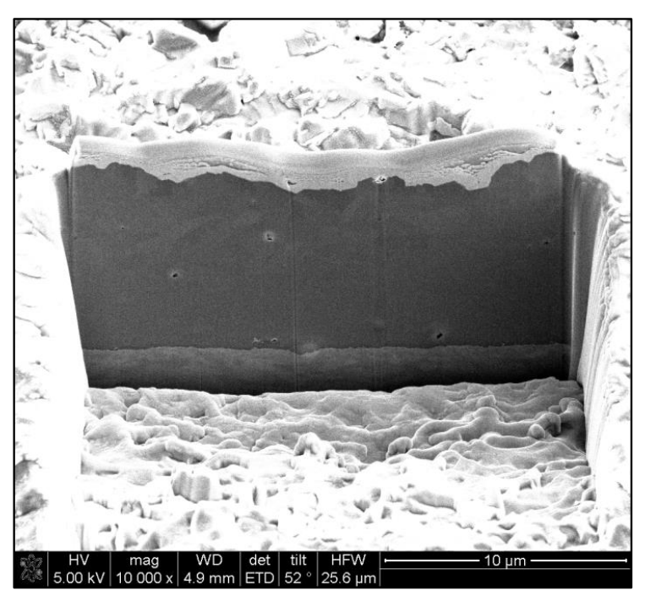
Karlsruhe Institute of Technology

Institute for Applied Materials
Material Process Technology (IAM-WPT)

Comparison of coating processes in the development of aluminum-based barriers for blanket applications

S.-E. Wulf, W. Krauss, J. Konys

Motivation



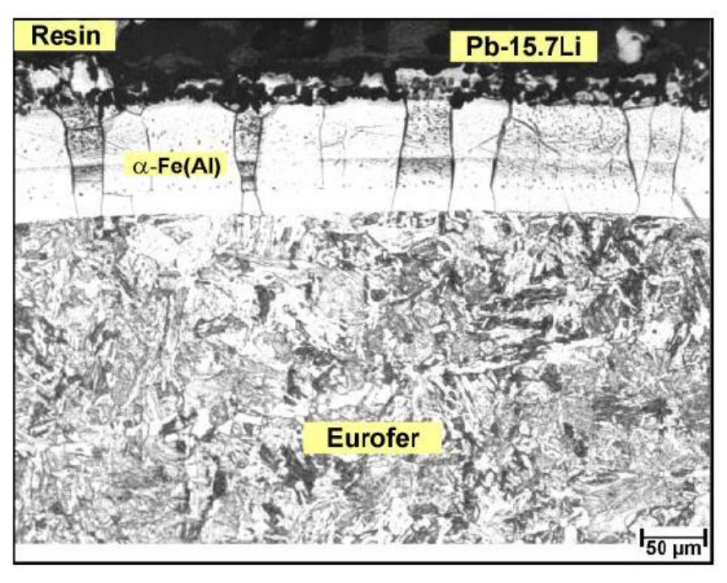
FIB image: 10 µm Al on Eurofer deposited by ECX

Reduced activation ferritic-martensitic steels (RAFM), e.g. Eurofer 97, are envisaged in future fusion technology as structural material, which will be in direct contact with a flowing liquid lead-lithium melt serving as breeder material.

Aluminum-based barrier layers had proven their ability to protect the structural material from corrosion attack in flowing Pb-15.7Li and to reduce tritium permeation into the coolant.

In the past, Hot-Dip Aluminization (HDA), showed its ability to produce Fe-Al scales but revealed some critical disadvantages. In the last years, electrochemical methods gained attention to produce defined aluminum-based scales on RAFM steels. Thereby, two different coating processes were introduced to the field of fusion technology: (a) ECA process and (b) the newer ECX process.

All three processes exhibit specific characteristics, for example in the field of processability, control of coating thicknesses (low activation criteria) and heat treatment behavior. In this study these different aluminization processes and their heat treatment behavior are compared, whereby the focus is on the comparison of the electrochemical processes ECA and ECX.

