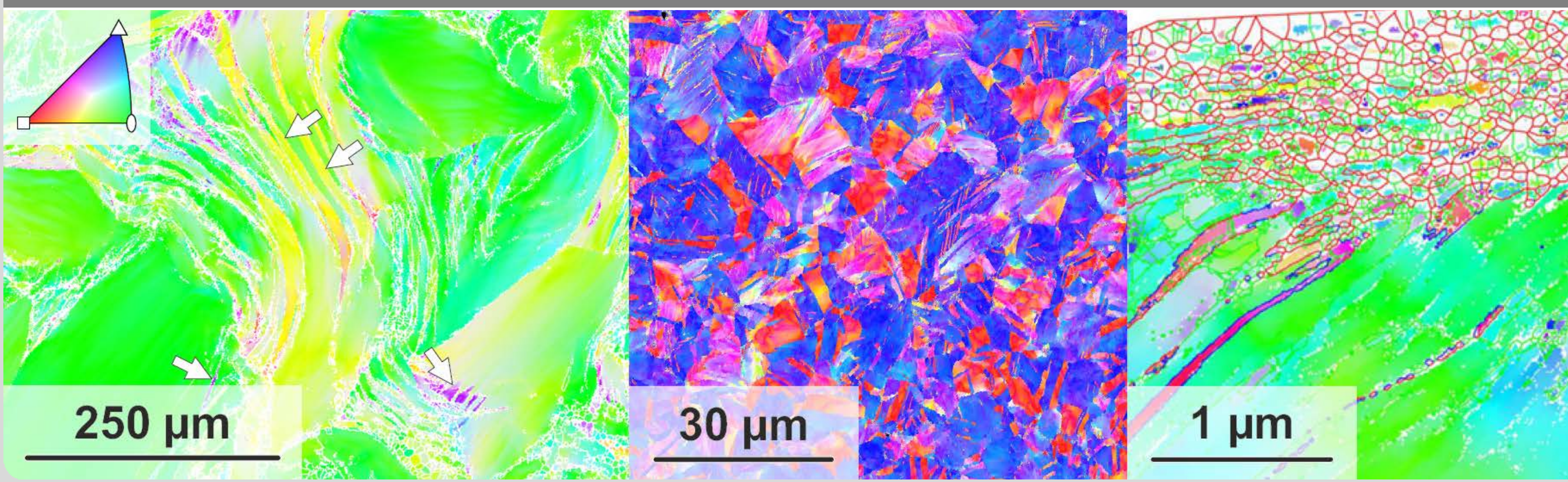
Features of plastic deformation in CCA-HEA

A. Kauffmann

A contribution to the priority programme SPP 2006
"Compositionally Complex Alloys – High Entropy Alloys (CCA-HEA)" by DFG

Institute for Applied Materials (IAM-WK)



Collaborative work

… within and outside the framework of the SPP

- at **KIT**:
  Hans Chen, Aditya Srinivasan Tirunilai, Stephan Laube, Martin Heilmaier (*IAM-WK*)
  Theresa Hanemann, Jan Sas, Klaus-Peter Weiss (*ITEP*)
  Antje Dollmann, Christian Greiner (*IAM-CMS*)
  Torben Boll, Sascha Seils, Dorothée Vinga Szabó, Sabine Schlabach (*KNMF*)
  Korbinian Ziegler, In-Chul Choi, Silva Basu, Ruth Schwaiger (*IAM-WBM*)
  Harald Leiste, Michael Stüber (*IAM-AWP*)
- at **University of Siegen**:
  Franz Müller, Steven Schellert, Bronislava Gorr, Hans-Jürgen Christ
- at **IFW Dresden**:
  Felix Thiel, David Geissler, Jens Freudenberger
- at **Brown University**:
  Sharvan K. Kumar
- at **MPIE Düsseldorf**:
  Christian Liebscher, Igor Moravčík
- at **IIT Madras**:
  Subramanya Sarma Vadlamani
- at **University of Bayreuth**:
  Christian Gadelmeier, Sebastian Haas, Uwe Glatzel
- at **Ruhr-Universität Bochum**:
  Guillaume Laplanche

High Entropy Alloys at KIT

… covering fundamental materials science and application driven research

model systems for fundamental research of the deformation in concentrated alloys

meeting the requirements for high temperature applications

- **Co Cr Fe Mn Ni**
  - mechanisms
  - **serrated plastic flow**
  - **microstructural changes during tribological loading**
- **Hf Nb Ta Ti Zr**
  - reproducability of manufacturing
  - **localized deformation**
- **Ta Nb Mo Cr Ti Al + X**
  - oxidation resistance, high temperature strength, ductility, density
  - **solid solution hardening**
  - **phase formation and thermodynamics**

A. S. Tirunilai et al. in Journal of Materials Research 33 (2018) 3287-3300
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B. Gorr et al. in Metallurgical and Materials Transactions A 47 (2016) 961
H. Chen et al. in Metallurgical and Materials Transactions A 49 (2018) 772-781
F. Müller et al. in Materials at High Temperatures 35 (2017) 168-176
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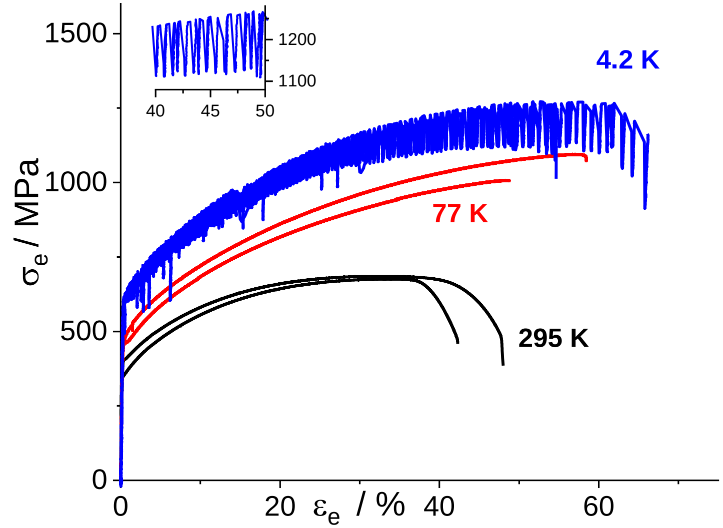
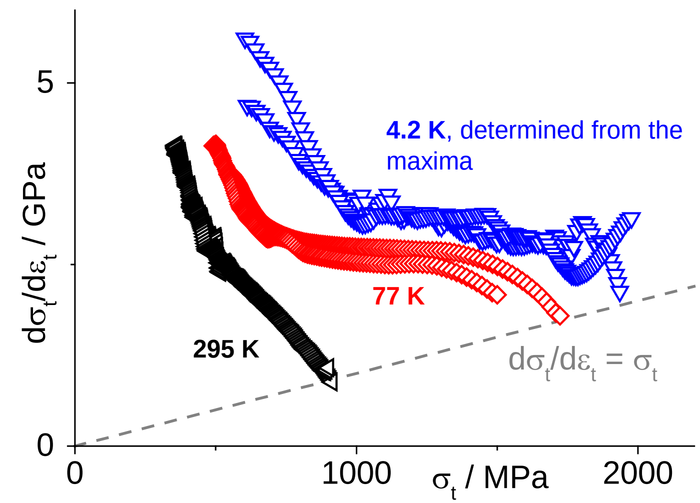
Deformation behavior of CoCrFeMnNi

… at cryogenic temperatures

- **high work-hardening rate with plateau** during deformation at cryogenic temperatures
- occurrence of **deformation twinning** in most and **martensite formation** in some alloys of the system
- **deformation is serrated** at very low temperatures
- increasing interest of the international community in the serrated flow behavior of HEA at very low temperatures





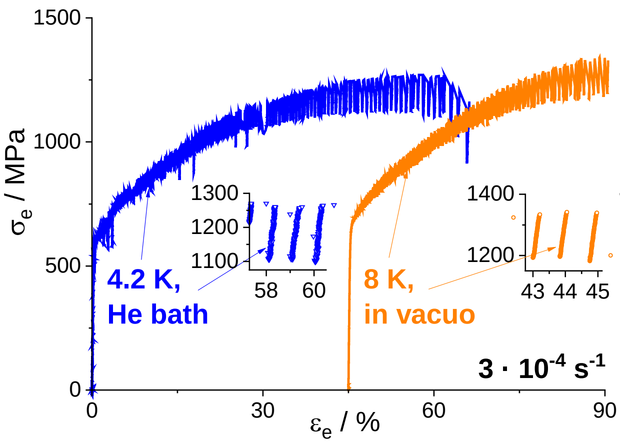
A. S. Tirunilai et al. in Journal of Materials Research 33 (2018) 3287-3300
J. Liu in Science China Materials (2018)
Y. Zhang in Progress in Materials Science 90 (2017) 358-460
J. Antonaglia in Journal of Materials 66 (2014) 2002–2008

