Ab-initio informed thermokinetic modeling of metallic alloys

Lorenz Romaner[1,2]

1 Department of Materials Science, Montanuniversität Leoben, Leoben, Austria.
2 Materials Center Leoben Forschung GmbH, Leoben, Austria.

GreenALM meeting
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Collaborators

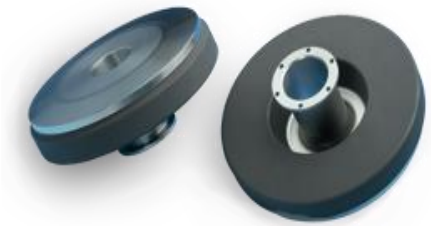
- Materials Center Leoben
  - Daniel Scheiber
  - Rishi Bodlos
  - Jürgen Spitaler
  - Andrei Ruban
- Montanuniversität Leoben
  - Tobias Spitaler
  - Franz Dieter Fischer
- Czech Academy of Sciences
  - Jiri Svoboda
- University of Vienna
  - Erwin Povoden-Karadeniz
  - Ernst Kozeschnik

Outline

- Ab-initio informed thermodynamic modeling of GB segregation.
  - Thermodynamic models
  - Example W-Re alloy
- Ab-initio informed thermokinetic modeling of GB segregation.
  - Kinetic models
  - Example Mo-Hf
- Ab-initio informed CALPHAD modeling of WTi

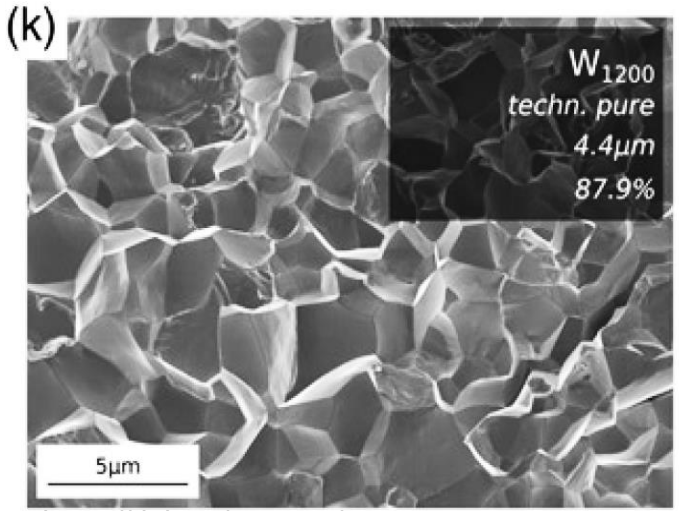
Metals where segregation matters

W, Mo



https://www.plansee.com

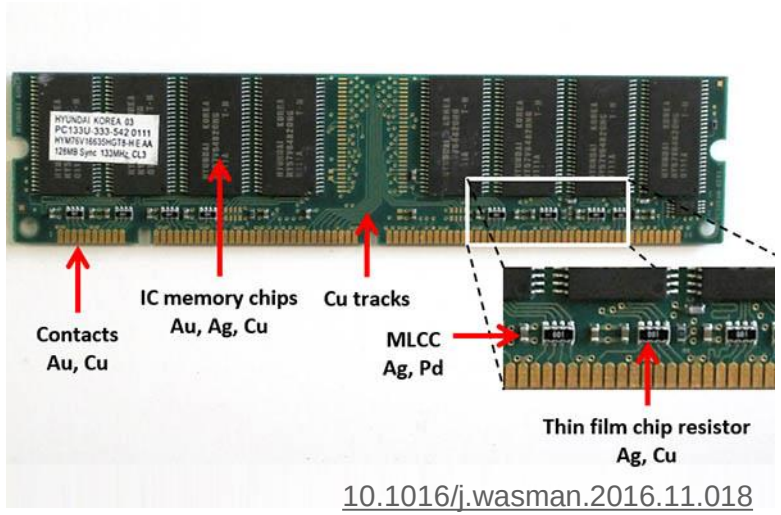
X-ray anodes



https://doi.org/10.1080/14786435.2011.558861

Intergranular fracture surface of W

Cu, Al



10.1016/j.wasman.2016.11.018

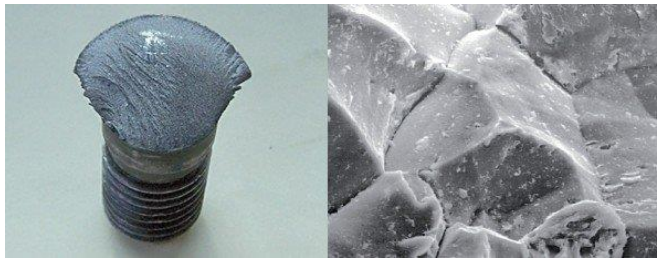
Microelectronics

www.indiamart.com

Busbars

Fe

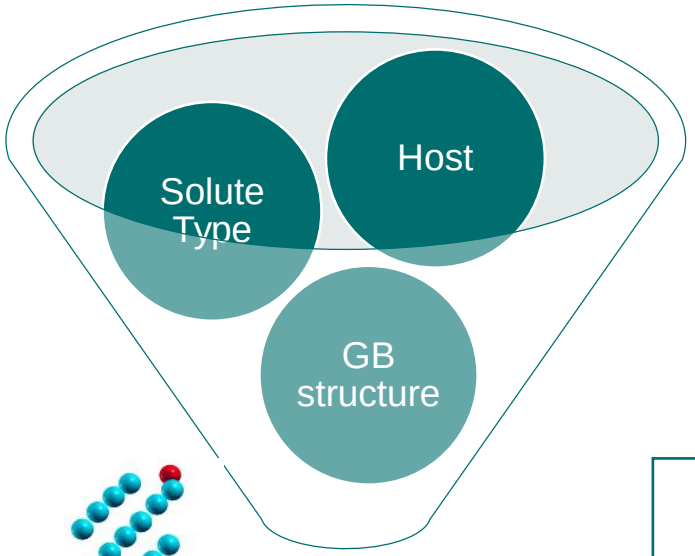
Source: WorldAutoSteel

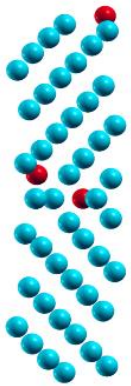


https://www.imetllc.com/hydrogen-embrittlement-steel/

H-embrittlement in steels

Multi-scale calculation work flow





DFT

E_{seg}

E_{stren}

Microstructure, Diff. Coeff. Heat treatment

Thermodynamic and kinetic modeling

Mechanical modeling

Plasticity parameters

accessible by experiment

Phase transformation kinetics

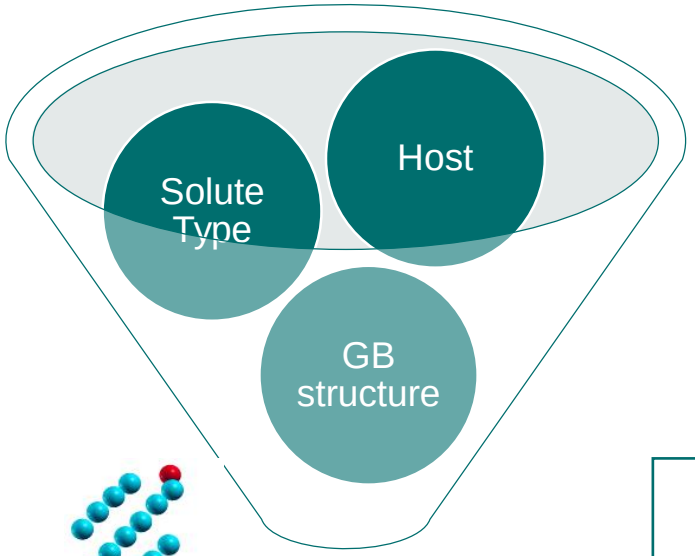
Grain growth

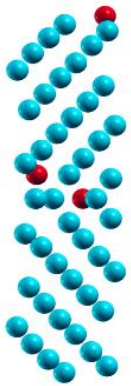
GB excess

Grain boundary toughness

Intergranular vs transgranular failure

Multi-scale calculation work flow





DFT

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accessible by experiment

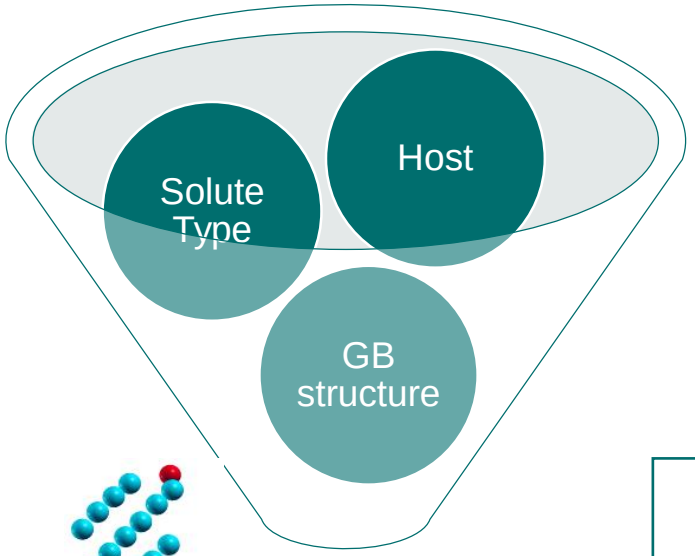
- Phase transformation kinetics
- Grain growth
- GB excess

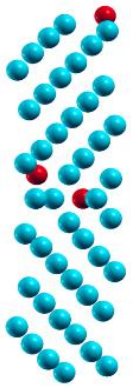
Solutes in Mo

R Janisch, et al. Physical Review B, 2003.
D Scheiber et al., Int. J. Refr. Met. Hard Mater. 2016.
D Scheiber et al., Mod. and Sim. in Mat. Sci. 2016.

