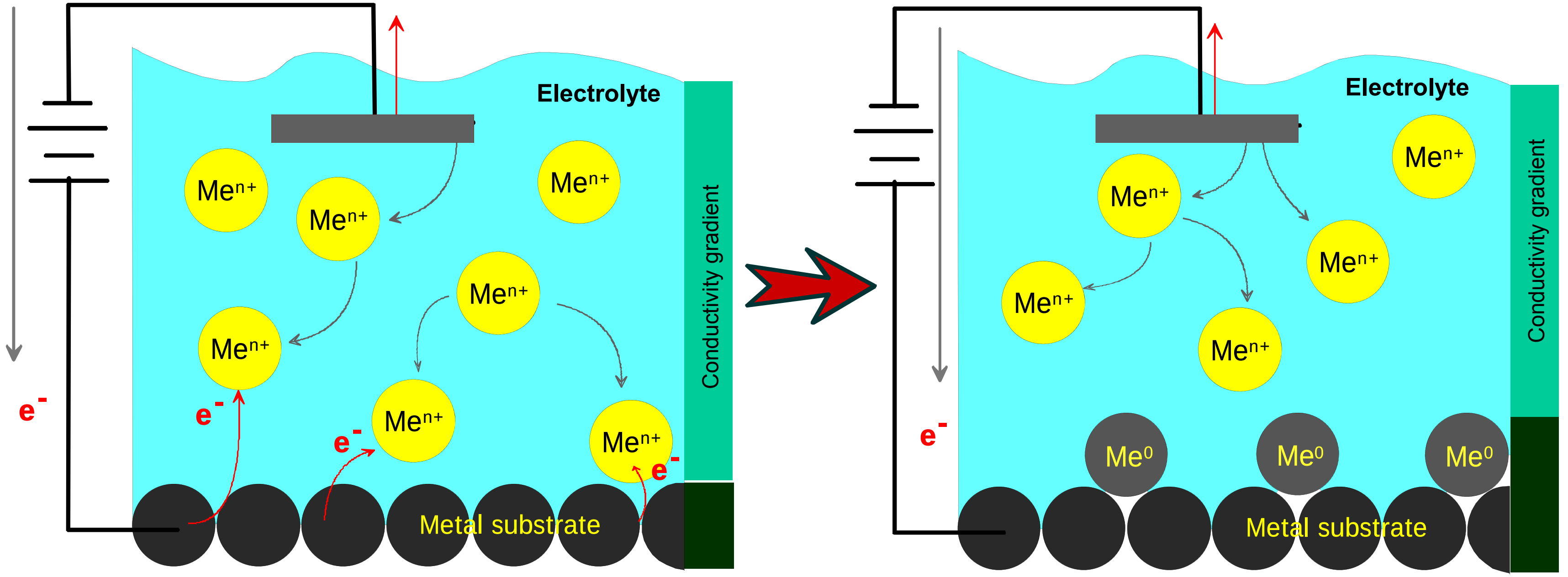
Heat treatment at 980°C / 0.5 h + 760°C / 1.5 h and an applied pressure of >250 bar (HIPing) reduces porosity and transforms the brittle Fe_2Al_5-phase into the more ductile phases FeAl and α-Fe(Al)

Electrochemistry for coating application



EC measurements of protic and aprotic metal deposition systems

Electrochemical deposition for barriers/coatings - advantages of galvanic coatings -



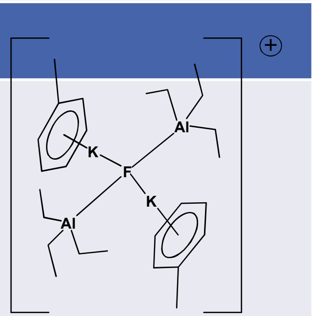
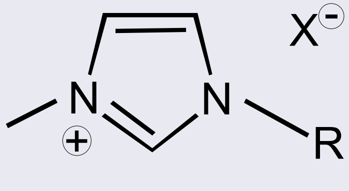
- By **anodic** dissolution, metal removal takes place without any mechanical stresses and at “low” temperatures

- **No gradients** ΔT, Δp (and resulting forces) between
  - electrolyte medium and metal surface
  - metal surface and metal bulk

