MatCalc
Engineering

MatCalc approach for the modelling of the vacancy concentration evolution

(MatCalc 5.60.0005)

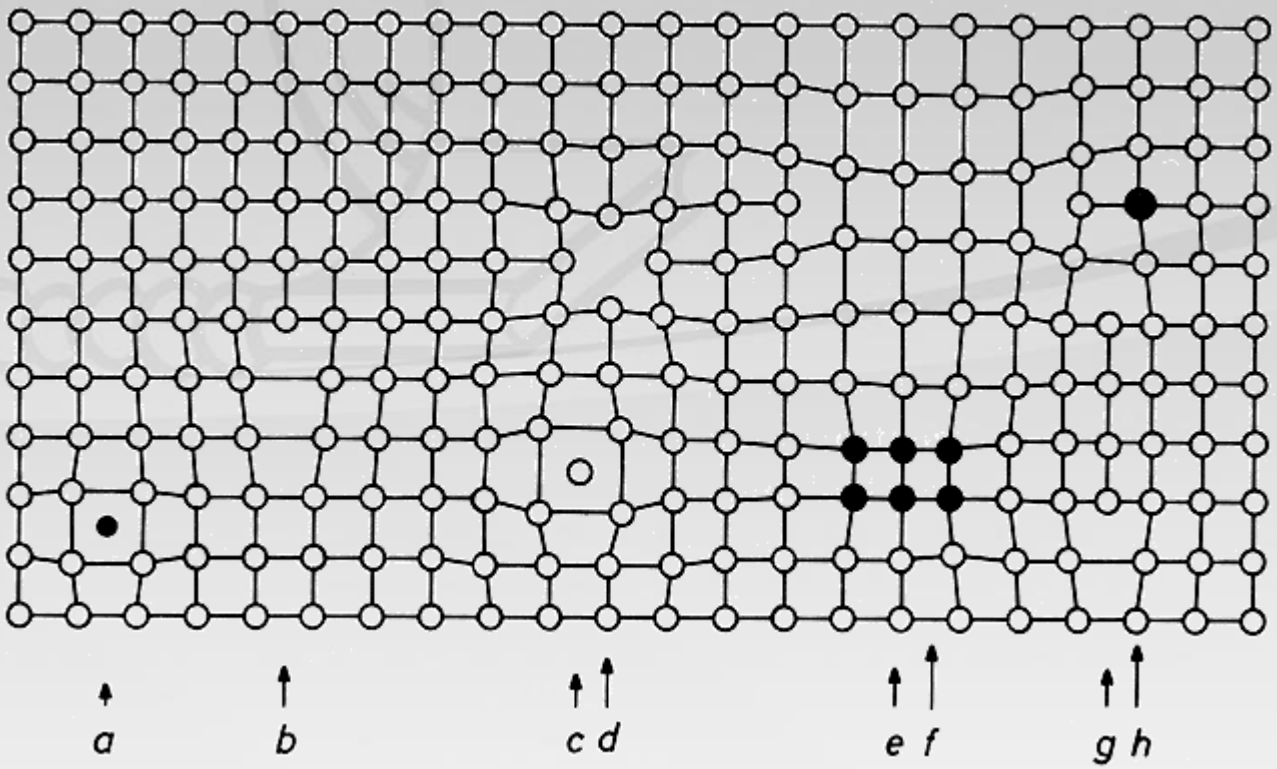
P. Warczok

Outline

- Vacancy concentration
  - What is it all about?
  - Why do we care about?
  - How does it evolve?
  - Why does it (sometimes) take so long to evolve?

What is it all about?

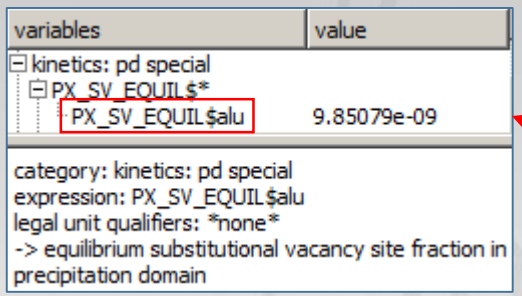
- Real materials are not perfect crystals...



