Outward diffusion through protective Alumina on NiAl-alloys

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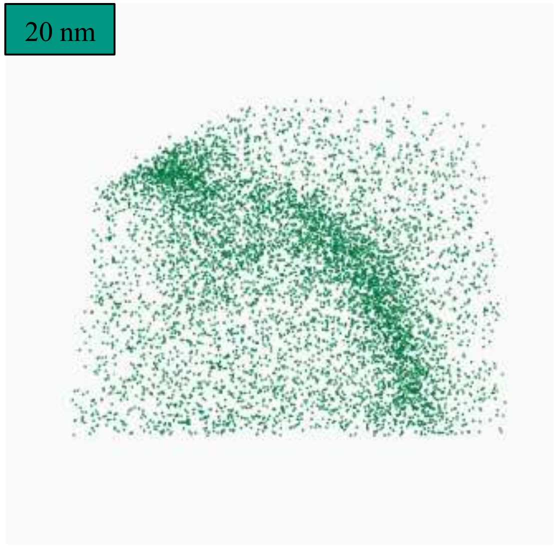
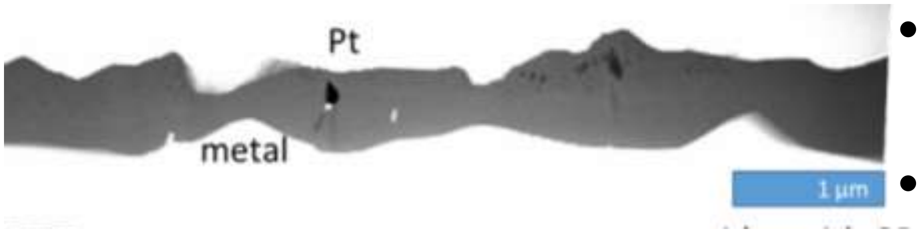
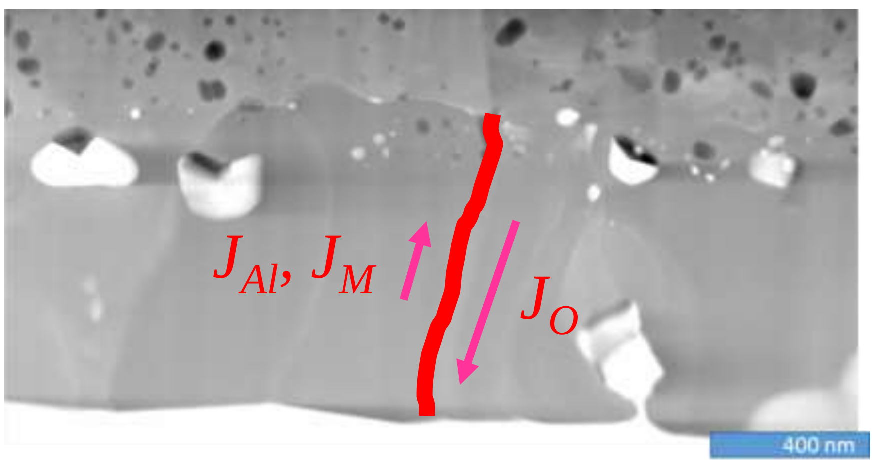


Atom Probe Tomography:
Zr at a grain boudary in Al_2O_3,
Each dot represents one atom,
Al and O atoms are not displayed