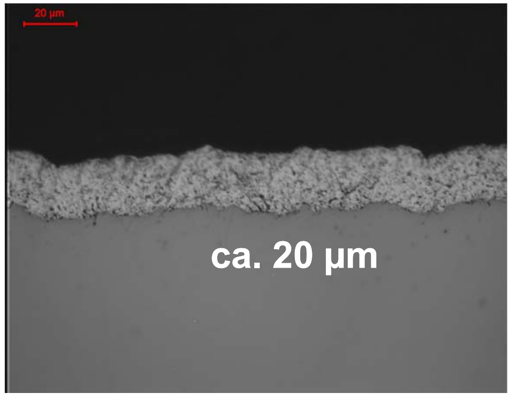
►no local heating as in EDM working

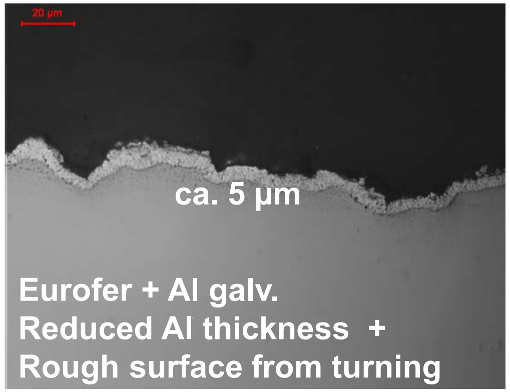
►no mechanical load (no residual stresses)

Electrochemical aluminium deposition
- properties of organic aprotic electrolyte systems -

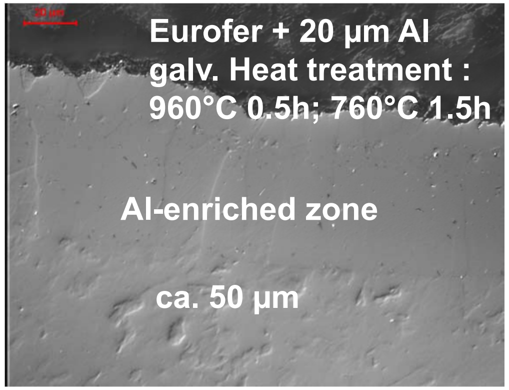
Solvens		**Toluol, Xylol** **Diisopropylether**	**Quarternay Amin salts** **e. g. Ethylmidazolium chloride**
Ionic solubility of solvens		**No**	**Yes**
Al-carrier system		KF·2Al(R)$_3$ R = C_nH_{2n+1} mit n= 2-6	$AlCl_3$
Temperature		100°C	RT … 200°C
Reactivity	Water	extremly high	modest
	Air	extremly high	low
	Temperature	modest	Stable up to 300°C
Toxicology | biodegrability		Aromates: ++/---	Amines: -/+
Max. conductivity [mS/cm]		19,5	22,0
		ECA	**ECX**
		Al-Alkyl- Acryl-Complex in Toluol resp. Alkylether 	Al^{3+} + 3 Cl- → EMIM-$AlCl_4$ 

Development of electrochemical Al coating process, toluol-based (ECA)





