Corrosion Behavior of Aluminum-based Coatings in a Liquid Metal Environment for Fusion Applications

Jürgen Konys,

Wolfgang Krauss, Sven-Erik Wulf

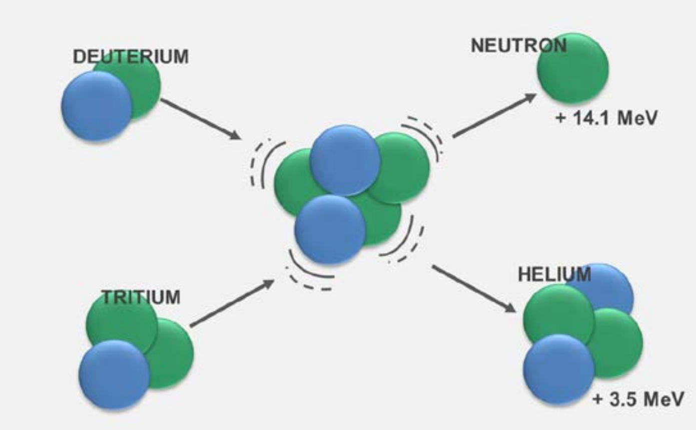
INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS | CORROSION DEPARTEMENT

Outline

- Introduction: Fusion as an Energy Option
- Corrosion Issue in Liquid PbLi alloy
- Requirements for Al-based Coatings
- Development of Coating Processes
- Corrosion Behavior in PbLi Environment
- Estimation of TPR Behavior of Al-coating
- Conclusions

Nuclear Fusion as a Long-term Option for the Worldwide Energy Demand

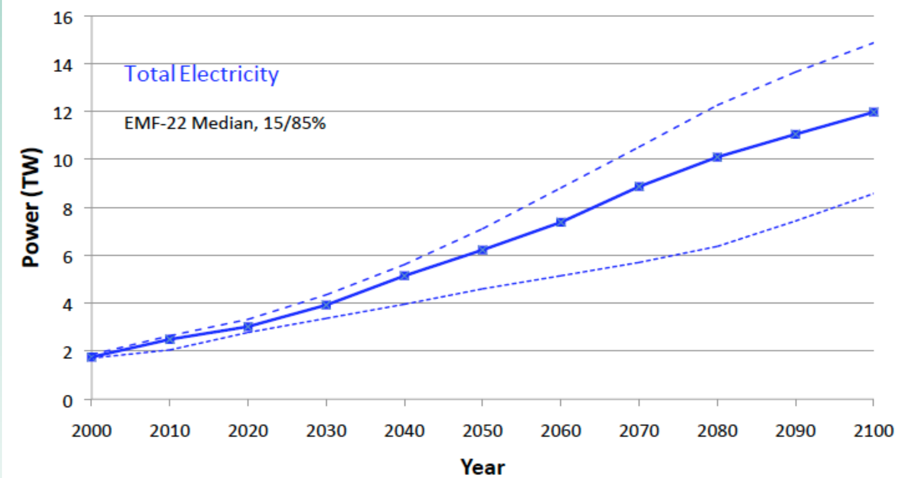
Deuterium – Tritium Fusion Reaction



Energy gain is about 450 : 1

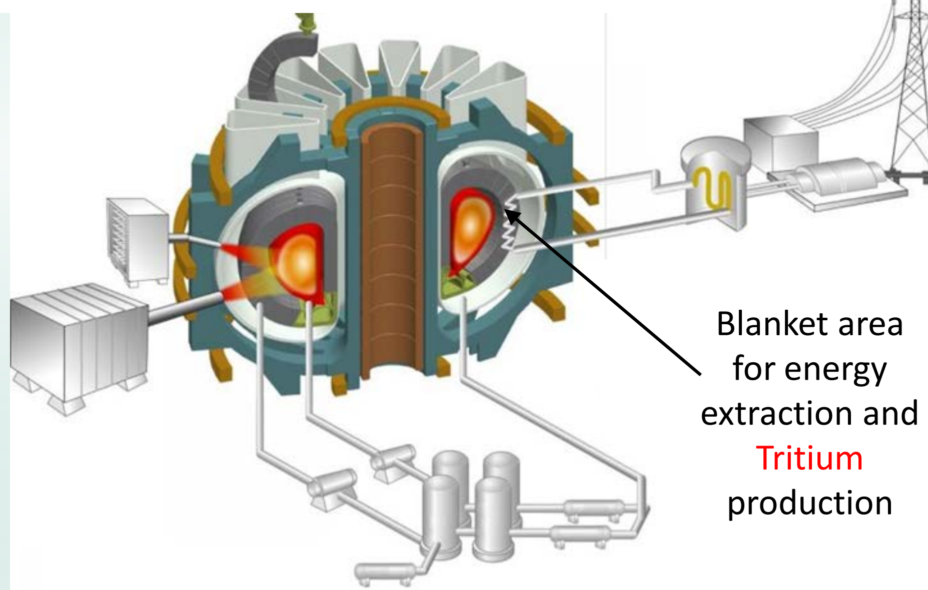
$$^{2}_{1}D + ^{3}_{1}T \Leftrightarrow ^{4}_{2}He\,(3.5\,MeV) + n\,(14.1\,MeV)$$

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
  - Typical for present base load power plants
- Potential fusion applications
  - Base load for large cities
  - Energy intensive industries
  - High temperature process heat for renewable economy



The He-PbLi Blanket Concept for ITER: Application of T-permeation and/or Anti-corrosion coatings

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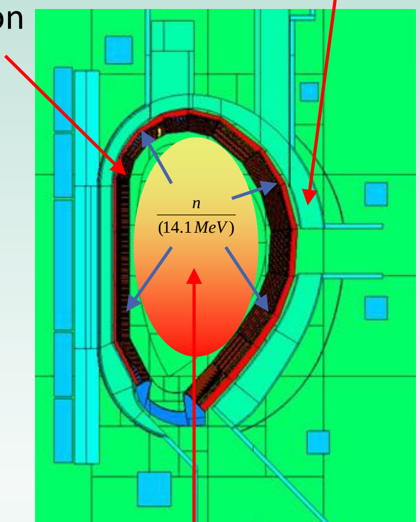
- **Deuterium (D) is highly available, e. g. in sea water**
- **Tritium (T) is naturally "extremely rare" on earth, but is**
  - **produced in heavy water-moderated reactors by neutron**
  - **capture and by nuclear reactions with Lithium**

$^{6}_{3}Li$ **(8%) + n (14.1 MeV) → T + He + 4.8 MeV →**	**enrichment is needed**
$^{7}_{3}Li$ **(92%) + n (14.1 MeV) → T + He - 2.87 MeV**	

- **Worldwide, blanket concepts are designed to use lithium in different chemical/physical form,**
  - **as ceramic breeder, e.g. Li_4SO_4, Li_2O pebbles**
  - **or as *liquid metal*, e.g. pure Li or Pb-16Li (T_m = 235°C, T_b ≈ 1730°C)**

