Status of Tritium Permeation Barrier Development in the EU

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- Introduction
- Experimental
  * Process parameter of coating techniques
- Results
  * Permeation data of barriers in H_2-gas and in H_2/Pb-17Li
- Conclusions

1: FZK, Germany, 2: ENEA, Italy, 3: CEA, France

Why do we need TPB's (Tritium Permeation Barriers)?

To reduce the Tritium release into the coolant significantly (water for WCLL and Helium for HCLL blanket concept)

- ☺ EU Fusion Technology program selected FeAl-based coatings with Al_2O_3 as a thin top layer✓

First phase in EU (up to ca. 1998):

3 coating processes have been selected ✓

- ☺ Chemical vapour deposition (CVD) CEA Grenoble (F)
- ☺ Vacuum plasma spraying (VPS) JRC Ispra (I)
- ☺ Hot-dip aluminizing (HDA) FZK Karlsruhe (D)

The preparation procedures and characterization of each coating were summarized in reports until about end of 1998✓

Second phase in EU (up to ca. "2002"):

Further consolidation to only two remaining coating processes as so-called "reference coatings": Hot-dip aluminization (HDA) and Chemical vapour deposition (CVD)

- Measurements of permeation rates in hydrogen gas (PRF > 1000) ✓
- Measurements of hydrogen permeation rates in Pb-17Li (PRF > 75) ✓
- Self-healing tests in Pb-17Li !!!!
- Irradiation experiments of coatings !!!!
- Compatibility studies of coatings in flowing Pb-17Li at relevant temperatures ✓

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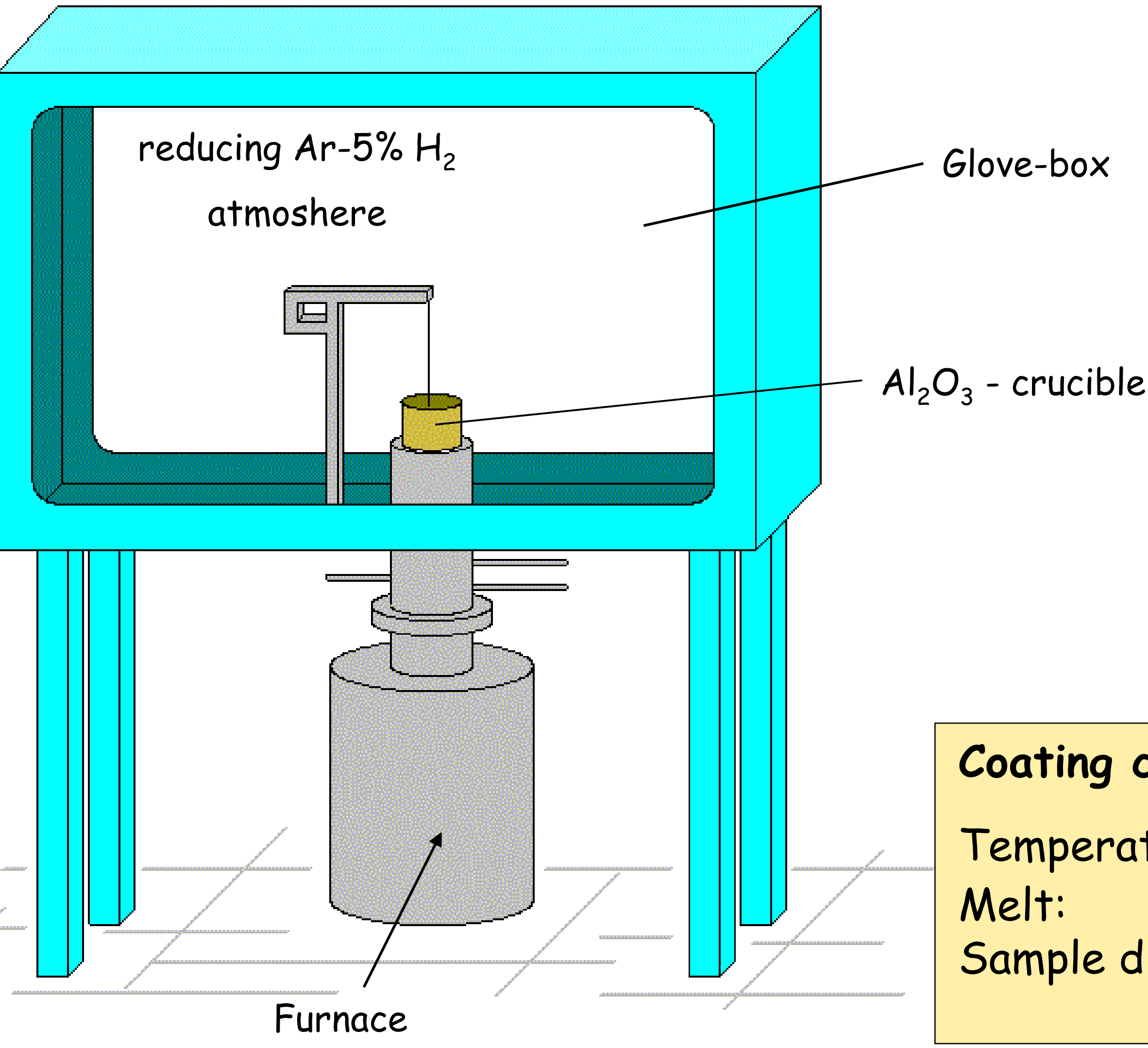
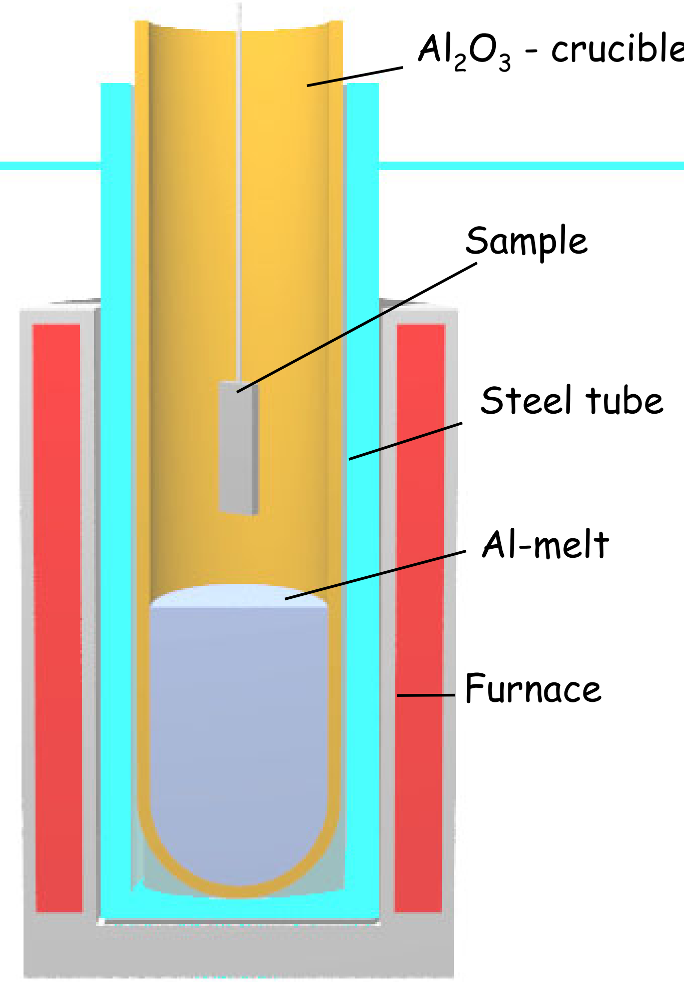
⇒ **Therefore, this 2nd phase has not been finished!!**