Eurofer + Al galv.
Reduced Al thickness +
Rough surface from turning



Eurofer + 20 µm Al galv. Heat treatment : 960°C 0.5h; 760°C 1.5h

Process specifics

Organic electrolyte, Al-alkyle, under cover gas

Deposition temperature ca. 100°C, rate ≈ 12 µ/h

More complex geometries can be coated; even inside tubes

EUROFER	8.82	0.47	0.20	1.09	0.13	--	0.11	0.02
(wt.-%)	Cr	Mn	V	W	Ta	Mo	C	Ni

Screws with nuts

Result of ECA development

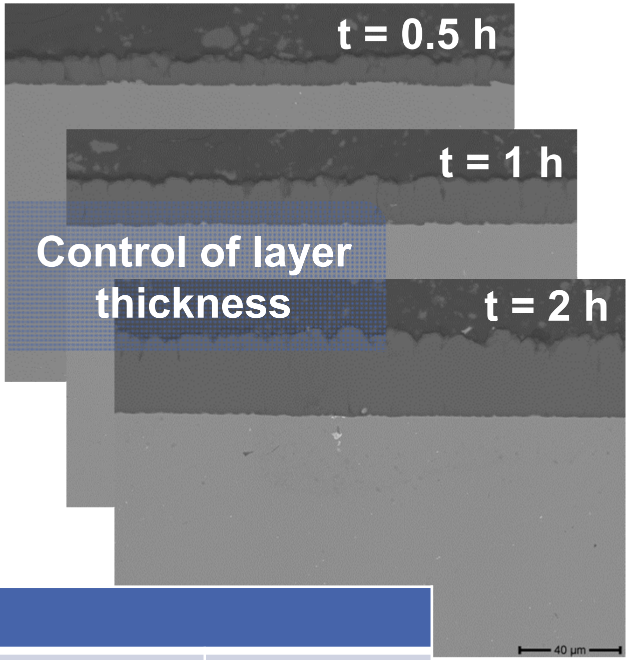
- Electrochemical coating **applicable** to functional scales in TBM's
- Barrier function tested in corrosion, successfully
- **Salt-based processes have to be developed** for higher compositional flexibility
- Reason: Electro-negativity of refractory metals and unique behavior

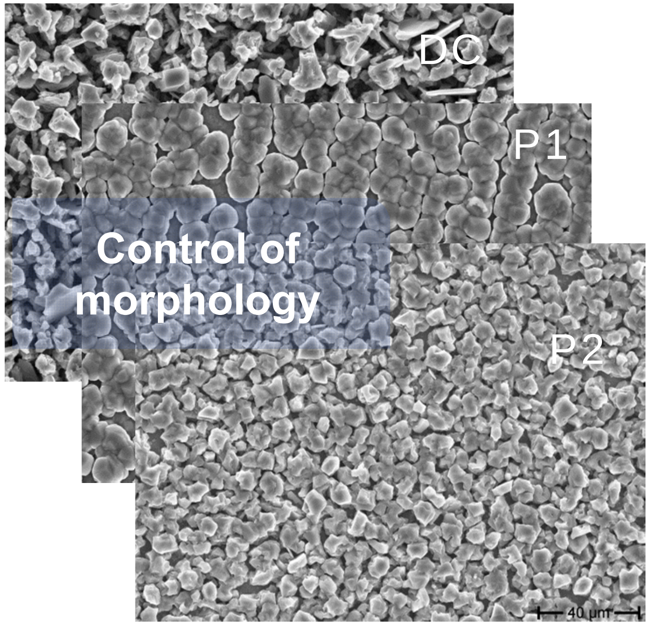
Development of coatings as corrosion T-permeation barriers (ECX)

Development of electrochemical aluminum coating process based on ionic liquids (ECX)

Advantages of ECX process based on ionic liquids:

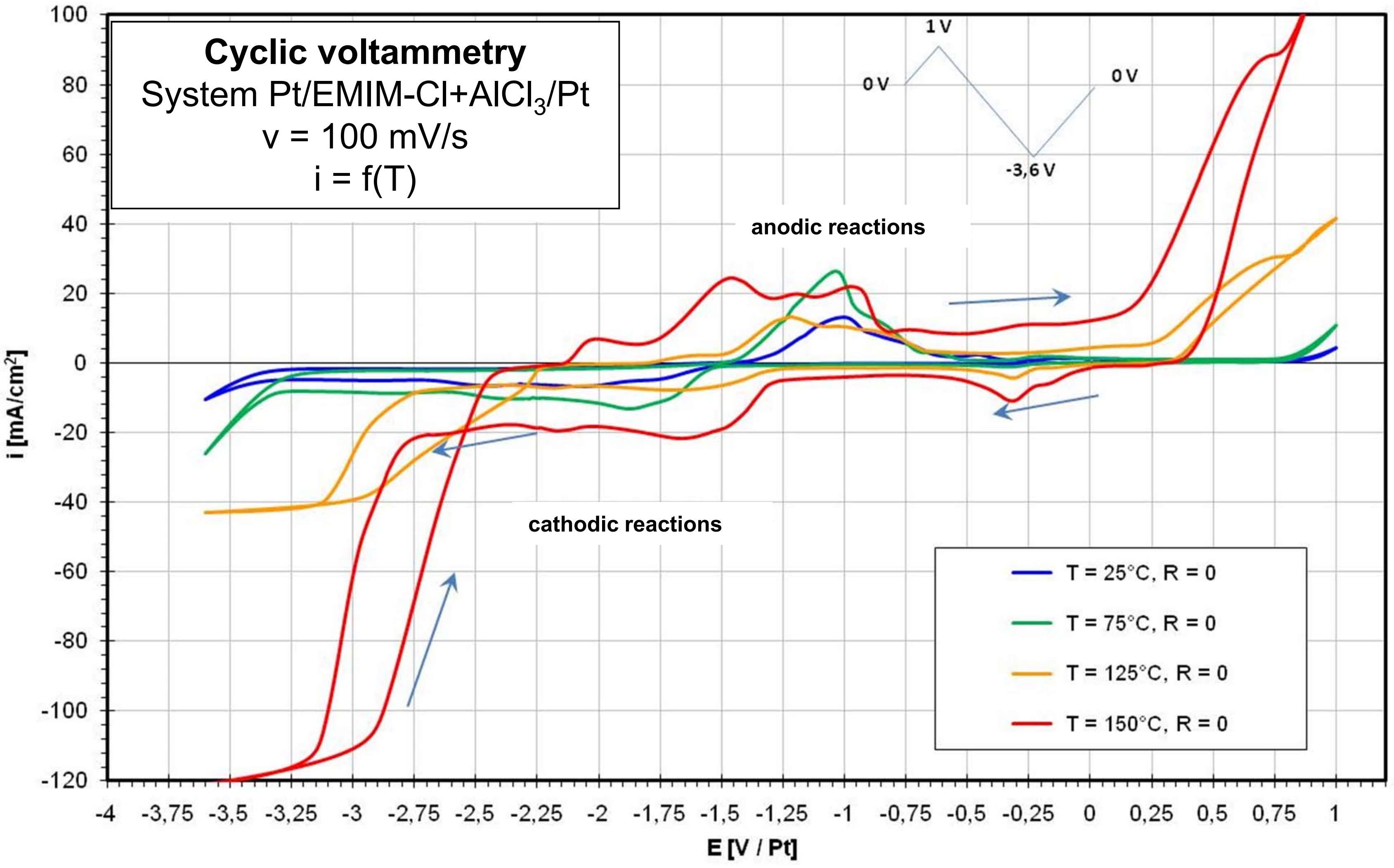
- Improved flexibility compared to ECA
- Improved security (inflammable, not volatile) compared to ECA
- Deposition parameters are customizable to produce coatings with specific properties (thickness, deposition rate, morphology)
- Controllable layer thickness (compared to HDA)





Deposition Parameters			
Parameter	DC	P1	P2
j_m	20 mA/cm^2	20 mA/cm^2	20 mA/cm^2
j_p	-	80 mA/cm^2	25 mA/cm^2
t	30 min	30 min	30 min
f	-	1 s^{-1}	1 s^{-1}
Θ	100 %	25 %	80 %

Electrochemistry of aluminum in ionic liquids



Cyclic voltammetry
System Pt/EMIM-Cl+$AlCl_3$/Pt
v = 100 mV/s
i = f(T)

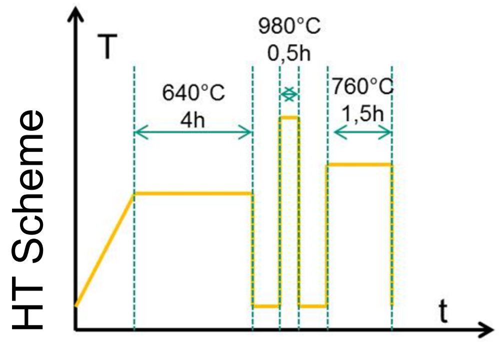
anodic reactions

cathodic reactions

Heat treatment of Al layers for corrosion and T-permeation barriers (pure Al is not stable in PbLi)

