# Metastable High Entropy Alloys

Max-Planck-Institut für Eisenforschung

**Short version**

# Max-Planck High Entropy Alloy Team

*Rao*

Magnetism

*Springer*

Combinatorial Metallurgy

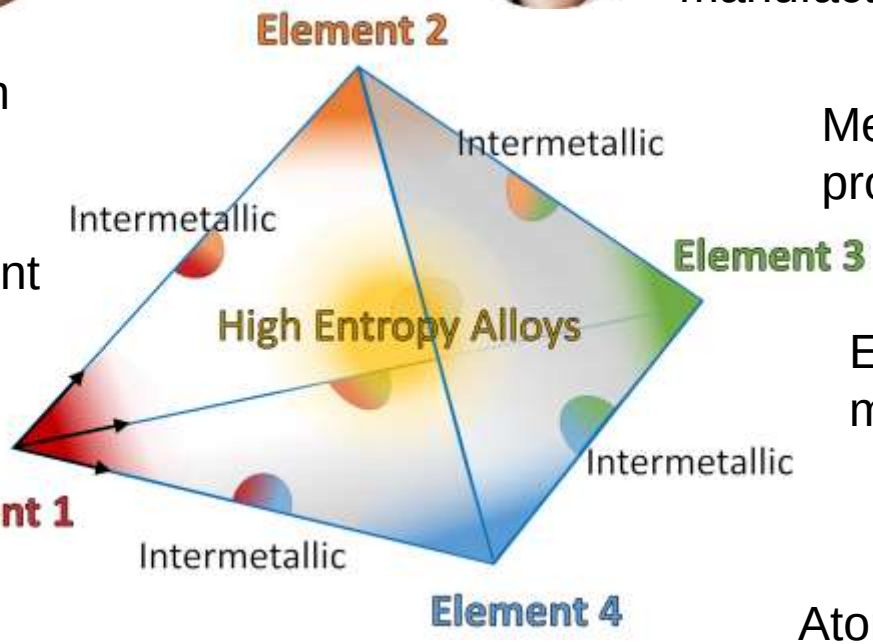
*Jägle*

Additive manufacturing

*Ponge*

*Luo*

Hydrogen Embrittlement




*Lu*

Mechanical properties

*Dehm*

Electron microscopy

*Kasian*

Corrosion

Electro-Catalysis

*Liebscher*

Atom probe

*Scheu*

Phase transformation

*Li*

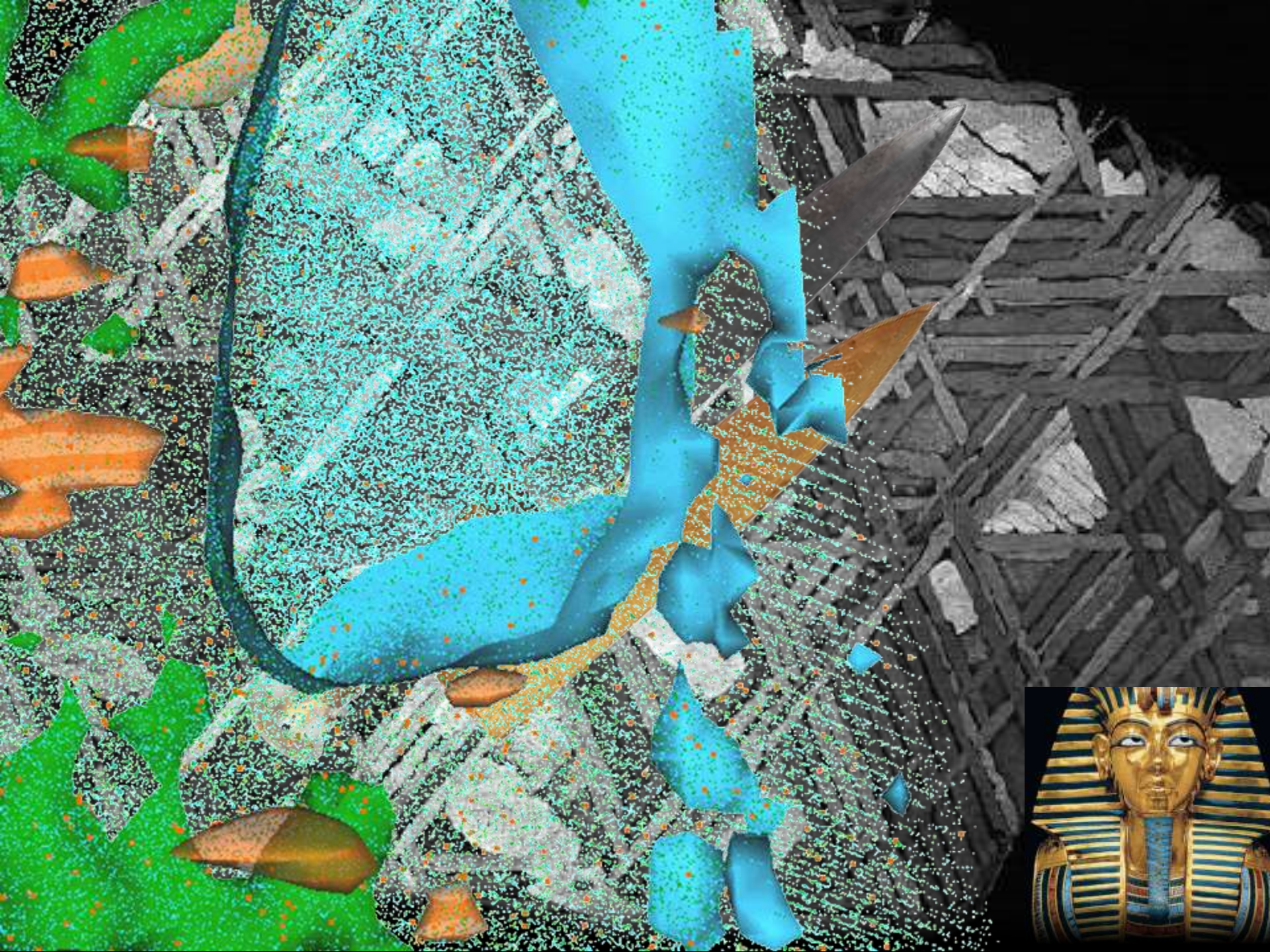
*Neugebauer*

Thermodynamics & kinetics

*Körmann*

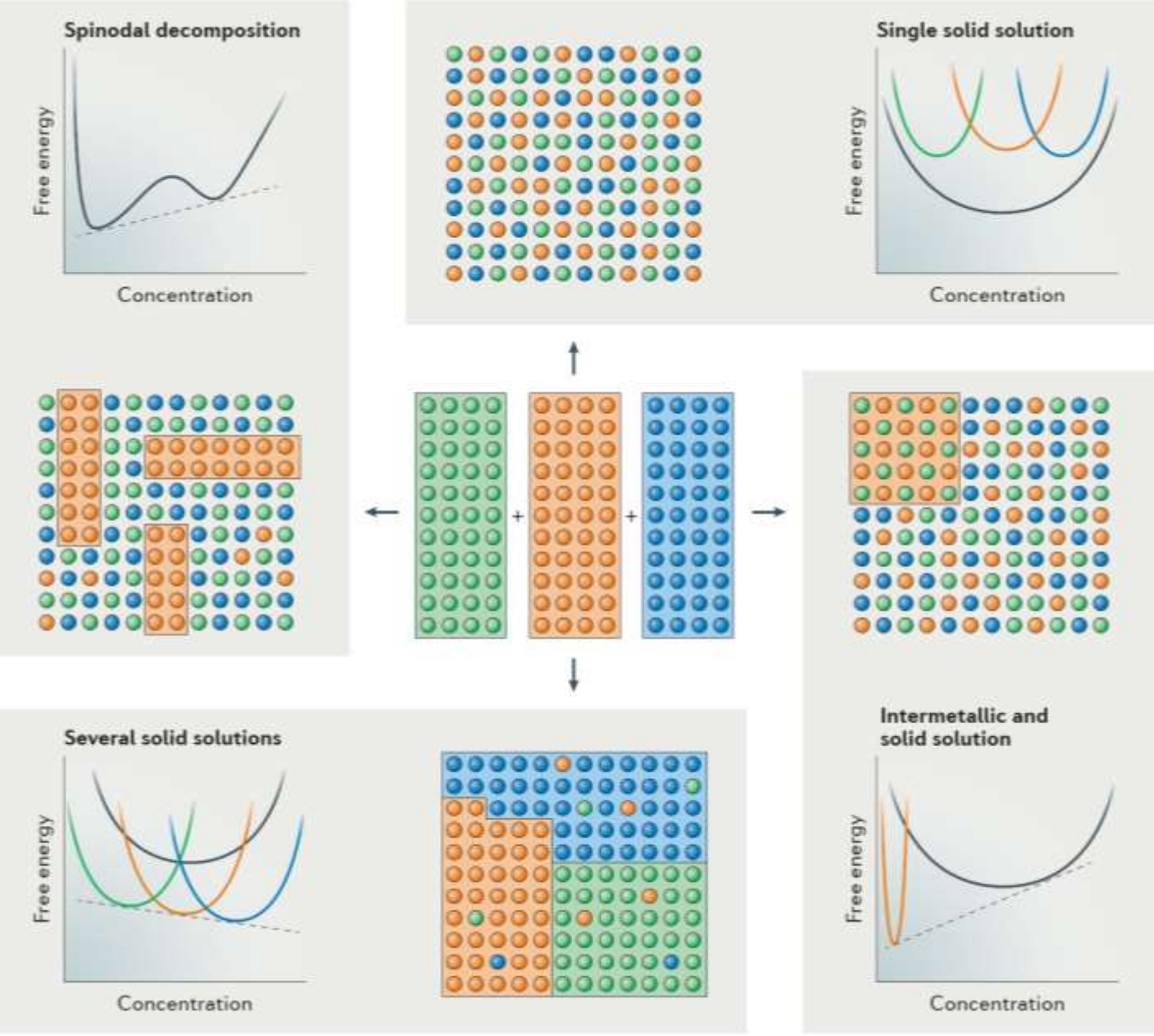
*Grabowski*

*Gault*

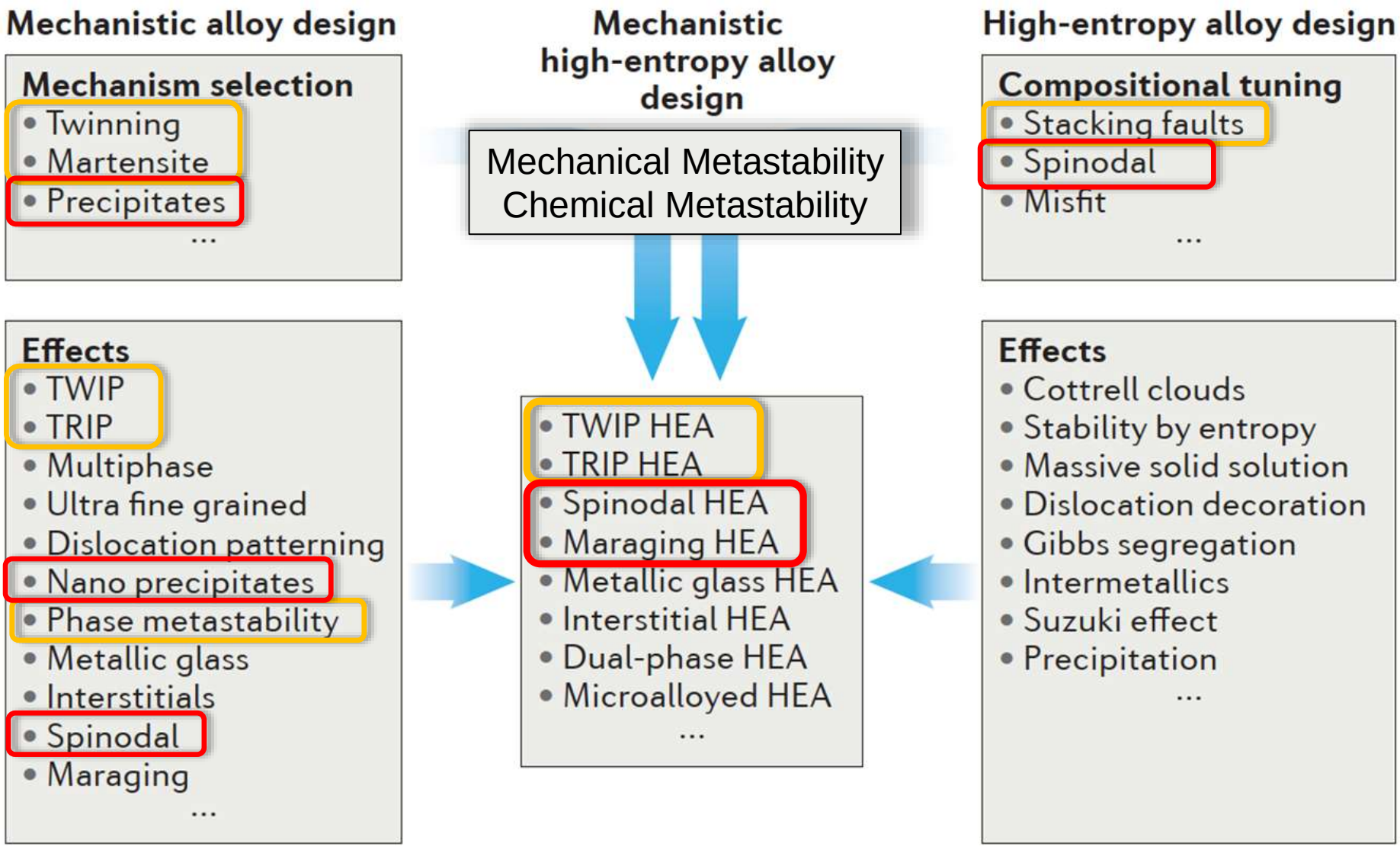


- Global metal market: 3000 billion € / year
- Green energy supply
- $e^-$ and H in transport and industry
- Sustainable production and $CO_2$ reduction