Hot-Dipping Facility





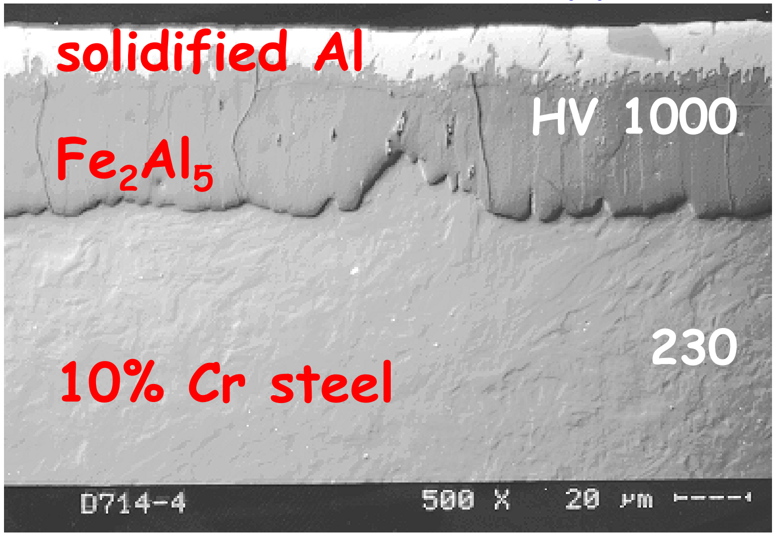
Coating conditions

Temperature:	700°C
Melt:	Al or Al-Si
Sample dimensions:	up to 200 mm in length up to 40 mm in diameter

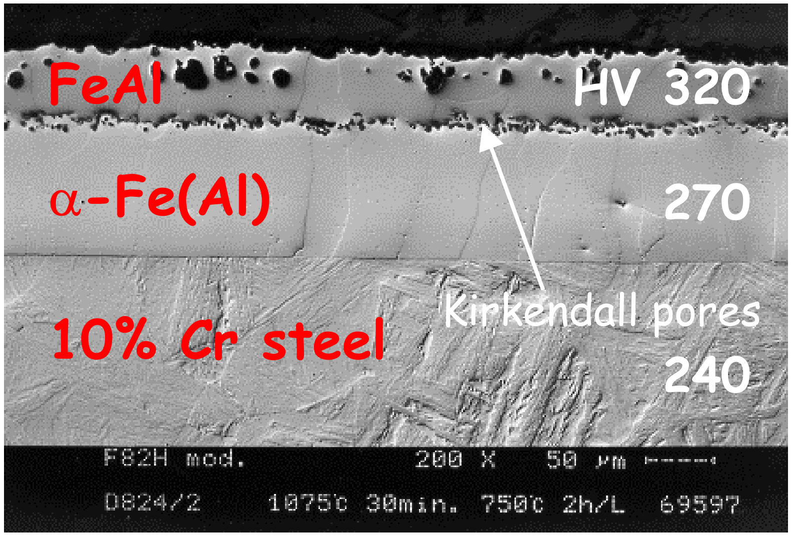
Hot-Dip aluminizing process

Parameters for hot dipping are: temperature at 700°C and dipping time of 30 s

Microstructure of hot dipped surface



Microstructure after heat treatmen



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

Heat treatment at 1040°C/0.5 h + 750°C/1 h incorporates the solidified Al and transforms the brittle Fe_2Al_5-phase into the more ductil phases FeAl and α-Fe(Al)

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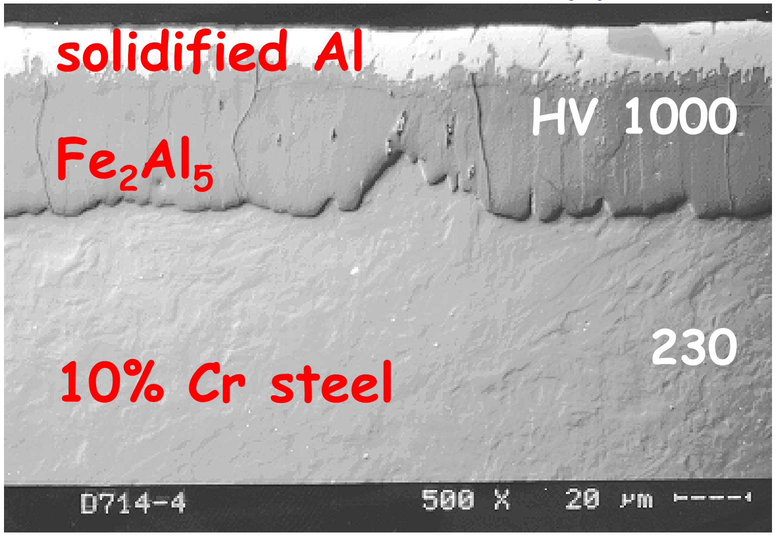

