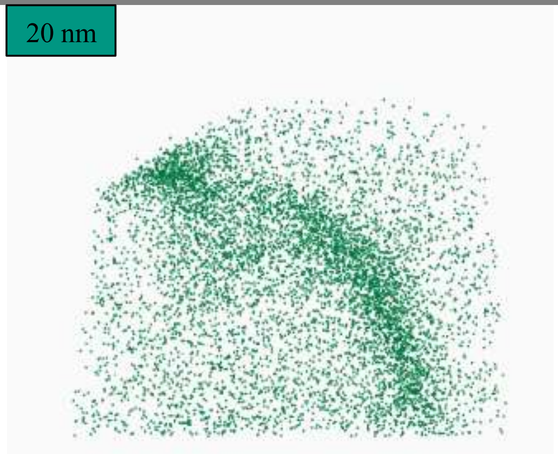
Karlsruhe Institute of Technology

Karlsruhe Micro Nano Facility

Institute for Applied Materials

# Atom Probe Tomography of Oxidation processes in NiAlCr-alloys

Torben Boll



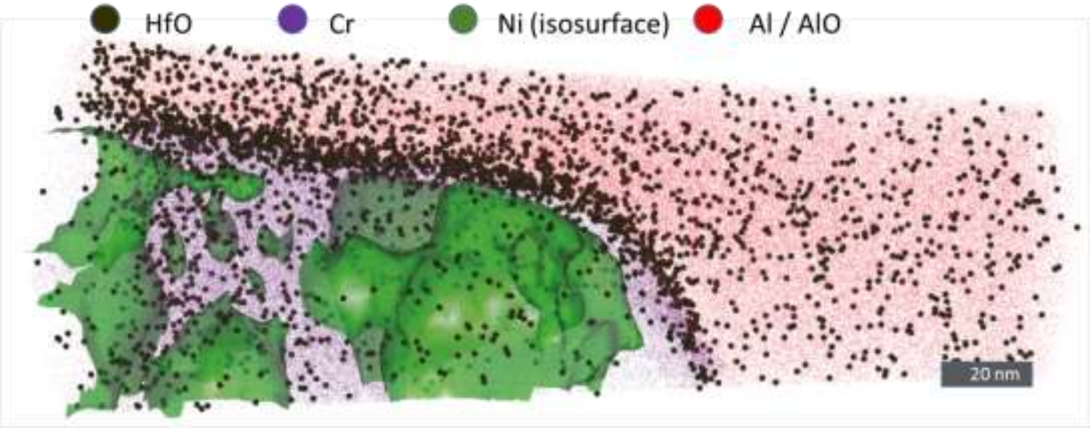
Zr at a grain boudary in $Al_2O_3$

- Field Ion Microscopy
- Atom Probe Tomography
- Investigated Materials @ KIT
- Oxidation of NiAlCr
- Outward diffsion through $Al_2O_3$

BAM Berlin 14.02.2018

# What can APT do for me?

- 3D-information of a sample up to 200 nm laterally and up to 1000 nm in depth
- Mass to charge ratio: Chemical information
- Atomic resolution (<0.1 nm) can be achieved in z-direction (in lateral directions 0.5 nm are typical)



# History

Erwin Wilhelm Müller (*1911, † 1977):

**1951** Field Ion Microscope: Atomic resolution was achieved the first time in October, 17th 1955.

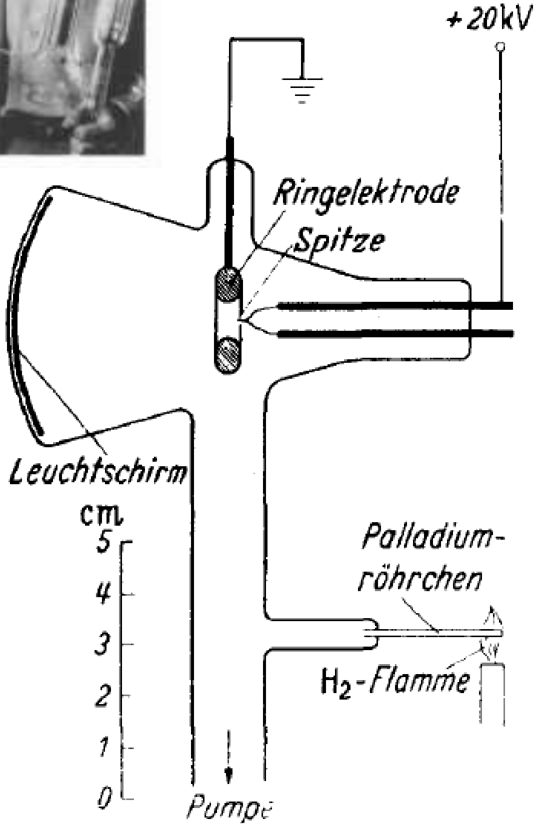
**1967** Chemical Analysis by time of flight measurement in Atom Probe Field Ion Microscope (APFIM)

**1989** Position Sensitive Atom Probe

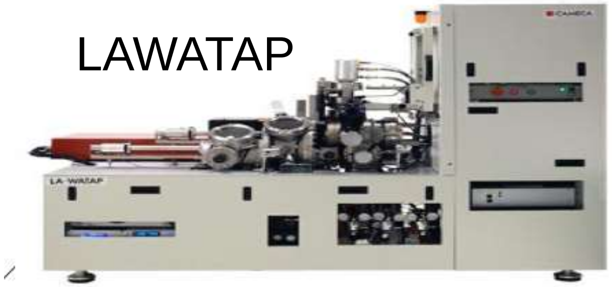
**2001** Local Electrode Atom Probe (LEAP)

**2013** Installation of LEAP 4000X HR at KIT

**2018** Installation of Laser Assisted Wide Angle Atom Probe (LAWATAP) at KIT



# History



| | |
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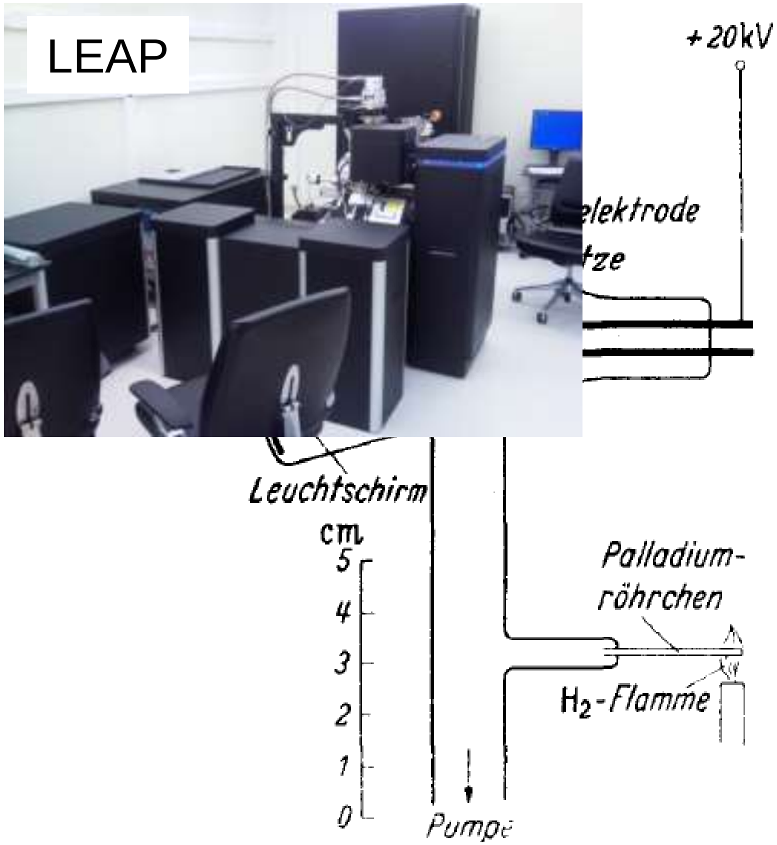
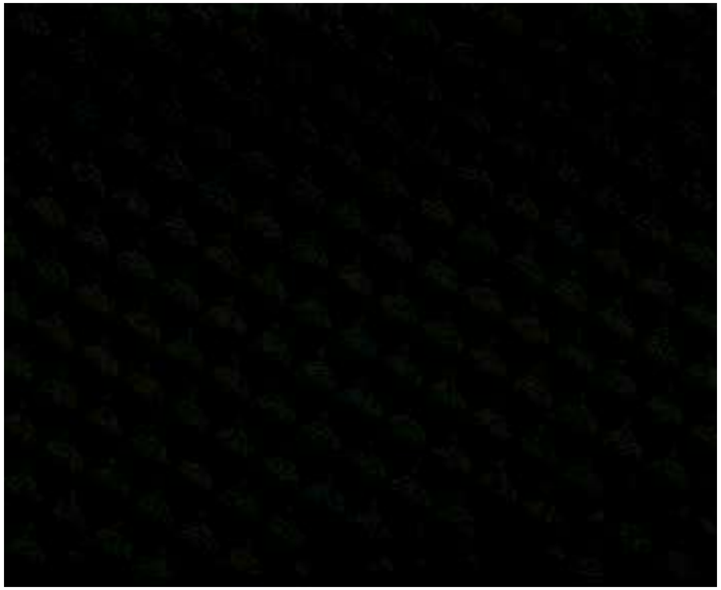
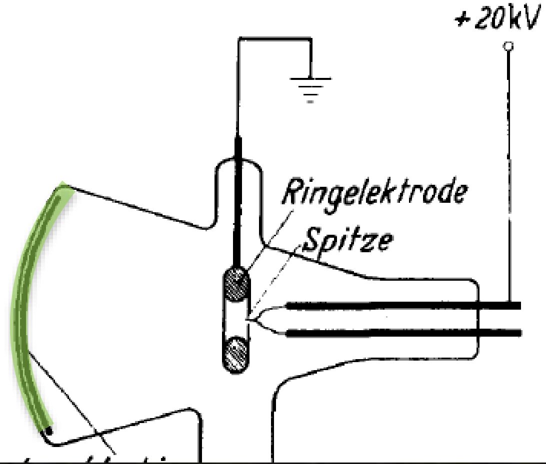
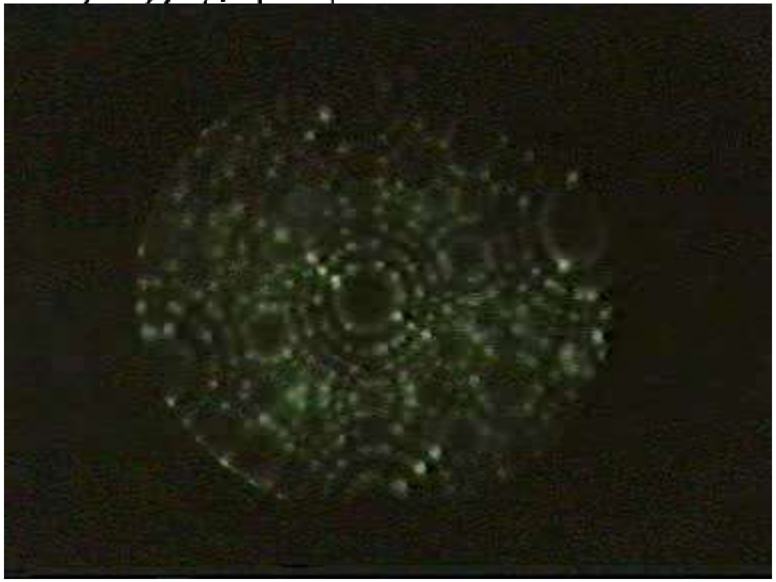


# Field Ion Microscopy



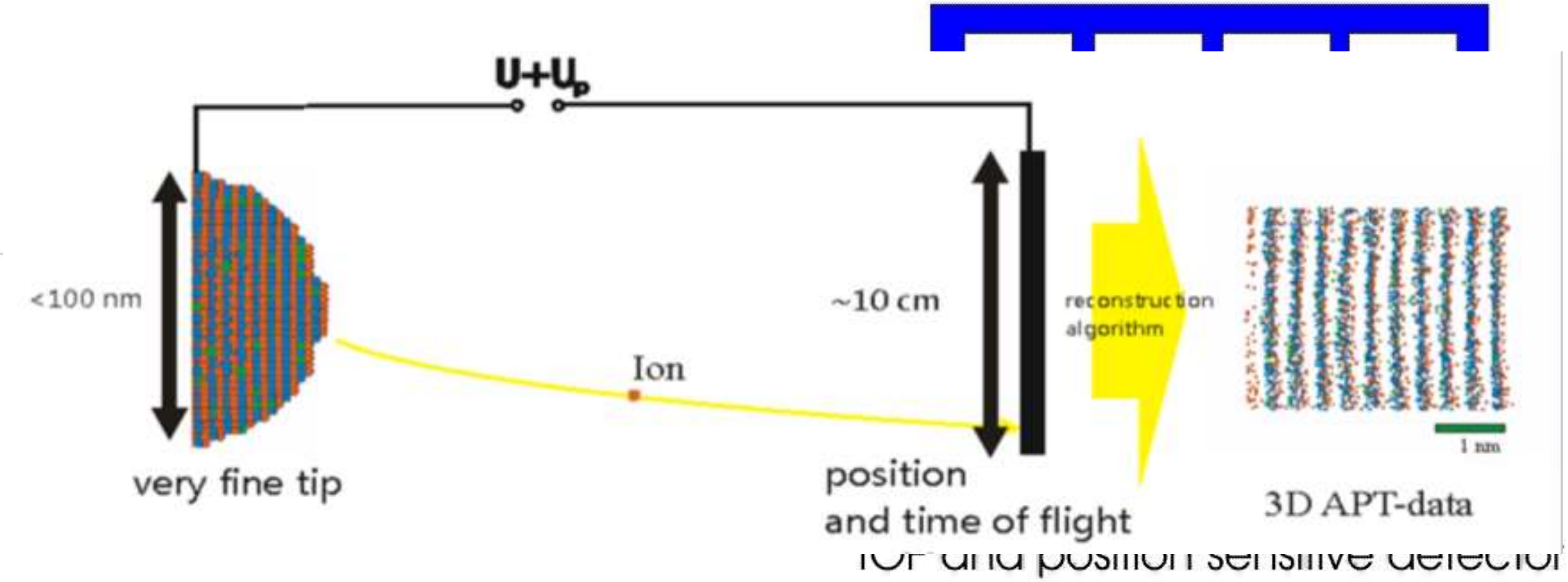
Video: B. Färber (Göttingen)





- Image gas ionizes on tip surface
- Ions are accelerated towards the screen
- Kinks (i.e. atoms) are imaged on the phosphorous screen
- If voltage is increased, tip atoms are evaporated, the image changes