H																	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Multi-scale calculation work flow





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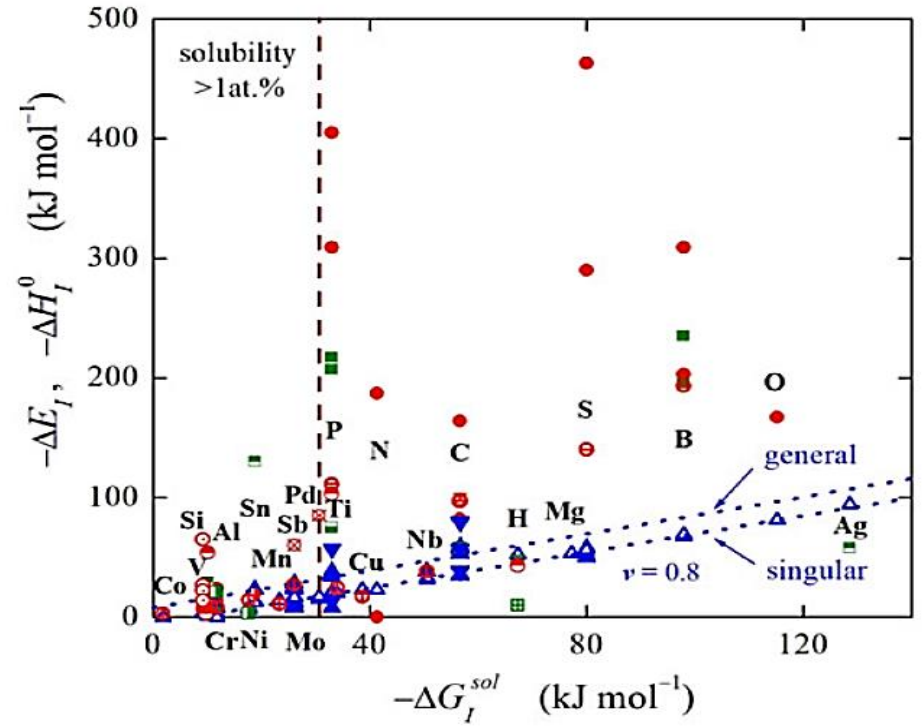


Grain boundary toughness

Intergranular vs transgranular failure

Thermodynamic Framework

- Minimization of grand potential W (Sutton&Baluffi) in a mean-field approach

$$\Omega = F(\{c_i\},\{r_i\}) - TS_c - \mu_A N_A - \mu_B N_B \qquad F(\{c_i\},\{r_i\}) = E(\{c_i\},\{r_i\}) - TS_V(\{c_i\},\{r_i\})$$

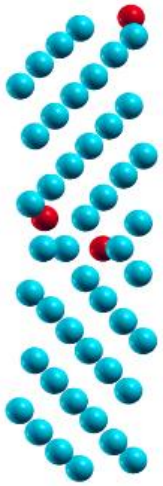
- Regular solution model: McLean equation:

$$-TS_c = kT\sum_k [c_k \ln c_k + (1-c_k)\ln(1-c_k)]$$

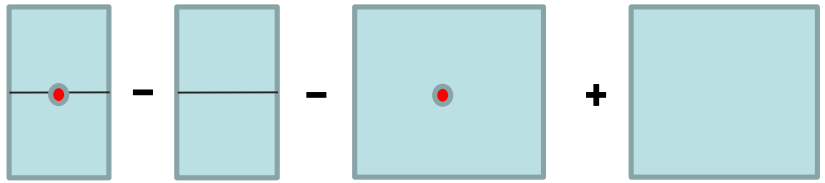
$$\frac{c_k}{1-c_k} = \frac{c_0}{1-c_0}\exp\left(-\frac{1}{kT}\left(\frac{\partial F}{\partial c_k} - \frac{\partial F}{\partial c_0}\right)\right)$$

- DFT Segregation energy evaluated at 0K.

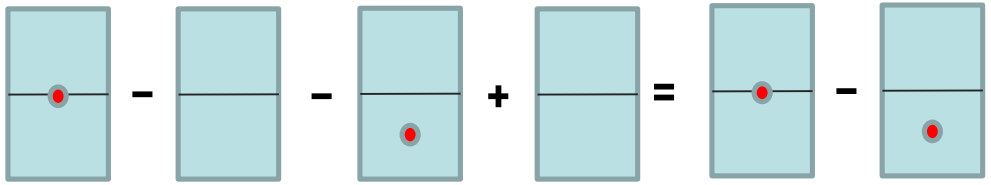
$$\Delta E_k^{seg} = \frac{\partial E(\{c_i\})}{\partial c_k} - \frac{\partial E(\{c_i\})}{\partial c_0}$$



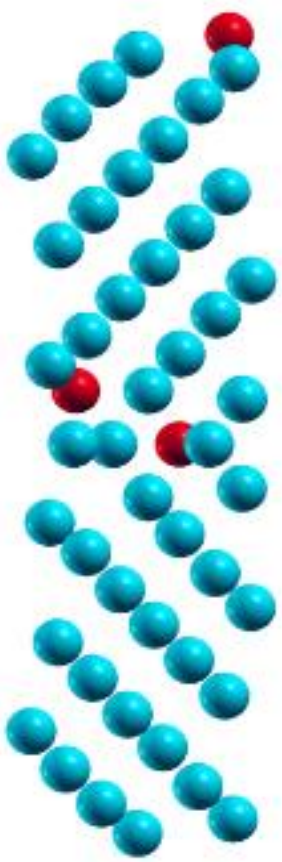
Method 1



Method 2

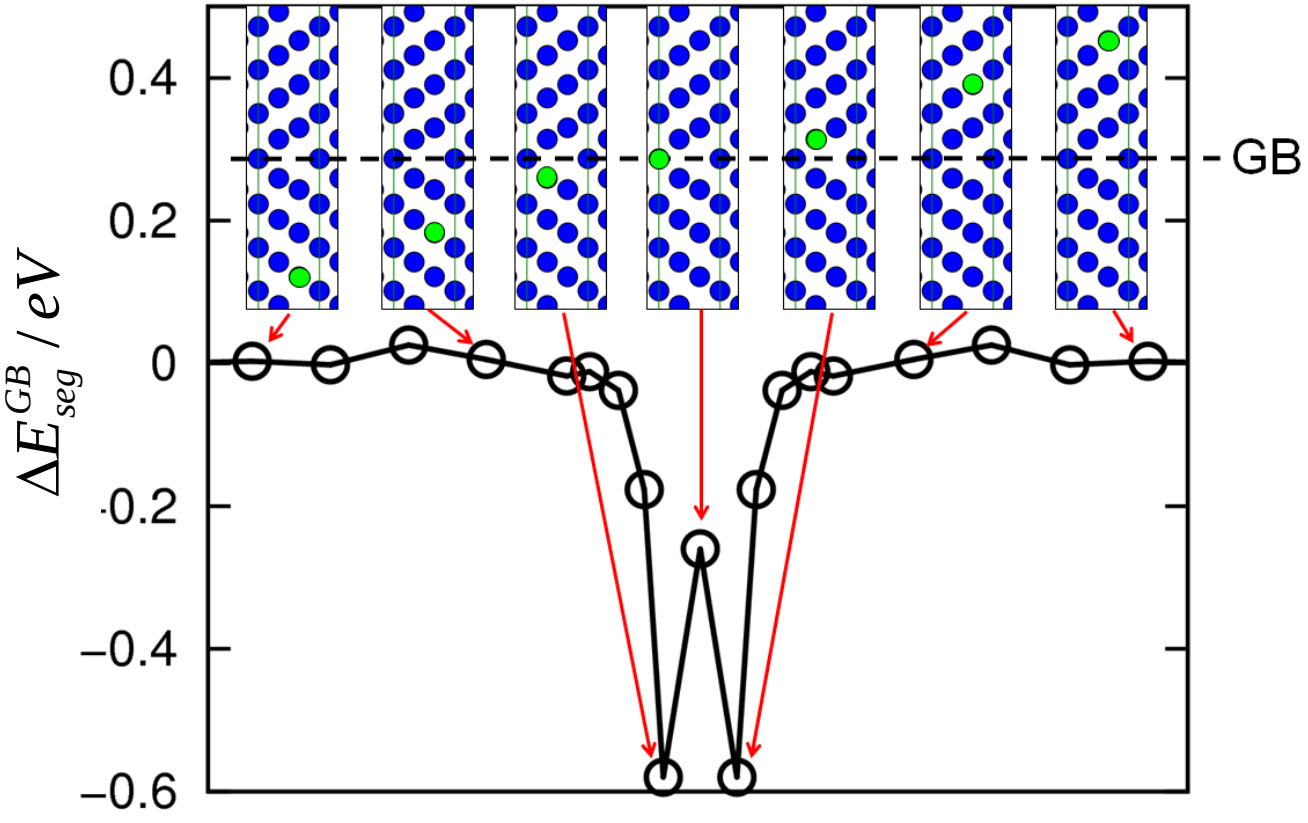


DFT calculations: Segregation energies



VSC Supercomputer Vienna

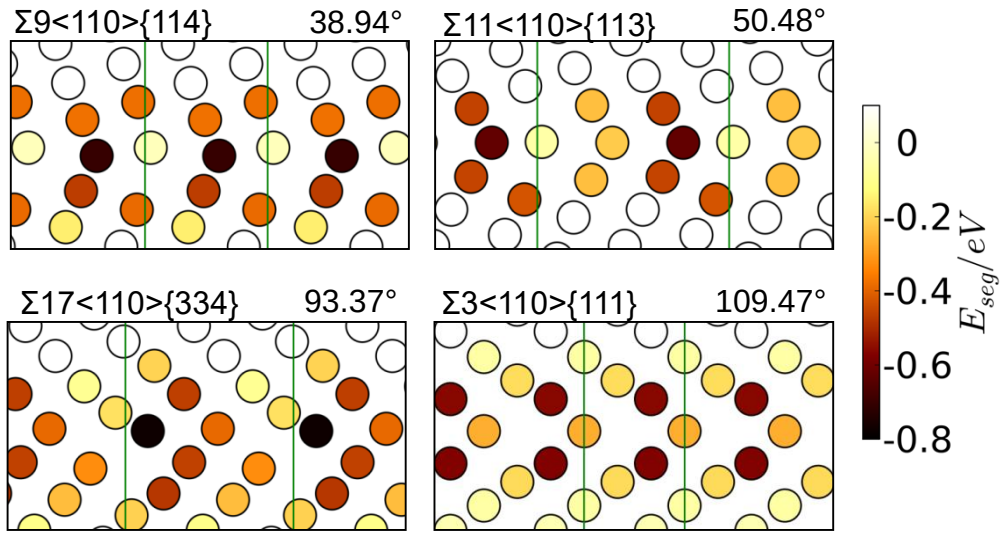
Segregation profile (Re in W)



