Karlsruhe Institute of Technology
Karlsruhe NANO MICRO Facility
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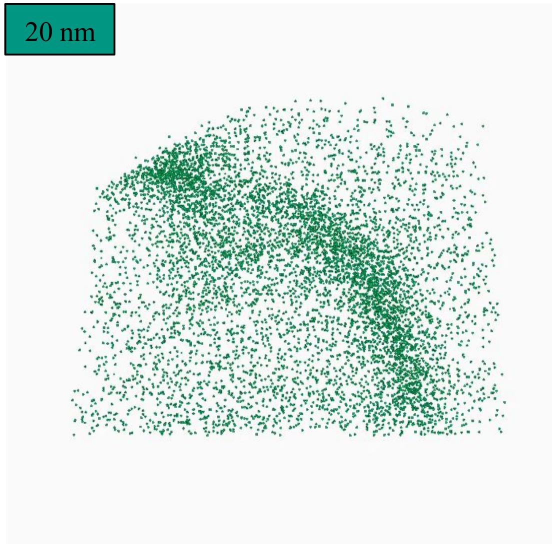
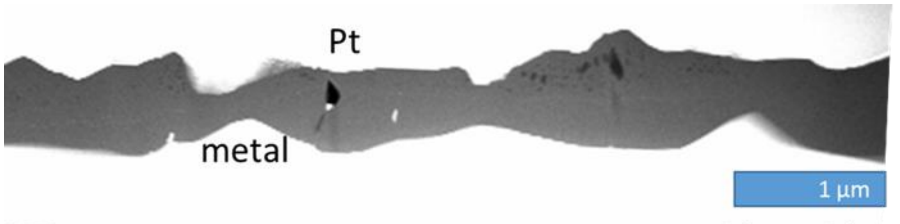
Transport along grain boundaries through alumina investigated by atom probe tomography

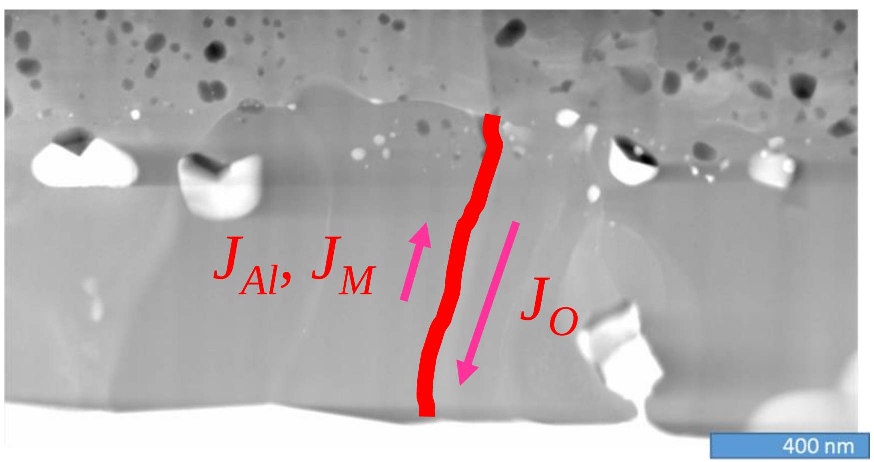
Torben Boll*, Kinga A. Unocic, Bruce A. Pint, Krystyna Stiller



Atom Probe Tomography:
Zr at a grain boudary in Al_2O_3,
Each dot represents one atom,
Al and O atoms are not displayed

TEM of typical oxide on NiAl



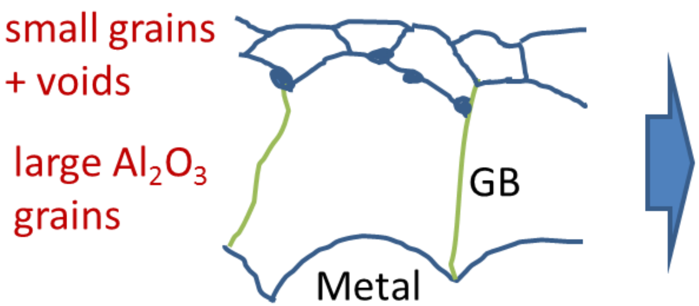


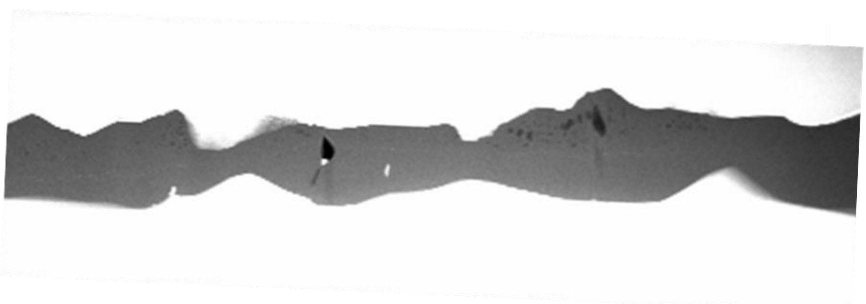
- Protective Al_2O_3 coating on NiAl-alloy
- O (and all other elements) in α-alumina diffuse mostly via grain boundaries (GBs)
- Minor outward diffusion of metal
- Decoration of GBs will influence the diffusion and thus oxidation
- Apparently grows inwards