Karlsruhe Institute of Technology

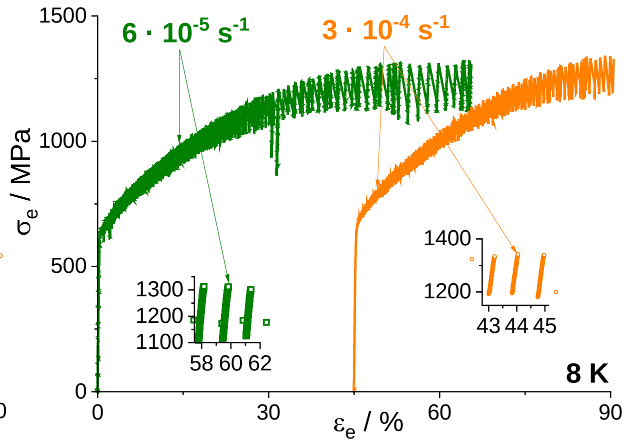
Serrated Plastic Flow at low temperatures

Origin and characteristics in HEAs

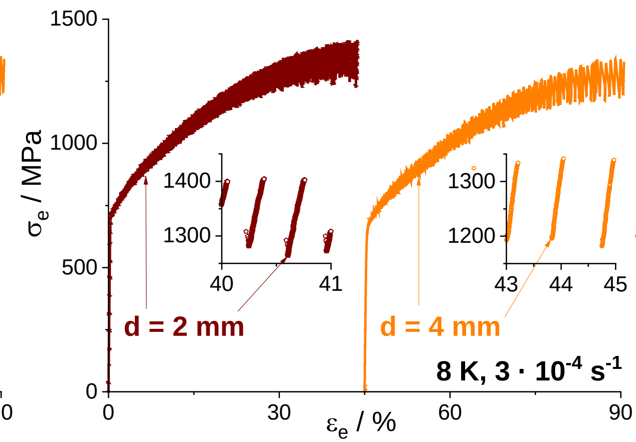
cooling medium



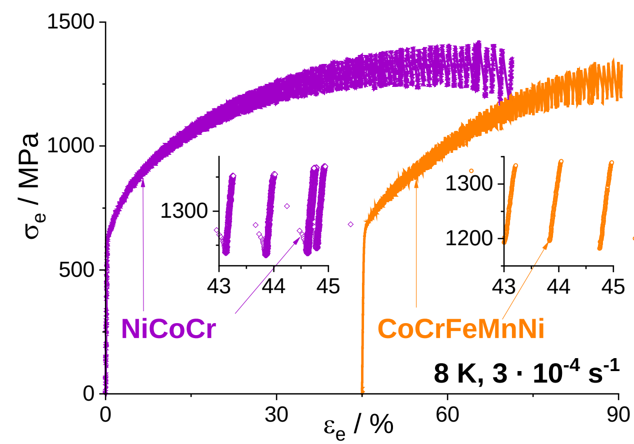
strain rate



gauge volume



lattice distortion, pre-deformation, etc.



- testing under various extrinsic and intrinsic conditions
- general deformation behavior is comparable for the tested extrinsic conditions (work-hardening & microstructure evolution)
- varying intrinsic conditions (activation of ε-martensite formation, interstitial solutes) are in progress

A. S. Tirunilai et al. in Journal of Materials Research 33 (2018) 3287-3300

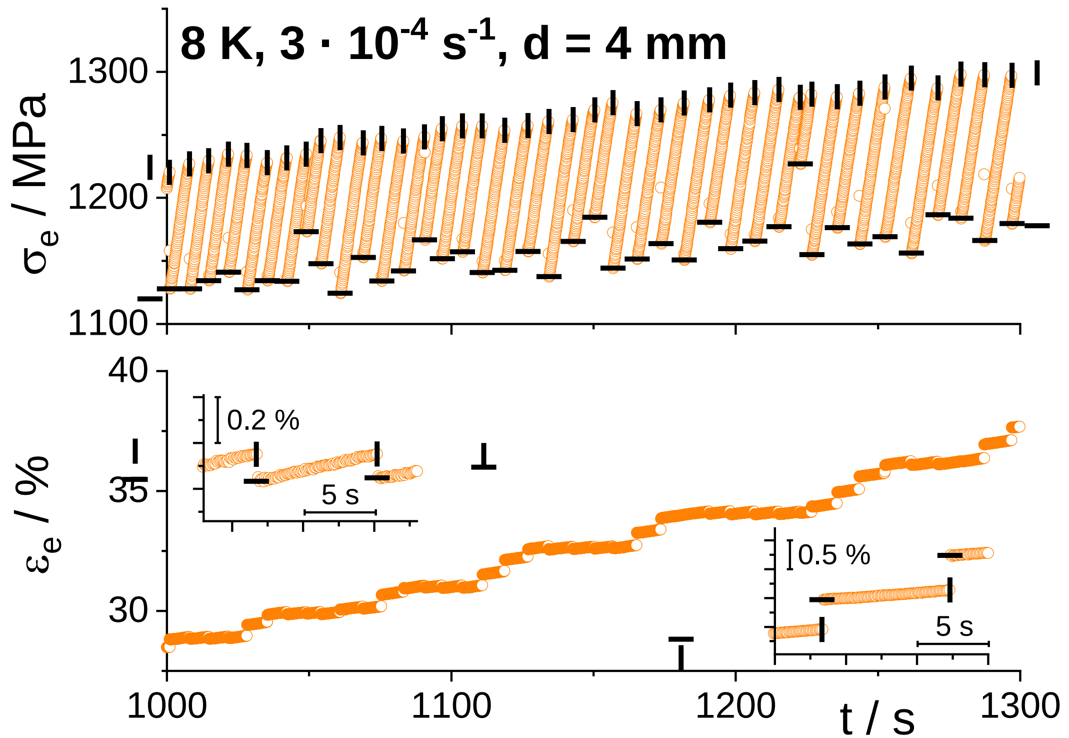
Cryogenic Materialtests Karlsruhe CryoMaK

IAM Institute for Applied Materials

Serrated Plastic Flow at low temperatures

Origin and characteristics in HEAs

- time-based statistical analysis
- at high sampling rate in order to cover all occurring events



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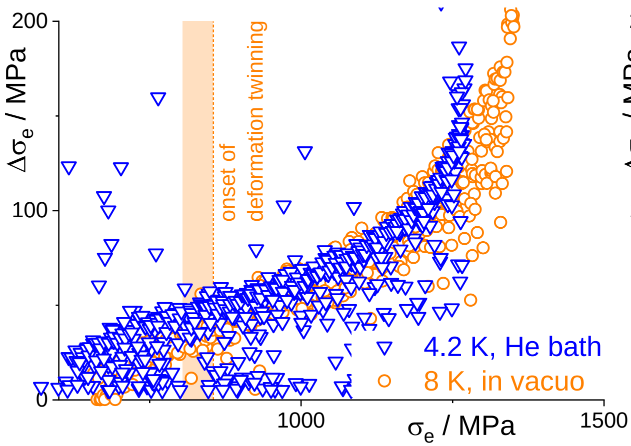
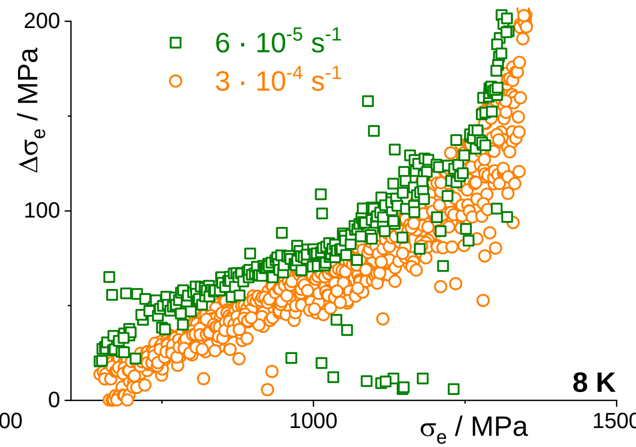
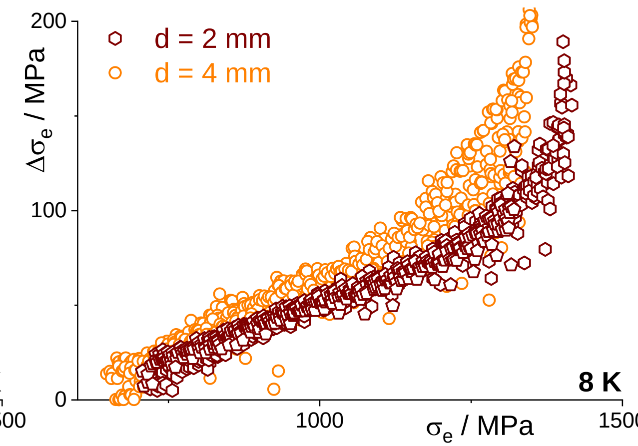


strain rate



gauge volume



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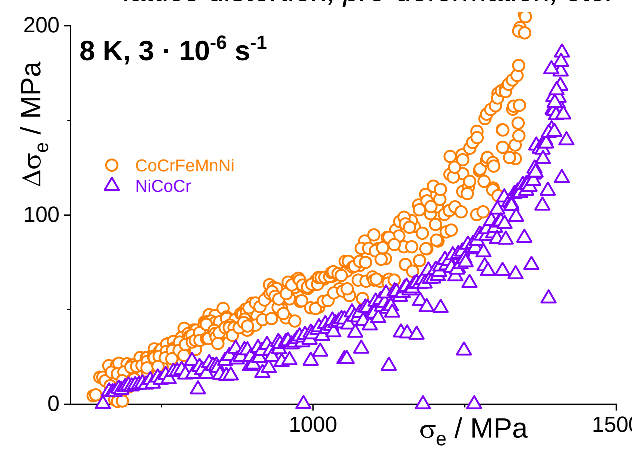