# Alloy thermodynamics

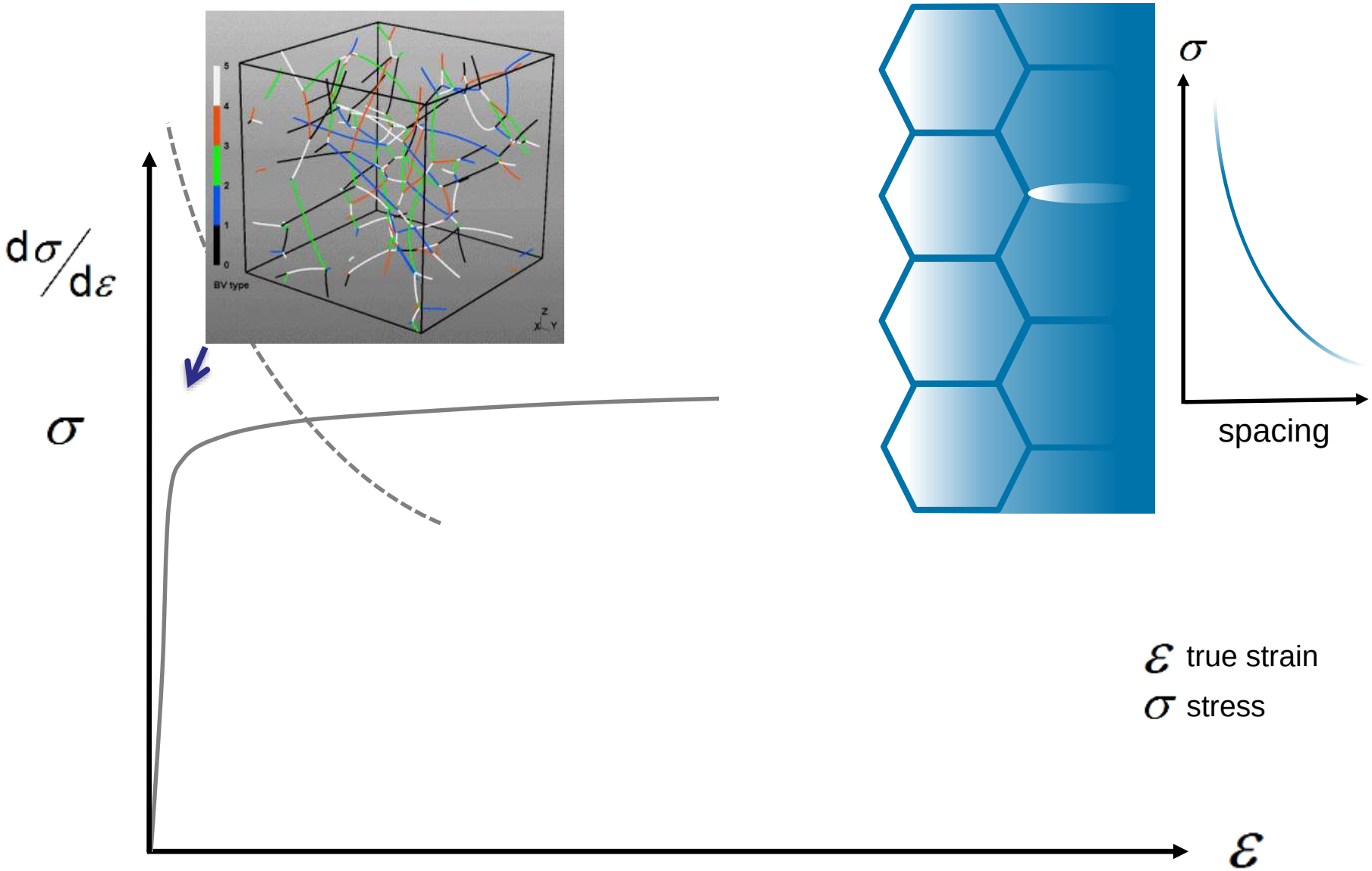


# Metastability high entropy alloy design

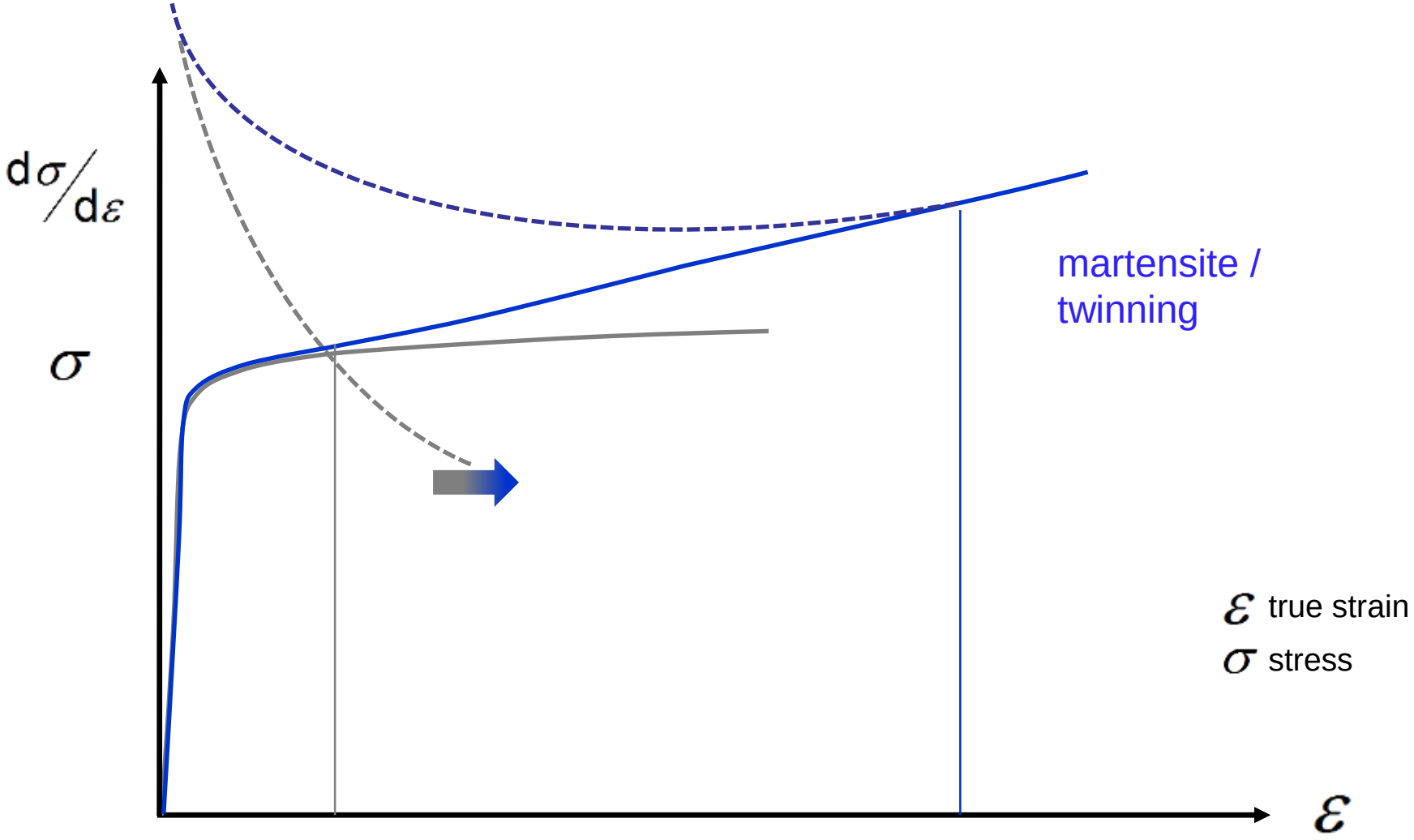



George et al. High entropy alloys, Nat. Rev. Mat. 4 (2019)

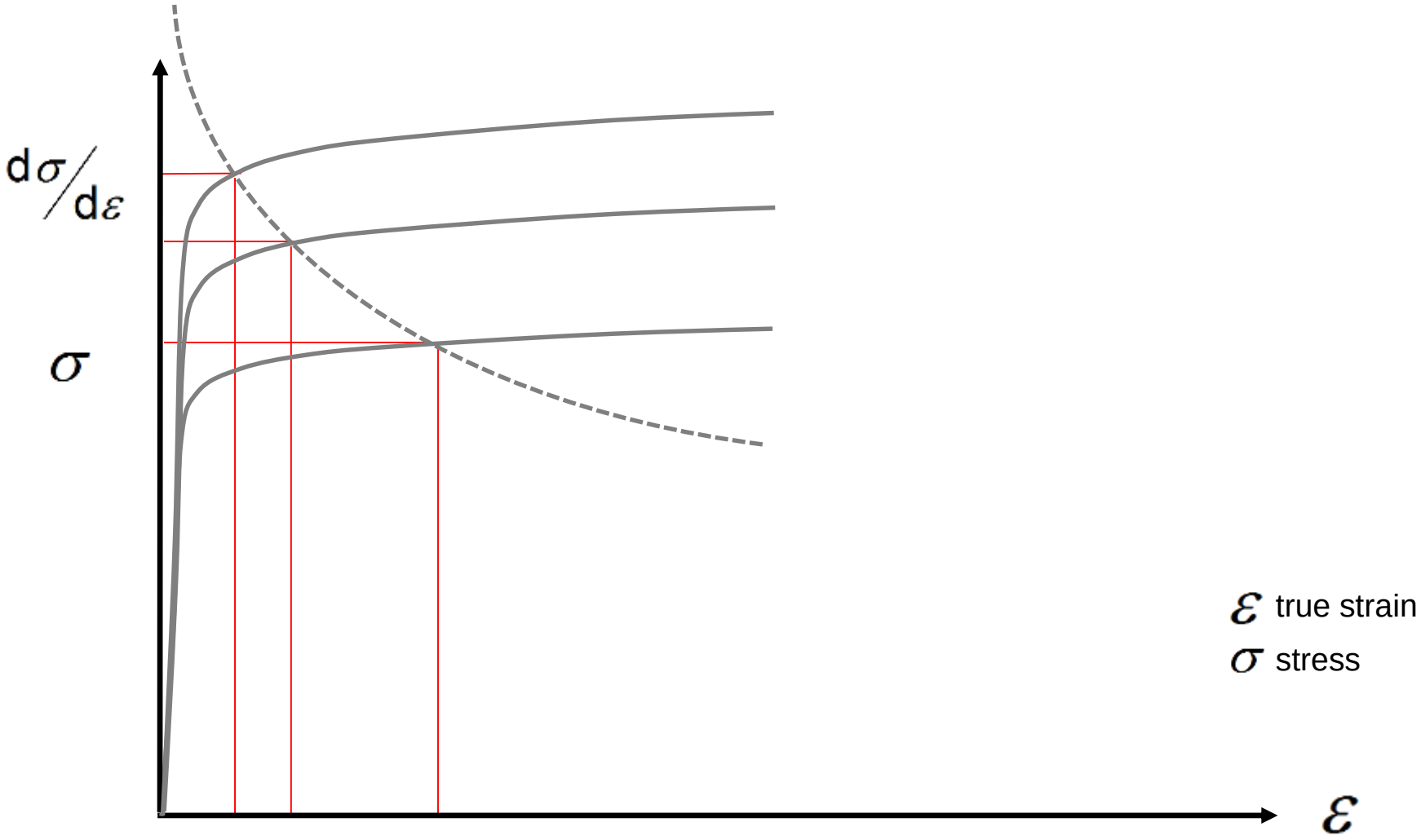
# Dislocations and strain hardening



# Dislocations and strain hardening



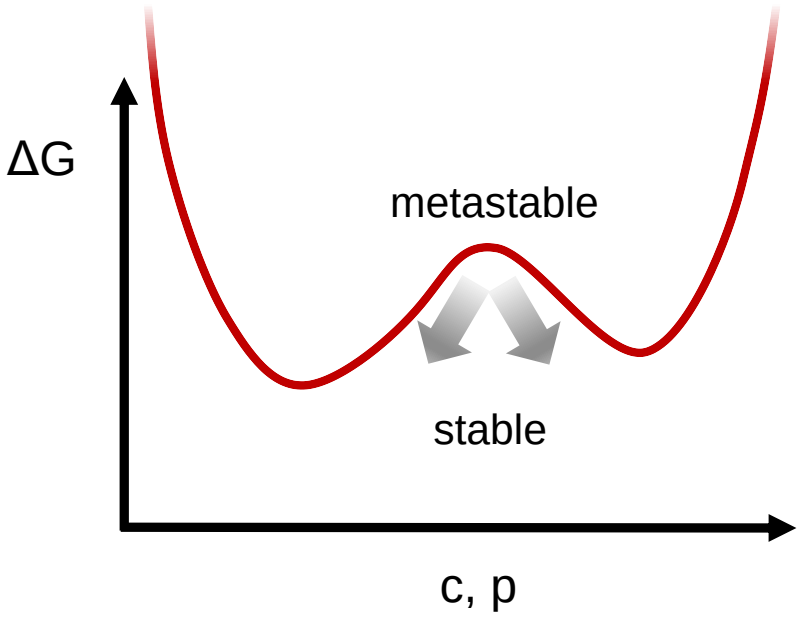
# Dislocations and strain hardening

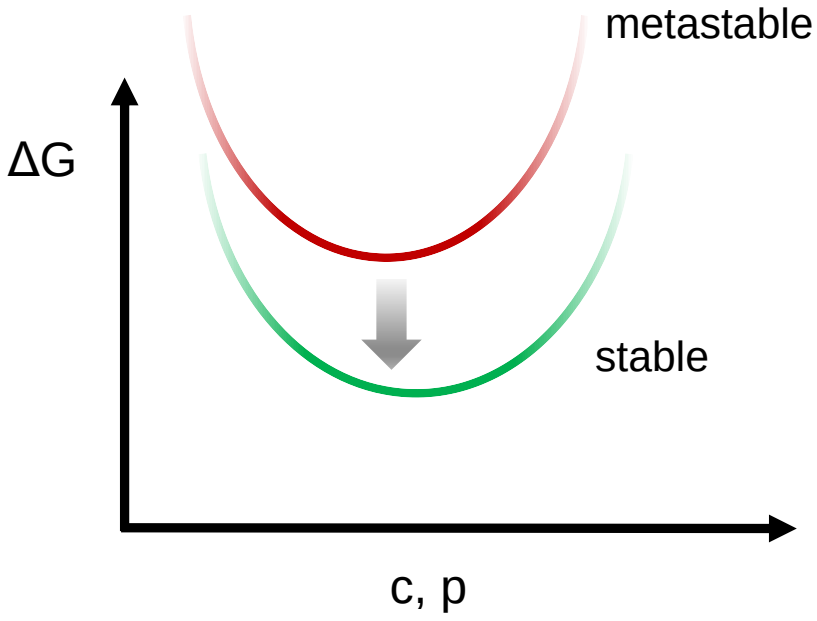


# Metastability Alloy Design

Mechanical Metastability

Chemical Metastability

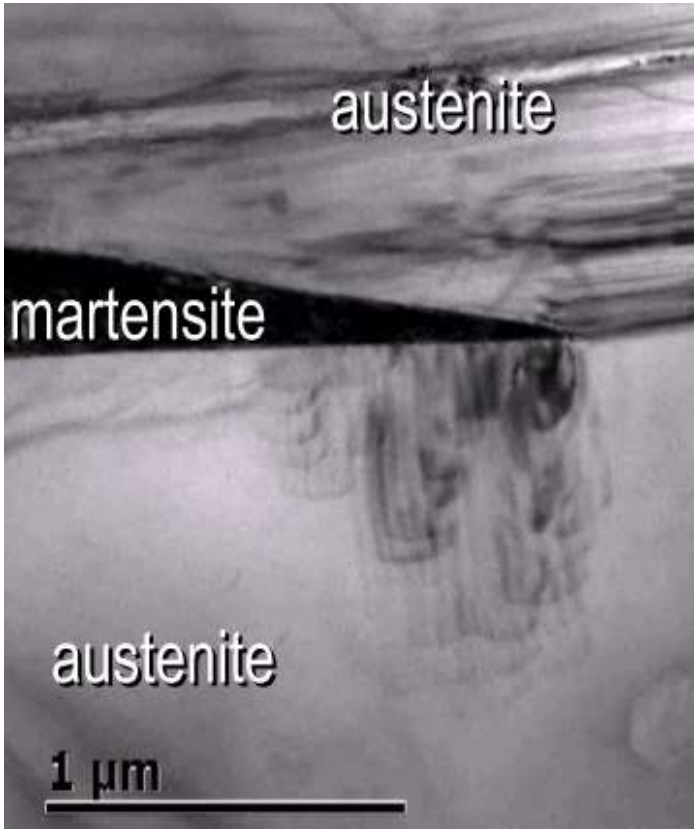


# Mechanical Metastability

**Athermal transformations not affine, not commensurate - high misfit deformation**

**Multiple strain hardening effects**

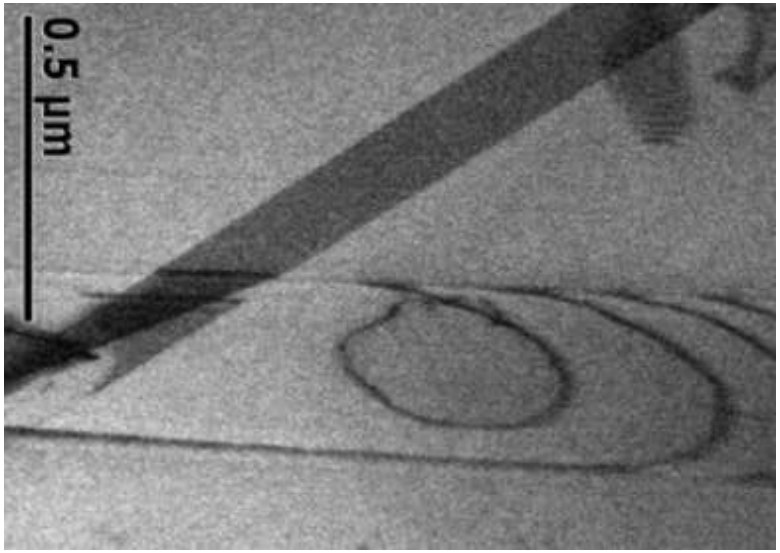


# Mechanical Metastability

**Confined at lattice defects**

**Chemical and structural size effects**

**Size effects in the bulk**
- **All for free and self-organized**
- **Thermodynamically tuned**




# Role of the stacking fault energy

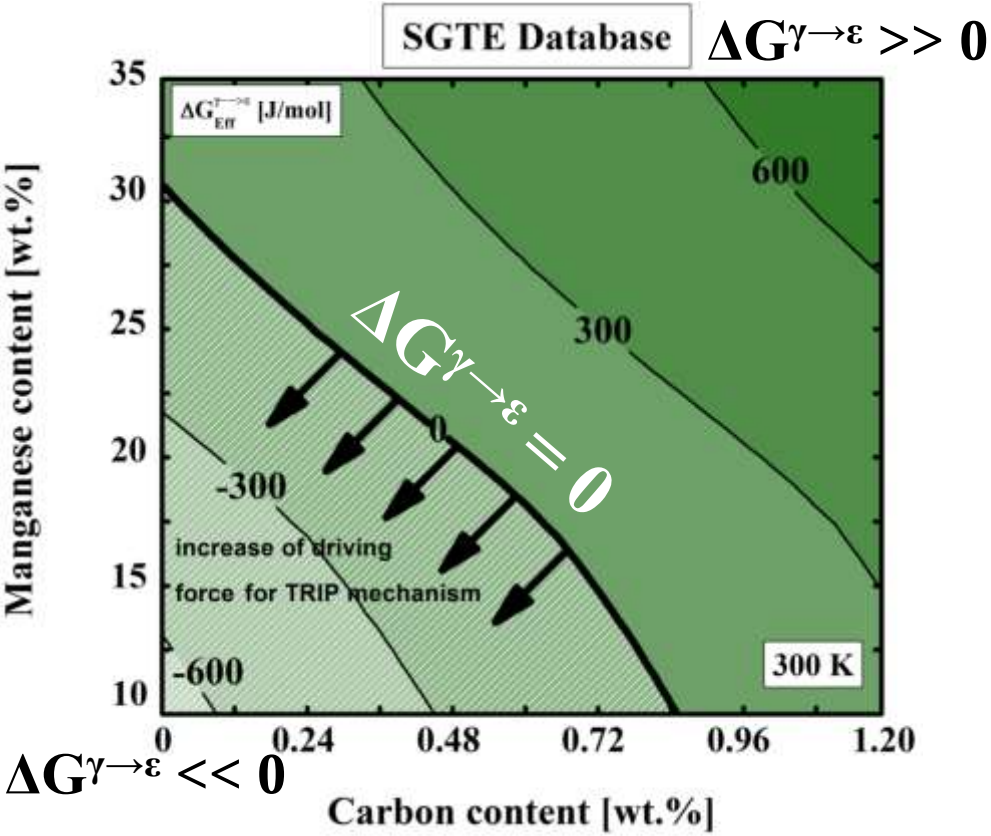
lower SFE →

high-Mn (15-30%), HEA

γ (fcc) cells → γ (fcc) planar → γ (fcc+order) planar → γ (fcc+twins) → ε (hcp) → α' (bcc/bct)

high-Mn+Al

medium-Mn (5-12%)