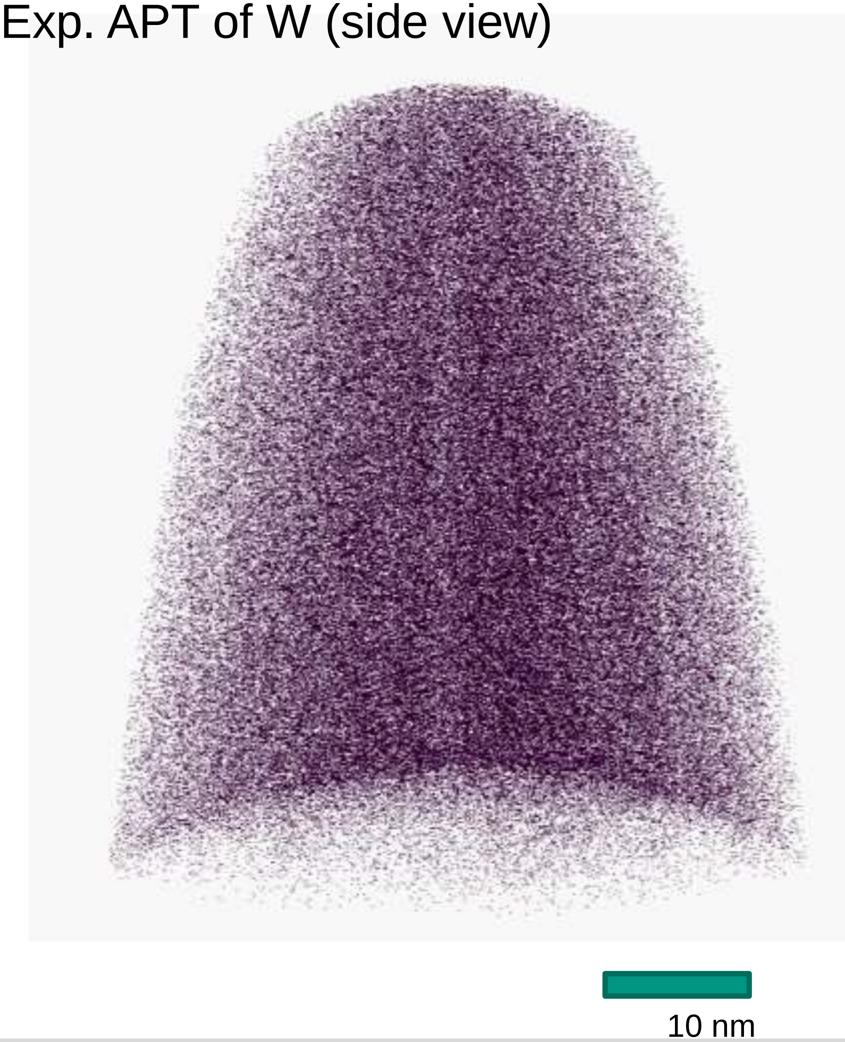
# Atom Probe Tomography (APT)



- High field applied, almost strong enough to evaporate atoms
- Additional pulse (laser or voltage): Atom is evaporated
- From the flight time the mass to charge ratio can be calculated
- (x,y)-dimension is known from the detector, z is determined from the sequence of arrival

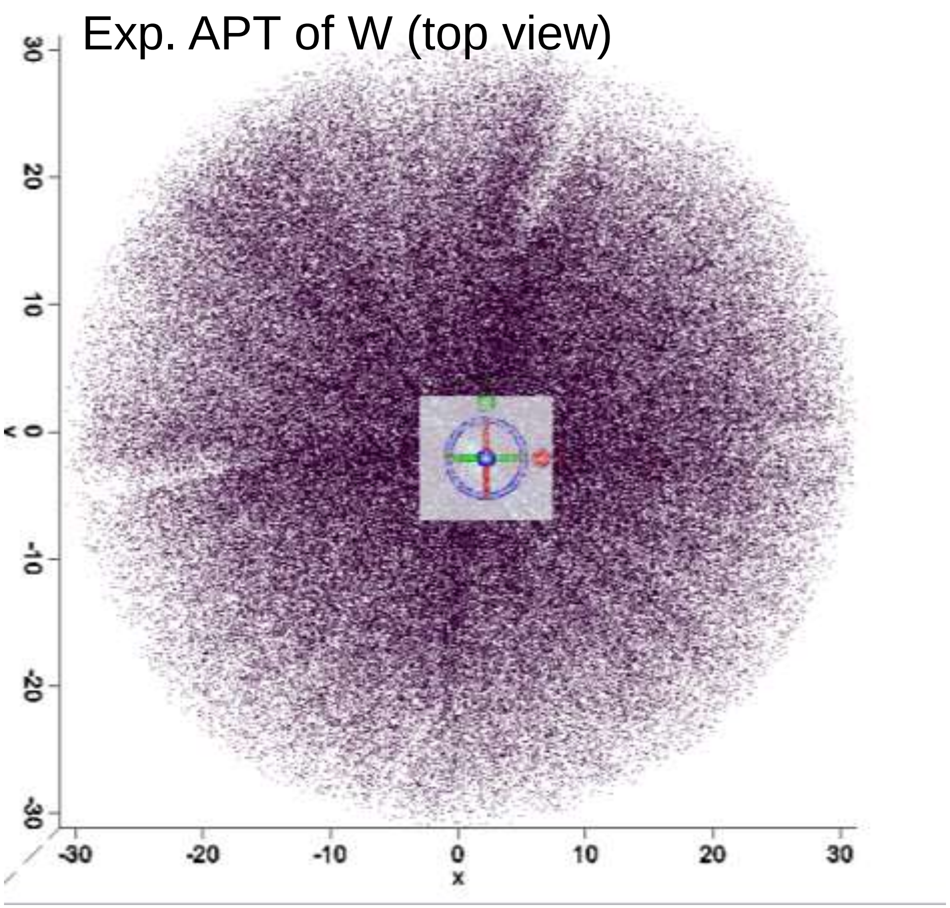
# Resolution

Exp. APT of W (side view)



- 3D- Atom Probe Tomography (APT) data often has atomic resolution in z-direction (crystallographic information)

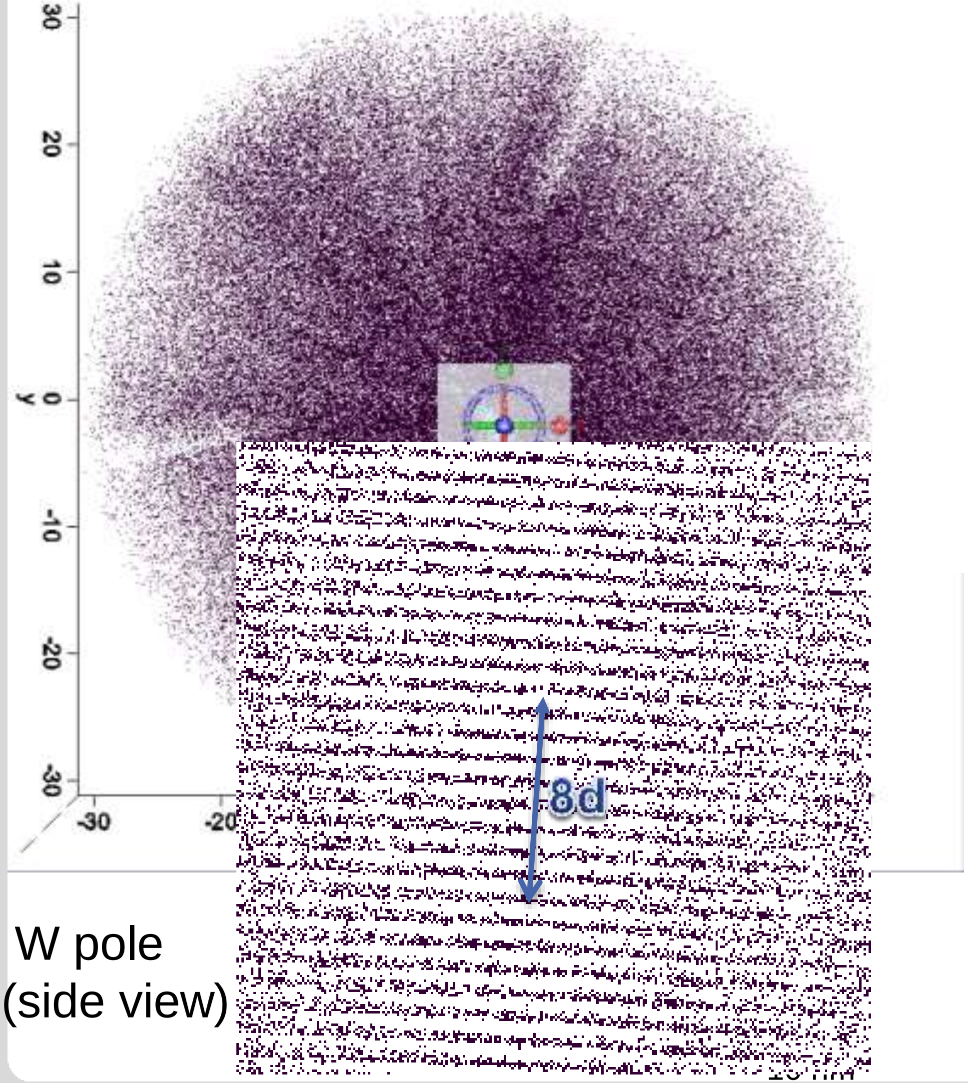
# Resolution



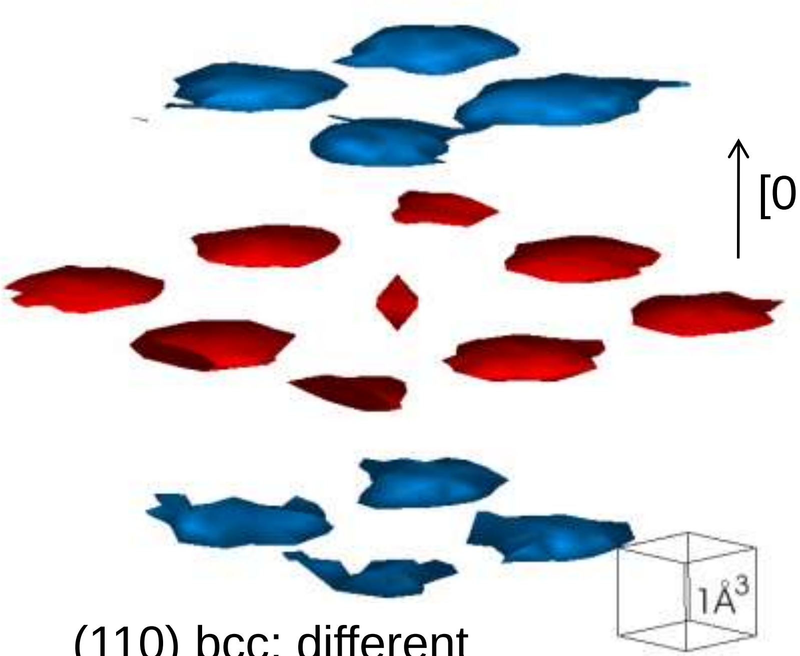
3D- Atom Probe Tomography (APT) data often has atomic resolution in z-direction (crystallographic information)

10 nm

# Resolution



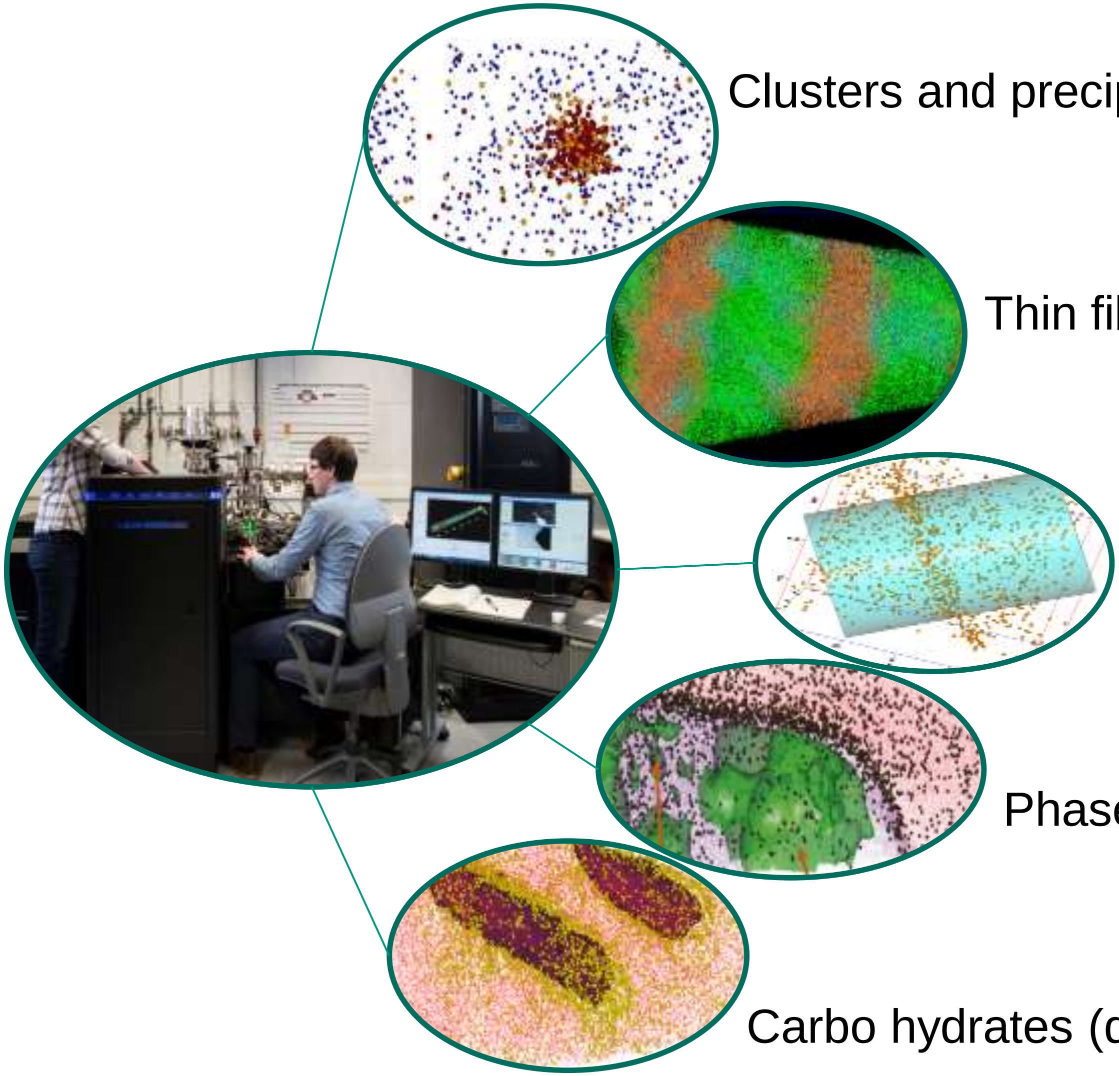
W pole
(side view)



(110) bcc: different planes emphasized by color

But often the resolution is not good enough -> data has to be processed to obtain this information

# What can APT do for me?



Clusters and precipitates

Thin films

Grain boundaries

Phase boundaries

Carbo hydrates (difficult)

# Sample preparation: options

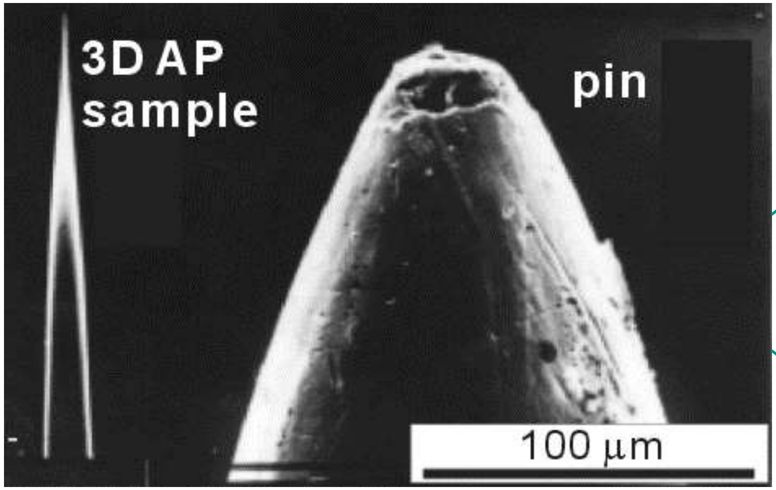
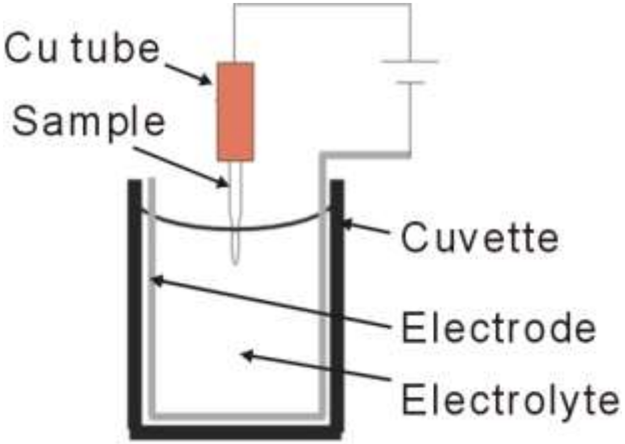