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Serrated Plastic Flow – current status

Origin and characteristics in CoCrFeMnNi

- **events are stress-critical**
  (varying gauge diameters do not lead to varying event on-sets and magnitudes of the stress drops)
- **events are localized plastic deformation**
  (stress drops lead to two different strain responses depending on whether the localized deformation occurs within or outside the strain gauge)
- **events occur immediately**
  (time scale of the drops is below 0.1 s in practically all cases)
- **events are not related to deformation twinning**
  (on-set stress is not linked to specific features/changes in the serration trends; single crystal tests with orientations unfavorable for twinning do exhibit serrated flow)

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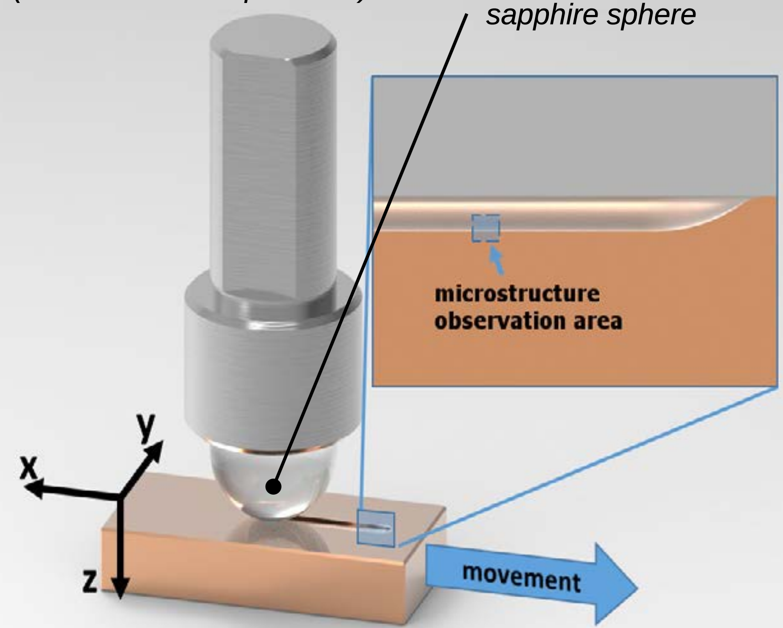
Deformation behavior of CoCrFeMnNi

… under tribological load

- promise of outstanding tribological properties of HEAs
- investigation of subsurface microstructural changes in the Cantor alloy under mild conditions
- mechanism-based interpretation of the tribological behavior
- effects that have to be considered:
  - dislocation slip
  - deformation twinning
  - development of shear bands
  - tribo-oxidation
  - mechanical mixing

(scheme of the experiment)



F_N = 2 N, v = 0.5 mm/s, stroke length 12 mm, 25 °C and rel. hum. of (50 ± 3) %

A. Dollmann et al. in preparation (2019)

work in the framework of a recently started DFG project on „Structure-properties relations in single phase fcc and bcc high entropy alloys under a tribological load“ (by C. Greiner and M. Heilmaier)

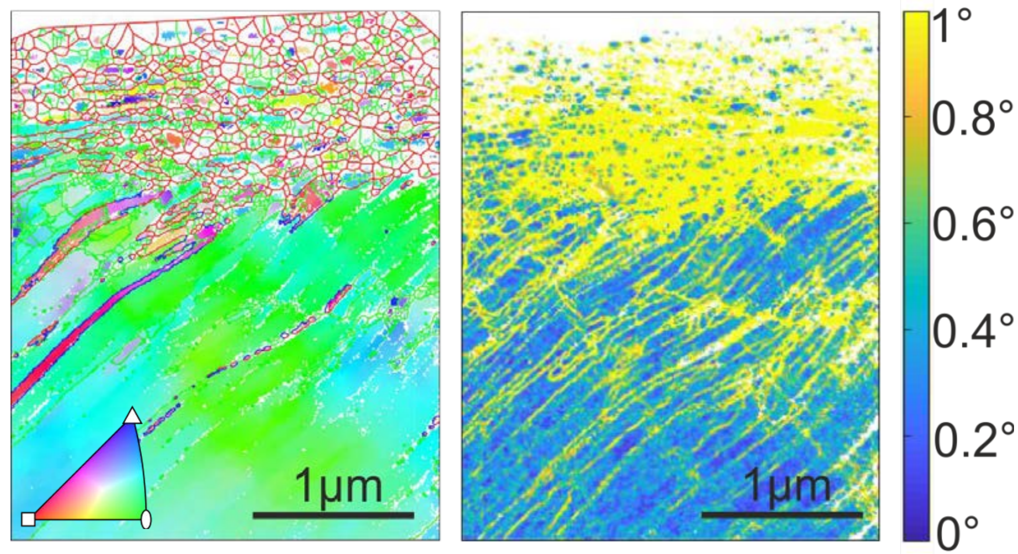
Subsurface changes in CoCrFeMnNi

… under tribological load

- significant microstructural changes already after single track, including regions with:
  - nanocrystalline grains
  - localized dislocation motion
  - deformation twins
- large adhesive forces (material transfer to the counter body)
- considerably different to Cu and brass!

sliding direction ⟶

by transmission Kikuchi diffraction

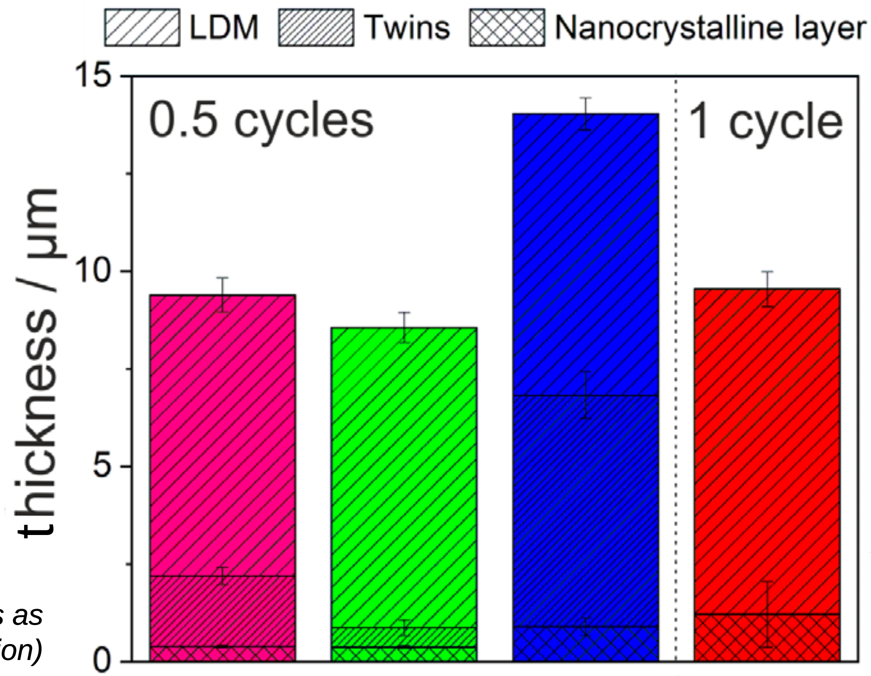


orientation (ND) *kernel average misorientation*

A. Dollmann et al. in preparation (2019)

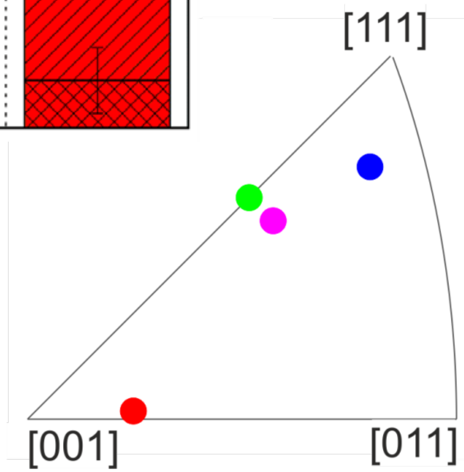
Subsurface changes in CoCrFeMnNi

… under tribological load



(thicknesses of the characteristic layers as a function of initial grain orientation)

