Advanced Processes for T-Permeation and Corrosion Barriers for the $DCLL_{mod.}$ concept

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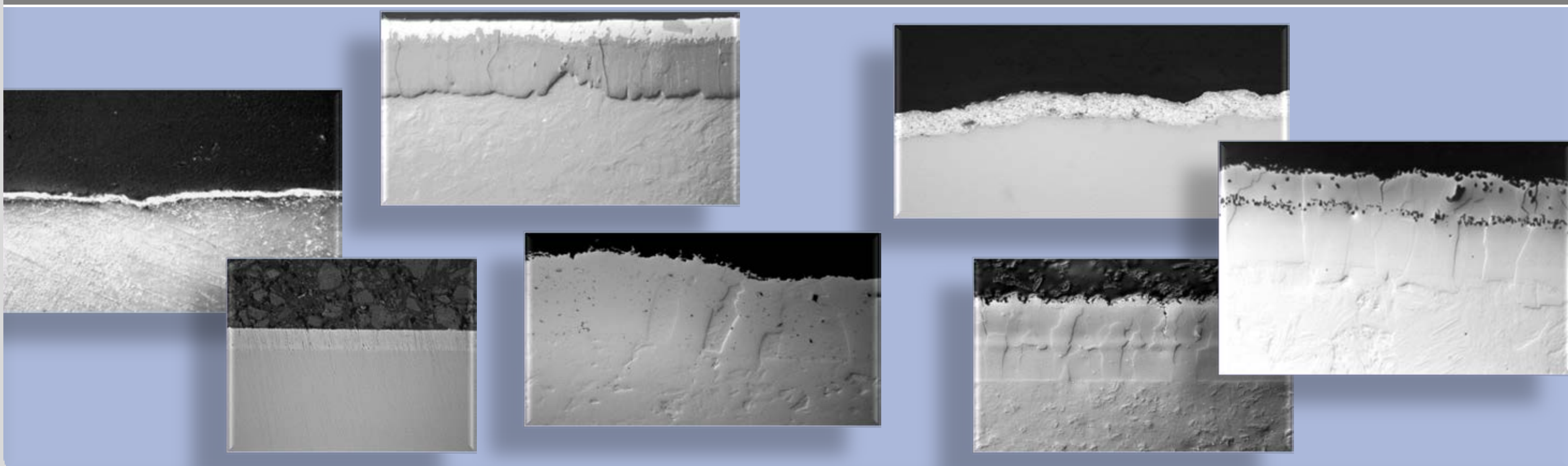

Advanced processes for T-permeation and corrosion barriers

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Outline

- T-permeation and/or anti-corrosion barriers for the $DCLL_{mod.}$ blanket in ITER (and for DEMO?)

  → why **Al-based** barriers?
- Overview of previous coating activities
- New electrochemical Al coating processes

  - **ECA**, Al deposition from organic aprotic electrolyte

  - **ECX** (X = Al, W, Ta …), deposition from ionic liquid + metal salt
- Conclusions

The HCLL (He-PbLi) TBM (and DEMO) blanket
Application of T-permeation and/or anti-corrosion barriers