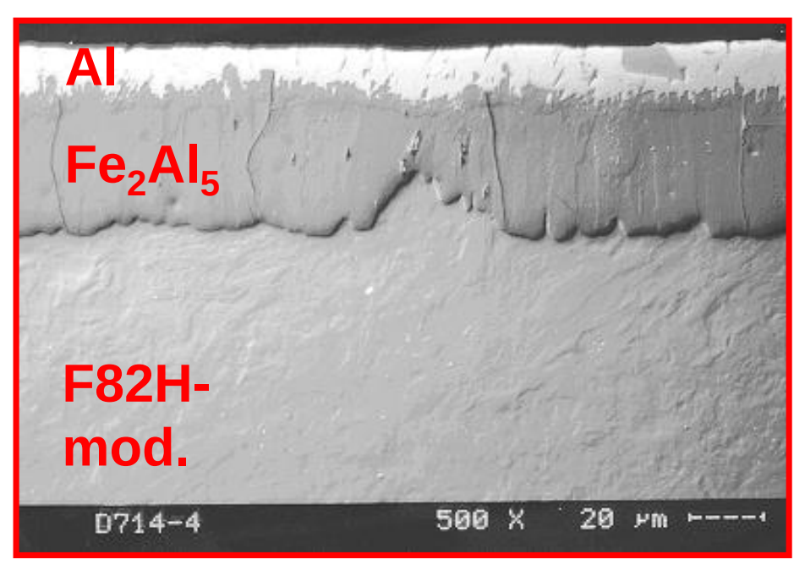


HDA coated Eurofer sample after exposure in flowing Pb-15.7Li, taken from [1]

Aluminization processes

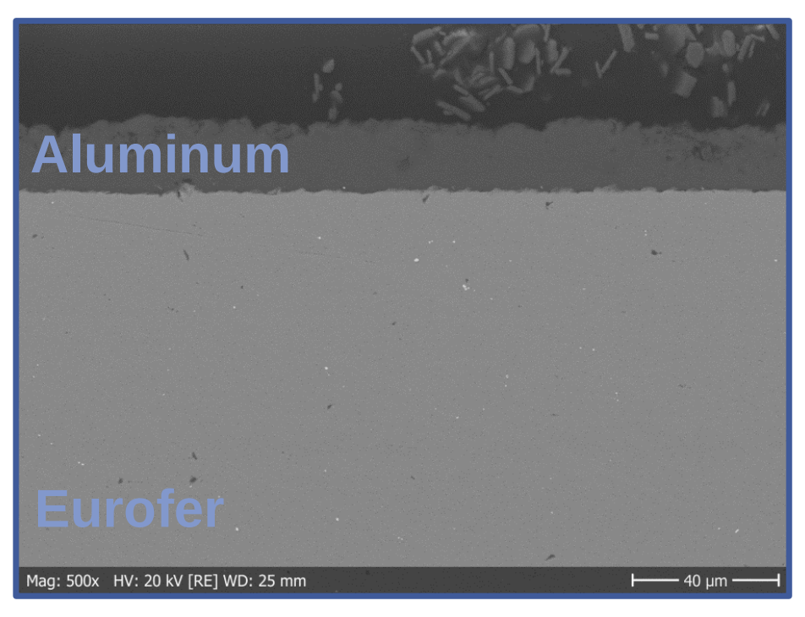
Hot-Dip-Aluminization (HDA)

- ► Steel parts to be coated are dipped into an Al melt (T=700°C)
- ► Residual Al upon brittle Fe_2Al_5 phase is formed on RAFM steels during aluminization
- ► Aluminized scale thickness depends on dipping time
  - Below a certain time (<30 s) insufficient wetting occurs
  - Reduction of coating thickness (Al amount) not possible
- ► Layer thickness not controllable, especially in edges, etc.
  - Nonuniform layer thickness distribution



Electrochemical processes in general

- ► No reaction with the substrate material
- ► Layer thickness easily controllable (in µm to mm range)
  - By controlling time and current density (*Faradays law*)
  - Comparatively uniform layer thicknesses
- ► Good adherence to the substrate
- ► Low temperature process (generally T<100°C)
  - Low energy costs