Phoenix, 14.03.2018

TEM of typical oxide on NiAl

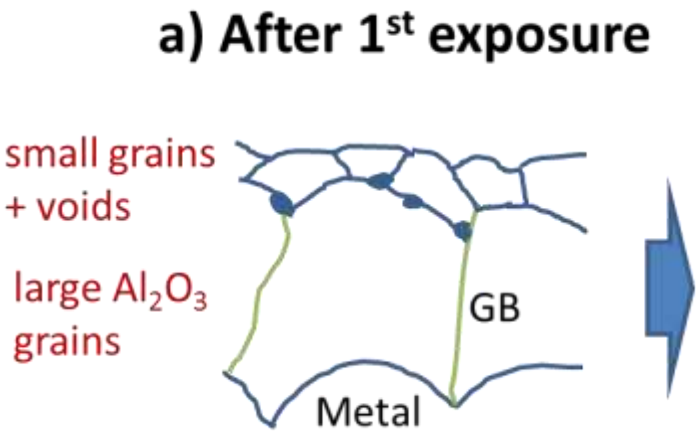


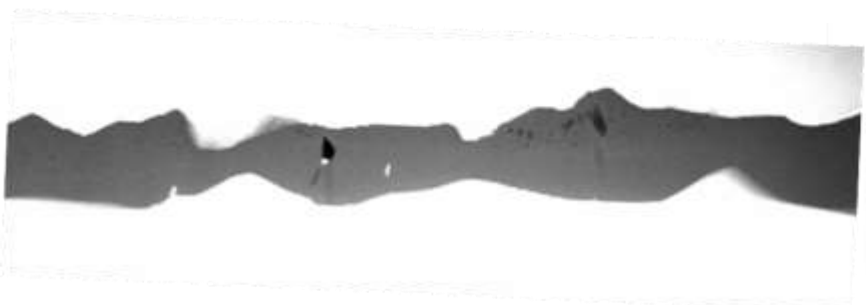


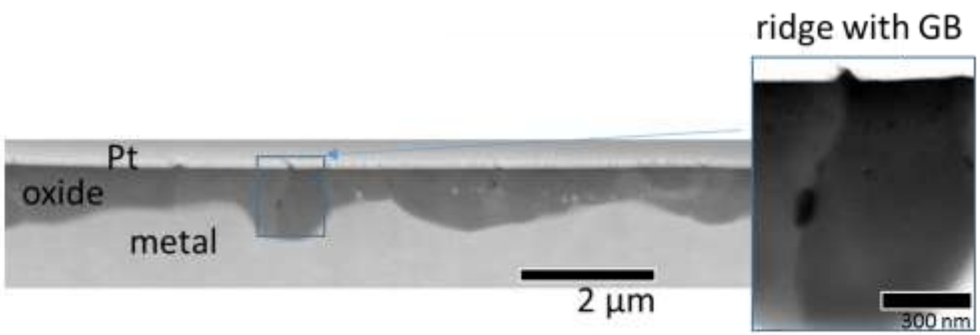
- Protective Al_2O_3 coating on NiAl-alloy
- O (and all other elements) in α-alumina diffuse mostly via grain boundaries (GBs)
- Minor outward diffusion of metal
- Decoration of GBs will influence the diffusion and thus oxidation
- Apparently grows inwards

Material	Ni at.%	Al at.%	Zr ppma	Hf ppma	C ppma	S ppma	Cr ppma
Zr-doped	49.95	49.99	520	0	0	3	0
Hf-doped	49.83	50.07	0	480	36	<3	100
undoped	49.9	50.1		<1	40	<4	<100