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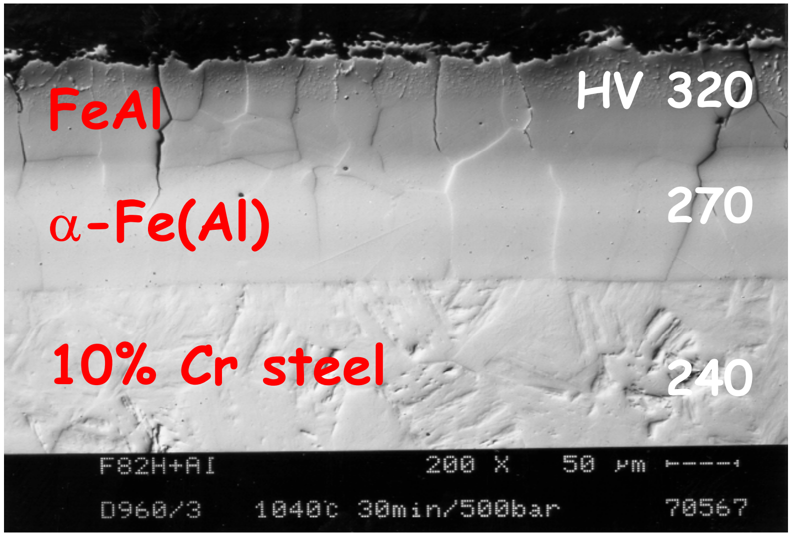


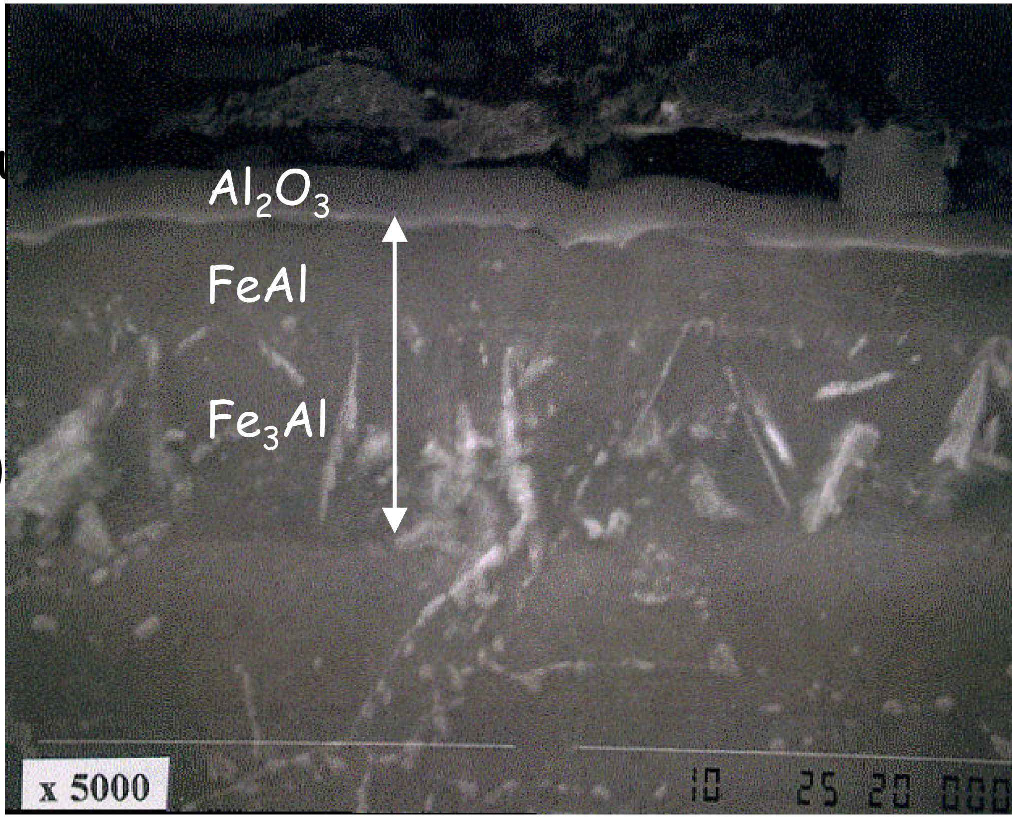
Heat treatment at 1040°C/0.5 h + 750°C/1 h and an applied pressure of >250 bar (HIPing) reduces porosity and transforms the brittle Fe_2Al_5-phase into the more ductile phases Fe and α-Fe(Al)