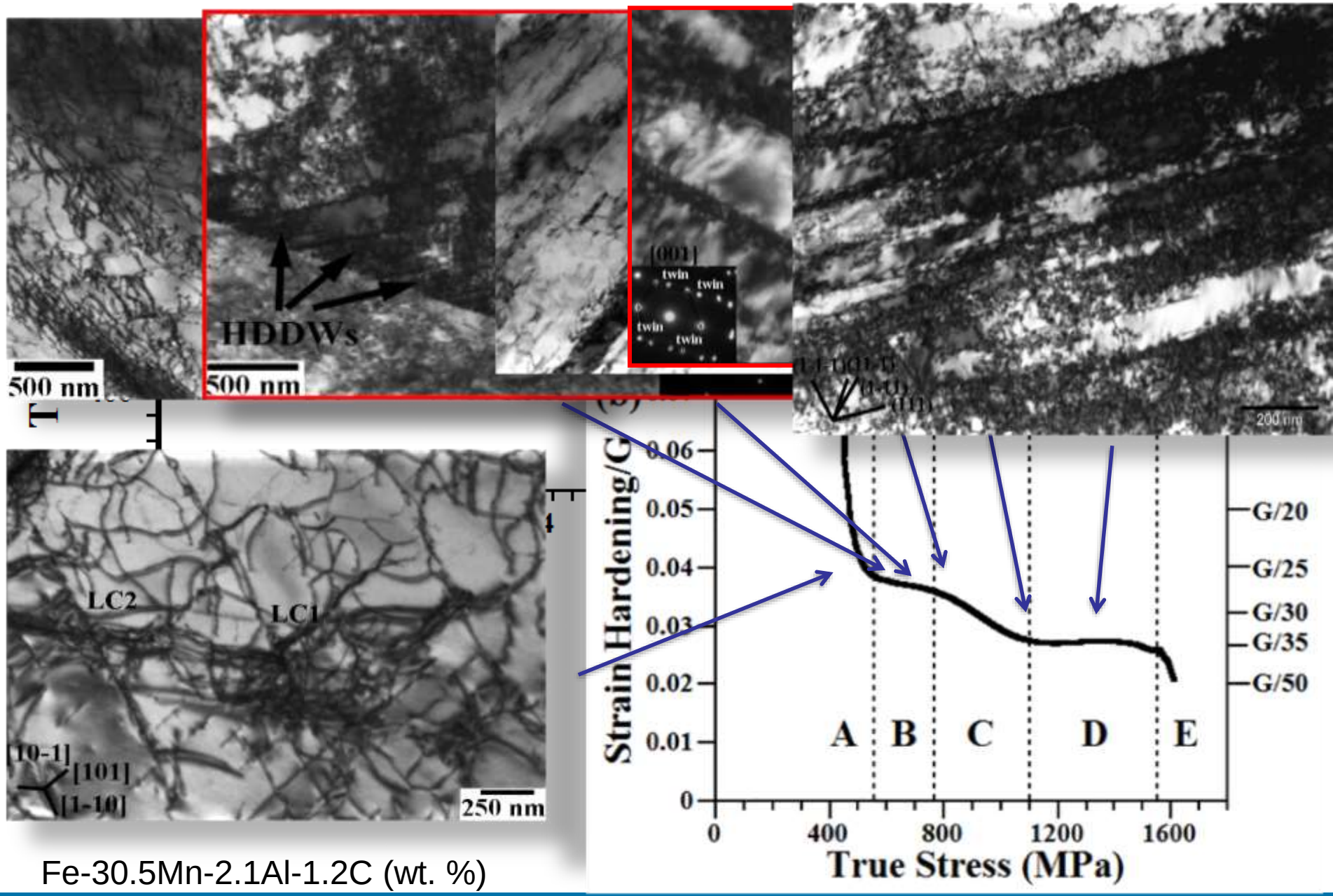

Critical stress for twin growth:

$$\tau_c = \frac{\gamma_{sf}}{3b_s} + \frac{3Gb_s}{L_0}$$

Critical stress for ε-martensite growth:

$$\tau_c = \frac{\gamma_{sf}}{3b_s} + \frac{3Gb_s}{L_0} + \frac{h\Delta G^{\gamma\to\varepsilon}}{3b_s}$$

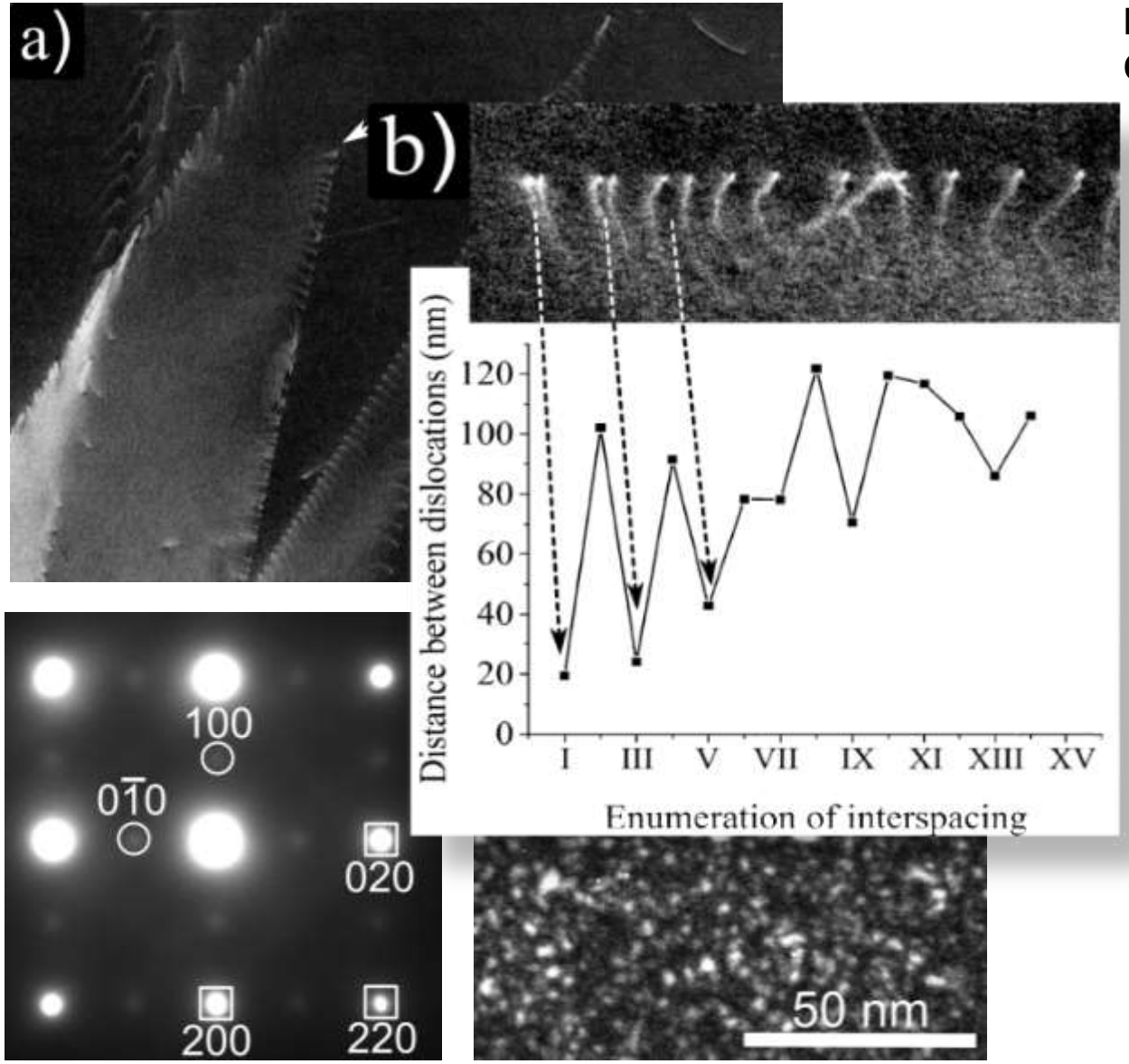
# Fe-Mn-Al-C solid solution




Fe-30.5Mn-2.1Al-1.2C (wt. %)

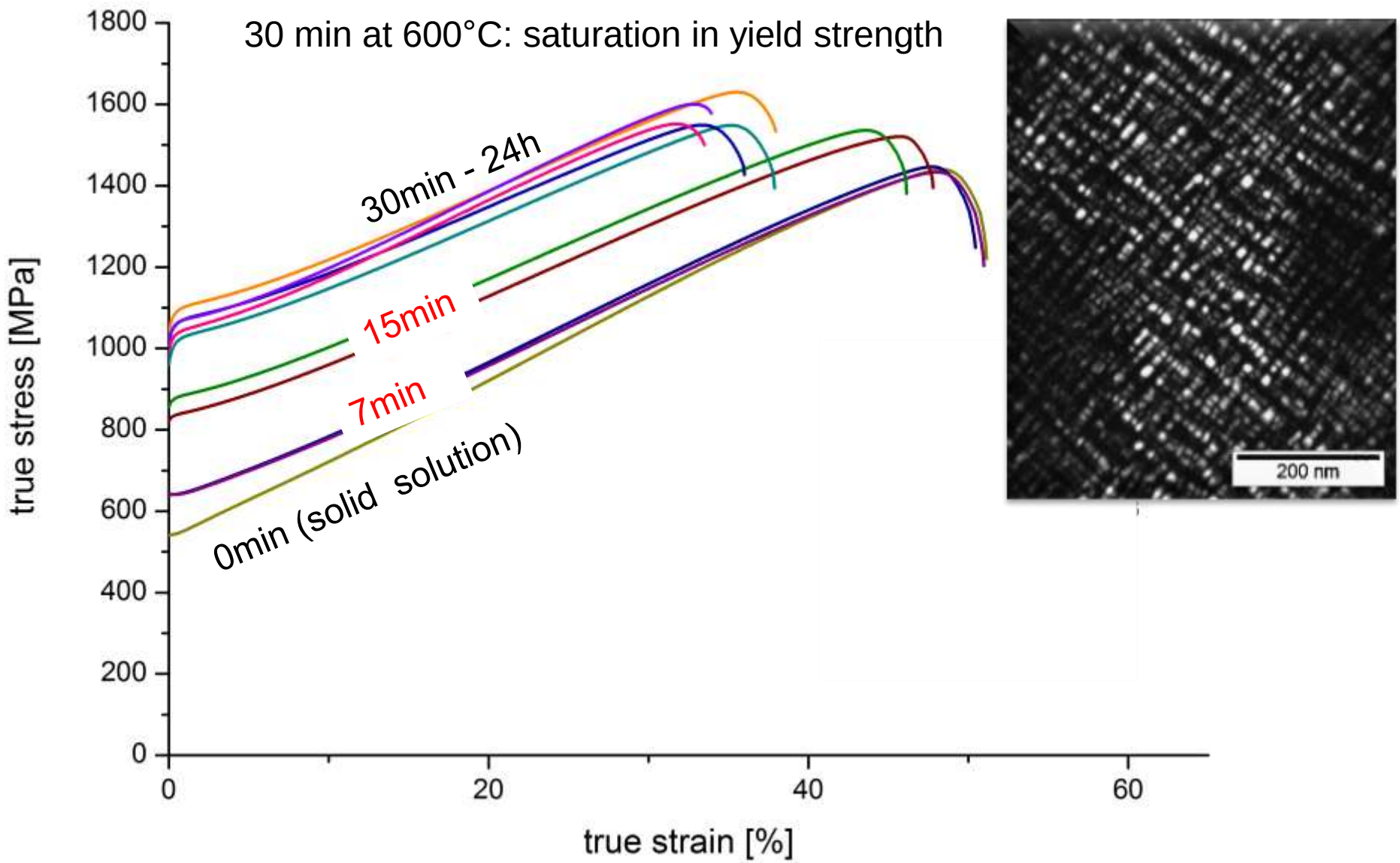
# Fe-30.4Mn-8Al-1.2C (wt%) quenched

**Electron Channeling Contrast Imaging ECCI**

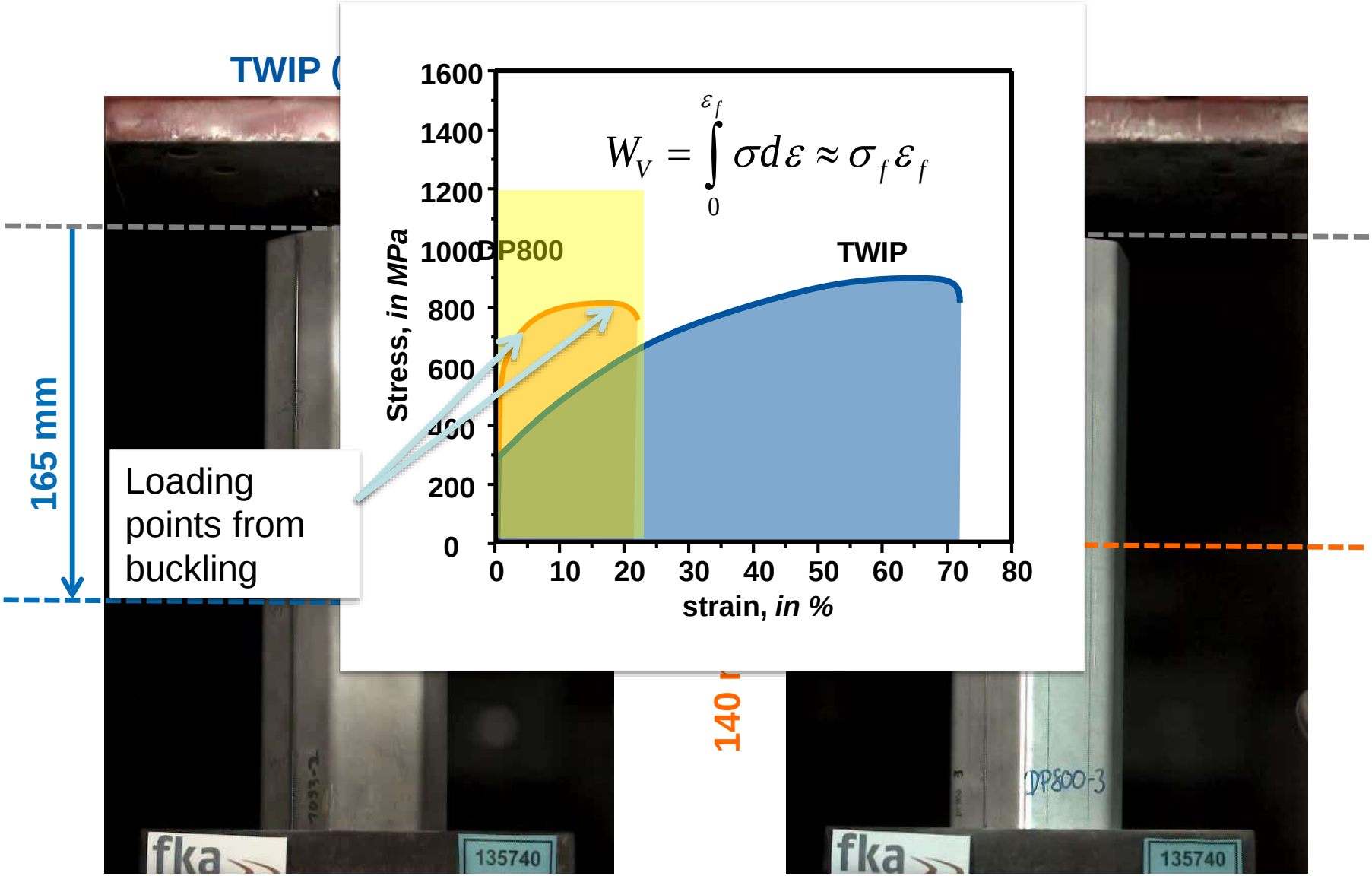



Yao Acta Mater. 106 (2016) 229; Welsch (2016) Acta Mater. 116, pp. 188

# Fe-30Mn-8Al-1.2C, annealing at 600°C



# Strain rate 800/s: TWIP steel & DP800



# Role of the stacking fault energy

$50\ mJ/m^2$ **Stacking fault energy** $\cong 0\ mJ/m^2$

**Dislocation slip**

**Stacking faults**

**Dislocation cell structures**

**Partial dislocations, reduced cross slip, planar slip**

**Chemical short range ordering and decomposition effects possible**

**Slip band formation**

**Dynamic slip band refinement**

**Mechanical twinning**

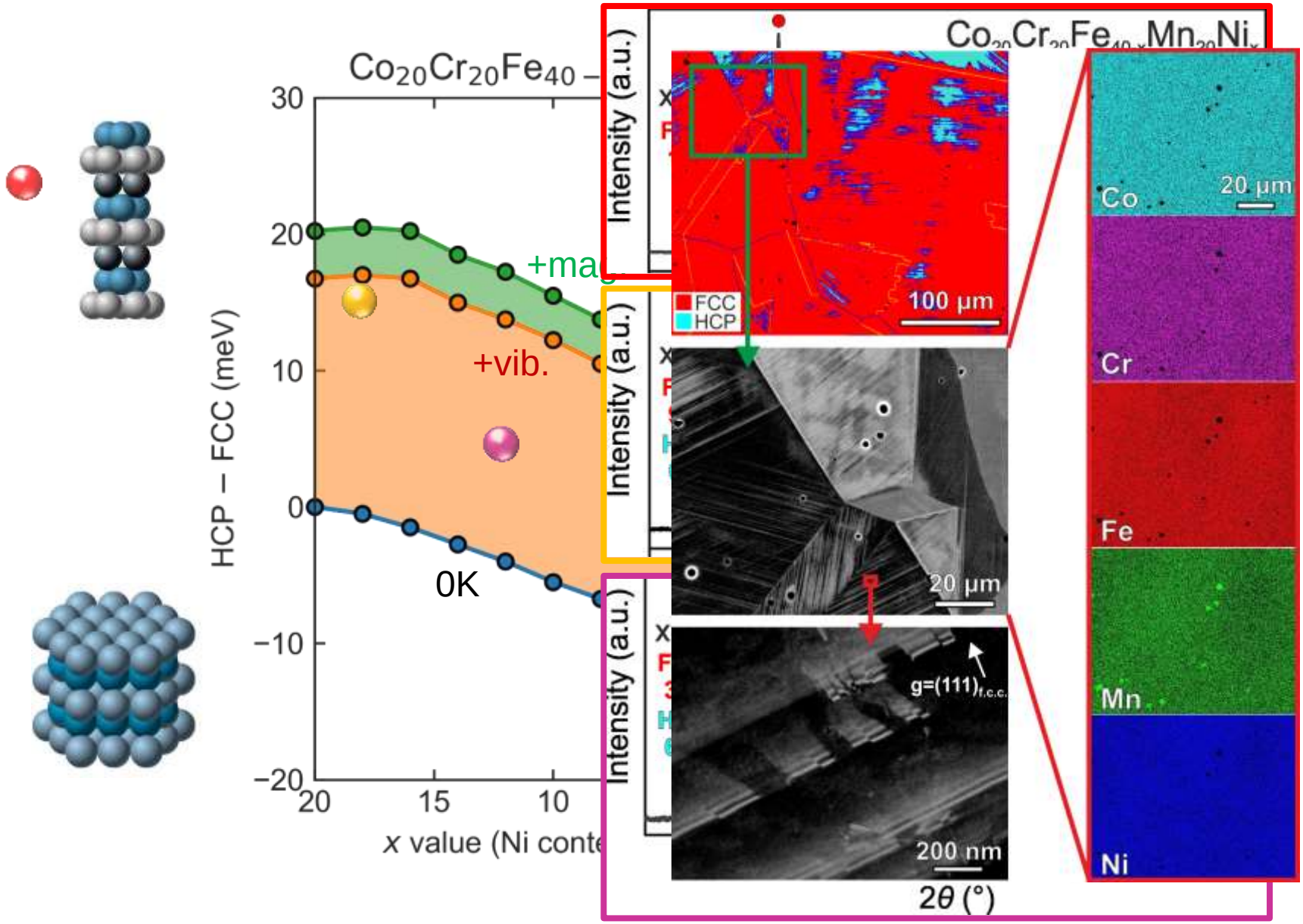
**Coexistence of fcc (γ), hcp (ε), bcc (α) / bct (α‘)**