- nanocrystalline layer is common feature independent of the grain orientation
- localized dislocation motion and deformation twinning exhibit significant orientation dependence



inverse pole figure of the sliding direction

A. Dollmann et al. in preparation (2019)

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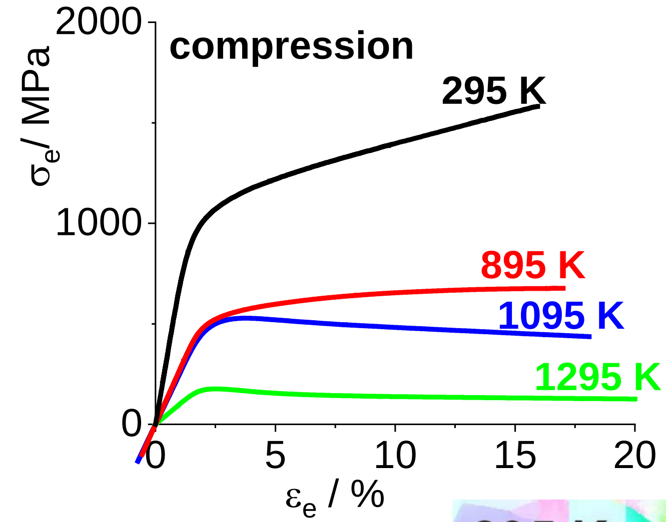
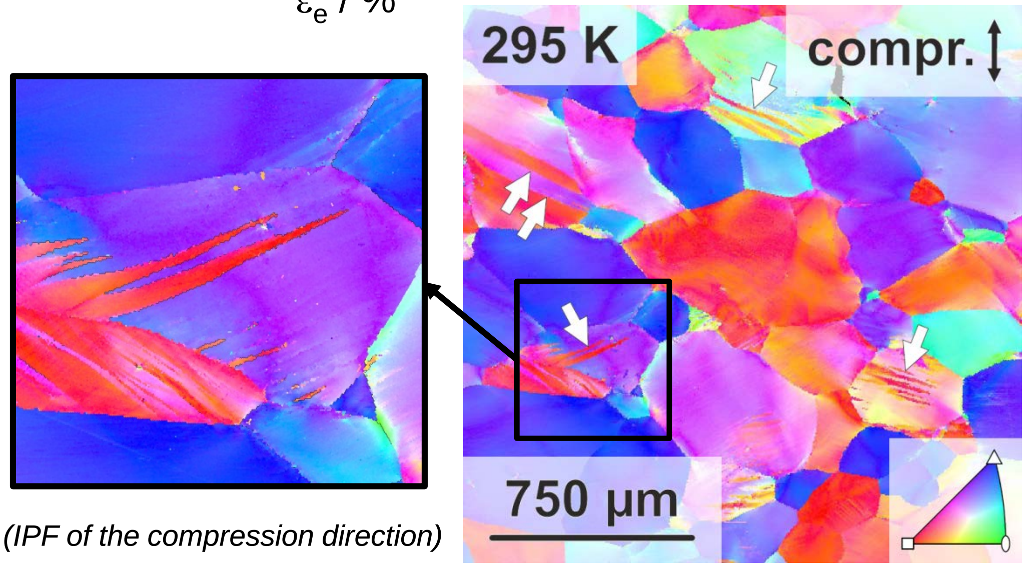
Deformation behavior of HfNbTaTiZr

… under various stress states

- HfNbTaTiZr exhibits **outstanding ductility** and workability
- **pronounced, localized plastic deformation** is frequently observed at large plastic strains:
  - **compression testing**
  - tensile testing
  - rotary swaging
  - rolling





(IPF of the compression direction)

T. Hanemann et al. in preparation (2019)

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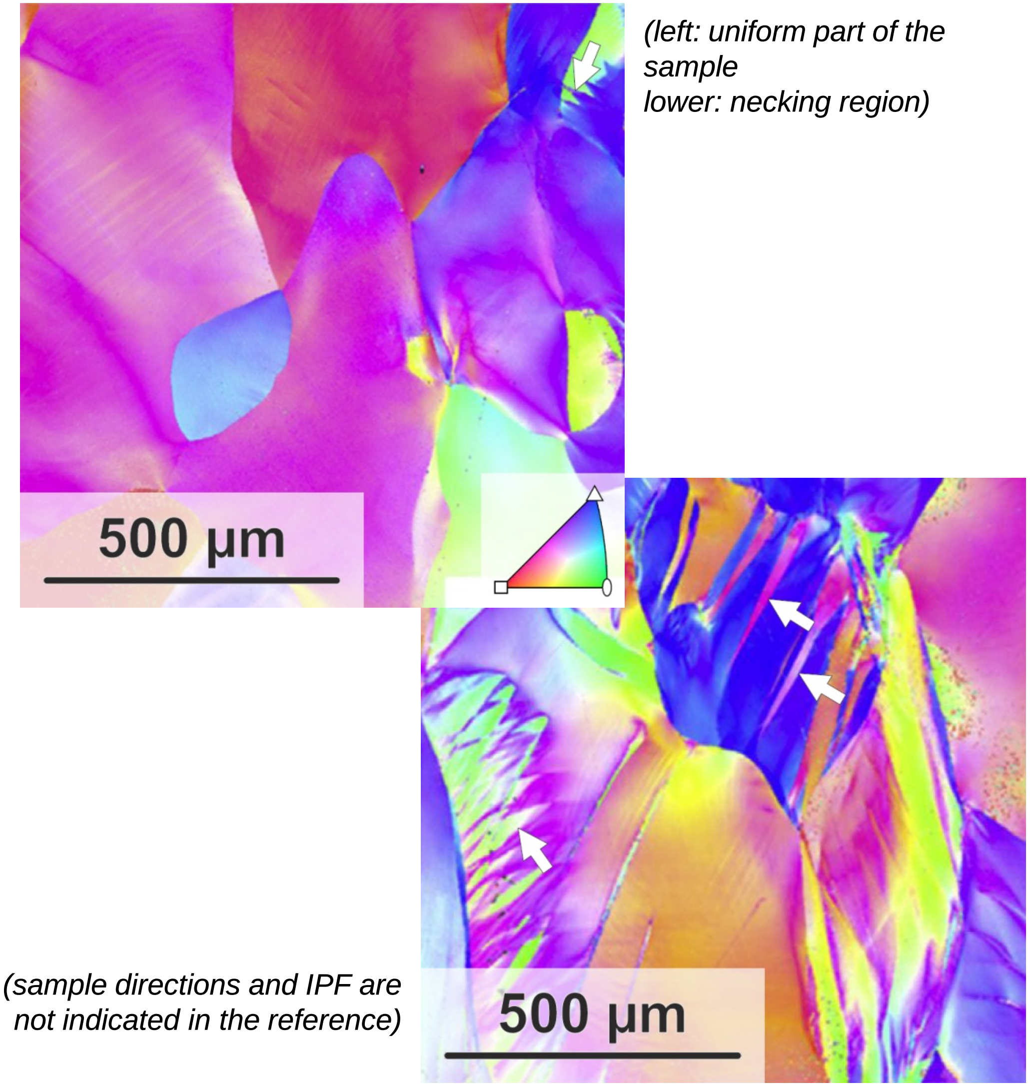

(left: uniform part of the sample
lower: necking region)

(sample directions and IPF are not indicated in the reference)

D. Dirras et al. in Materials Science and Engineering A 654 (2016) 30-38

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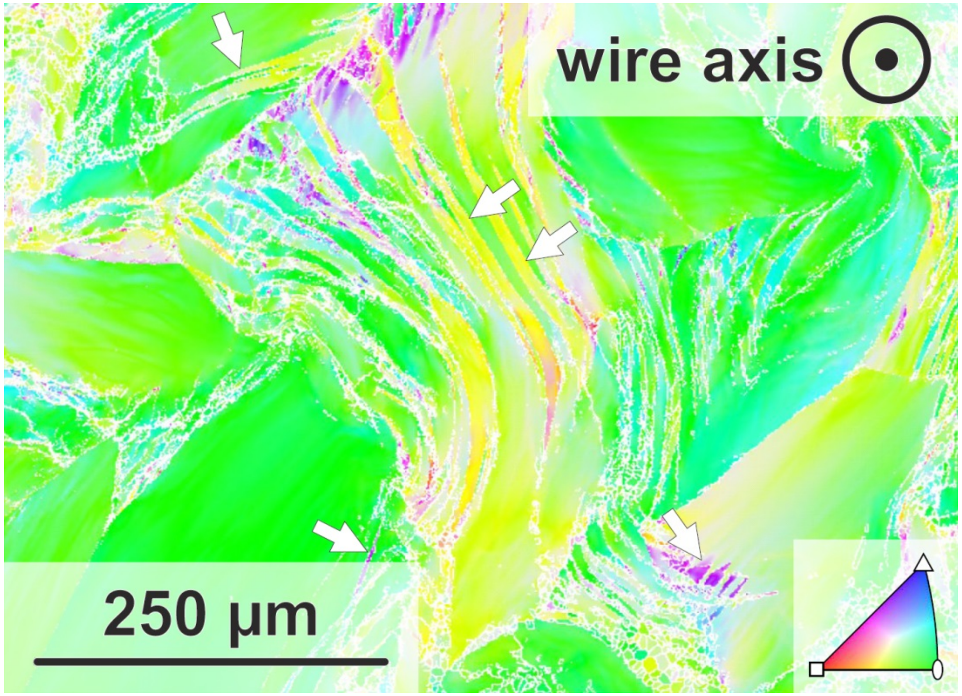

(IPF of the wire axis at a true strain of about 1.4)