Chemical vapour deposition (CVD) by CEA

Industrial established 2-step process

FeAl coating

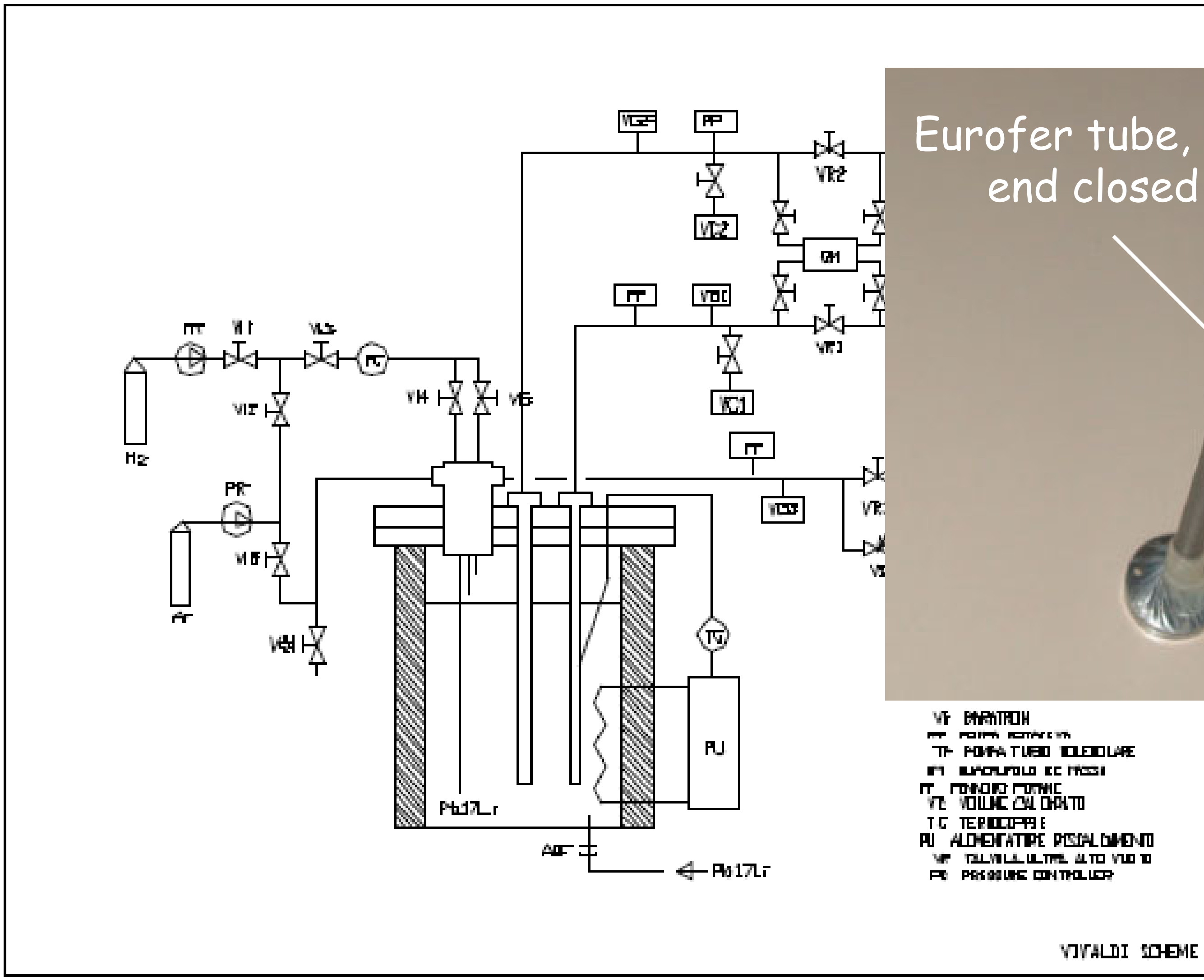
- Powder mixture: Fe-Al, NH_4Cl and Al_2O_3
- T = 650-750°C, p < 10 mbar Ar, t = 1-5 hou