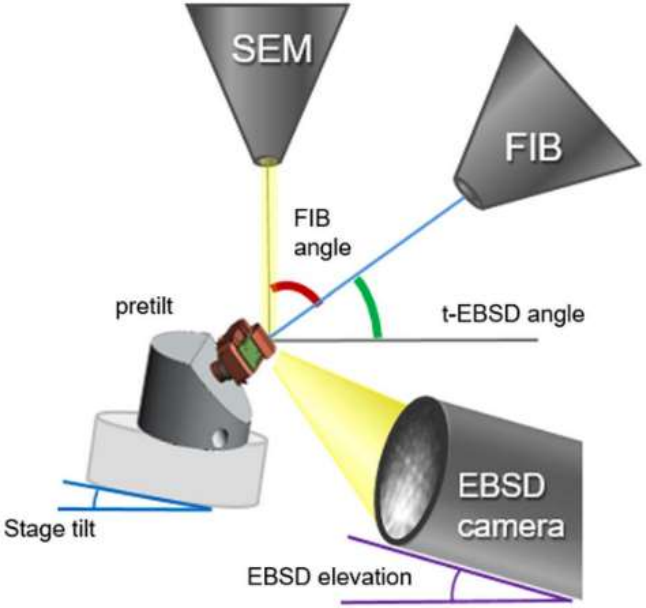
Image: B. Färber (Göttingen)

Electropolishing



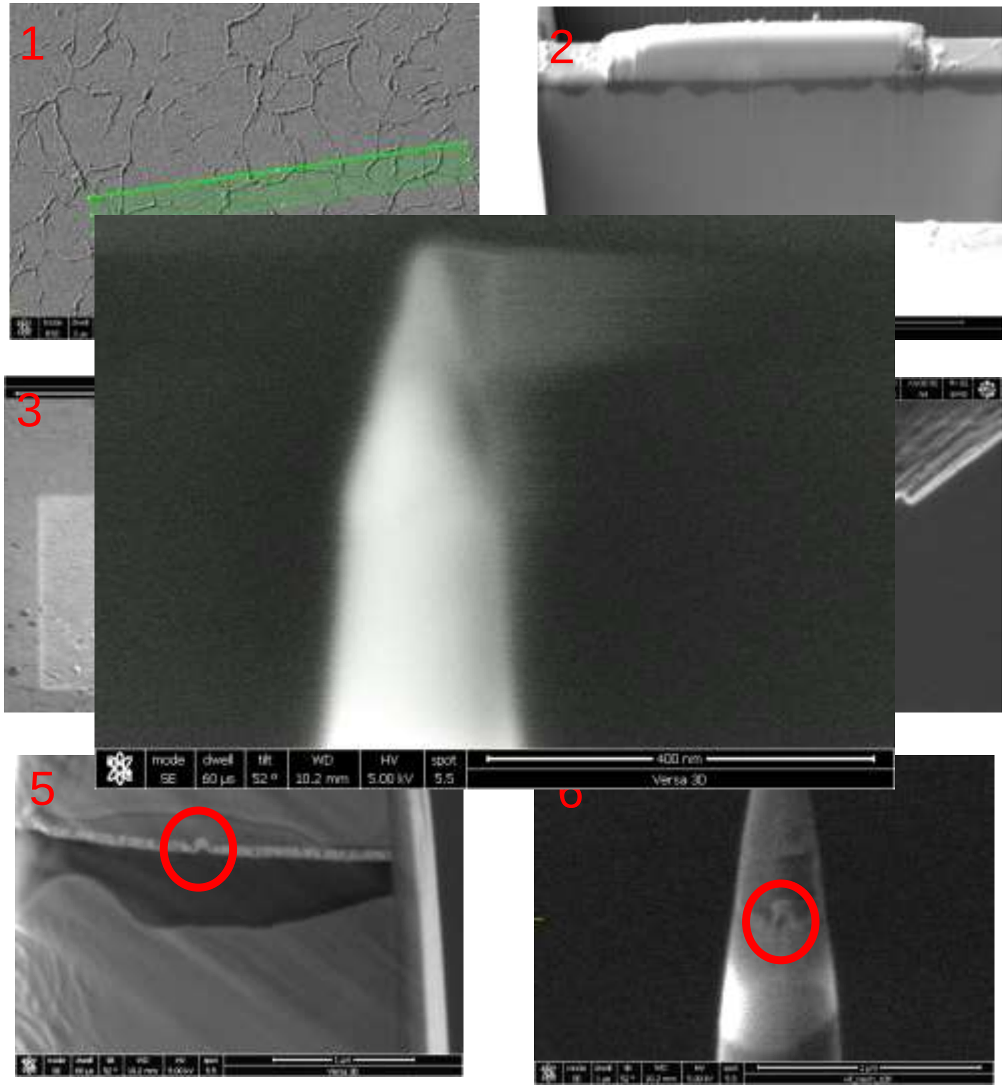
PhD thesis C. Wille 2010, Göttingen

Focused Ion Beam (FIB)



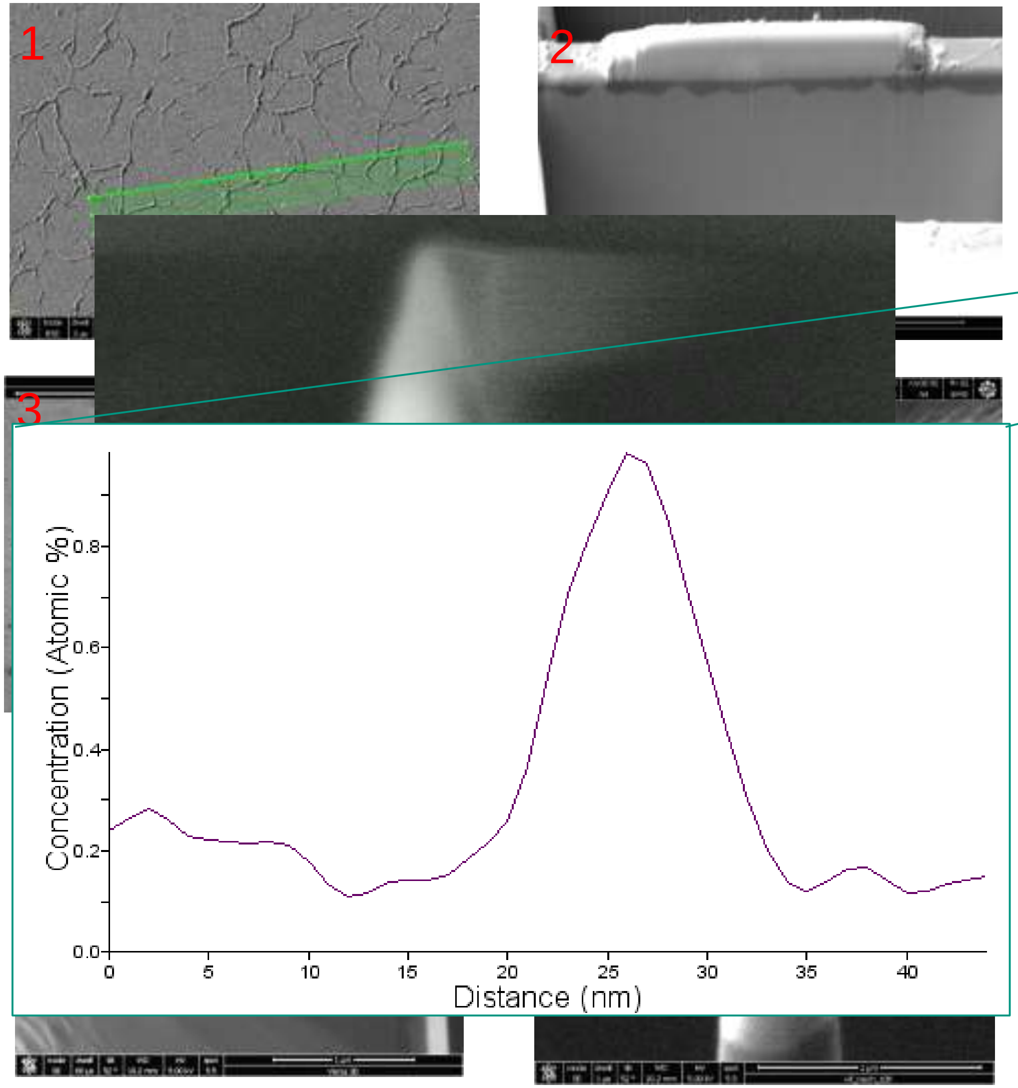
D. Larson et al, Microsc. Microanal. 2017

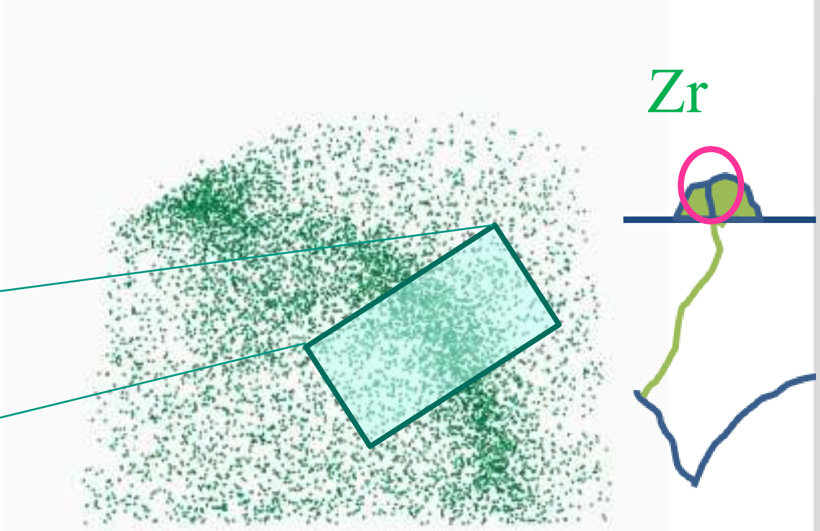
# Sample preparation of surface features with FIB



- 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

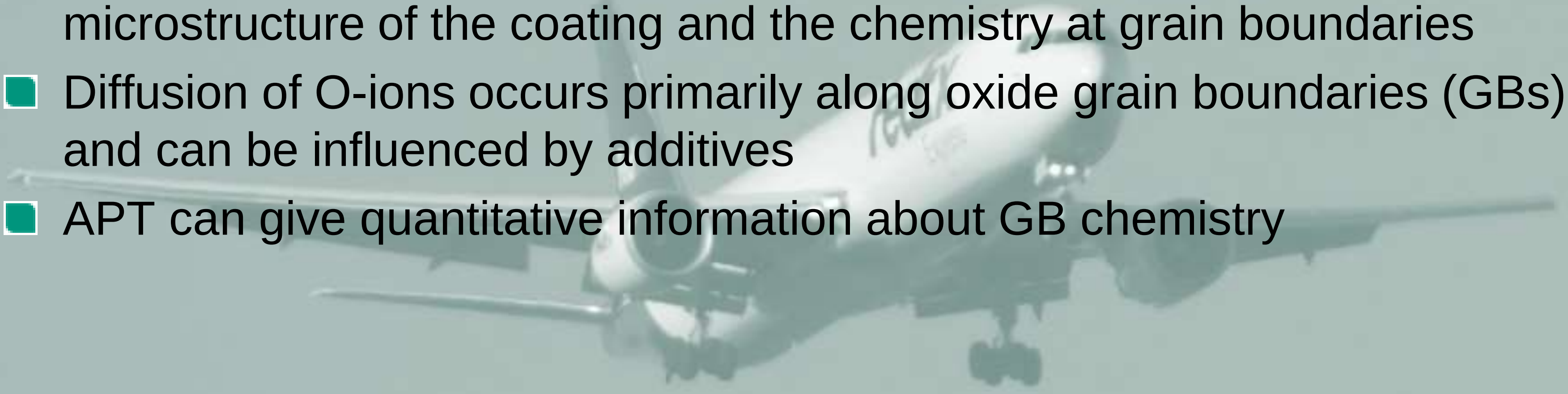
# Sample preparation of surface features with FIB





- Protective Ag on top of ridge-GB
- Zr enrichment at GB
- Gibbsian excess $\Gamma_{Zr}$: 2.5 $nm^{-2}$

# Overview for NiAl-alloys



- Ni base superalloys are good at high temperatures (e.g. air plane engines)
- Corrosion potentially dangerous
- Stable protective coating (oxide scale) is required: $\alpha$-$Al_2O_3$
- Cr and reactive elements (e.g. Y,Hf) are added to change microstructure of the coating and the chemistry at grain boundaries
- Diffusion of O-ions occurs primarily along oxide grain boundaries (GBs) and can be influenced by additives
- APT can give quantitative information about GB chemistry

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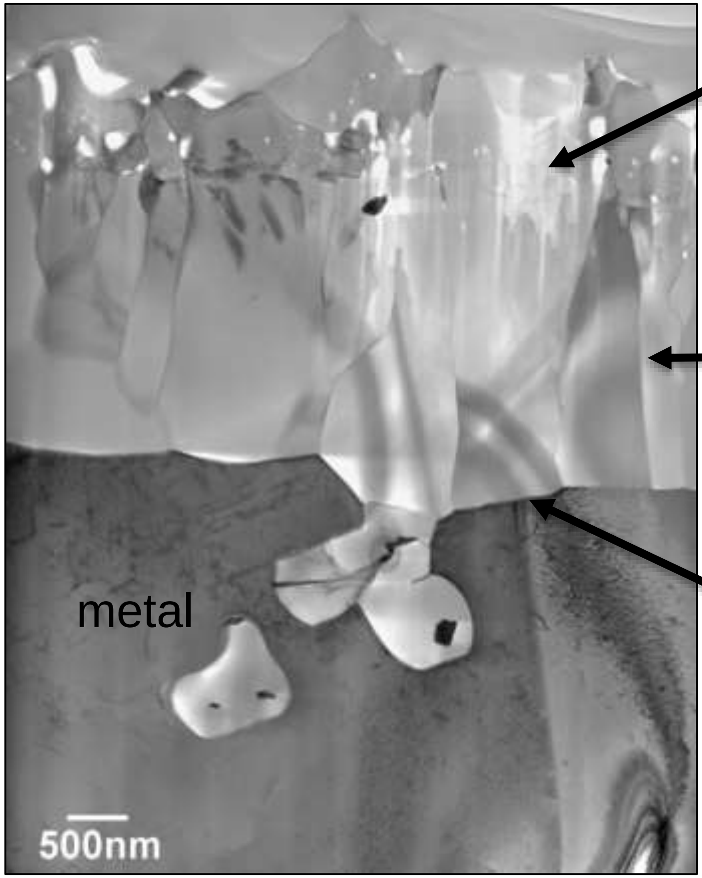
# Overview:NiAlCr