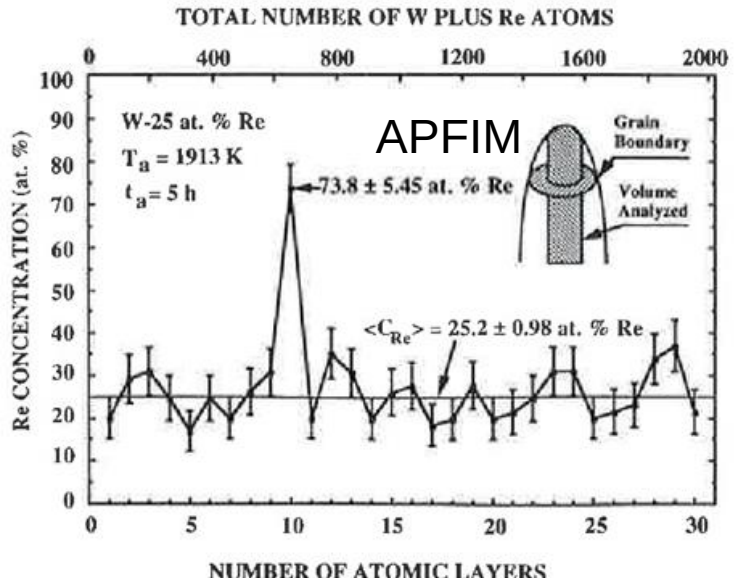
Re atom is trapped by the GB

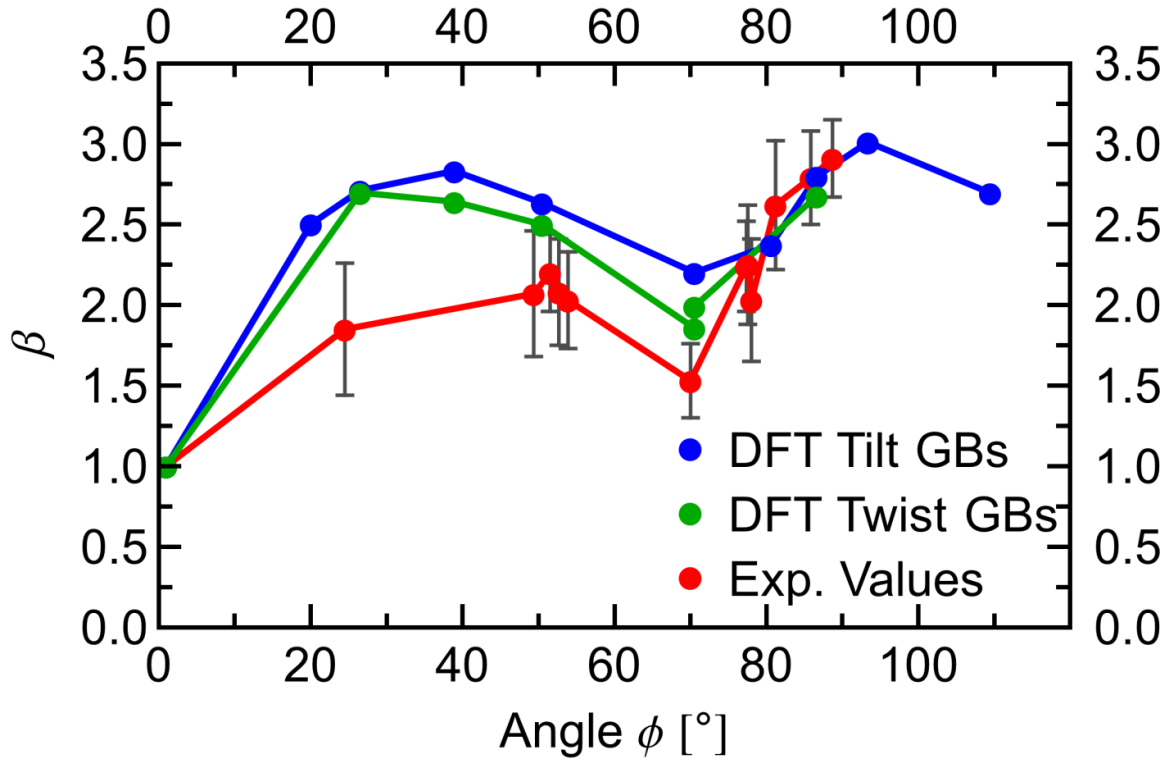
Validation GB excess: W-Re

DFT



$$\frac{c_k}{1-c_k} = \frac{c_0}{1-c_0}\exp\left(-\frac{\Delta E_{seg}^{GB}}{kT}\right) \Rightarrow \beta = \frac{\sum_{k\in GB} c_k}{N_{GB}c_0}$$





D. N. Seidman, Mat. Sci. Eng. A137, 57, (1991).

D. Scheiber et al. Acta Materialia, Vol. 88, 2015, p.180-189

Relevant approximation for comparison with experiment

- Model:
  - Segregation energy depends on XC functional
  - No vibrational entropy
  - No solute-solute interactions
  - Mean-field approximation
  - Regular solution assumption
  - ….

- Experiment:
  - Errors in determining excess.
  - Thermodynamic equilibrium (segregation while cooling?).
  - Precipitates modify bulk composition with respect to nominal composition.
  - In case segregation energies are extracted: assumption of a single segregation energy
  - …..

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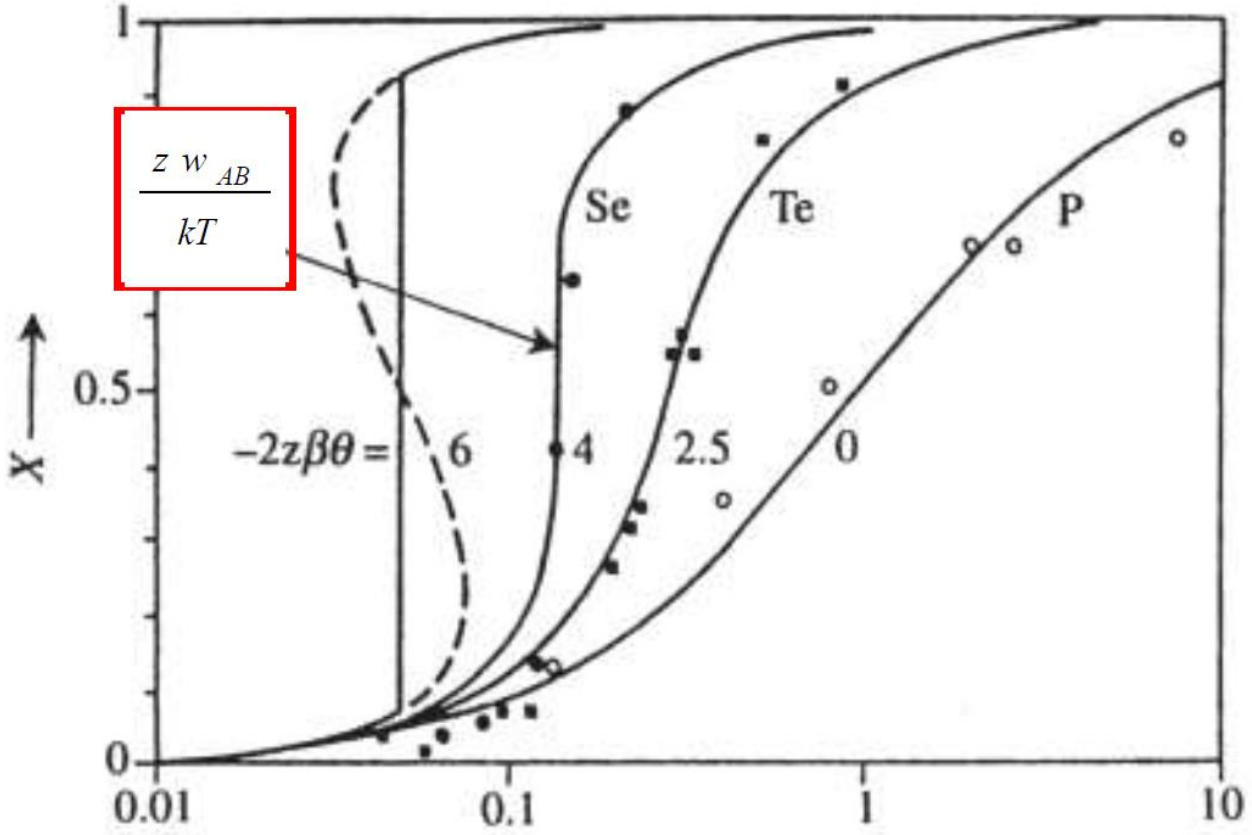
Solute-solute interactions

- Solute-solute interactions need to be included for Fowler-Guggenheim behavior.

$$\frac{c_k}{1-c_k} = \frac{c_0}{1-c_0}\exp\left(-\frac{\Delta E_k^{seg}\left(\{c_i\}\right)}{kT}\right)$$



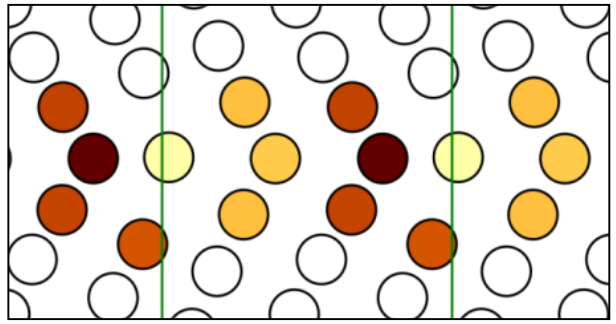
Sutton,Baluffi Interfaces in crystalline materials

Solute-solute interactions

- Iterative procedure is required for including solute-solute interactions

$$\frac{c_k}{1-c_k} = \frac{c_0}{1-c_0}\exp\left(-\frac{\Delta E_k^{seg}\left(\{c_i\}\right)}{kT}\right)$$

$$\Delta E_k^{seg} = \frac{\partial E\left(\{c_i\}\right)}{\partial c_k} - \frac{\partial E\left(\{c_i\}\right)}{\partial c_0}$$



- GreenALM could be an efficient and highly precise code for this purpose.

Relevant approximation for comparison with experiment

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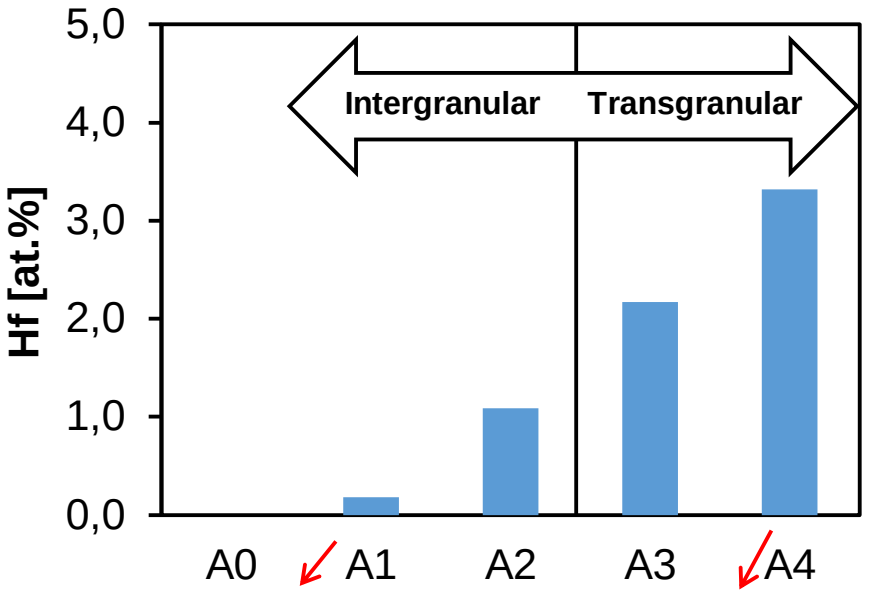
  - …..

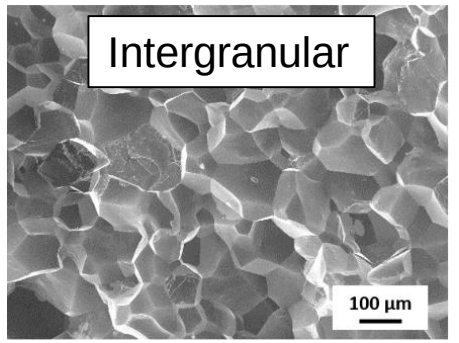
Validation GB excess: Mo-Hf-C

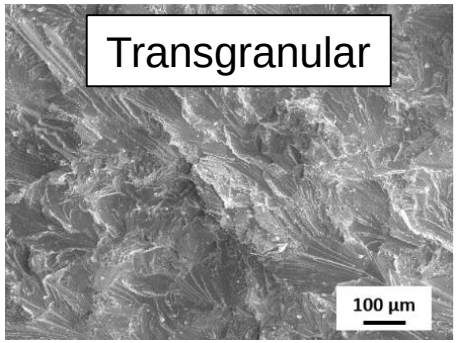
Mo-Hf-C alloy (MHC)

Pöhl et al. Mater. Sci. Eng. A **559,** 643, (2013).
Pöhl et al. J. Alloys Compd. ***576****,* 250, (2013).

→ technological alloy produced by powder metallurgy.