What is it all about?

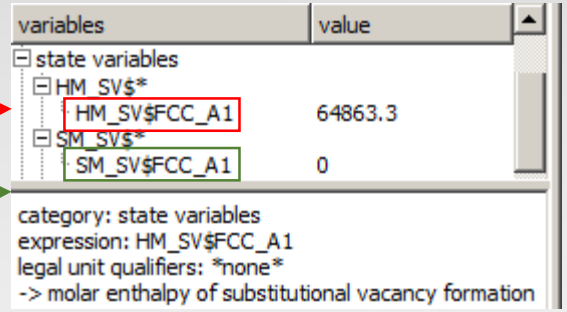
- Equilibrium vacancy concentration → thermodynamics make them appear

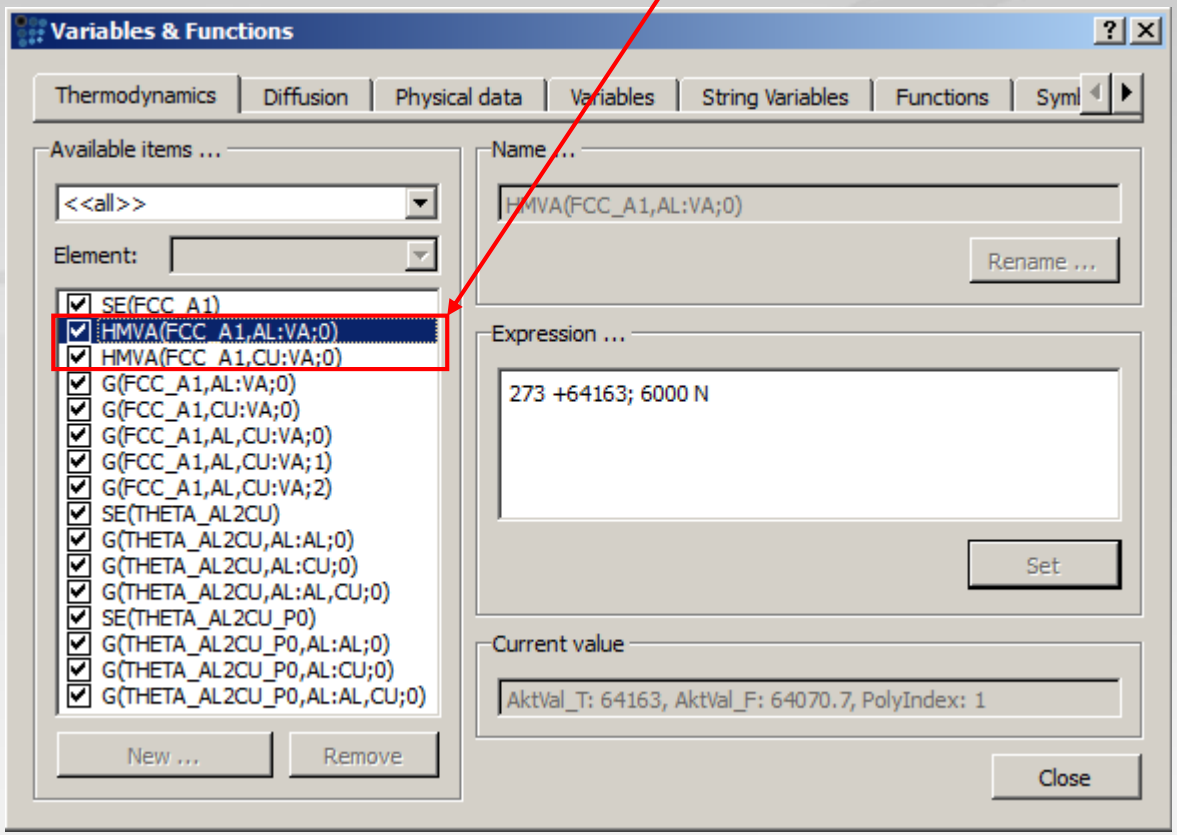
$$H_{Va}^{f} = \sum_{i} y_i H_{Va,i}^{f}$$