T. Hanemann et al. in preparation (2019)

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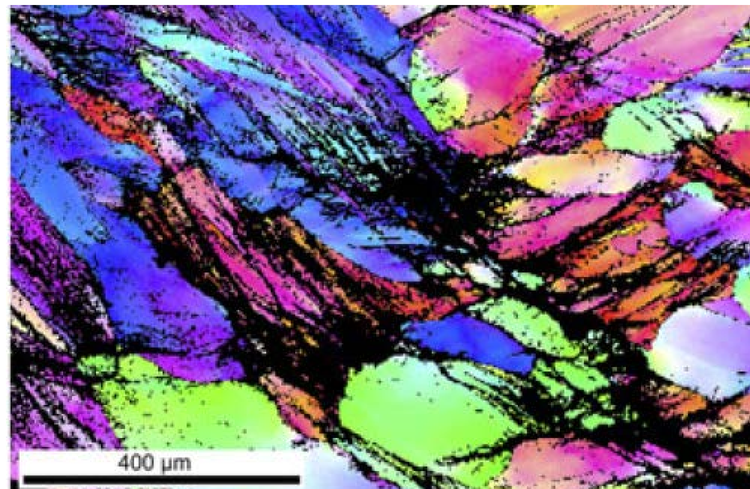
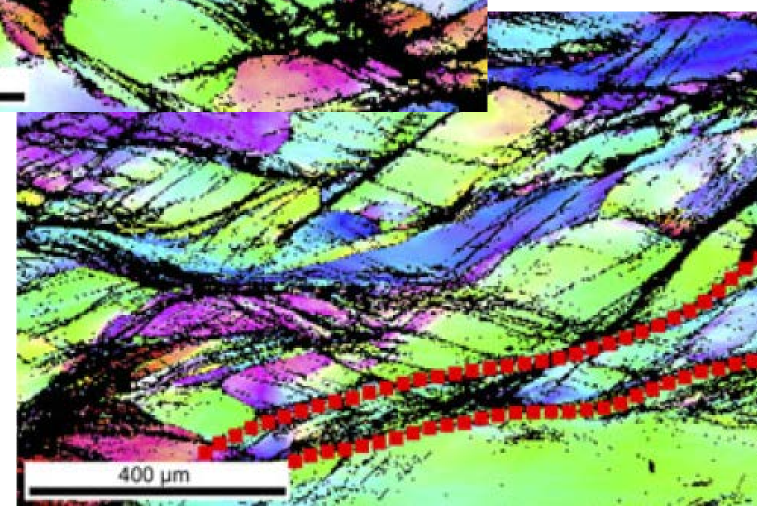


(left: thickness reduction of 40 % lower: 60 %)



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W. Wu et al. in Journal of Materials Research 31 (2016) 3815-3823

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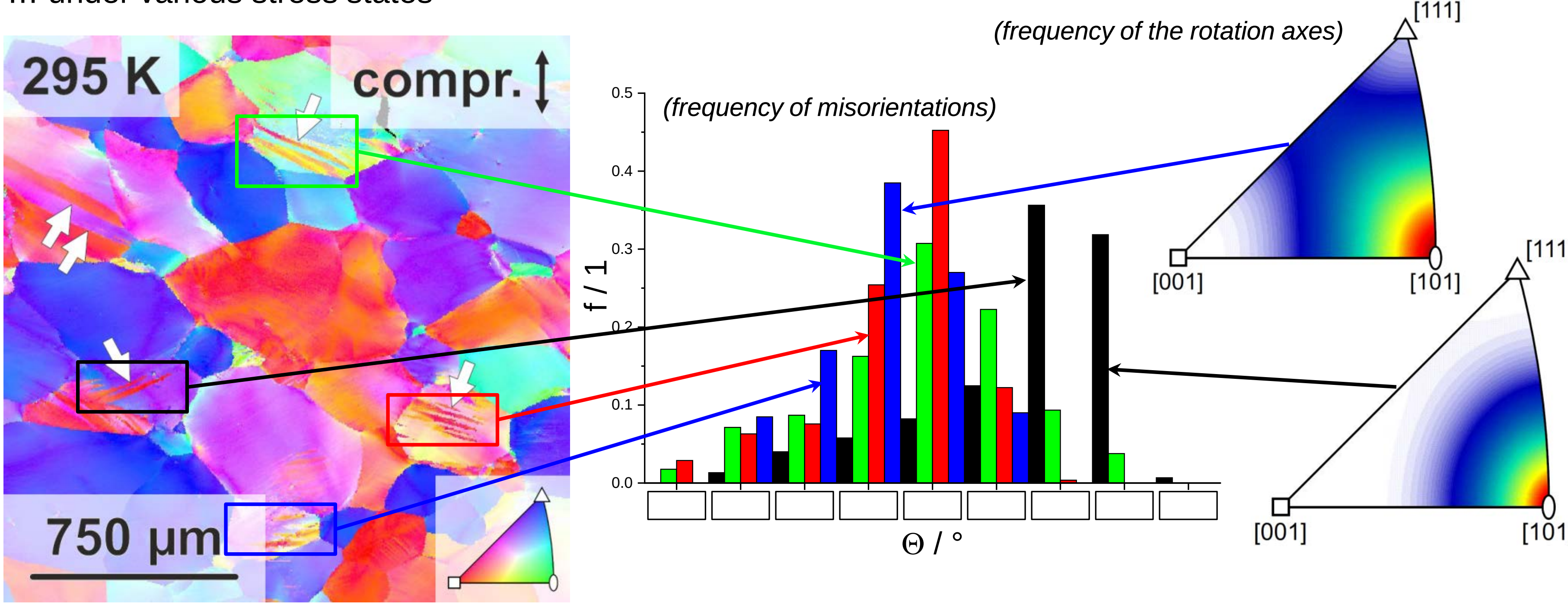

- detailed analysis of the features yield rotations of (20 … 60)° about close to ⟨110⟩ (EBSD data)
- interface coincides with {110} (FIB cut in conjunction with EBSD)
- cannot be related to common or uncommon twin systems

T. Hanemann et al. in preparation (2019)

Karlsruhe Institute of Technology

Cryogenic Materialtests Karlsruhe CryoMaK

IAM Institute for Applied Materials

Deformation behavior of HfNbTaTiZr

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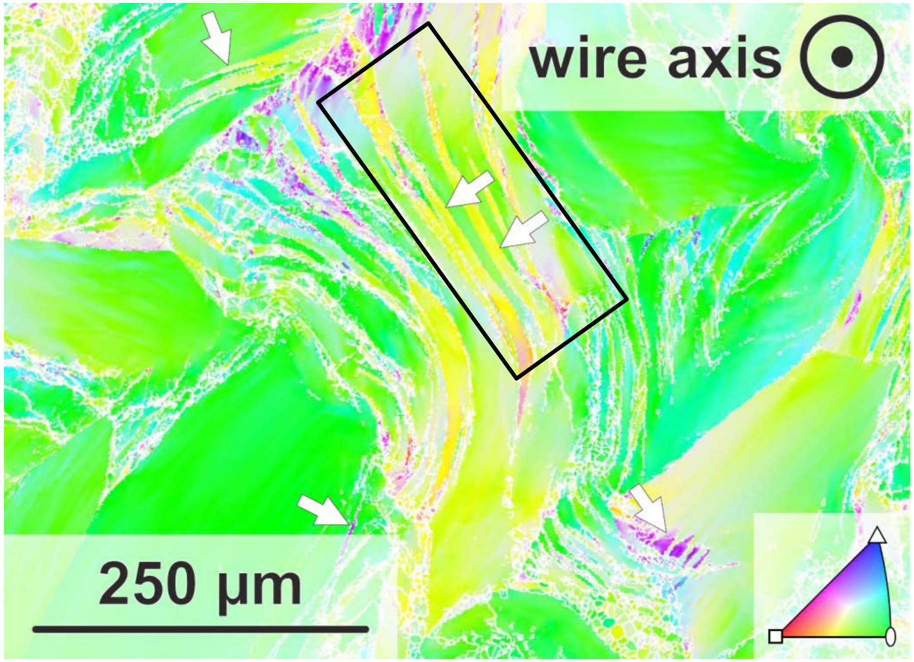