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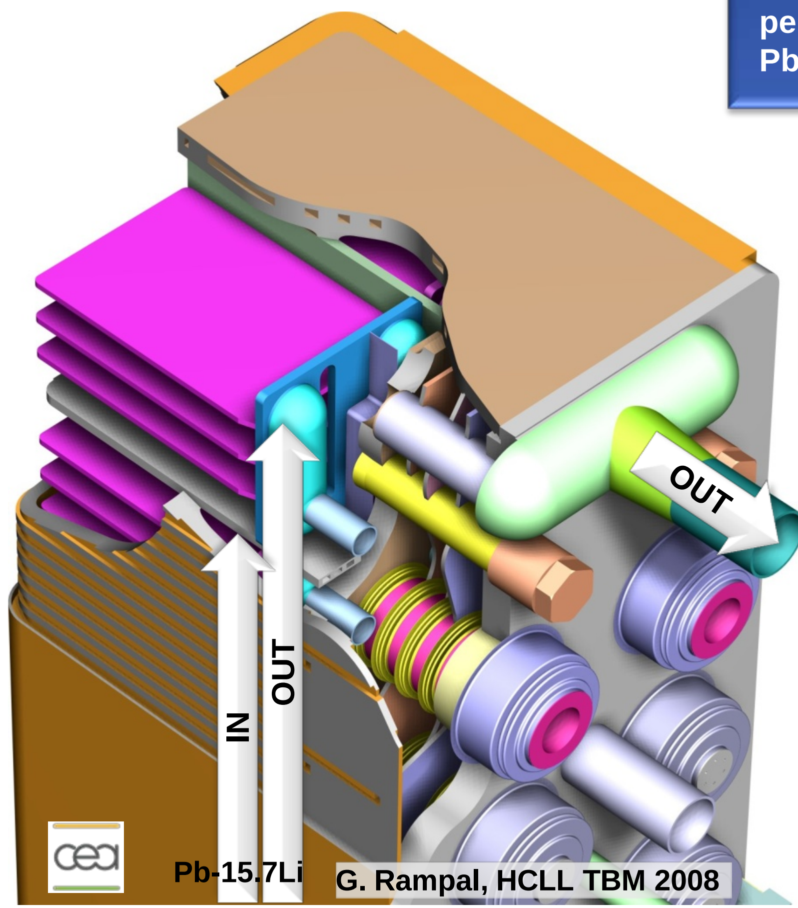
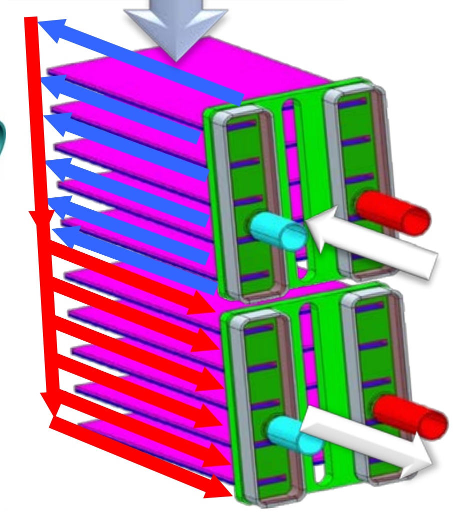
DEMO HCLL MAIN FEATURES
2m x 2m modules
RAFM steel (EUROFER)
He (8 MPa, 300-500°C)
Liquid Pb-15.7Li (eutectic) as breeder and multiplier
PbLi slowly re-circulating (10/50 rec/day)
90% ^{6}Li in PbLi Pb-Li velocities in breeding unit ~ 1 cm/s range
TBR = ≤1.15 with 550mm Breeder radial depth
Lifetime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



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

PbLi flow velocity ~ 1 mm/s



Why do we need TPB's (Tritium Permeation Barriers) for Liquid Breeder Concepts?

Safety and cost
Its to reduce the tritium release from the PbLi into the coolant significantly (water for WCLL and helium for $DCLL_{mod.}$ blanket concept)
→ limit for ITER site 1gT/a