Electrochemical deposition of aluminum

- ► Aluminum exhibit an highly electronegative standard potential of E_0= -1.7V vs. NHE
  - Al can not be deposited from common and well known water-based electrolytes
  - Non-aqueous electrolytes are recommended for Al-deposition:

ECA

- Based on volatile solvents, e.g. toluene
- Metal source: Al-alkyls, NaF-Al$(C_nH_{2n+1})_3$
- Process temperature: 95°C-103°C
- Current density (j): ~ 10 mA/cm²
- Deposition rates = f(j): ~ 12 µm/h

High vapor pressure, highly sensitive to O_2 and H_2O → High safety requirements

Limited current density range → restricted deposition rates and use of pulse plating

ECX

- Uses new class of electrolytes: Ionic liquids (ILs)
  - Ionic compounds with T_m<100°C
  - Imidazolium-based ILs used for Al deposition
    - e.g. [Emim]Cl, [Bmim]Cl
- Metal source: e.g. $AlCl_3$ + soluble Al anode
- Process temperature: e.g. ≤100°C
- Current density (j): ~ 20 mA/cm²
- Deposition rates = f(j): ~ 25 µm/h

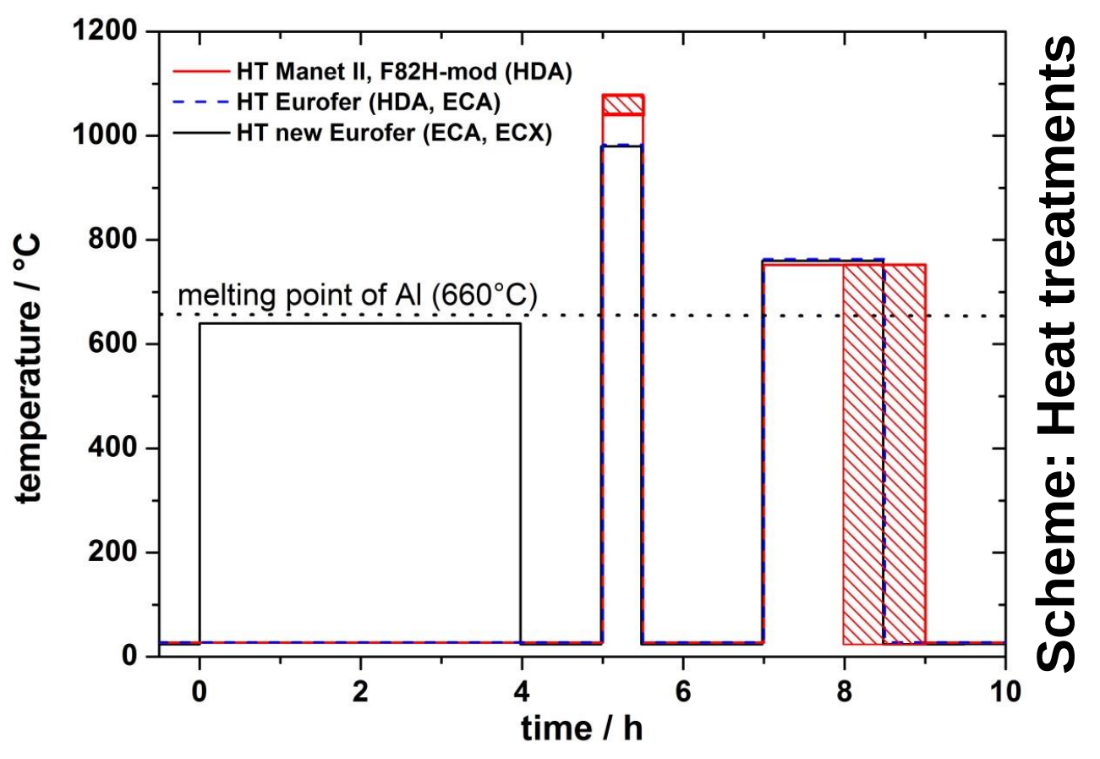
No/ very low vapor pressure, only sensitive to H_2O
→ Reduced safety requirements