Blanket area for energy extraction and Tritium production

Vacuum vessel SS 316

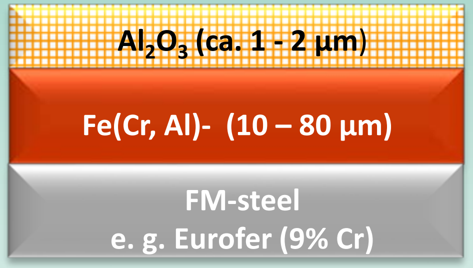


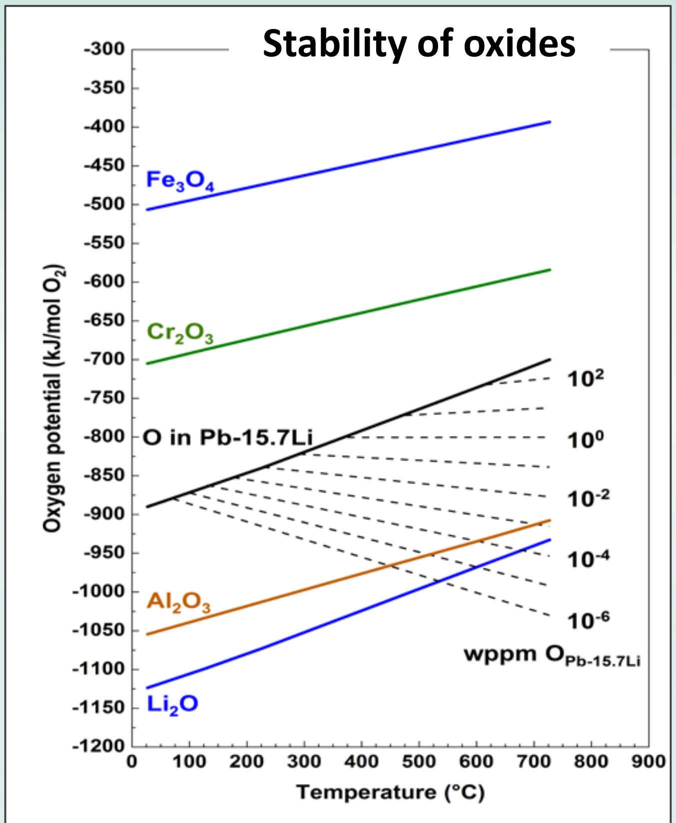
Burning D-T plasma

Corrosion of blanket structures by PbLi and permeation of T from PbLi into coolant gas

Coatings on structural components are required!

Structure and Technical Requirements for an Al-based T-permeation and/or Corrosion Coating





Requirements for coatings

- Reduction of T-permeation by a factor of <100 in Pb-16Li (1000 in gas phase)
- Self-healing of (mechanically) damaged layer must be thermodynamically possible in Pb-16Li (re-oxidizing)
- Long-term corrosion resistant in flowing Pb-16Li up to ca. 550°C (protecting the underlying structural material)
- High content of low activation elements (minimizing Al content)
- No negative influence on mechanical properties of the steel due to the coating process
- The coating process must be of industrial relevance

Need for Corrosion Coatings on Eurofer Steel

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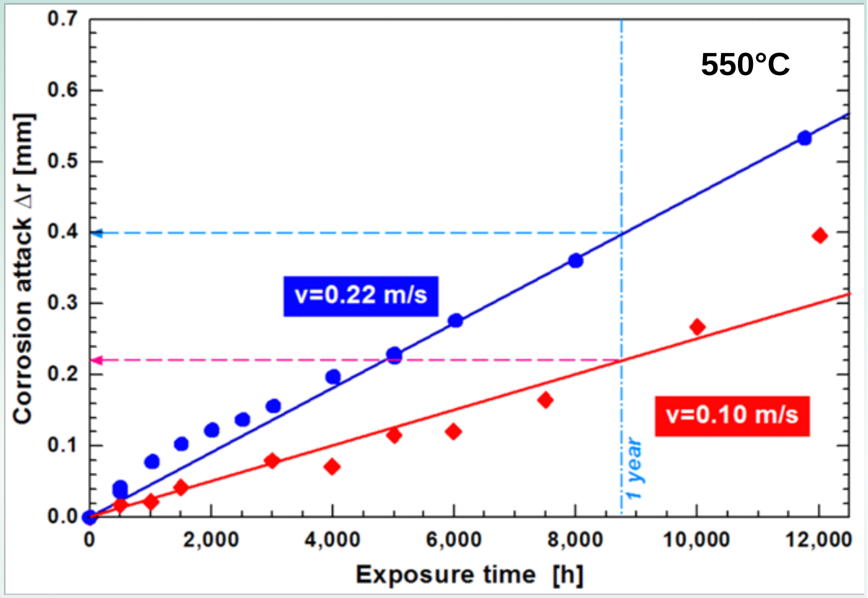
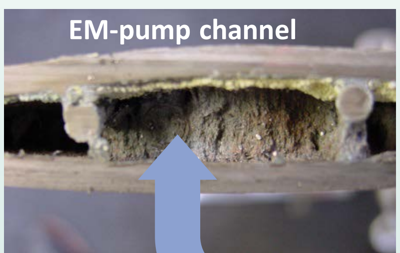
Alloying elements in RAFM steel Eurofer (wt.%)

Cr	Mn	V	W	Ta	C	Ni
8.82	0.47	0.2	1.09	0.13	0.11	0.02

- Reduced activation ferritic-martensitic steels (RAFM) e.g. Eurofer suffer from severe corrosion attack in flowing Pb-16Li
- Corrosion rates up to 400 µm/y at 550°C are reported depending on:
  - Temperature, flow velocity, (time)
- Mechanism → dissolution corrosion in Pb-16Li

from: J. Konys et. al, *J. Nucl. Mater.*, vol. 455, issues 1-3, (2014), p.491





Risk for precipitation of corrosion products → tube plugging

Corrosion protection layers needed for a reliable and save operation

Development of Al-based coating processes

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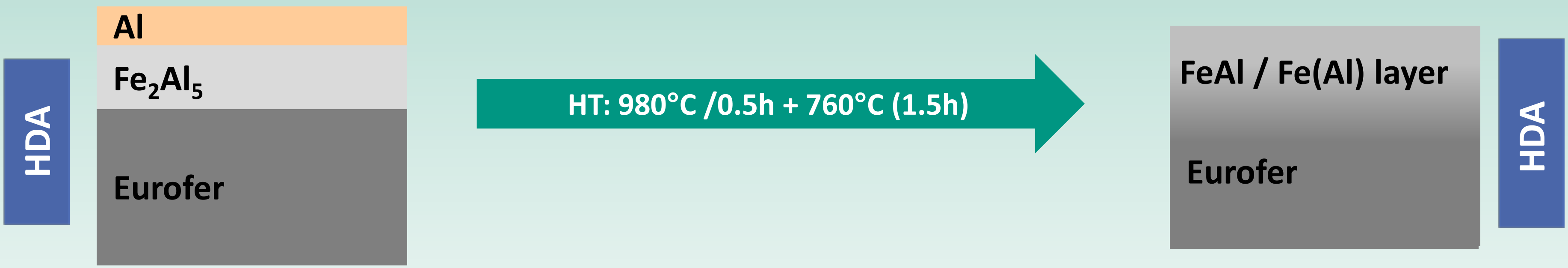
Fabrication routes for aluminum-based coatings on Eurofer steel