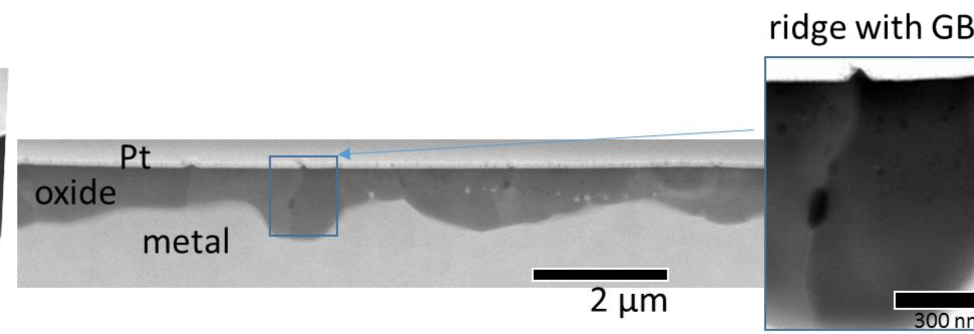
Material	*Ni* at.%	*Al* at.%	*Zr* ppma	*Hf* ppma	*N* ppma	*C* ppma	*Sxx* ppma	*O* ppma	*B* ppma	*Cr* ppma
Zr-doped	49.95	49.99	520	0	0	0	3	48	30	0
Hf-doped	49.83	50.07	0	480	30	36	0	43	0	100