**Unidirectional TRIP effect**

**Bidirectional TRIP effect**

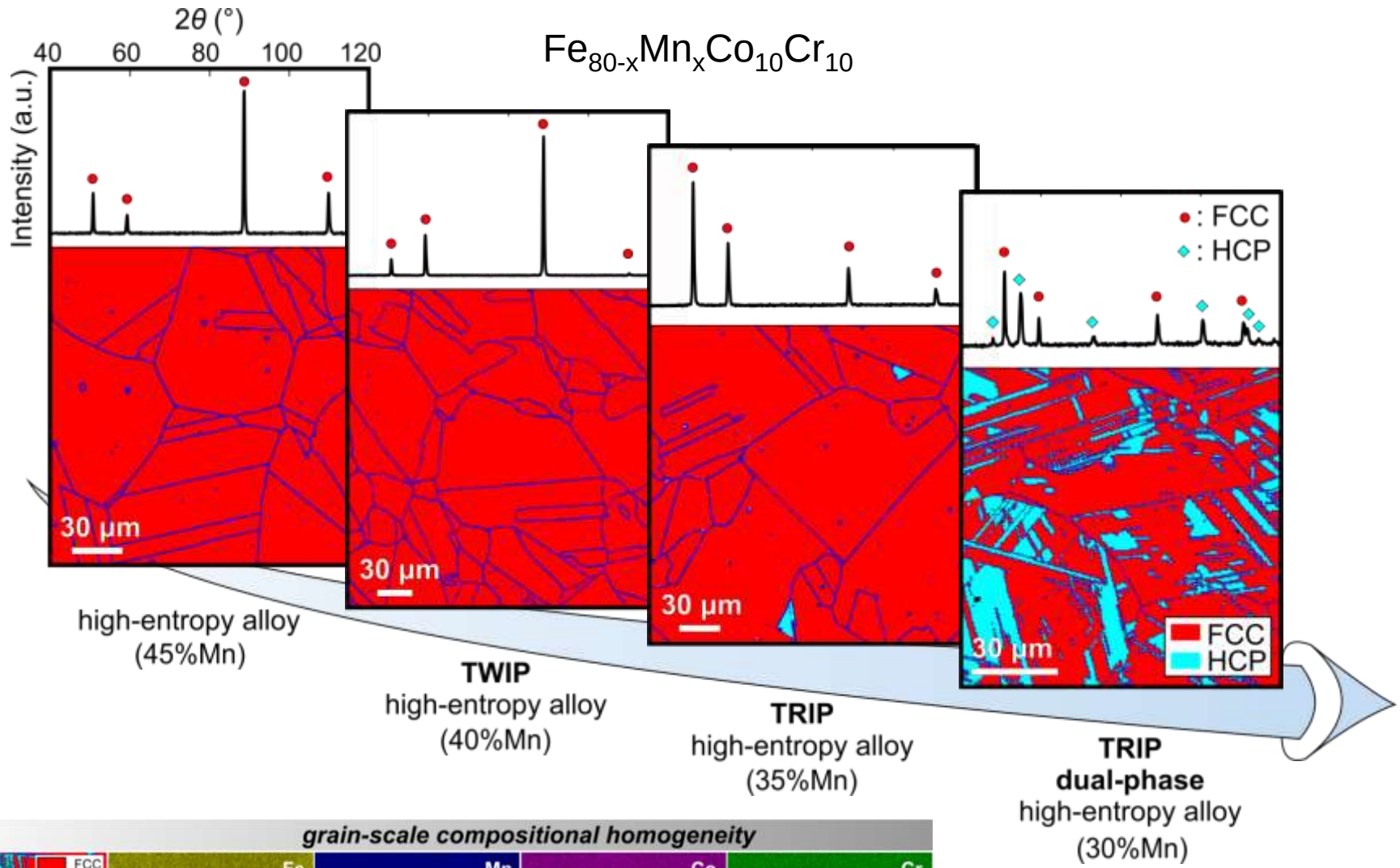
**Less** **More**

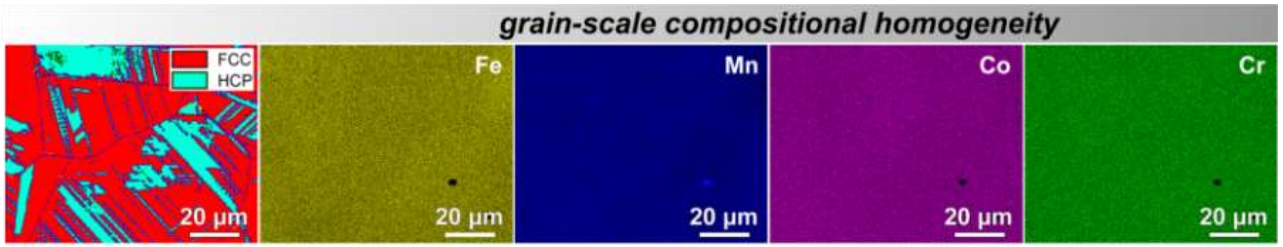
# Dual phase high entropy alloy




D. Ma et al. Acta Mater. 100 (2015) 90 & Acta Mater 98 (2015) 288, Z. Li et al. Acta Mater. 136 (2017) 262

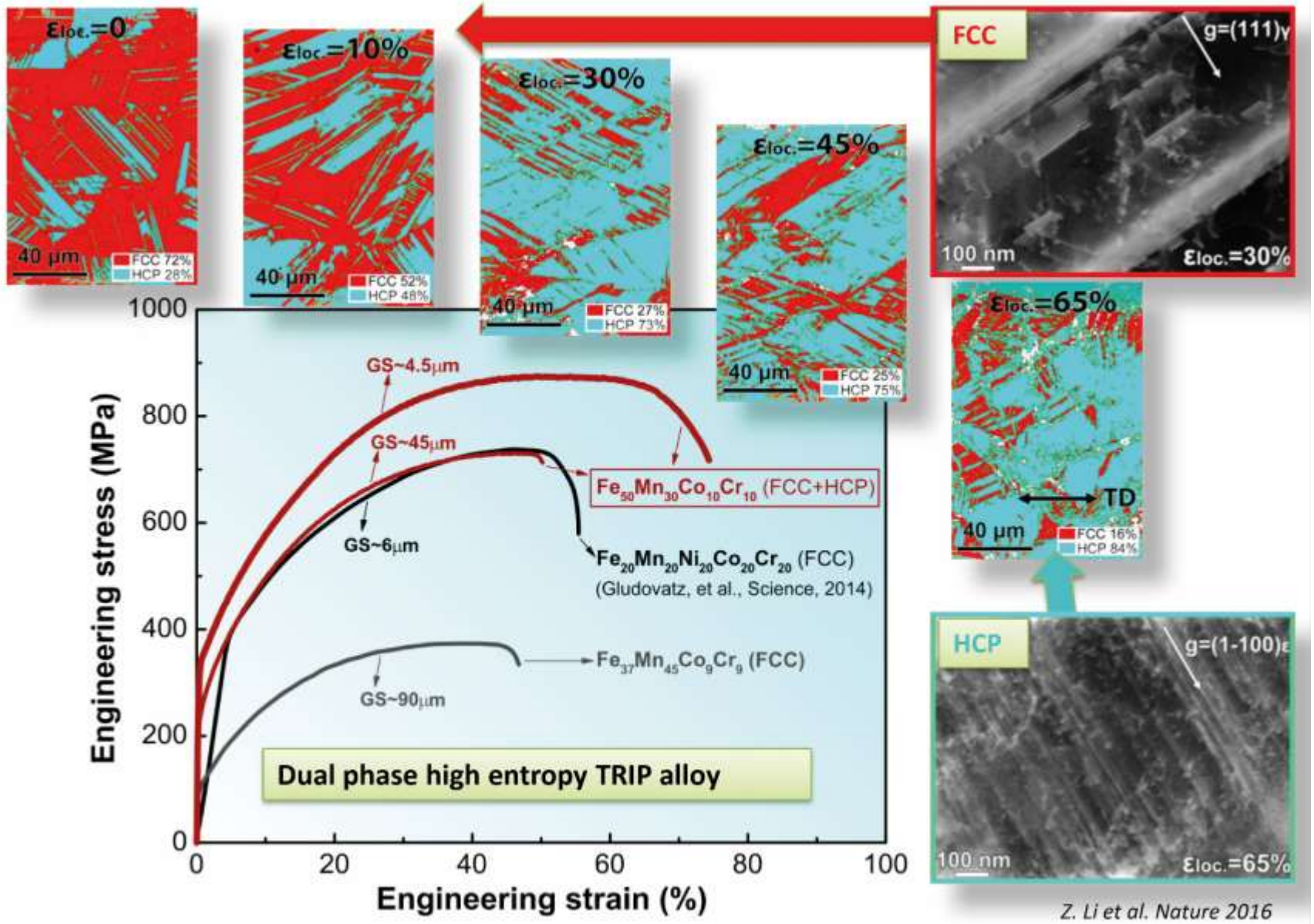
# Dual phase high entropy alloy




2 homogeneous solid solution HEA phases

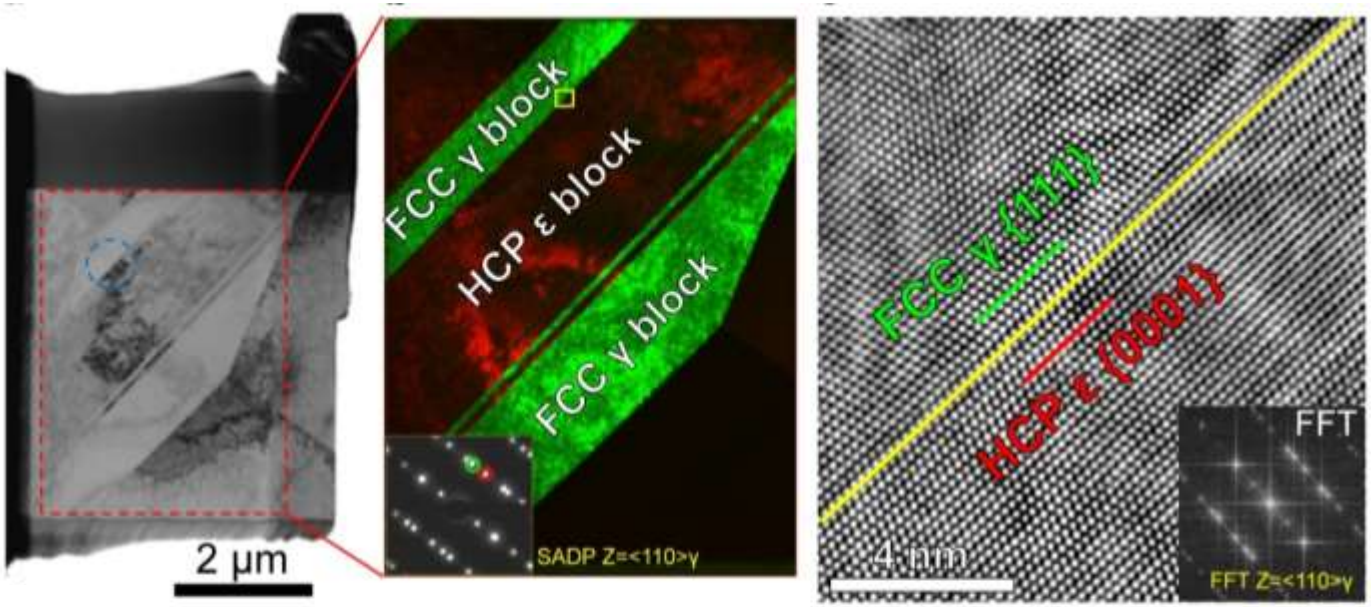
# Dual phase high entropy alloy

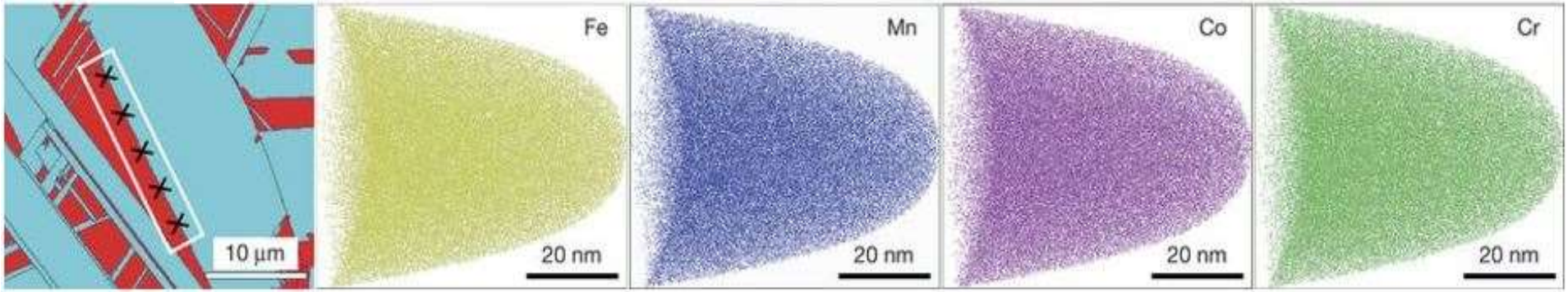



Z. Li et al. Acta Mater. 136 (2017) 262, D. Ma et al. Acta Mater, 100 (2015) 90, Z. Li et al., Nature (2016)

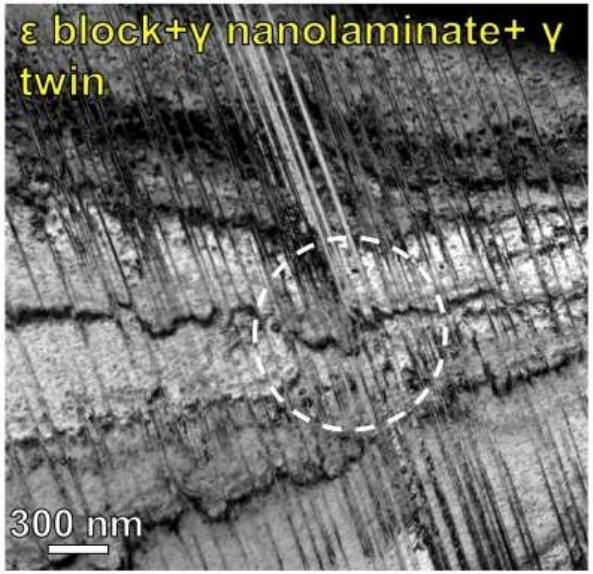
# Interface between ε and γ (quenched)

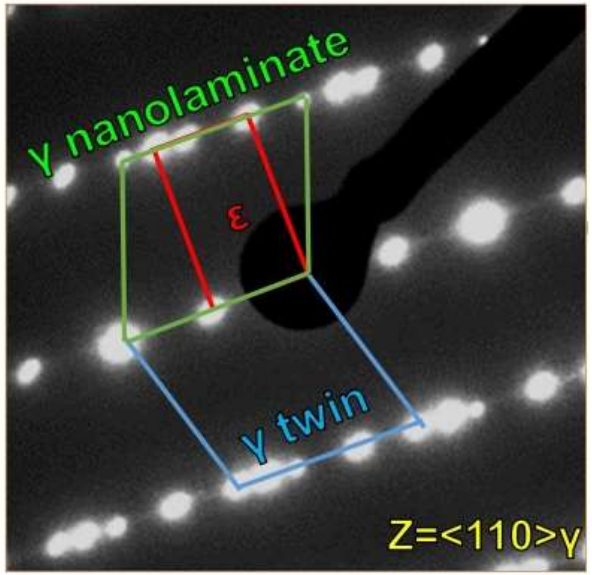
- Fe50Mn30Co10Cr10
- STEM-EDS / APT / z-contrast: both phases chemically homogeneous
- SAED: <11-20> ε //<110> γ; {0001} ε //{111} γ