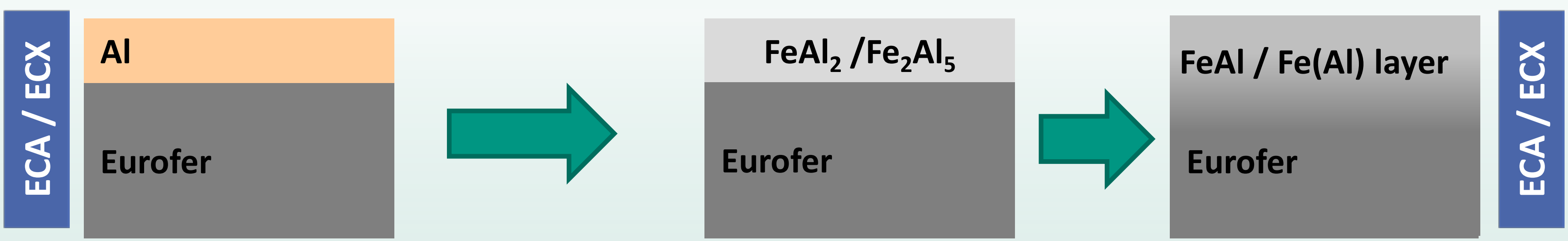
Coating application | **Heat treatment (HT) procedure**



Dipping in liquid Al
700°C/30 s

Mid 1990s: Hot dip aluminizing

Electrochemical processes



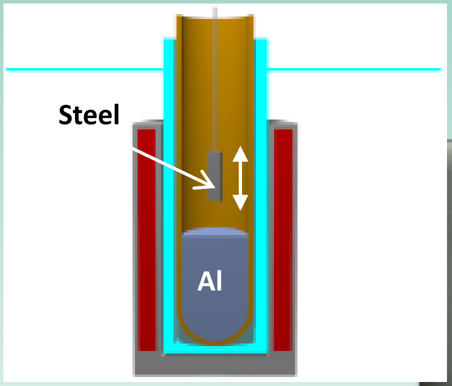
Electrodeposition of Al from (a) organic electrolytes (ECA) ; (b) ionic liquids (ECX)

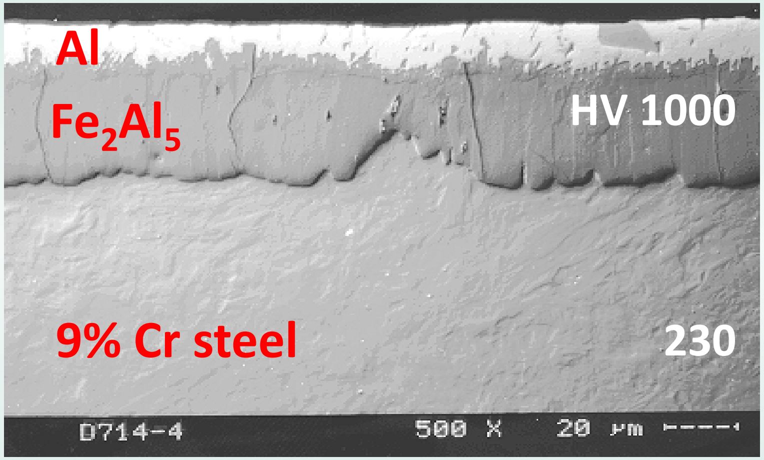
1st HT step:
640°C / 4h

2nd + 3rd HT step:
980°C / 0.5h + 760°C/1.5h

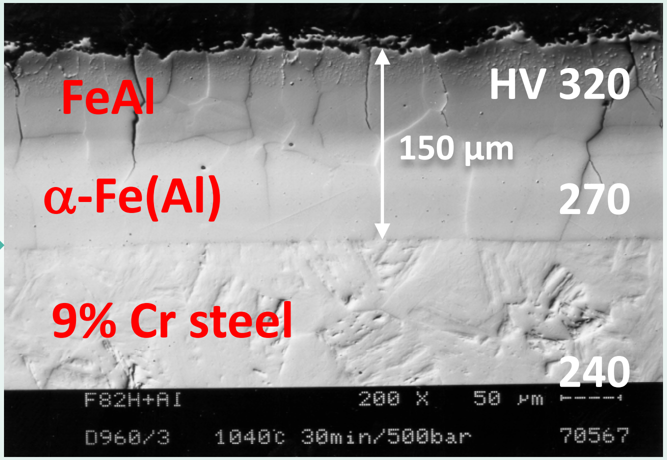
Hot-Dip Aluminizing Process (HDA)

- Temperature Al melt T_{dip} = 700°C
- Dipping time of 30 s in Al + Ar-5%H_2
- Formation of Al-rich brittle phases (Fe_2Al_5)
- Inhomogeneous thickness distribution (at edges, etc.) → Crack formation (e.g. during HT)
- Relatively thick coatings → >100µm (after HT)
  - High Al content (low activation?)





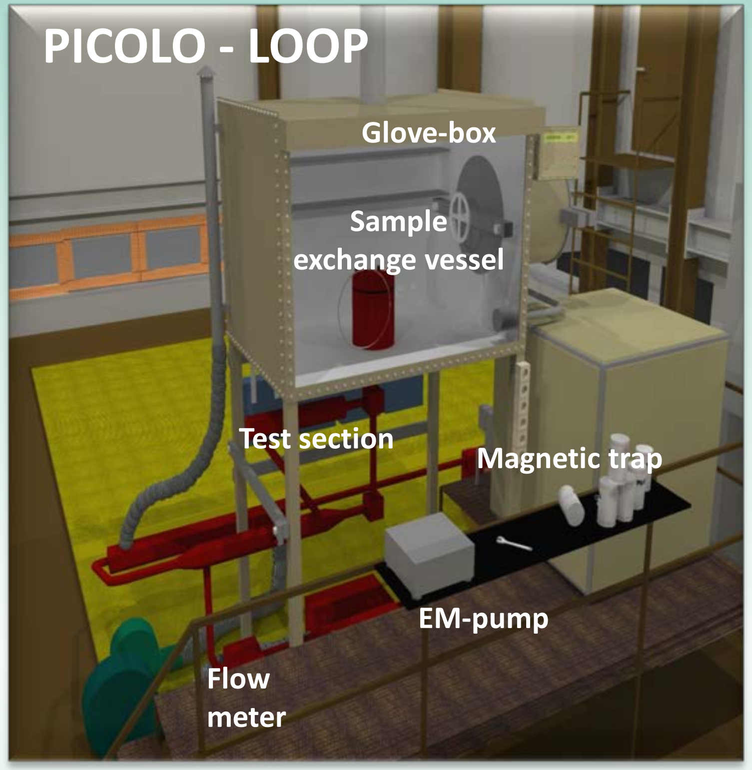
HT: 980°C + 760°C (1.5h)

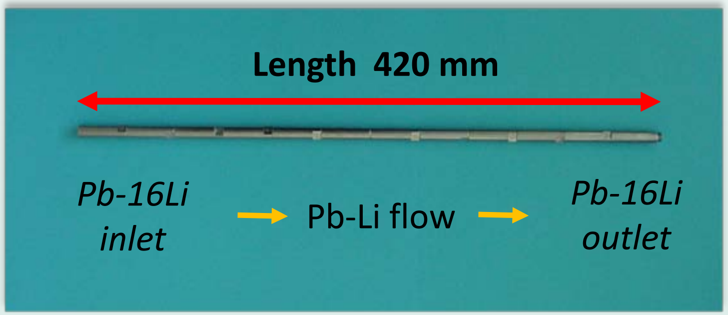


Improved coatings required!