Outward diffusion: Exp. idea

a) After 1st exposure

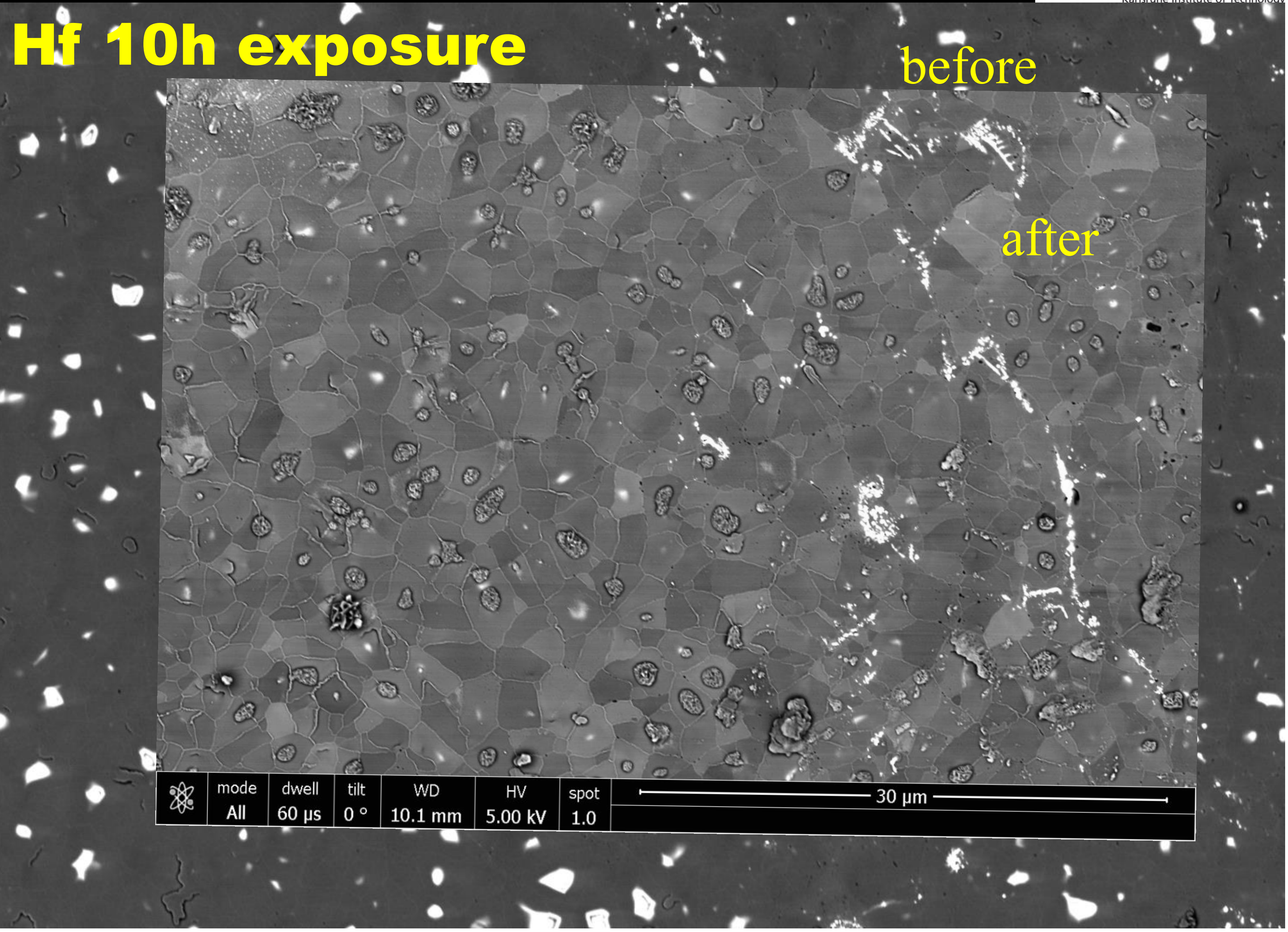




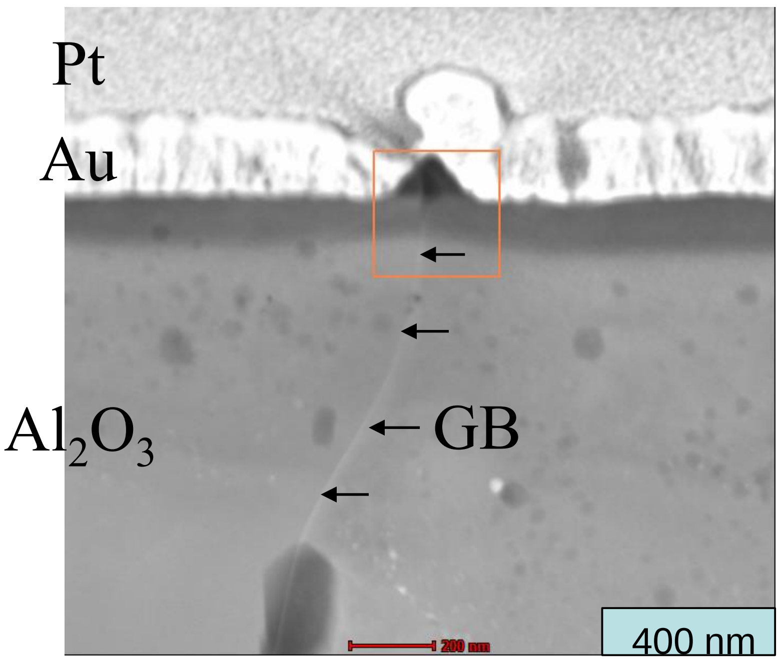


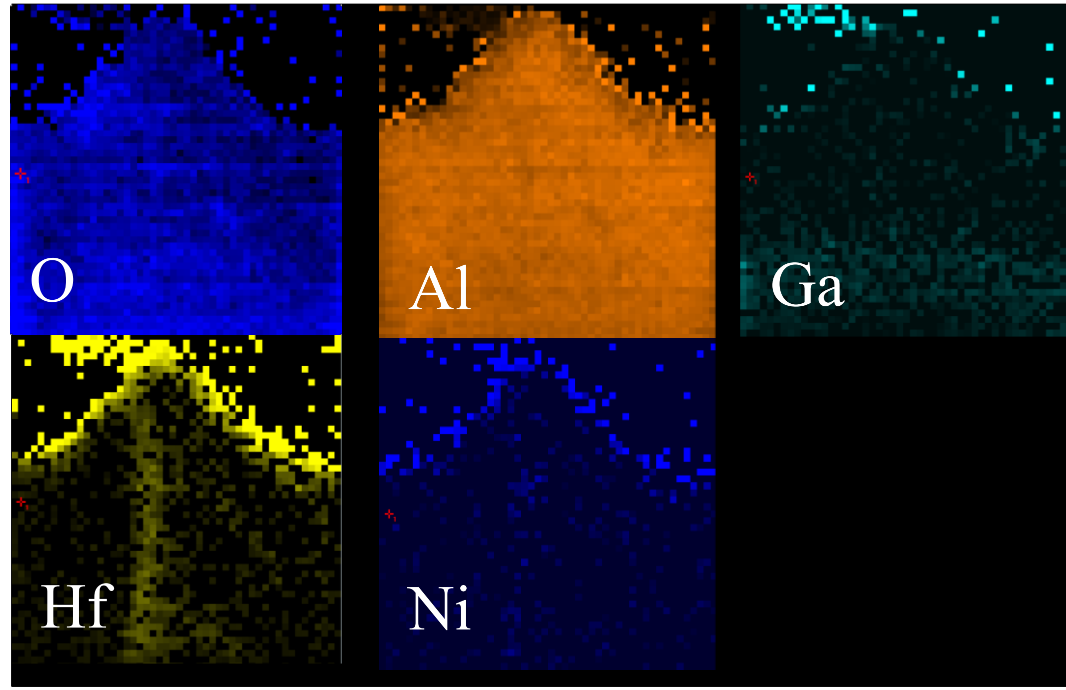
[1] V. K. Tolpygo and D. R. Clarke, *Mater. High Temp.*, vol. 20, no. 3, pp. 261–271, 2003
[2] J. a. Nychka and D. R. Clarke, *Oxid. Met.*, vol. 63, no. 5–6, pp. 325–352, 2005