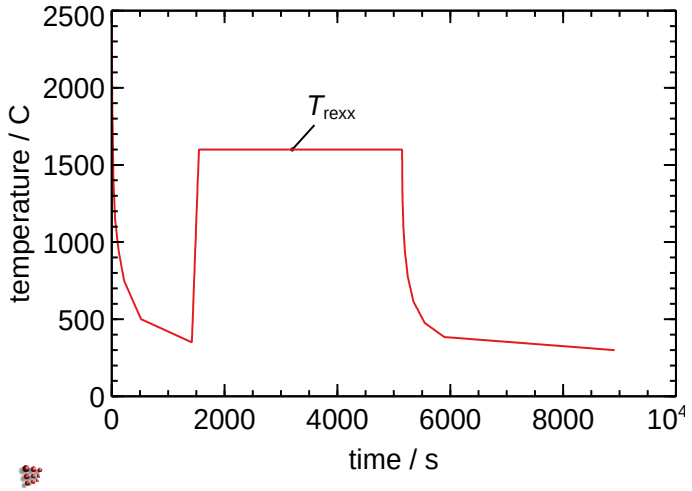






Fracture tests showed transition from intergranular fracture to transgranular fracture

Heat treatment:



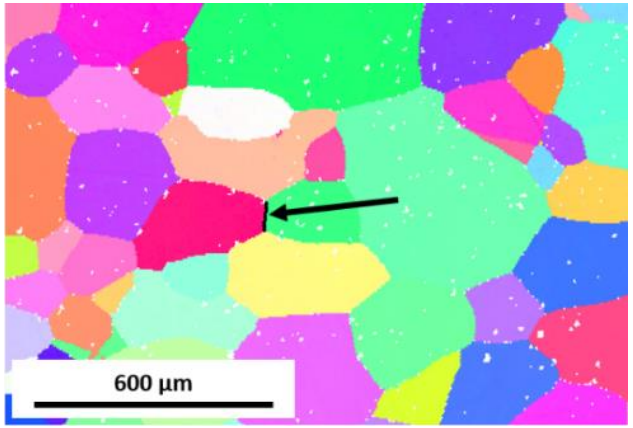
Chemistry :

	Total content			
Alloys	**Hf**	**C**	**O**	**B**
	at. %	at. %	at. %	at. ppm
A0	0.00	0.011	0.010	0.0
A1	0.18	0.010	0.021	0.1
A2	1.09	0.011	0.338	0.1
A3	2.18	0.020	0.553	0.5
A4	3.32	0.013	0.601	0.7

Validation of GB excess: Mo-Hf-C

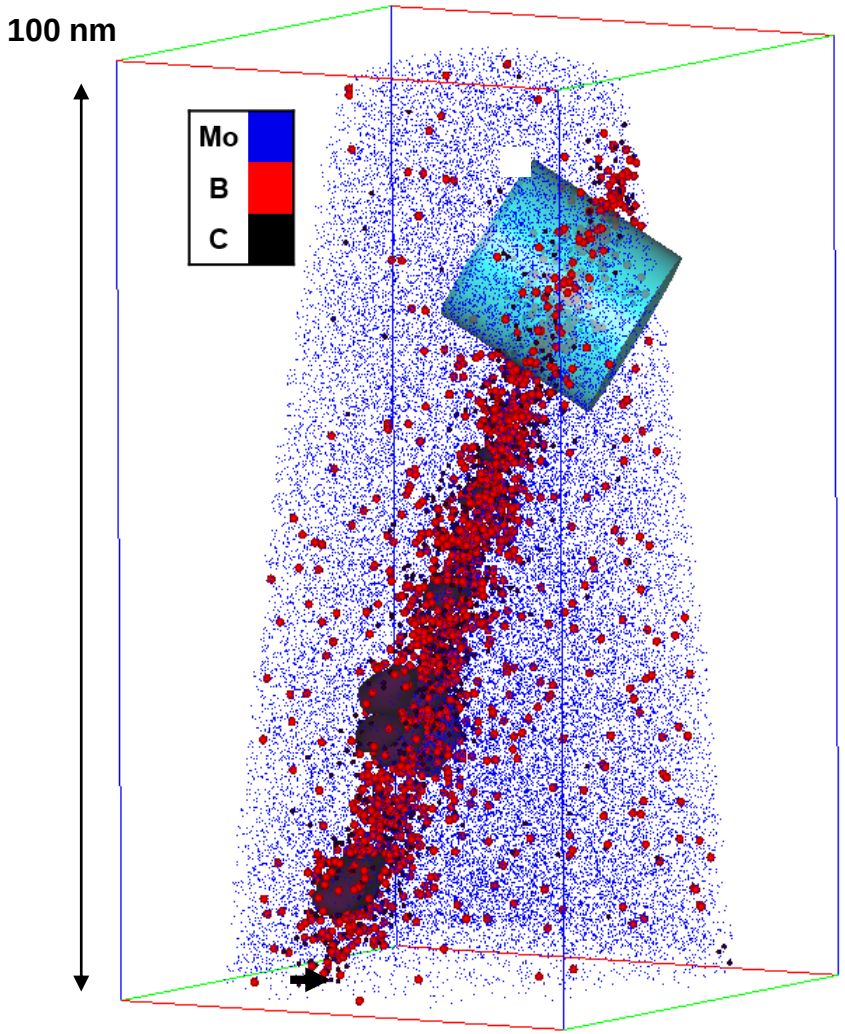
Leitner et al, Materials & Design 2018, 142, 36.

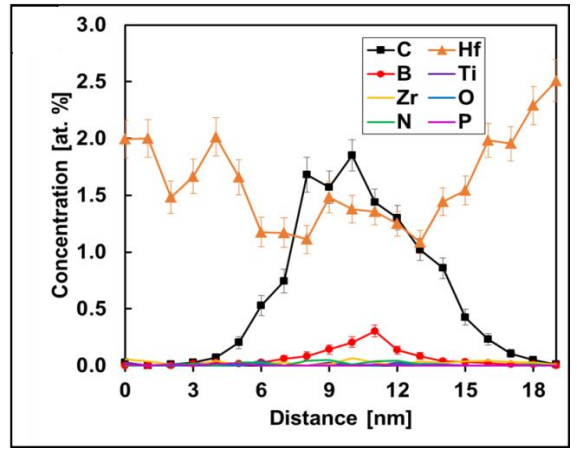
Measurement of GB chemistry with atom probe tomography (APT):
→Two or more GBs were studied for each alloy



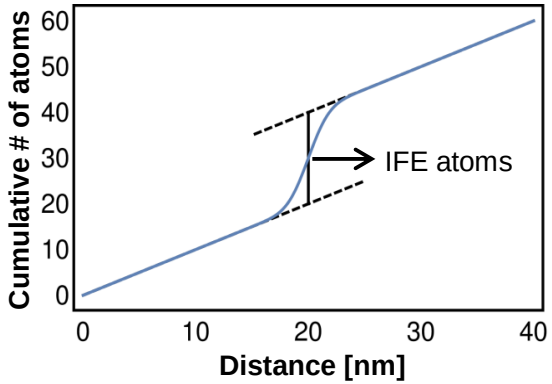
Microstructure of Alloy A4

APT analysis of the Σ11 GB



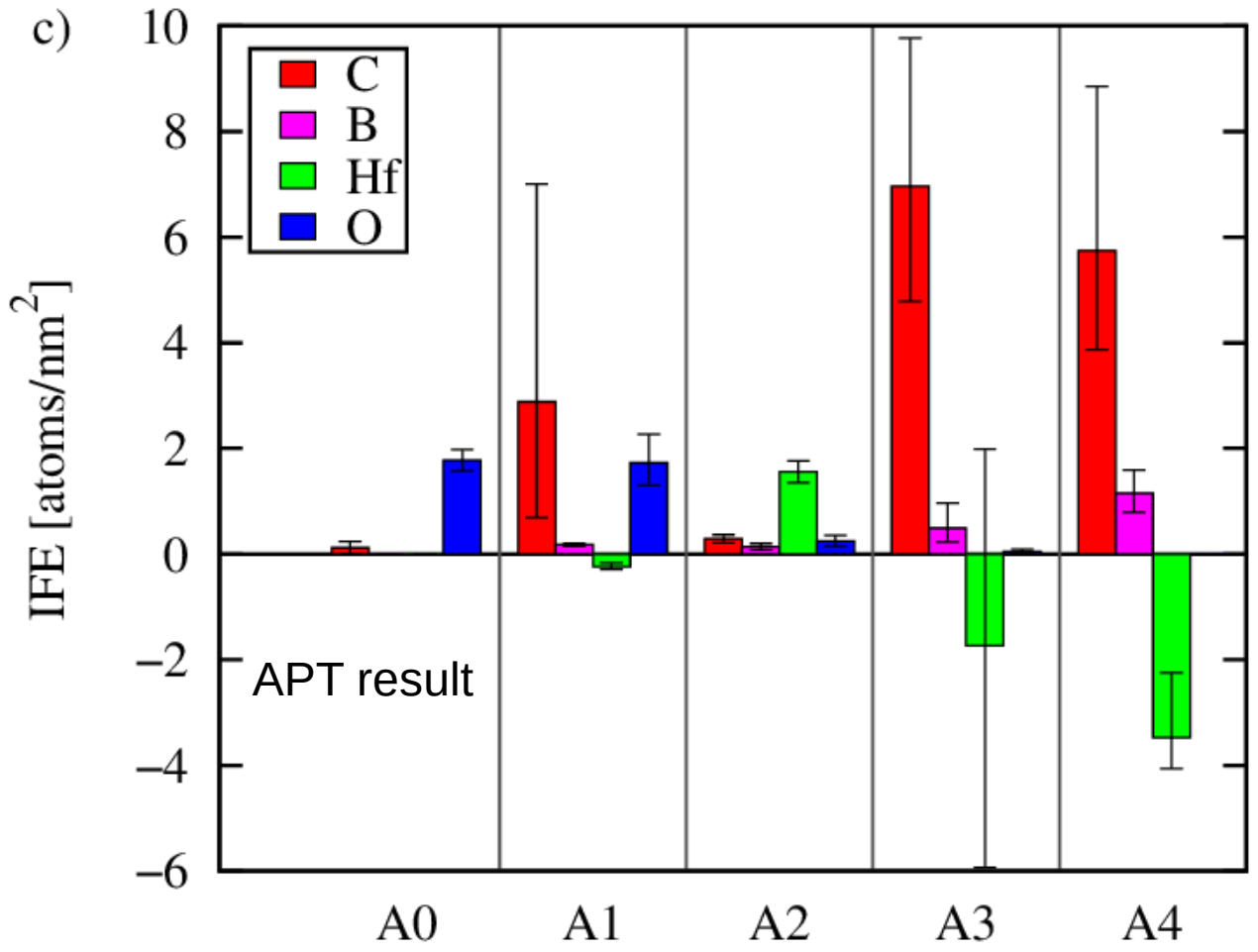


Segregation profile in region of interest



Interfacial excess (IFE) values
→ # of atoms that are more/less at interface per area

Validation of GB excess: Mo-Hf-C



Leitner et al, Materials & Design 2018, 142, 36.