Mid 1990s: Hot-Dip-Aluminization | 2010: ECA process | Since 2011: ECX process

Corrosion testing of coated and uncoated steel specimens in a Pb-16Li loop (PICOLO)





Parameters of Pb-16Li Loop PICOLO

Test temperature:	480-550°C
T_{max} in test section:	**550°C**
T_{low} at EM-pump:	350°C
Pb-16Li volume:	20 litres
Flow velocity range:	0.01 - 1 m/s
Test velocity up to 2007:	0.22 m/s
Since 2011:	**0.1 m/s**
Loop materials:	
Cold legs:	18 12 CrNi steel
Hot legs:	10 % Cr steel
Total loop operation:	
at 480°C	> 120,000 h
at 550°C	> 40,000 h

Corrosion behaviour of HDA coated Eurofer in flowing Pb-16Li

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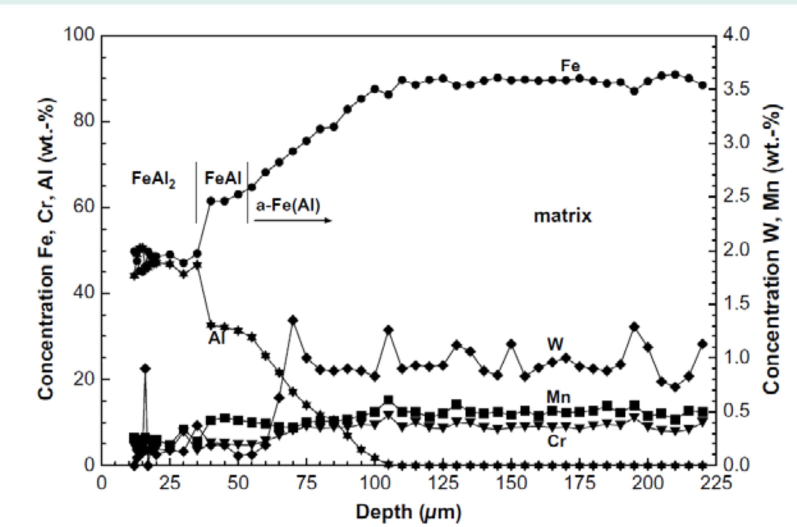
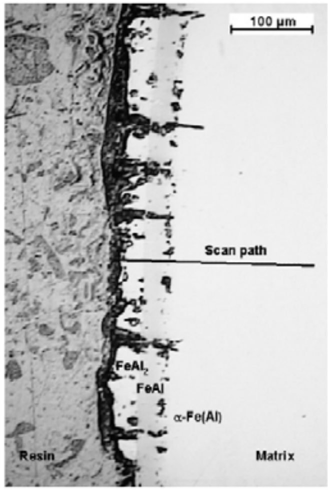
- Exposure to flowing Pb-16Li for up to approx. 7,000h (480°C)
- Coating protects underlying RAFM steel from corrosion
- Local corrosion of the coating itself
- Al-rich phase ($FeAl_2$) attacked and partially removed
- Corrosion attack decreased/stopped in case of FeAl and Fe(Al) phase





from: J. Konys et. al, *J. Nucl. Mater.*, 367-370, (2007), 1144-1149.

Lower Al amounts seem favorable concerning corrosion resistance

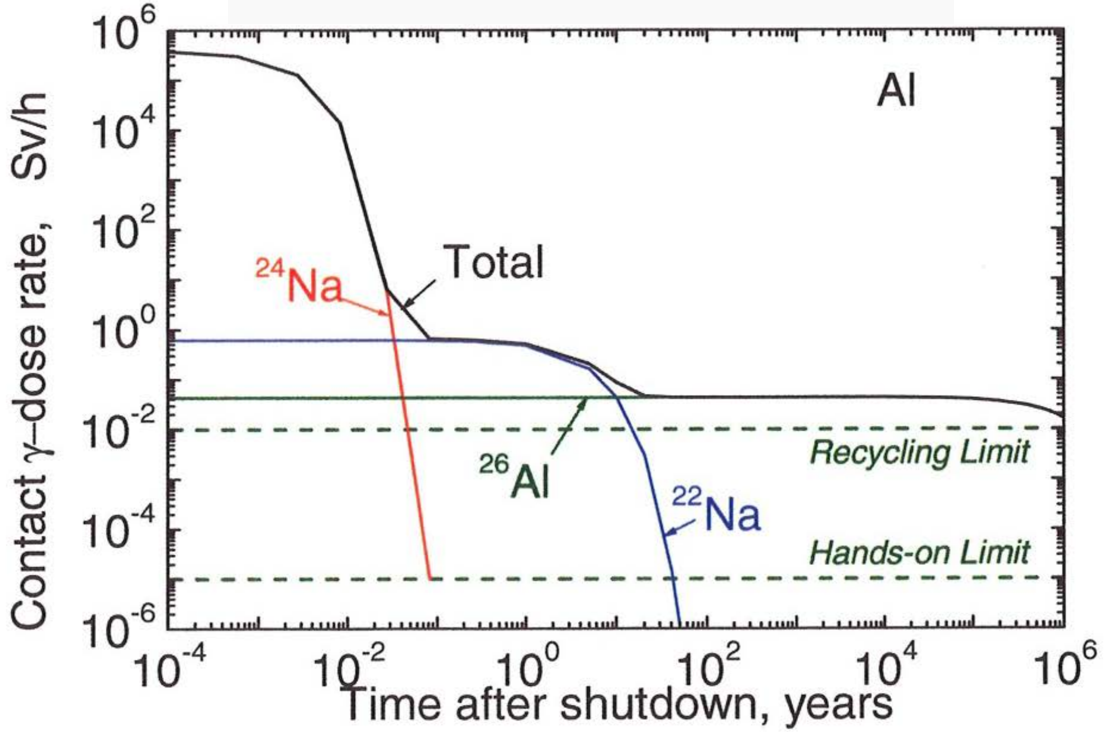
Improved coating techniques required to deposit homogeneous and thinner Al coatings

Electroplating of Aluminum

Mid 1990s: Hot-Dip-Aluminization | 2010: ECA process | Since 2011: ECX process

Activation of Al from Al-based coatings in a "fusion irradiation environment"

Aluminium irradiation for 2 years

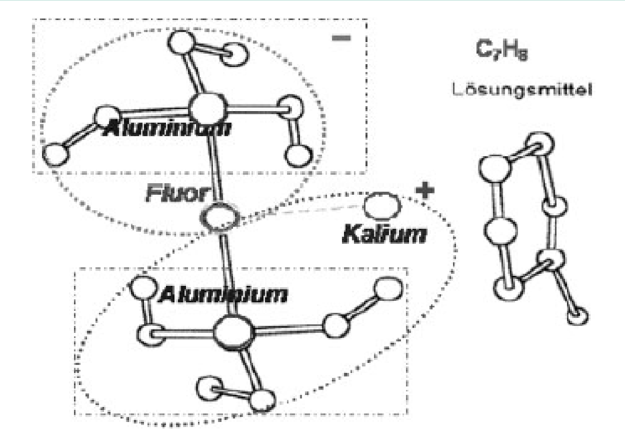


→ **Consequence: Minimization of the amount of Al in the surface of steel**

Al-Electroplating from volatile organic electrolytes: ECA process

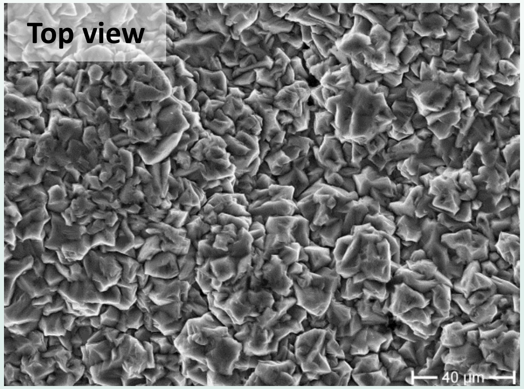
Water-free electrolytes required for Al electrodeposition