Outward diffusion: Exp. idea

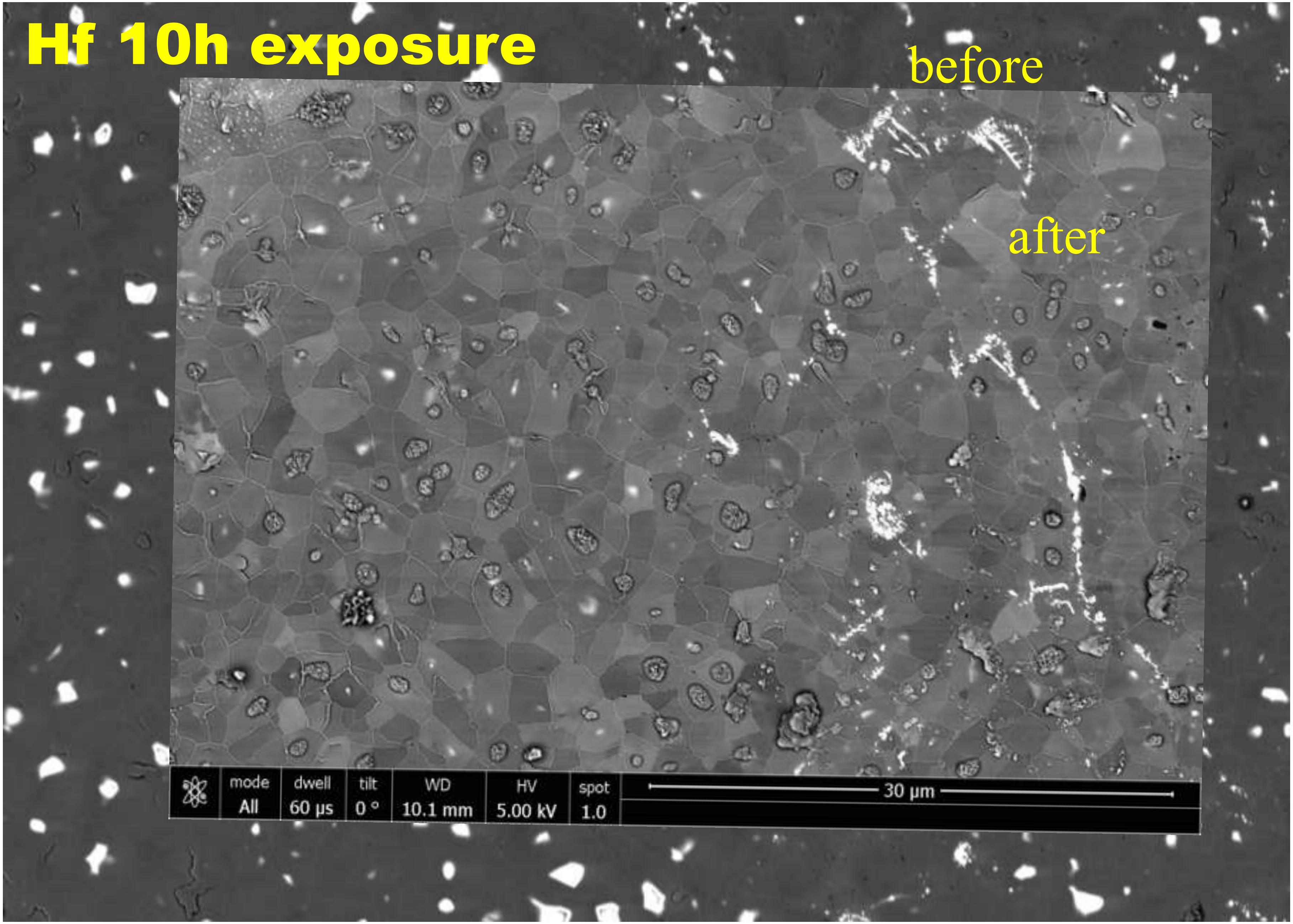




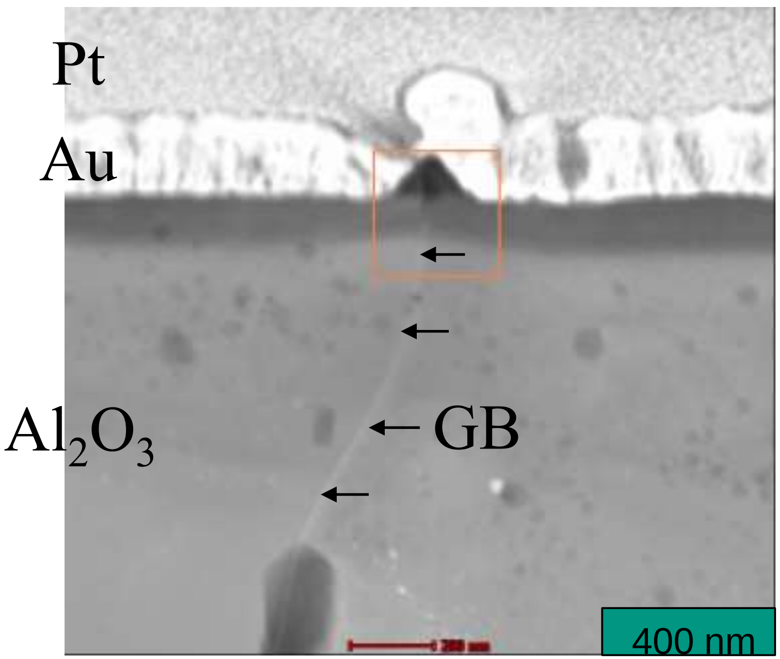


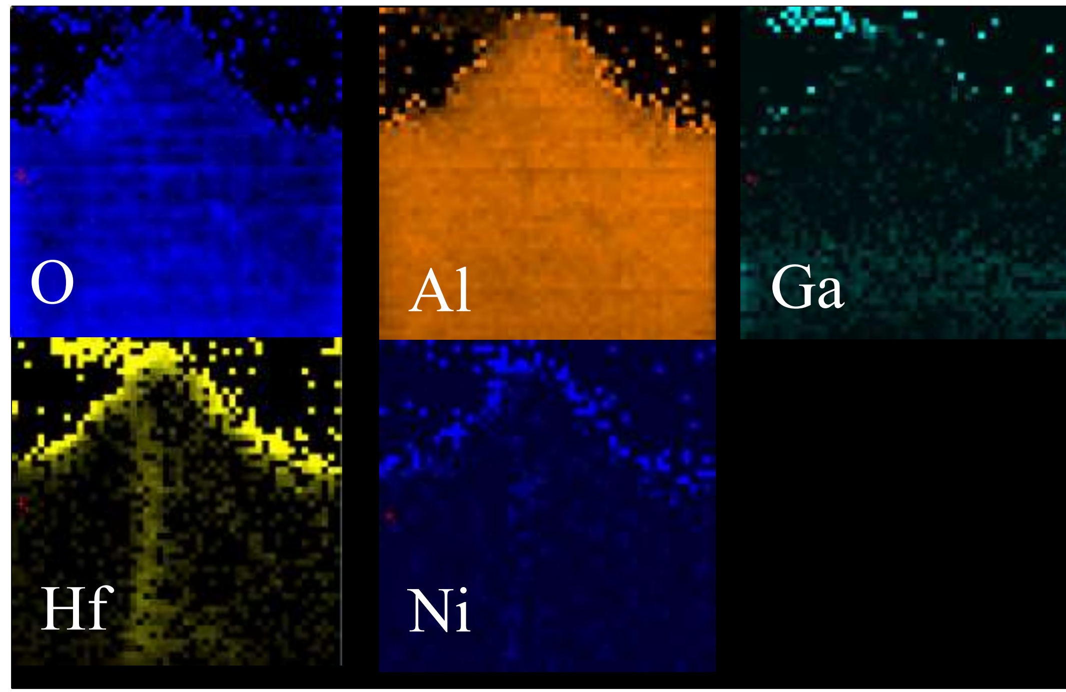
[1] V. K. Tolpygo and D. R. Clarke, *Mater. High Temp.*, vol. 20, no. 3, pp. 261–271, 2003
[2] J. a. Nychka and D. R. Clarke, *Oxid. Met.*, vol. 63, no. 5–6, pp. 325–352, 2005