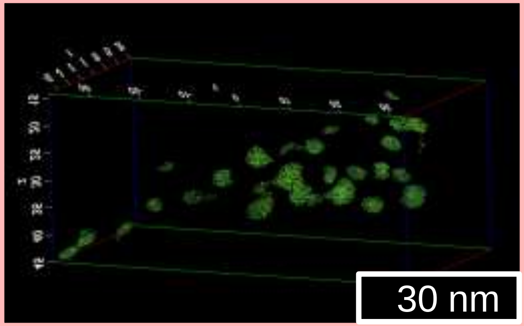
## TEM



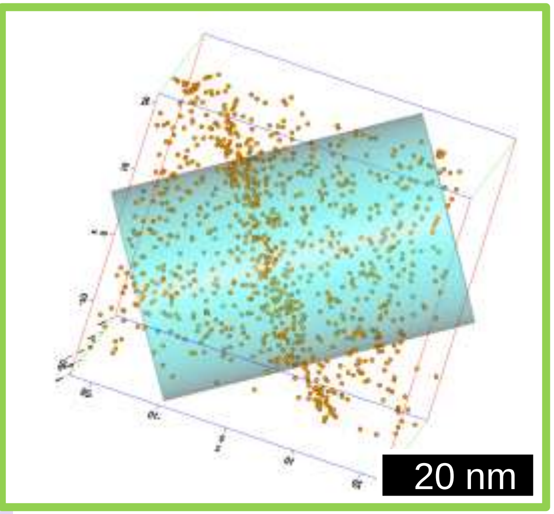
TEM of oxidized NiCrAl after 100h@1100°C

## APT

Outer oxide: Phase boundaries (PB) between different oxides



Inner oxide: Grain boundaries (GB) between different $Al_2O_3$-grains



Phase boundary (PB) between the metal and the $Al_2O_3$-grains

# Overview:TEM

YHfB: $Ni_{60.6}Cr_{16.8}Al_{22.2}Y_{0.015}Hf_{0.037}B_{0.33}C_{0.028}$
YHfTi: $Ni_{61.9}Cr_{15.2}Al_{22.6}Y_{0.020}Hf_{0.043}Ti_{0.31}C_{0.017}$
YHf: $Ni_{62.3}Cr_{15.1}Al_{22.5}Y_{0.03}Hf_{0.04}C_{0.024}$

TEM of oxidized NiCrAl after 100h@1100°C

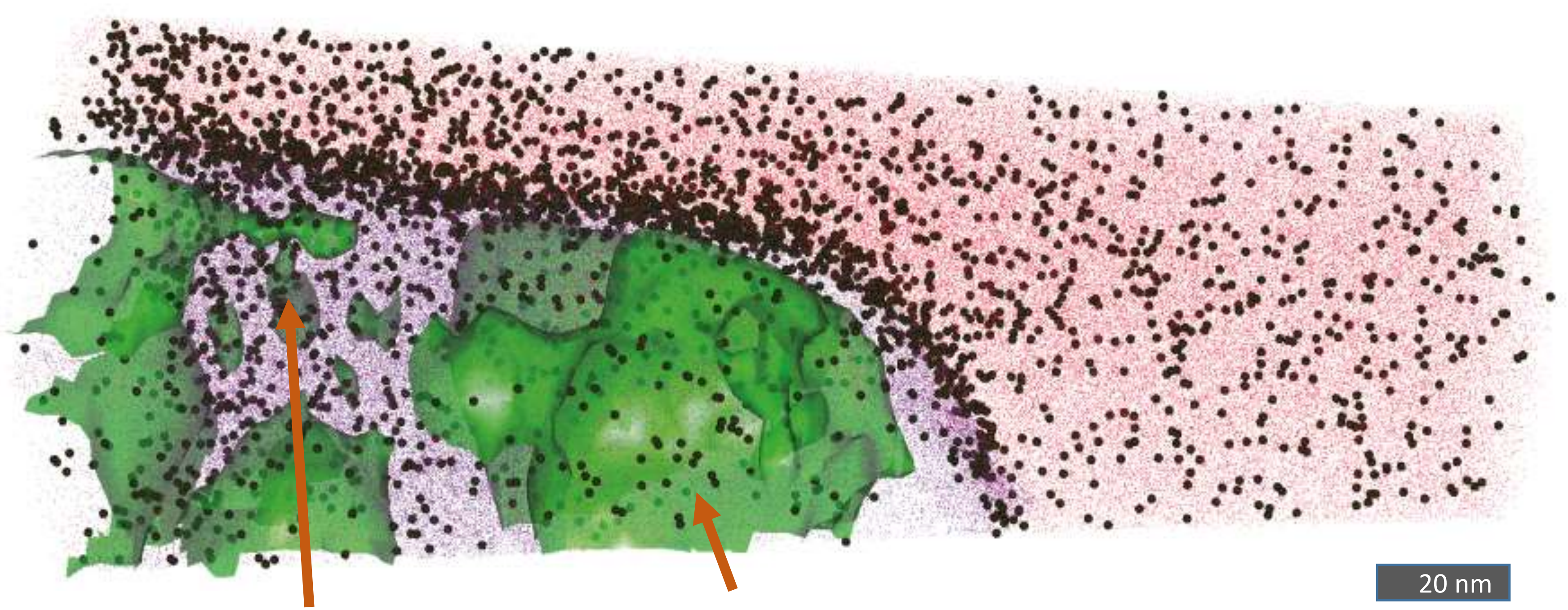
| | Metal-$Al_2O_3$ | $Al_2O_3$-$Al_2O_3$ | $Al_2O_3$-$M_yO_x$ |
|---|---|---|---|
| **Hf** | Y | Y | Y |
| **Y** | N | Y | Y |
| **Ti** | N | N | N |
| **B** | N | N | N |
| **Ni** | | Y | |
| **Cr** | | Y | |

APT: Quantitative enrichment at different interfaces

BOLL, T., UNOCIC, K. A., PINT, B. A. & STILLER, K. (2017). Microscopy & Microanalysis

# Atom Probe: YHfTi M/O interface

● HfO ● Cr ● Ni (isosurface) ● Al / AlO



γ: Cr-rich grain
$Ni_{59}Al_{16}Cr_{24}Ti_{0.1}$

γ`:Al-rich grain
$Ni_{70.2}Al_{21.3}Cr_{5.9}Ti_{0.7}$

- Hf but no Ti or Y at metal-oxide interface
- γ/ γ` metal nanosrucure. Ti is enriched in γ`

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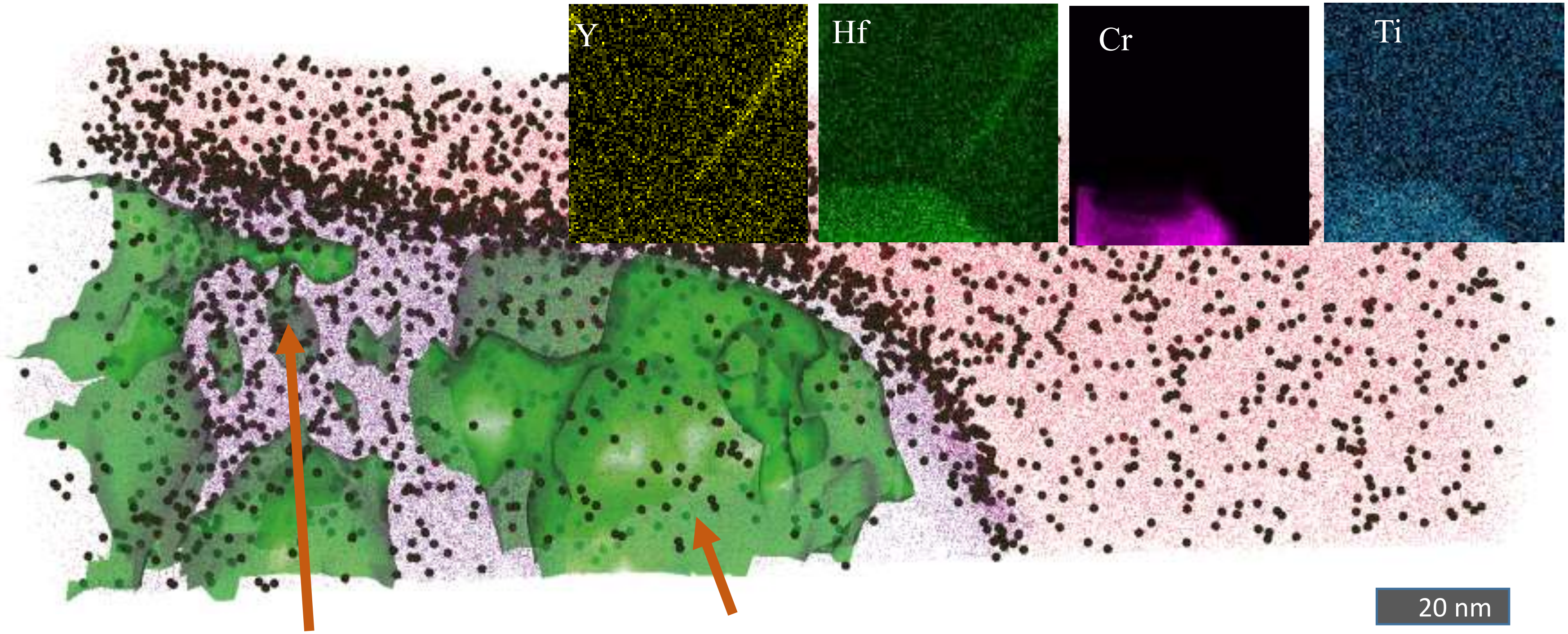

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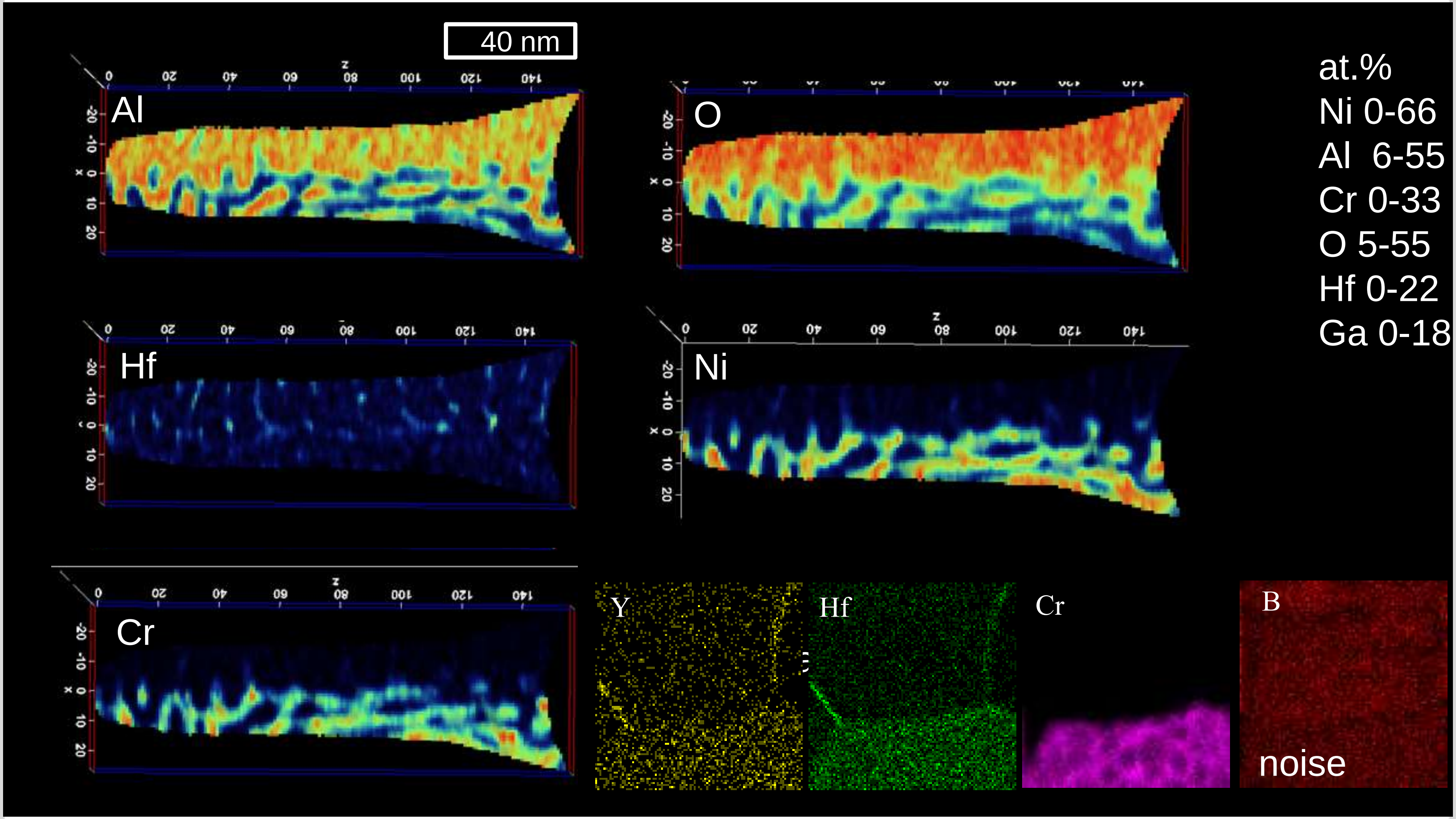
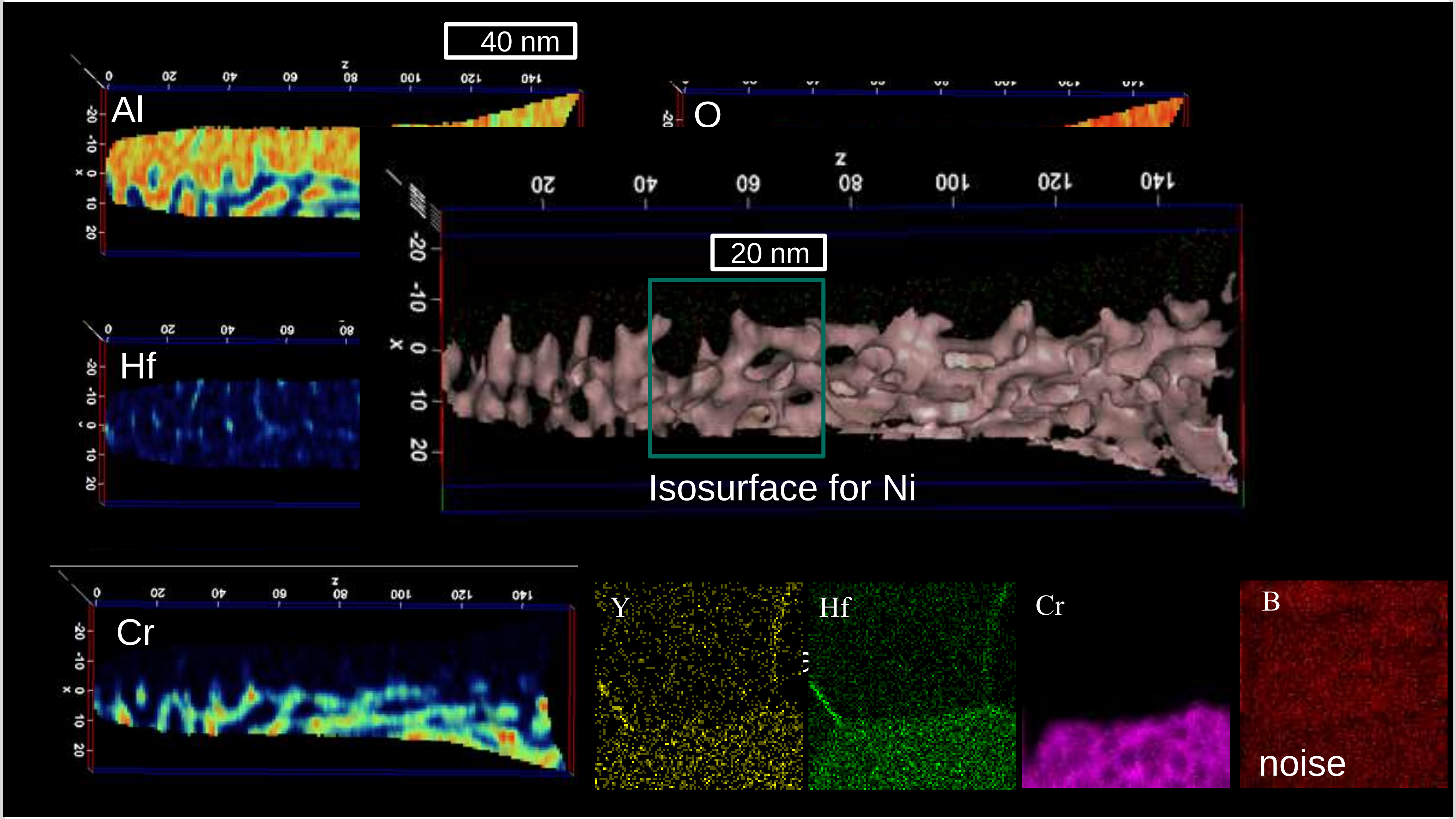
# Atom Probe:YHfB: Metal-oxide interface



