DFT-based modeling of interface segregation in metals

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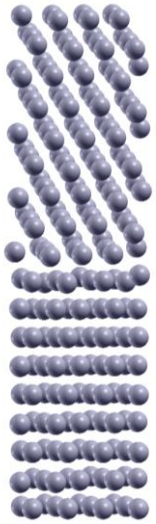
Motivation

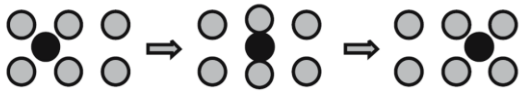
Thermo-dynamics

$$\frac{c_k}{1-c_k} = \frac{c_0}{1-c_0} exp \frac{-E_{seg}^{gb}}{k_B T}$$

Structure



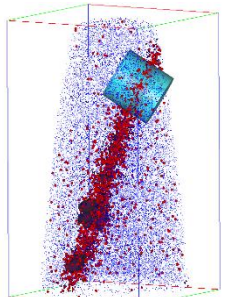
Kinetics



Goal:GB chemistry simulation

Validation with experiment

Goal: GB property simulation



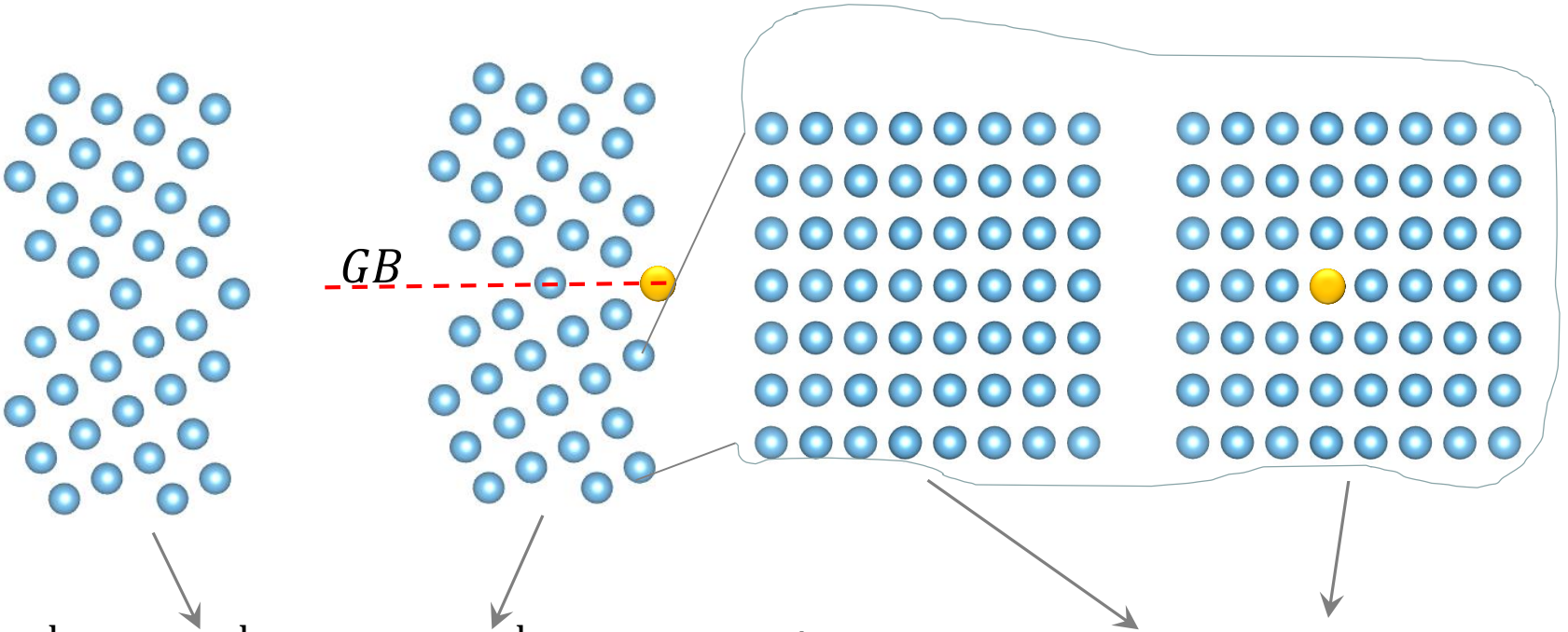
Introduction: impurity segregation from DFT

Impurity segregation to grain boundaries:

- Even tiny amounts of impurities segregating to interfaces can affect properties of Cu

Characteristic fundamental quantity:

- Segregation energy E^{seg} : from density functional theory (DFT)