Hf 10h exposure



TEM of mech. pol. Hf sample





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

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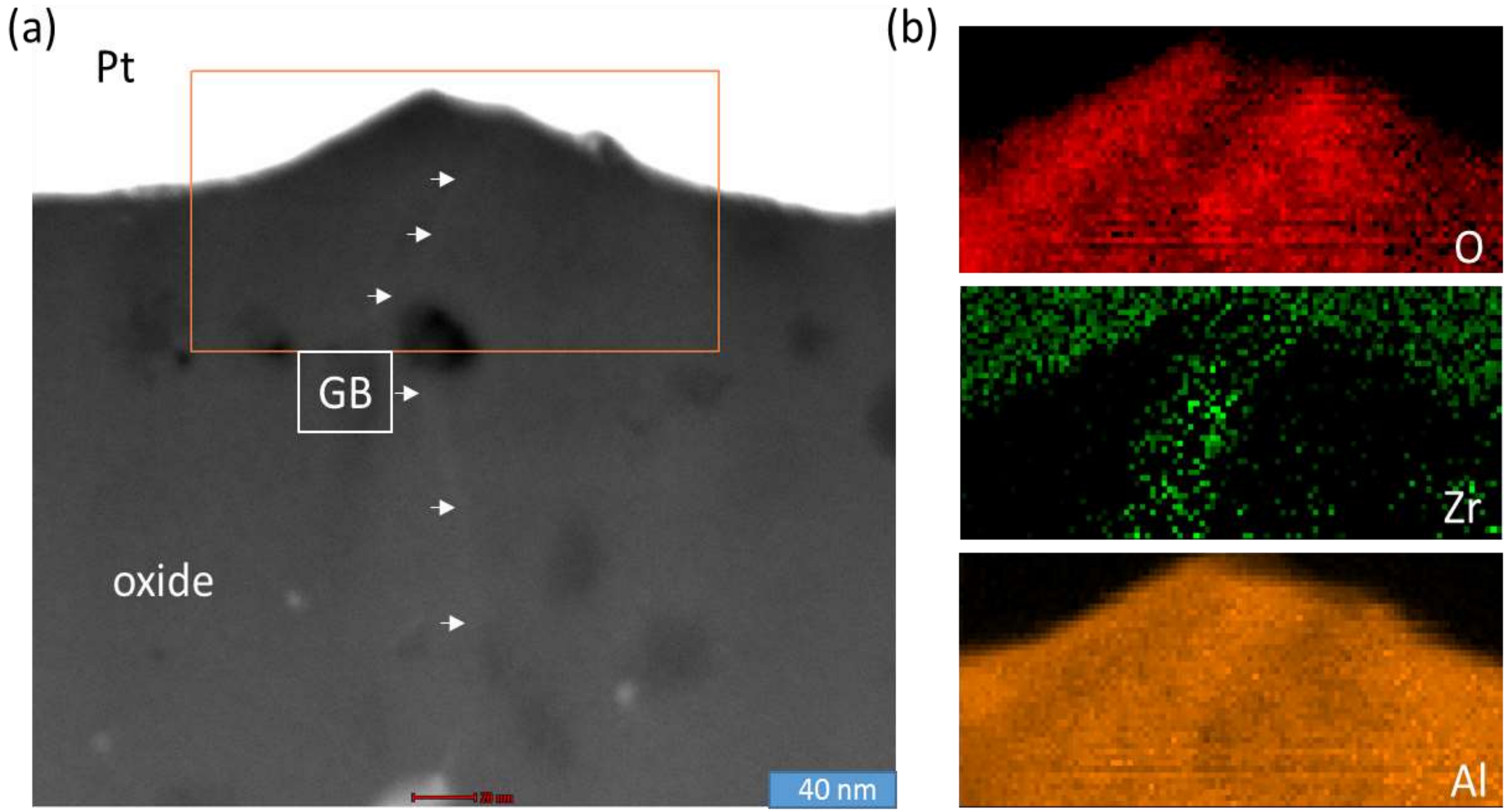
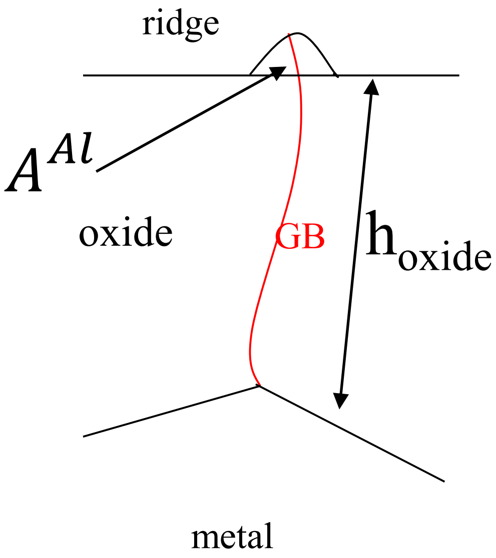
TEM of Zr sample



- 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

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

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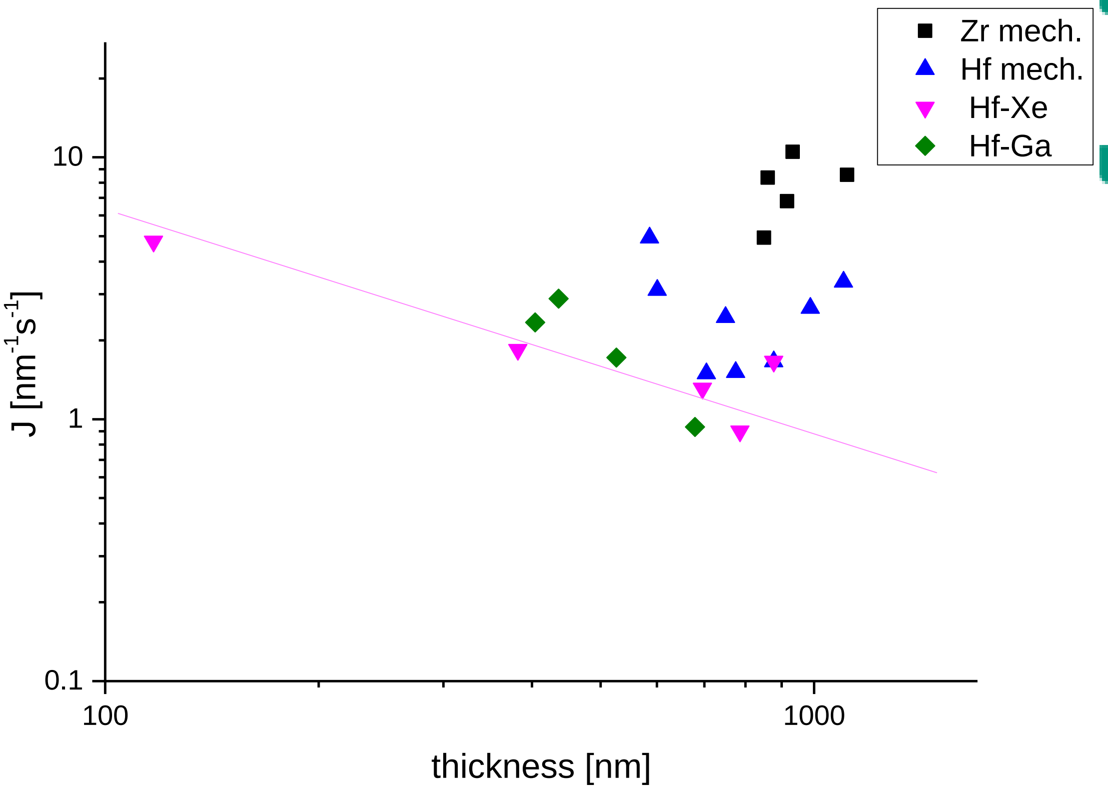
Flux of Al through GBs at 1100°