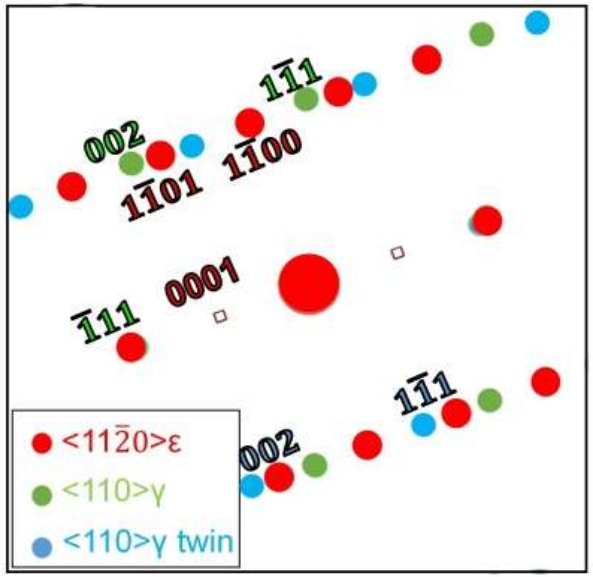


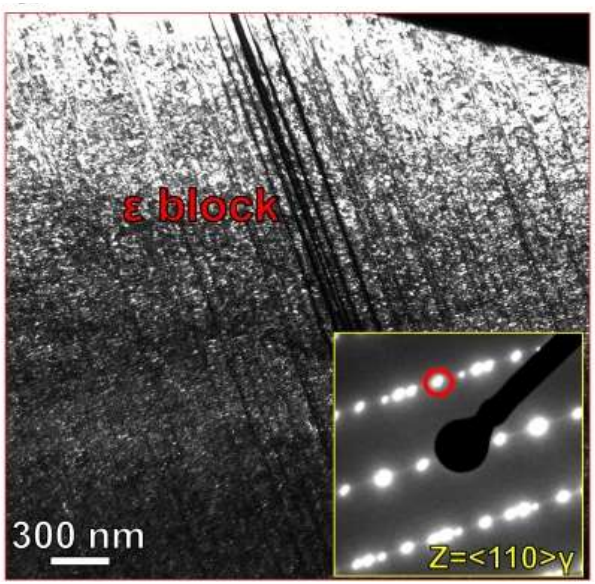



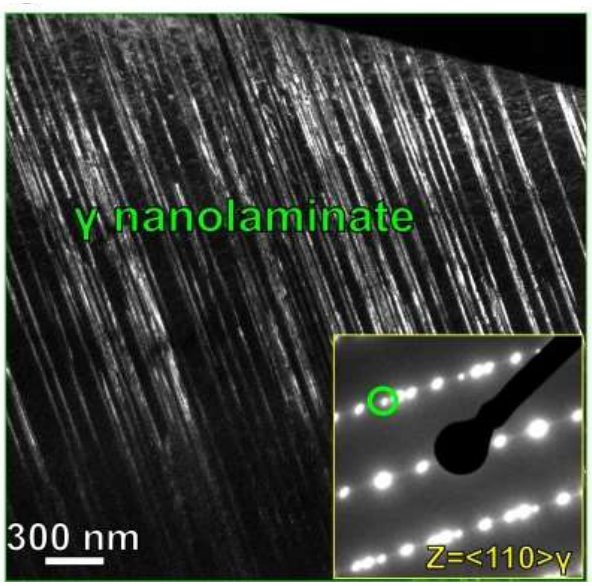
# Nano-γ lamellae in ε under load

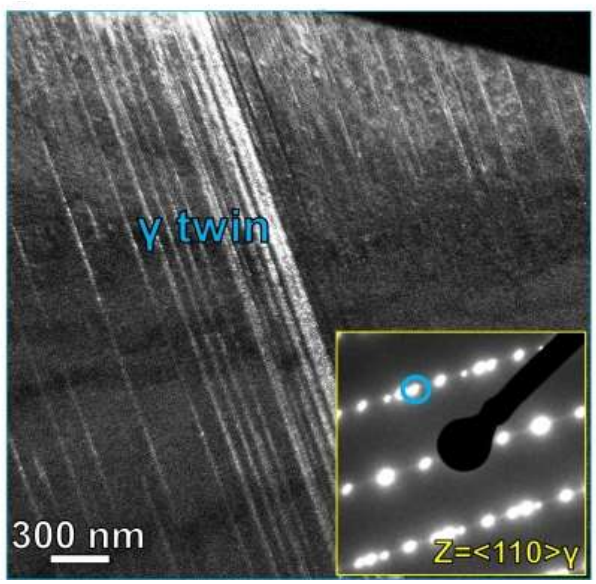



Z. Li, et al. Nature 2016; W. Lu, et al. Adv. Mater. 2018

# Transformation inside ε block (ε → γ)

## Process 1 (perfect FCC)

Leading Trailing

**HCP→Nano-FCC:**

BCBCBCBCBCBCBC

1 BCBCABABABAB

2 BCBCABCACACA

3 BCBCABCABCBC

R. Bauer, et al. Philosophical Magazine, 2010.

## Process 2 (nano-twin)

Leading Trailing

**HCP→Nano-FCC:**

BCBCBCBCBCBCBC

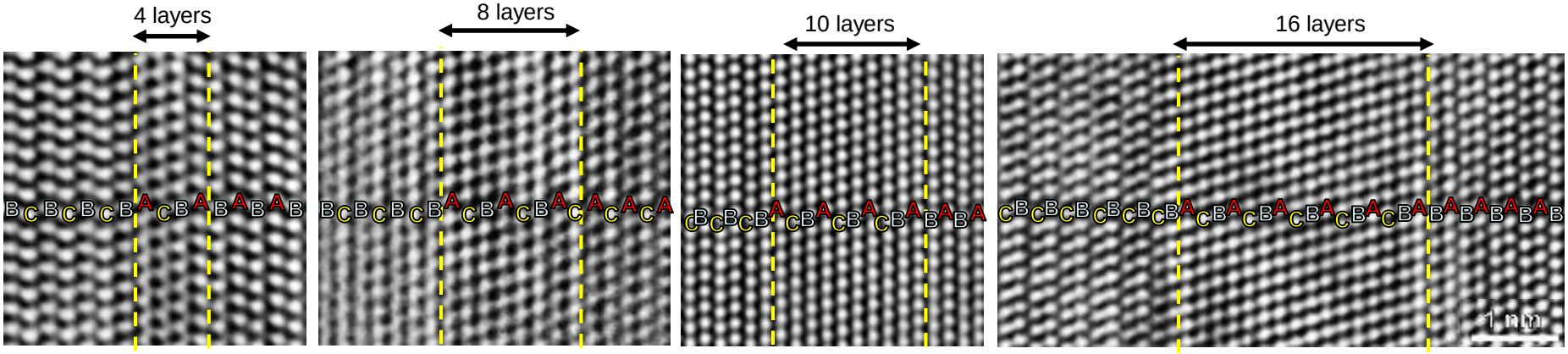
1 BCBACACACACA

2 BCBACBABABAB

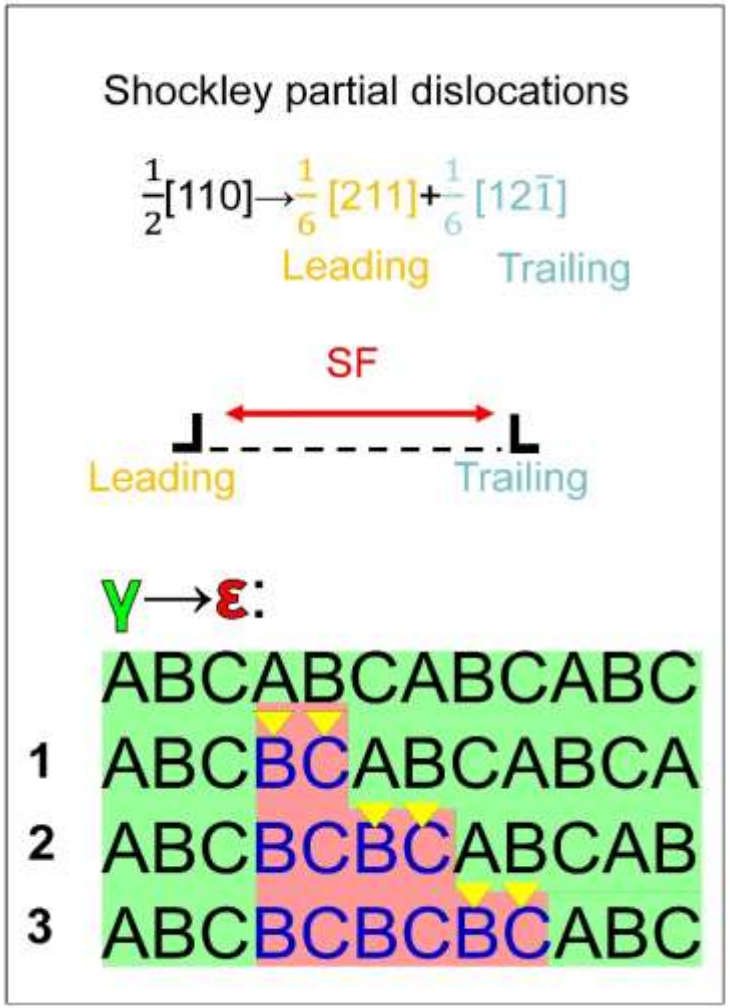
3 BCBACBACBCBC

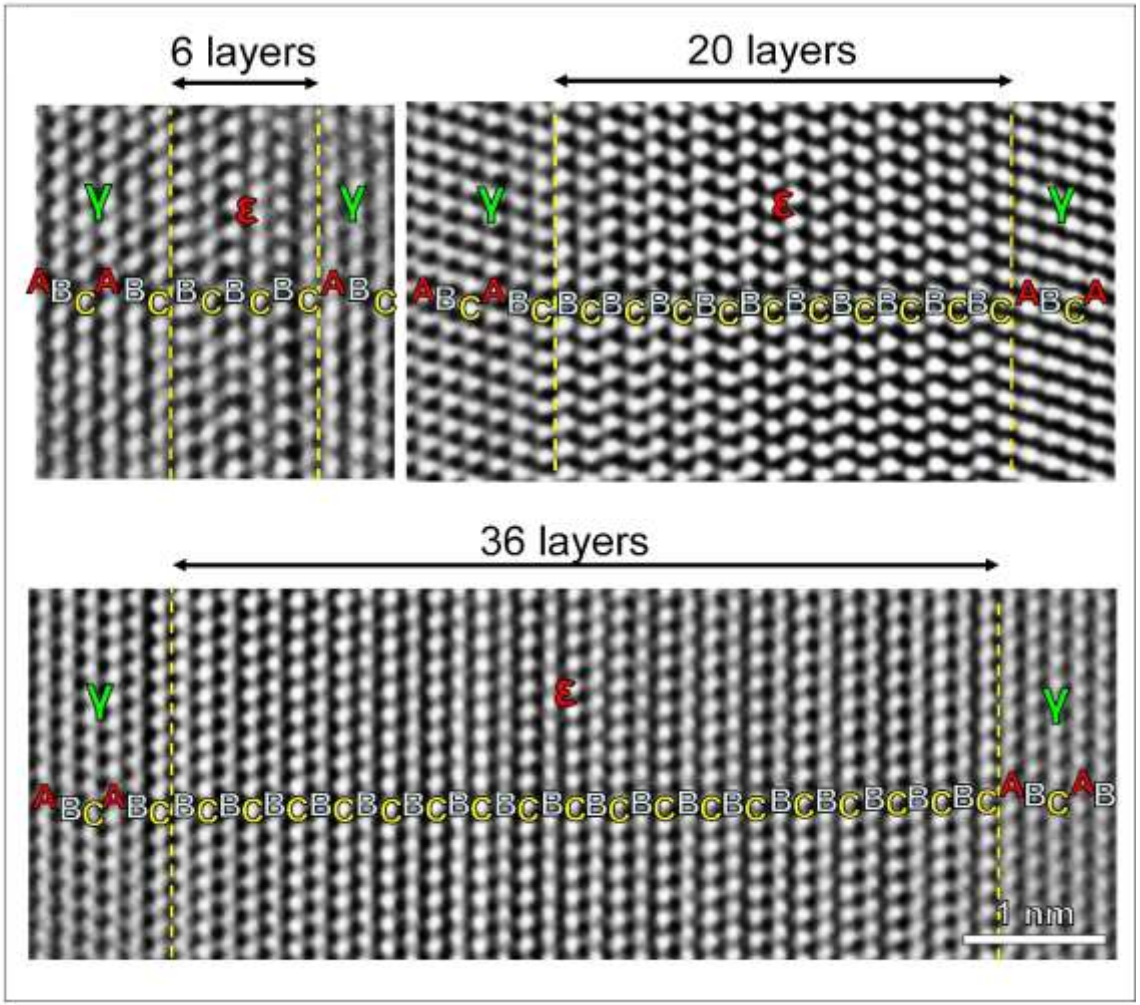
H.T. Wang, et al. Scripta Mater, 2018.

## Deformed sample (twin relation)



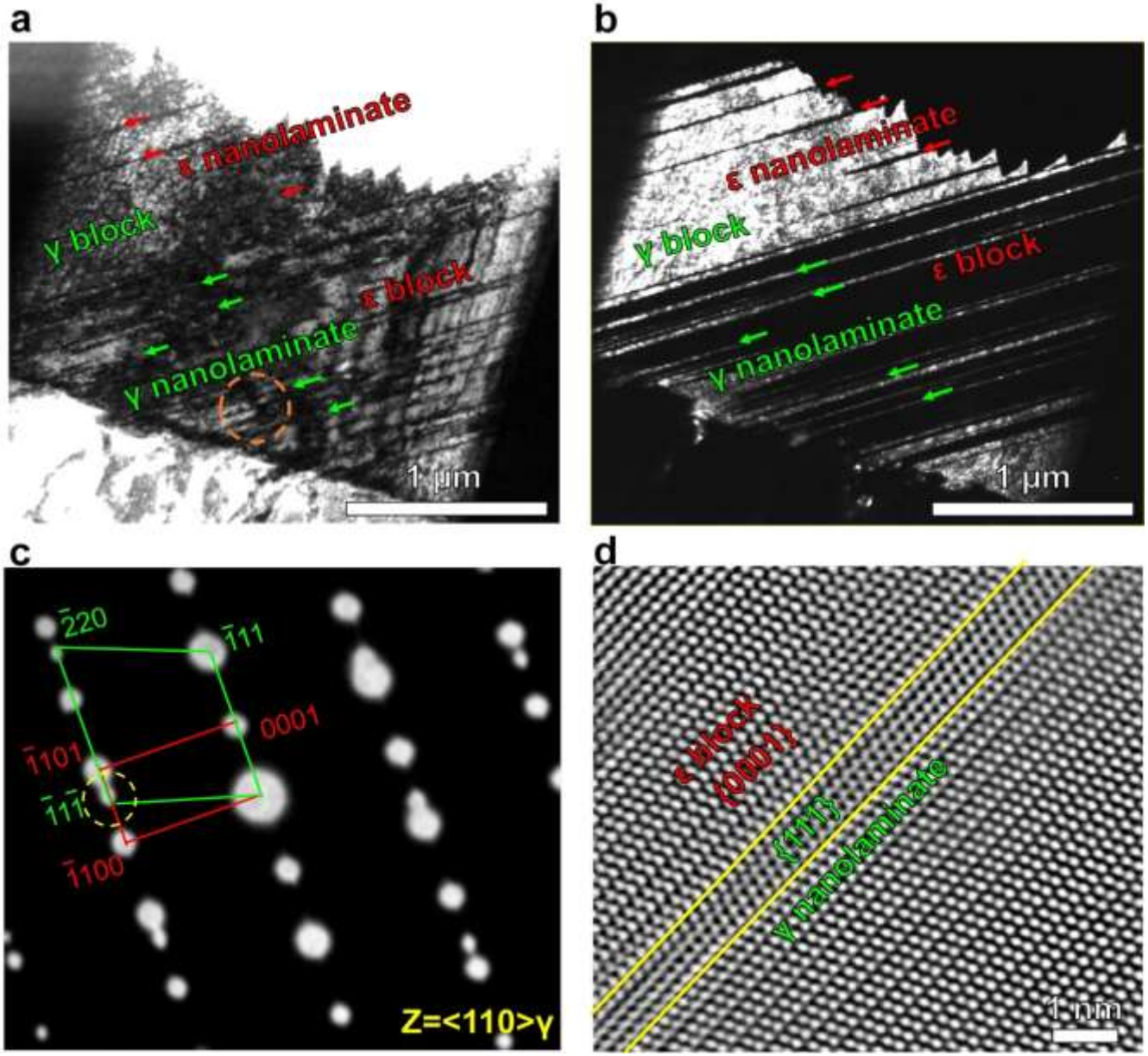
# Transformation inside γ block (γ → ε)



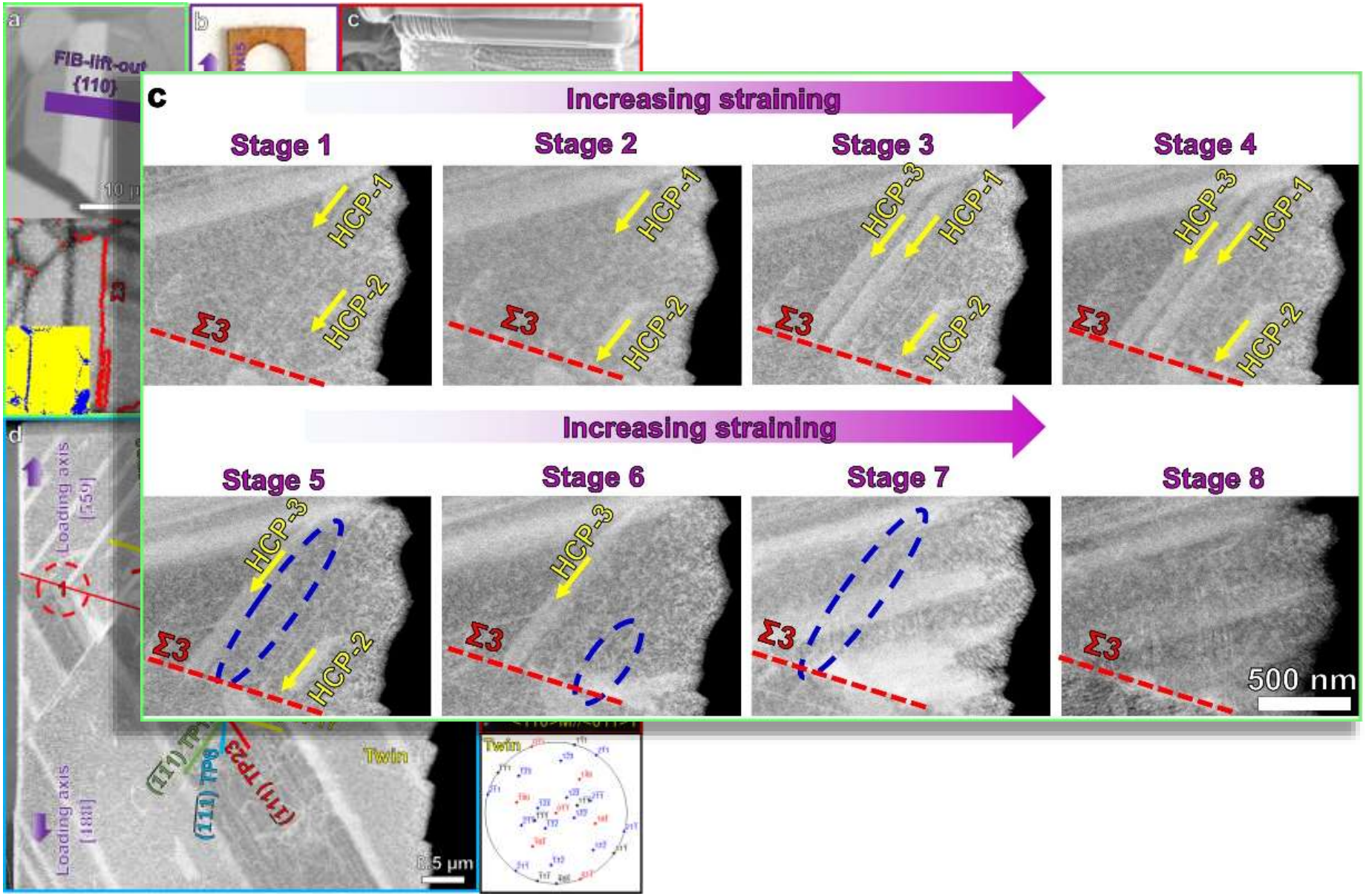



# Nano-lamellae in ε and γ (quenched)

- Linear features in both the ε and γ blocks (DF-TEM)
- SFs (γ nano-lamellas): 87.6±5.4 nm
- Thermodynamic stable at RT

