Hydrogen Permeation through Fusion Materials

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Motivation

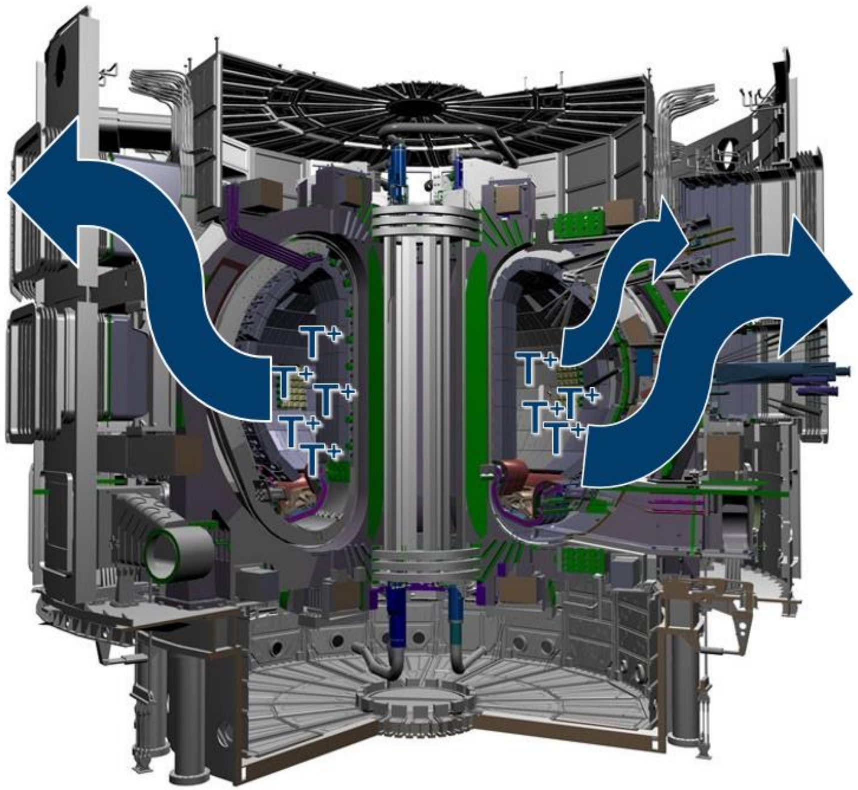


Figure (edited): http://www.iter.org/

Estimation and prevention of tritium permeation:

→ Fuel loss
→ Tritium accumulation
→ Release into the environment

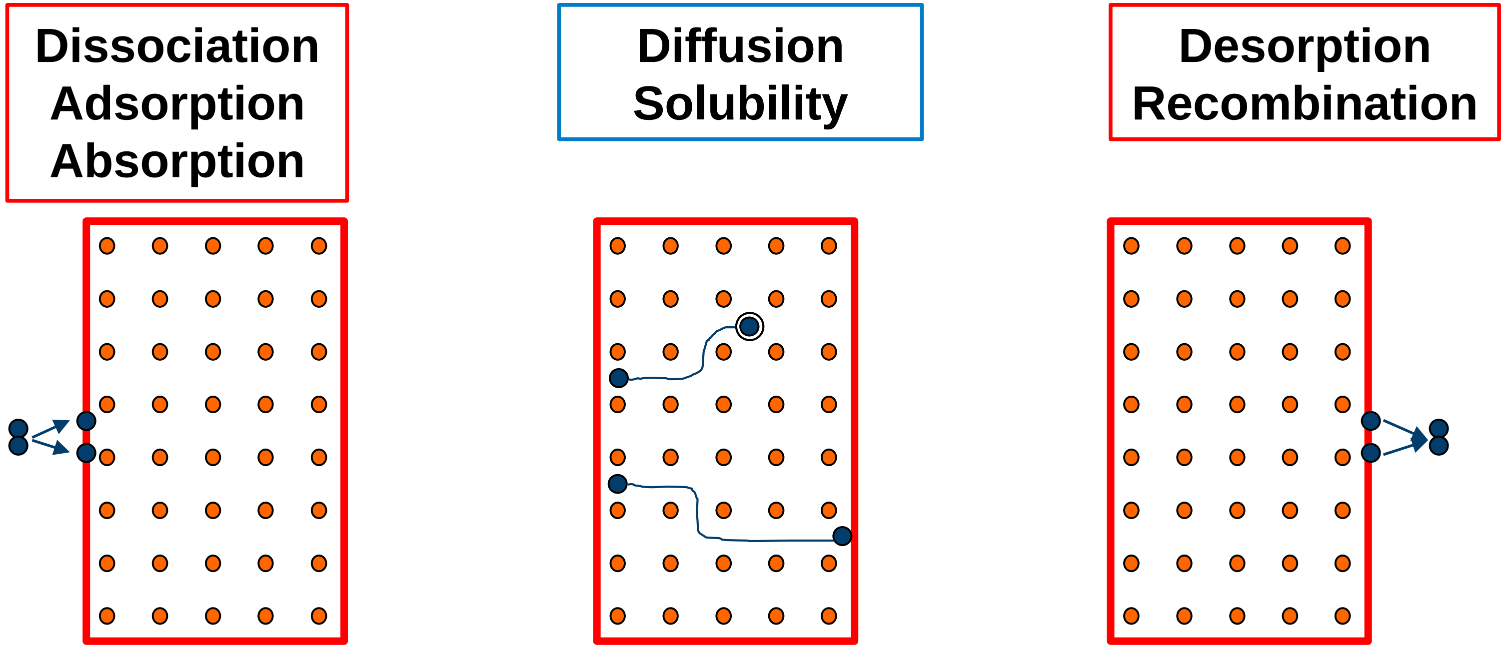
Deuterium permeation studies:

→ 'Pure' materials: Eurofer97, 316L(N)-IG, Cu, CuCrZr-IG
→ Combined material systems:
    → Cu/316L(N)-IG
    → W/CuCrZr-IG
    → W/Eurofer97

Investigation of the Influence of:

→ Interfaces
→ Microstructure

Permeation



Dissociation
Adsorption
Absorption

Diffusion
Solubility

Desorption
Recombination

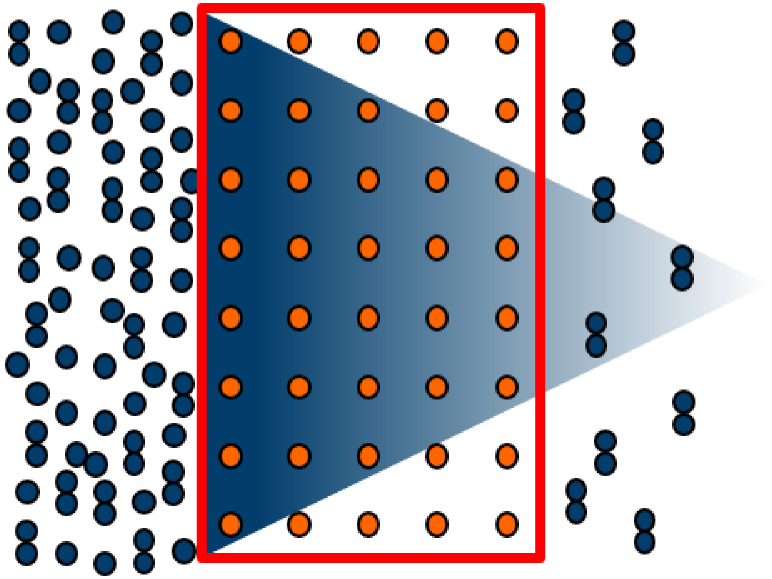
Effective Permeability: → Microstructure, grain size, pores

→ Contamination of the surface

→ Interfaces

Effective permeability can be higher or lower as the ‘pure’ or ‘bulk’ permeation, in order to verify the influence on the permeation → measurement of samples with different microstructure, surface modifications…

Gas / Ion Driven Permeation



high concentration/
high pressure side

low concentration/
low pressure side

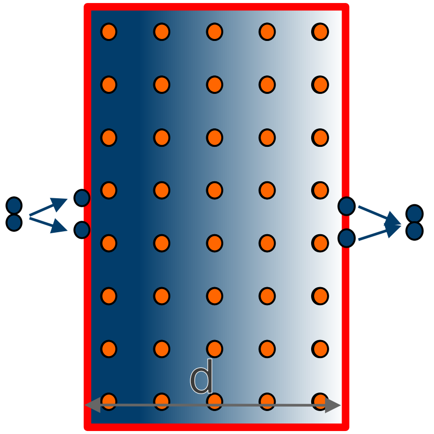
Gas-driven:

- → General permeation behavior (physical understanding)
- → Measurement does not influence the surface and bulk
- → Pressure, temperature and sample thickness dependent measurements

Gas Driven Permeation

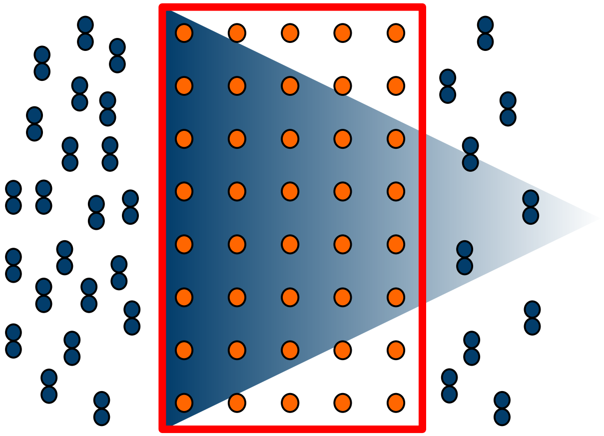
Diffusion-limited:
Dependent on thickness

$$J \sim {}^{1}/_{d}\sqrt{p}$$



$$J = -\frac{DK_s}{d}\left(\sqrt{p_l} - \sqrt{p_h}\right)$$

$$\xrightarrow{p_h \gg p_l} J = \frac{P}{d}\sqrt{p_h}$$



Pressure dependence:

$$J = ap^n$$

Temperature dependence:

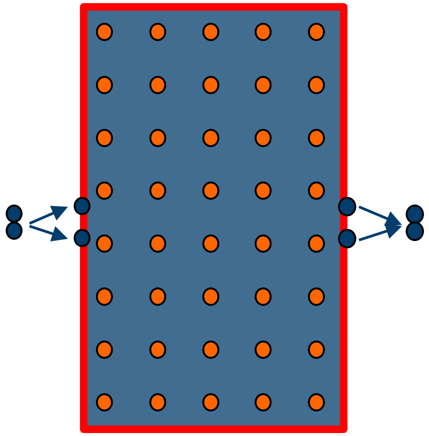
$$P = P_0 \exp\left(-\frac{E_P}{RT}\right)$$

Lag-Time measurement:

$$D = \frac{d^2}{6L}$$

Surface (Interface) -limited:
Independent on thickness

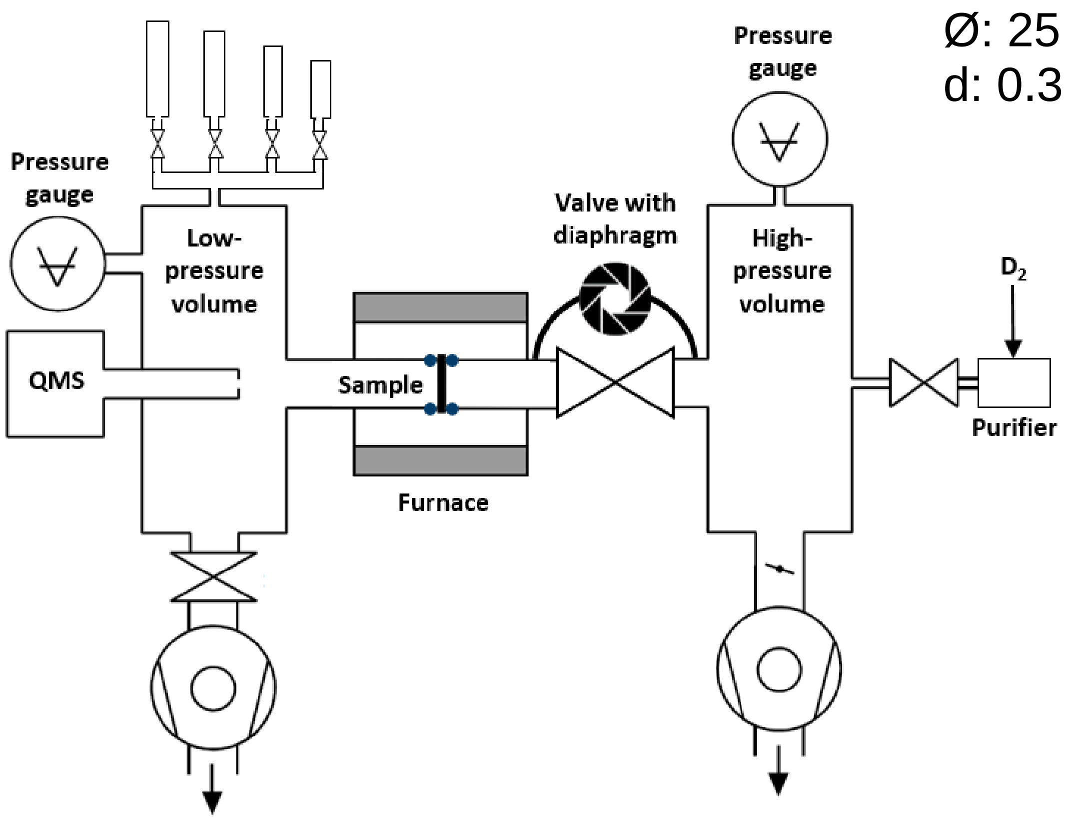
$$J \sim p$$

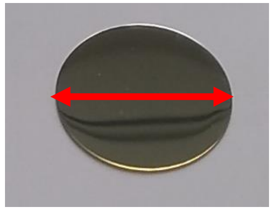


$$J = \sigma K p$$

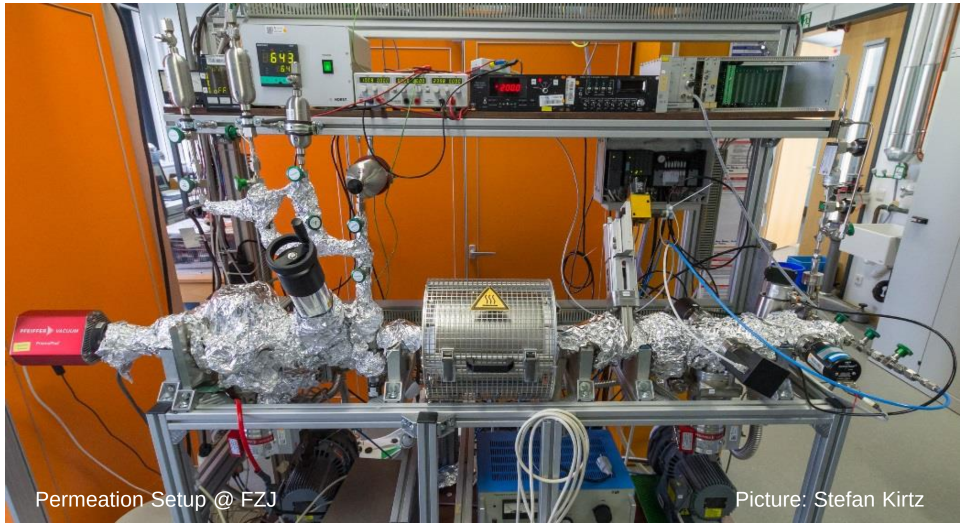
Experimental Setup

Gas-driven:





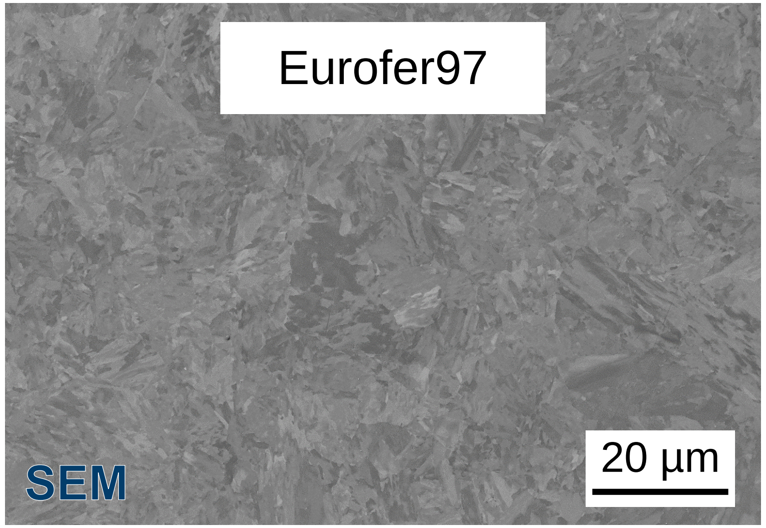
Ø: 25 mm
d: 0.3 mm

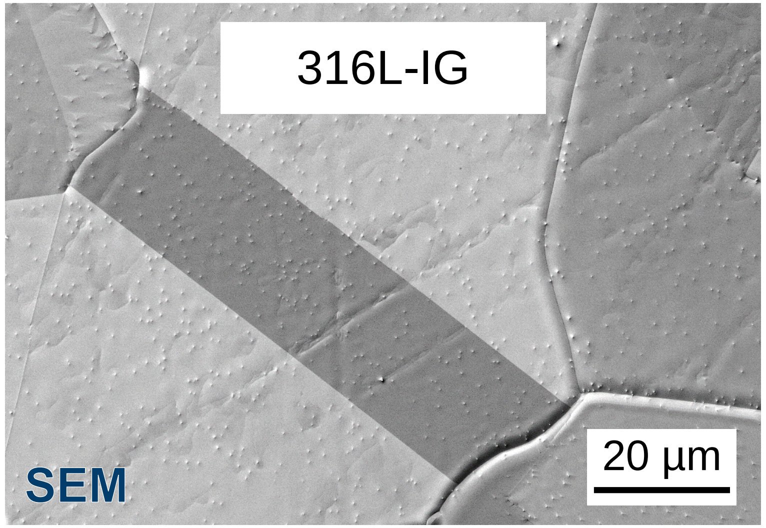

Permeation Setup @ FZJ
Picture: Stefan Kirtz

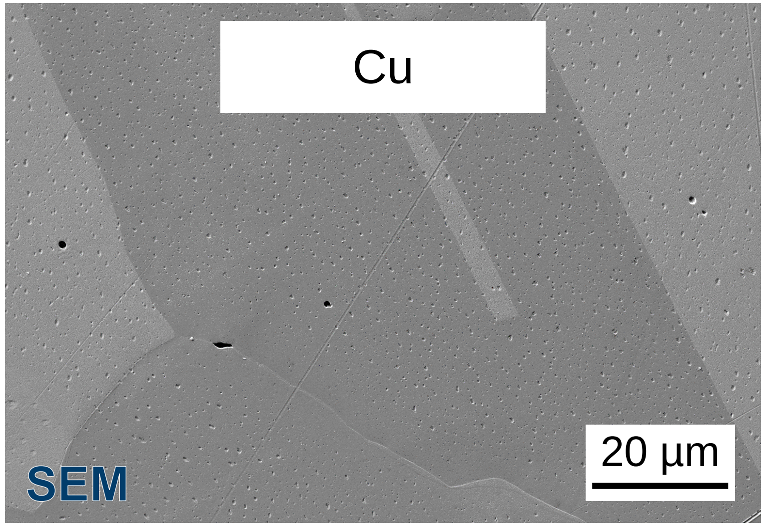
Measuring procedure:

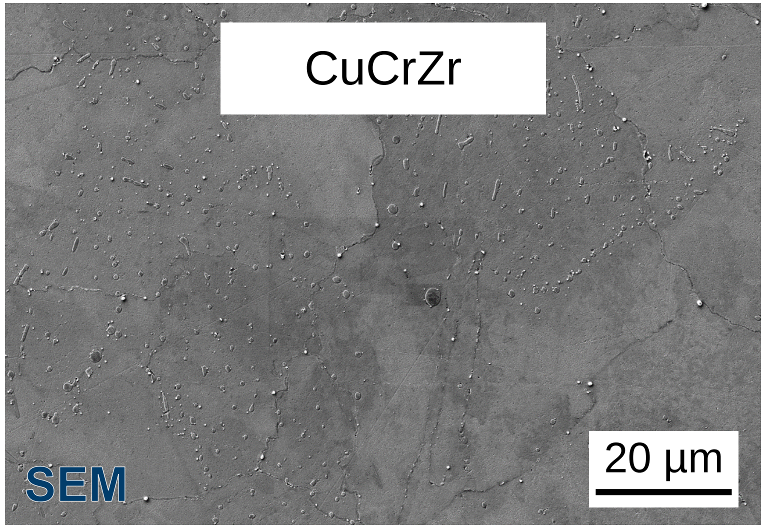
→ Sample preparation
→ Evacuation: HPV/LPV ~10^{-9} mbar
→ Calibration
→ Pressure/temperature dependent measurement
→ Lag-Time measurement -> Diffusion

Comparison ‘pure’ Materials









Fusion Steels:

- → Eurofer97 (DEMO):
  - → Reduced activation steel
  - → Martensitic/ferritic, distorted bcc
- → 316L(N)-ITER Grade
  - → Nitrogen enhanced 316L
  - → Austenitic, fcc

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Cu and Cu Alloy

- → Cu:
  - → Oxygen-free copper (commercial)
  - → Small voids
- → CuCrZr-ITER Grade
  - → ITER first wall panels
  - → Cu with Cr precipitates

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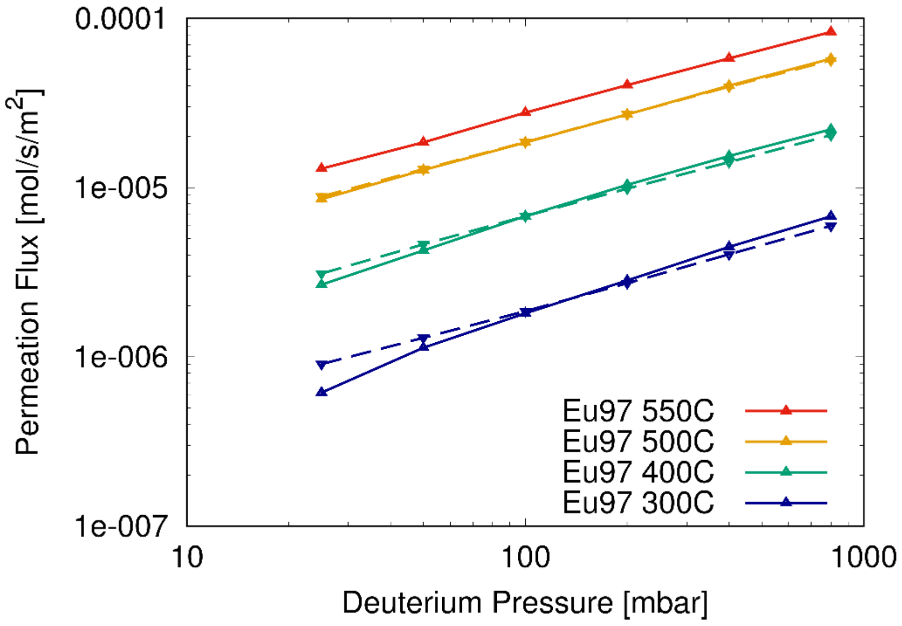
Measurement and Analysis

All 'pure' samples and substrates are 'mirror' polished, annealed and the thickness is ~ 0.3 mm
Gas-driven deuterium permeation flux measurements (measurement range: 300-550°C, 25-800 mbar):

Example Eurofer97:

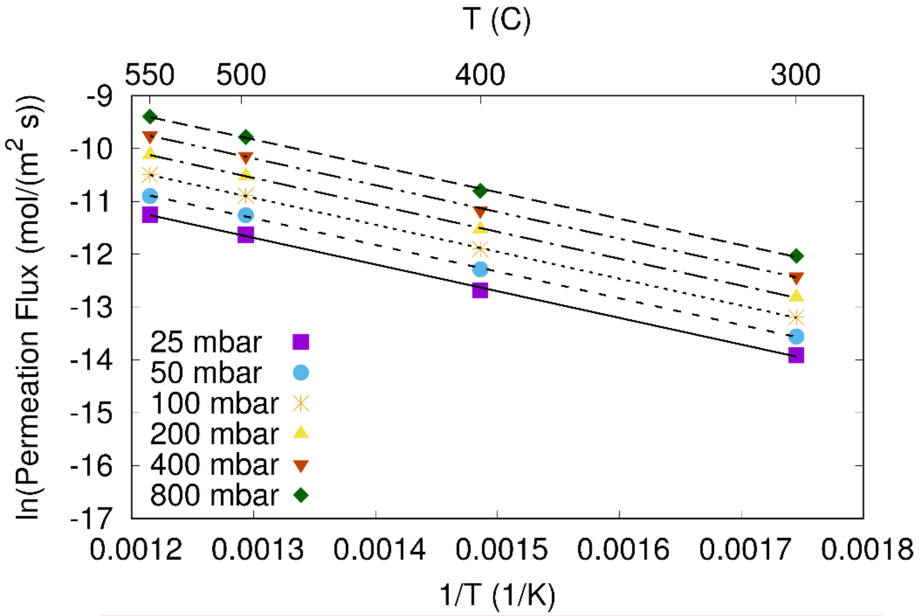
$$P = P_0 \exp\left(-\frac{E_P}{RT}\right)$$

Temperature dependence of stabilized permeation flux:



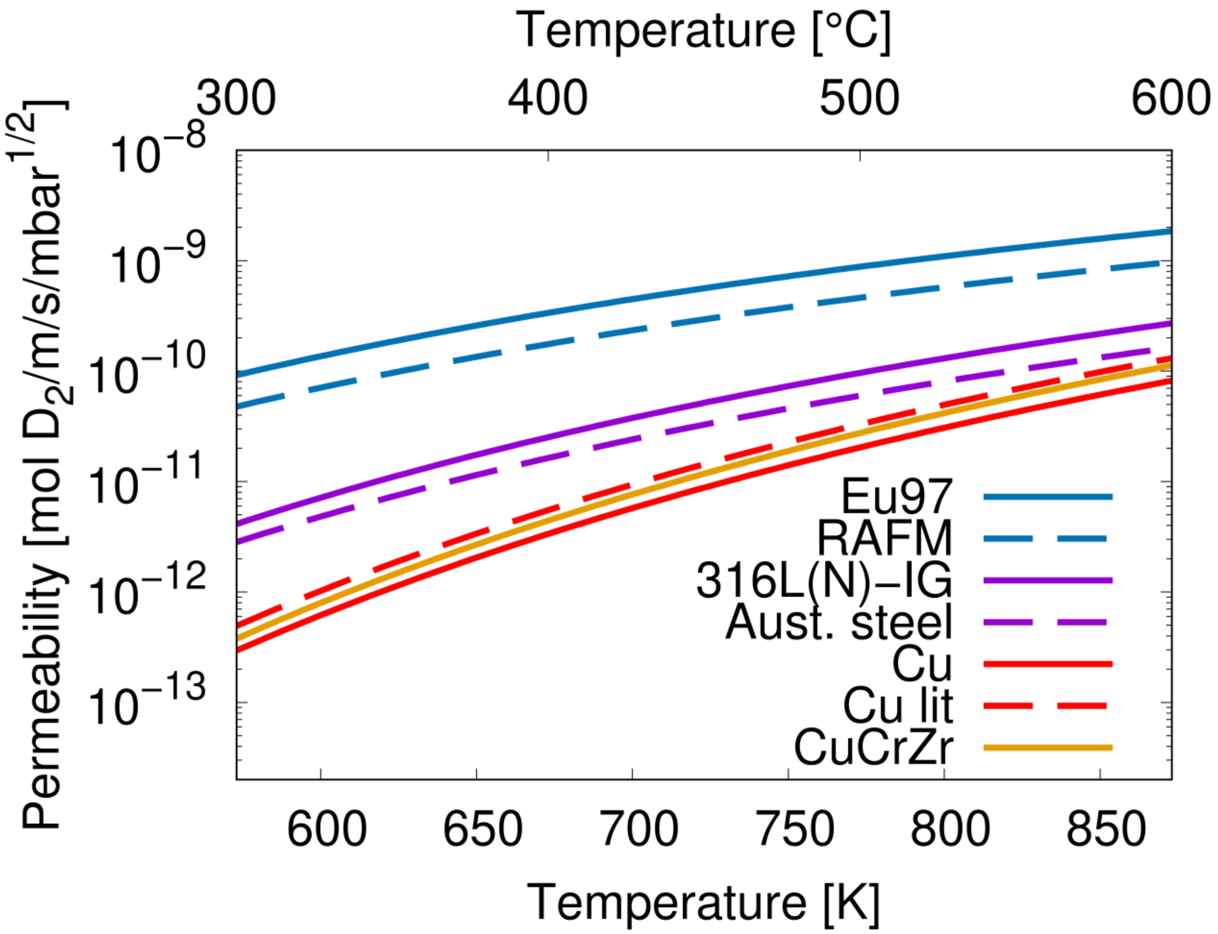
→ Slope: ~ 0.5 → $J \sim \sqrt{p}$ → **diffusion limited**
→ No change of sample during measurement