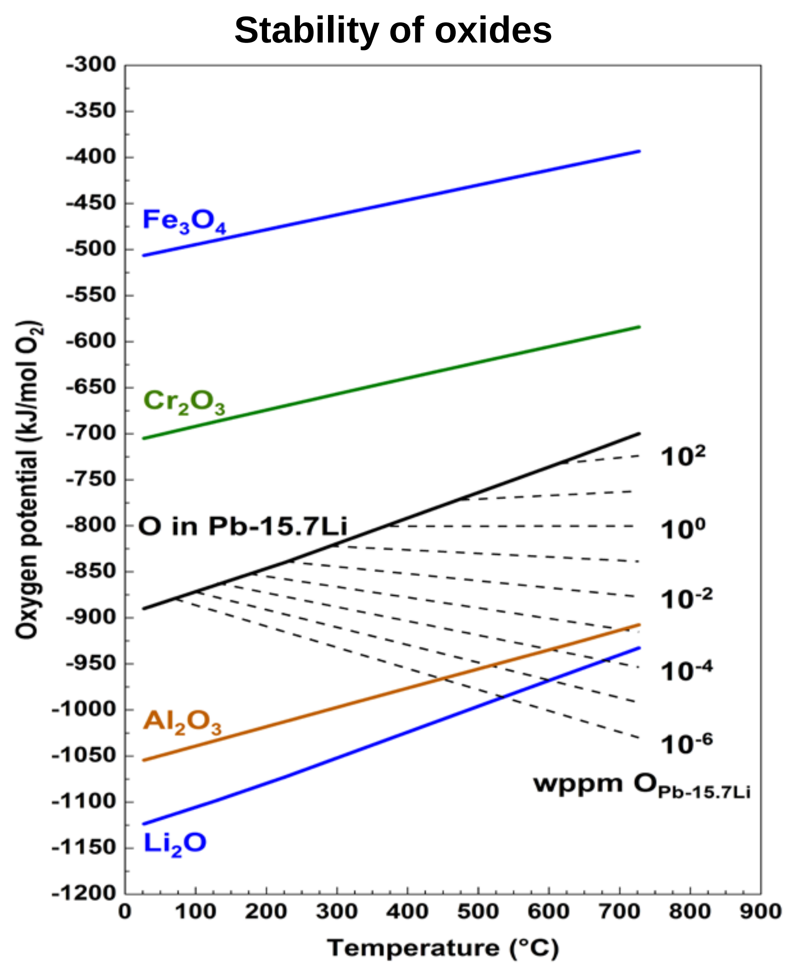
- EU Fusion Technology program started to select FeAl-based coatings with alumina as a thin top layer in the mid 90's. Later on, other type of coatings were also investigated, but with much less intensity and less claim for industrial relevance (ca. 2007+).
- During the phases one and two of the European R&D process, the manufacturing technologies for the coatings and their technical characterization were summarized in reports between 1998 and 2003.