$$y_{Va,eq} = exp\left(-\frac{G_{Va}^{f}}{RT}\right)$$

$$G_{Va}^{f} = H_{Va}^{f} - TS_{Va}^{f}$$





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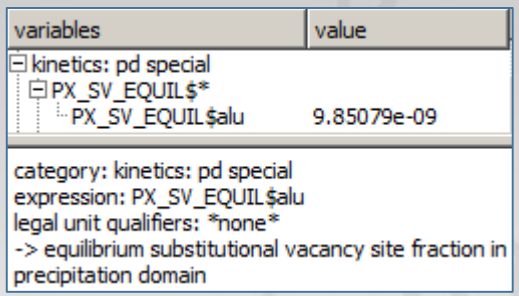
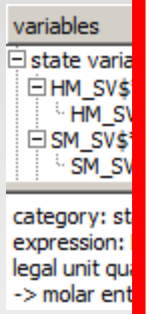


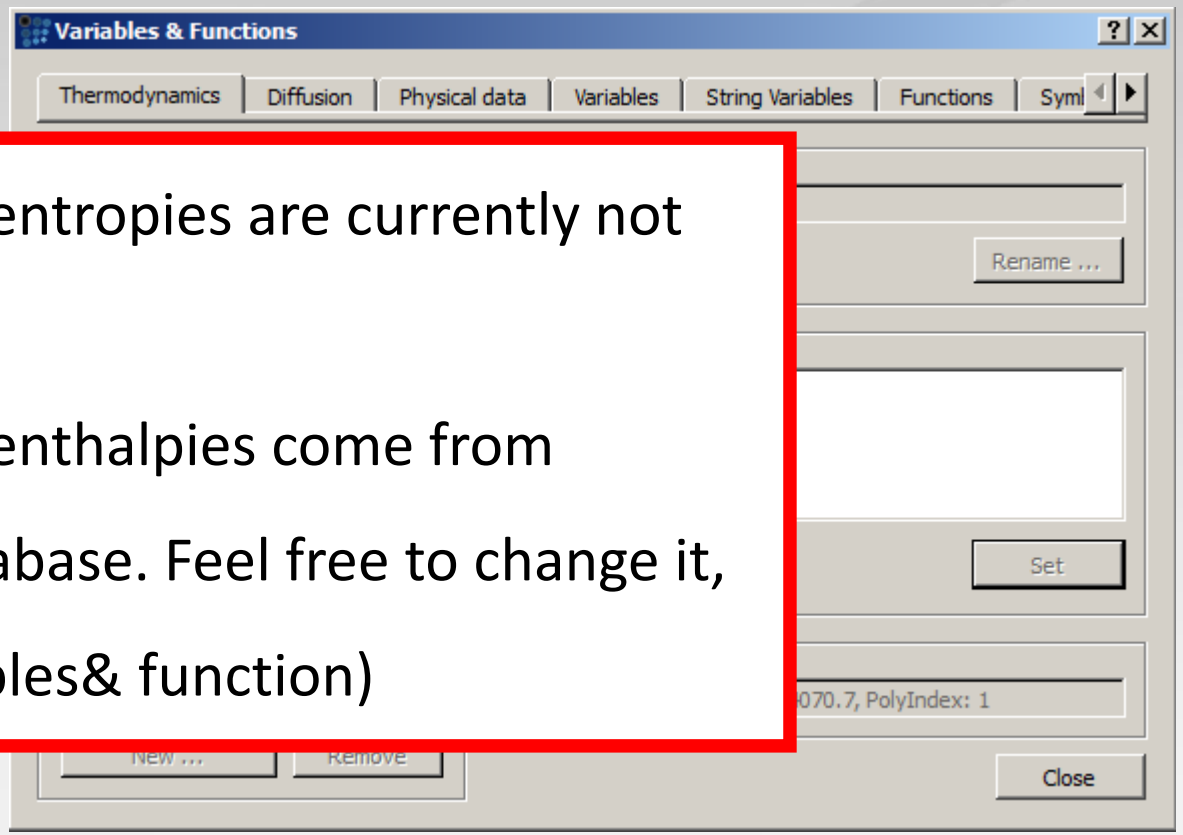
$$y_{V}\left(\frac{G_{Va}^{f}}{}\right)$$



$$G_{Va}^{f} = H_{Va}^{f} - TS_{Va}^{f}$$

-Vacancy formation entropies are currently not used in MatCalc

-Vacancy formation enthalpies come from thermodynamic database. Feel free to change it, if you need it (Variables& function)