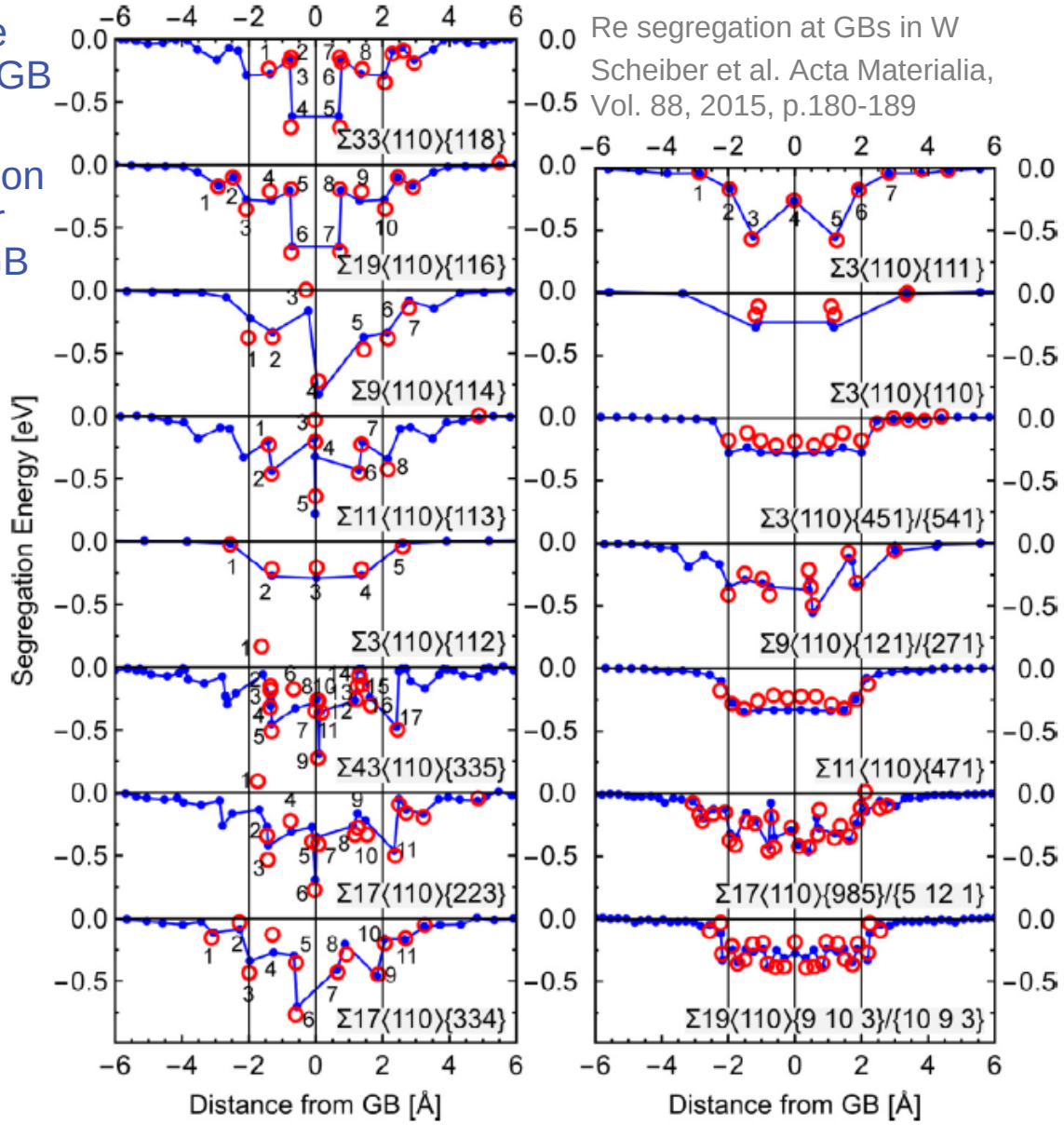


$$E_{\text{seg}}^{\text{gb}} = -E_{\text{slab}}^{\text{gb}}[\text{N},0] + E_{\text{slab}}^{\text{gb}}[\text{N},1] + \Delta_{\text{bulk}}^{\text{Ni}\rightarrow\text{X}} \qquad \Delta_{\text{bulk}}^{\text{Ni}\rightarrow\text{X}} = E_{\text{bulk}}^{\text{Ni}} - E_{\text{bulk}}^{\text{Ni+X}}$$

Introduction: impurity segregation from DFT at 0K

Segregation profiles:

- More than 1 GB site can be occupied (valid regardless GB type)
- Most efficient GB segregation sites are located at a rather narrow distance from the GB plane (GB width $\delta \approx 5\text{Å}$)



Re segregation at GBs in W
Scheiber et al. Acta Materialia, Vol. 88, 2015, p.180-189

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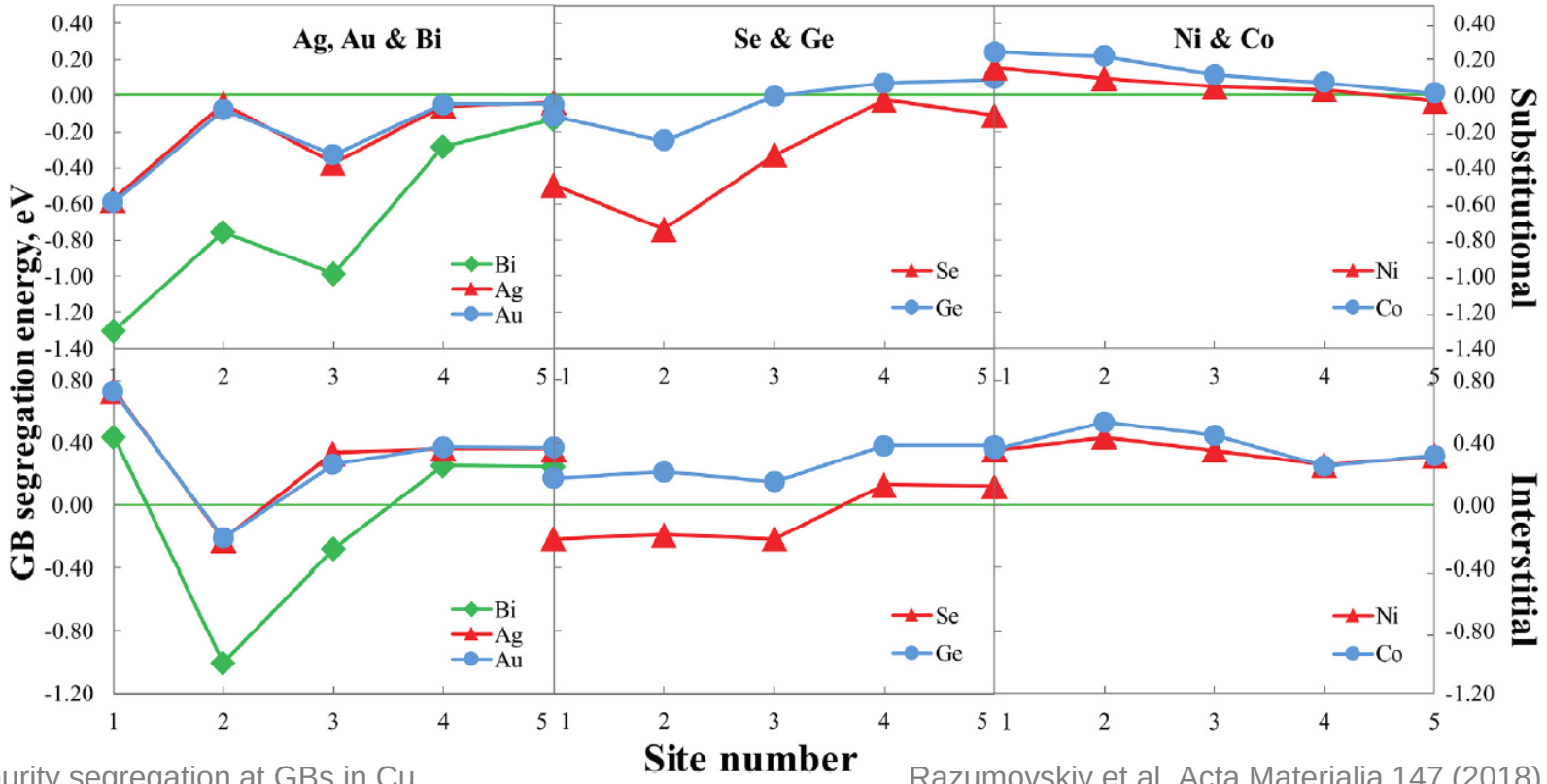