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

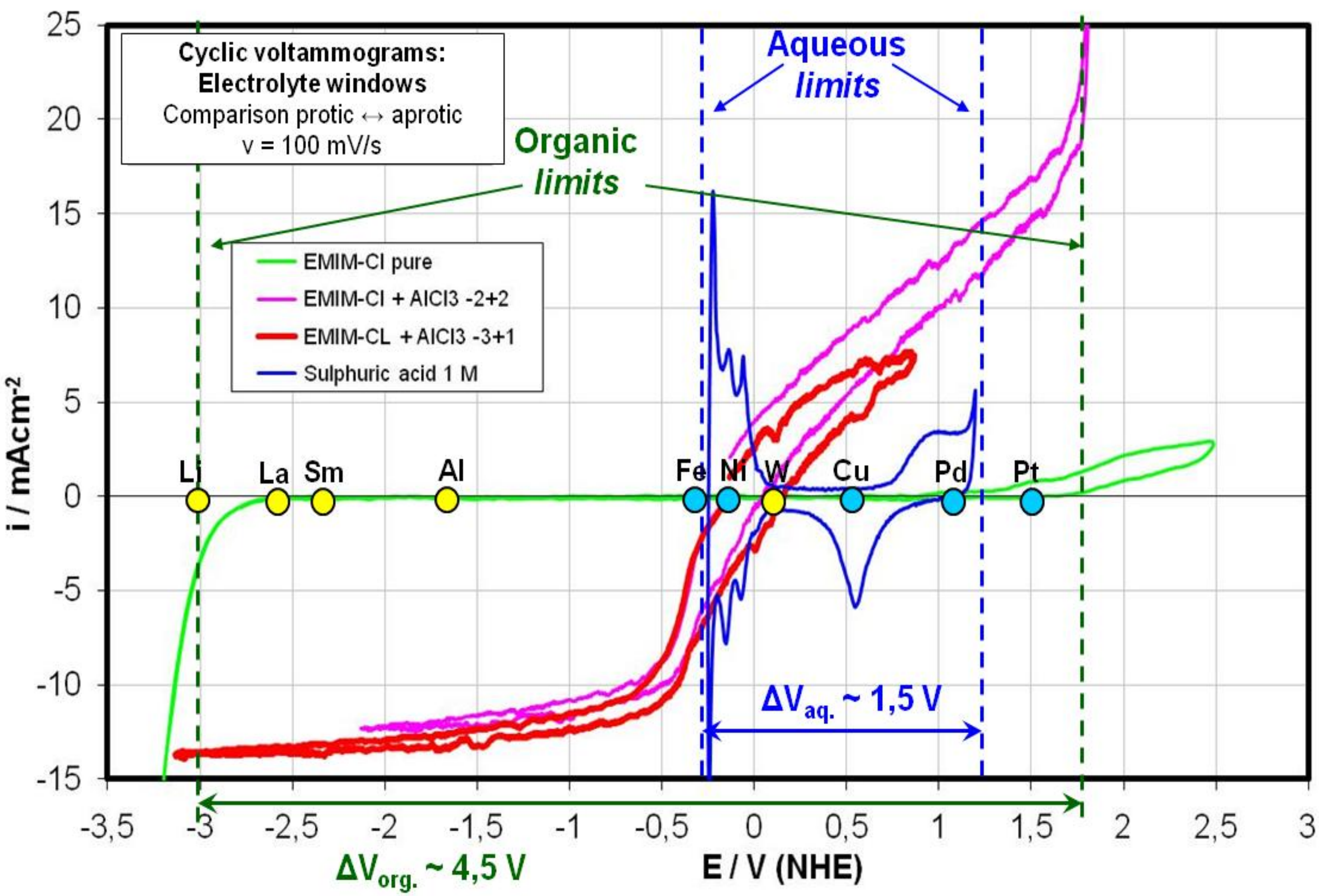
Requirements for a tritium permeation barrier

- 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

Thermodynamics of Al/Al_2O_3-based T-permeation barriers

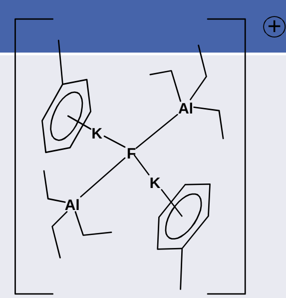
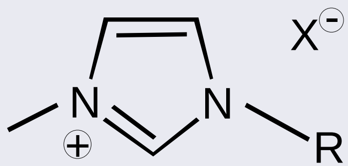


Electro-chemistry for coating application

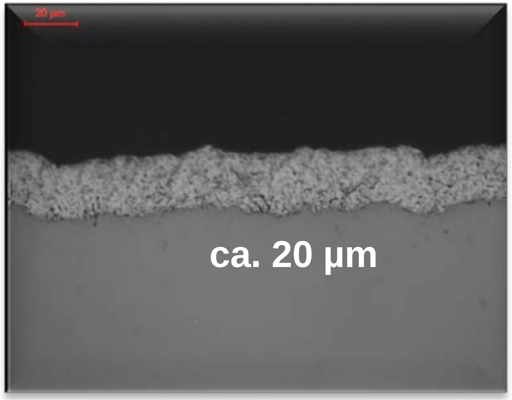


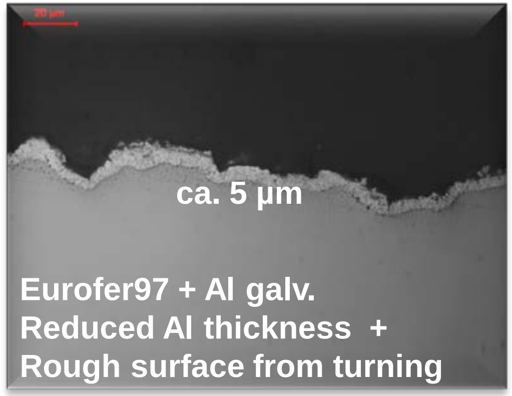
EC measurements of protic and aprotic metal deposition systems