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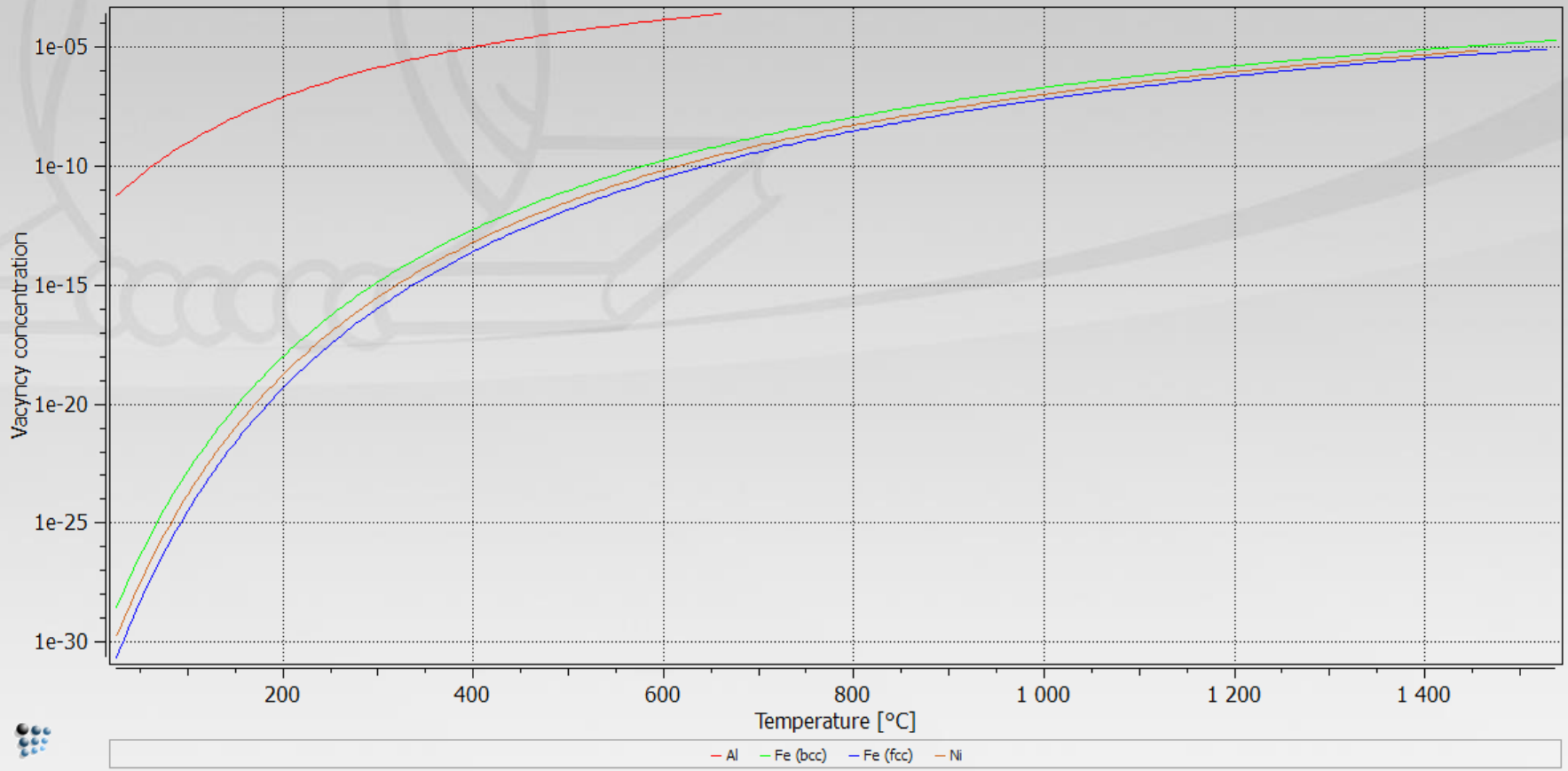