Hf 10h exposure



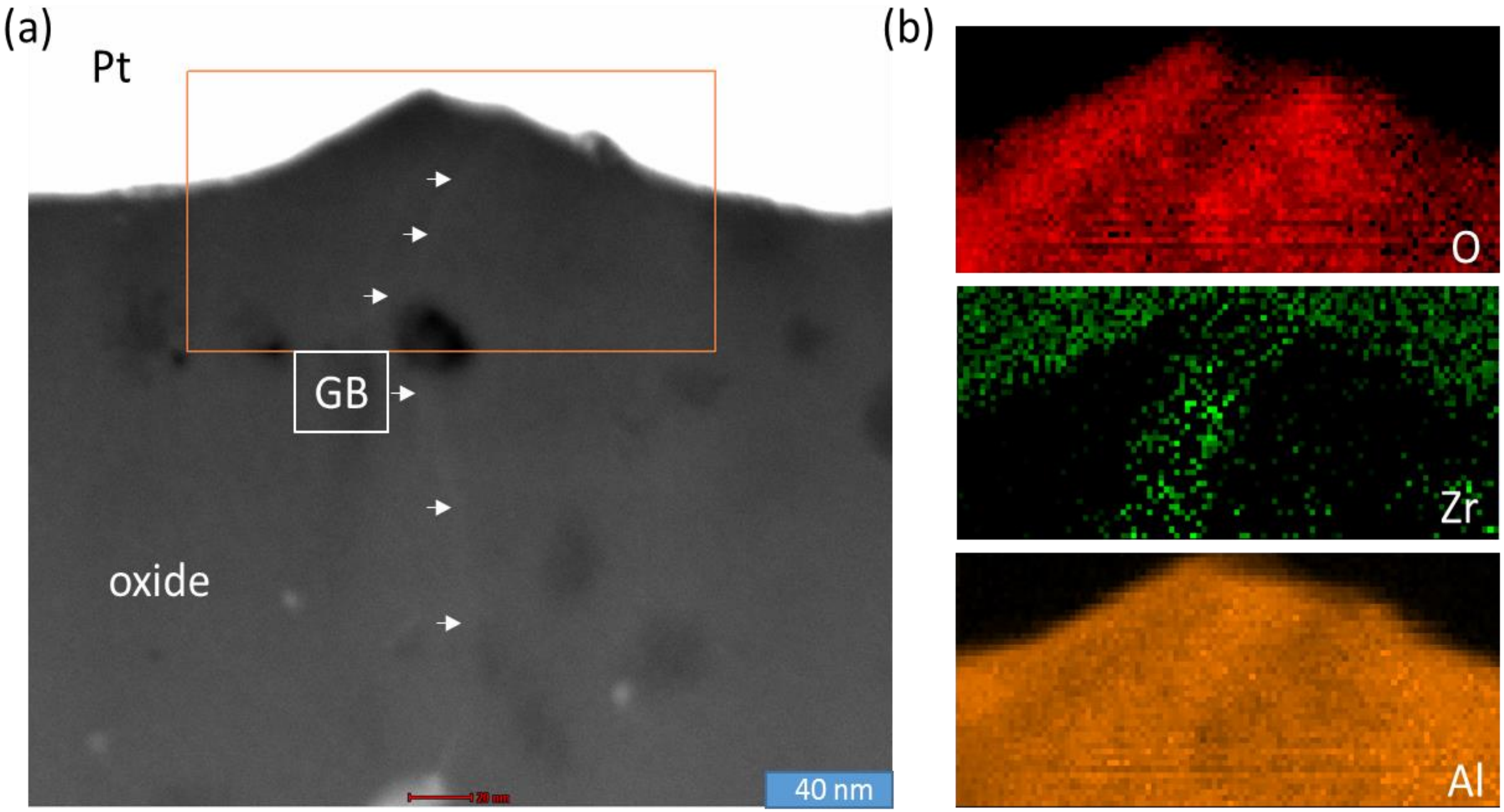
TEM of mech. pol. Hf sample





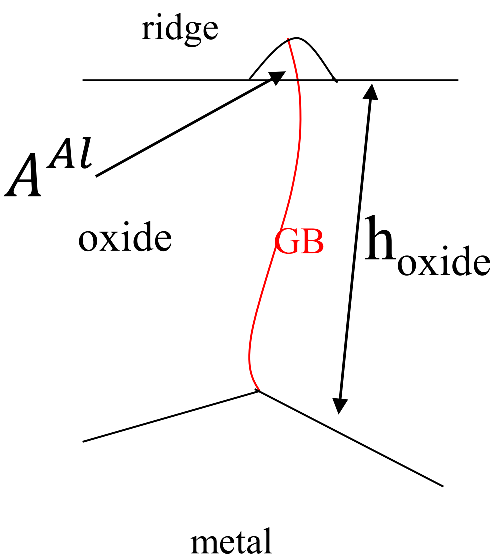
- No Ga contamination
- GB enriched with Hf and some Ni