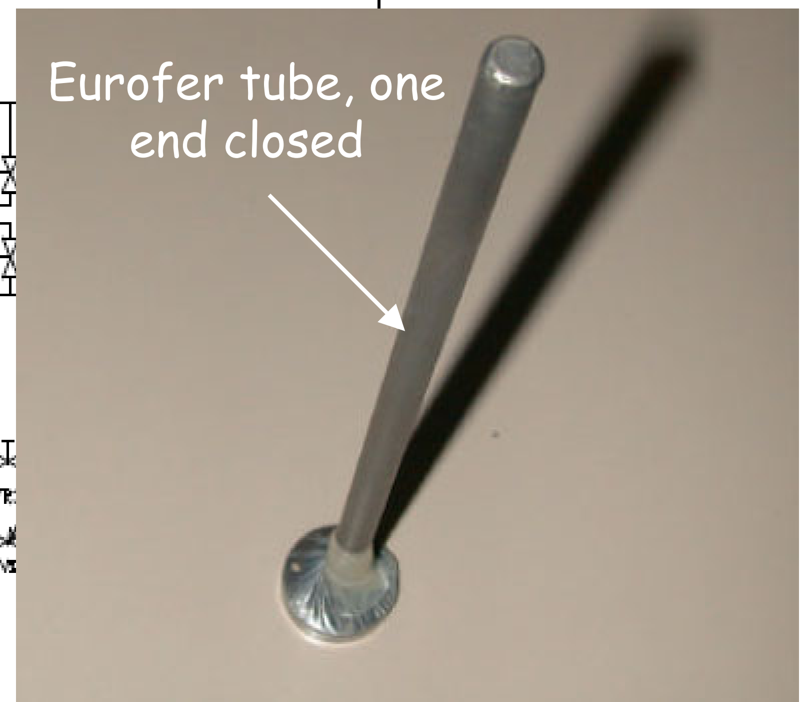


Al_2O_3 deposition

- MOCVD process (metalorganic precursor)
- T = 400-500°C, t = 1-2 hours

VIVALDI facility at ENEA, Brasimone, Italy, 2001-2003



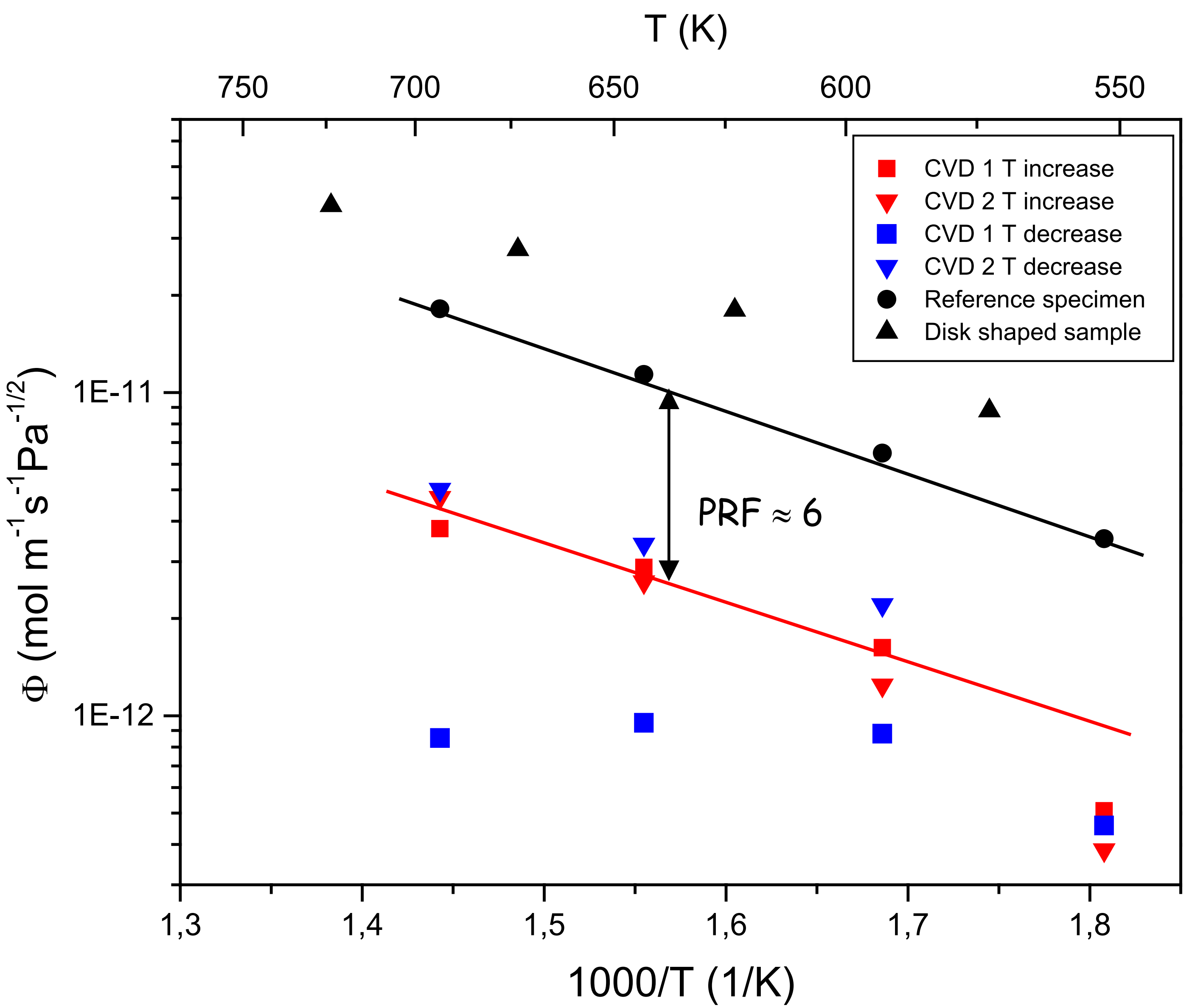


Permeation tests in VIVALDI facility

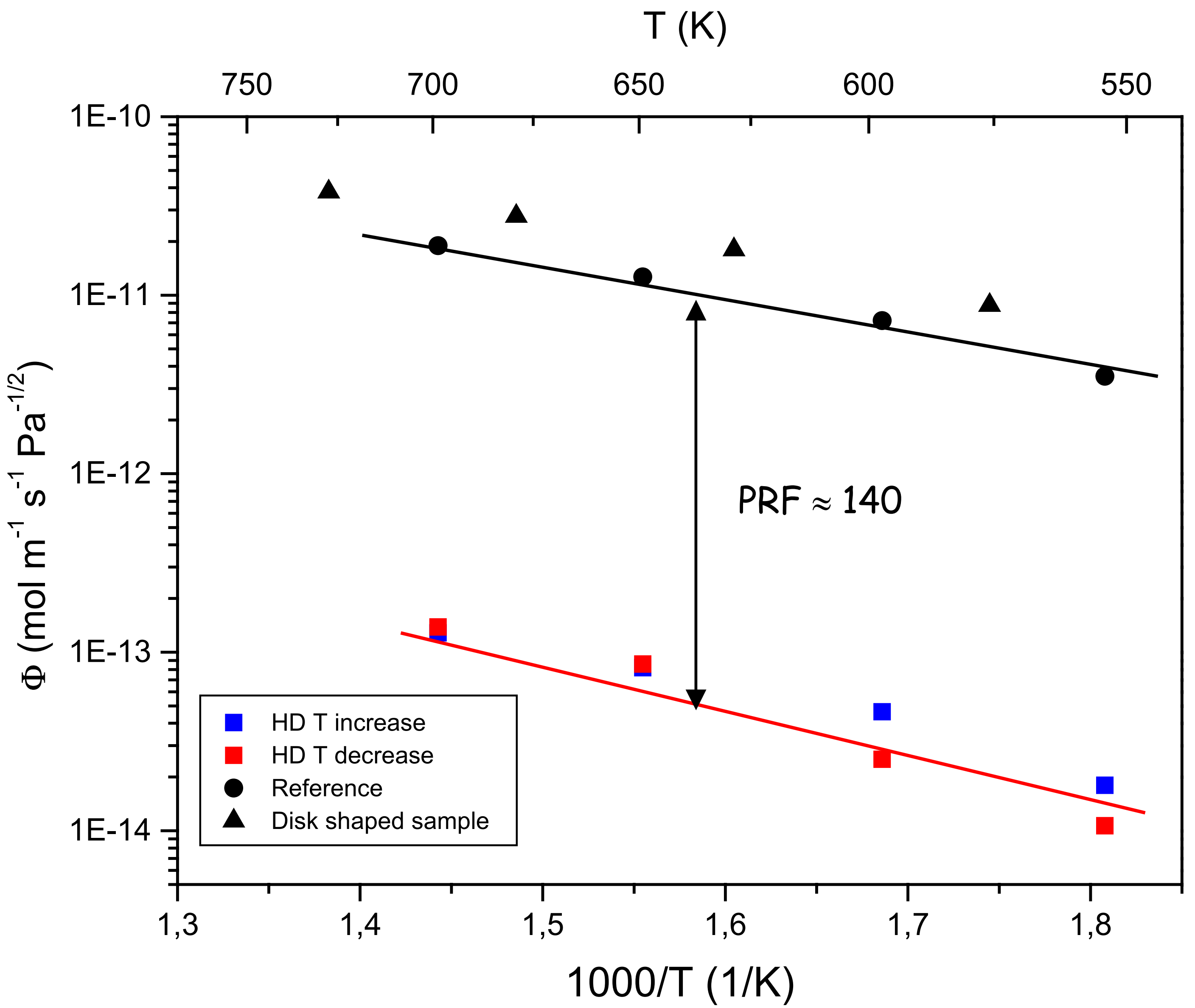
- The coated samples were tested in sequence and compared with the bare samples, both placed together in the permeation chamber.
- Hydrogen gas at a kn… …ased into the permeation chamber. The gas per… …used a pressure rise in the inner calibrated v…
- This pressure rise co… …holes of gas permeating per unit area of the s…
- By comparing the steady state fluxes of the coated and bare samples, one could calculate the Permeation Reduction Factor PRF.