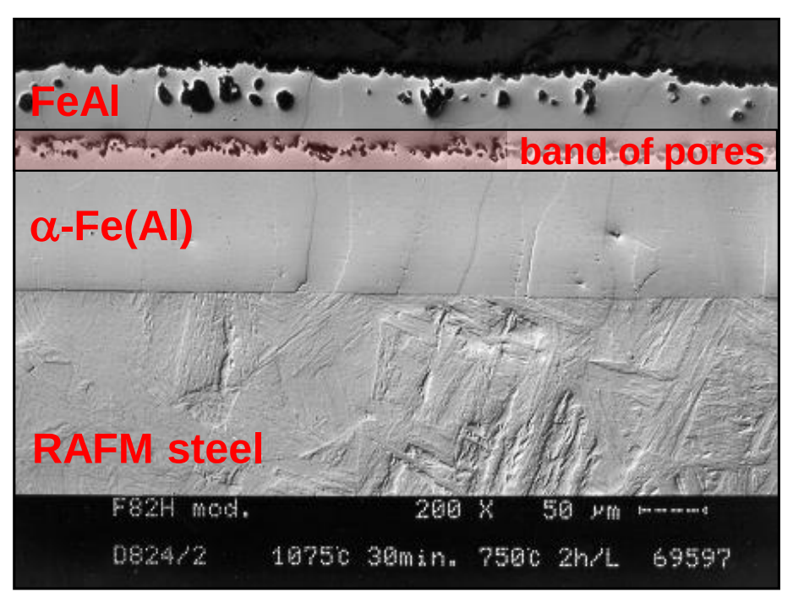
Extended current density range
→ Flexible use of different j possible
→ Provides use of pulse plating (PP)

Heat treatment behavior

Heat treatment

- Subsequent heat treatment is required for all three processes to enable the formation of desired ductile and protective Fe-Al phases, e.g. FeAl, α-Fe(Al)
- Heat treatment procedures depend on steel type
  - 2-step process (HDA and formerly for ECA)
  - Improved 3-step HT process for heat-treating electroplated Al on RAFM steels