TEM of Zr sample



- Zr enriched at the GB

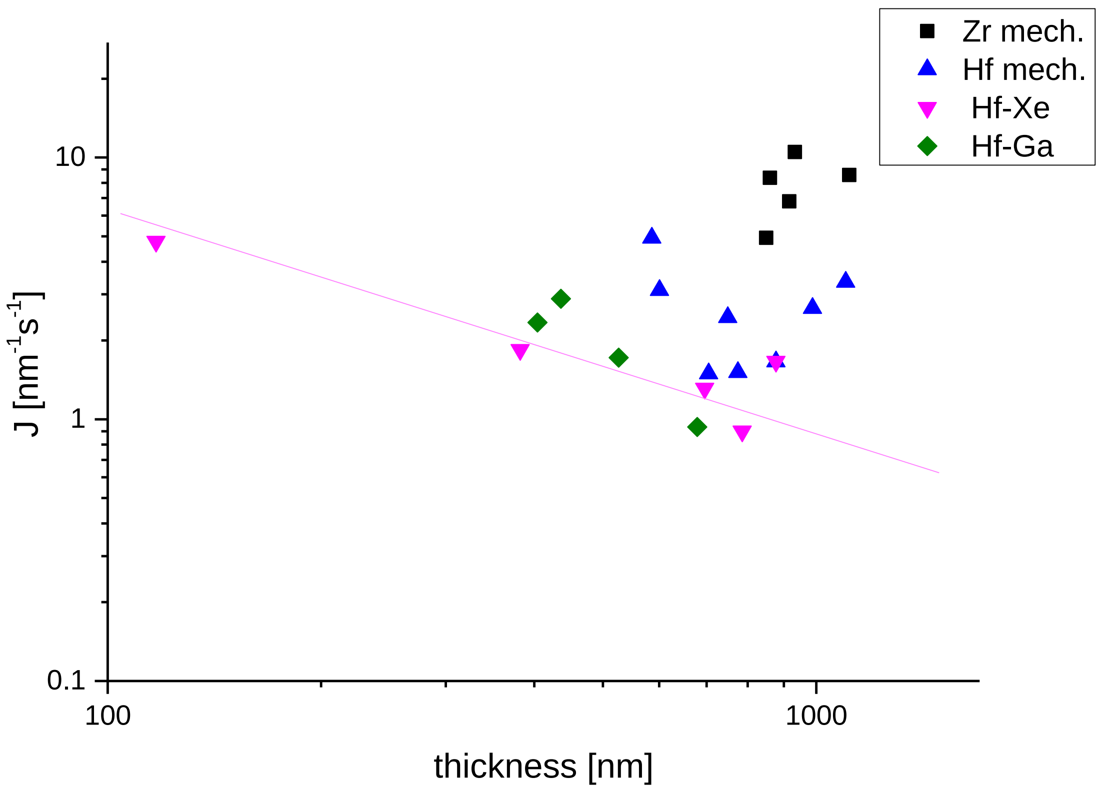
How to calculate the flux



- Calculate the flux
  - Number of diffused Al-atoms N_{GB}^{Al}
  - Exposure time Δt (10h)
- Calculate number of atoms
  - Volume of ridge V^{Al}=A^{Al} L_{GB}
  - Length of GB L_{GB}(not height!)
  - Cross section area of ridge A^{Al}
  - Volume of Al_2O_3 unit cell: V_u=2.54 10^{-22} cm^3
  - Number of Al atoms per unit cell: 12

$$J_{Al} = \frac{N_{GB}^{Al}}{L_{GB}\Delta t} \qquad N_{GB}^{Al} = \frac{12\, V^{Al}}{V_u} \qquad J_{Al} = \frac{12\, A^{Al}}{V_u}$$

Flux of Al through GBs at 1100°



- Mech. polishing enhances ridge growth
- Zr allows higher outward flux than Hf

Should follow Fick's 1. law (assuming h_{oxide} is constant)