Arrhenius plot → fulfilled (measured T and p range)



→ E_P = 41.6(5) kJ/mol
P_0 = 5.7(4)*10^{-7} mol/(ms$\sqrt{mbar}$)

Conclusion – 'Pure' Materials



R. Causey et al., Comprehensive Nuclear Materials 2012, 511–549

Solid line: measured values

Dotted line: adapted literature values Causey, 'mean value' of published effective permeation data (bulk)

→ Comparable to literature values

→ Permeability of Eu97 higher than 316L

→ Permeability Cu / CuCrZr similar

→ Diffusion limited regime

Study combined material systems:

→ Influence of interfaces

→ Influence of microstructure

Interfaces and Microstructure

The measurement of hydrogen permeation flux through a ‘real’ component is not possible:

→ Permeation measurements through several combination of bulk and layered substrates

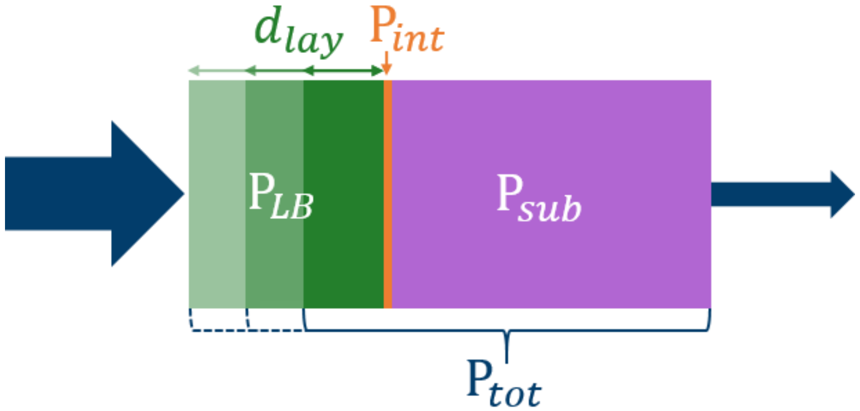
→ Enables estimation of the hydrogen permeation through a component / permeation mechanism

First studied system: Cu coated 316L-IG

→ For better estimation of the influence of the interface: measurement of several samples

→ Microstructure of the coatings is ‘identical’, thicknesses will be varied in order to vary the layer bulk/interface ratio

→ Separation of the influence of the microstructure (P_{LB}) and the influence of the interface (P_{int}) on the permeation flux



Major influence:

Microstructure:

- P_{tot} would vary with layer thickness
- Diffusion limited

Interface:

- P_{tot} would be identical for all layer thicknesses
- Surface limited

Deuterium permeation studies on 316L(N)-IG, Cu and 316L(N)-IG with Cu layer:

- Comparison of pure, bare materials and the combination of steel and Cu

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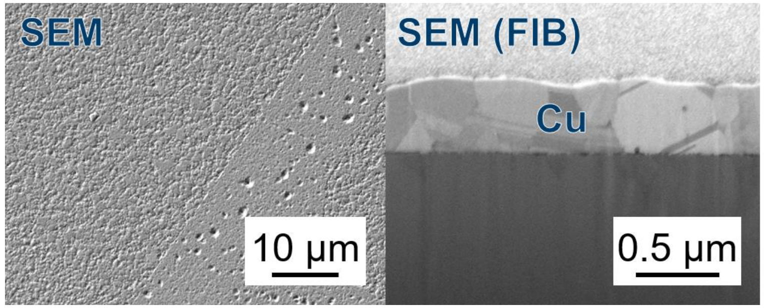
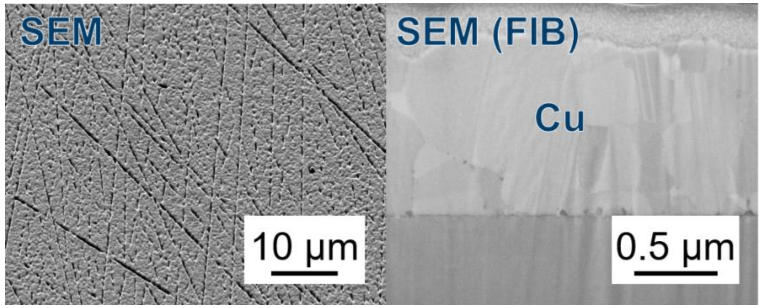
Cu coated 316L

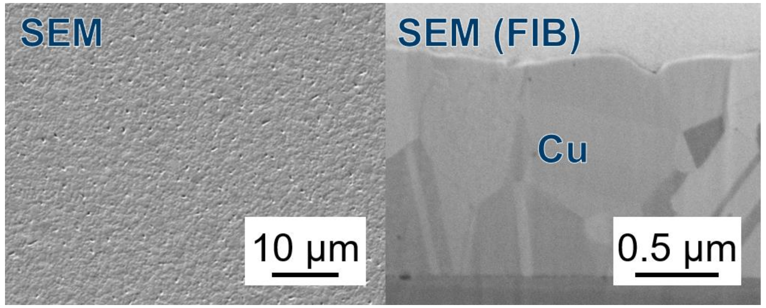
316L-IG with Cu layer 'thin' (316L_Cu_thin):



316L-IG with Cu layer 'thick' (316L_Cu_thick):



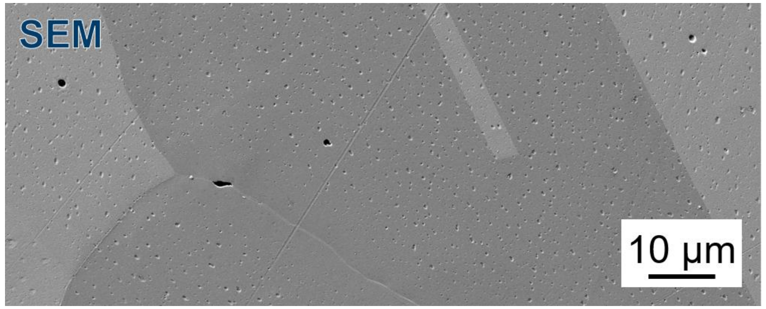
316L-IG with Cu layer 'very thick' (316L_Cu_very_thick):



Cu layered 316L substrates:

- Magnetron sputter deposition, coated on one side
- Annealed after deposition
- Layer thickness: **316L_Cu_thin :** ~490 nm
  316L_Cu_thick: ~980 nm
  316L_Cu_very_thick: ~1400 nm
- 'Clean' interface, no cracks, no voids
- Microstructure similar between layers
- Surface different between layers
- Microstructure very different to bulk Cu (no voids!):

Polished Cu (Cu):



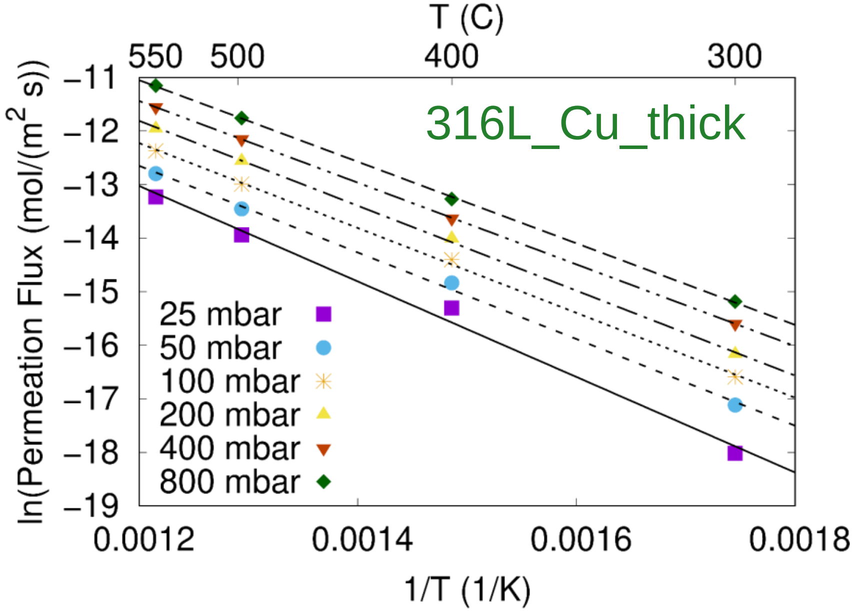
Measurements and Analysis

Gas-driven deuterium permeation flux measurements (measurement range: 300-550°C, 25- 800 mbar):
From the permeation flux (J_P) the effective permeability (P) can be obtained:

p/T-dependent measurements:

$$J_P = \frac{P_0 \sqrt{p}}{d} e^{\frac{-E_P}{RT}}, \ P = P_0 e^{\frac{-E_P}{RT}}$$