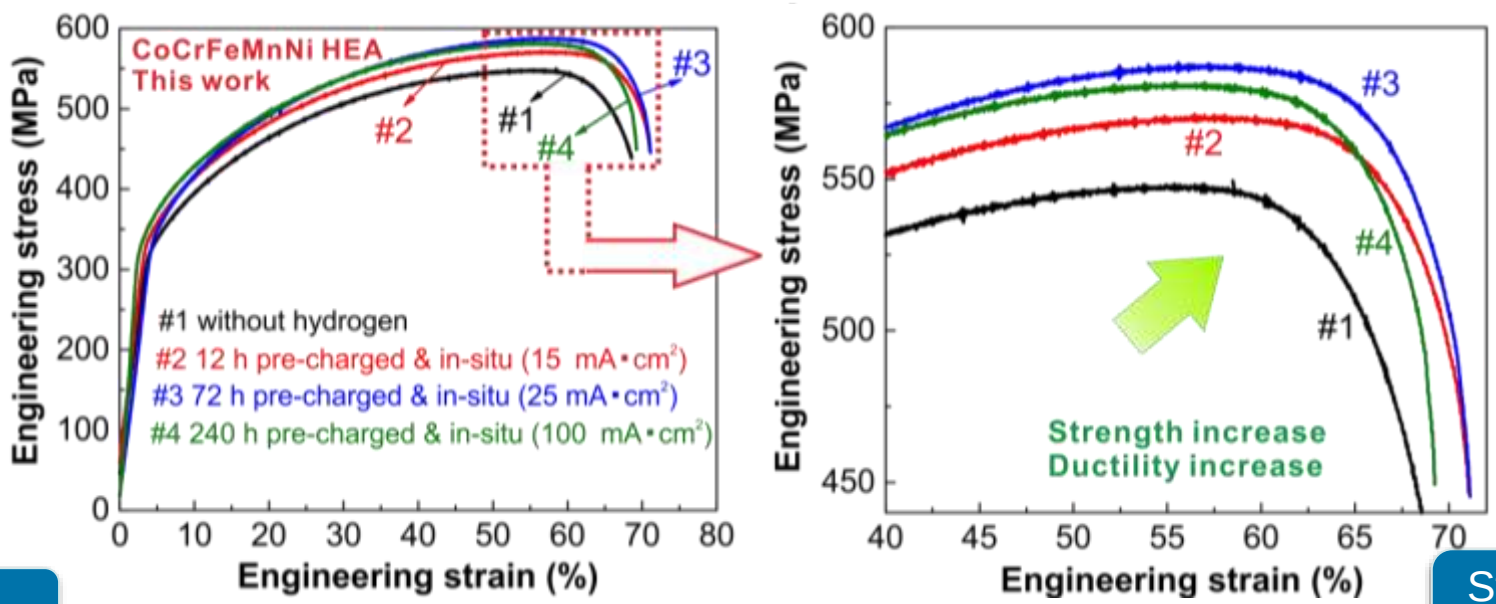


# In-situ LAADF-STEM reverse transformation (ε → γ)

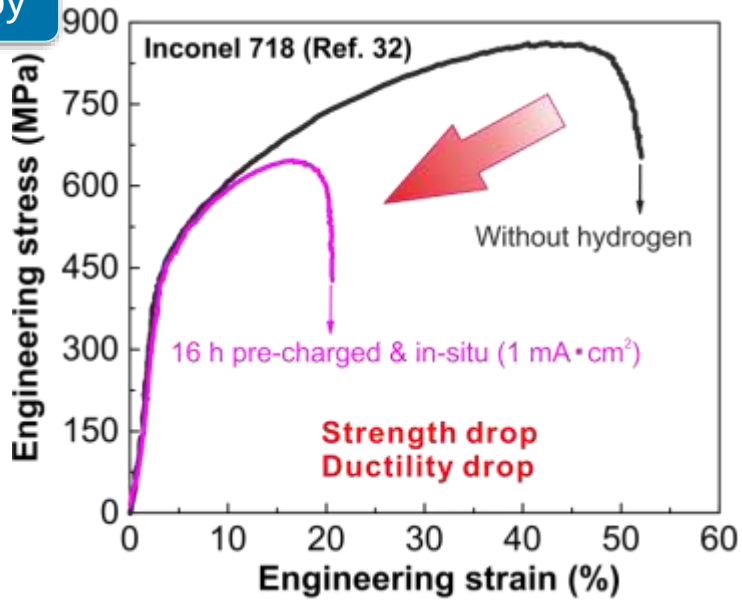


# Effect of Hydrogen: equim.-FeNiCrMnCo

HEA

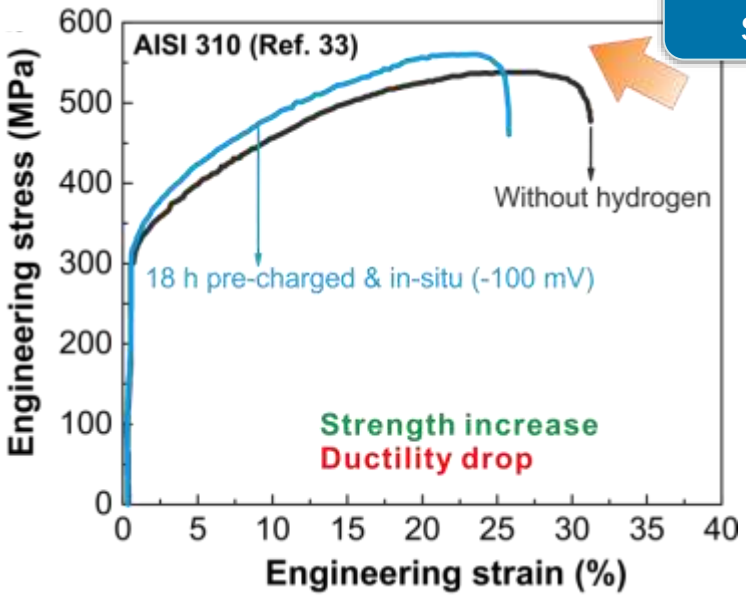



Superalloy




56Ni-18Fe-18Cr-5Nb-3Mo

Stainless steel



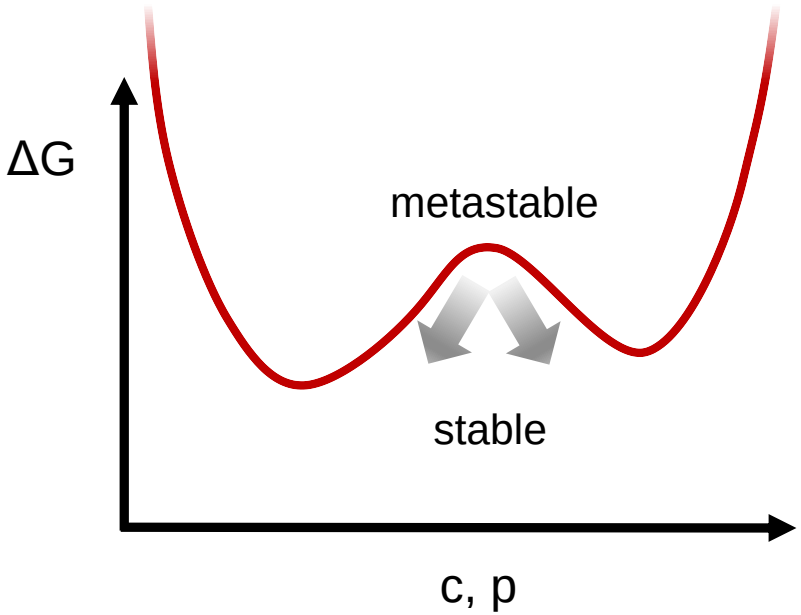

55Fe-25Cr-20Ni

H. Luo et al. Materials Today 21 (2018) 1003; H. Luo et al. Scientific Reports 7 (2017) 9892

# Metastability Alloy Design

Mechanical Metastability

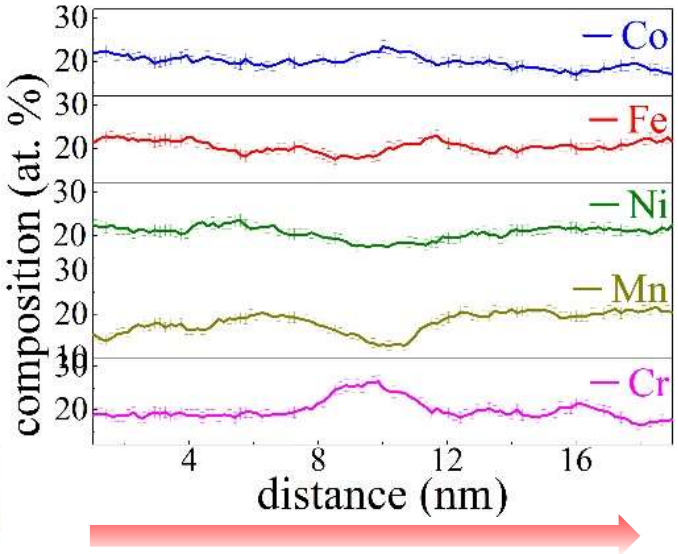
Chemical Metastability

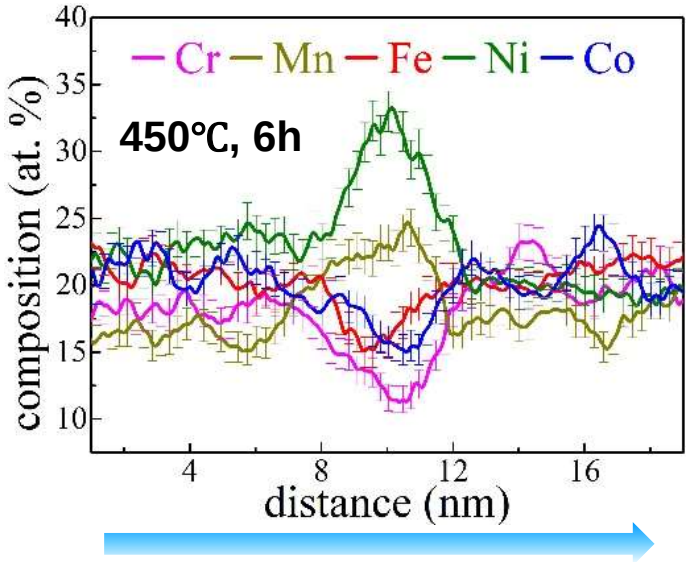


# Interface co-segreation in FeMnCrNiCo

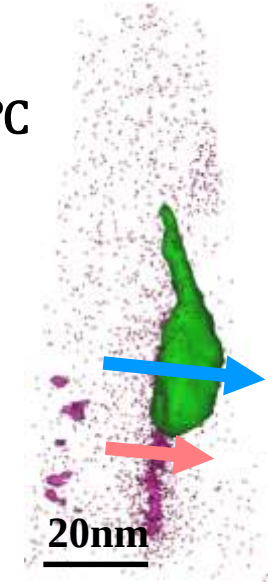
**Analysis <u>perpendicular</u> to grain boundary**

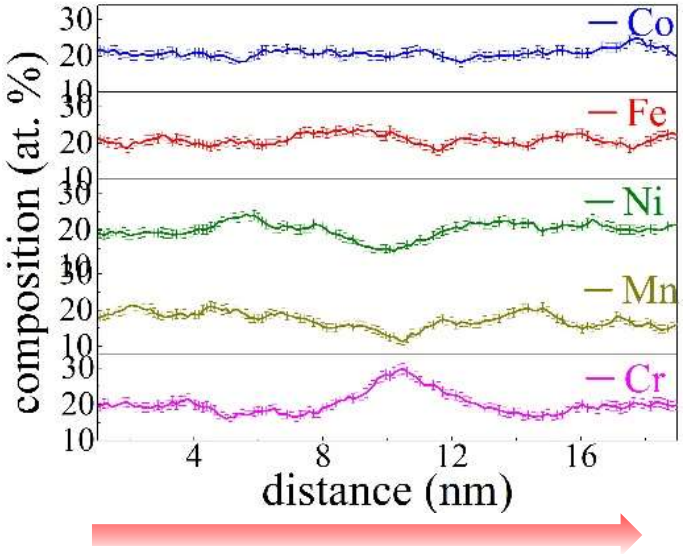
**450°C**
**6h**

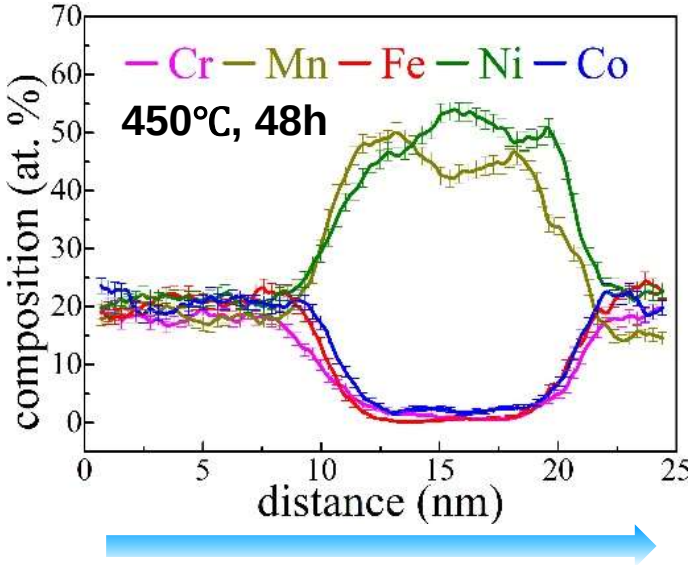




**450°C**
**48h**

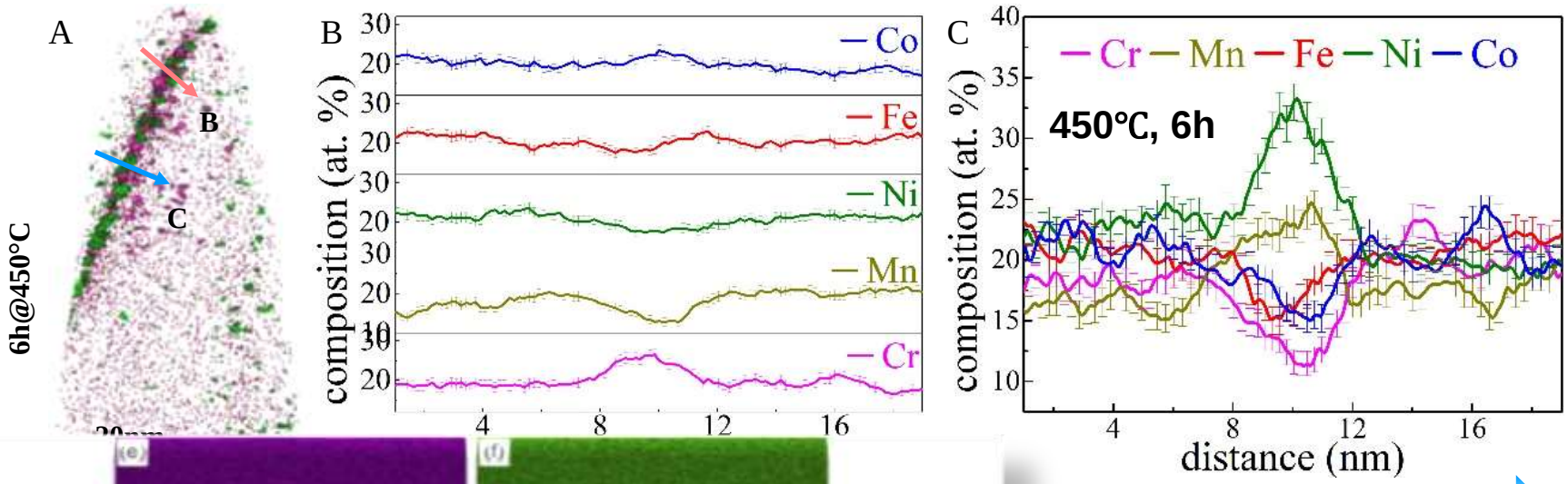


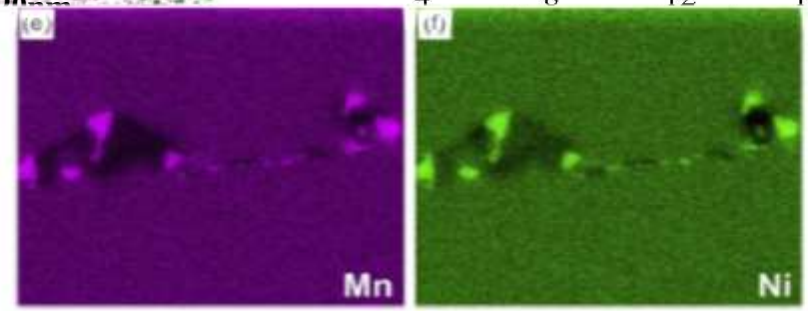



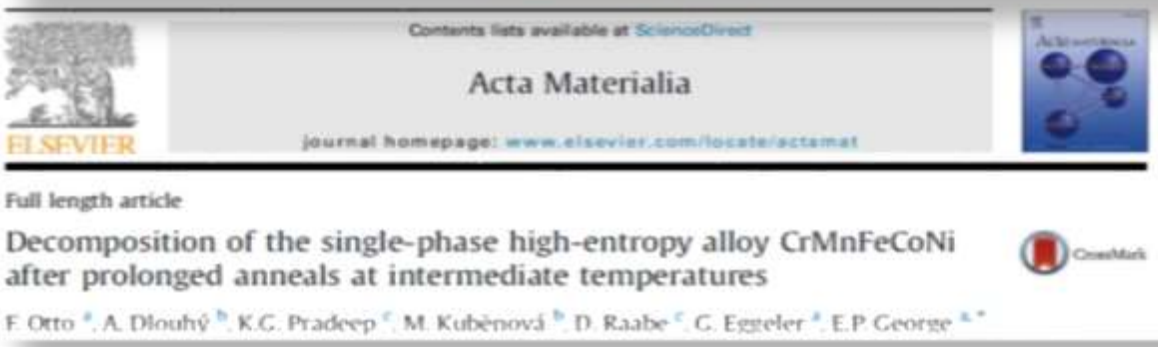



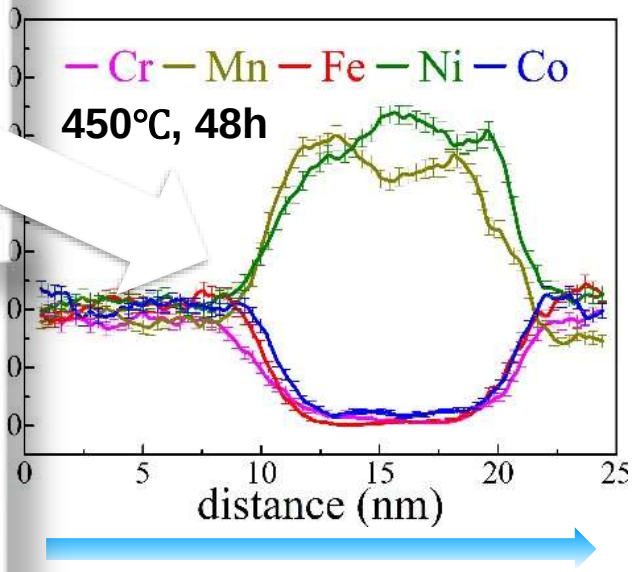

Otto et al. Acta Materialia,112,,40-52,2016; L. Li, Z. Li, A. Kwiatkowski da Silva et al. Acta Materialia 178 (2019)