Razumovskiy et al. Acta Materialia 147 (2018) 122

Introduction: impurity segregation from DFT at 0K

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- This result is valid for all types of impurities (interstitial & substitutional)
- This result is valid for all studied (by us) materials

D. Scheiber et al. MSMSE 24 (2016) 085009

Effect on GB cohesion of s- and p-elements in Mo

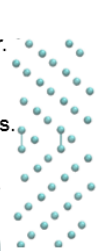
H						
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

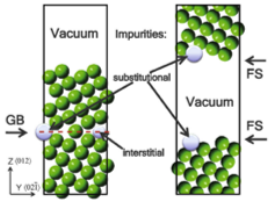
Effect on GB cohesion of transition metals in W

3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5d	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

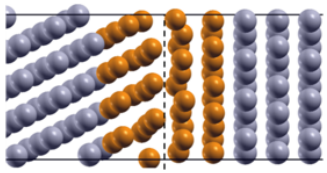
D. Scheiber et al. Int. J. Ref. Met. Hard Mat. 60 (2016) 75

Butrim et al. Adv. Mater. Res. 1119 (2015) 569
Razumovskiy Adv. in Cond. Mat. Phys. (2018) (in press)

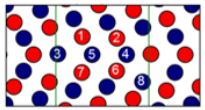




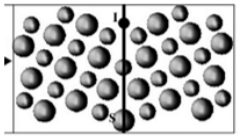
V. Razumovskiy Acta Mater. **82** (2015) 369



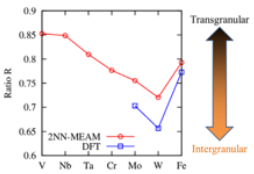
K. Leitner, D. Scheiber et al. Materials&Design 142 (2018) 36



D. Scheiber et al. Acta Mater. **88** (2015) 180



V. Razumovskiy Scripta Mater. **65** (2011) 926

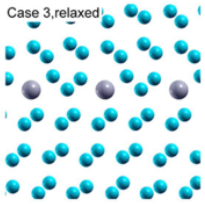


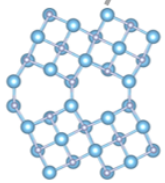
D. Scheiber et al. Modelling Simul. Mater. Sci. Eng. **24** (2016) 035013

GB @ MCL

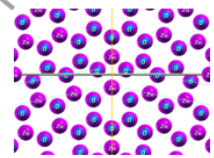
W
Cr
Ti
Ni
Al
Cu
ZnO
TiN
Si
Fe
Mo

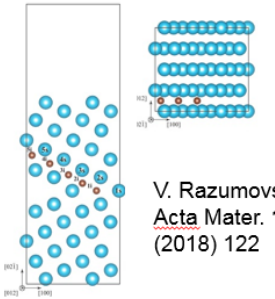
J. Li et al. Scientific Reports **5** (2015) 13802





M. Popov et al., Acta Mater. **144** (2018) 496





V. Razumovskiy Acta Mater. **147** (2018) 122

How to process DFT segregation profiles:

- segregation isotherms (GB concentration & effective segregation energies)

DFT+ McLean vs. Experiment: methodology

Segregation at T>0

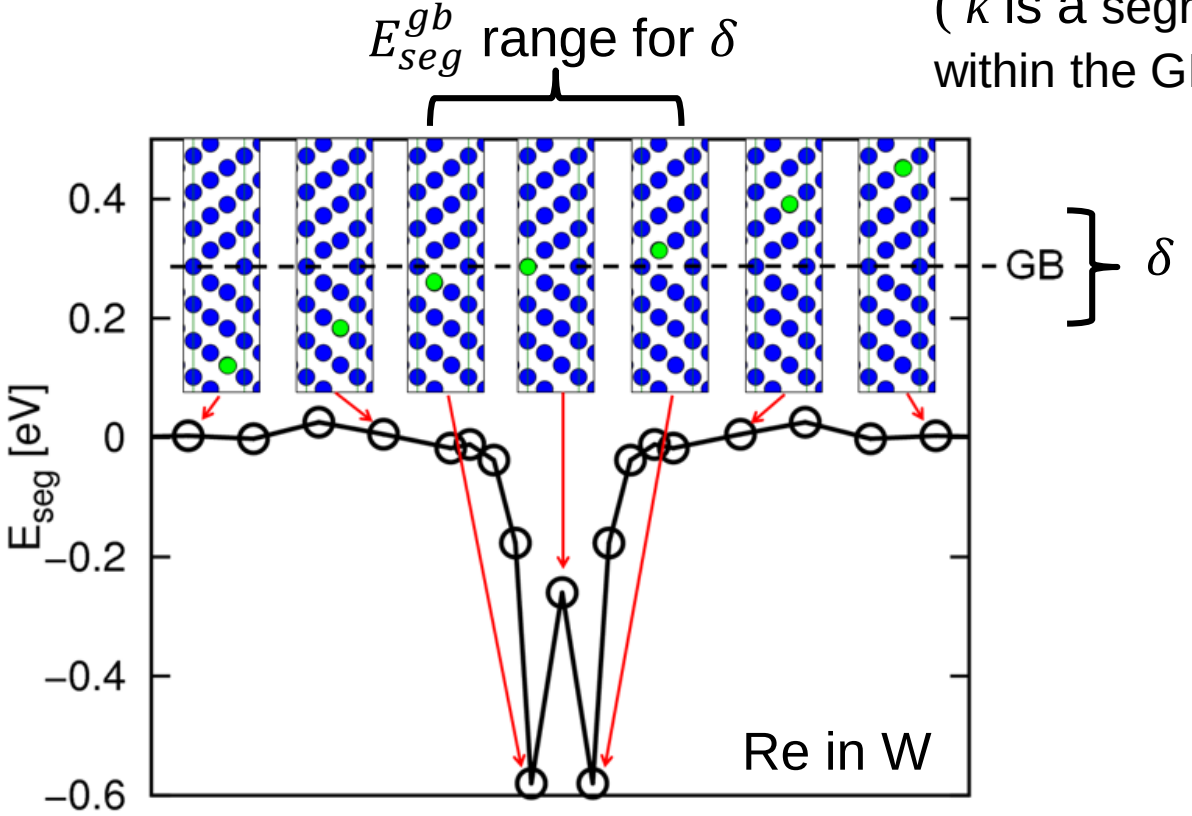
Langmuir-McLean segregation isotherm (Oriani's equation):