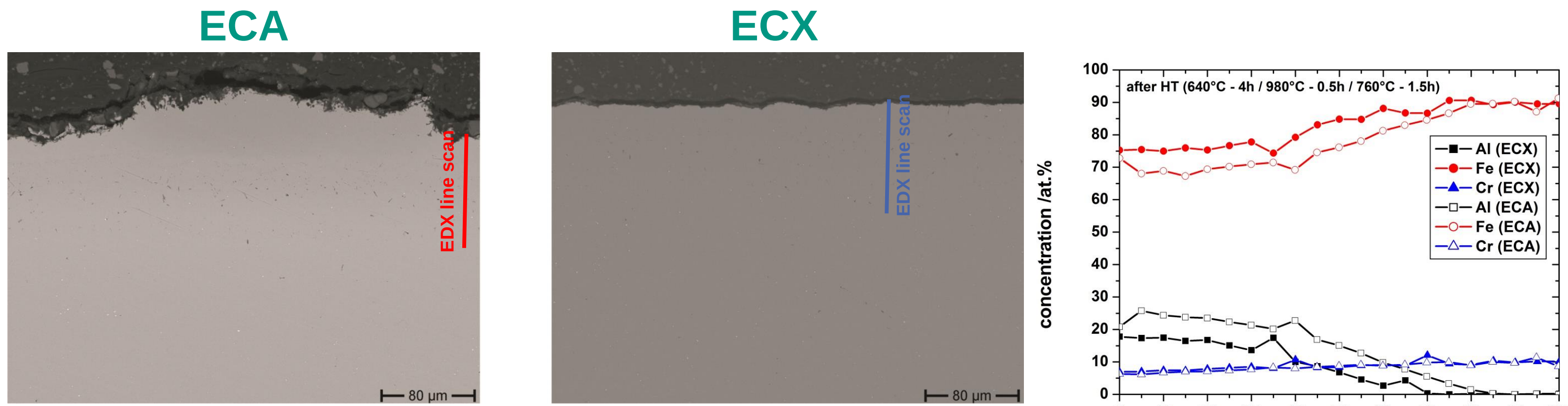




Heat treated HDA sample (F82H-mod.) 1075°C/0.5h + 750°C/2h

HDA samples after HT

- ► Residual Al and brittle Fe_2Al_5 phase are transformed to desired ductile FeAl and α-Fe(Al) phases
- ► Band of pores: presumably *Kirkendall* pores
  - Pores can be avoided by HT under superimposed high pressure → but crack formation occurs
- ► Overall scale thickness 150 µm – 250 µm → relatively high amounts of Al (conflict to low activation criteria)