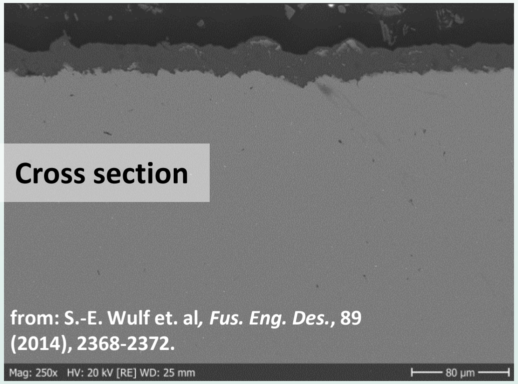
- Electrodeposition from toluene-based electrolytes + Al-alkyls (e.g. (Na,K)F*2 Al-R_3)
  - Electrolytes are very sensitive to oxygen and humidity → safety is a big issue!
- Process temperature: 100°C / growth rates: 12 µm/h
- Dense coatings (relatively big crystallite sizes)
- After HT relatively rough surfaces
- Available in industry: e.g. *Rasant-Alcotec* (Germany), *Alumiplate* (USA)



from: Reinold et. al, *Mat.wiss. und Werkstofftechn.*, 39 (12), (2008), 907-913.

ECA: after deposition

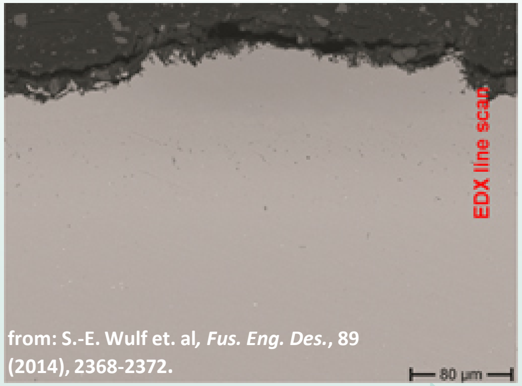




from: S.-E. Wulf et. al, *Fus. Eng. Des.*, 89 (2014), 2368-2372.

HT

ECA after HT



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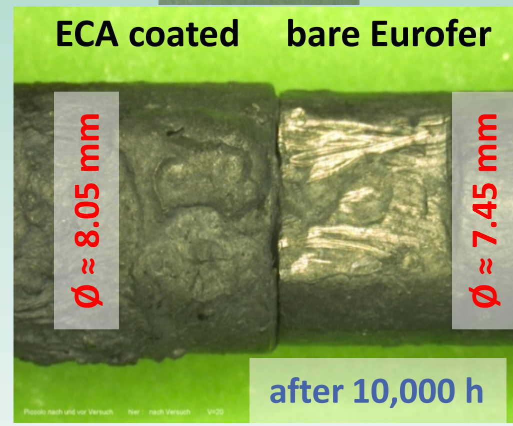
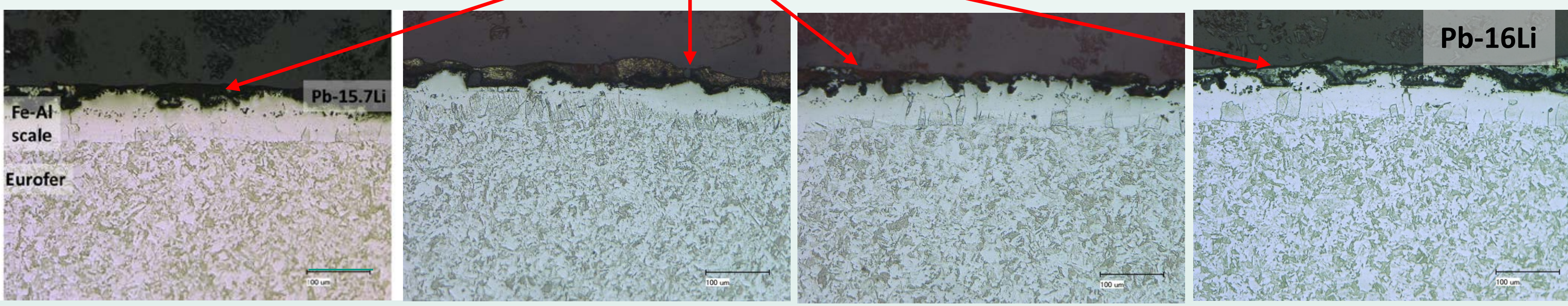
Mid 1990s: Hot-Dip-Aluminization | 2010: ECA process | Since 2011: ECX process

Corrosion behaviour of ECA-coated Eurofer in flowing Pb-16Li (550°C; 0.1m/s)

- ECA coated Eurofer test specimens:
  - Al-based coatings protect the underlying base material (i.e. Eurofer steel) from corrosion in flowing Pb-16Li even at long exposure times of up to 12,000h.
  - Fe-Al coating still remains after 12,000 h of exposure
  - Reduced corrosion attack of the coating layer itself
    → Formation of local steps to uncoated sample

Before test





4,006 h | 6,024 h | 10,000 h | 12,012 h

from: W. Krauss et. al, *J. Nucl. Mater.*, 455 (2014), 522-526.

Mid 1990s: Hot-Dip-Aluminization → 2010: ECA process → Since 2011: ECX process

Corrosion behaviour of ECA-coated Eurofer in flowing Pb-16Li (550°C; 0.1m/s)

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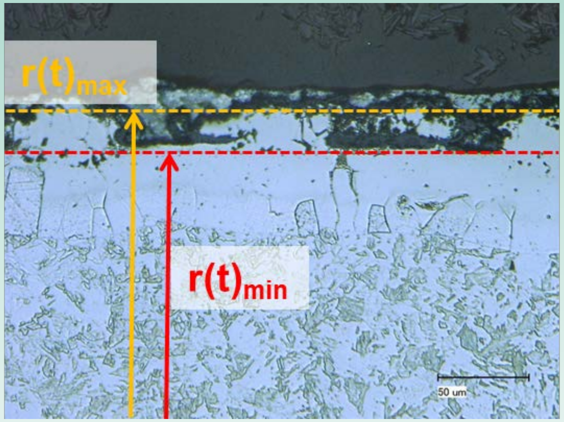
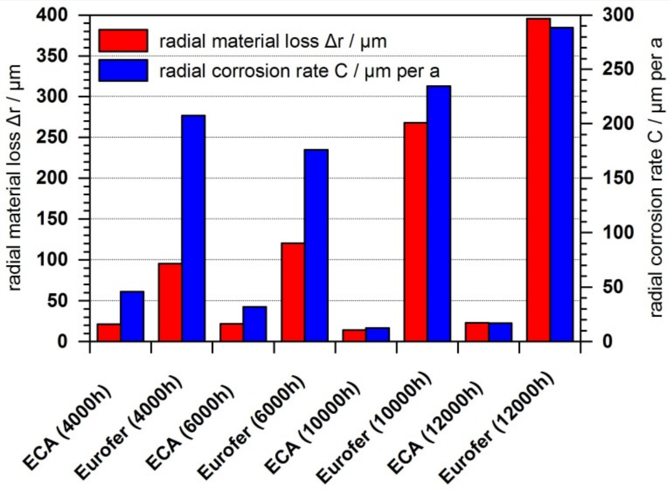
- Plateaus → two measured values for the radial material loss: Δr_{min} u. Δr_{max} → $\Delta r_{min, max} = r(t=0) - r(t)_{min, max}$
- Material loss slightly depended on the exposure time
- Calculated corrosion rates at high exposure times below 20 µm/y
- Reduction of corrosion rate in comparison to bare Eurofer steel by a factor of >10