P_0: permeation constant, E_P: activation energy

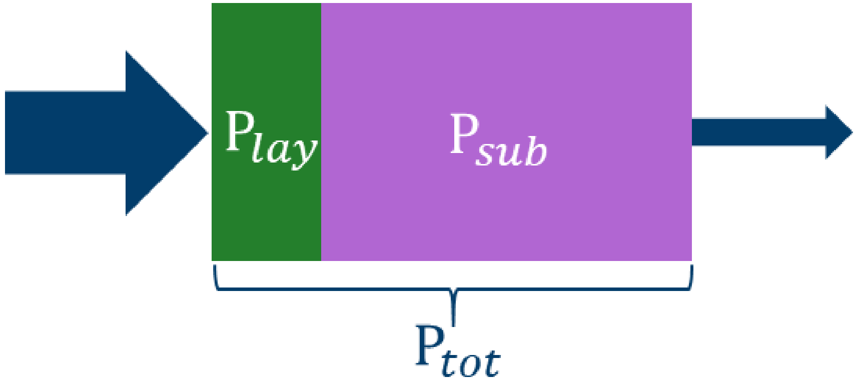


For this 316L_Cu_thick sample:

$$P_0 = 2.3(5) \cdot 10^{-6} \frac{\mathrm{mol}}{\mathrm{ms}\sqrt{\mathrm{mbar}}}, \ E_P = 66(2) \frac{\mathrm{kJ}}{\mathrm{mol}}$$

Calculation of the layer permeability (substrate and layer thickness independent, valid in Diffusion limited regime):

As resistivity (R) in series connection: $R_{tot} = R_1 + R_2$ and $R = \frac{1}{\sigma} \approx \frac{1}{P}$



$$P_{lay} = \frac{d_{lay}}{\left(\frac{d_{tot}}{P_{tot}} - \frac{d_{sub}}{P_{sub}}\right)}$$

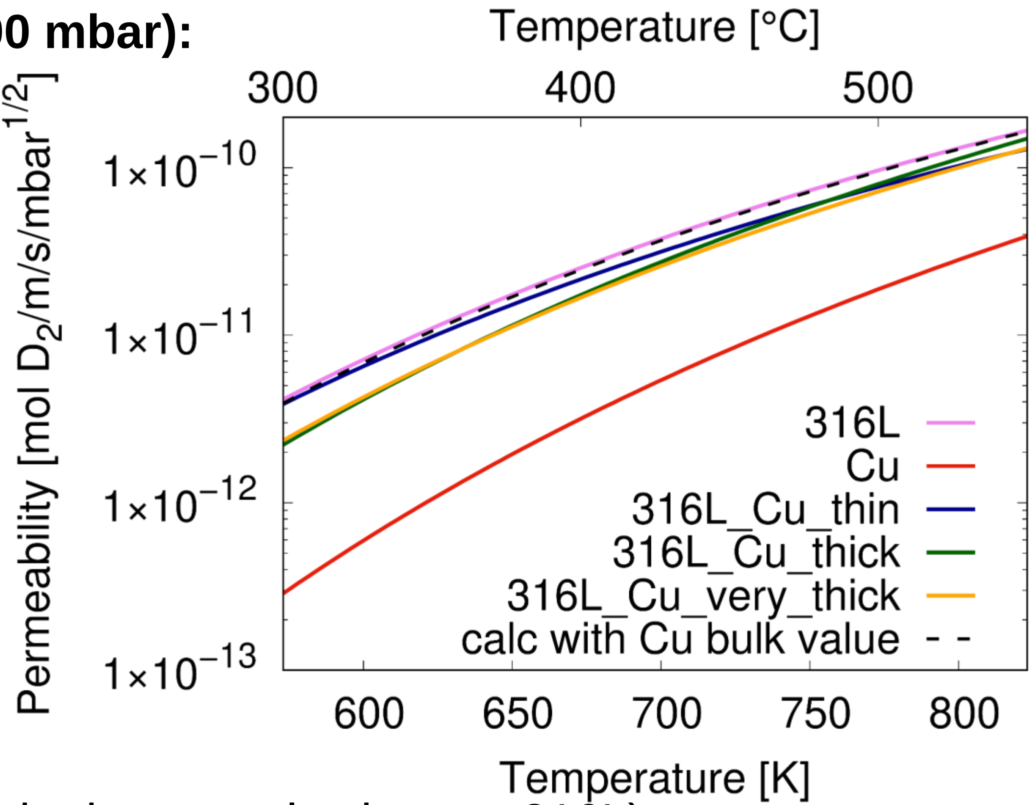
lay: layer
tot: total,
sub: substrate

Layer permeability (contains P_{LB} and P_{int}!) :
Microstructure: $P_{tot} \sim d_{lay}$ → similar P_{lay} for all d_{lay}
Interface: $P_{tot} \nsim d_{lay}$ → increased P_{lay} for thicker d_{lay}

Results Cu coated 316L

Effective permeability (measurement range: 300-550°C, 25-800 mbar):

Sample	$P_0 \left[\frac{\mathrm{mol}}{\mathrm{ms}\sqrt{\mathrm{mbar}}}\right]$	$E_P \left[\frac{\mathrm{kJ}}{\mathrm{mol}}\right]$	p^x
316L	$8(1)*10^{-7}$	58(1)	0.5
Cu	$3(2)*10^{-6}$	77(2)	0.55
316L_Cu_thin	$4(2)*10^{-7}$	55(2)	0.6
316L_Cu_thick	$2.3(5)*10^{-6}$	66(2)	0.6
316L_Cu_very_thick	$1.3(5)*10^{-6}$	63(2)	0.65



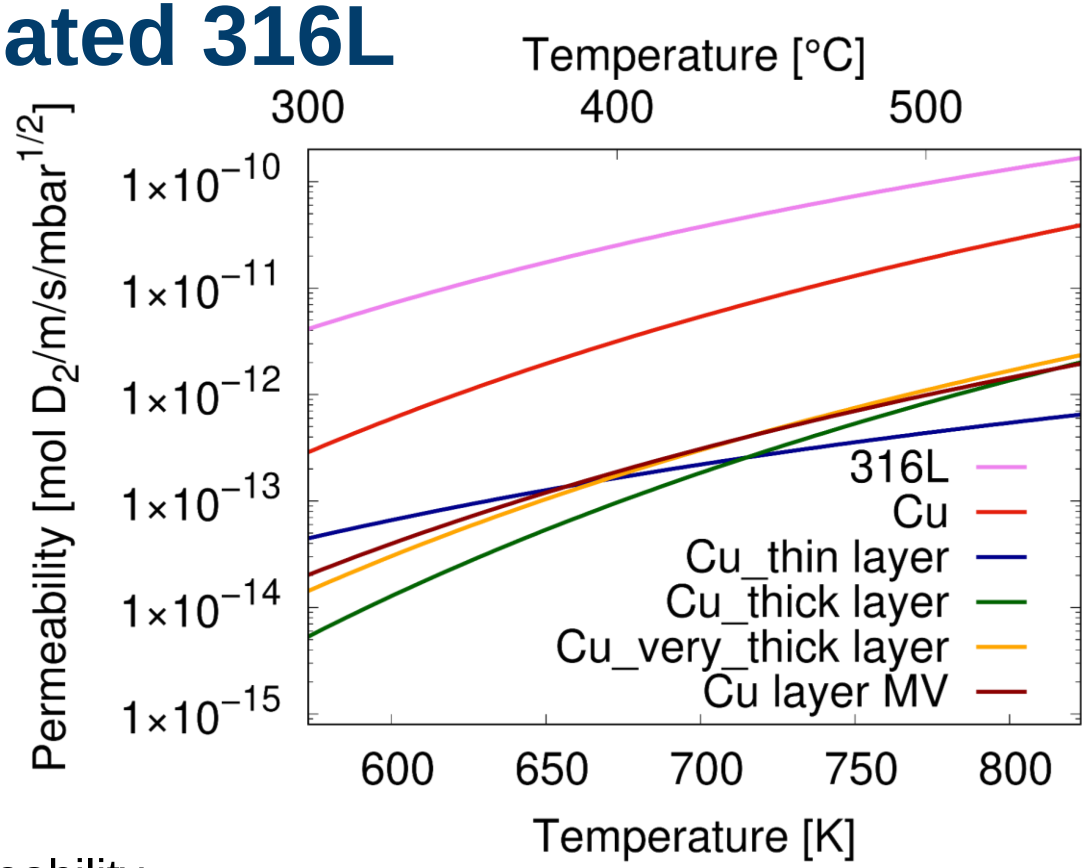
- → Reduction of permeability due to the coating (compared to the bare steel substrate 316L)
- → Reduction is larger as expected from calculation of the permeability with values 316L / Cu bulk
- → Permeabilities of layered substrates are different, dependent on layer thickness
- → Diffusion limited regime (only slight increase), similar ‘up’ and ‘down’ measurement values

Results Cu coated 316L

Layer permeability for Cu in 316L_Cu:

$$\left.\begin{array}{l} sub\text{: 316L} \\ tot\text{: 316L\_Cu\_thick}\end{array}\right\} \rightarrow \begin{array}{l} P_{lay}: P_0 = 2\cdot 10^{-6}\ \frac{\mathrm{mol}}{\mathrm{ms}\sqrt{\mathrm{mbar}}} \\ E_P = 93\ \frac{\mathrm{kJ}}{\mathrm{mol}}\end{array}$$

Sample	$P_0\left[\frac{\mathrm{mol}}{\mathrm{ms}\sqrt{\mathrm{mbar}}}\right]$	$E_P\left[\frac{\mathrm{kJ}}{\mathrm{mol}}\right]$
316L	$8(1)*10^{-7}$	58(1)
Cu	$3(2)*10^{-6}$	77(2)
Cu_thin layer	$3*10^{-10}$	42
Cu_thick layer	$2*10^{-6}$	93
316L_Cu_very_thick	$3*10^{-7}$	80



→ Cu layer permeabilities are smaller as the Cu bulk permeability

→ Effective permeability of Cu layers is very different, but order of magnitude is similar