$$\frac{c_{gb}}{1-c_{gb}} = \frac{c_{bulk}}{1-c_{bulk}} exp \frac{-E_{seg}^{gb}}{k_B T}$$

Average concentration within a GB width δ:

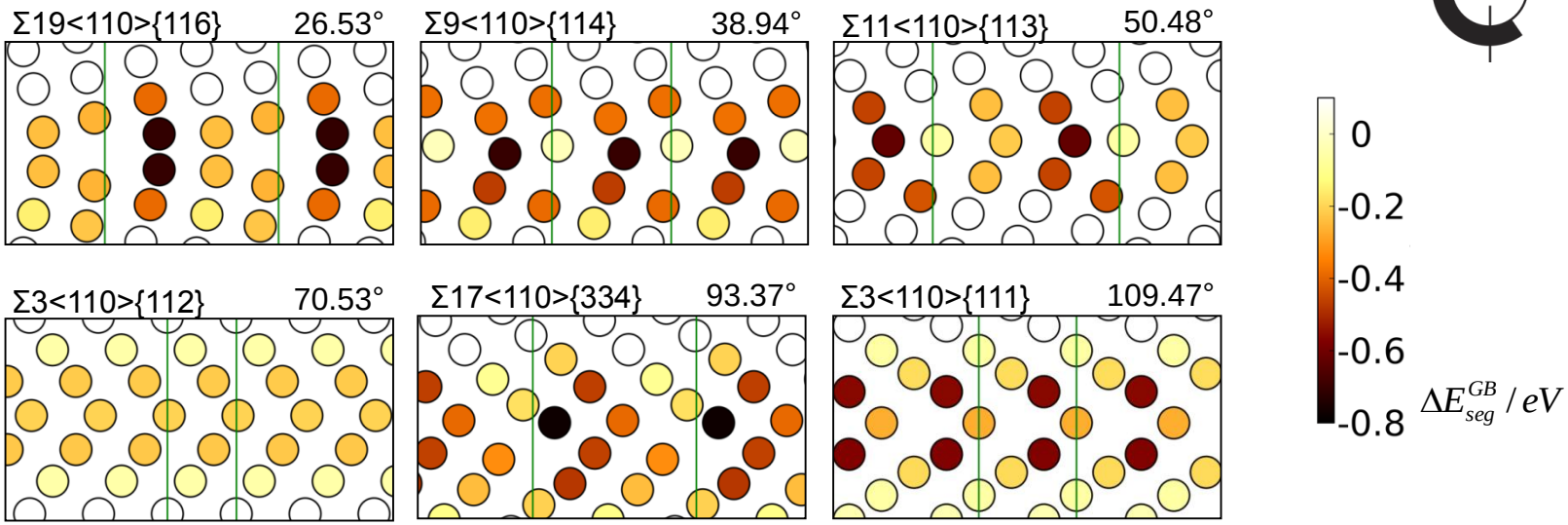
$$c_{gb} = \langle c_k \rangle = \frac{1}{N(k)} \sum_{k \in \delta} c_{gb}^{k}$$

(k is a segregation site within the GB width δ)



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

DFT+ McLean vs. Experiment: direct comparison

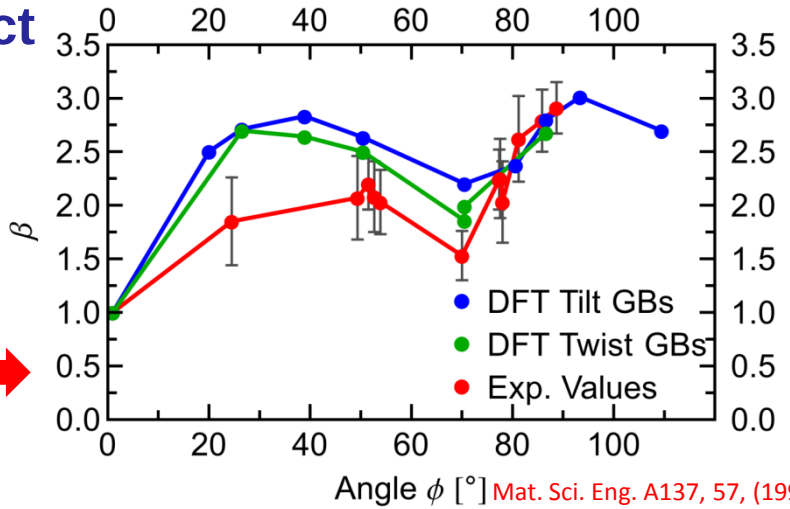


Re segregation at GBs in W)

DFT+ McLean vs. Experiment (direct comparison)

- Enhancement factor β of Re as a function of misorientation angle φ at 1913 K in a WRe_{25} alloy.

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



Mat. Sci. Eng. A137, 57, (1991)

- Good agreement with experiment!
- Prediction possible with simple McLean!

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

DFT+ McLean vs. Experiment: indirect comparison

Segregation at T>0

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Average concentration within a GB width δ:

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Effective (thermally activated) impurity segregation energy in Cu for multiple interfacial sites k at any temperature T:

$$\tilde{E}_{seg}^{gb} = k_B T \left[ln\left(\frac{c_{bulk}}{1-c_{bulk}}\right) - ln\left(\frac{\langle c_{gb}^{k} \rangle}{1-\langle c_{gb}^{k} \rangle}\right) \right]$$

Ag & Bi segregation to ∑5 GB in Cu:

Energy, kJ/mol	Ag	Bi
E_{seg}^{gb}(min) @ 0K [1]	-55	-126
$\tilde{E}_{seg}^{gb}$ @ 800K [1]	-40	-84
Experiment [2-3]	-28 (+/15)	-89 (+/4)

[1] Razumovskiy et al. Acta Materialia 147 (2018) 122;
[2] Alber et al. Acta Mat. 47 (1999) 4047;
[3] Divinski et al Prys. Rev B 85 (2012) 144104.