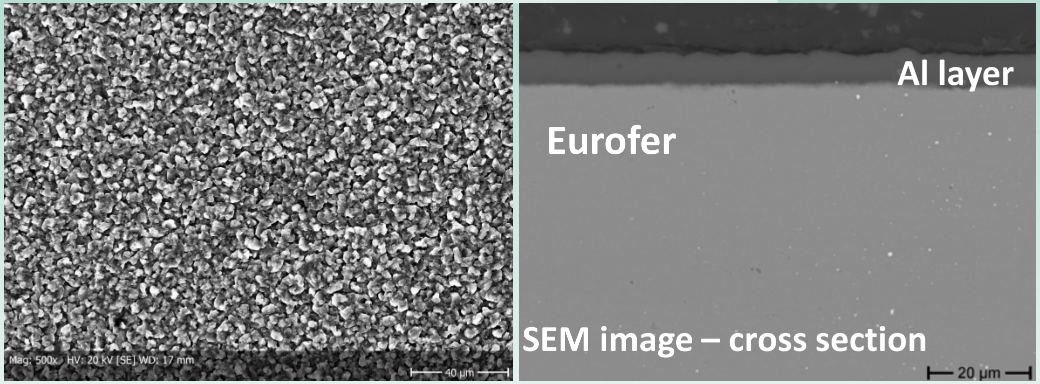
Comparison ECA coated Eurofer vs. bare Eurofer steel



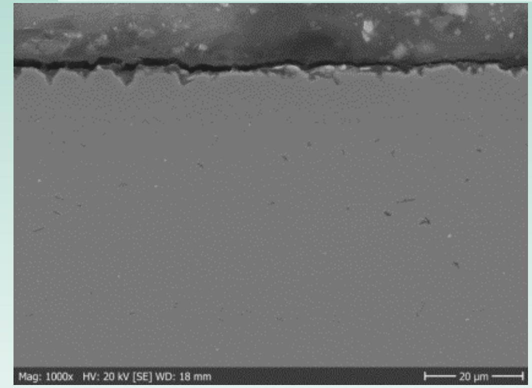
Mid 1990s: Hot-Dip-Aluminization | **2010: ECA process** | Since 2011: ECX process

Al-Electroplating from ionic liquids: ECX process

ECX after electrodeposition

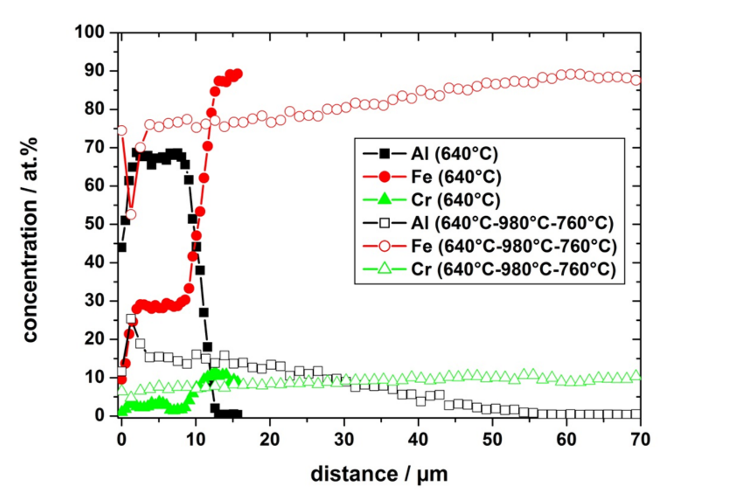


ECX after complete HT



Water-free electrolytes required for Al electrodeposition

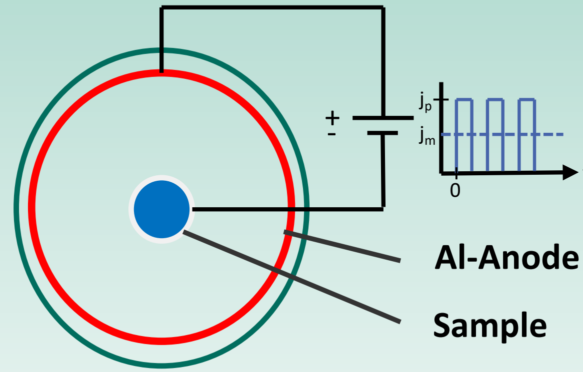
- Electrodeposition from *ionic liquids*
- Electrolyte: [Emim]Cl:$AlCl_3$ (1:1.5, lewis acidic)
  - Electrolytes are "only" sensitive to humidity
- Use of pulse plating possible (improved surfaces)
- Process temperature: 100°C / Growth rates: 10 - 25 µm/h
- Good adhesion to the substrate (no delamination)



Mid 1990s: Hot-Dip-Aluminization | 2010: ECA process | Since 2011: ECX process

Al-Electroplating from ionic liquids: ECX process

- Dense 10-13 µm thick Al coatings with fine grained morphology
- 1st HT step → Formation Al rich phases
- 2nd + 3rd HT step → ductile Fe-Al phases
    - Al content < 20 atomic percent
- Overall Fe-Al thickness after HT: approx. 55 µm
- Smooth surfaces even after HT



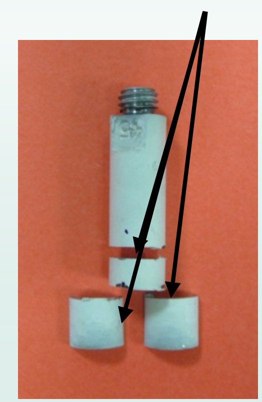
Al-coated test samples (ECX)

Appearance after HT

after 1st HT step

2nd + 3rd HT step

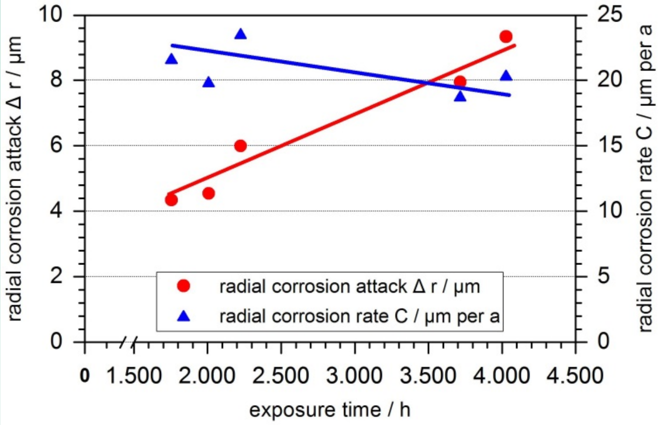
No delamination



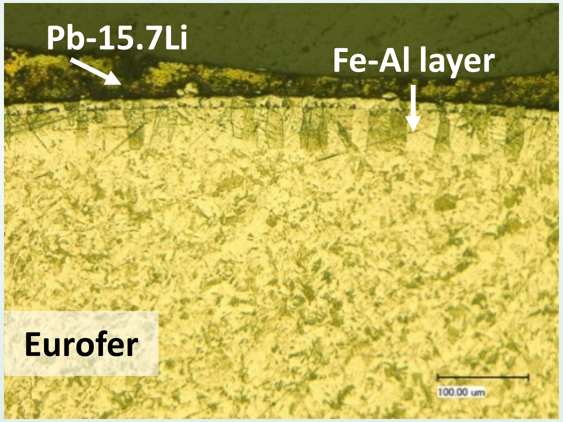
Mid 1990s: Hot-Dip-Aluminization | 2010: ECA process | Since 2011: ECX process