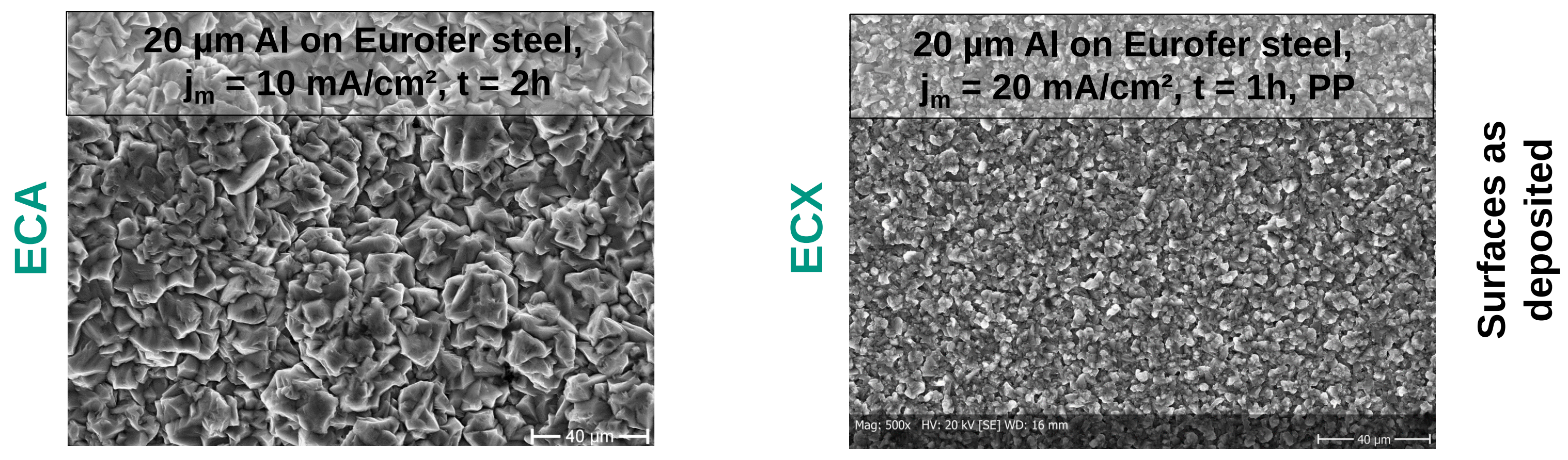


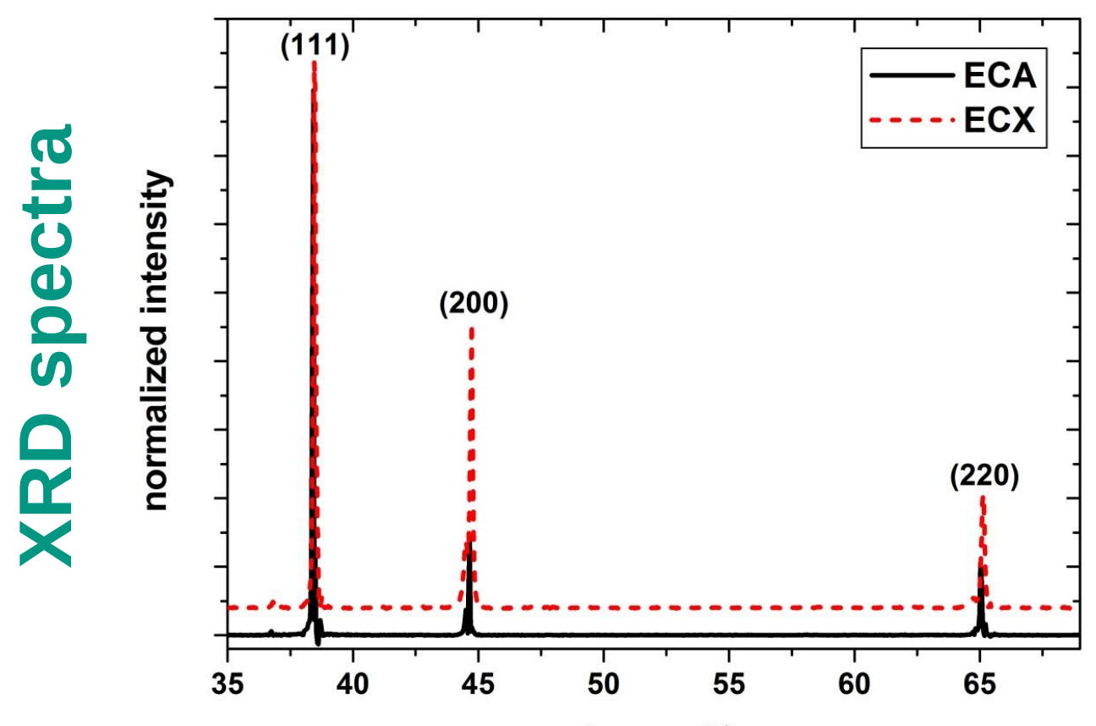
Cross sections of Al coated Eurofer samples after HT: 640°C/4h + 980°C/0.5h + 760°C/1.5h

ECA and ECX samples after HT

- ► Aluminum layer converted completely to ductile FeAl and α-Fe(Al) phases
- ► No pores observable after HT in cross sections of ECA and ECX coated samples
- ► Overall scale thickness below 90 µm → lower amounts of Al (low activation criteria)
  - Could be reduced in future by applying thinner Al layers
- ► Surface of ECX plated sample is smoother and even compared to ECA sample
  - Presumably due to initially coarse crystalline surface after deposition by ECA

Electrodeposited Aluminum made by ECA and ECX





- ► Dense Al-layers on Eurofer were achieved electrochemically by both processes
- ► ECX provides higher deposition rates than ECA due to higher current densities
- ► Smoother surfaces and fine grained Al layers achieved by ECX
- ► XRD spectra revealed slightly different crystallographic orientations

Conclusions

Electrochemical processes ECA and ECX are suitable for Al deposition on RAFM steels and exhibit advantages compared to HDA process:

- ➧ Controllable, uniform layer thickness even at more complex shaped parts
- ➧ Thinner Al coatings possible → Reduced scale thicknesses after HT → Lower amounts of Al (low activation)
- ➧ No or less pore formation observable after subsequent heat treatment

ECX process favorable to ECA process

- ➧ Lower safety requirements → might lead to lower costs
- ➧ More flexible in adjusting process parameters (due to larger current density range)
- ➧ Use of pulse plating possible → Improved Al coatings possible: Lower thicknesses, fine grained (microcrystalline) Al layers + improved surface morphologies after HT

Testing of scale properties made by ECA and ECX is necessary

- ➧ Corrosion tests in flowing Pb-15.7Li (PICOLO) are in progress (ECA, ECX)
- ➧ T-permeation behavior tests are still lacking for ECA and ECX coated RAFM steels

References:

[1] Konys, J. et al.: Impact of heat treatment on surface chemistry of Al-coated Eurofer for application as anti-corrosion and T permeation barriers in flowing Pb-15.7 environment, Fus. Eng. Des., 87 (2012), 1483.

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

www.kit.edu