$$J_{GB}^{Al} = -\frac{A}{h_{oxide}}$$

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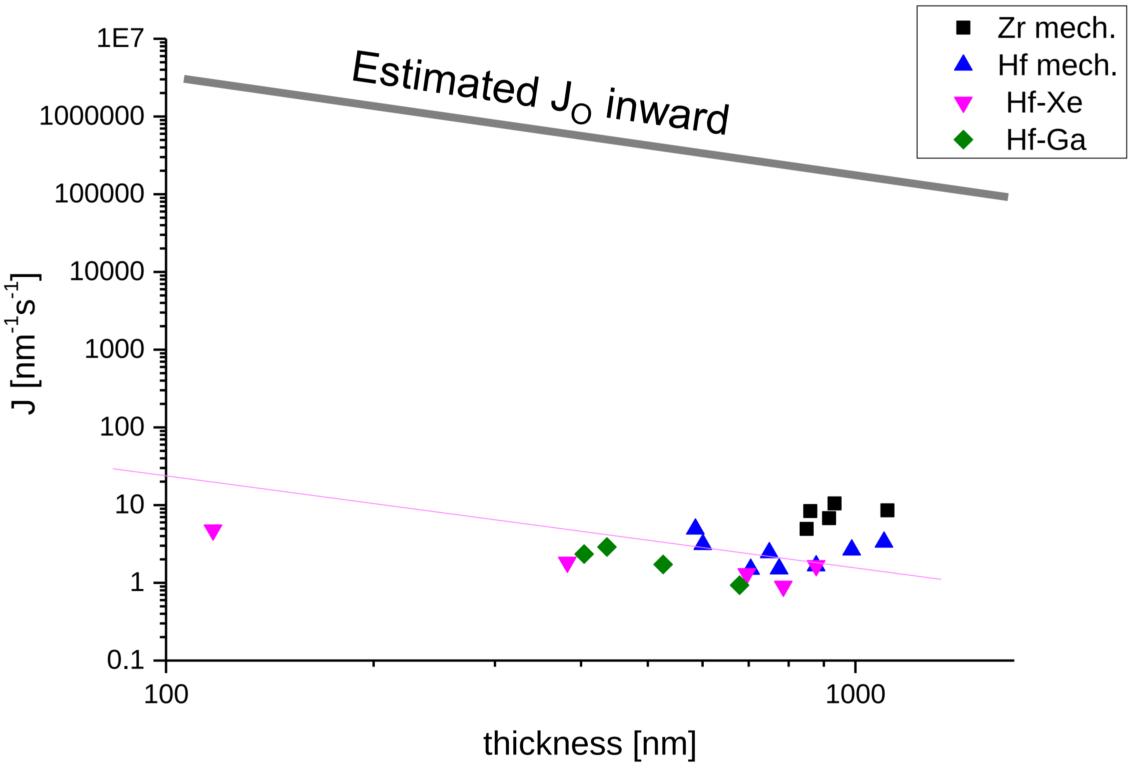
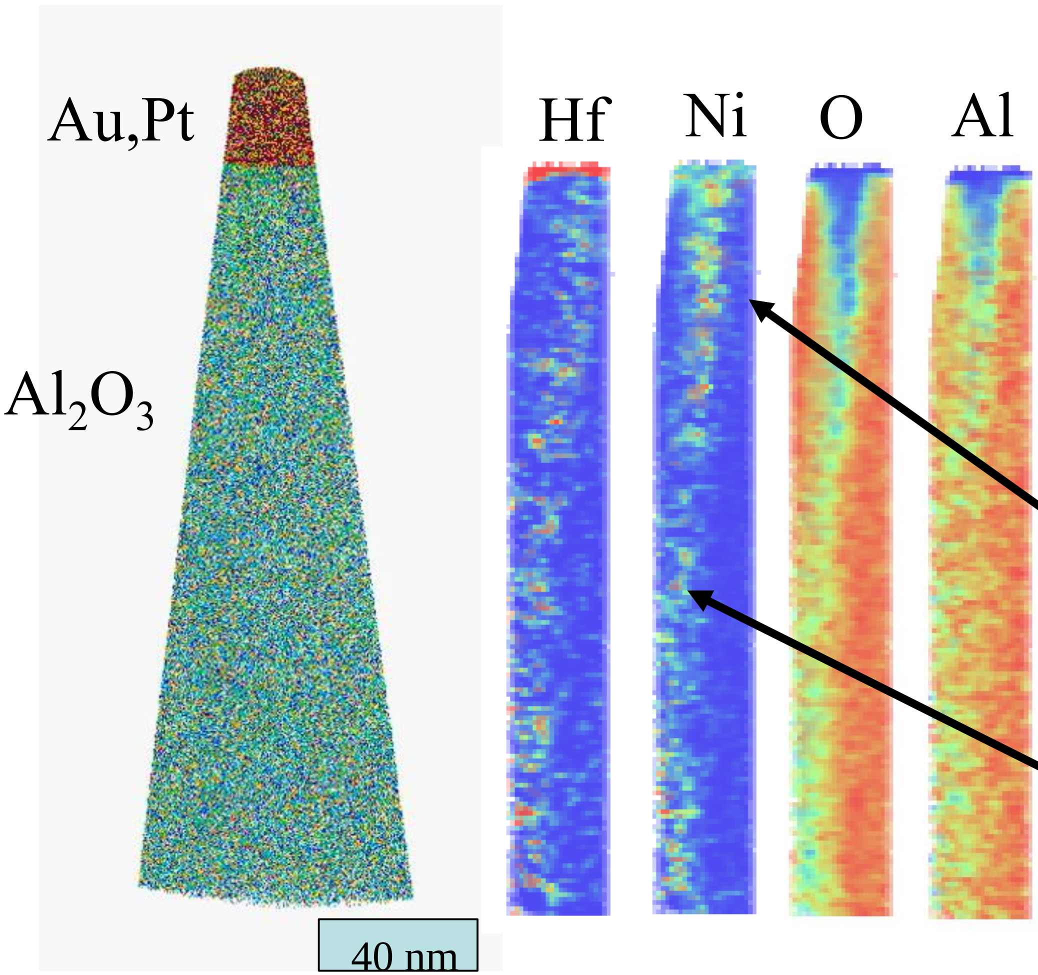
Flux of Al through GBs at 1100°



- Mech. polishing enhances ridge growth
- Zr allows higher outward flux than Hf
- Inward flux six orders of magnitude larger

Should follow Fick's 1. law (assuming h_{oxide} is constant) $J_{GB}^{Al} = -\frac{A}{h_{oxide}}$