$$J = \frac{\Phi \sqrt{P_h}}{R_{out} \ln \frac{R_{out}}{R_{in}}}$$

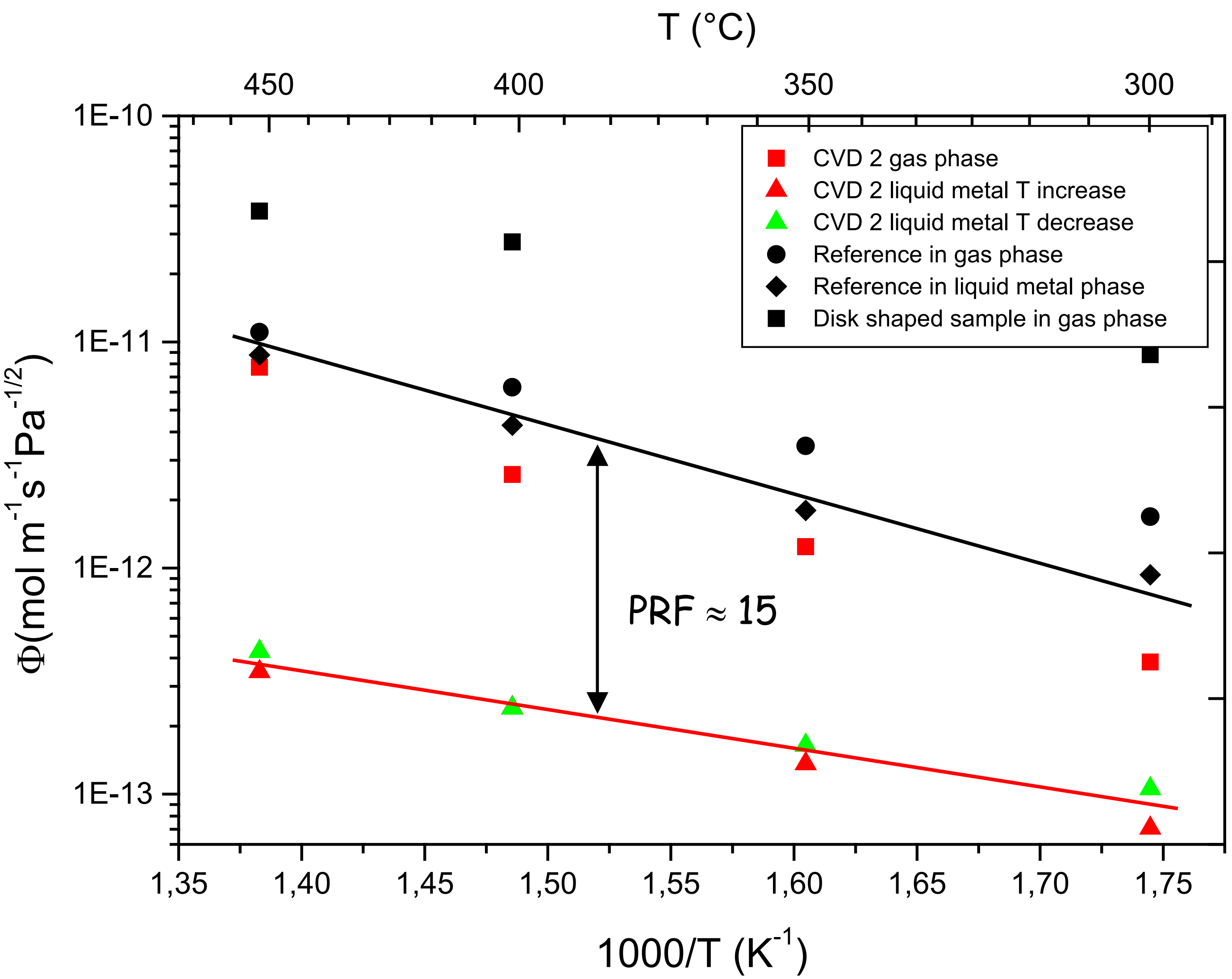
Permeabilities of CVD-coated tubes in H_2-gas