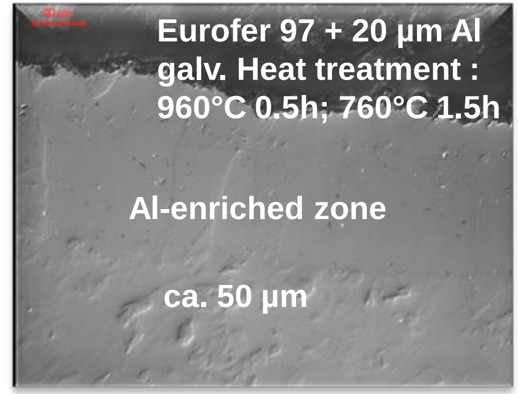
Electrochemical aluminium deposition
- properties of organic aprotic electrolyte systems -

Solvens		Toluol, Xylol Diisopropylether	Quarternay Amin salts e. g. Ethylmidazolium chloride
Ionic solubility of solvens		**No**	**Yes**
Al-carrier system		$KF{\cdot}2Al(R)_3$ $R = C_nH_{2n+1}$ 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- → $EMIM\text{-}AlCl_4$ 

Development of electrochemical Al coating process (ECA)







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

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 electrochemical Al coating process (ECX, X=Al, W, Ta…)

- Ionic liquids (IL's) + metal salts as new advanced electrolytes -

Ionic liquids as electrolytes

- Structure like ionic salts (similar to solid ionic crystals: e. g. NaCl), 100% ionic
- No additional solvent is necessary
- Mostly liquid at "room temperature" (≤ 100°C)

Major properties

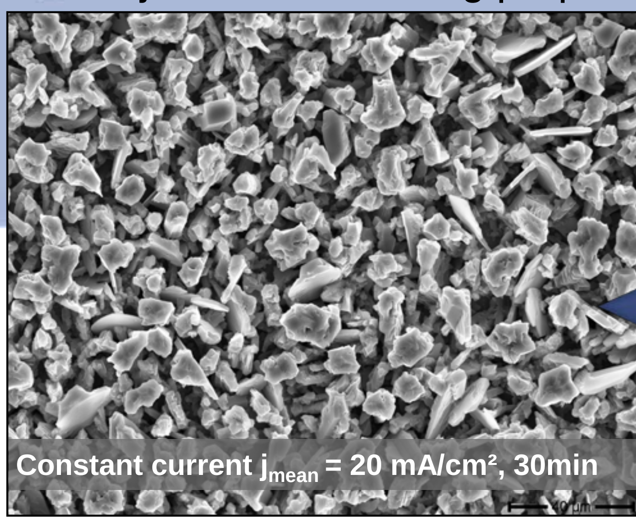
- Thermally very stable (> 300°C) → low vapor pressure
- Not flammable
- High variability of chemical structure
- Good miscibility with inorganic metal salts as "carriers" for metal deposition, e.g. $AlCl_3$
- High electrical conductivity
- Electrochemically very stable against oxidation and/or reduction
- High bio-compatibility

IL's are superior for use for electrochemical Al deposition

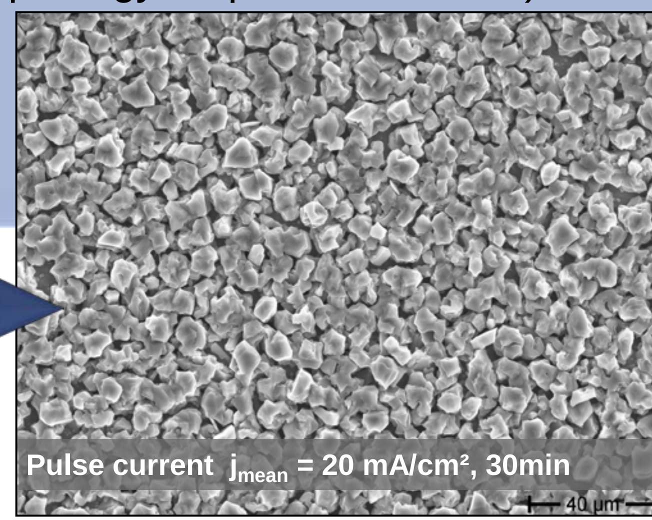
Development of coatings for corrosion / T-permeation barriers