APT of Hf sample

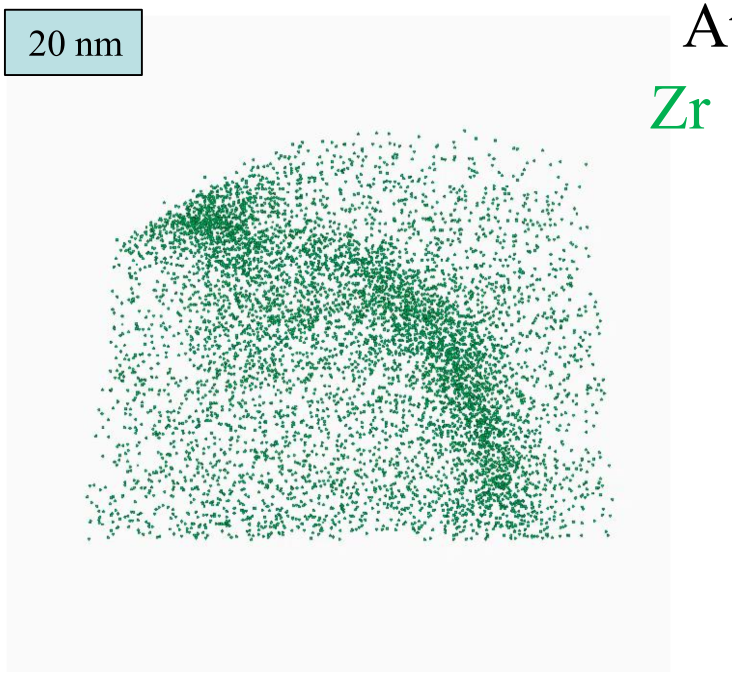


- Protective Au,Pt coating
- GB with Hf, Ni
- Ni enriched at surface
- Gibbsian excess Γ (Number of additional atoms per area in GB):

Hf: 0.5 nm^{-2}
Ni: 2.6 nm^{-2}

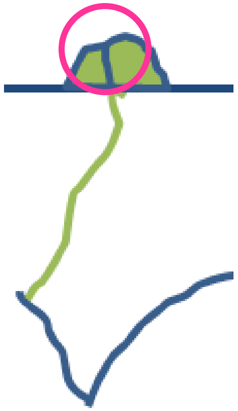
Hf: 0.35 nm^{-2}
Ni: 0.59 nm^{-2}

APT of Zr sample



At the ridge

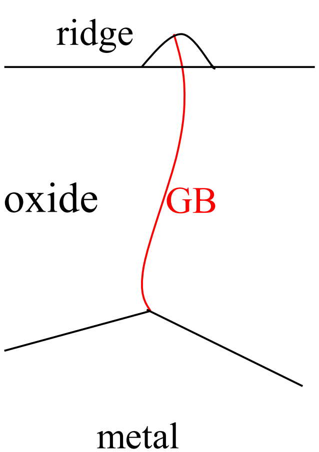
- Protective Ag on top of ridge-GB
- No Ni found
- Γ_{Zr}: 2.5 nm^{-2}