Validation GB excess: Kinetic modeling

- Several models exist for treating GB segregation kinetics
  - Models based on second Fick‘s Law
  - Layer-by-Layer Models

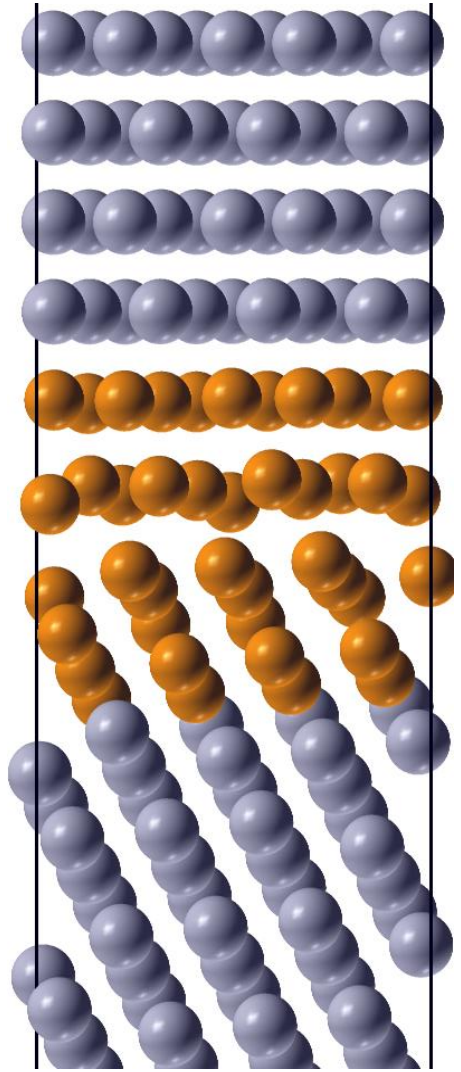
    Book, P. Lejcek, Grain Boundary Segregation in Metals

  - Model based on Thermodynamic Extremal Principle (TEP)

    Svoboda et al. Philos. Mag. Letters 95 (2015) 458-465.

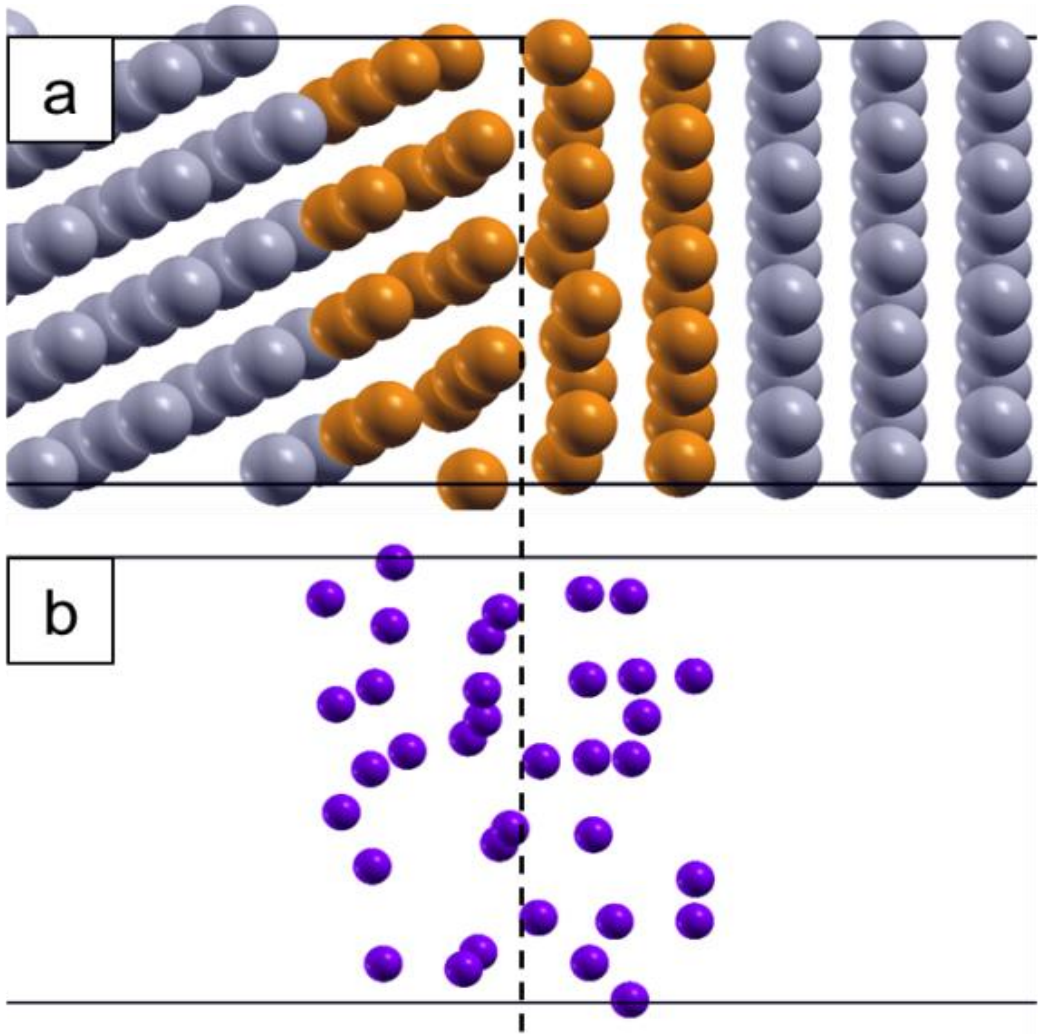
- GB is treated with one GB site

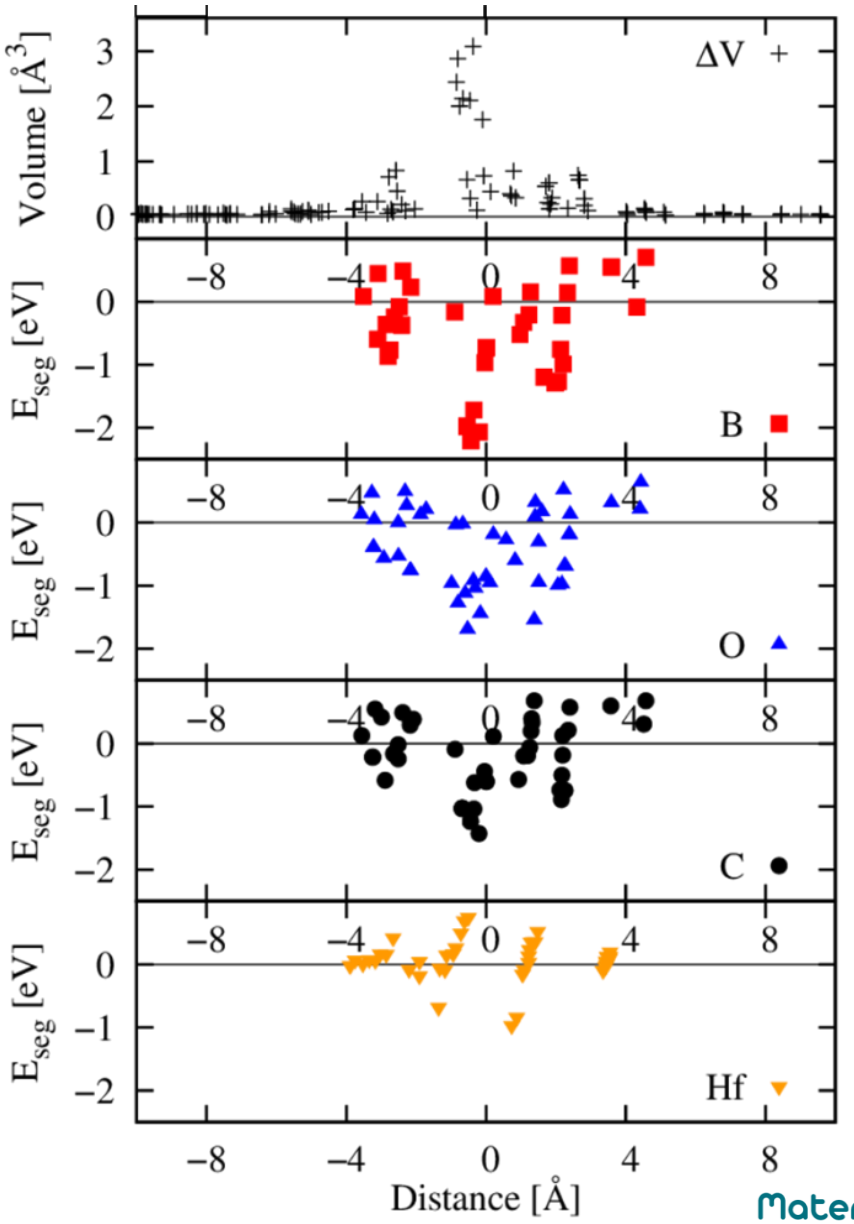
- **Develop a model for multiple GB sites and multiple solutes which directly couples to DFT simulations**



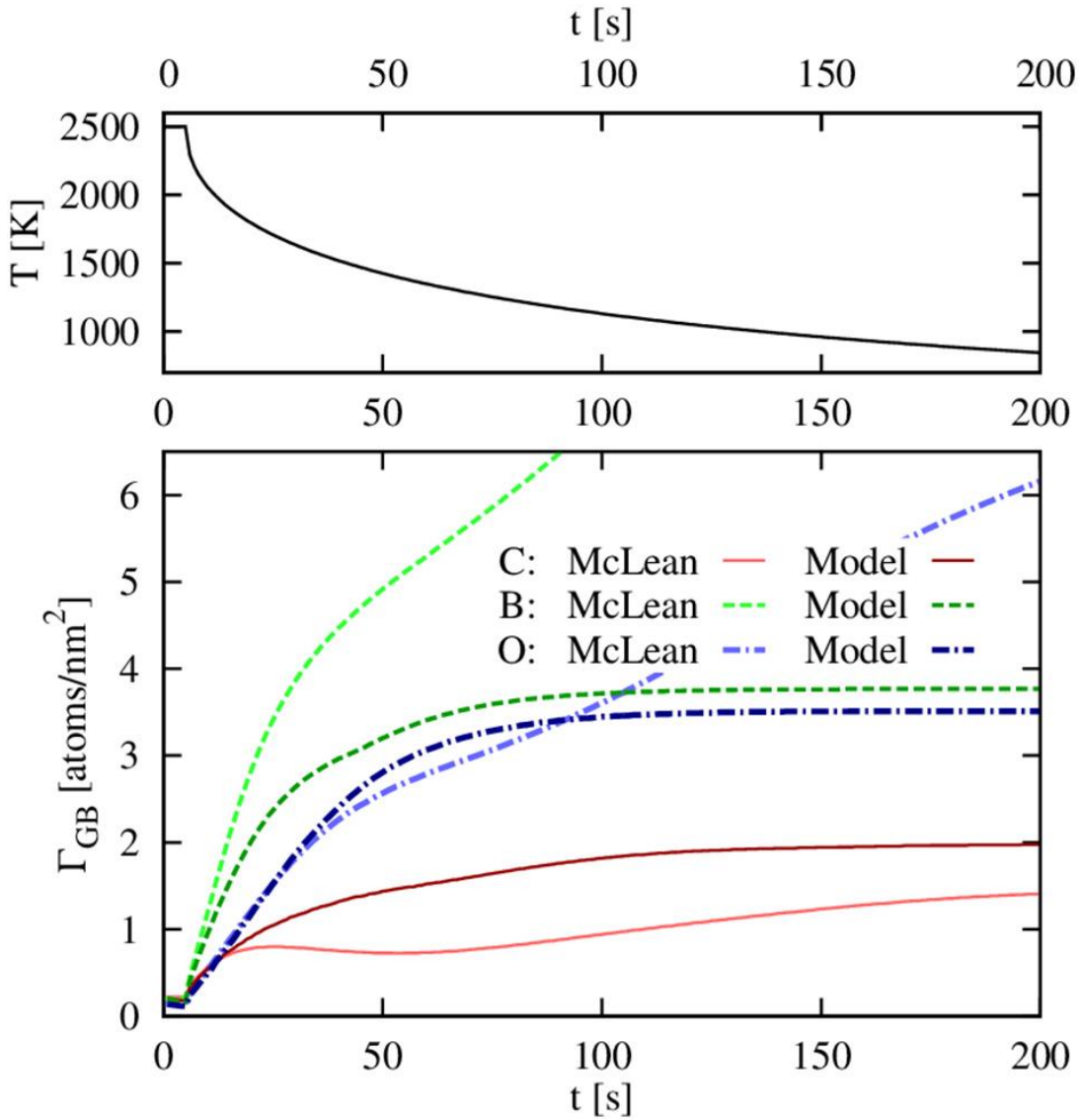
Σ11 CSL GB

Validation GB excess: Kinetic modeling





Validation GB excess: Kinetic modeling



Kinetic equation for GB excess

$$\frac{R_G^2}{15\bar{c}_k D_k}\sum_{j=1}^{n} f^j \dot{\hat{c}}_k^j + \tilde{U}_k^i f^i \dot{\hat{c}}_k^i = \ln\left[\frac{\hat{c}_k^i\left(1-\sum_{l=1}^{N}\bar{c}_l\right)}{\bar{c}_k\left(1-\sum_{l=1}^{N}\hat{c}_l^i\right)}\right] + \frac{\Delta E_k^i}{kT}$$

Scheiber, Romaner, Fischer, Svoboda, Scripta Mater. 150 (2018) 110.