How to process DFT segregation profiles:

- segregation isotherms (GB concentration & effective segregation energies)
- impurity depletion in the bulk (GB size effect)

Introducing grain size effects

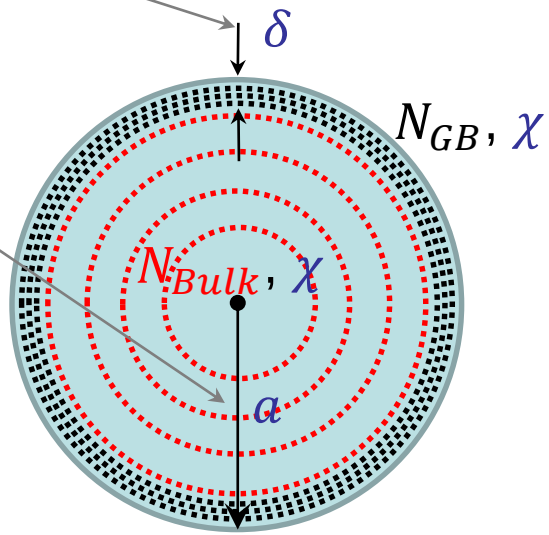
Ratio of GB/bulk sites:

Site density

Half of the GB width (it is assumed that 2 grains share a GB)

$$f = \frac{N_{GB}}{N_{Bulk}} = \frac{\delta A_{GB} \chi}{V_{Bulk} \chi} = \frac{6\delta a^2}{2a^3} = \frac{3\delta}{a}$$

Grain size



additional condition to McLean

$$\frac{c_k}{1 - c_k} = \frac{c_{bulk}}{1 - c_{bulk}} exp \frac{-E_{seg}^{gb}(k)}{k_B T}$$

occupancy of bulk sites

ocuupancy of GB sites

$$c_{bulk}^0 = (1 - f) c_{bulk} + f \sum_k \frac{c_k}{N_k}$$

Number of GB segregation sites (from DFT)

Nominal composition (bulk)

Scheiber et al. Scripta Materialia, Vol. 150, 2018, p.110-114

Methodology: GB impurity concentration at T>0

Segregation at T>0

McLean segregation isotherm (Oriani's equation):

$$\frac{c_{gb}}{1-c_{gb}} = \frac{c_{bulk}}{1-c_{bulk}} exp \frac{-E_{seg}^{gb}}{k_B T}$$

Grain size dependence at T>0

Actual c_{bulk} depends on the ration of the GB to bulk sites $f = \frac{N_{GB}}{N_{Bulk}}$ and on the nominal bulk concentration of the solute c_{bulk}^0:

$$c_{bulk}^0 = (1-f)c_{bulk} + f\sum_k c_{gb}^k$$

Methodology: GB impurity concentration at T>0

Segregation at T>0

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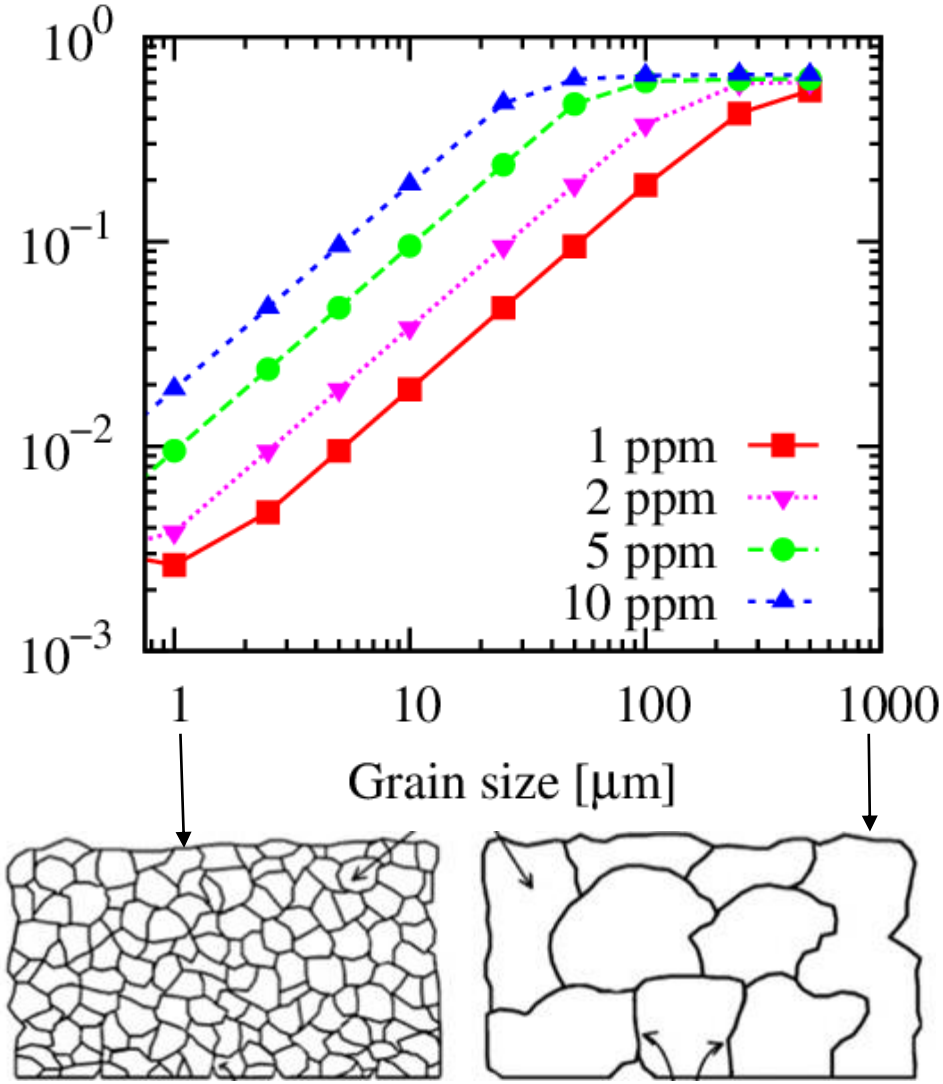
Grain size dependence at T>0