at.%
Ni 0-66
Al  6-55
Cr 0-33
O 5-55
Hf 0-22
Ga 0-18

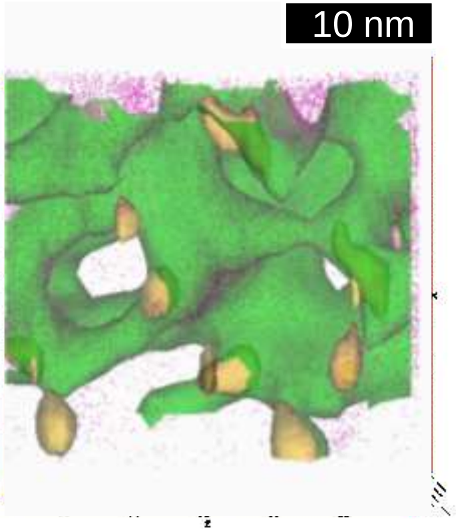
Unexpected interface roughness

# Atom Probe:YHfB: Metal-oxide interface

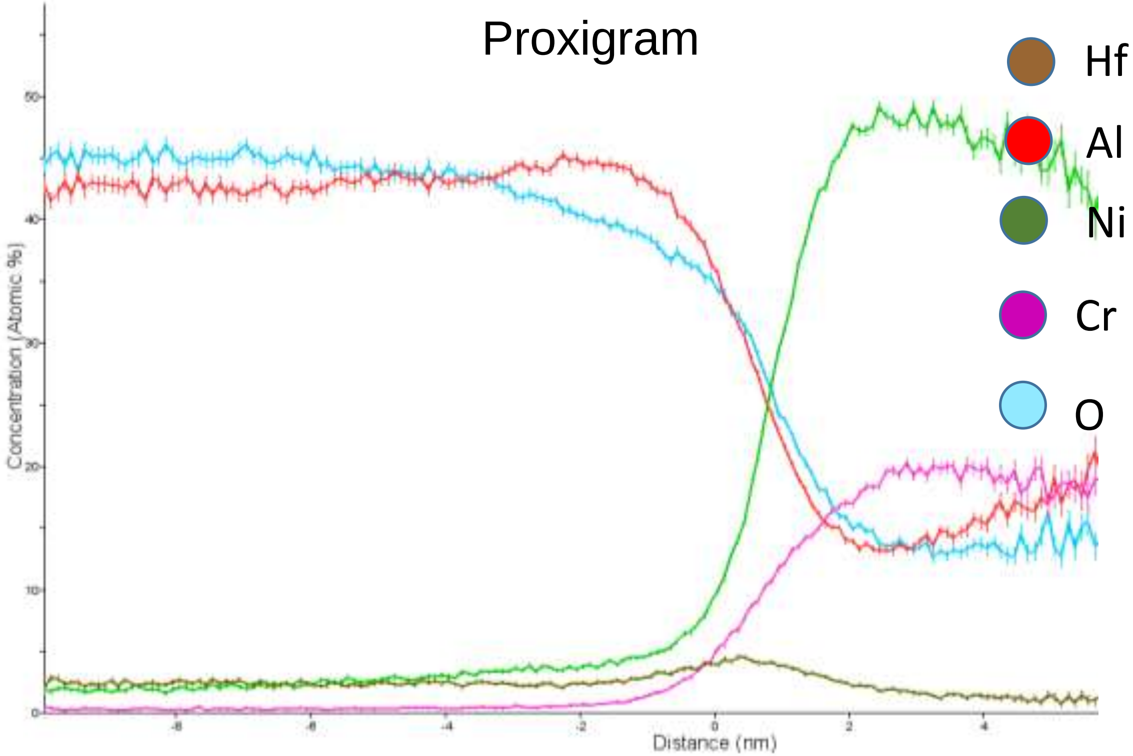


Unexpected interface roughness

# M/O interface

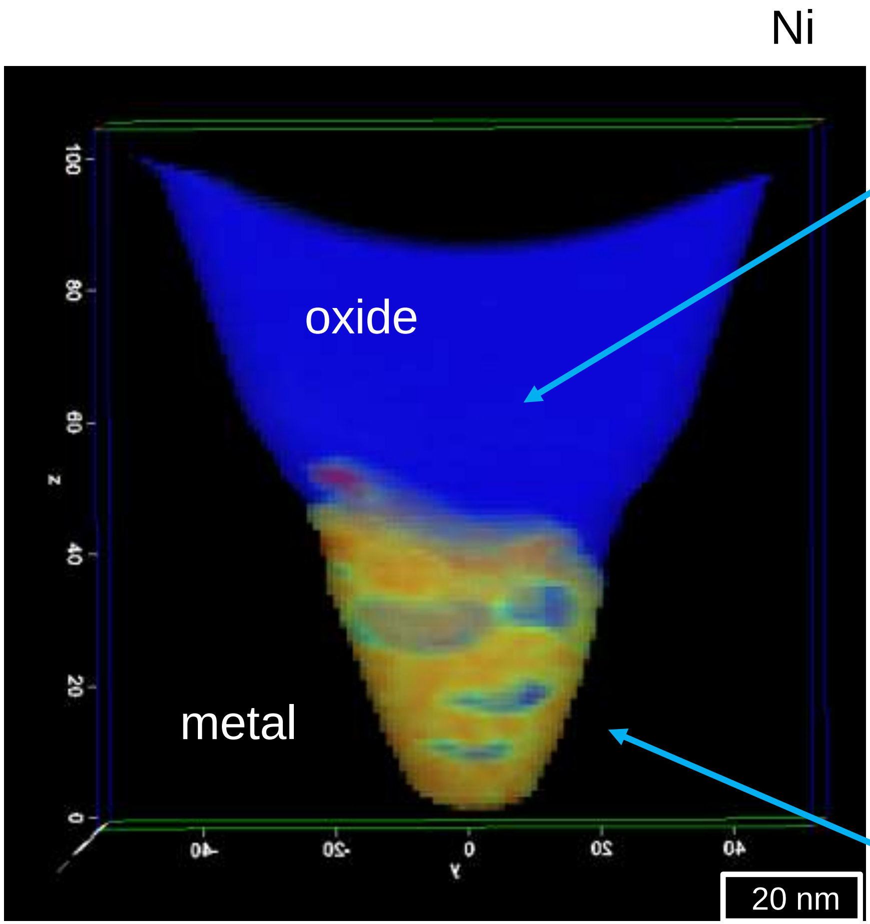


Green: 17 at.% Ni
brown: 2at.%Hf



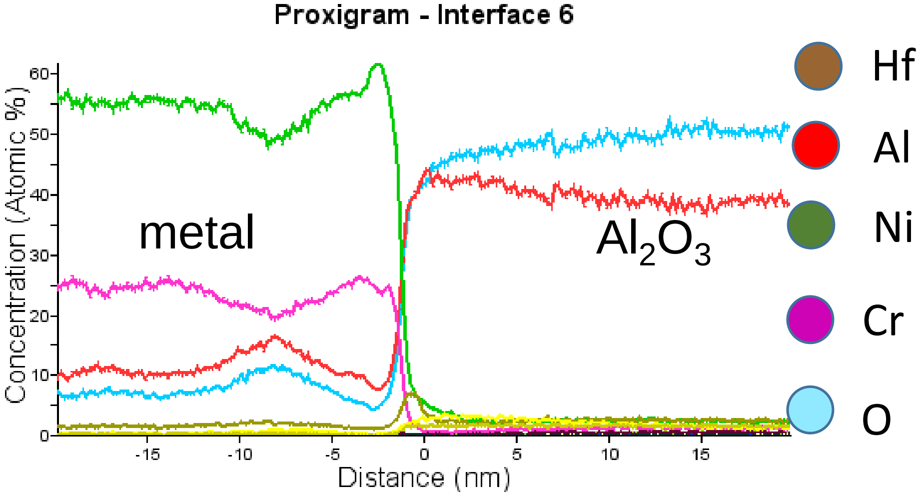
- $Al_2O_3$ interface
- Al depleted, Ni enriched in the metal close to the interface
- Hf enriched at interface
- Nothing else is enriched at the interface

# APT: YHfB- M/O-interface: non stoichiometric AlO in metal

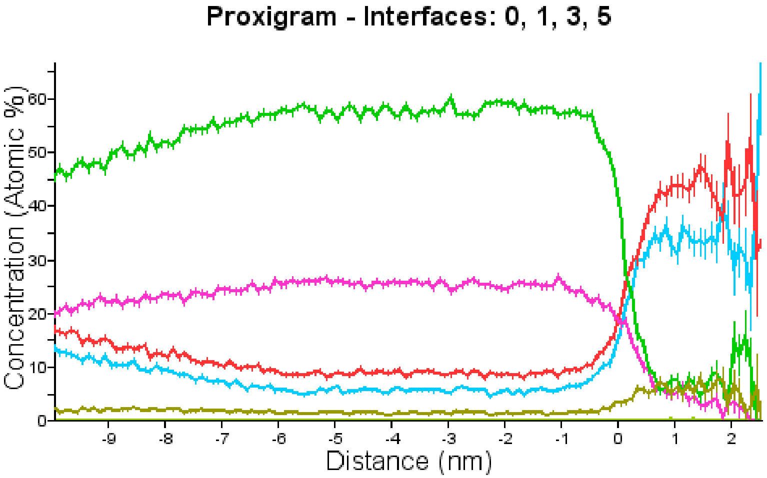


Particles not stoichimetric $Al_2O_3$

Isosurface 34 at.% O



Isosurfaces 13 at.% O



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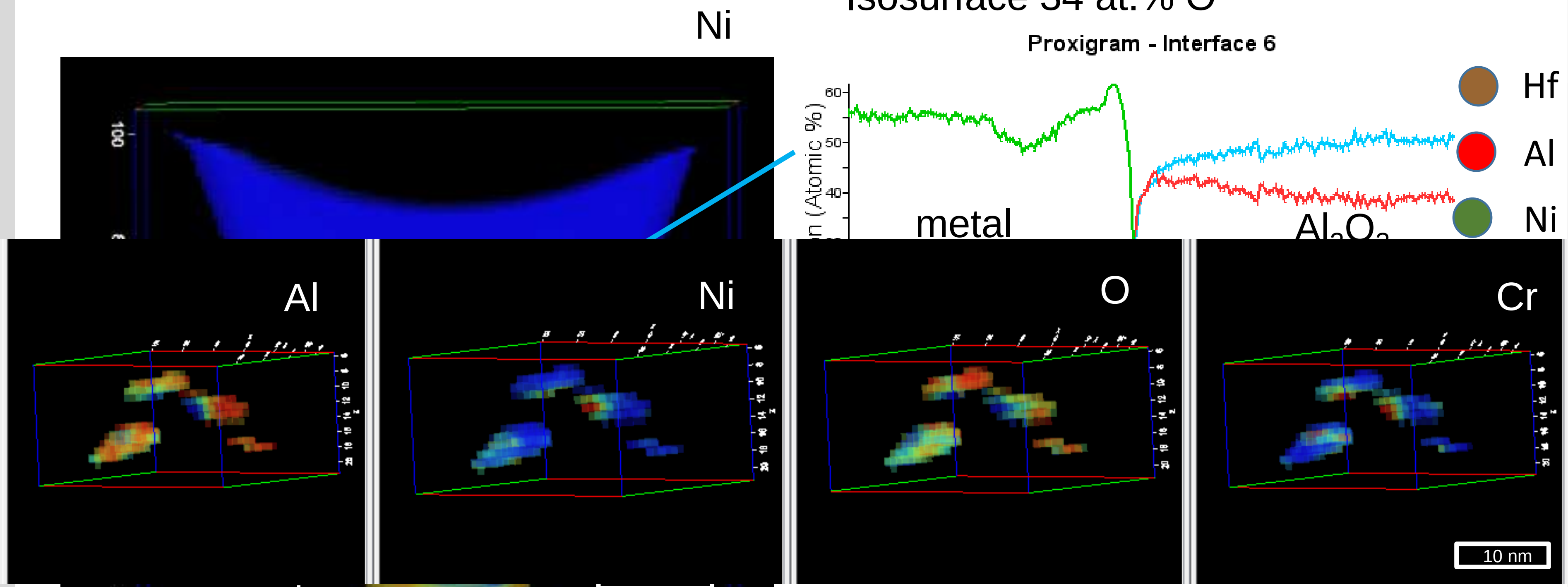
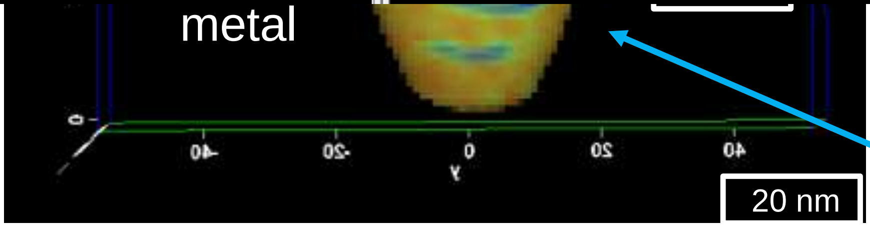
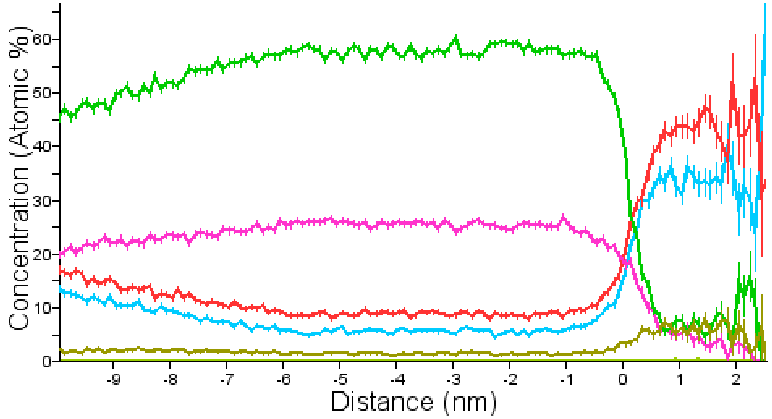
# APT: YHfB- M/O-interface: non stoichiometric AlO in metal

Isosurface 34 at.% O







Particles not stoichimetric $Al_2O_3$ but contain NiO and CrO

# Conclusions I

- The solutes
  - Ti not found at phase or grain boundaries
  - Hf segregates to metal/oxide PBs, oxide/oxide PBs and oxide GBs
  - Y segregates to oxide/oxide GBs and PBs but not to metal-oxide PBs
  - B shows no segregation to PBs or GBs
  - $Al_2O_3$-$Al_2O_3$ GBs contain Ni and Cr
  - Hf and Y could influence the transport of O, Ni and Cr in these GBs