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

- The use of **$AlCl_3$:[Emim]Cl** (1,5:1, *Lewis acidic*) ionic liquids (**IL**s) as electrolyte for Al-electrodeposition provides advantages in comparison to Lewis basic or neutral electrolytes
  - Increased electrochemical stability during electrodeposition
  - Commercially available: constant composition and quality, available in great quantities
    - **Industrial relevance is given**
- ECX process provides better flexibility than ECA process
  - Adjustable deposition parameters: current density, temperature, pulse plating possible, …
  - Adjustable Al coating properties (morphology, deposition rate, …)



Constant current j_{mean} = 20 mA/cm², 30min



Pulse current j_{mean} = 20 mA/cm², 30min

Development of electrochemical aluminium coating process (ECX)

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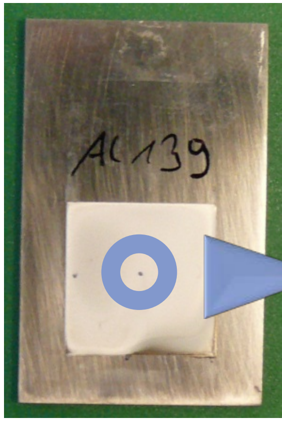
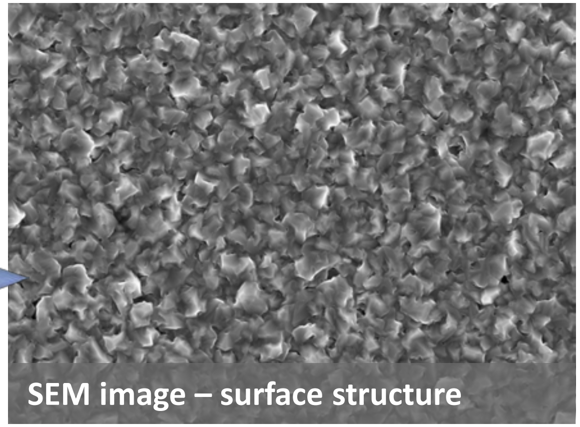
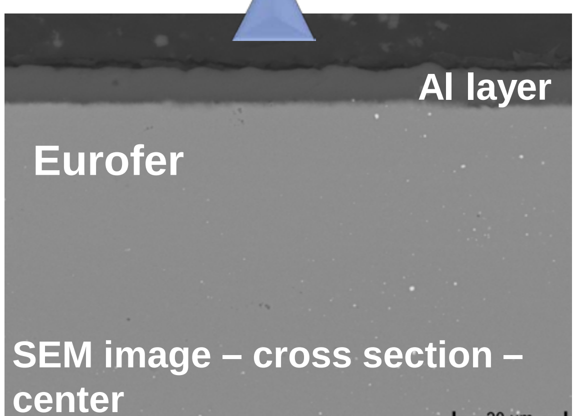




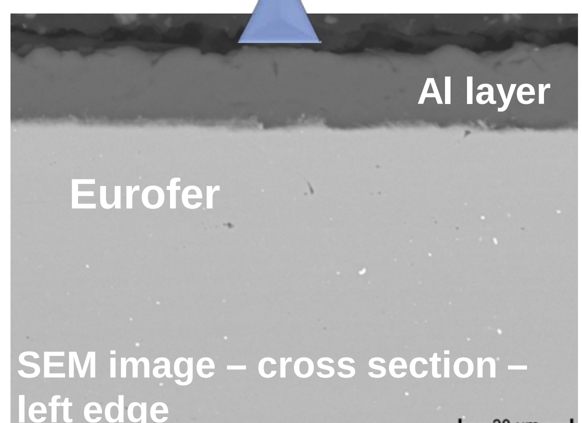
SEM image – surface structure

- Good adhesion of the coating to Eurofer substrate: depends on pre-treatment of the sample
- No delamination of layers during cutting process