# GB co-segreation in Cantor HEA



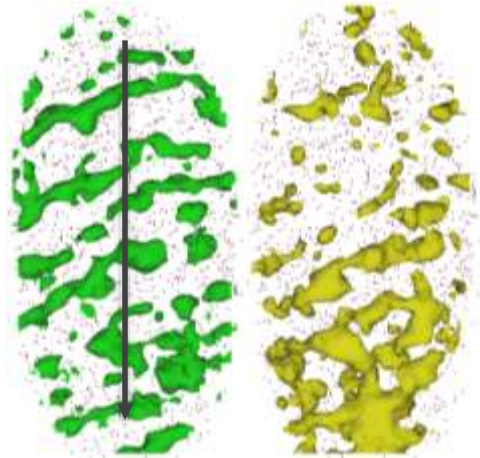




Ongoing work, Li, Gault; see also Otto et al. Acta Materialia,112,,40-52,2016

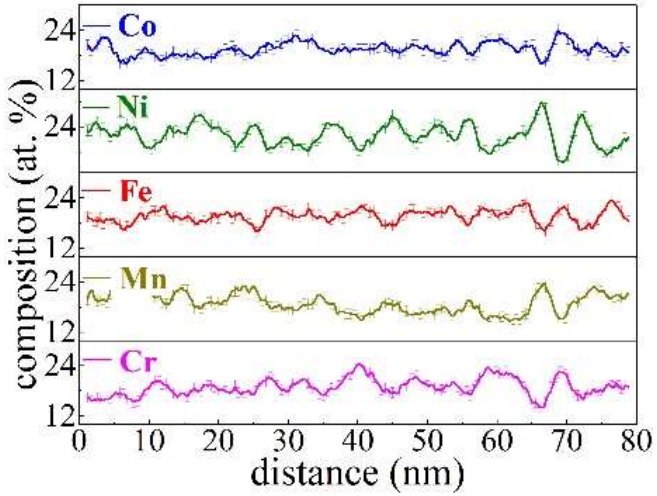
# Interface co-segreation in FeMnCrNiCo

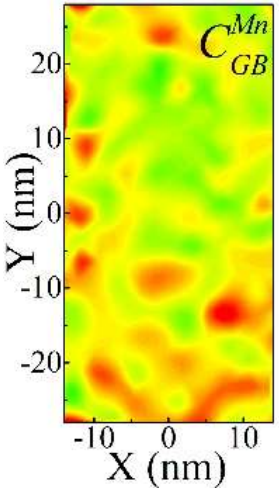
**450℃, 6h**

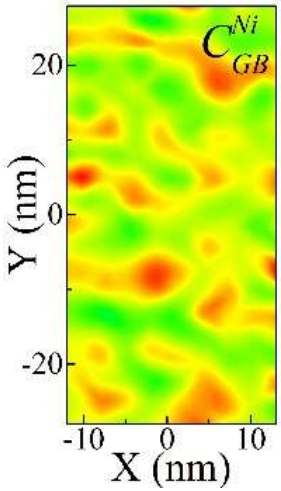
**Analysis <u>inside</u> grain boundary plane**

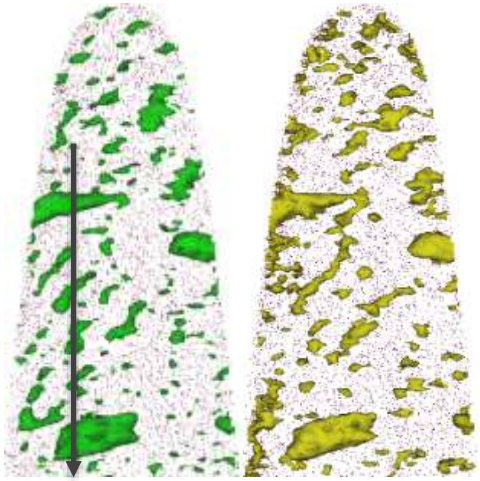


25at. % Ni 21.5at. % Mn

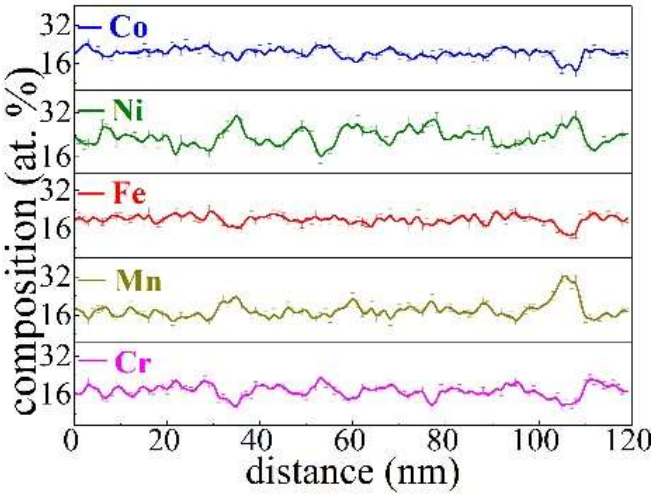


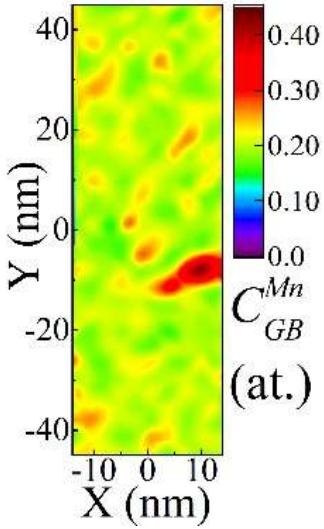



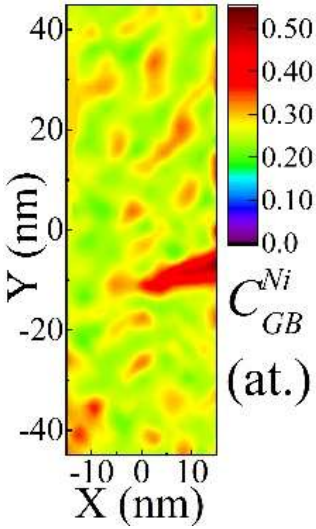



25.5at. % Ni 19.5at. % Mn

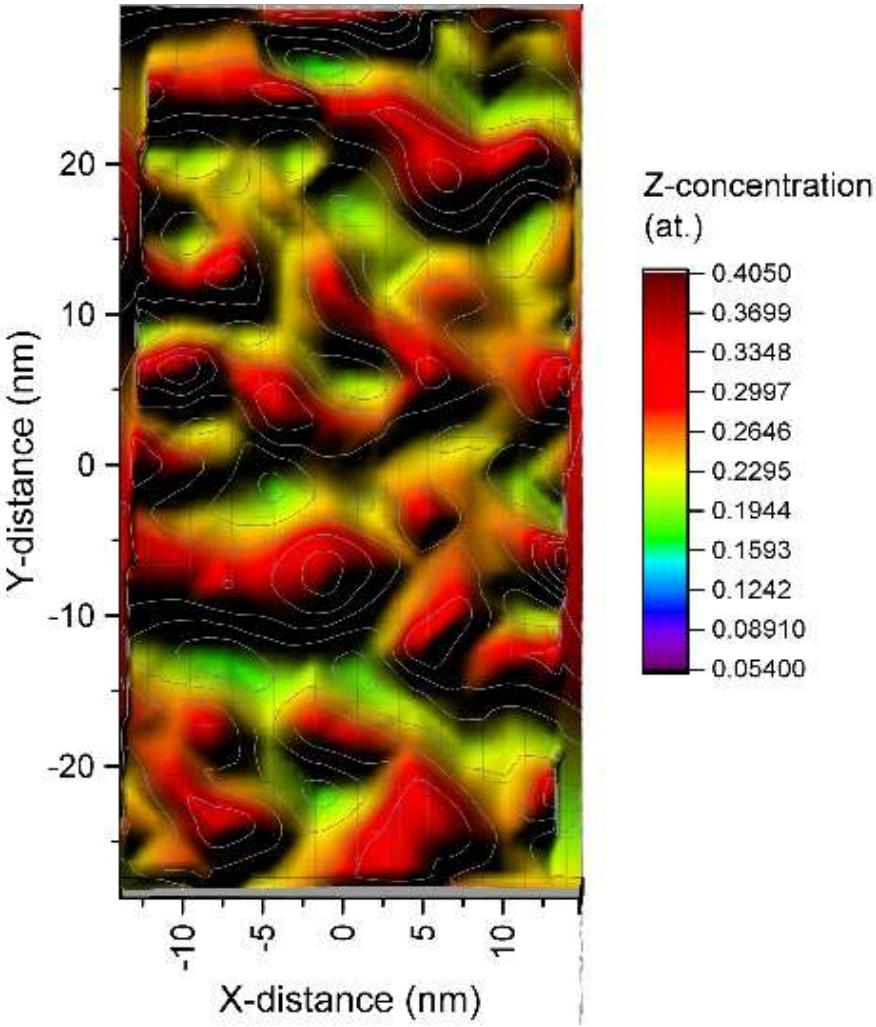


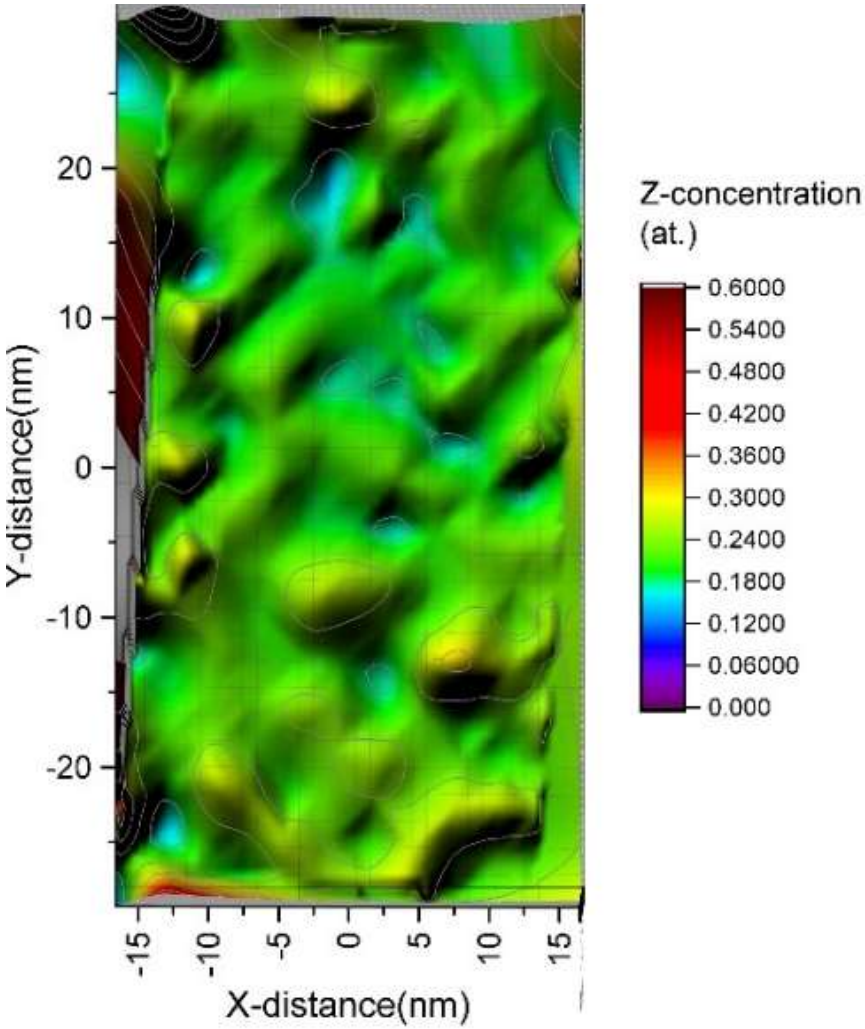




**450℃, 18h**

# Interface co-segreation in FeMnCrNiCo




**Ni in GB plane, 450℃, 6h**




**Mn in GB plane, 450℃, 6h**

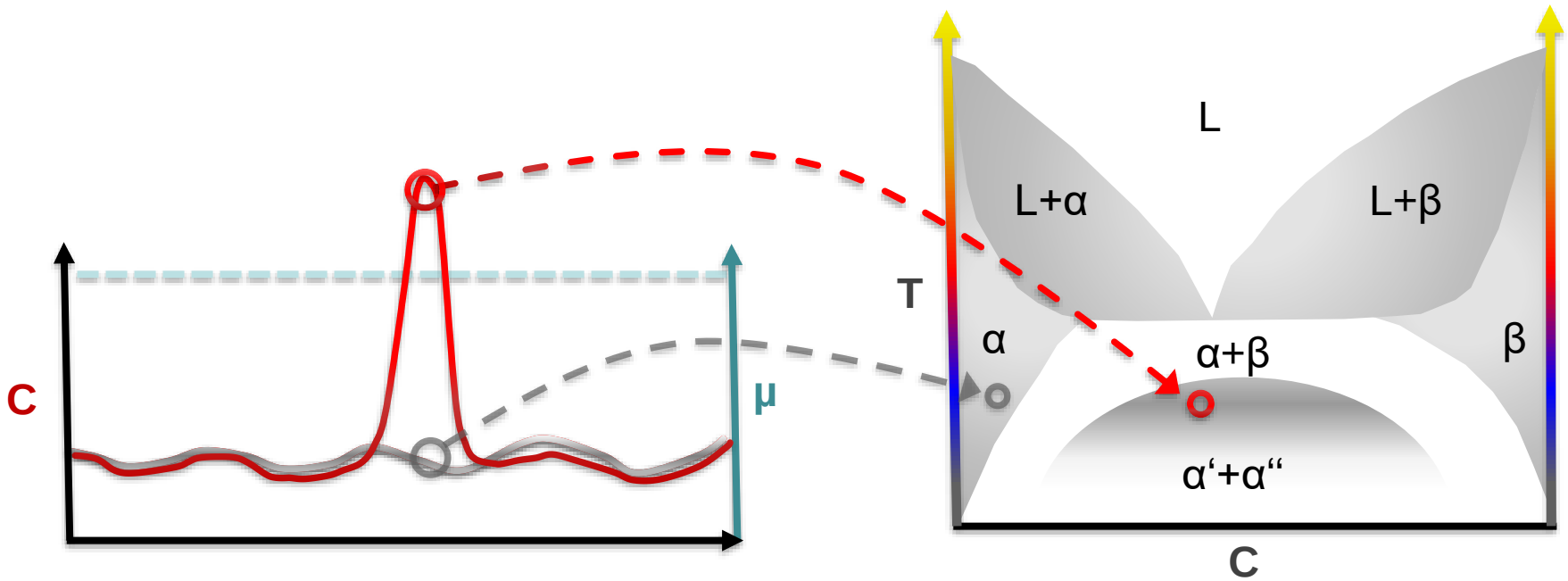
L. Li, Z. Li, A. Kwiatkowski da Silva et al. Acta Mater. 178 (2019); A Kwiatkowski da Silva et al. Acta Mater. 168 (2019)

# Defect decoration & thermodynamics

1. GB is NOT part of equilibrium, it is frozen in
2. BUT local composition / segregation is in equilibrium (Gibbs isotherm)
3. YET, segregants can interact (Fowler & Guggenheim, Hart, Guttmann isotherms)