- The oxidation progress
  - Rough oxide/metal interface
  - Oxidation in the metal progresses along γ/γ`-PBs into Al-rich γ'-phase
  - Small oxides in metal are not stoichiometric $Al_2O_3$
  - Only observed due to APT

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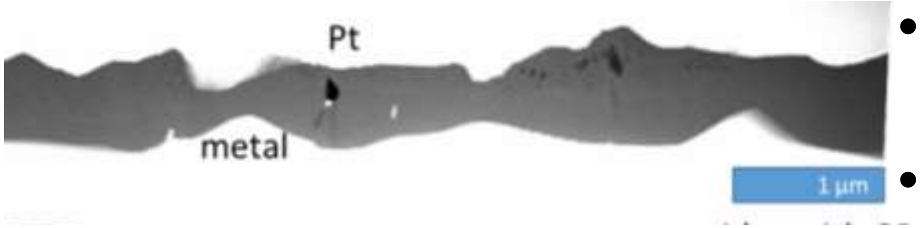
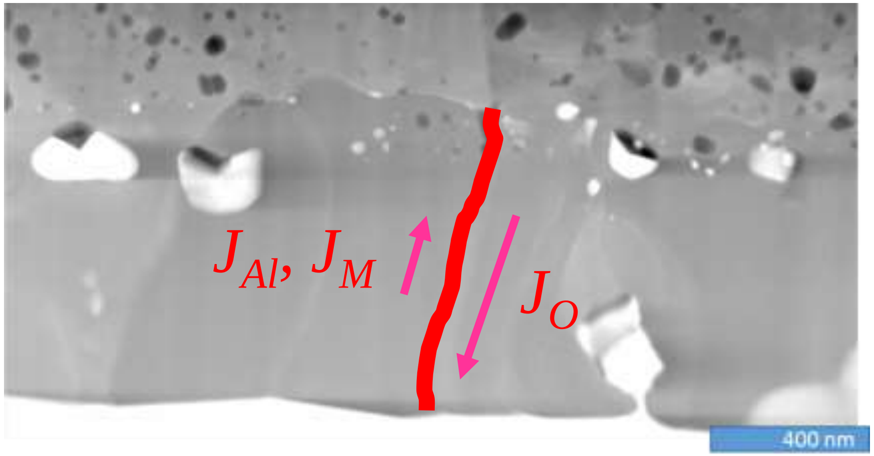
# Outward diffusion in oxide scale on NiAl



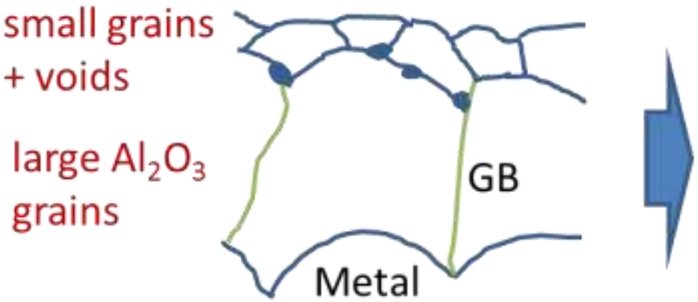


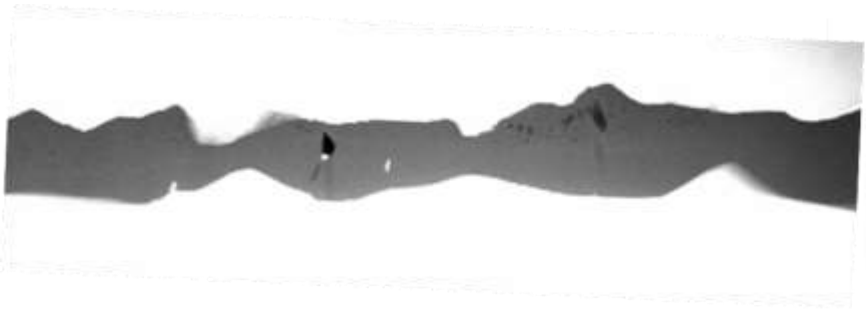
- Protective $Al_2O_3$ coating on NiAl-alloy
- O (and all other elements) in α-alumina diffuse mostly via grain boundaries (GBs)
- Minor outward diffusion of metal
- Decoration of GBs will influence the diffusion and thus oxidation
- Apparently grows inwards

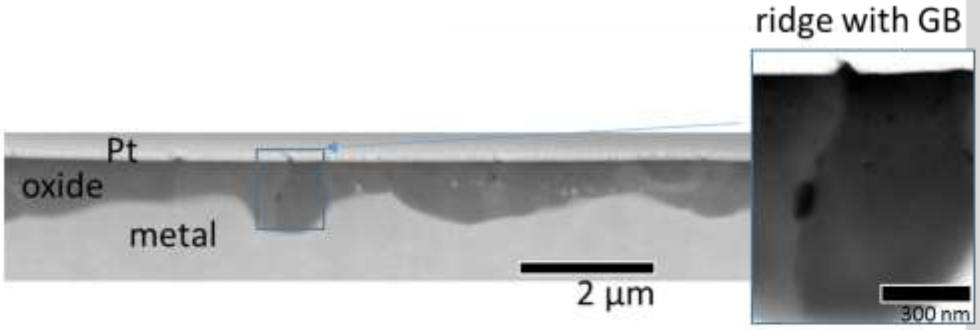
| *Material* | *Ni at.%* | *Al at.%* | *Zr ppma* | *Hf ppma* | *N ppma* | *C ppma* | *Sxx ppma* | *O ppma* | *B ppma* | *Cr ppma* |
|---|---|---|---|---|---|---|---|---|---|---|
| *Zr-doped* | 49.95 | 49.99 | 520 | 0 | 0 | 0 | 3 | 48 | 30 | 0 |
| *Hf-doped* | 49.83 | 50.07 | 0 | 480 | 30 | 36 | 0 | 43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

# Outward diffusion: Exp. idea

## a) After 1st exposure

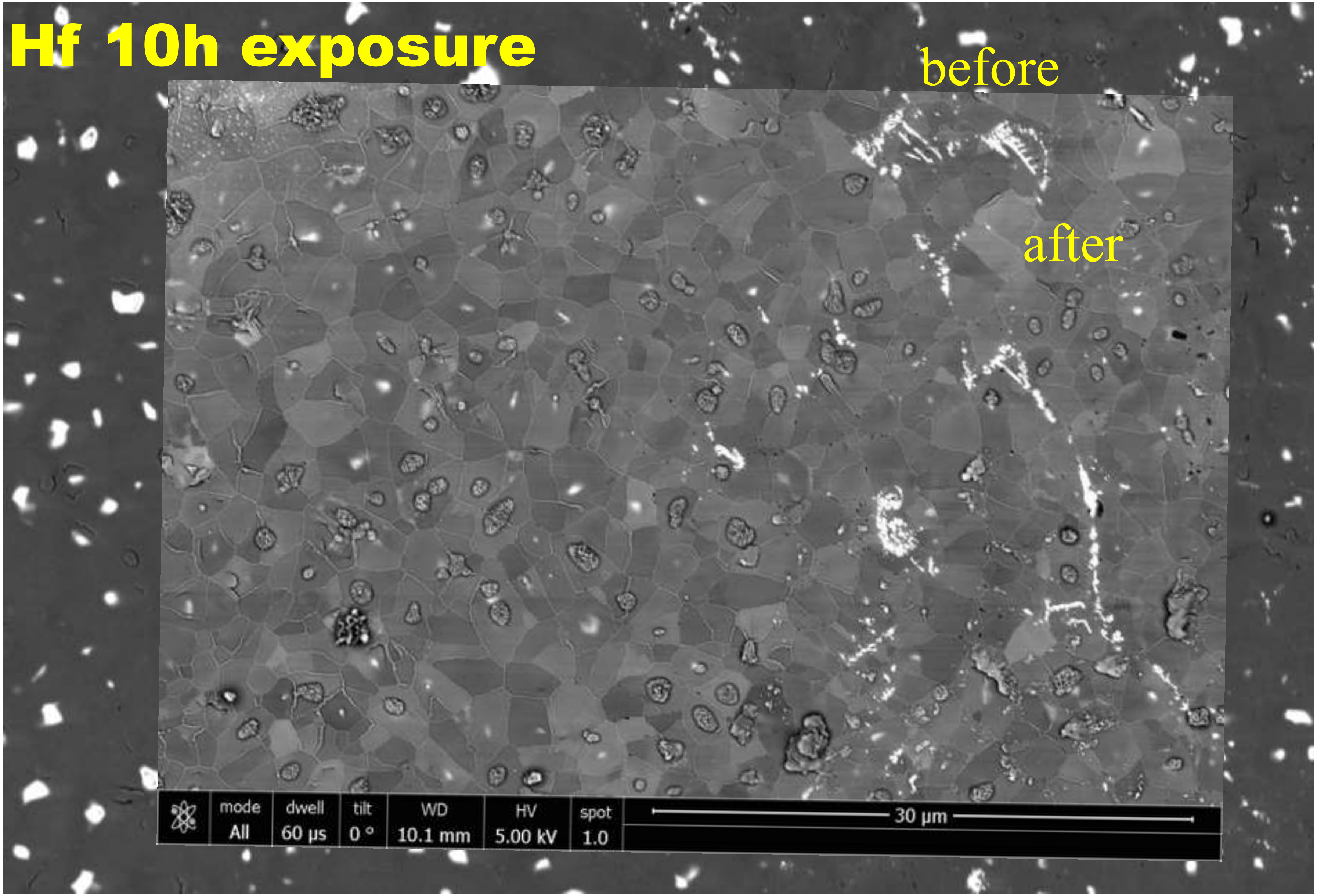




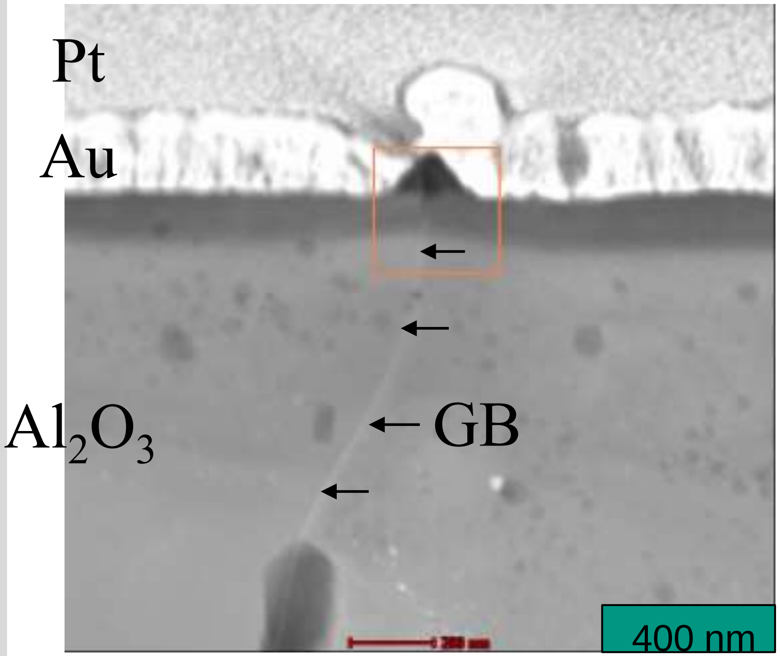


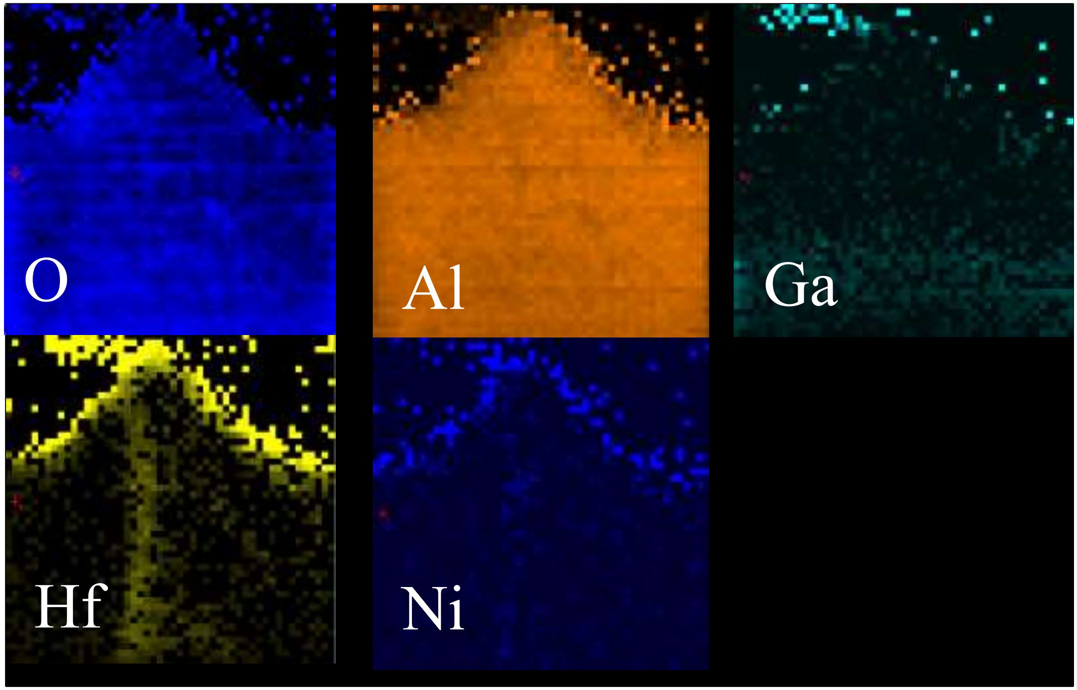
[1] V. K. Tolpygo and D. R. Clarke, *Mater. High Temp.*, vol. 20, no. 3, pp. 261–271, 2003
[2] J. a. Nychka and D. R. Clarke, *Oxid. Met.*, vol. 63, no. 5–6, pp. 325–352, 2005