- 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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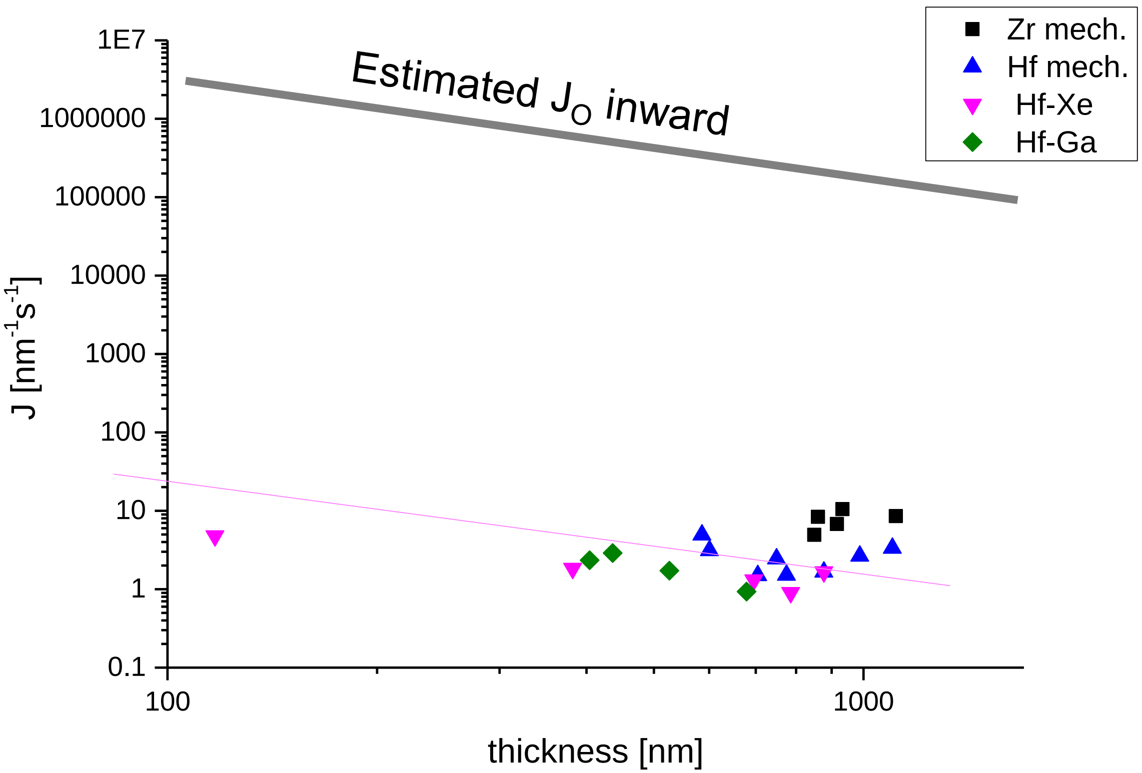
Flux of Al through GBs at 1100°