Extension to solute depletion in the grain

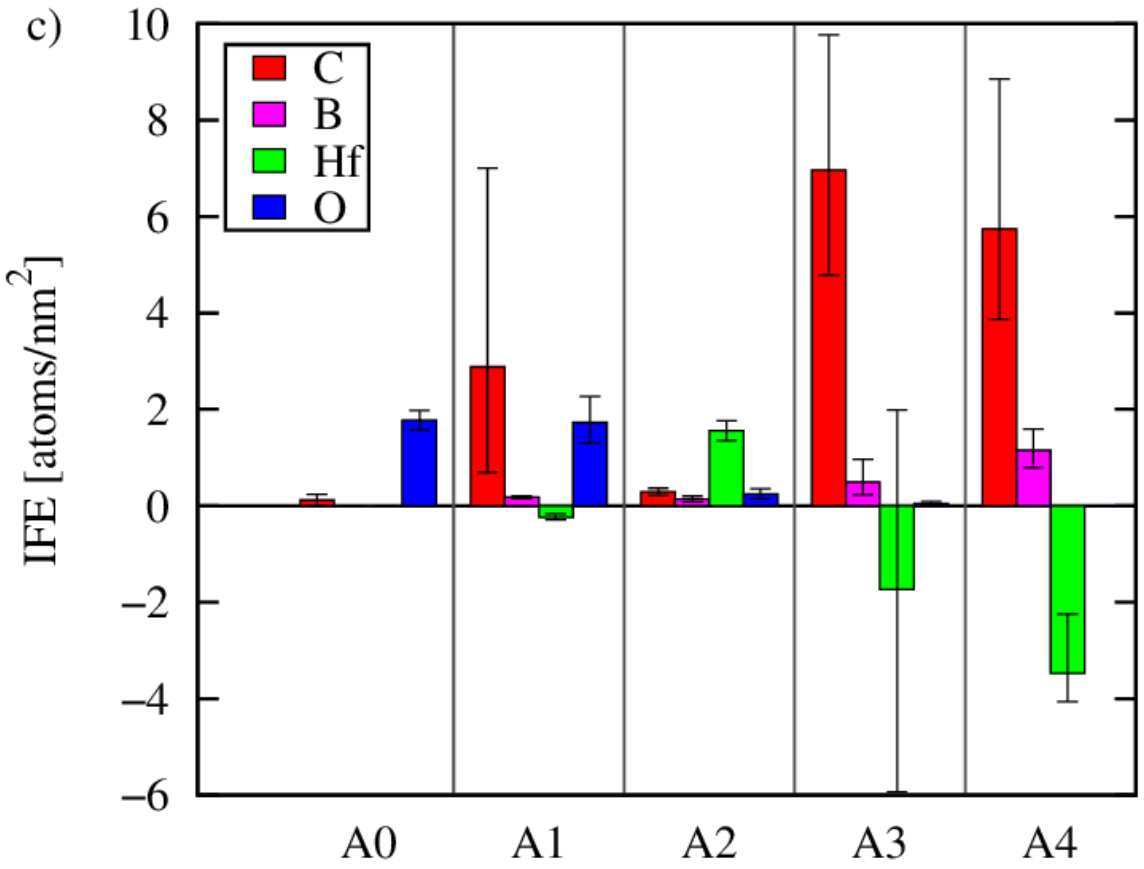
Scheiber, Jechtl, Svoboda, Fischer, Romaner, Acta Materialia, 182, (2020), 100.

Extension to precipitation and segregation

Under review

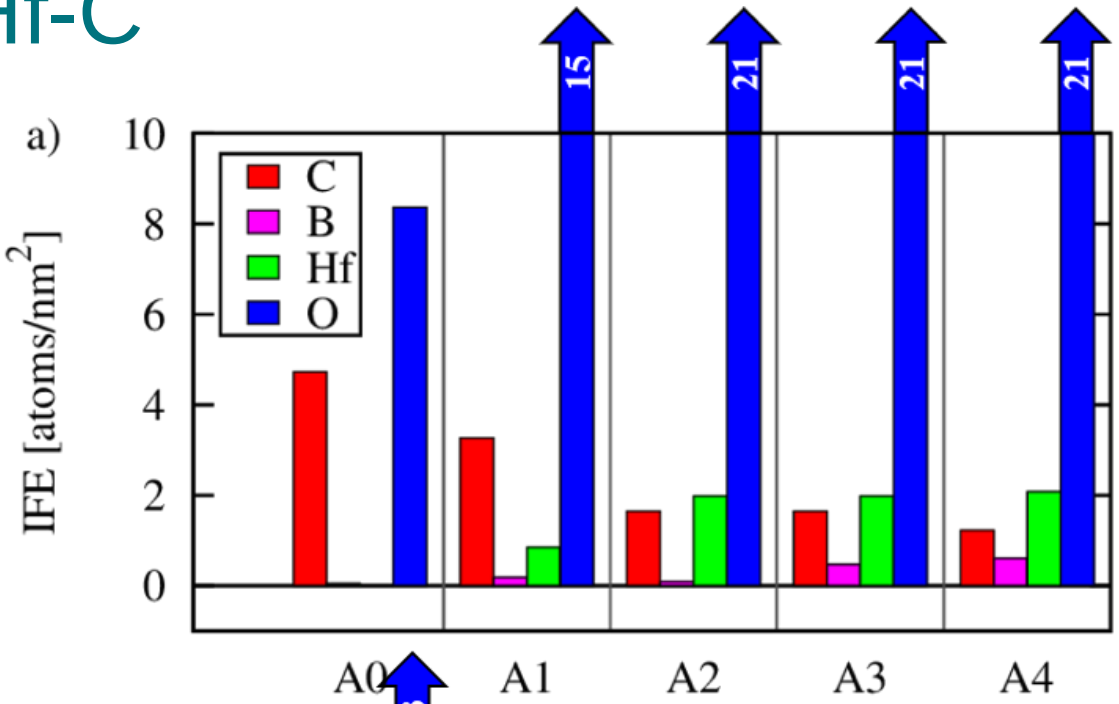
Validation of GB excess: Mo-Hf-C

APT result

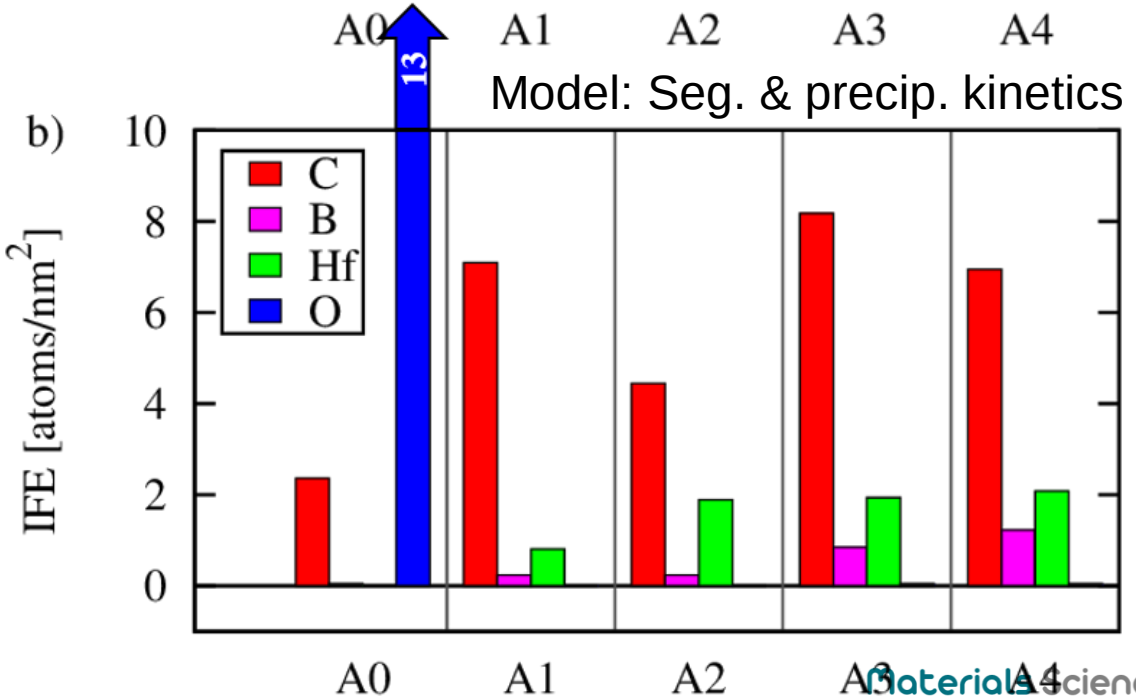


Leitner et al, Materials & Design 2018, 142, 36.