Corrosion behaviour of ECX-coated Eurofer in flowing Pb-16Li (550°C; 0.1m/s)

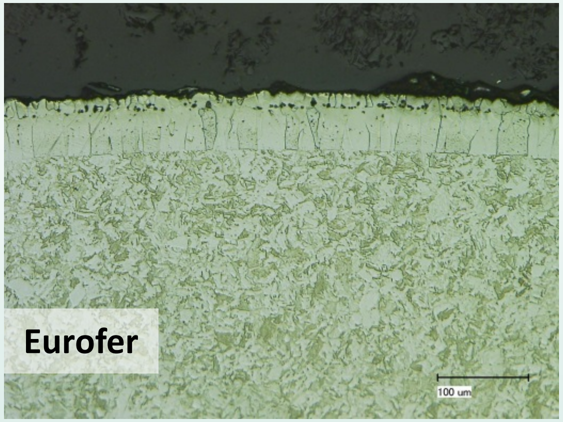
- ECX coated Eurofer test specimens:
  - Al-based coatings protect the underlying base material (i.e. Eurofer steel) from corrosion in flowing Pb-16Li for ≥ 6,000 h
  - Fe-Al coating thickness after 6,000 h of exposure > 40 µm
  - No formation of local plateaus as in the case of ECA
    - Smooth surface preserved



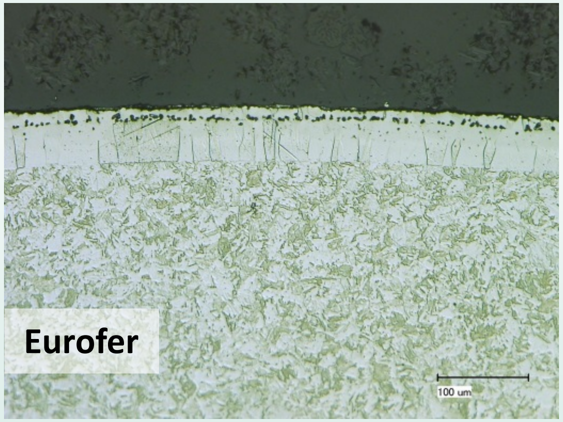
from: S.-E. Wulf et. al, *Nucl. Mater. & Energy.*, (2015), accepted.



2,000 h



4,000 h



6,000 h

Mid 1990s: Hot-Dip-Aluminization | 2010: ECA process | Since 2011: ECX process

Corrosion behaviour of ECX-coated Eurofer in flowing Pb-16Li (550°C; 0.1m/s)

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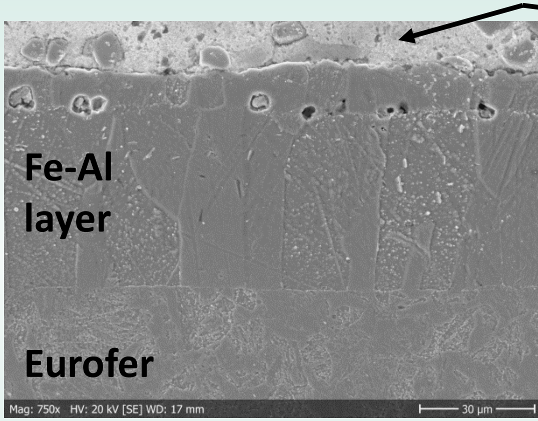
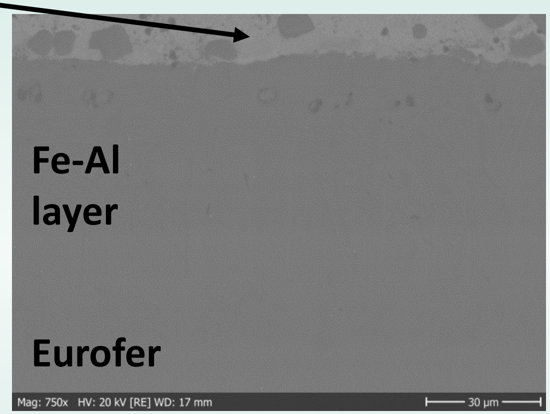
- Microstructure remains columnar
- No/very low roughening in the contact zone between Pb- 16Li and coating
- No penetration of Pb-16Li into the Fe-Al coating