→ Mean Value (MV): $E_P = 72\ \frac{\mathrm{kJ}}{\mathrm{mol}}$, $P_0 = 7*10^{-8}\ \frac{\mathrm{mol}}{\mathrm{ms}\sqrt{\mathrm{mbar}}}$

→ Clear statement of the influence of the interface is not possible from these measurements

→ But: Strong indication that in this case the **influence of the interface is minor** compared to the **large influence of microstructure** on the permeability

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W coated CuCrZr-IG

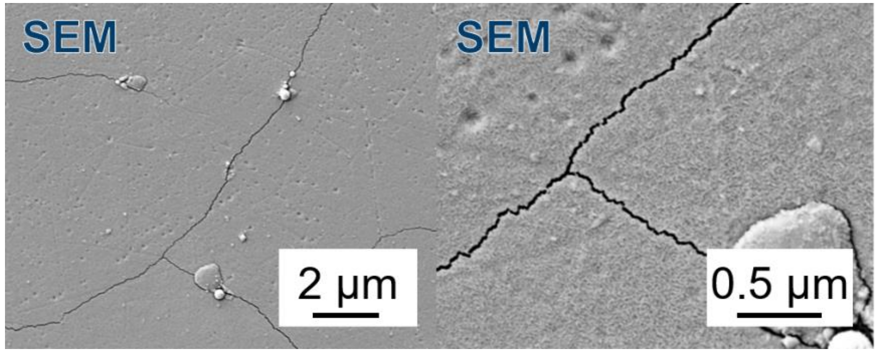
Second studied system: W coated CuCrZr-IG

In order to avoid cracking of W layer due to differences in thermal expansion:

→ First attempt: thin W layer, max. temperature 450°C

→ Second attempt: W deposition at elevated substrate temperature of around 300°C

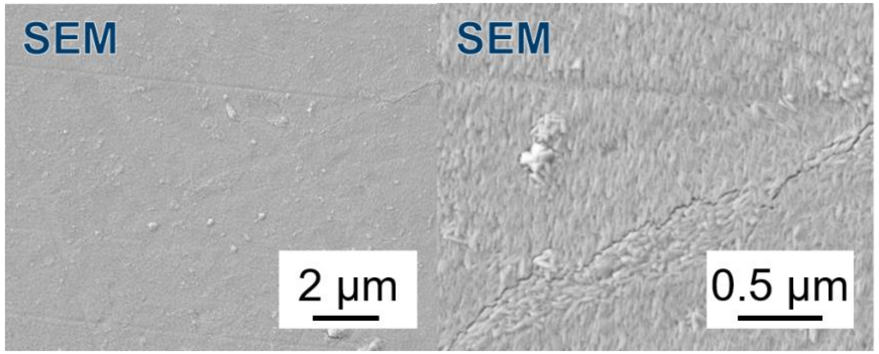
CuCrZr-IG with W layer 'thin/cold':



- Magnetron sputter deposition, coated on one side
- Layer thickness: ~100 nm
- Annealed at 450°C after deposition
- Cracks after annealing
- Permeation measurement (T_{max}= 450°C): very similar to CuCrZr substrate (reasons: too thin layer, cracks?)

→ No conclusion can be drawn from the result!

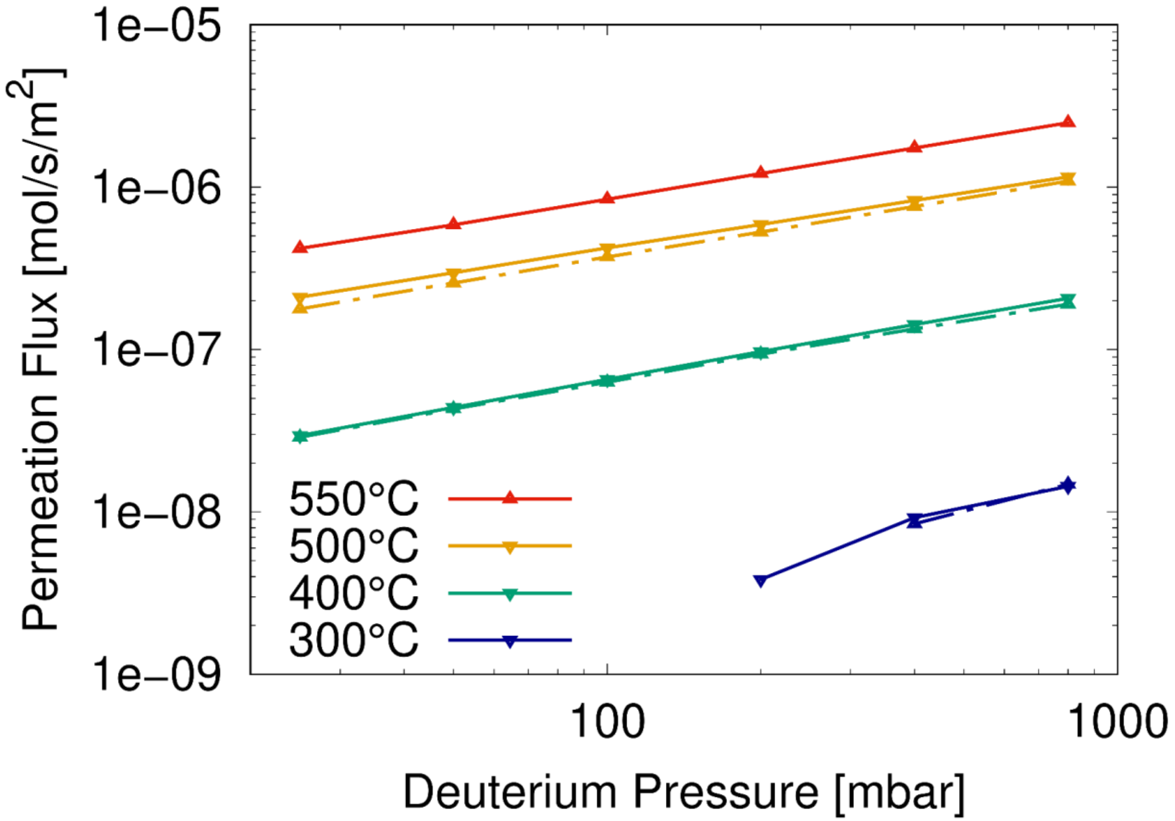
CuCrZr-IG with W layer 'hot' (CuCrZr_W_hot):



- Magnetron sputter deposition, coated on one side, T_{sub}~300°C
- Layer thickness: ~ 350 nm
- Annealed at 550°C after depositon
- Very small cracks after annealing
- W phase confirmed by XRD

→ Permeation measurement (T_{max}= 550°C)

W coated CuCrZr-IG



Permeation Flux Measurement CuCrZr_W_hot:

→ Very similar up and down measurement

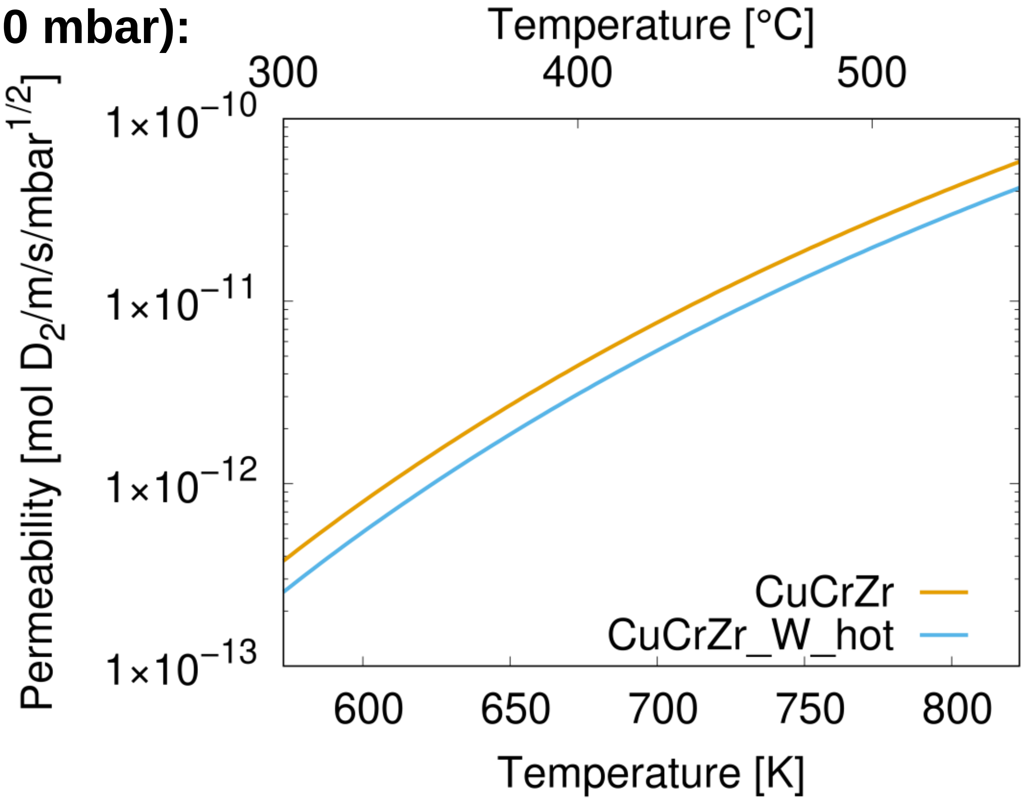
→ No change of sample during measurement expected

→ Slope: ~ 0.5 → $J \sim \sqrt{p}$ → **diffusion limited**

Results W coated CuCrZr

Effective permeability (measurement range: 300-550°C, 25-800 mbar):