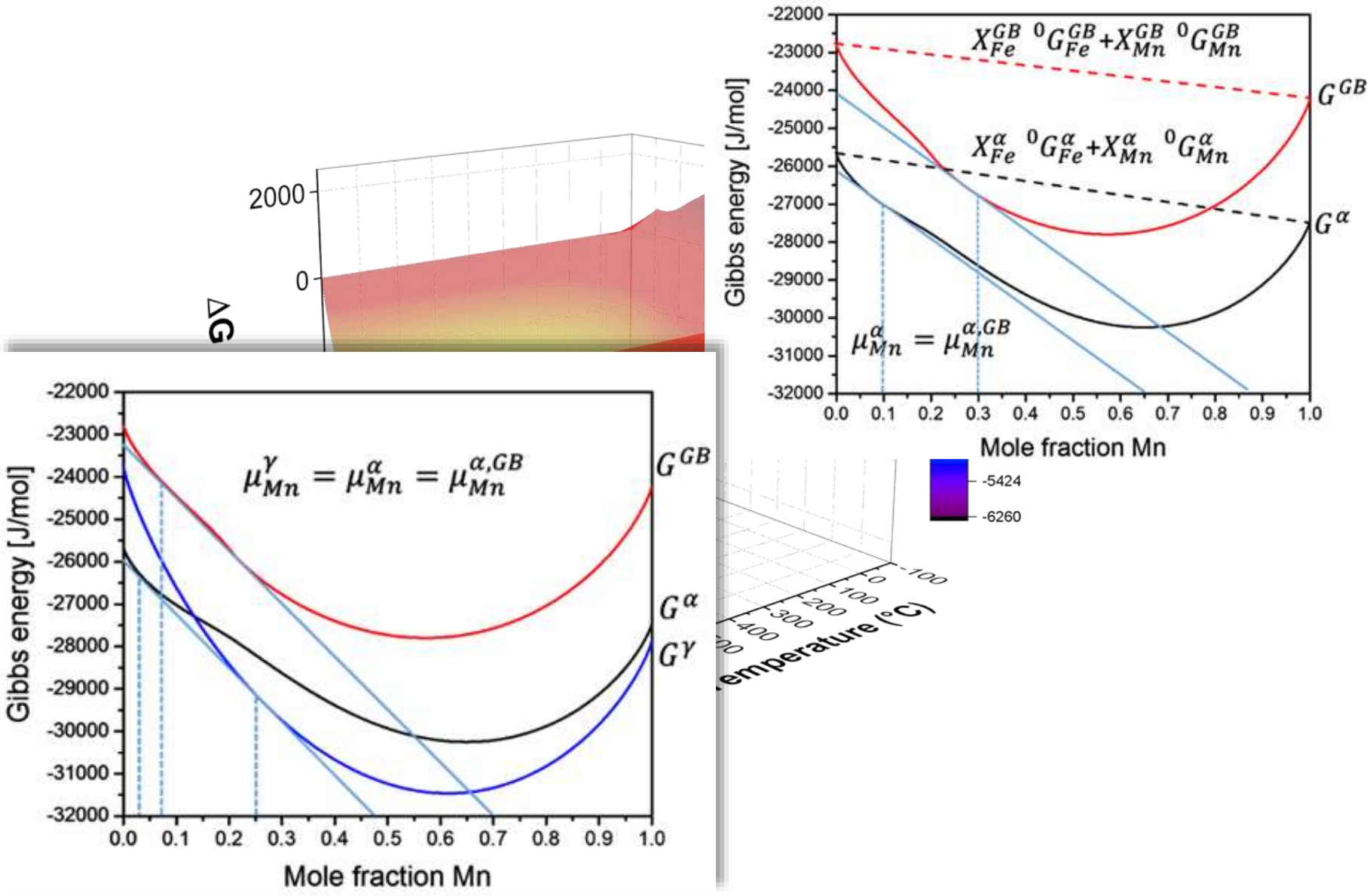
‘Heterogeneous‘ nucleation:

- Different compositional equilibrium working point
- Different driving force
- Different interface energy (isotherm)
- GP-like precursor states or other…




Kuzmina et al. Science (2015) 80; Kwiatkowski da Silva et al. Acta Mater. 168 (2019); Acta Mater. 124 (2917); Nat. Com. 9 (2018)

# Defect decoration & thermodynamics




Kwiatkowski da Silva et al. Acta Mater. 168 (2019); Acta Mater. 124 (2917); Nat. Com. 9 (2018)

# Bulk spinodal: tuning for ferromagnetism

$Fe_{15}Co_{15}Ni_{20}Mn_{20}Cu_{30}$

↓

**Cast**

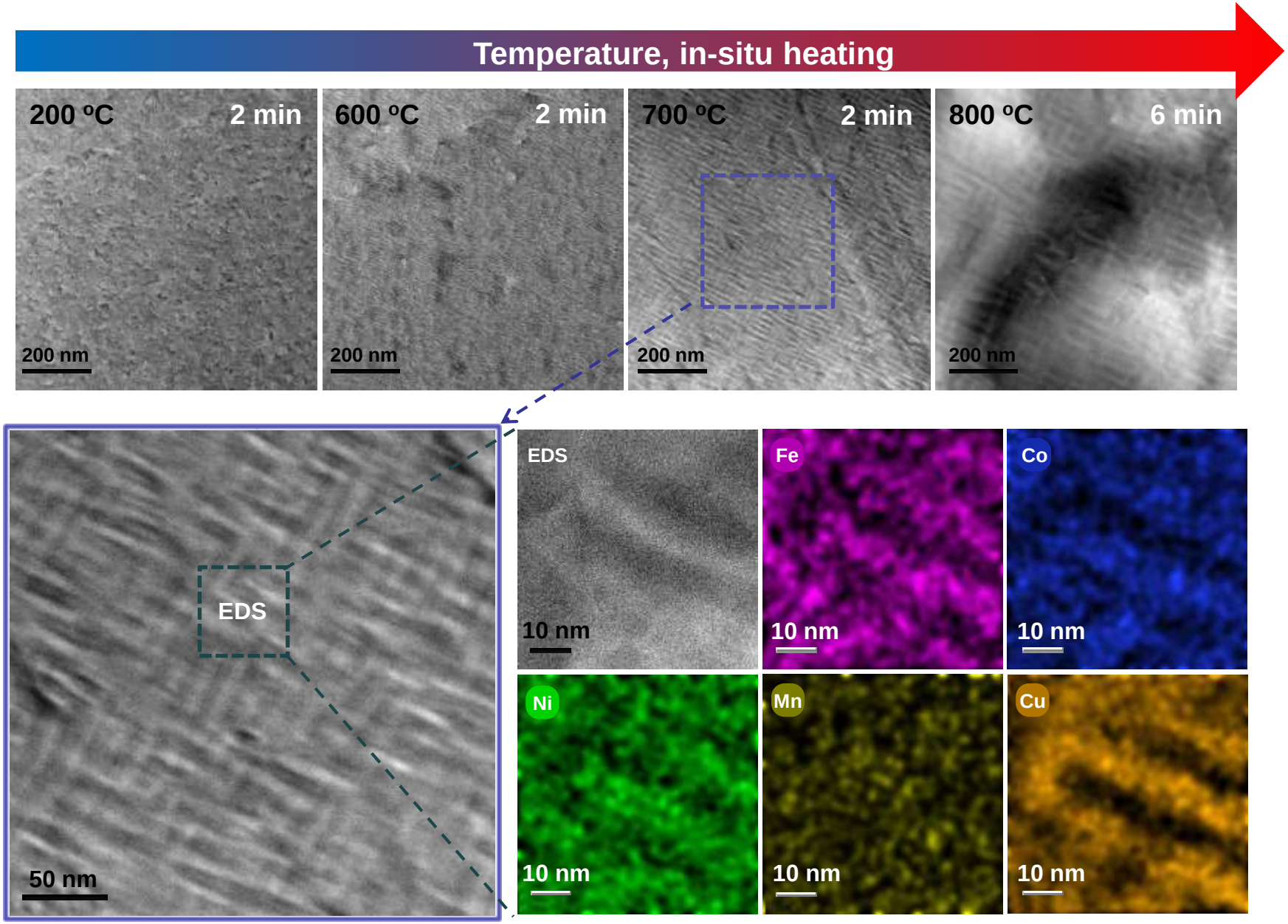
↓

**Homogenization (1000 $^{o}$C 24h)**

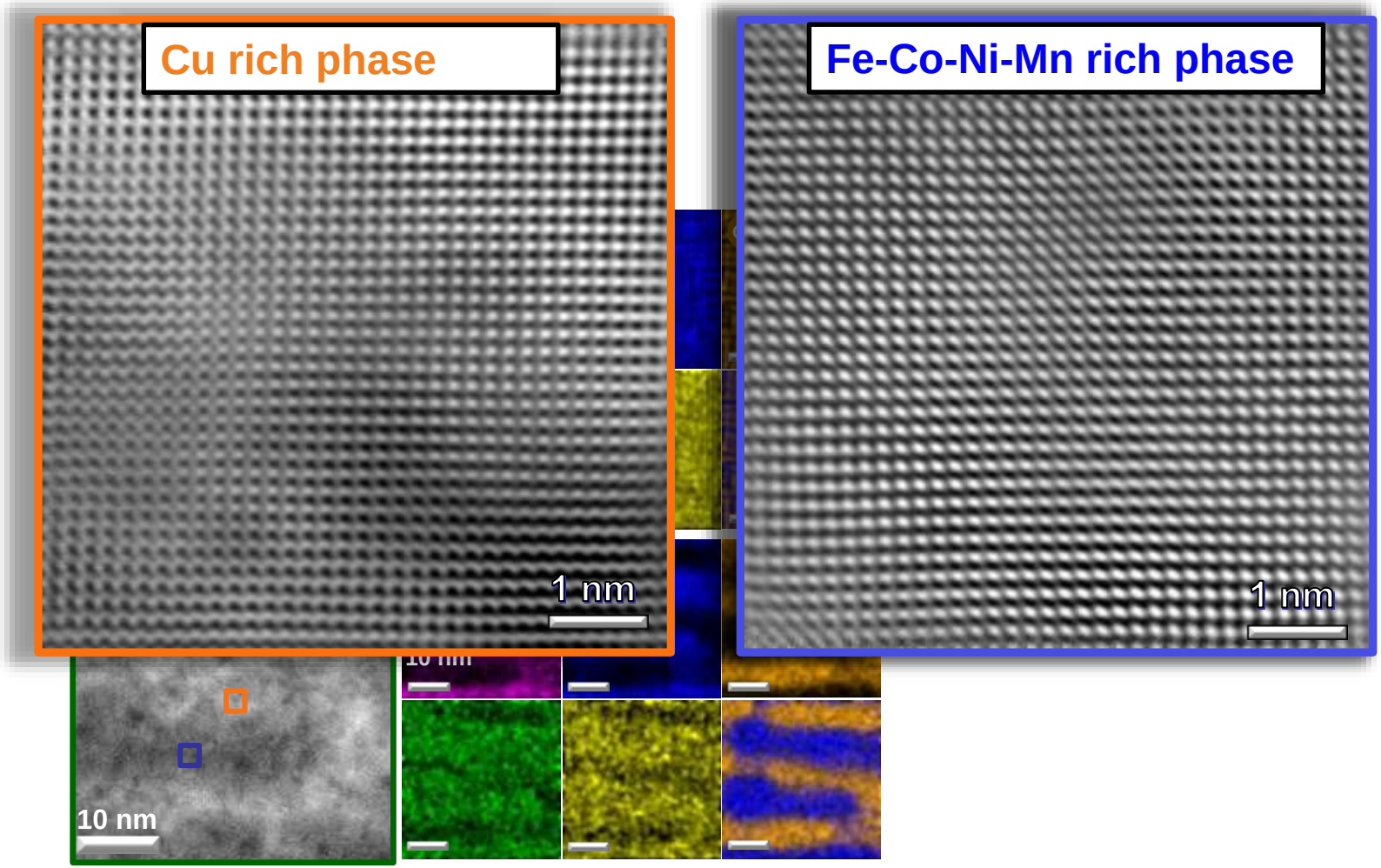
↓

**Anealing (600 $^{o}$C 2h, 6h, 24h)**

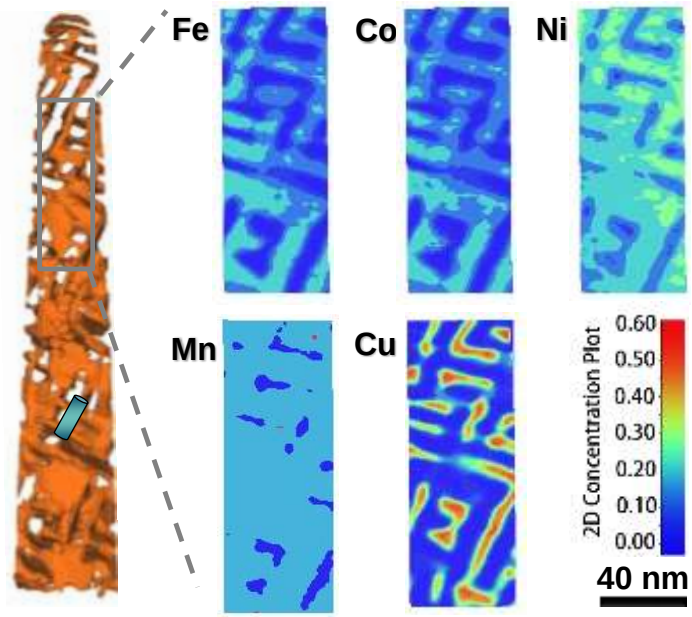
# Bulk spinodal: tuning for ferromagnetism

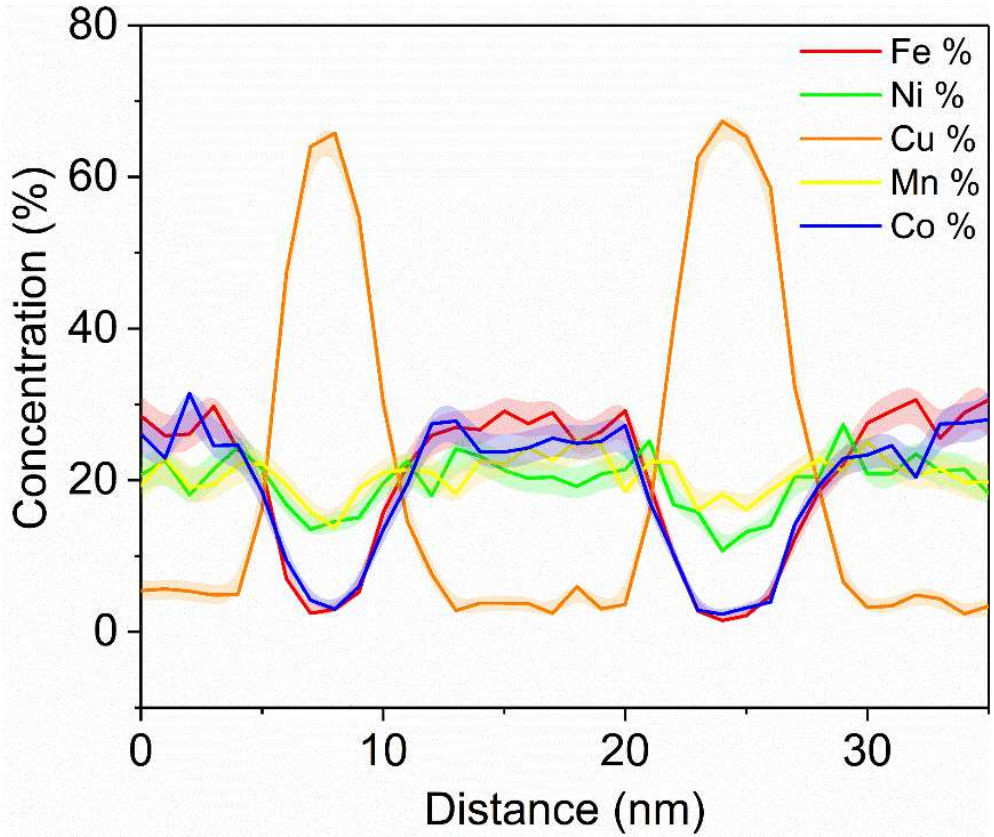


# FeCoNiMnCu annealed at 600°C for 6 h



# FeCoNiMnCu annealed at 600°C for 6 h



# FeCoNiMnCu annealed at 600°C

Annealing time

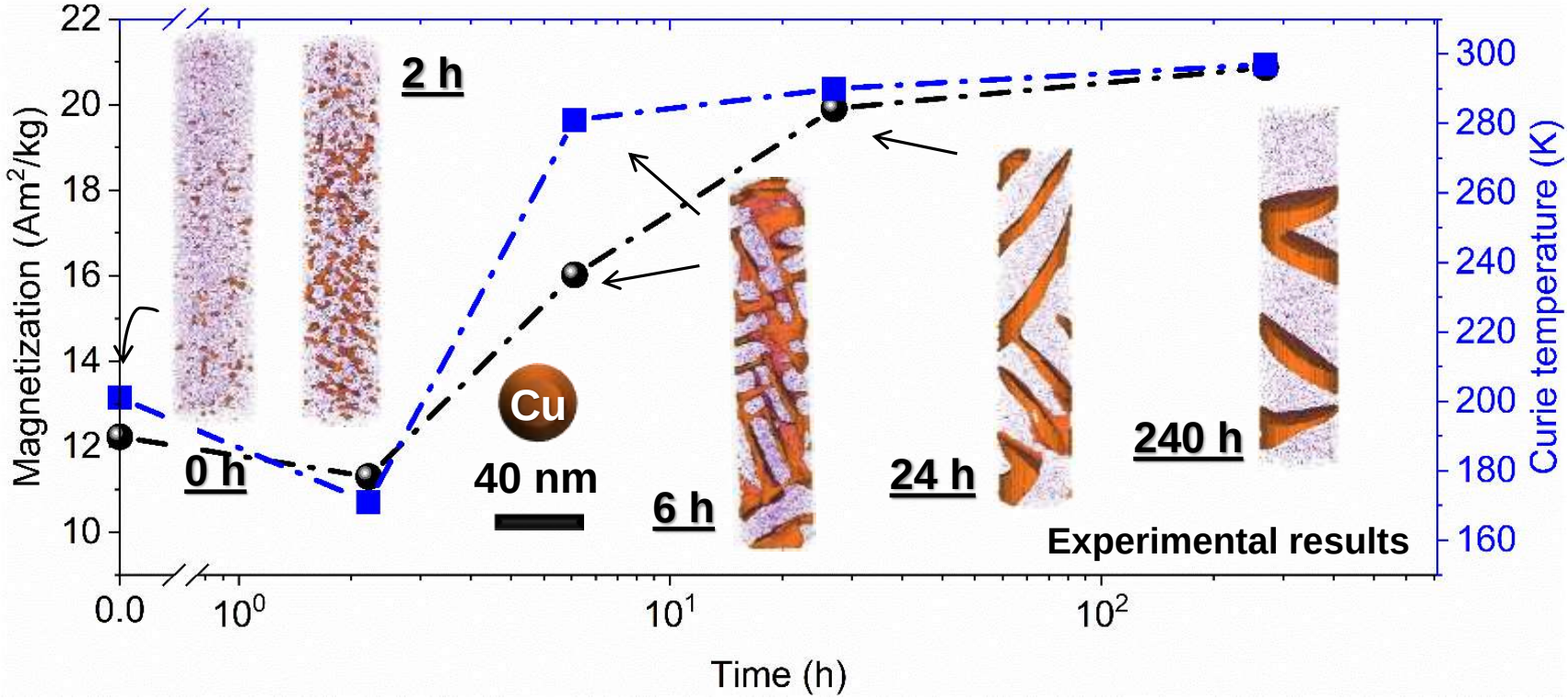
**0 h** **2 h** **6 h** **24 h** **240 h**

*Iso-surface:*
*50 at% Cu*

Cu

**20 nm**

# FeCoNiMnCu annealed at 600°C



# Message & Conclusions

- Metastability alloy design (displacive, spinodal)
- Multicomponent thermodynamics, also at confined scales

- Combine mechanical properties with magnetism, corrosion, H-resistance,…

# Thank you for the attention

*Kindly sponsored by:*
**European Research Council**
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