Permeabilities of HDA-coated tubes in H_2-gas



Comparison of permeabilities of CVD-coated tubes in H_2-gas and Pb-17Li



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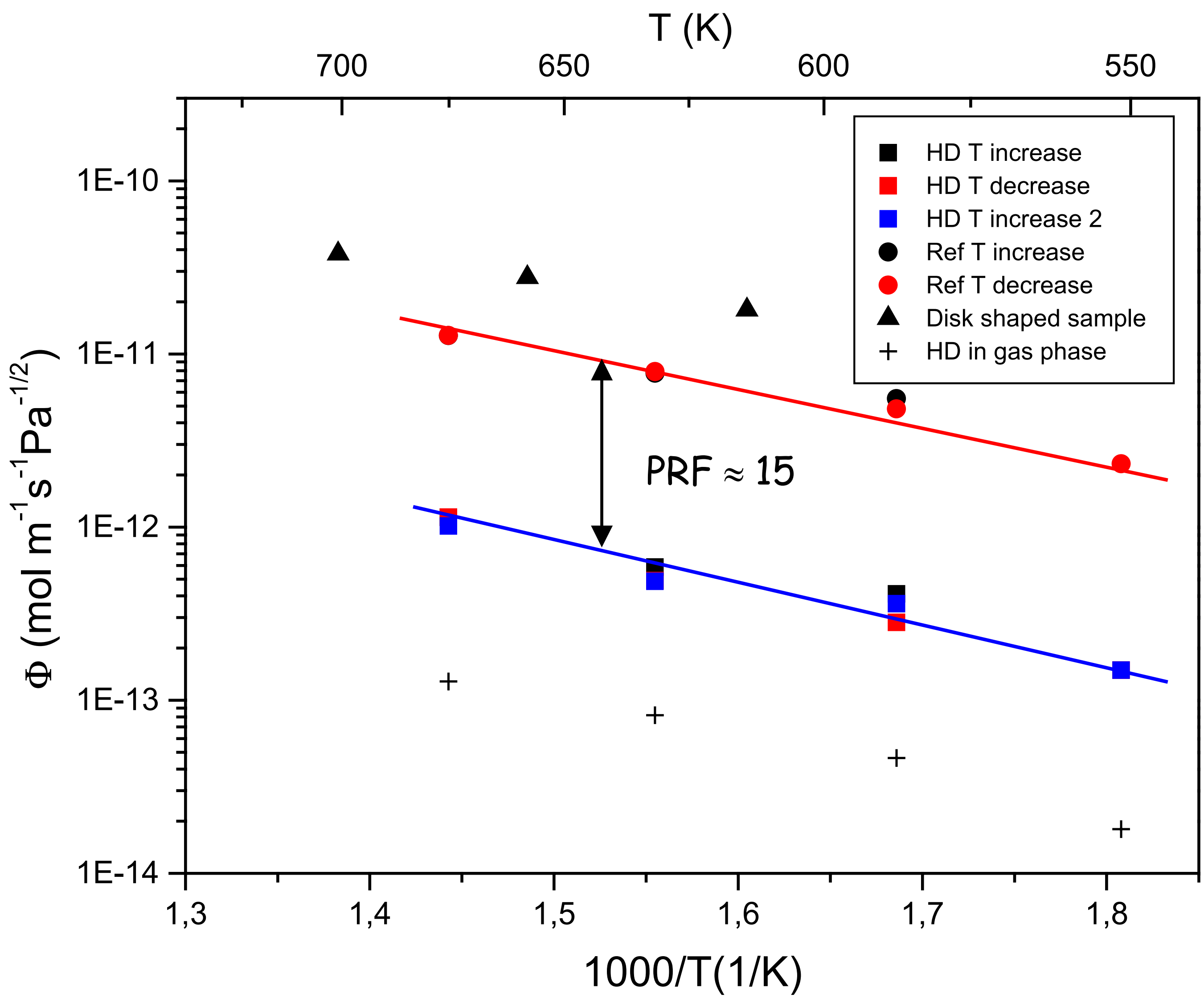


PRF values of bare and coated samples

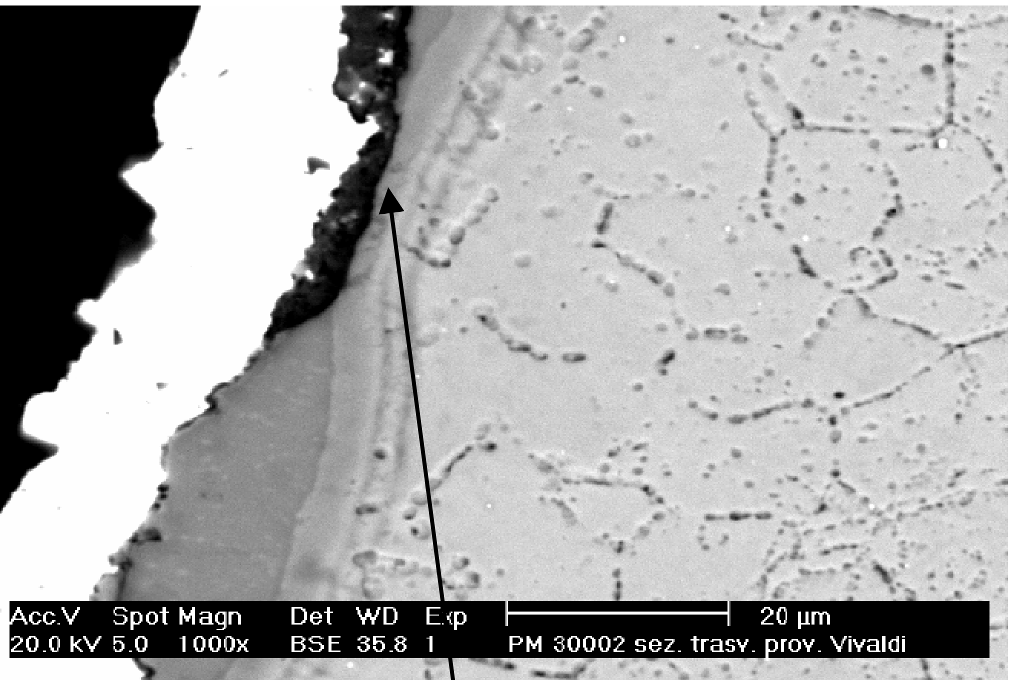
T (°C)	CVD sample 1 gas phase P (mol m^{-1} s^{-1} Pa$^{-1/2}$)	Bare Eurofer P (mol m^{-1} s^{-1} Pa$^{-1/2}$)	PRF	Disk sample Eurofer 97 P (mol m^{-1} s^{-1} Pa$^{-1/2}$)	PRF tube versus disk
280	$5.08 \cdot 10^{-13}$	$3.53 \cdot 10^{-12}$	7	$8.79 \cdot 10^{-12}$	17
320	$1.63 \cdot 10^{-12}$	$6.50 \cdot 10^{-12}$	4	$1.80 \cdot 10^{-11}$	11
370	$2.88 \cdot 10^{-12}$	$1.14 \cdot 10^{-11}$	4	$2.77 \cdot 10^{-11}$	10
420	$3.79 \cdot 10^{-12}$	$1.82 \cdot 10^{-11}$	5	$3.79 \cdot 10^{-11}$	10
	HDA sample 2				
280	$1.80 \cdot 10^{-14}$	$3.53 \cdot 10^{-12}$	196	$8.79 \cdot 10^{-12}$	489
320	$4.64 \cdot 10^{-14}$	$6.50 \cdot 10^{-12}$	140	$1.80 \cdot 10^{-11}$	388
370	$8.19 \cdot 10^{-14}$	$1.14 \cdot 10^{-11}$	139	$2.77 \cdot 10^{-11}$	338
420	$1.28 \cdot 10^{-13}$	$1.82 \cdot 10^{-11}$	141	$3.79 \cdot 10^{-11}$	296
	HDA sample 2 Pb-17Li	Bare Eurofer Pb-17Li			
280	$1.49 \cdot 10^{-13}$	$2.32 \cdot 10^{-12}$	15	$8.79 \cdot 10^{-12}$	59
320	$2.81 \cdot 10^{-13}$	$4.82 \cdot 10^{-12}$	17	$1.80 \cdot 10^{-11}$	64
370	$4.91 \cdot 10^{-13}$	$7.91 \cdot 10^{-12}$	16	$2.77 \cdot 10^{-11}$	56
420	$1.14 \cdot 10^{-12}$	$1.28 \cdot 10^{-11}$	11	$3.79 \cdot 10^{-11}$	33