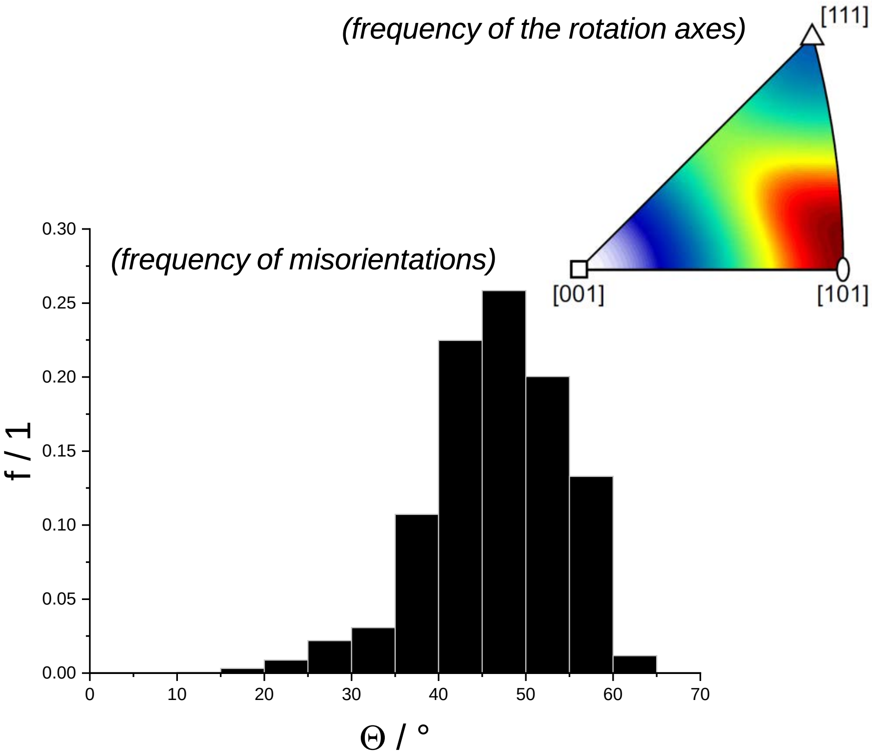

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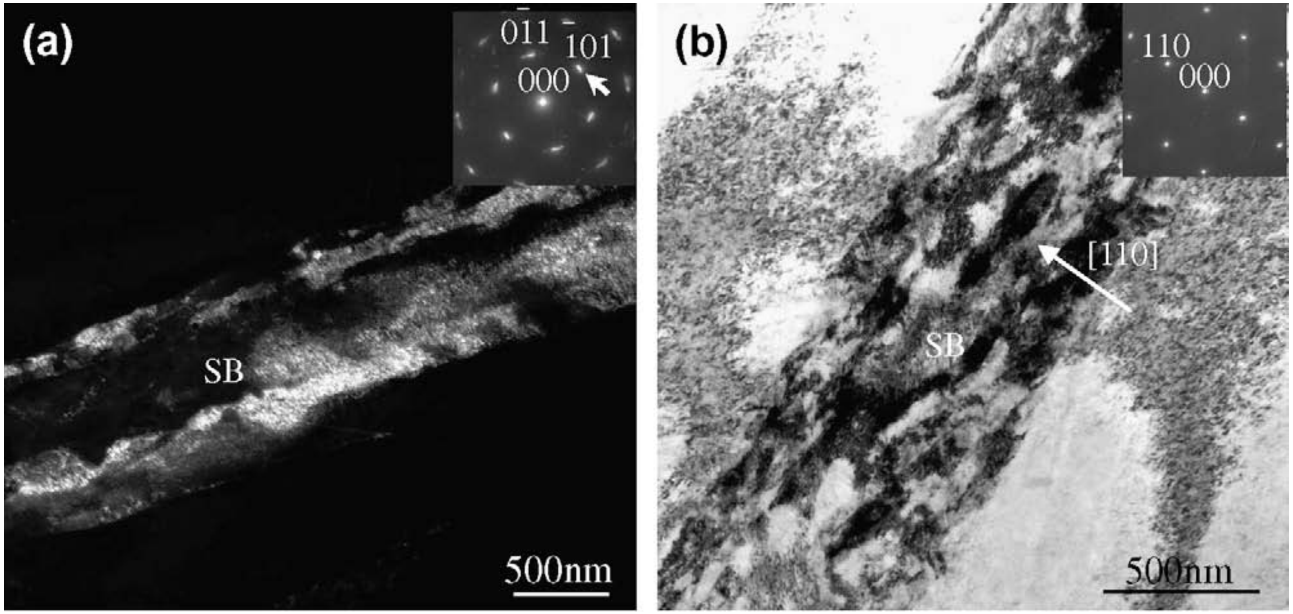

(localized plastic deformation in Ti-22.4Nb-0.73Ta-2Zr-1.34O with common {110} after straining to 60 % in compression at room temperature)

- similar features were previously found in “gum metals” (β-stabilized Ti alloys with substantial amounts of O)
- in Ti-22.4Nb-0.73Ta-2Zr-1.34O, these features with common {110} are linked to shear band formation due to texture evolution (towards ⟨100⟩ || CD)
- contradicting orientation dependence to the observations an unusual orientation change across the features in HfNbTaTiZr
- inherent instability of the bcc-phase has to be taken into account

T. Saito et al. in Science 300 (2003) 464-467
Y. Yang et al. in Acta Materialia 58 (2010) 2778-2787

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Assessment of solid solution strengthening

NbMoTiAl

$NbMoCr_{0.25}TiAl$

$NbMoCr_{0.5}TiAl$

$NbMoCr_{0.75}TiAl$

Suppression of Cr_2Nb and $Al(Mo,Nb)_3$

Cr reduction ← **NbMoCrTiAl** → Nb reduction

$Nb_{0.75}MoCrTiAl$

$Nb_{0.5}MoCrTiAl$

$Nb_{0.25}MoCrTiAl$

MoCrTiAl

- within the metallurgical constraints (competing phases, homogenization treatment, etc.)

H. Chen et al. in Metallurgical and Materials Transactions A 49 (2018) 772-781

Obtaining proper atomic radii

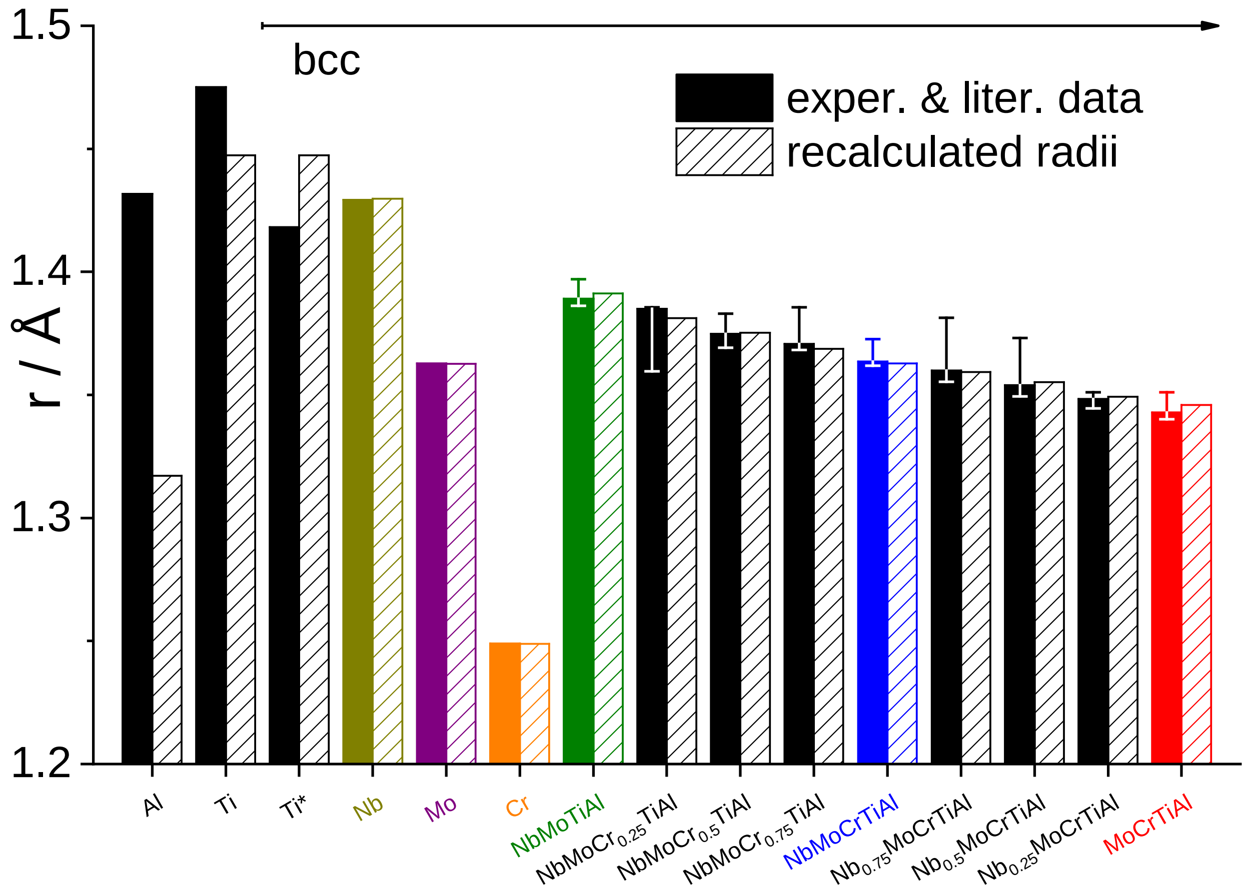
Karlsruhe Institute of Technology

- Recalculation of metallic radii (with bcc coordination) using (experimental) interatomic spacings and Vegard's rule
- Error minimization on the (overdetermined) set of linear equations (nine alloys plus three bcc elements)

$$\underbrace{\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ x_{\mathrm{Nb},1} & x_{\mathrm{Mo},1} & x_{\mathrm{Cr},1} & x_{\mathrm{Ti},1} & x_{\mathrm{Al},1} \\ x_{\mathrm{Nb},2} & x_{\mathrm{Mo},2} & x_{\mathrm{Cr},2} & x_{\mathrm{Ti},2} & x_{\mathrm{Al},2} \\ x_{\mathrm{Nb},3} & x_{\mathrm{Mo},3} & x_{\mathrm{Cr},3} & x_{\mathrm{Ti},3} & x_{\mathrm{Al},3} \\ & & \vdots & & \end{pmatrix}}_{\text{Solid solution composition by EDX}} \underbrace{\begin{pmatrix} r_{\mathrm{Nb}} \\ r_{\mathrm{Mo}} \\ r_{\mathrm{Cr}} \\ r_{\mathrm{Ti}} \\ r_{\mathrm{Al}} \end{pmatrix}}_{\textbf{Recalculated atomic radii}} = \underbrace{\begin{pmatrix} r_{\mathrm{Nb}} \\ r_{\mathrm{Mo}} \\ r_{\mathrm{Cr}} \\ r_1 \\ r_2 \\ r_3 \\ \vdots \end{pmatrix}}_{\text{Interatomic spacings}}$$