Sample	$P_0 \left[\frac{\text{mol}}{\text{ms}\sqrt{\text{mbar}}}\right]$	$E_P \left[\frac{\text{kJ}}{\text{mol}}\right]$	p^x
CuCrZr	$6(2)*10^{-6}$	79(1)	0.55
CuCrZr_W_hot	$5(2)*10^{-6}$	80(1)	0.5



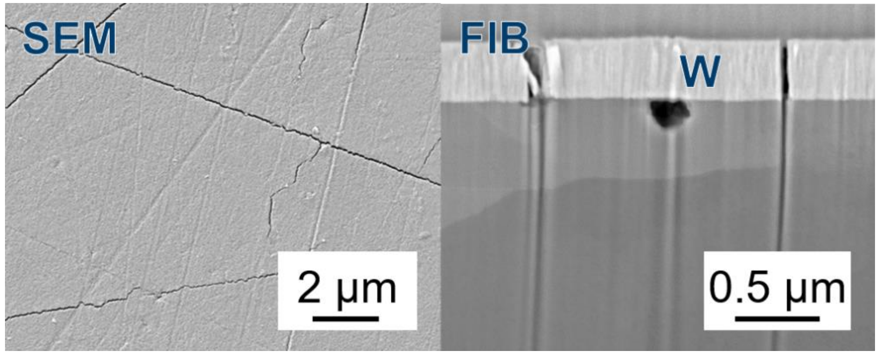
→ Reduction of permeability due to the coating (compared to the bare CuCrZr)

→ Diffusion limited regime, similar ‘up’ and ‘down’ measurement values

→ Assumption: no measurable influence of interface

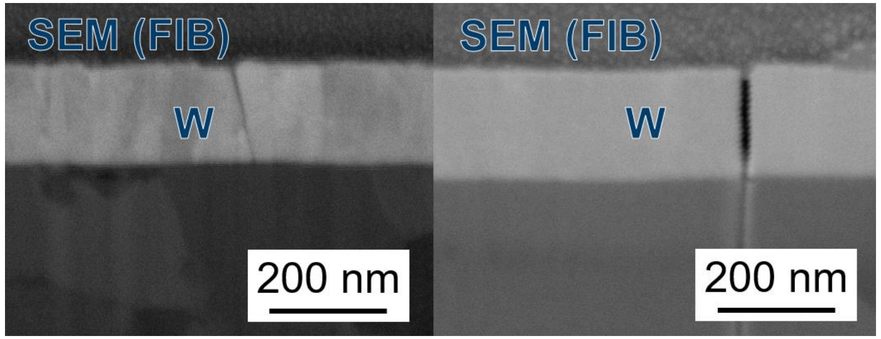
Comparison W coatings

CuCrZr_W_hot FIB/SEM after permeation measurement:



- ‘Clean’ interface: no intermediate phase
- In addition to small cracks: straight lines
- Straight cracks going completely through the W layer

Eu97_W FIB/SEM after annealing/permeation measurement:



A. Houben *et al*., NME **24** (2020), 100752

- W deposition without substrate heating
- Crack propagation during measurement (non stable measurement)
- Cracked W layer on Eurofer97: shortcuts to substrate
- Large influence on permeation flux (increase)

→ In CuCrZr_W_hot **no influence** of cracks on permeation measurement → ?

Results W coatings

Layer permeability for W in CuCrZr_W_hot:

sub: CuCrZr

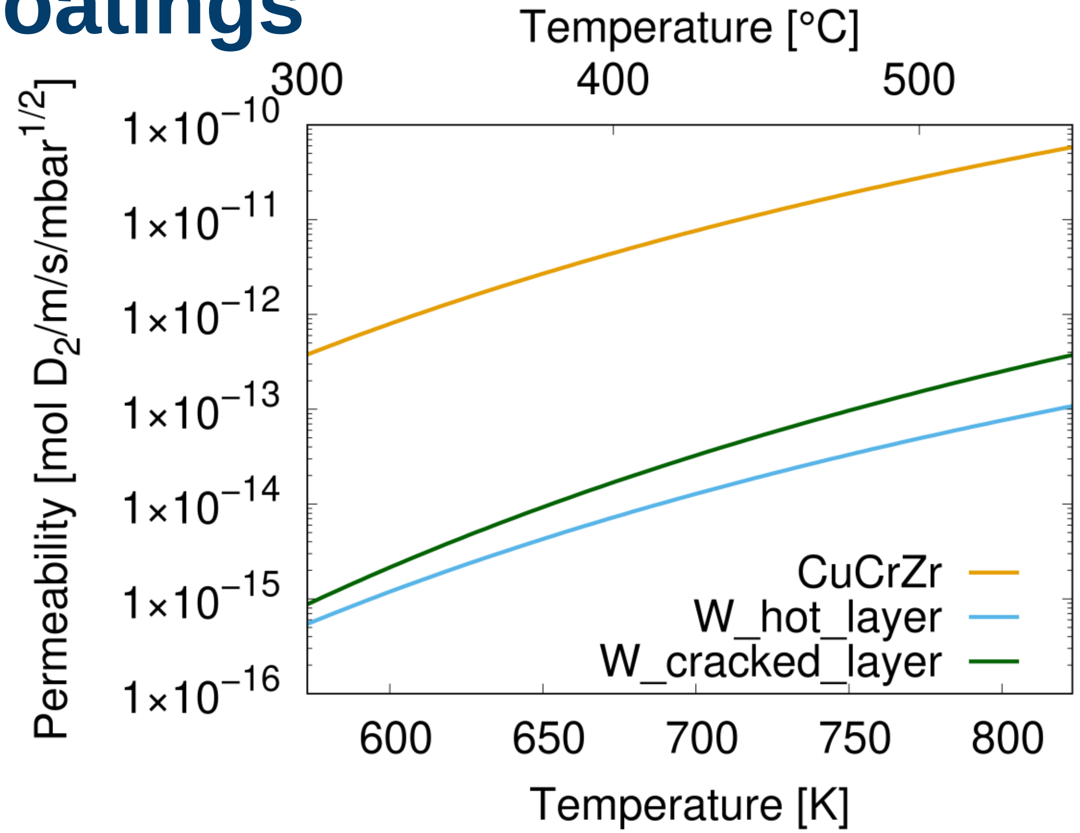
tot: CuCrZr_W_hot

$$\left.\begin{matrix} \\ \\ \end{matrix}\right\} \longrightarrow \; P_{lay}: P_0 = 2 \cdot 10^{-8} \ \frac{\text{mol}}{\text{ms}\sqrt{\text{mbar}}}$$

$$E_P = 83 \ \frac{\text{kJ}}{\text{mol}}$$

Sample	$P_0 \left[\frac{\text{mol}}{\text{ms}\sqrt{\text{mbar}}}\right]$	$E_P \left[\frac{\text{kJ}}{\text{mol}}\right]$
CuCrZr	$6(2)*10^{-6}$	79(1)
W_hot_layer	$2*10^{-8}$	83
W_cracked_layer*	$4*10^{-7}$	95

* W on Eu97: A. Houben *et al*., NME **24** (2020), 100752



→ W layer permeability is more than two orders of magnitude smaller compared to the CuCrZr permeability

→ The permeabilities of W coatings deposit on different substrates a similar (calculation of layer permeability)

Results W coatings

Layer permeability for W in CuCrZr_W_hot / Eu97_W:

Sample	$P_0 \left[\frac{\mathrm{mol}}{\mathrm{ms}\sqrt{\mathrm{mbar}}}\right]$	$E_P \left[\frac{\mathrm{kJ}}{\mathrm{mol}}\right]$
CuCrZr	$6(2)*10^{-6}$	79(1)
Eu97**	$5.7(4)*10^{-7}$	41.6(5)
W_hot_layer	$2*10^{-8}$	83
W_cracked_layer*	$4*10^{-7}$	95

* W on Eu97: A. Houben *et al.*, NME **24** (2020), 100752

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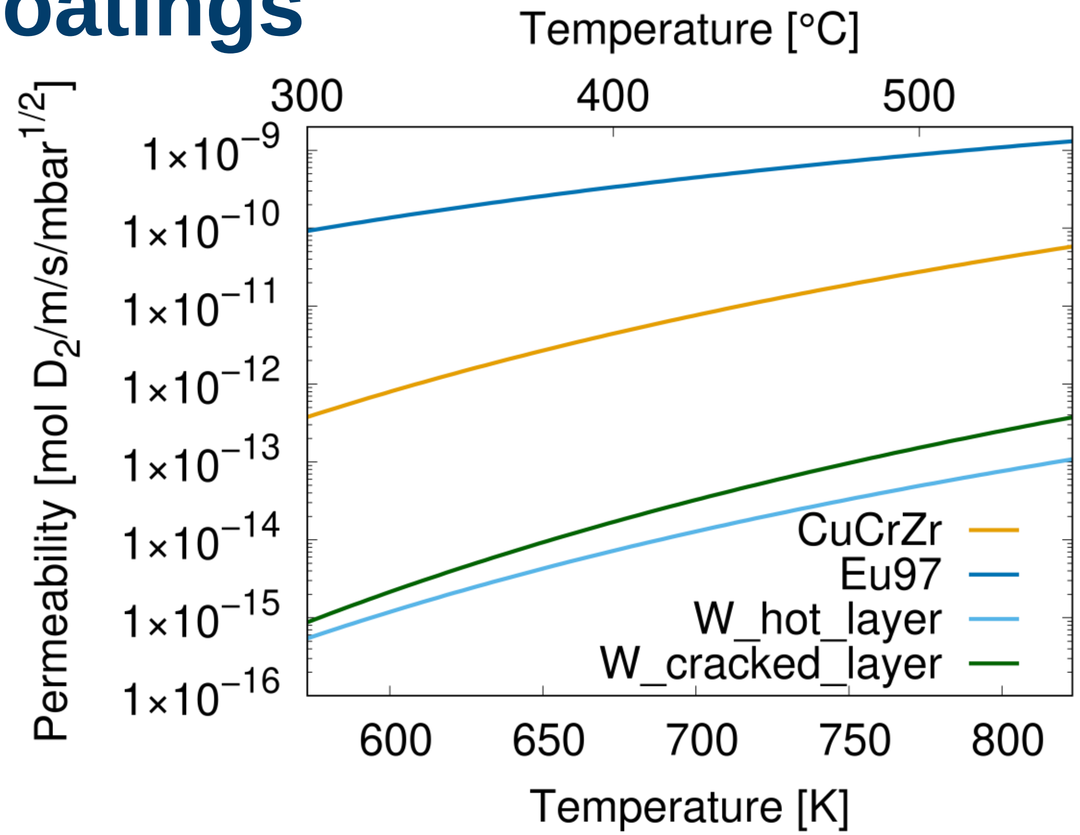