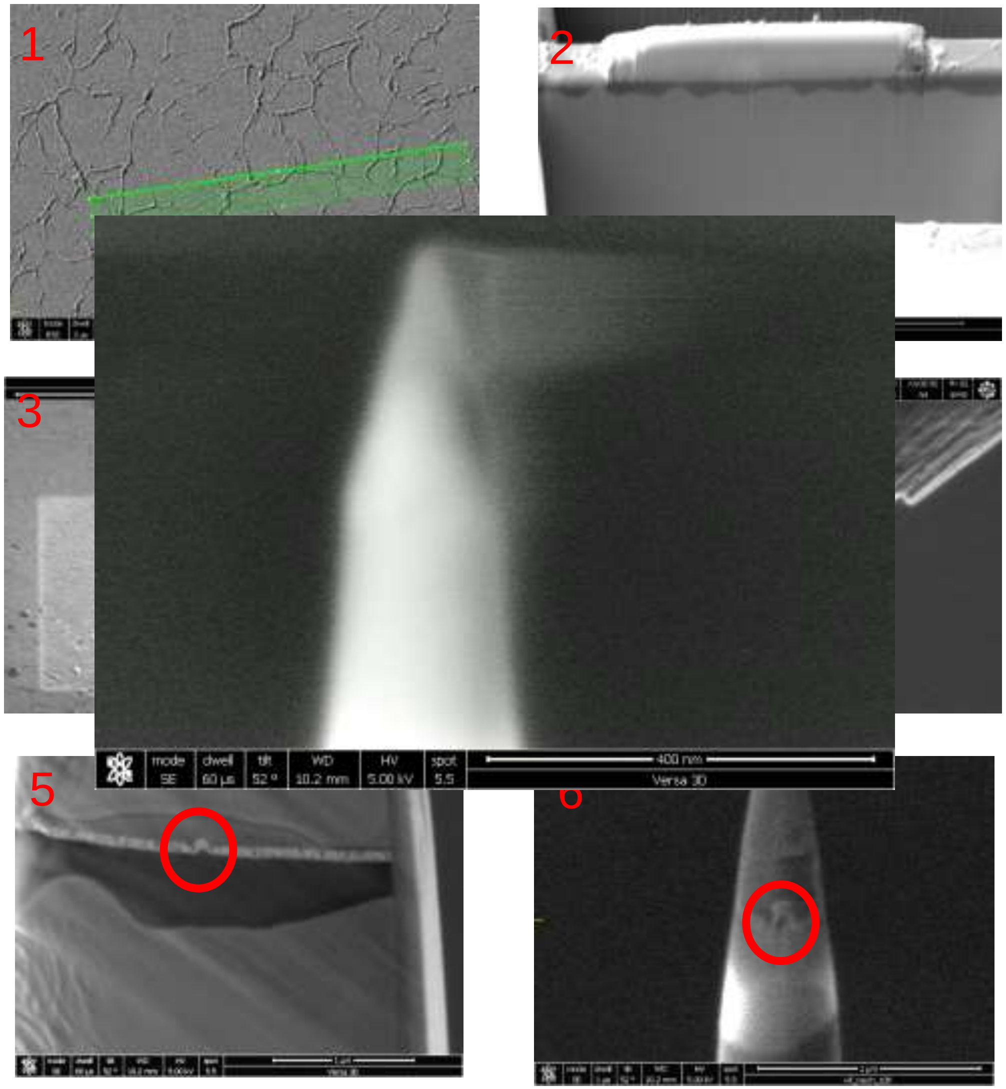
- Mech. polishing enhances ridge growth
- Zr allows higher outward flux than Hf
- Inward flux six orders of magnitude larger

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

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

[1] T. Boll, K. A. Unocic, B. A. Pint, A. Mårtensson, and K. Stiller, "Grain Boundary Chemistry and Transport Through Alumina Scales on NiAl Alloys," *Oxid. Met.*, pp. 1–11, 2017.

Sample preparation of surface features with FIB



- Protective sample coating (Au, Ag)
- Mark area with Pt, deposit 2 µm Pt on 2x10 µm
- Cut lamella
- Lift out
  - Attach lamella to OP
  - Cut lamella loose
  - Attach to micro tip
  - Cut loose
- Find feature (ridge)
- Annular milling at feature (ridge) while controlling position

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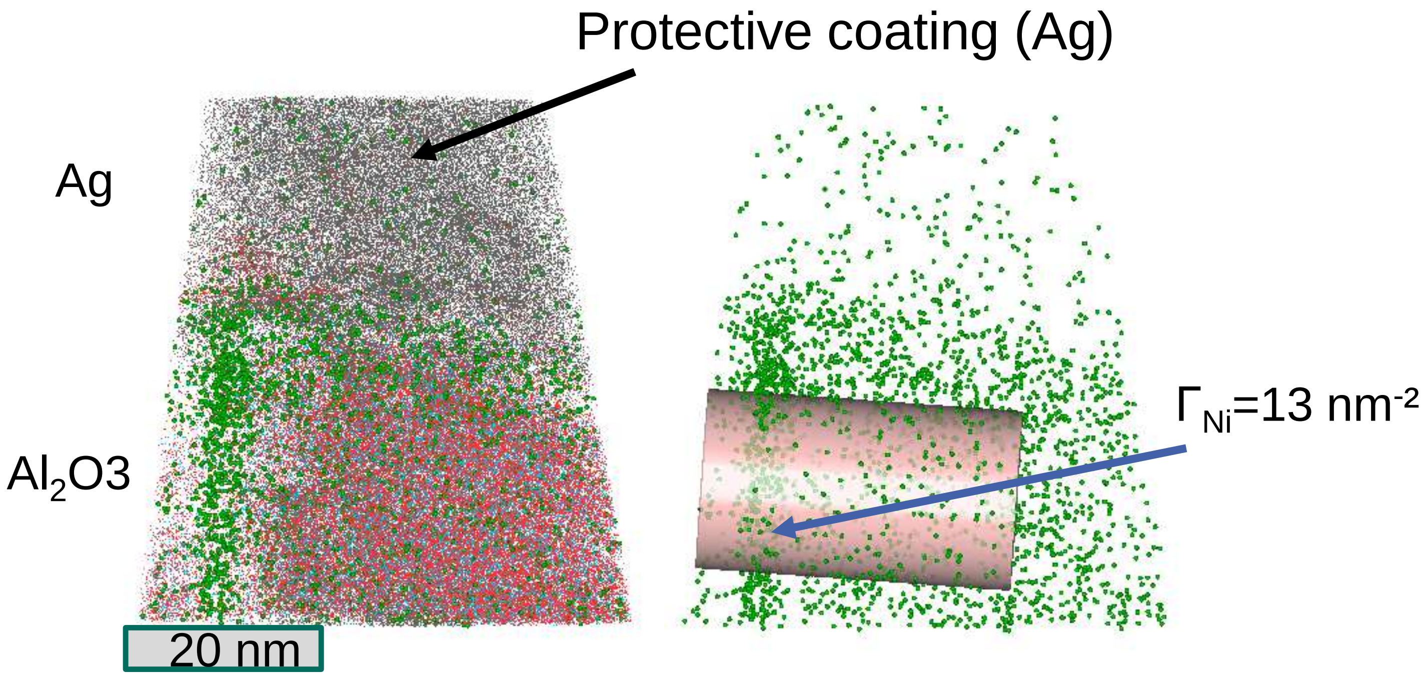
Undoped NiAl