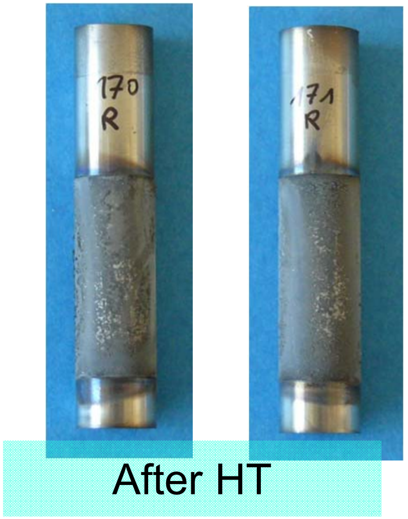
Treatment of Al coatings produced by ECX

- **Heat treatment necessary to convert Al coatings to desired protective Fe-Al scales for corrosion protection and T-permeation**




tube furnace used for HT


After deposition

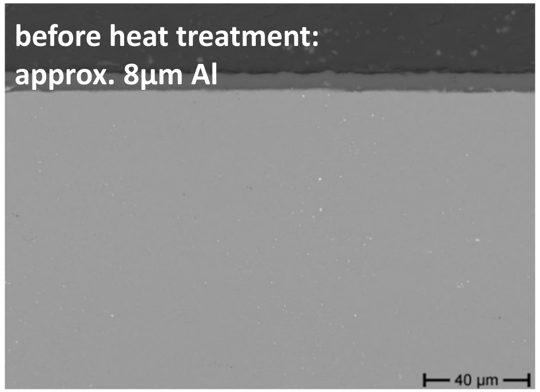


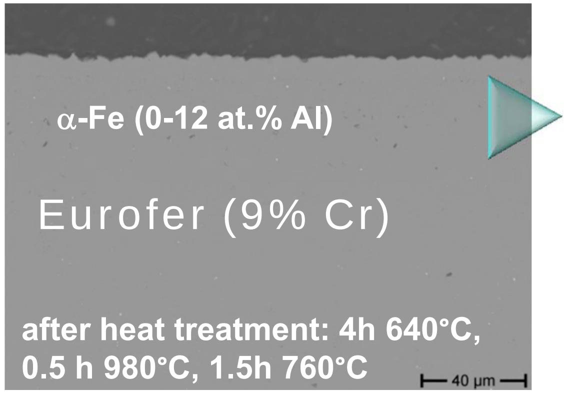
After HT

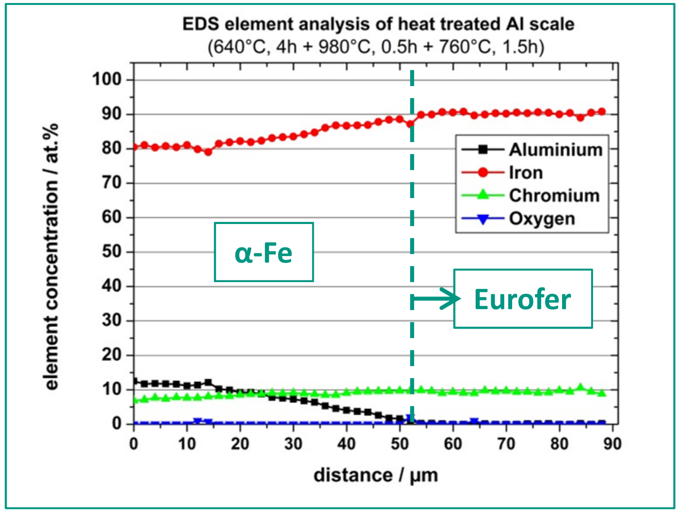
- **Homogeneous conversion of Al coatings and formation of desired Fe-Al phases on 1.2210 steel**
- **No delamination visible**

Heat treatment of Al layers for corrosion and T-permeation barriers

Treatment of Al coatings produced by EDX process (Lewis acidic IL)