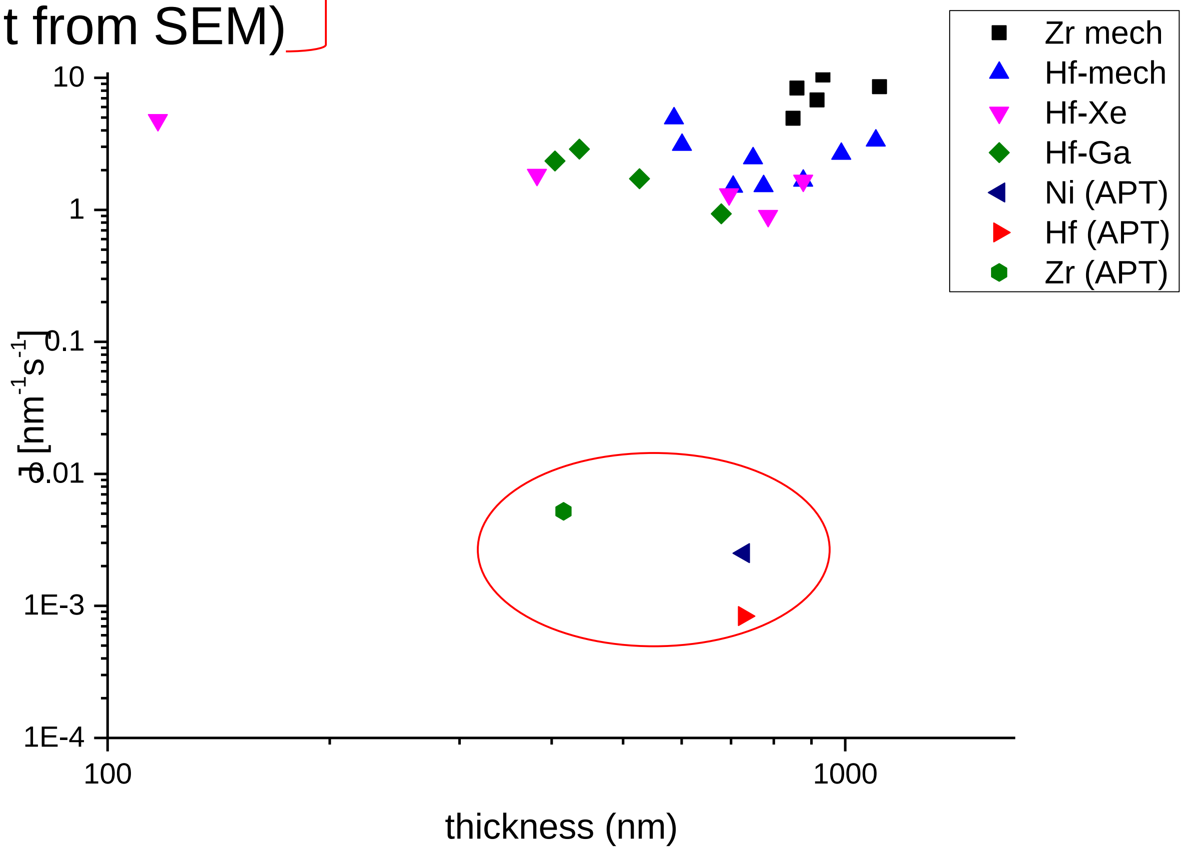


Outward flux of Ni, Hf, Zr

- Outward flux into ridge GB
- Gibbsian excess
- Additional GB length (ridge height from SEM)
- $J_X = \Gamma_X \, h_{ridge}$

→ amount of diffused material





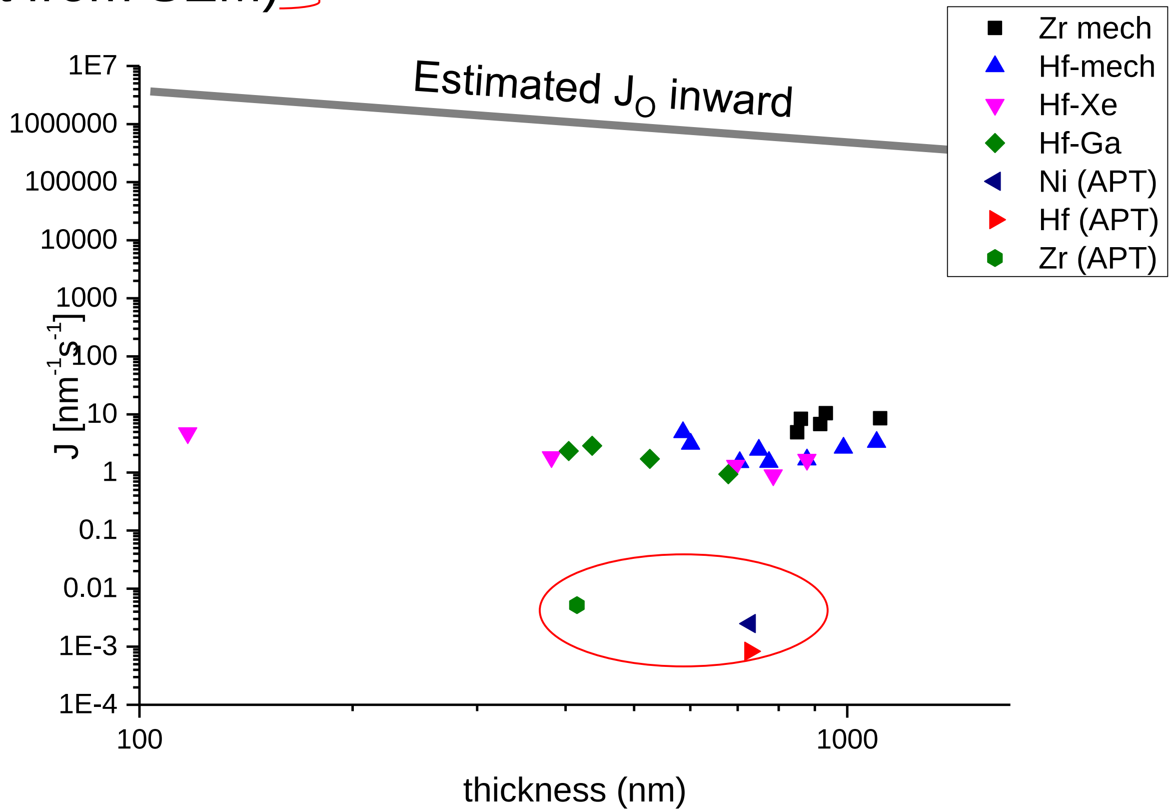
Outward flux of Ni, Hf, Cr

- Outward flux into ridge GB
- Gibbsian excess
- Additional GB length (ridge height from SEM)

→ amount of diffused material

- $J_X = \Gamma_X h_{ridge}$

$J_O >> J_{Al} >> J_{Hf,Ni,Zr}$



Conclusions

- Outward Diffusion of Al along Al_2O_3 GBs is observed by STEM
  Mechanical polishing introduces defects that promote diffusion
  - Hf reduces Al-outward diffusion stronger than Zr

- Zr is enriched at GBs
- Hf is enriched at GBs

→ Outward diffusion of Zr, Hf

- Ni is found at the GB and at the top of the ridge in the Hf sample

→ Outward diffusion of Ni

- $J_O \sim 10^6\ nm^{-1}s^{-1} >> J_{Al} \sim 1\ nm^{-1}s^{-1} >> J_{Hf,Ni,Zr} \sim 10^{-3}\ nm^{-1}s^{-1}$

Thank you for your attention

You also want APT results: knmf.kit.edu, or contact me
KNMF grants APT time to suitable projects

Acknowledgements
For help with 2nd exposure and sputter coating:
Patrik Alnegren