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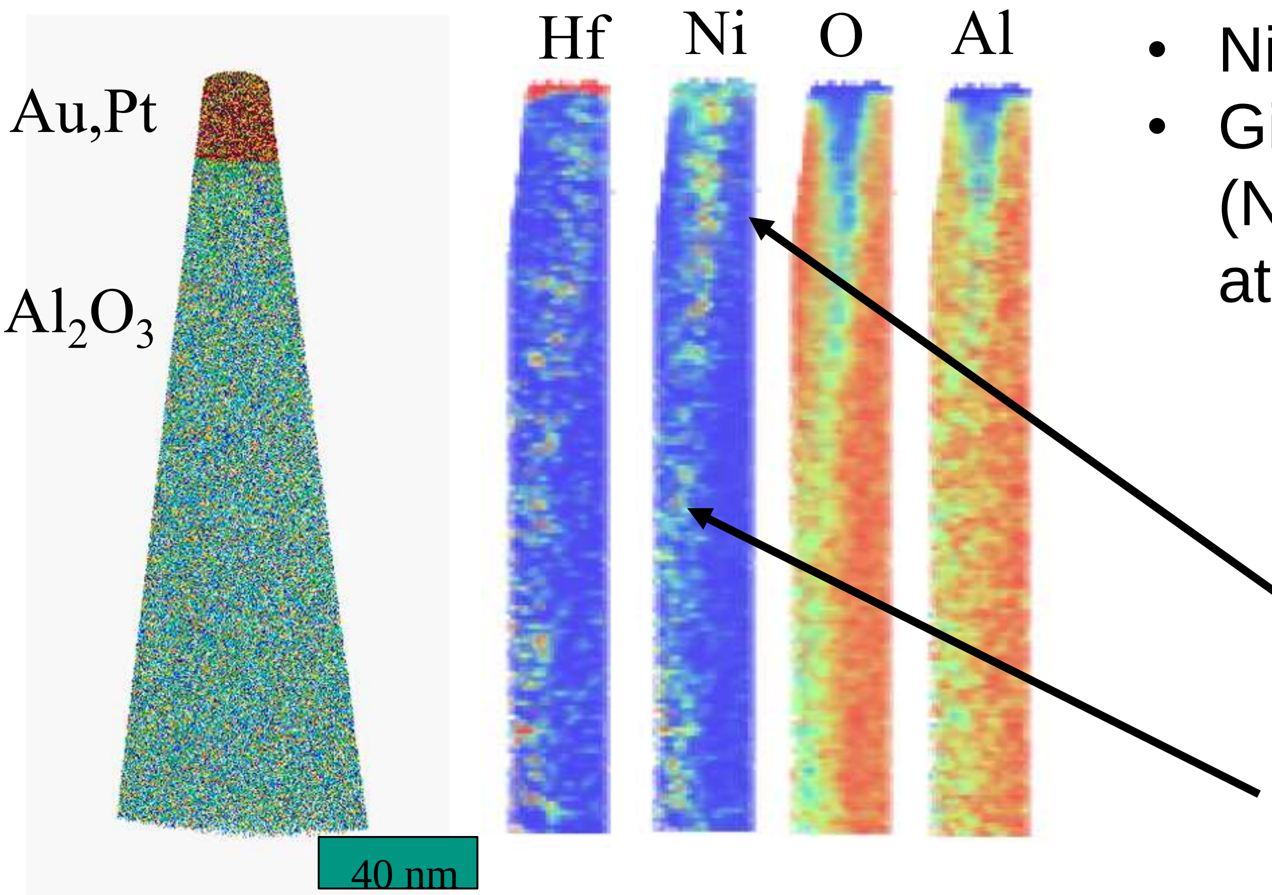
APT of Hf sample

- 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}

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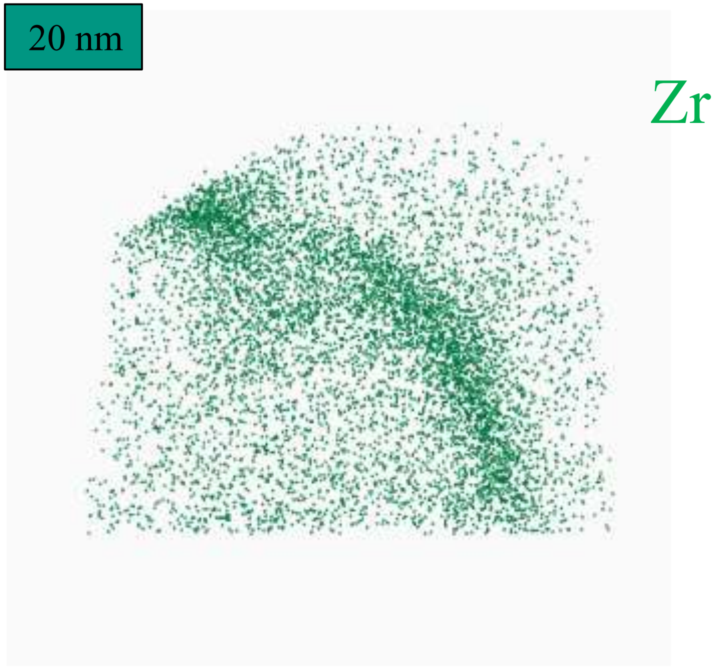
APT of Zr sample