Actual c_{bulk} depends on the ration of the GB to bulk sites $f = \frac{N_{GB}}{N_{Bulk}}$ and on the nominal bulk concentration of the solute c_{bulk}^{0}:

Sulfur in Ni @ 1000K



(Based on ∑5(210) GB segregation profile DFT calculations)

How to process DFT segregation profiles:

- segregation isotherms (GB concentration & effective segregation energies)
- impurity deplition in the bulk (GB size effect)
- site competition at GB

Site competition model

One segregating element:

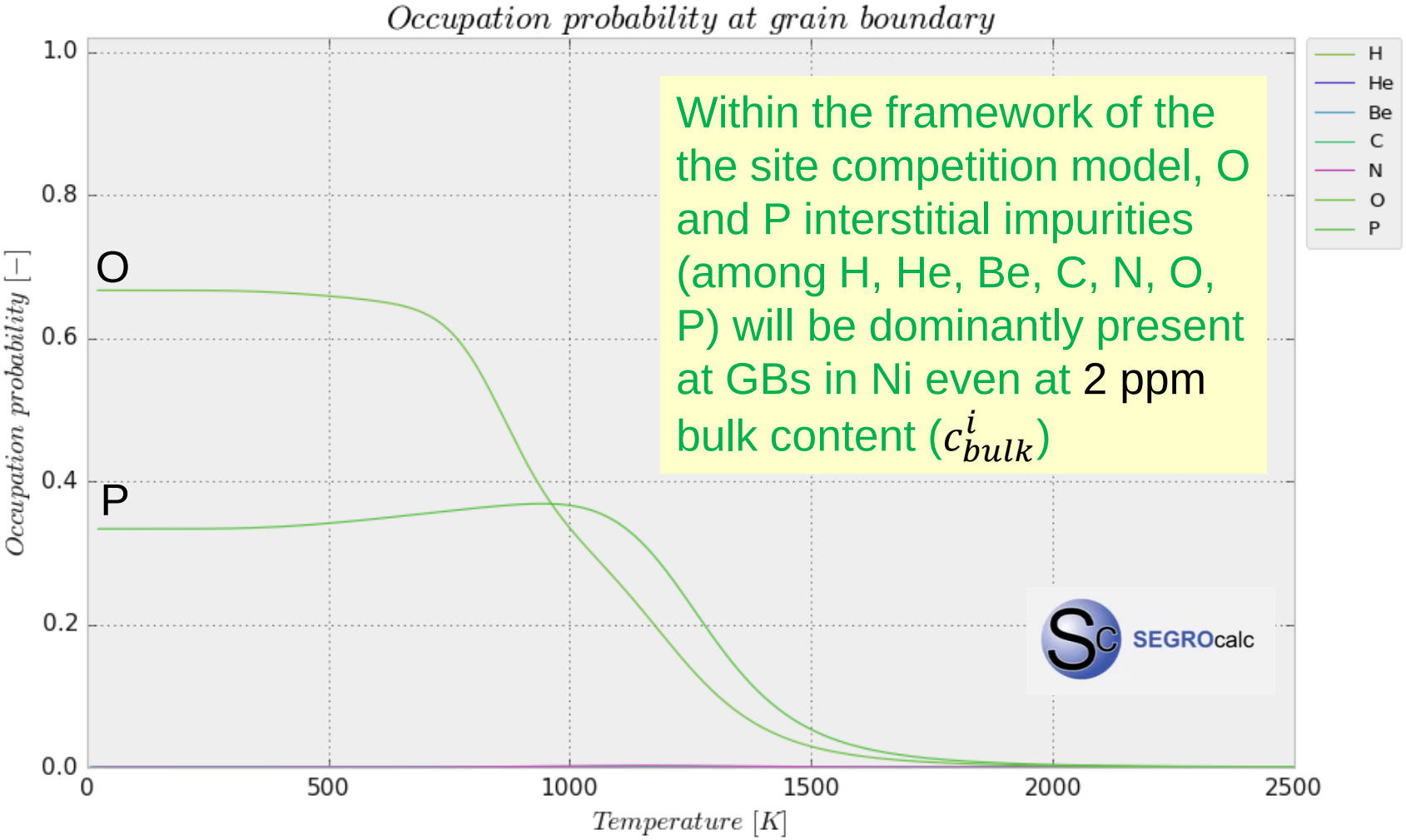
$$\frac{c_k}{1-c_k} = \frac{c_0}{1-c_0} exp \frac{-E_{seg}^{gb}(k)}{k_B T}$$

Multiple segregating elements:

$$\frac{c_k^i}{1-\sum_i c_k^i} = \frac{c_0^i}{1-\sum_i c_0^i} exp \frac{-E_{seg}^{i,gb}(k)}{k_B T}$$

c_k^i of a solute i depends on the GB concentration and bulk concentration of all other solutes

Interstitial element site competition with H



Within the framework of the the site competition model, O and P interstitial impurities (among H, He, Be, C, N, O, P) will be dominantly present at GBs in Ni even at 2 ppm bulk content (c^i_{bulk})

For a multicomponent system c^i_{gb} of solute i depends on the GB concentration and bulk concentration of all other solutes:

$$\frac{c^i_{gb}}{1-\sum_i c^i_{gb}} = \frac{c^i_{bulk}}{1-\sum_i c^i_{bulk}} exp \frac{-E^{gb}_{seg}}{k_B T}$$

How to process DFT segregation profiles:

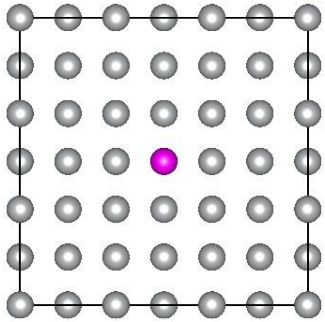
- segregation isotherms (GB concentration & effective segregation energies)
- impurity deplition in the bulk (GB size effect)
- site competition at GB
- combine with cohesive energy calculations for evaluation of the cohesive strength of alloys