H. Chen et al. in Metallurgical and Materials Transactions A 49 (2018) 772-781

Recalculated atomic radii



- good agreement of experimental and re-calculated data
- substantial differences of radii of non-bcc alloying elements vs. their elemental metallic radii

H. Chen et al. in Metallurgical and Materials Transactions A 49 (2018) 772-781

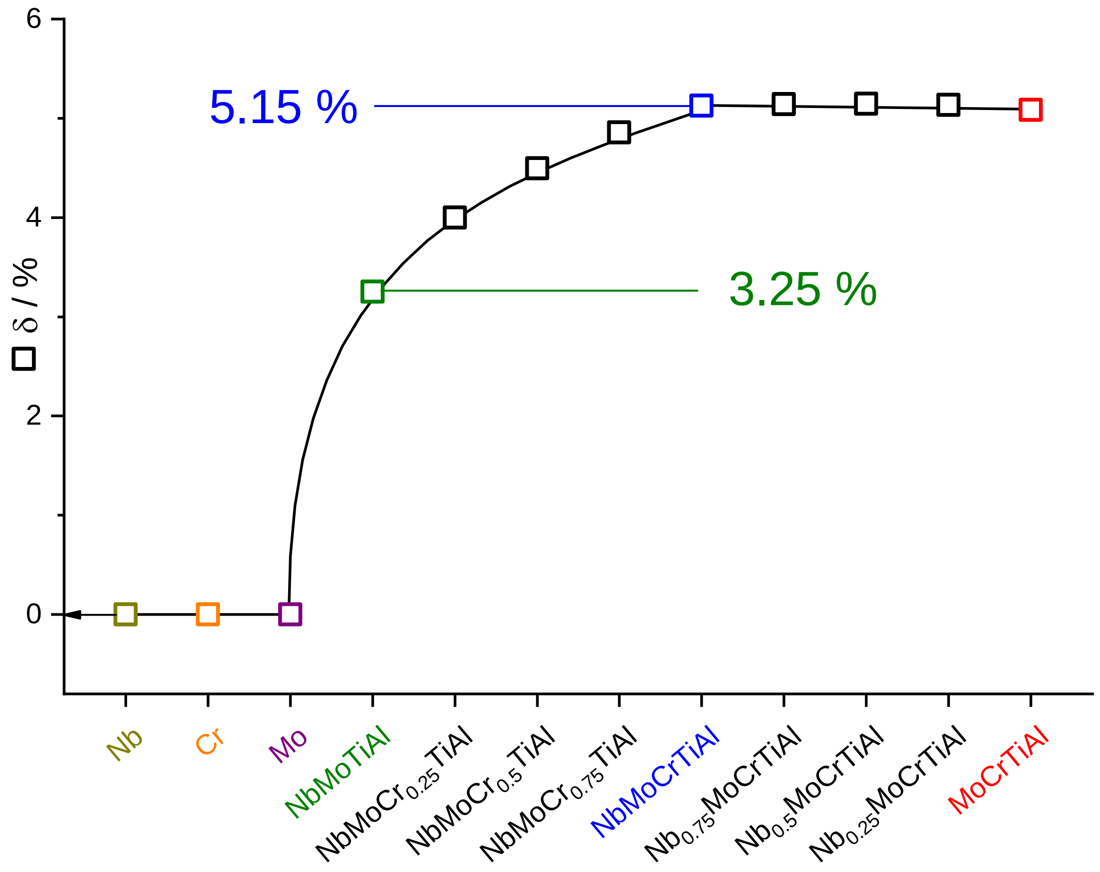
Lattice distortion

- Description based on the atomic size difference δ:

$$\delta = \sqrt{\sum_i x_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}$$

x_i … concentration of the alloying element; r_i … radius of the alloying element; $\bar{r}$ … mean radius of the alloys

- $x_{\mathrm{Cr}} \downarrow \;\rightarrow\; \delta \downarrow$
  $x_{\mathrm{Nb}} \downarrow \;\rightarrow\; \delta \approx \mathrm{const.}$



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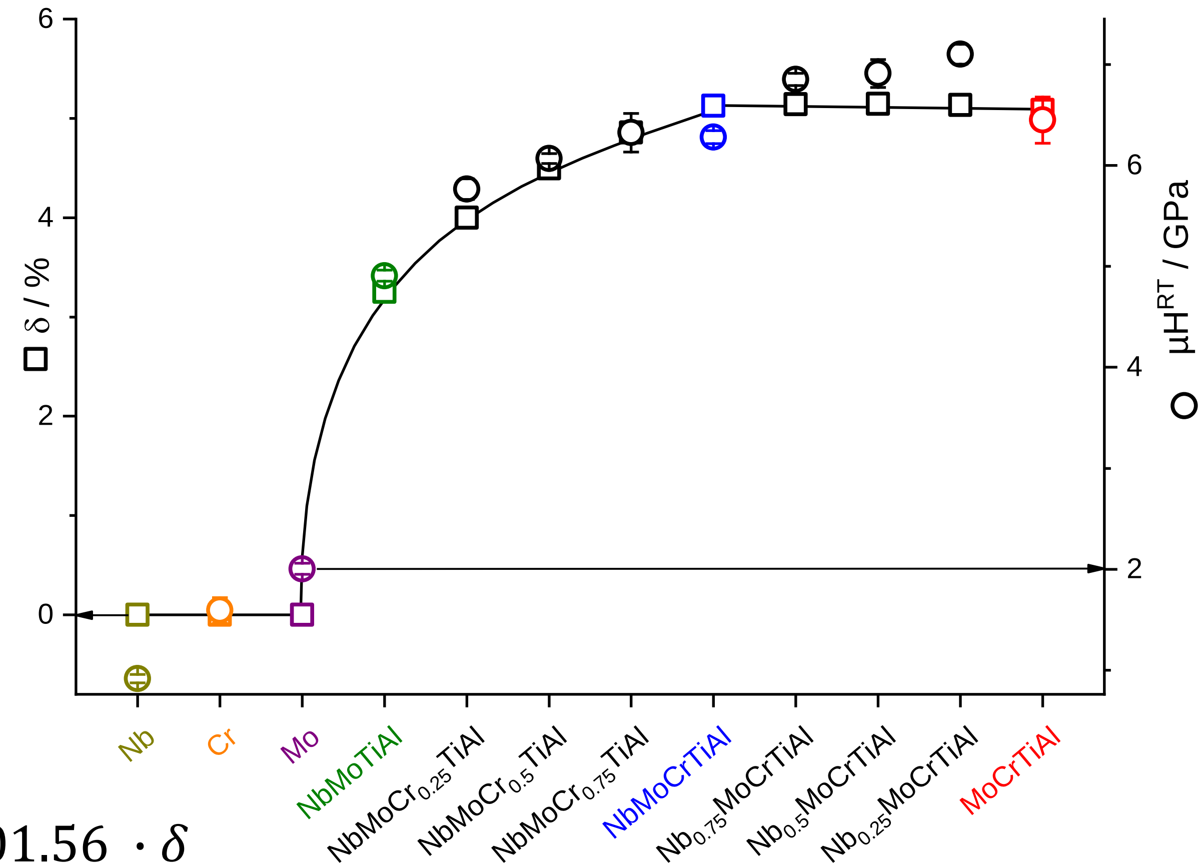
Lattice distortion

- Description based on the atomic size difference δ:

$$\delta = \sqrt{\sum_i x_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}$$

- Correlation of microhardness at room temperature μH^{RT} and δ:

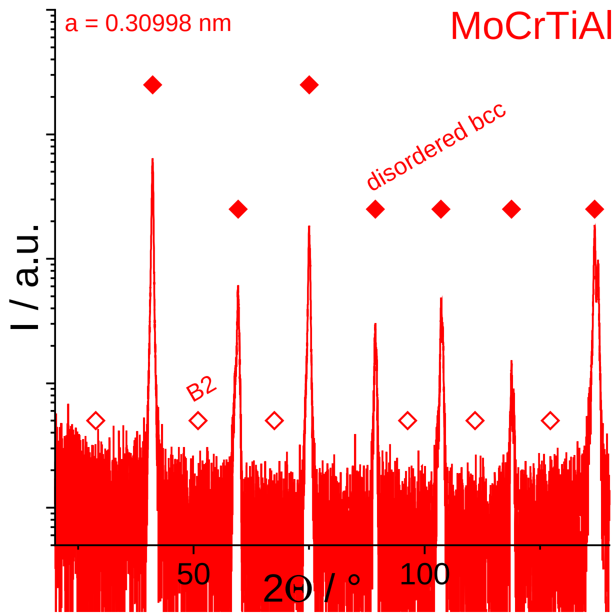


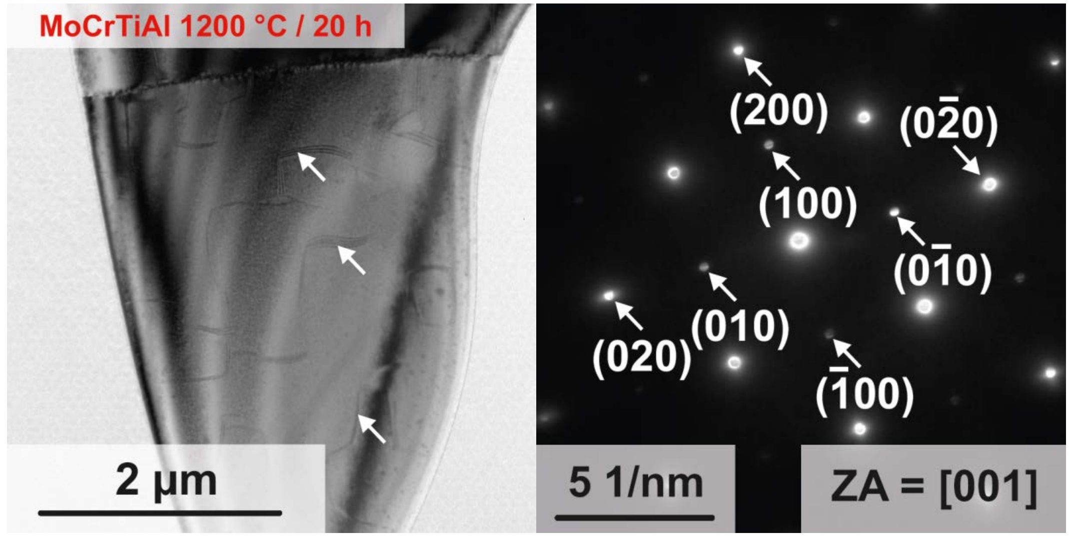
$$\mu H^{RT} = 1.52 \text{ GPa} + 101.56 \cdot \delta$$

with $R^2_{\text{adj}} = 0.98$

H. Chen et al. in Metallurgical and Materials Transactions A 49 (2018) 772-781

Order





- XRD & APT:
  - no superlattice reflections
  - negligible correlation factors

- DSC, TEM-SAD, TEM-BF & STEM:
  - second order phase transition
  - superlattice spots
  - planar faults are visible
  - filtered imaging of domains
  - chemical segregation at APBs

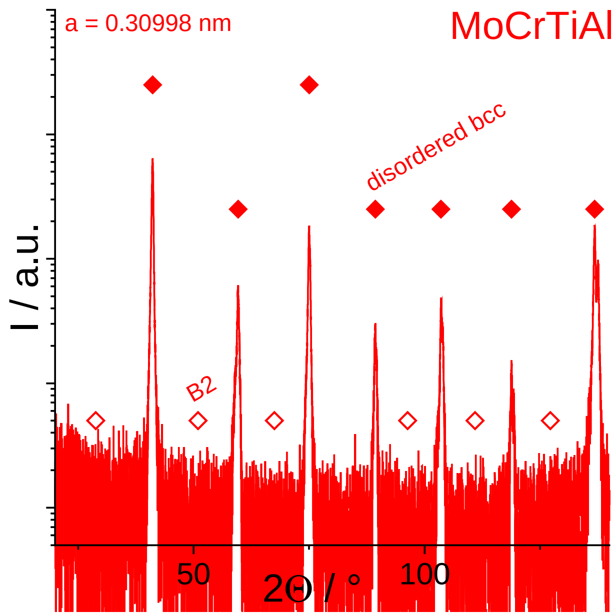
H. Chen et al. in preparation (2019)

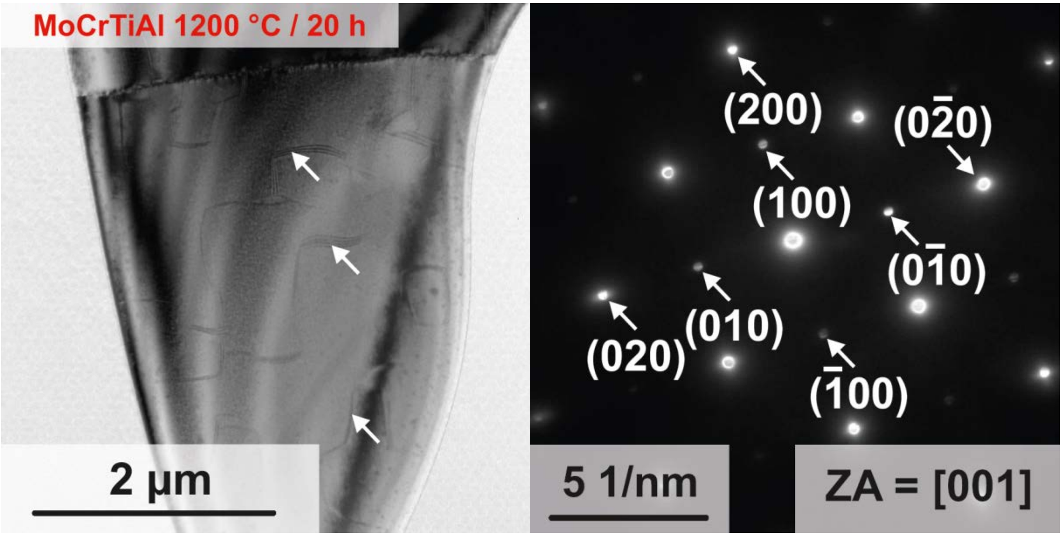
Karlsruhe Institute of Technology

UNIVERSITÄT SIEGEN

IAM Institute for Applied Materials

Order

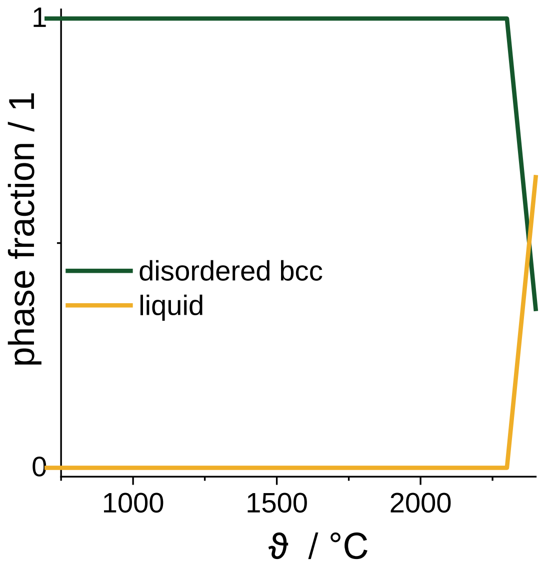


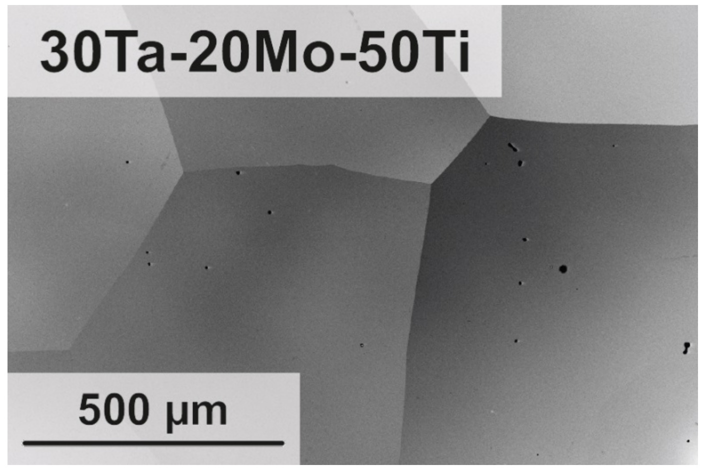


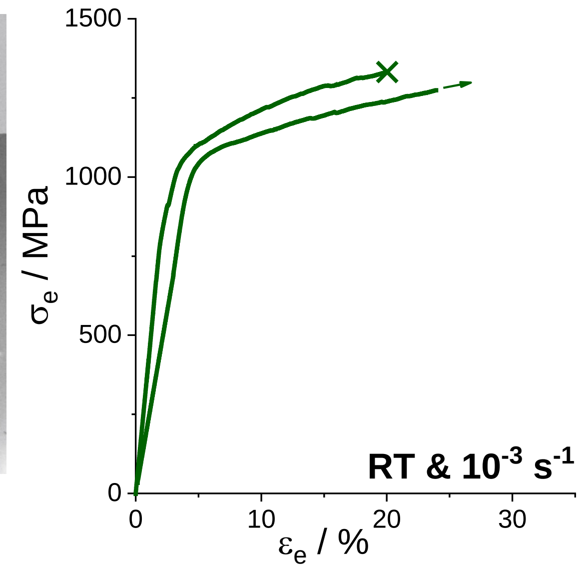
- consequences for mechanical behavior:
  - intrinsic brittleness?
  - impact of partial order and anti-phase domain boundaries on solid solution hardening?

H. Chen et al. in preparation (2019)

Order







- Search for **off-stoichiometric**, **B2-free alloys** within Ta-Nb-Mo-Cr-Ti-Al **by thermodynamic calculations** (own-built FactSage database at University of Siegen):
  - no ordering transformation down to low temperatures, e.g. 30Ta-20Mo-50Ti

Conclusions

- localized deformation plays an important role in many HEA:
  - serrated plastic flow at very low temperatures
  - plastic deformation of HfNbTaTiZr at room temperature at strains
  - deformation of CoCrFeMnNi under tribological load
- plastic response of bcc HEA significantly depends on the presence of (partial) order which is rather difficult to detect ↔ tailoring order provides perspectives for further development

A contribution to the priority programme SPP 2006
“Compositionally Complex Alloys – High Entropy Alloys (CCA-HEA)” by DFG

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