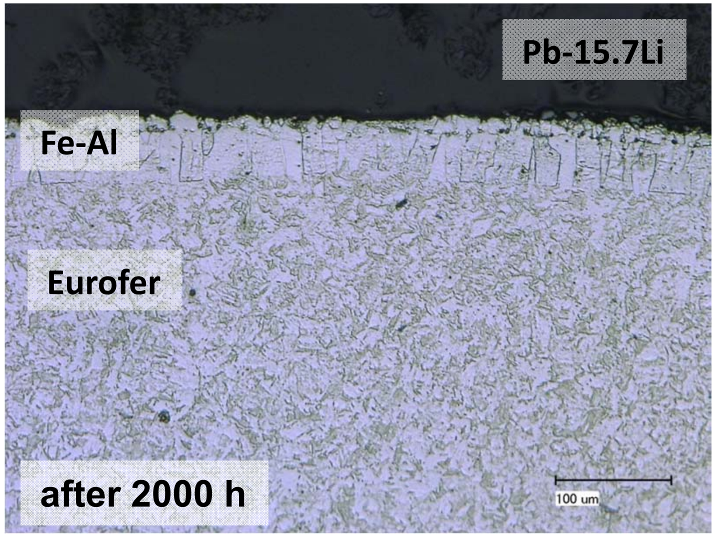

EDS element analysis of heat treated Al scale (640°C, 4h + 980°C, 0.5h + 760°C, 1.5h)

- Heat treatment under Ar atmosphere (preventing of strong surface oxidation) + additional annealing step at 640°C (4h)
- Relatively smooth surface after heat treatment
- Layer thickness after heat treatment: approx. 50µm (center)

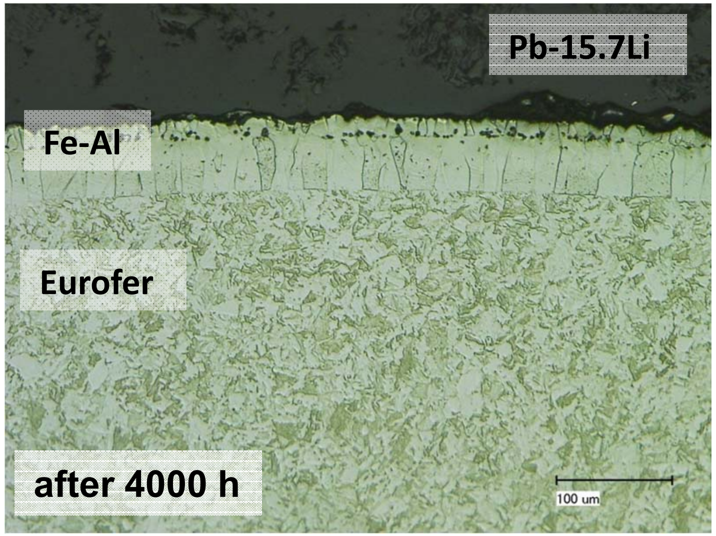
  Actual work:
  - Ongoing examination of deposition parameters:
    - Adhesion to the substrate, reproducibility, influence on coating properties
    - Influence of sample geometry
- Optimization of heat treatment parameters (depending on parameters during ECX process)

Development of electrochemical aluminum coating processes (corrosion tests in Pb-15.7Li for ECX process)

- Barriers produced by ECX process:
  - Corrosion protection of Eurofer in flowing Pb-Li is shown for “short-term“ exposure times up to 4.000h
  - Remaining protective scale thickness after 4000 h: >50 µm
  - Radial mass loss: ca. 10 µm → corrosion rate ca. 20 µm/year
  - Homogeneous corrosion attack of the scale itself → No formation of plateaus (!) visible as in the case scales produced by ECA process



after 2000 h



after 4000 h

Conclusions

- **Barriers**, based on Fe-Al/Al_2O_3, are appropriate to fulfill the requirements for T-permeation reduction and corrosion protection in liquid PbLi.
- **Hot-dip aluminizing** is an excellent tool to investigate the formation of aluminide layers on FM-steels (interdiffusion). But HDA coatings have drawbacks because of the high Al content in the surface
  - ► high activation under neutron irradiation: **^{26}Al**
    and the low flexibility for coating of complex-shaped parts.
- Electrochemical deposition processes like **ECX** have shown their applicability for manufacturing of thin Al coatings with **high reproducibility,** even for complex geometries.
- The development of appropriate **heat treatments** has to be further optimized, followed by new permeation tests in H-, D- and finally T- environments.
- The new electrochemical Al-based coatings have also a **high potential in other energy applications** at elevated temperatures and aggressive environments.