Model: Seg. kinetics

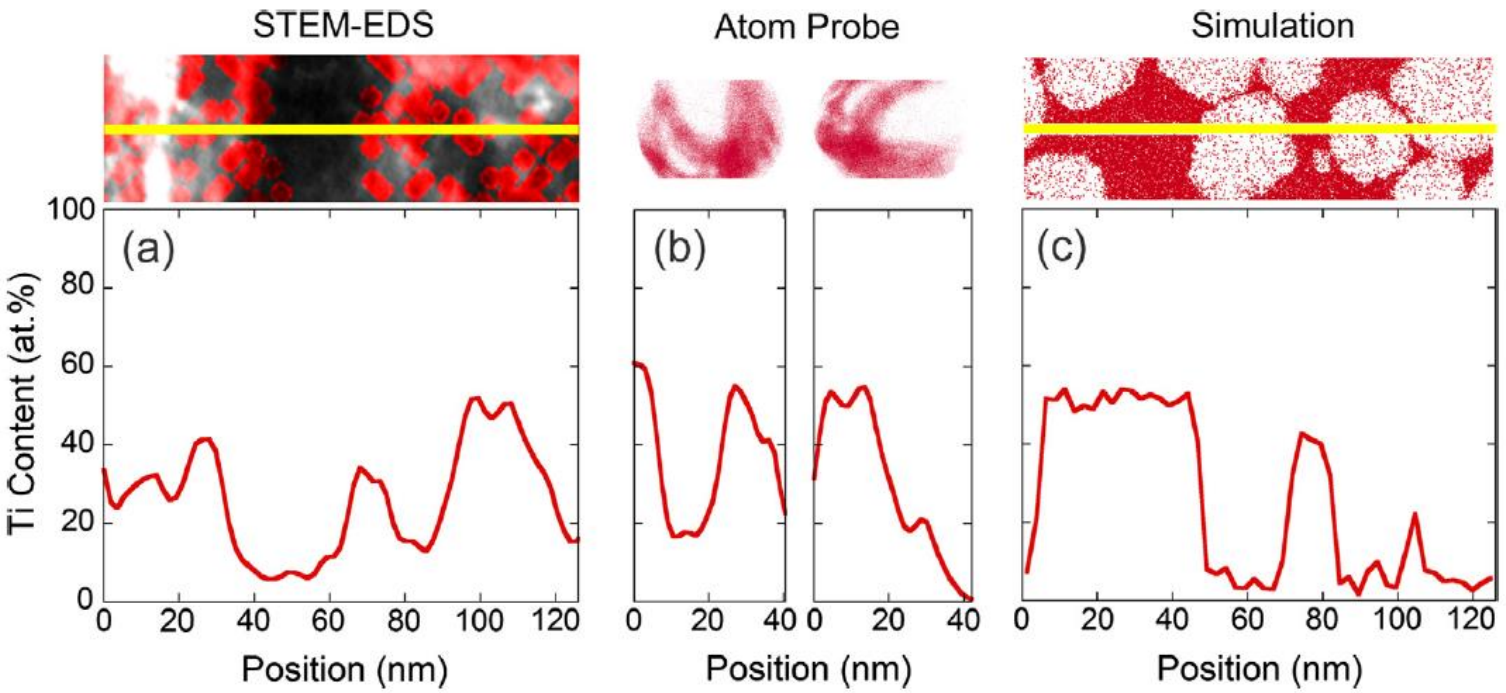


Model: Seg. & precip. kinetics



Nanoscale segregation in WTi

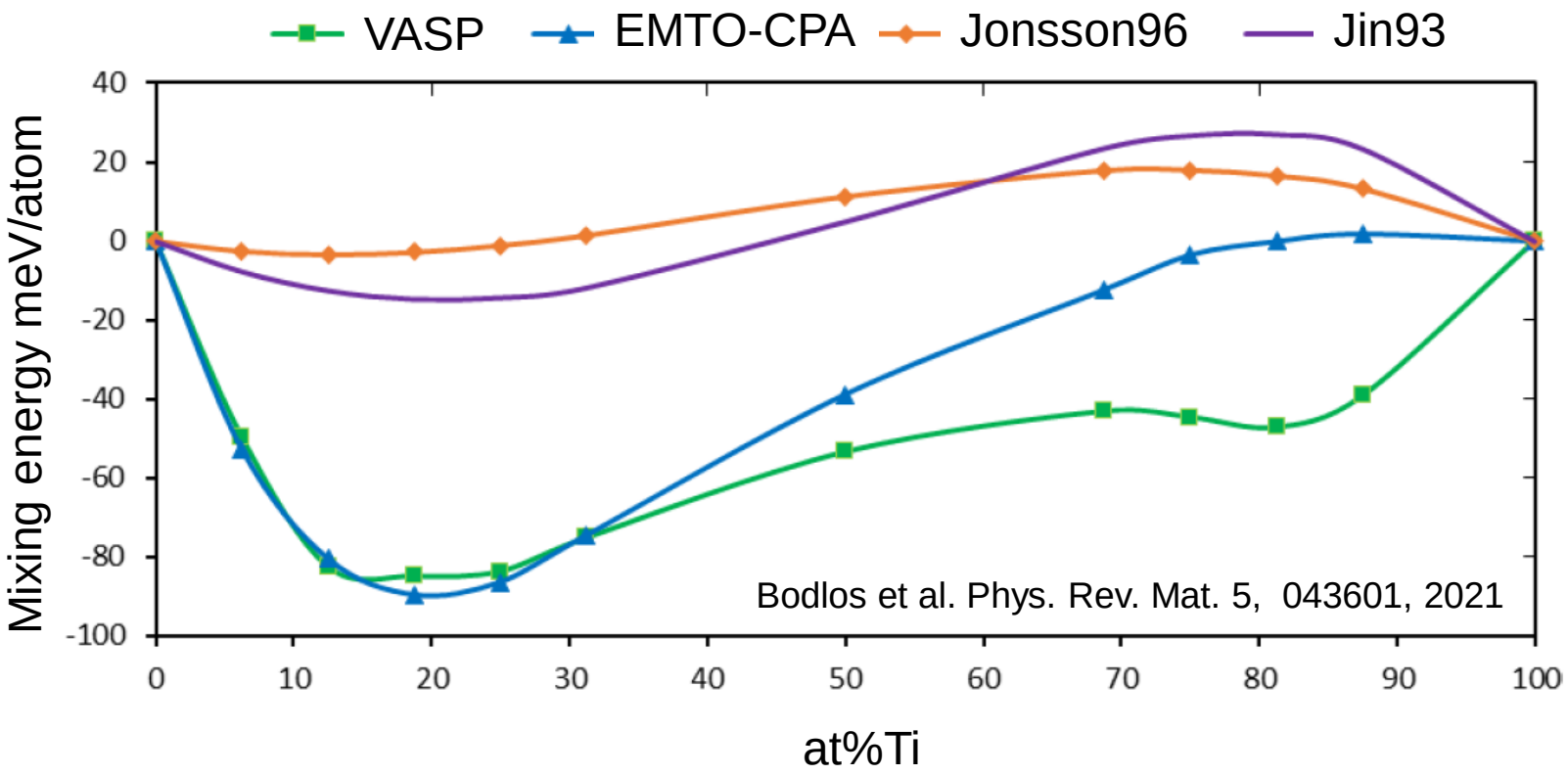
- Decomposition of W20at%Ti into two bcc phases proposed.



Chookajorn&Schuh, Acta Materialia 73 (2014) 128–138

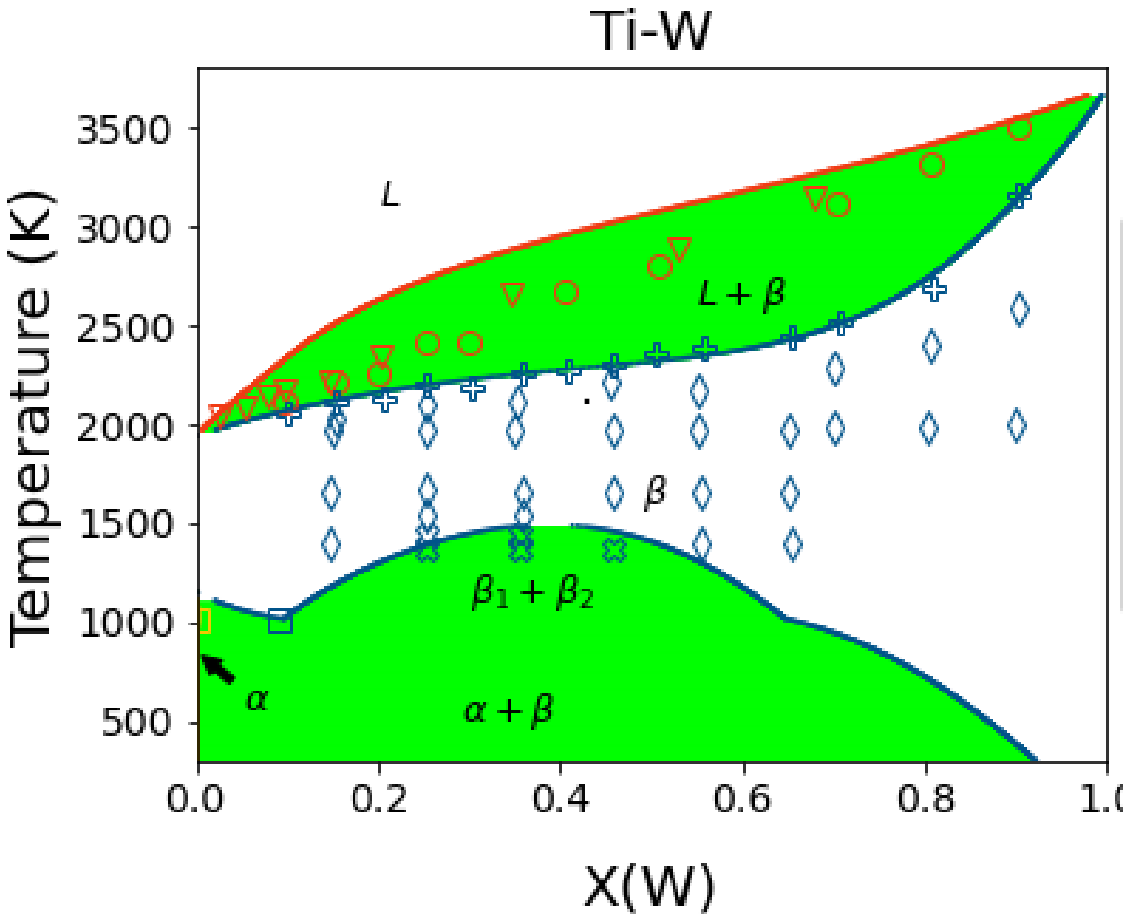
- However, underlying thermodynamics of MC simulation questionable.
- Segregation energy of -0.5 eV in the dilute limit from Miedema model.
- Positive mixing energy of 0.2 eV assumed to capture miscipility gap

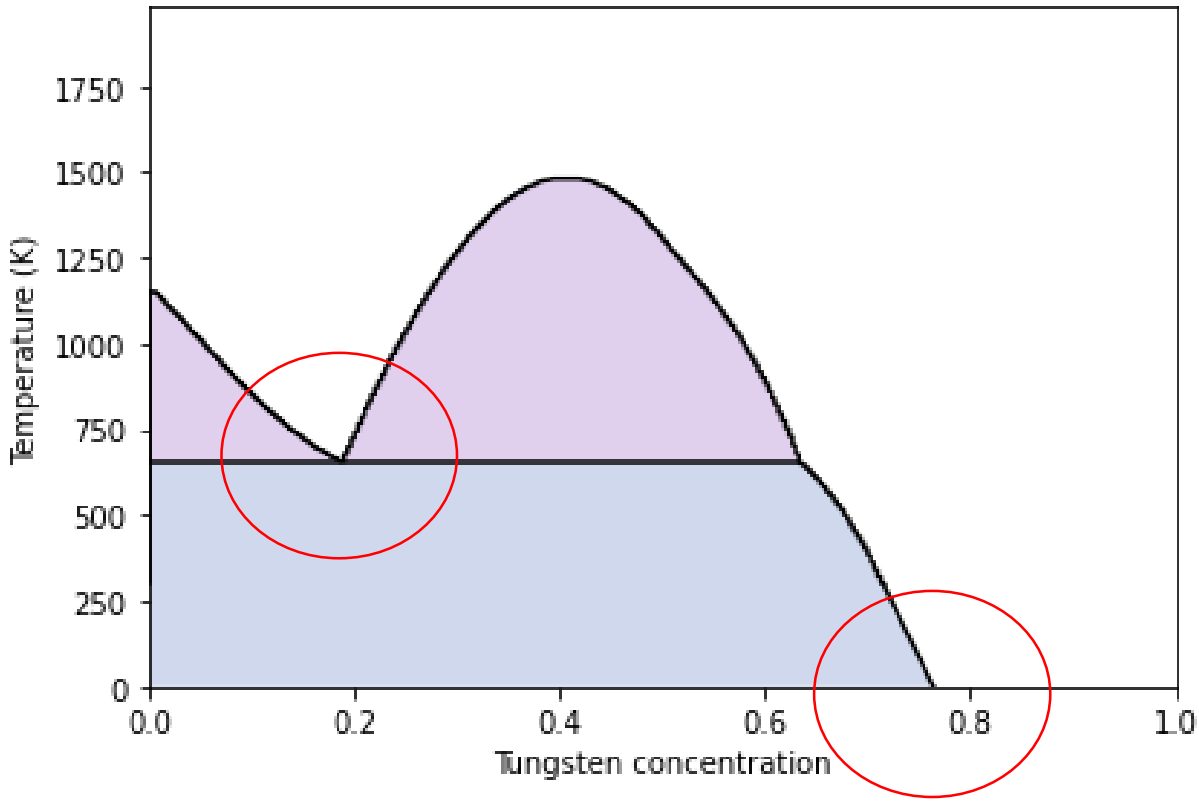
WTi: Mixing energies



- EMTO-CPA and VASP supercell calculations both predict negative mixing energies.
- Calphad assessments rely on mixing energies which are mostly positive.