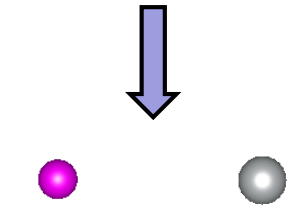
Effect of solutes on cohesive strength

Bulk cohesion

Partial cohesive energy

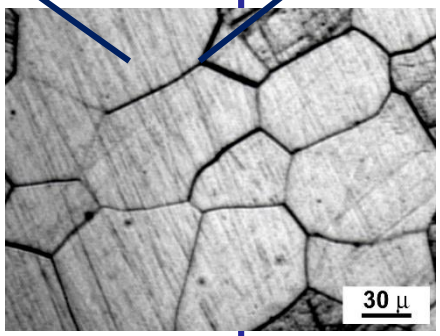
$$\chi_i = \frac{\partial E_{\mathrm{coh}}}{\partial c_i}$$





Free atoms

$\chi > 0$: **strengthening**
$\chi < 0$: **destrengthening**



Crystal

GB cohesion

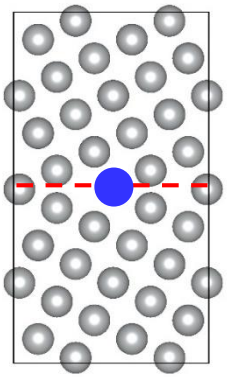
Work of separation change

$$\eta = \frac{W_{sep}^{0} - W_{sep}^{imp}}{\Gamma}$$

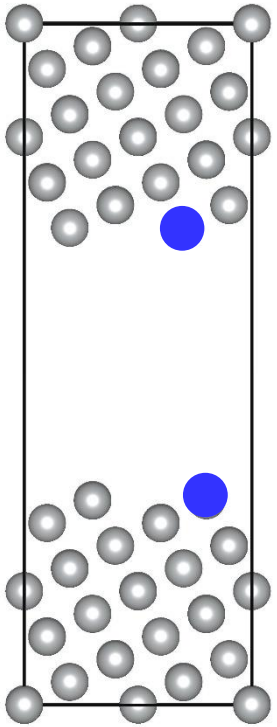
$\eta < 0$: **strengthening**
$\eta > 0$: **embrittlement**

Free Surface (FS)