Activation energies of bare and coated samples

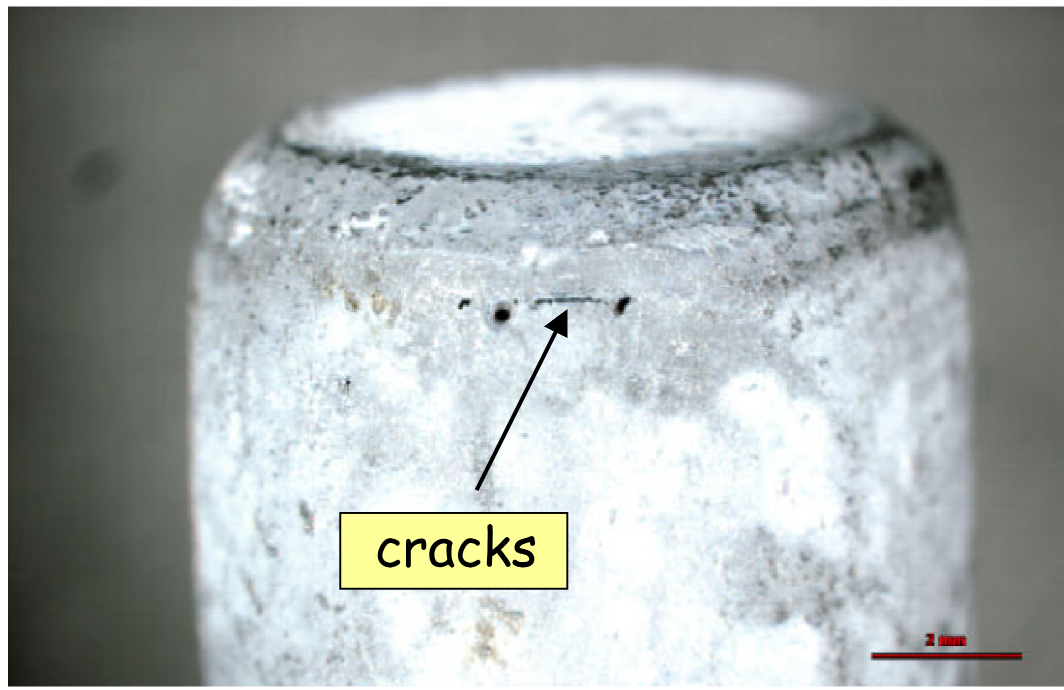
Material	Activation energy (kJ/mol)
Bare Eurofer 97	37.1
CVD coating (gas phase)	44.9
CVD coating (Pb-17Li)	39.0
HD coating (gas phase)	40.0
HD coating (Pb-17Li)	45.0

Defects in CVD and HDA coatings, visible after permeation testing in Pb-17Li

CVD coating



HDA coating



Conclusions

- A large R&D activity regarding the development of coating techniques for TPB's was launched in the EU during the last 10 years.
- FeAl-type coatings were identified as potential materials for TPB's and qualified in gas permeation tests. They fulfill the requirement of PRF ≥ 1000. ✓
- CVD and HDA process were selected as "reference coatings" for TPB's. A final selection between both coatings has not yet been made up to now.
- The low PRF's in Pb-17Li (required was a PRF ≥ 75) obtained in the VIVALDI experiments, demonstrated a distinct sensitivity of the PRF to the coating quality.
- Nevertheless, the reason for the too low PRF's in the presence of Pb-17Li is not fully understood (facility and/or material specific?). A reaction of Al_2O_3 to form $LiAlO_2$ as discussed in literature, is not believed to fully explain the current result

Conclusions

- Since 2001/2002, the development of coating processes in the EU was "frozen" because the "design" wanted to continue without TPB's in the existing WCLL blanket concept.
- Therefore, the funding from the EU was reduced and/or maintained on a low level. Only a small budget for the permeation measurements at ENEA Brasimone, Italy, was launched.
- In 2003, a change from WCLL to HCLL blanket concept was made, due to budget reasons in the EU.
- In the new HCLL concept, temperatures up to 550°C (or maybe higher) are envisage in the "Pb-17Li area" of the blanket structure. This was or is the return of the necessity of coatings for the reduction of tritium permeation into the coolant (He) and also for so-called" corrosion barriers", because of the increasing dissolution-corrosion of structural steels in high-temperature Pb-17Li.
- A new programme for the continuation of the TPB/corrosion barrier development would be necessary to clearify the still existing technological questions.