- Deposition rates up to 25 µm/h, depending on current density
- Smooth surface in the center of the sample, at the edges even higher layer thicknesses, due to current density focusing



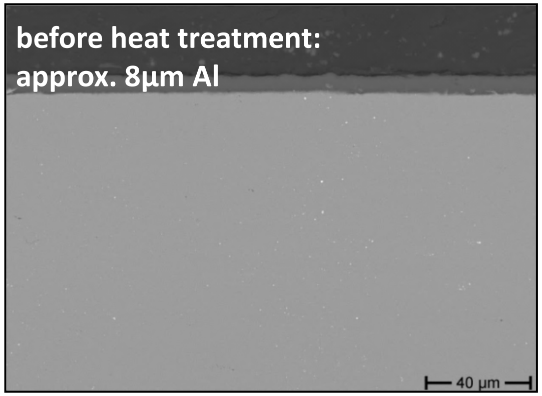
SEM image – cross section – center

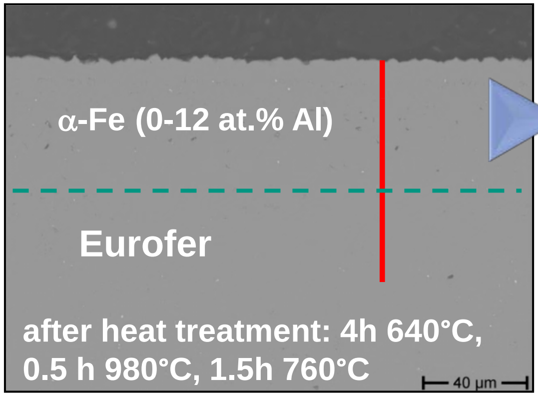


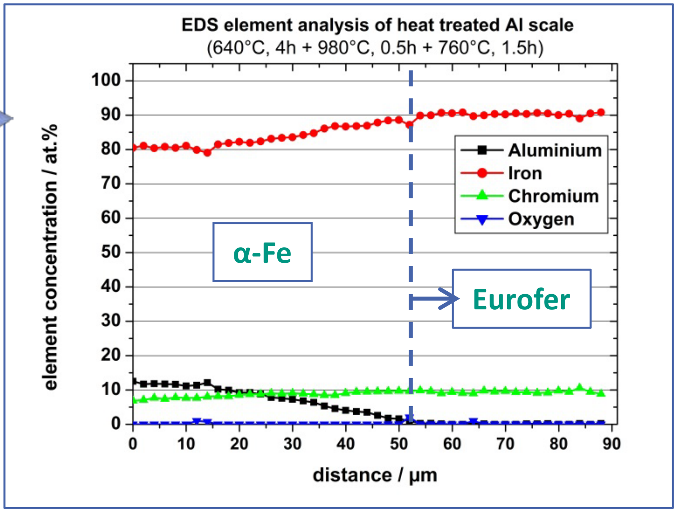
SEM image – cross section – left edge

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

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







- 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)

Conclusion and outlook

- **Barriers** on Eurofer steel structures, based on Fe-Al/Al_2O_3, are appropriate to fulfill the requirements for T-permeation reduction and corrosion protection in PbLi operated systems, including $DCLL_{mod.}$ blankets.

- Electrochemical deposition process **ECX** has shown its appropriateness for manufacturing of thin Al-based coatings with **high reproducibility**. The development of suitable **heat treatment sequences** to form the outermost alumina layer has been successful, too.

- Qualification outstanding concerning corrosion stability, T-permeation, thermal cycling and irradiation
- Development towards real application necessary under ITER TBM
- Transfer to $DCLL_{mod.}$?