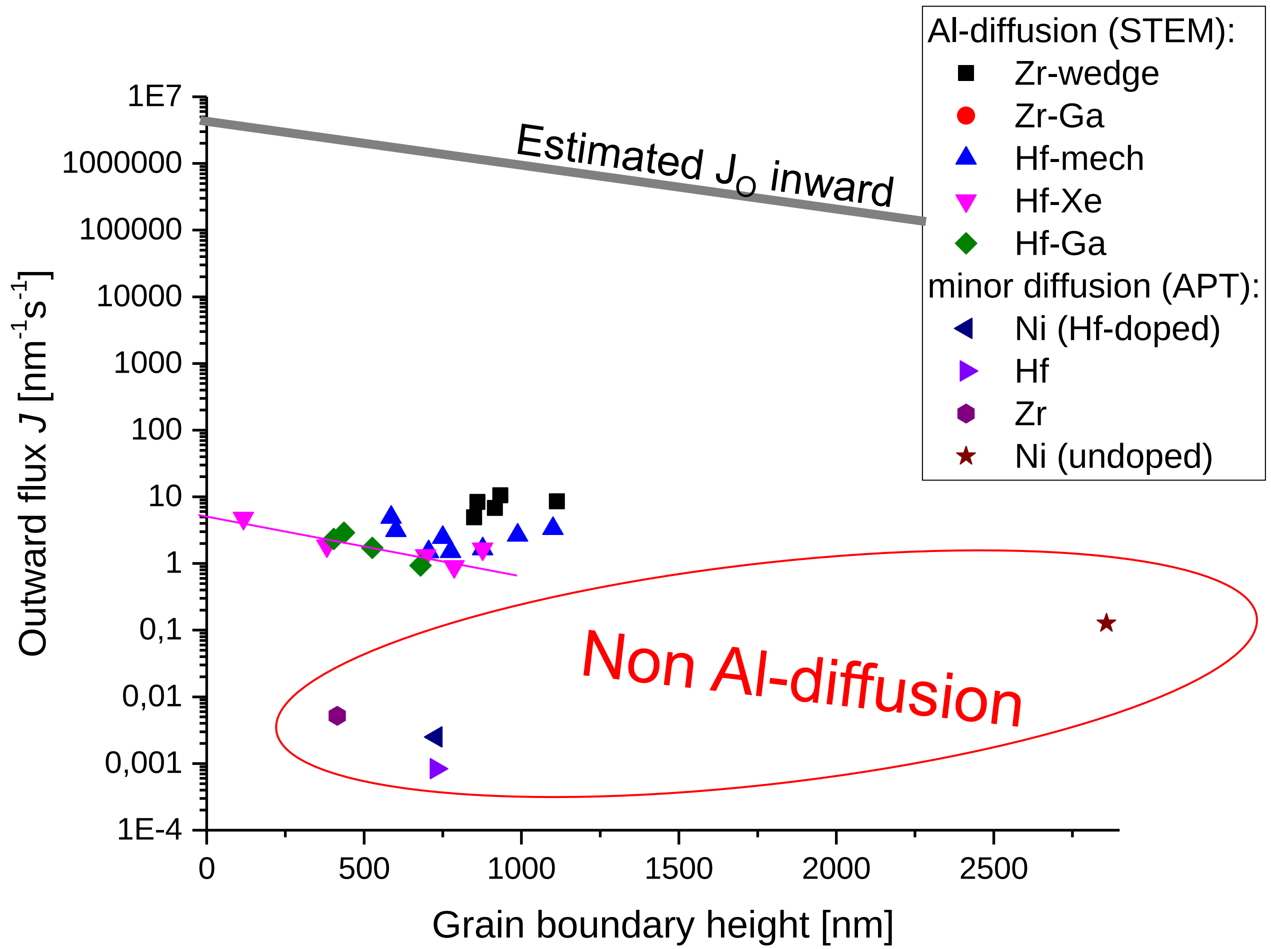
- Protective Ag on top of ridge-GB
- No Ni found
- Γ_{Zr}: 2.5 nm^{-2}

Outward flux of Ni, Hf, Cr

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

→ amount of diffused material

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



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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 at the GB and at the top of the ridge

→ Outward diffusion of Ni

- $J_O \sim 10^6\ nm^{-1}s^{-1} >> J_{Al} \sim 1\ nm^{-1}s^{-1} >> J_{Hf,Ni,Zr} \sim 10^{-3}\ nm^{-1}s^{-1}$
- *Absence or reactive elements* -> $J_{Ni} \sim 10^{-2}\ nm^{-1}s^{-1}$

Thank you for your attention

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

Acknowledgements
Kinga A. Unocic, Bruce A. Pint (ORNL): NiAl+Hf and NiAl+Zr samples
Patrik Alnegren: Help with 2nd exposure and sputter coating:

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