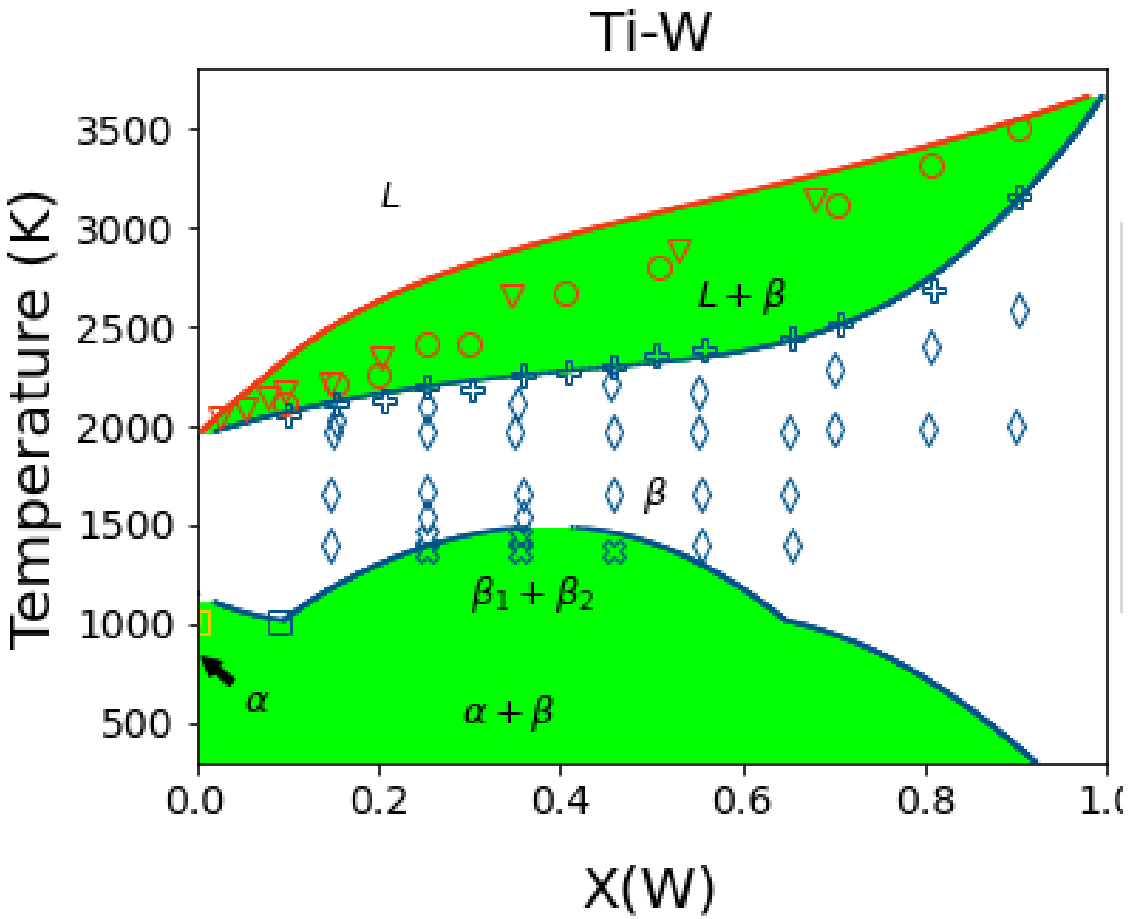
WTi CALPHAD assessment

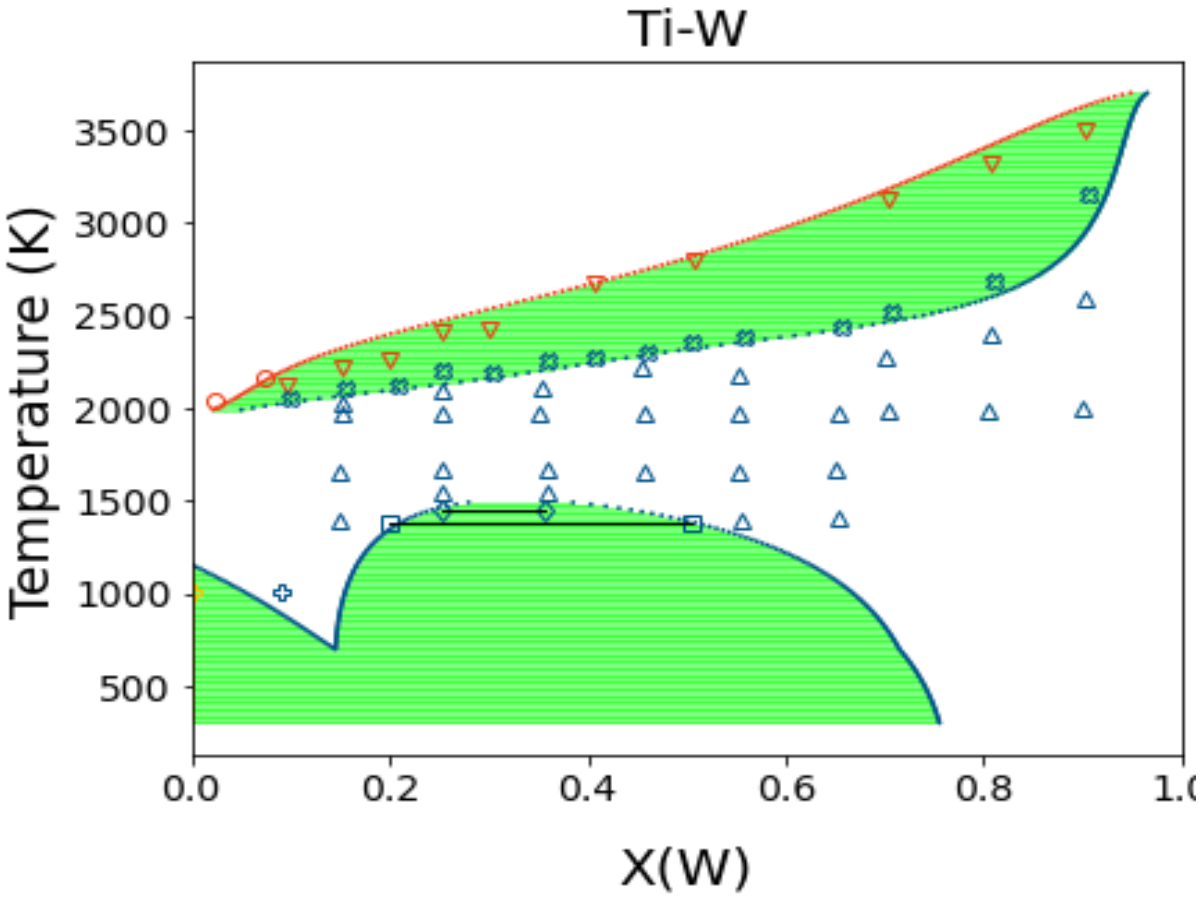




- Assessment by Jonsson, Z. Metallkd. 87, 784 (1996).
- Ab-initio prediction by Ångqvist, Phys. Rev. Mater. 3, 073605 (2019).

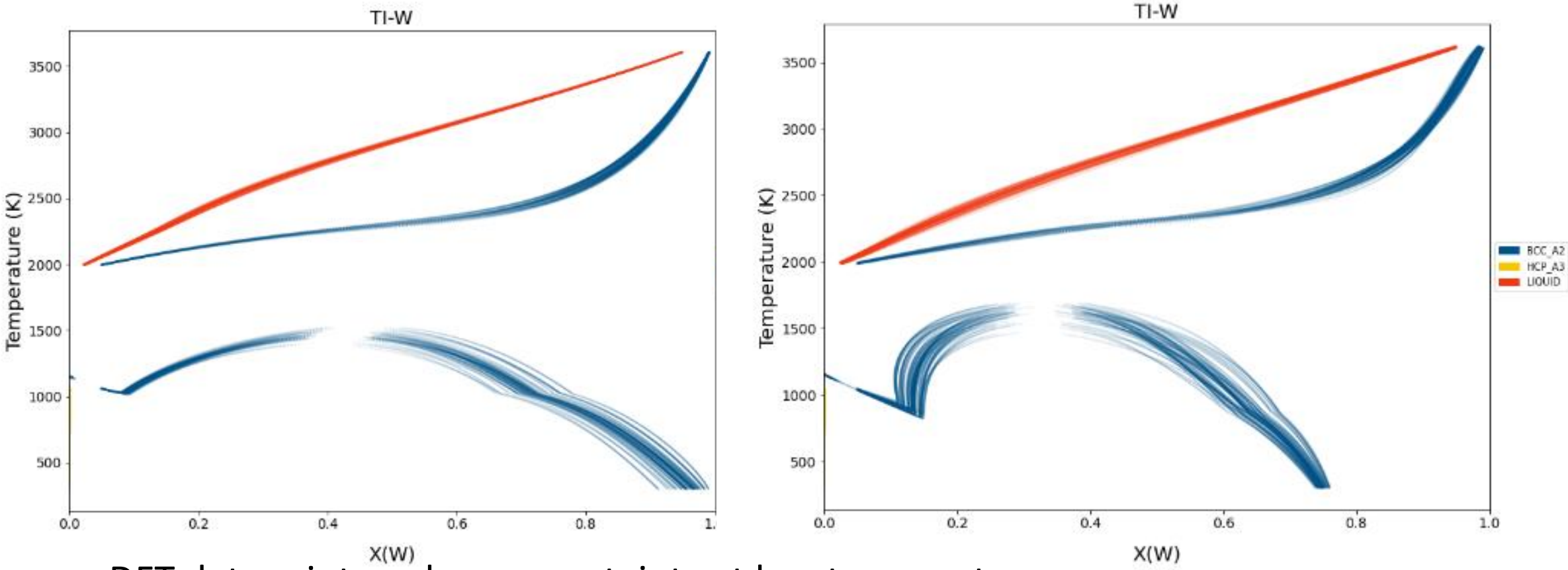
WTi CALPHAD assessment





- Assessment by Jonsson, Z. Metallkd. 87, 784 (1996).
- New ESPEI assessment including experimental data and 0K DFT mixing energies

WTi: Uncertainty quantification



- DFT datapoints reduce uncertainty at low temperatures.
- At eutectic point data points are in conflict.

Conclusion

- DFT segregation energies combined with thermokinetic models allow close validation with experiment
  - For W-Re already a Mc-Lean type approach gives good agreement.
  - Techological alloys, e.g. Mo-HF, require more complex treatments
- A complete description requires also a good understanding of bulk thermodynamics
  - W-Ti system

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