GB



Split

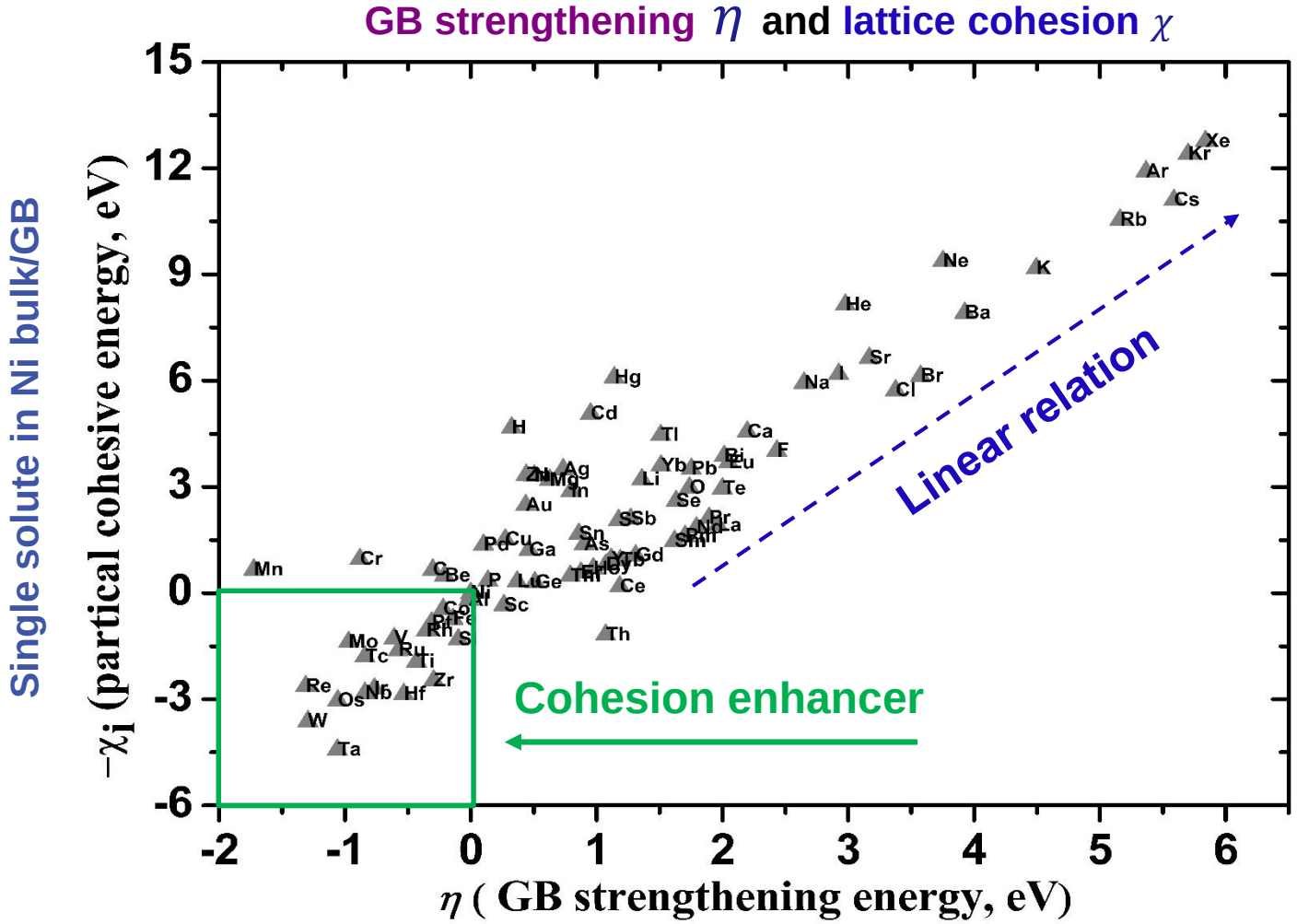


I.M. Razumovskii, et al. Mater.Sci.Eng. A,497(2008)18

J.R. Rice and J.-S. Wang: Mater. Sci. Eng. A 107 (1989), 23

Solute effect on the cohesion of Ni bulk and GB

new (extended) data



Solute effect on the cohesion of Ni bulk and GB

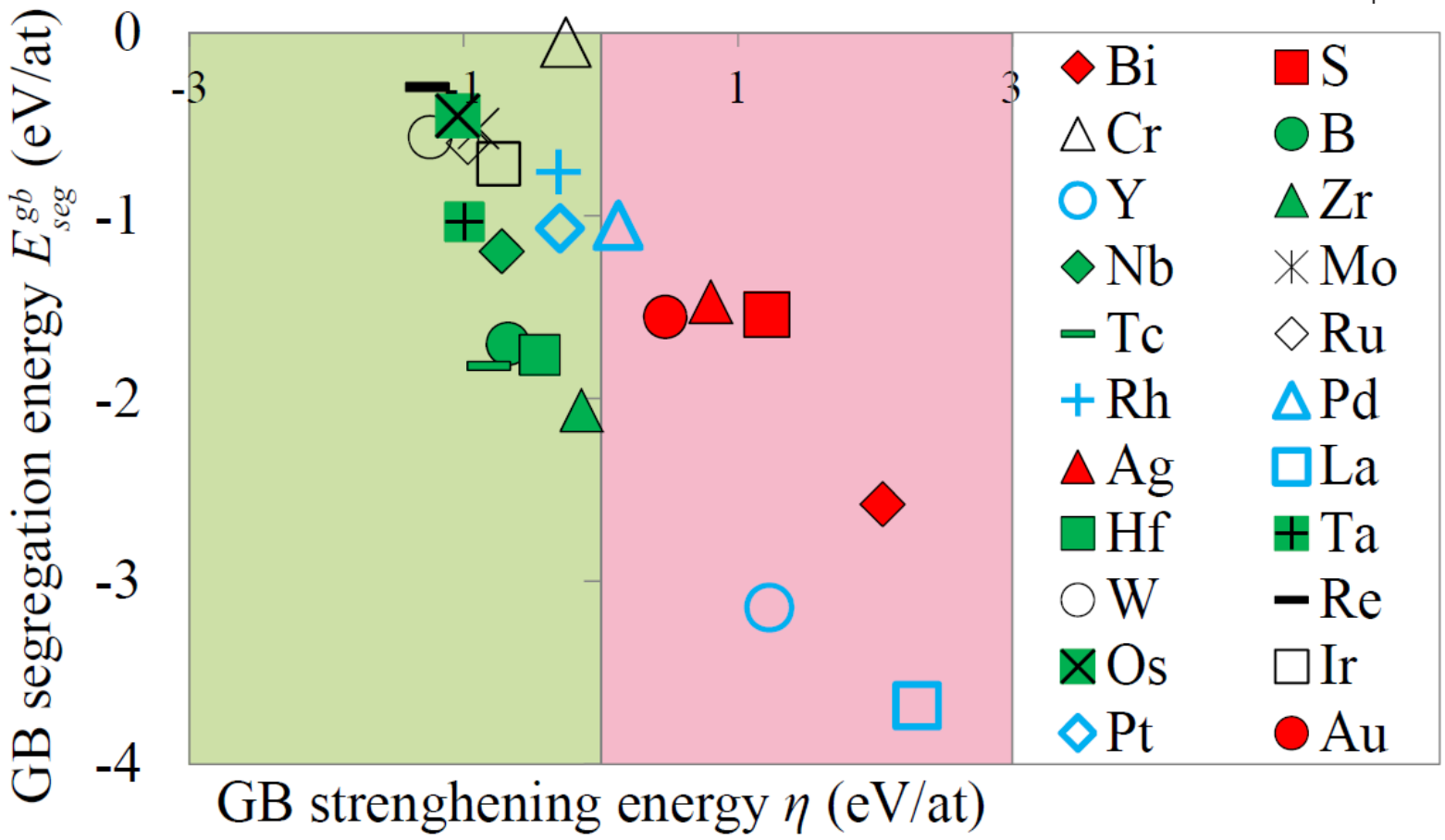


Fig. 3. $E_{seg}^{gb} - \eta$ map (GB segregation energy vs. GB strengthening energy). Elements that strengthen GB are located on the left side of the figure (green area of the plot); elements that embrittle the GB are located on the right side of the figure (red area of the plot). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Razumovskiy et al. Acta Materialia 82 (2015) 369

Summary: towards ICGBE

Segregation at T>0

McLean segregation isotherm for a GB with multiple sites k

$$\frac{c_{gb}}{1-c_{gb}} = \frac{c_{bulk}}{1-c_{bulk}} exp \frac{-E_{seg}^{gb}}{k_B T};$$

$$c_{gb} = \langle c_k \rangle = \frac{1}{N(k)} \sum_{k \in \delta} c_{gb}^{k}; \quad \tilde{E}_{seg}^{gb} = k_B T \left[ln\left(\frac{c_{bulk}}{1-c_{bulk}} \right) - ln\left(\frac{\langle c_{gb}^{k} \rangle}{1-\langle c_{gb}^{k} \rangle} \right) \right]$$

Grain size dependence at T>0

additional condition:

$$c_{bulk} = (1-f) c_{bulk}^{0} + \frac{f}{N_k} \sum_{k} c_k$$

Combine

Site competition at T>0

c_{gb}^{i} of solute i dependence on the GB concentration $c_{gb}^{j,j \neq i}$ and bulk concentration $c_{bulk}^{j,j \neq i}$ of other solutes:

$$\frac{c_{gb}^{i}}{1-\sum_i c_{gb}^{i}} = \frac{c_{bulk}^{i}}{1-\sum_i c_{bulk}^{i}} exp \frac{-E_{seg}^{gb}}{k_B T}$$

GB and bulk cohesion

$$\eta = E_{seg}^{gb} - E_{seg}^{fs}; \chi_i = \frac{\partial E_{\mathrm{coh}}}{\partial c_i}$$

Thank you for your attention

Acknowledgements

The authors gratefully acknowledge the financial support under the scope of the COMET program within the K2 Center "Integrated Computational Material, Process and Product Engineering (IC-MPPE)" (Project No 859480). This program is supported by voestalpine BÖHLER Edelstahl GmbH, Plansee SE, the Austrian Federal Ministries for Transport, Innovation and Technology (BMVIT) and for Digital and Economic Affairs (BMDW), represented by the Austrian research funding association (FFG), and the federal states of Styria, Upper Austria and Tyrol.