# Outward diffusion: SEM



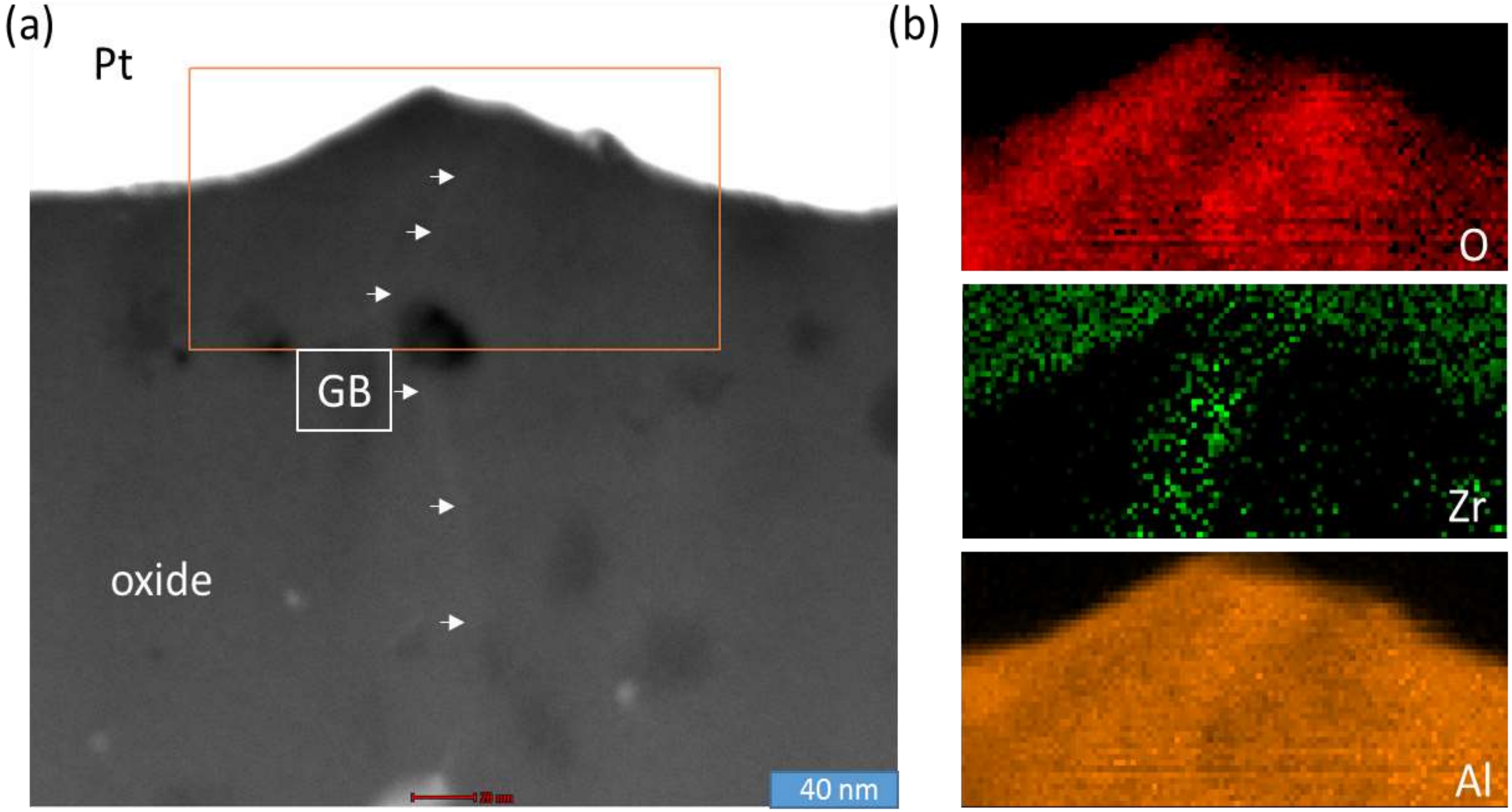
# TEM of mechanically polished Hf sample





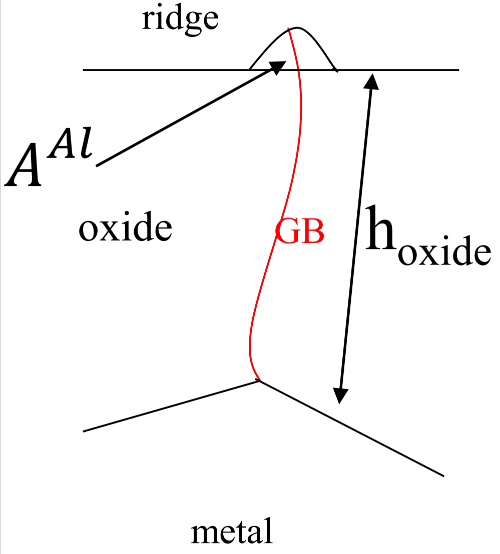
- No Ga contamination
- GB enriched with Hf and some Ni

# TEM of Zr sample



Zr enriched at the GB

# How to calculate the flux

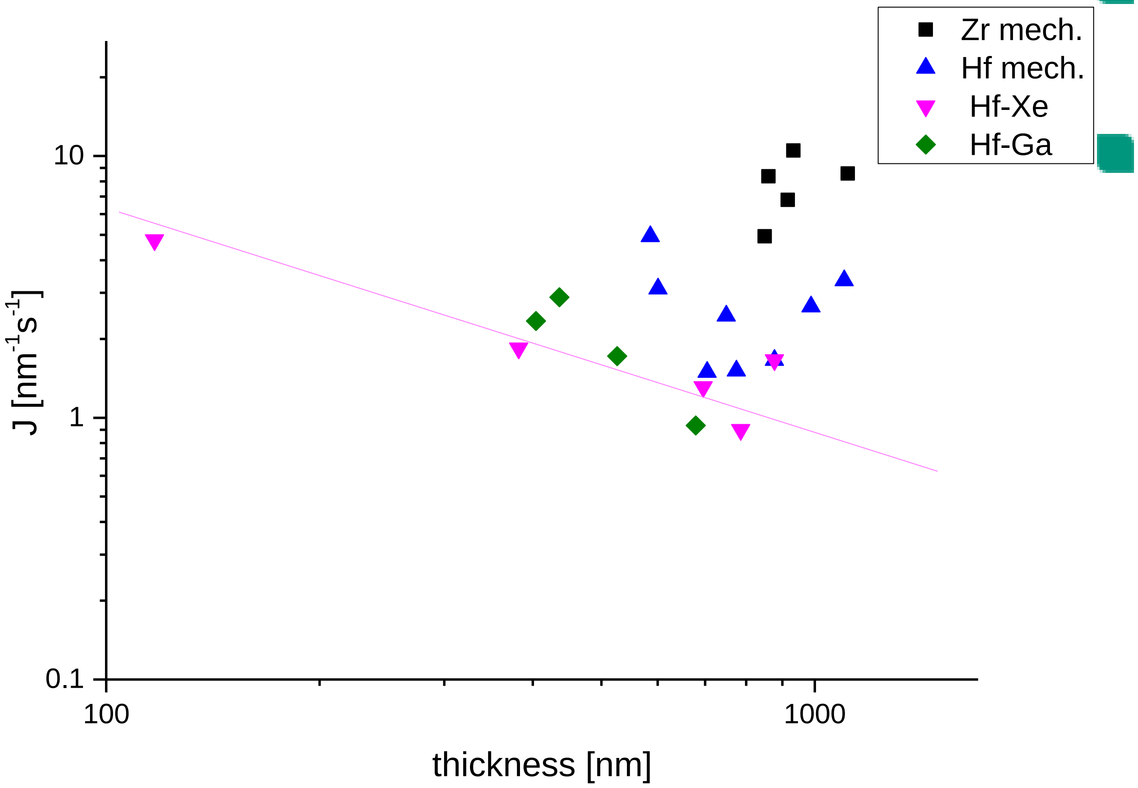


- Calculate the flux
  - Number of diffused Al-atoms $N_{GB}^{Al}$
  - Exposure time $\Delta t$ (10h)

- 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

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

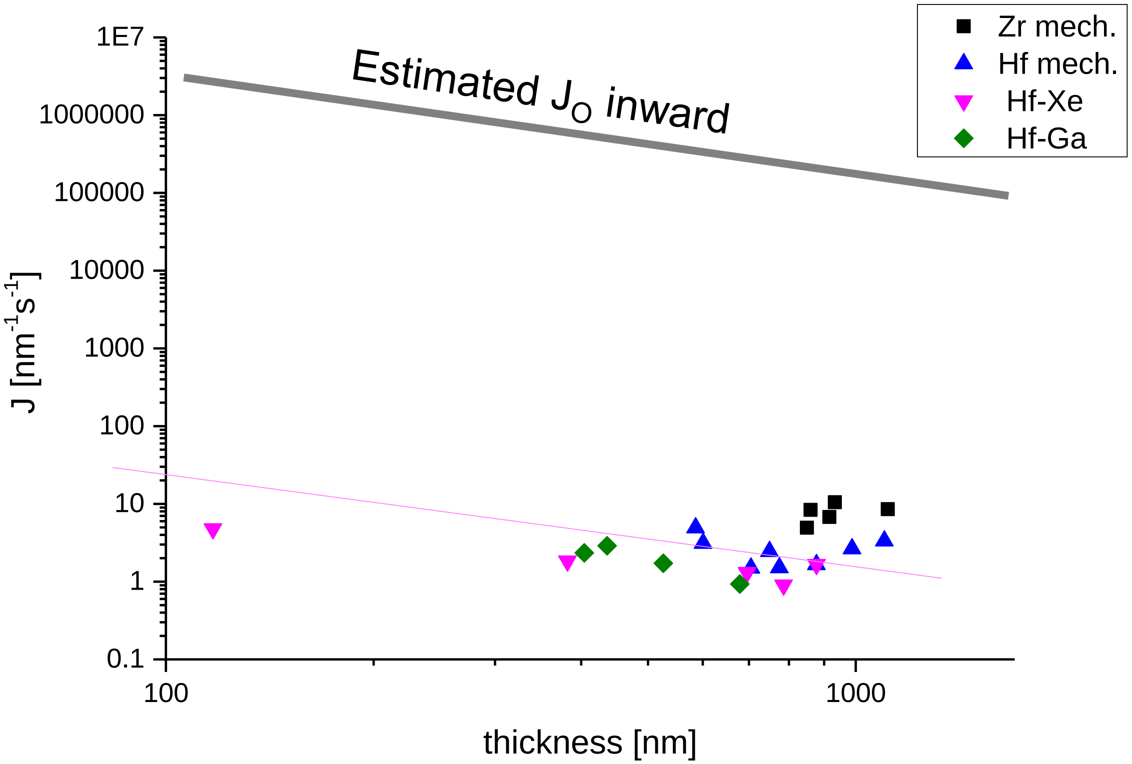
# Flux of Al through GBs at 1100° C



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

follows Fick's 1st law

# Flux of Al through GBs at 1100° C

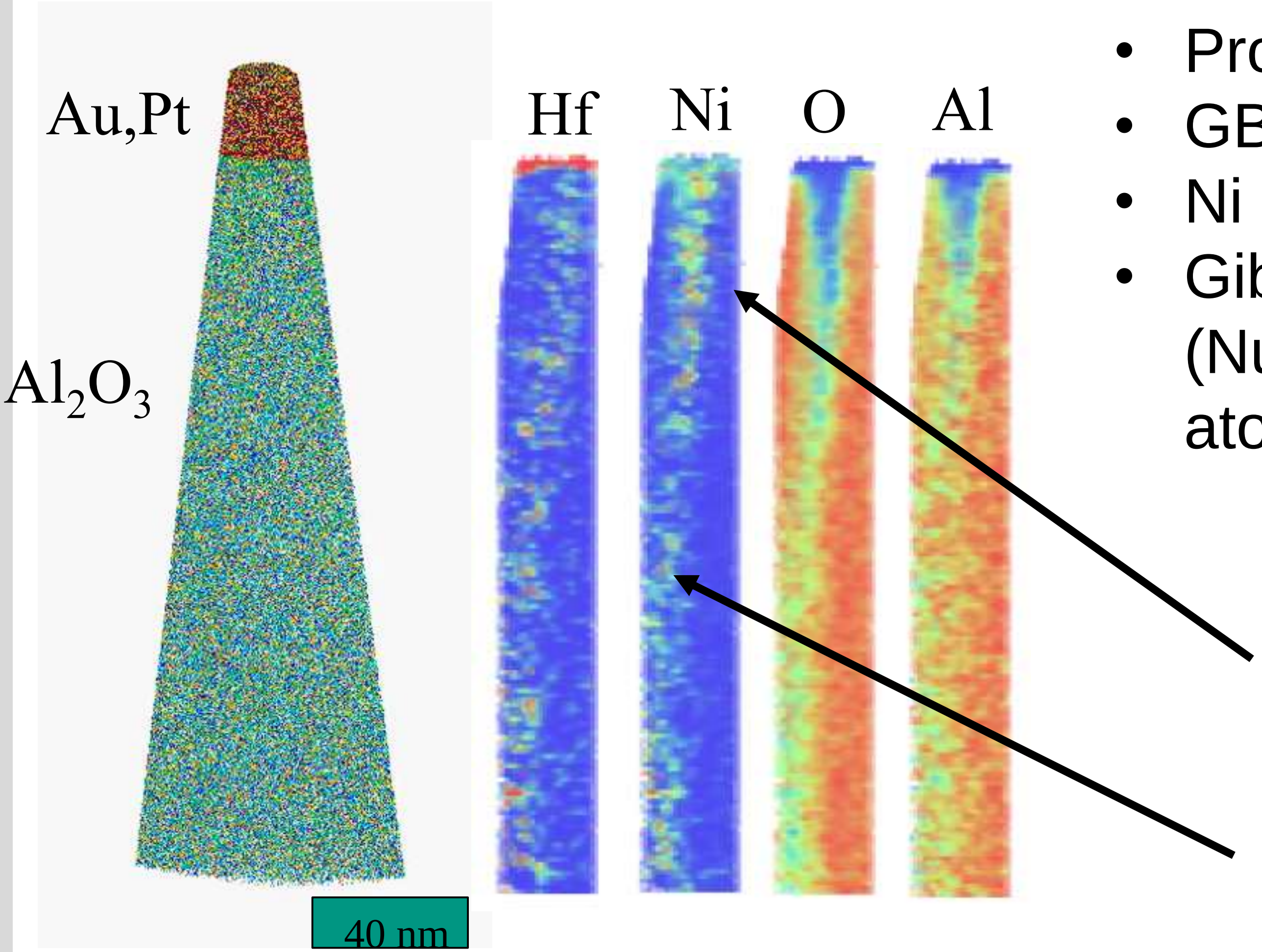


- Mechanical polishing enhances ridge growth
- Zr allows higher outward flux than Hf
- Inward flux six orders of magnitude larger

follows Fick’s 1st law

# APT of NiAl + Hf sample

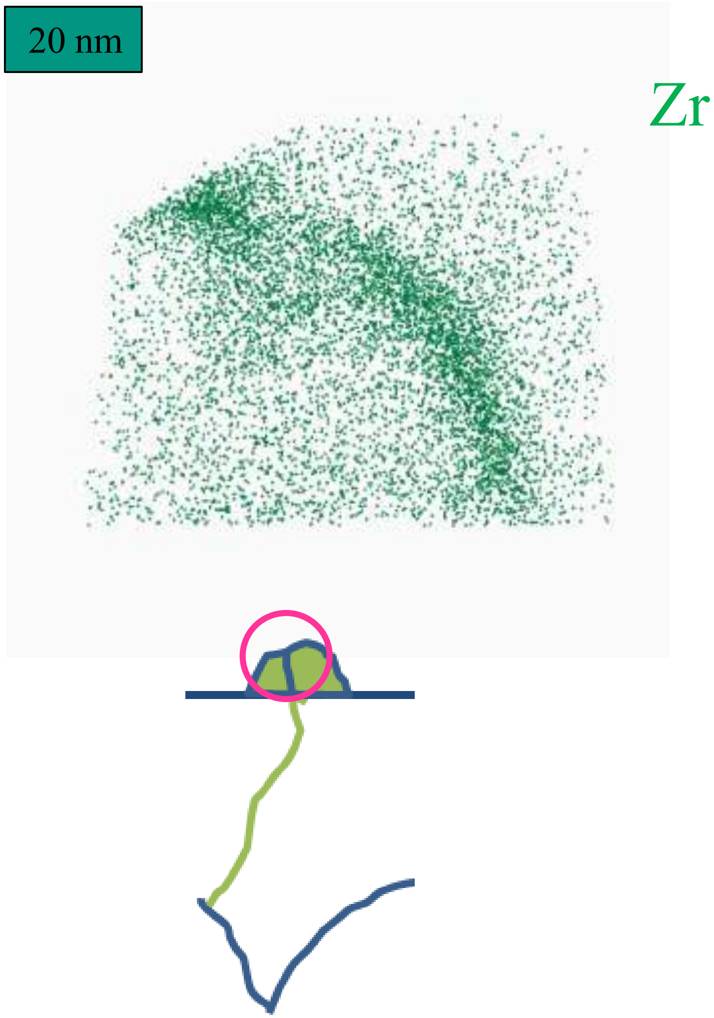
- Protective Au,Pt coating
- GB with Hf, Ni
- Ni enriched at surface
- Gibbsian excess Γ (Number of additional atoms per area in GB):