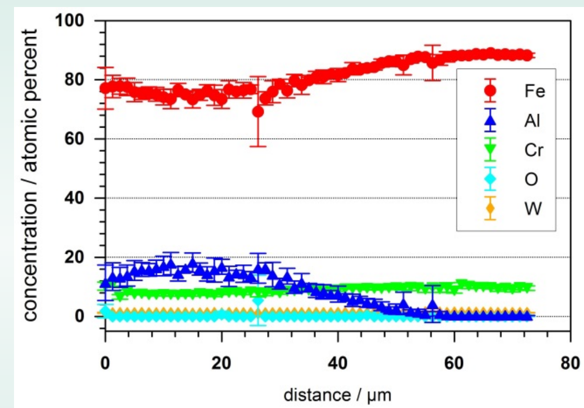
Pb-16Li



SEM image



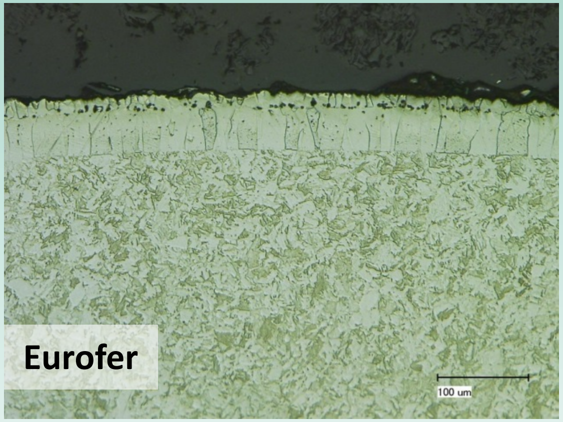
BSE image



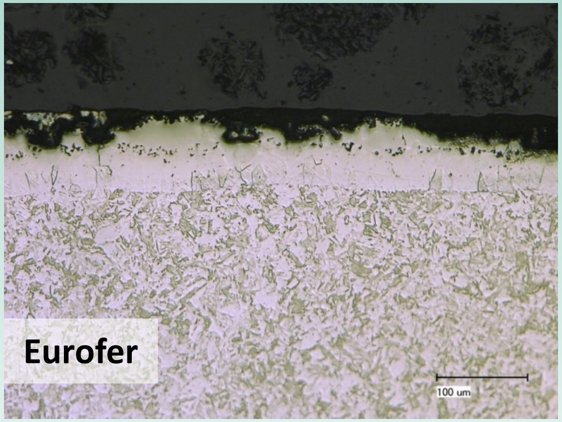
EDS average line scan

Mid 1990s: Hot-Dip-Aluminization | 2010: ECA process | Since 2011: ECX process

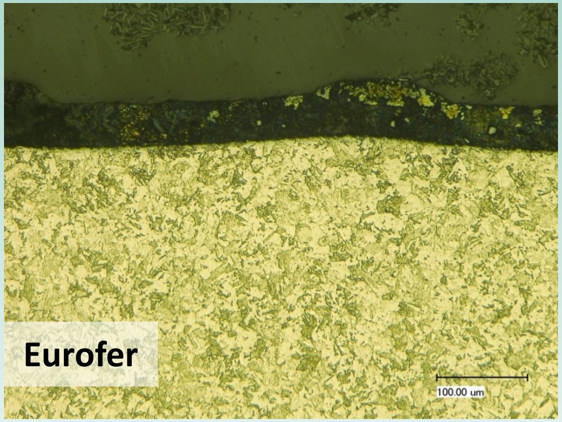
Comparison of the corrosion behaviour of coated and uncoated Eurofer in flowing Pb-16Li (550°C; 0.1m/s)



ECX (4,026h)

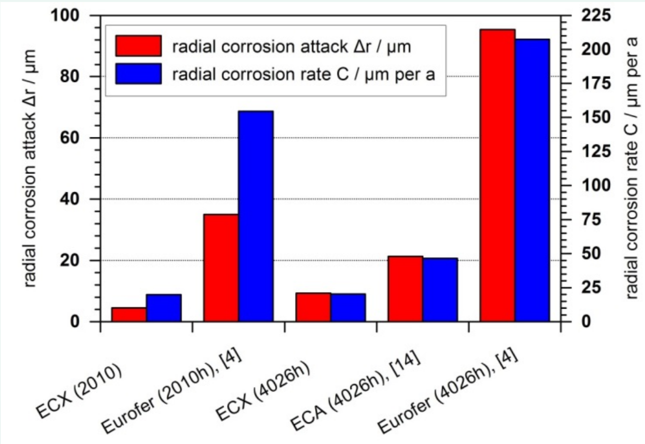


ECA (4,026h)



Eurofer (4,026h)

- **Fe-Al coatings showed good corrosion resistance**
- **Corrosion rates could be reduced by a factor of 10 in case of ECX coated samples (after 4,000h)**
- **No formation of local plateaus in case of ECX coatings**
- **Corrosion rates reduced by a factor of 2 in case of ECX coated samples compared to ECA coated ones**

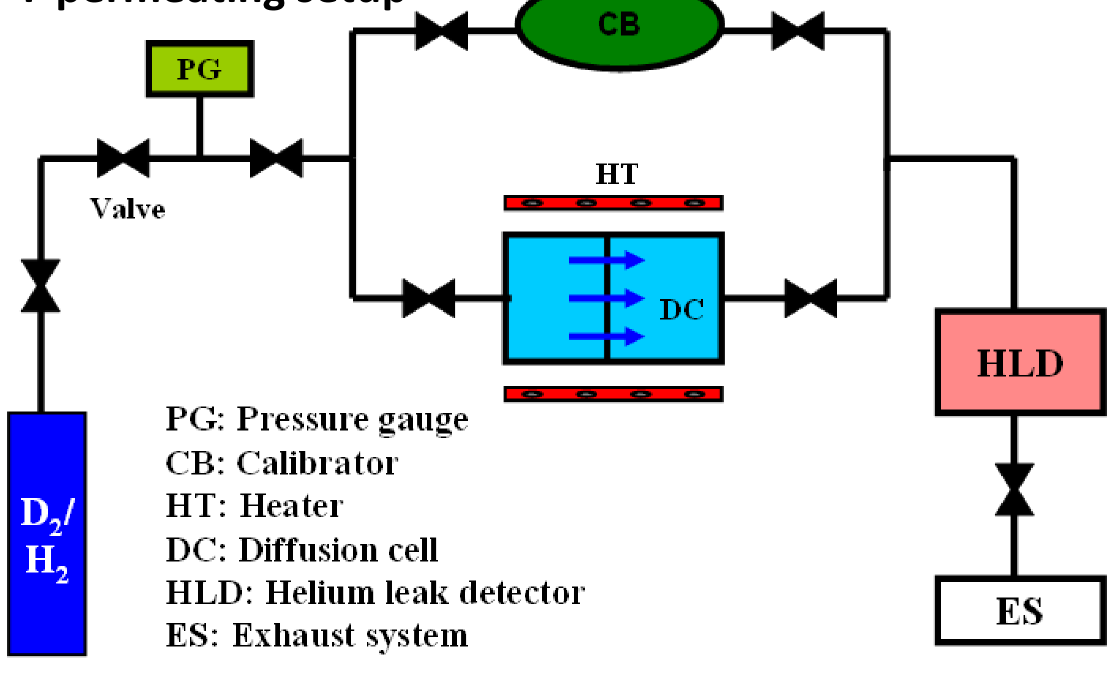


Mid 1990s: Hot-Dip-Aluminization | 2010: ECA process | Since 2011: ECX process

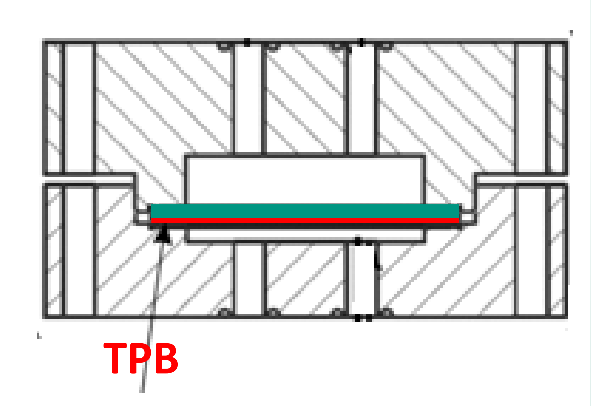
Characterization of T-permeation Behavior

- T-permeating setup have been designed, in which H and D-permeability is measured by helium leak detector, thus interference of residual hydrogen existed on/in most materials can be neglected.
- Permeation reduction factor (PRF) is the rate of T -permeability in steel before and after TPB coated, and tests will be performed in 2016.

T-permeating setup



$$PRF = \frac{\phi_{steel}}{\phi_{coated \cdot\ steel}}$$



DC details

Conclusions

- **Aluminum-based coatings** have proven their ability to protect 9%Cr-steels (Eurofer) sufficiently from heavy corrosion attack in flowing liquid Pb-16Li.
- Although, **coatings by Hot-dip aluminizing** have drawbacks due to their "high" Al content in the steel surface
  ► activation under neutron irradiation: → ^{26}**Al** (slightly above recycling limit)
- Electrochemical-based processes like **ECA**, **ECX** have shown better behavior concerning homogeneity, Al thickness and reproducibility, even for complex geometries.
- **Fe-Al** coatings made by **ECX** process showed smoother and more uniform surfaces with additional advantages regarding lifetime, cost and safety.
- Applying Fe-Al layers by **ECX** process can **reduce corrosion rates** in flowing Pb-16Li by a **factor of 10,** compared to uncoated Eurofer steel.
- The Al-based coatings made by electrodeposition from ionic liquids have also proven their high potential in other energy applications at elevated temperatures and aggressive environments (gas, steam etc.).