→ W layer permeability is more than two orders of magnitude smaller compared to the CuCrZr permeability

→ The permeabilities of W coatings deposit on different substrates a similar (calculation of layer permeability)

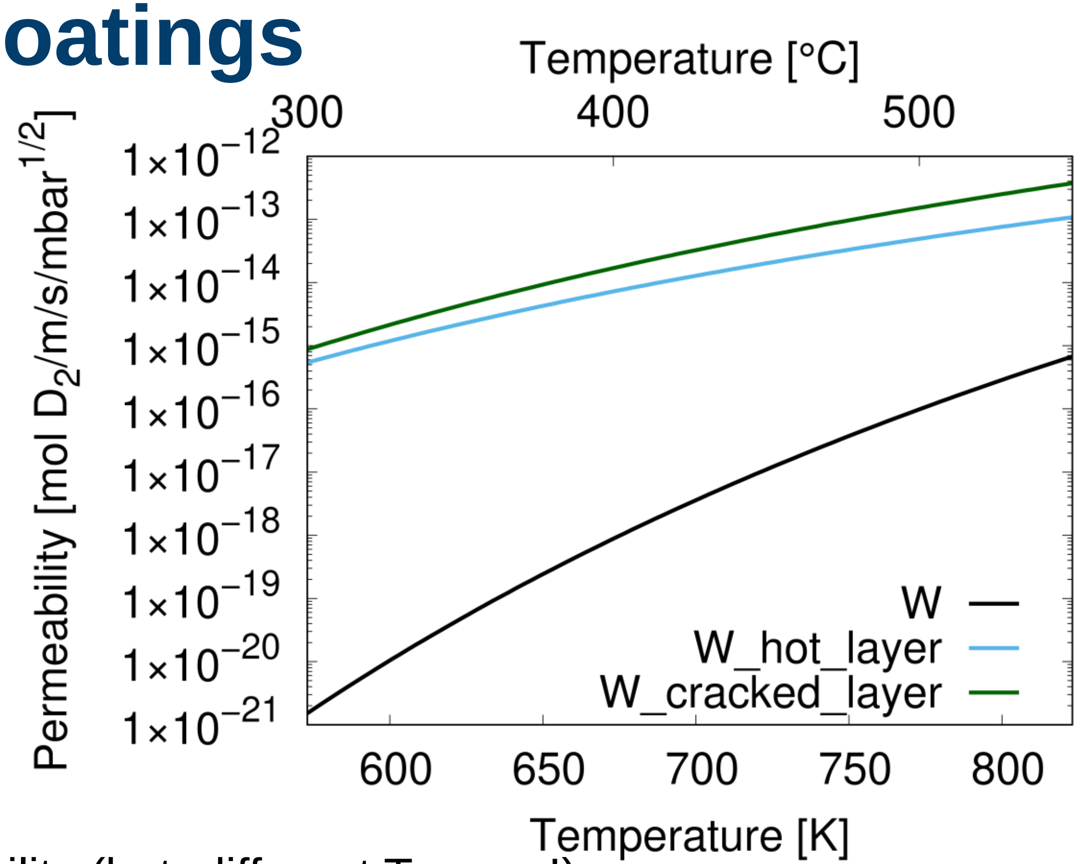
→ Strong indication that in this case the **influence of the interface is minor** as well

Results W coatings

Layer permeability for W in comparison to W bulk:

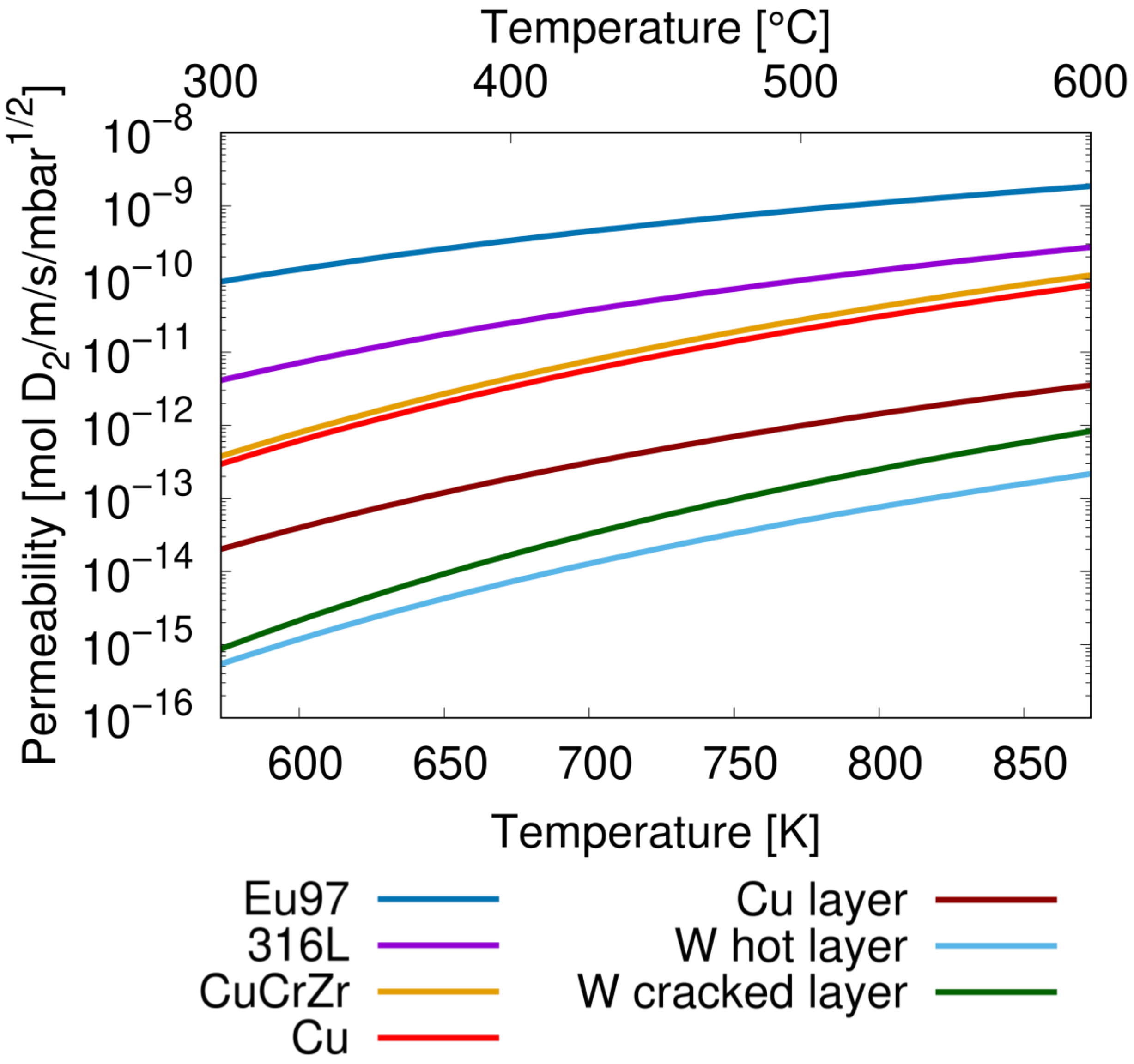
Sample	$P_0\left[\frac{\mathrm{mol}}{\mathrm{ms}\sqrt{\mathrm{mbar}}}\right]$	$E_P\left[\frac{\mathrm{kJ}}{\mathrm{mol}}\right]$
CuCrZr	$6(2)*10^{-6}$	79(1)
W*	$6*10^{-3}$	204
W_hot_layer	$2*10^{-8}$	83
W_cracked_layer	$4*10^{-7}$	95

* W bulk measured between 1100 K and 2400 K, adapted value from R. Causey et al., Comprehensive Nuclear Materials 2012, 511–549 (Frauenfelder)



- → W layer permeabilities are larger as the W bulk permeability (but: different T range!)
- → Strong indication that in this case the **influence of the interface is minor** compared to the **large influence of microstructure** on the permeability
- → Substrate heating during deposition leads to a reduction of cracks in the layer and an avoidance of crack propagation (stable permeation flux measurement, lower layer permeability)
- → Future plan for this year: same W deposition parameter (hot) for a W coated Eu97 sample

Conclusions



‘Pure’ Materials:

→ Polished samples → diffusion limited

→ Permeability of Eu97 higher than 316L

→ Permeability Cu / CuCrZr similar

Coated Substrates:

→ Influence of the interface is minor

→ **Influence of the microstructure is large**

→ Permeability of layer different to bulk permeability

→ Comparison of coatings deposited on different substrates is possible

→ Increase of permeability due to cracks in layer

→ Substrate heating during deposition leads to a stable coating

Future Plans:

→ W hot coated Eurofer97

→ Permeation measurements on p-damaged Eurofer97

Thank you for your attention!

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