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

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

# APT of NiAl + Zr sample: At the ridge

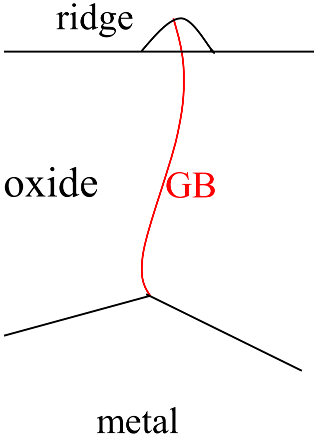


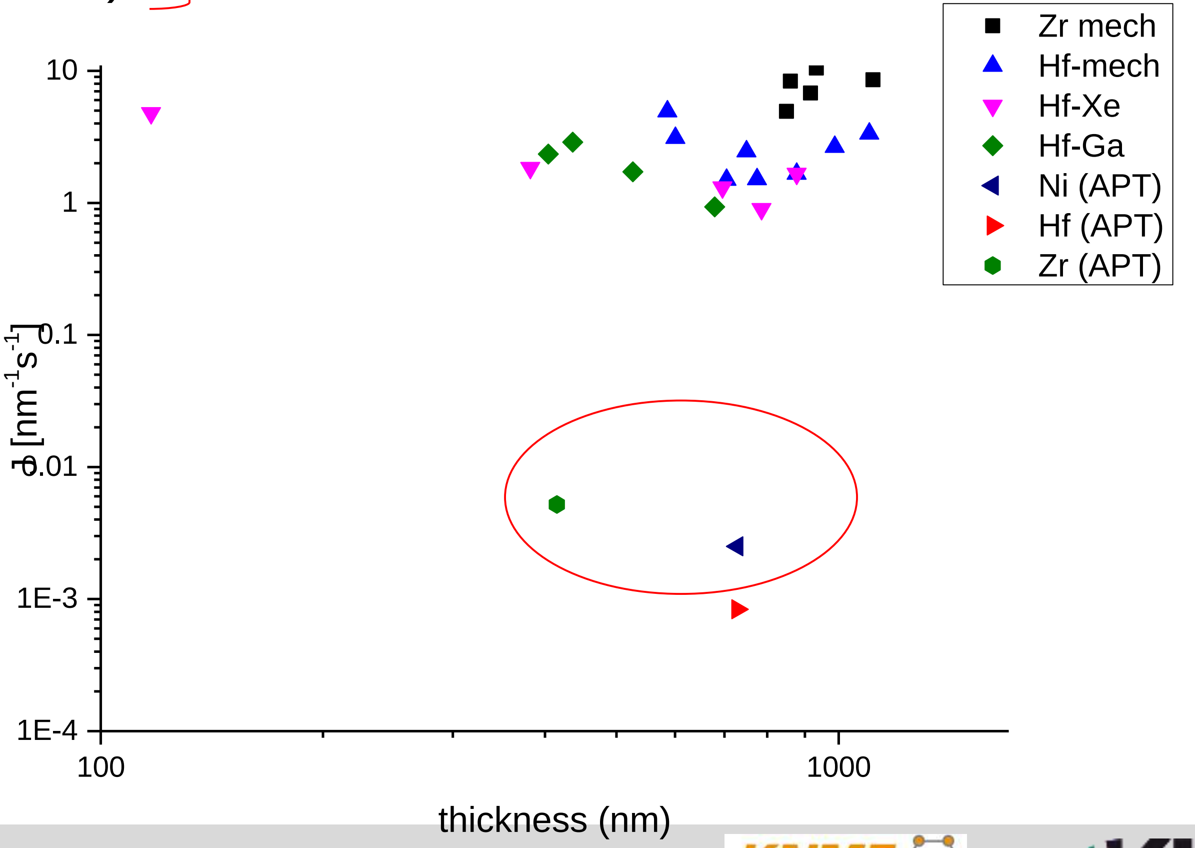
- Protective Ag on top of ridge-GB
- No Ni found
- $\Gamma_{Zr}$: 2.5 nm$^{-2}$

# Outward flux of Ni, Hf, Zr

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

→ amount of diffused material



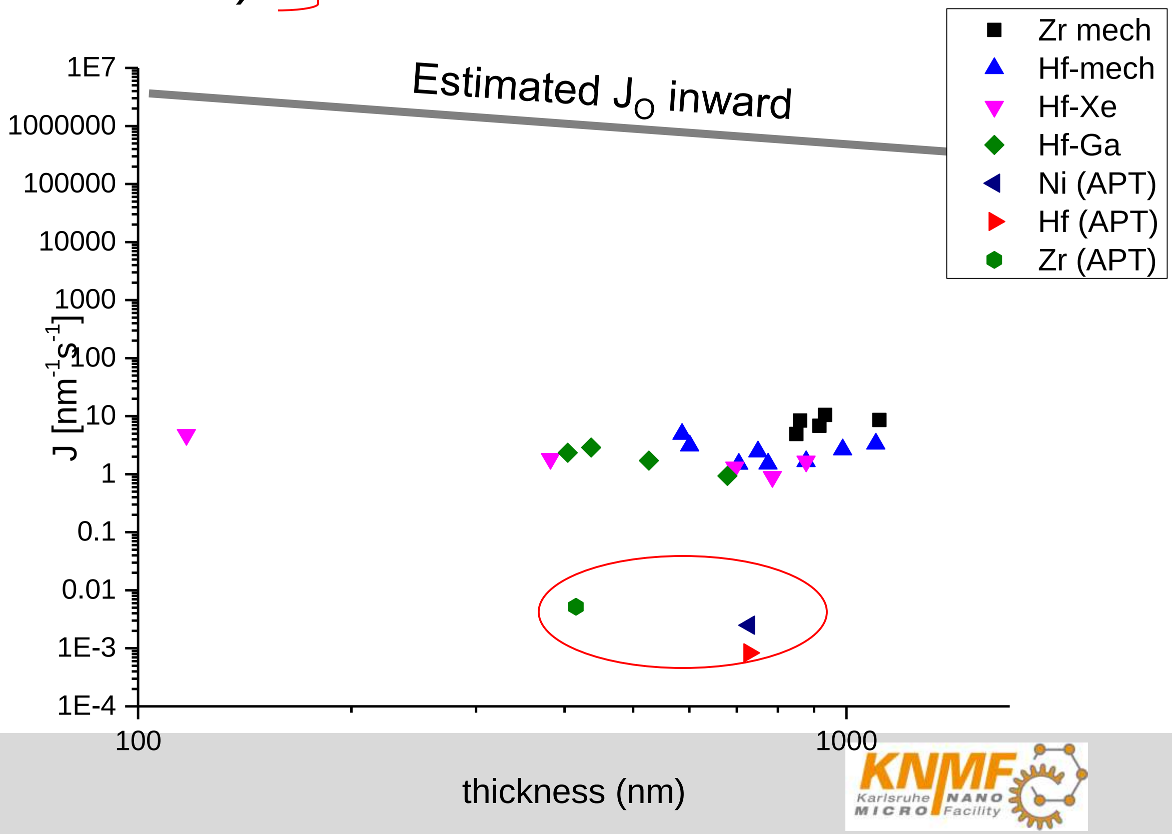


# Outward flux of Ni, Hf, Cr

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

→ amount of diffused material

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



# Conclusions II

- 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

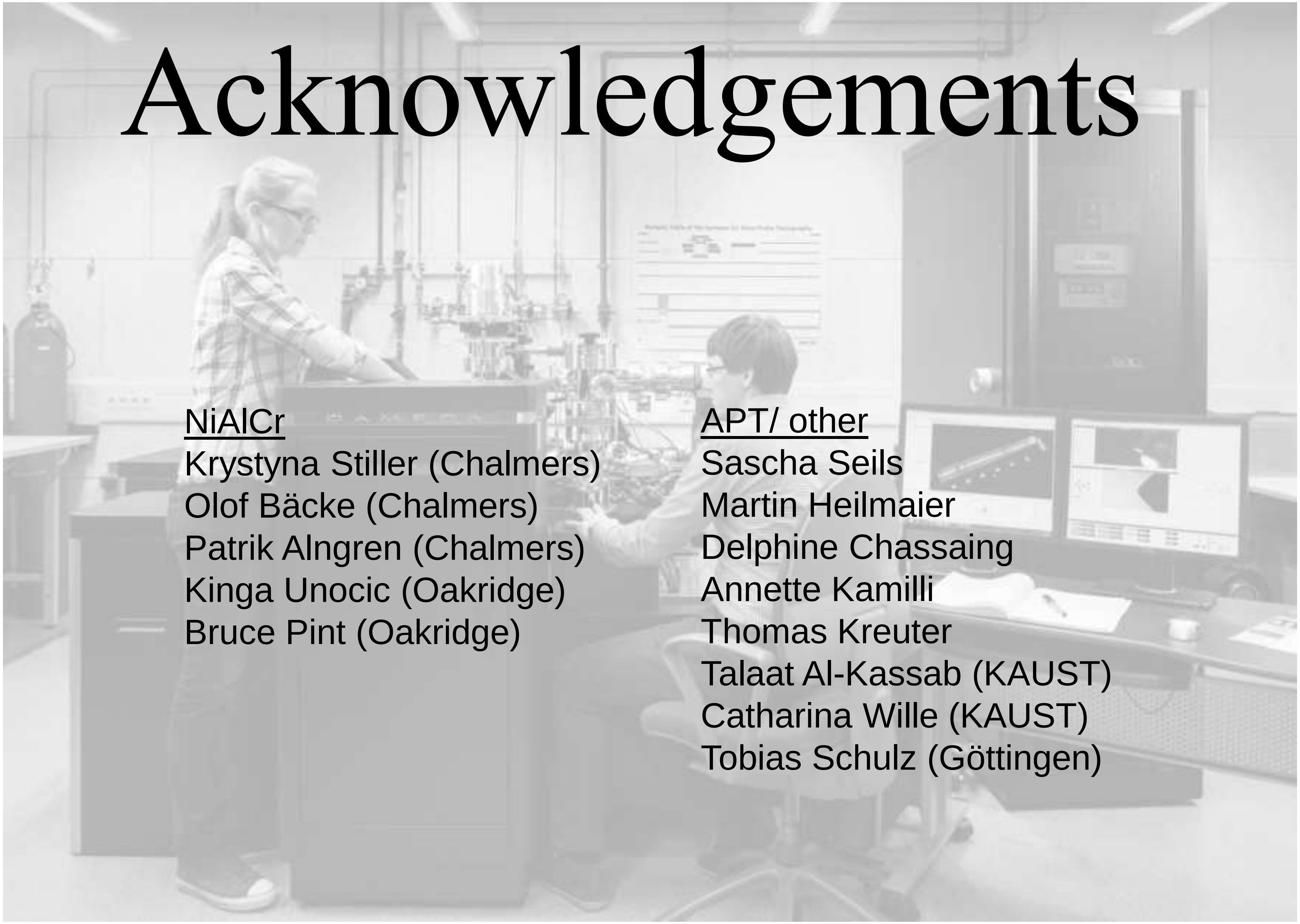
→ Outward diffusion of Ni

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

# Atom Probe Tomography: fast facts

- Small tip (d < 400 nm),high field (10-50 V/nm) in UHV -> atoms almost field evaporate
- Additional event: Laser /voltage ->evaporate single atoms
- Evaporation time and arrival time -> time of flight mass spectrometer -> elements and molecules can be identified
- Detection on a 2D detector ->(x,y)-position of atom
- Z-position from arrival sequence
- APT can analyze (in order of difficulty): metallic alloys, semi-conductors, multi-layer systems, ceramics, non-organic compounds; organic materials are problematic
- Atomic resolution for a volume of 20-300 nm in diameter and 20-2000 nm in length

# Acknowledgements



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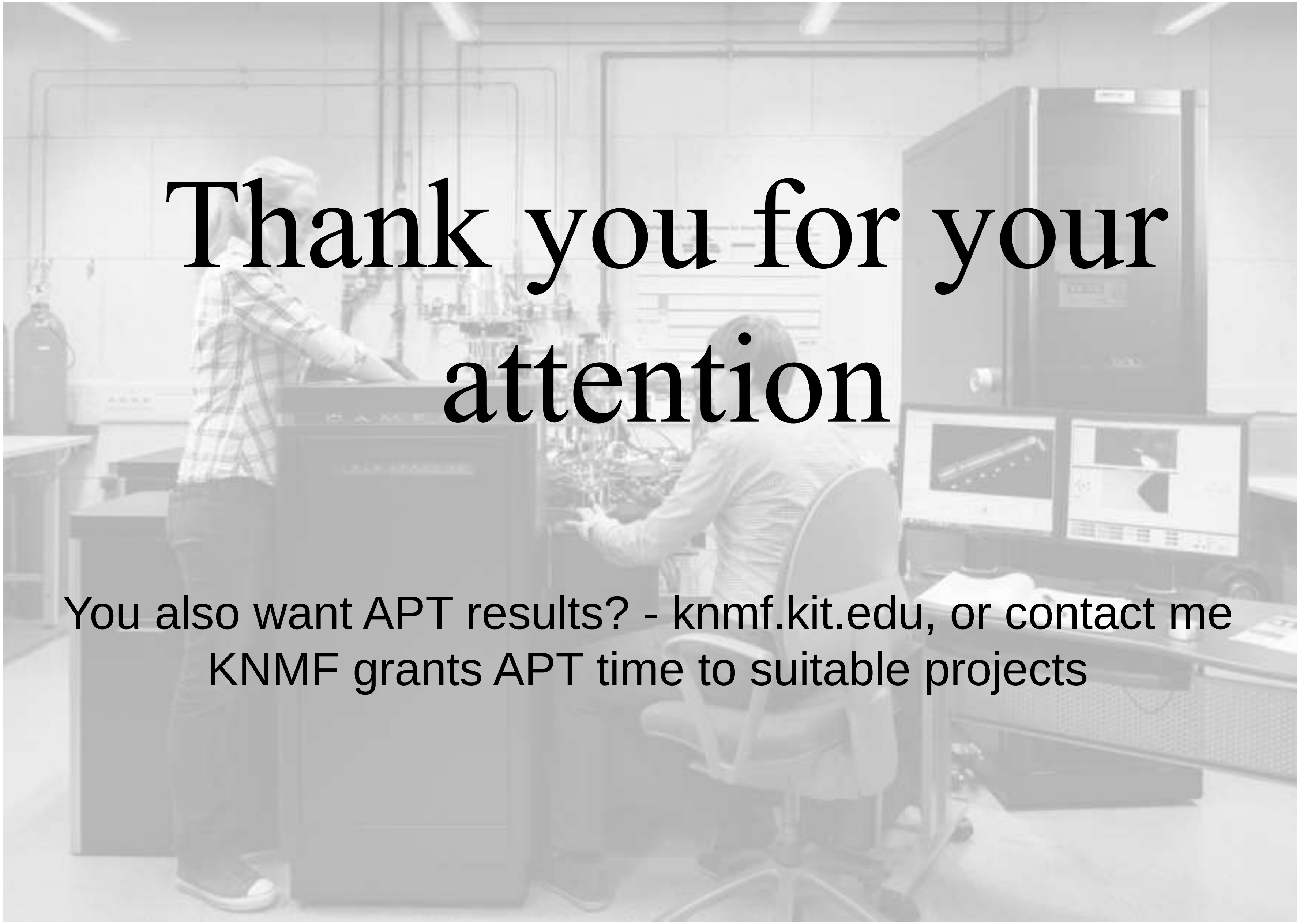

# Thank you for your attention

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

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