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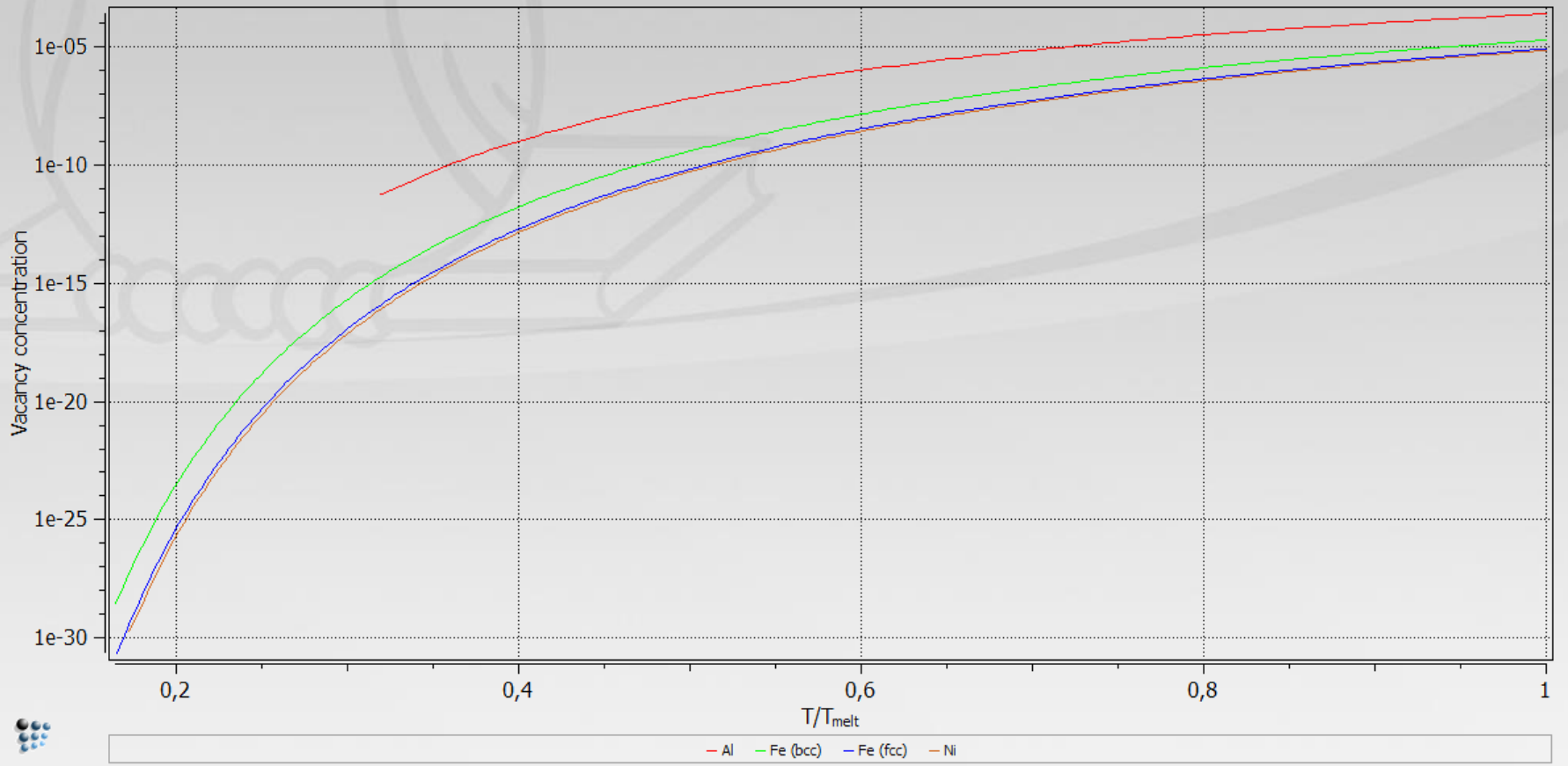

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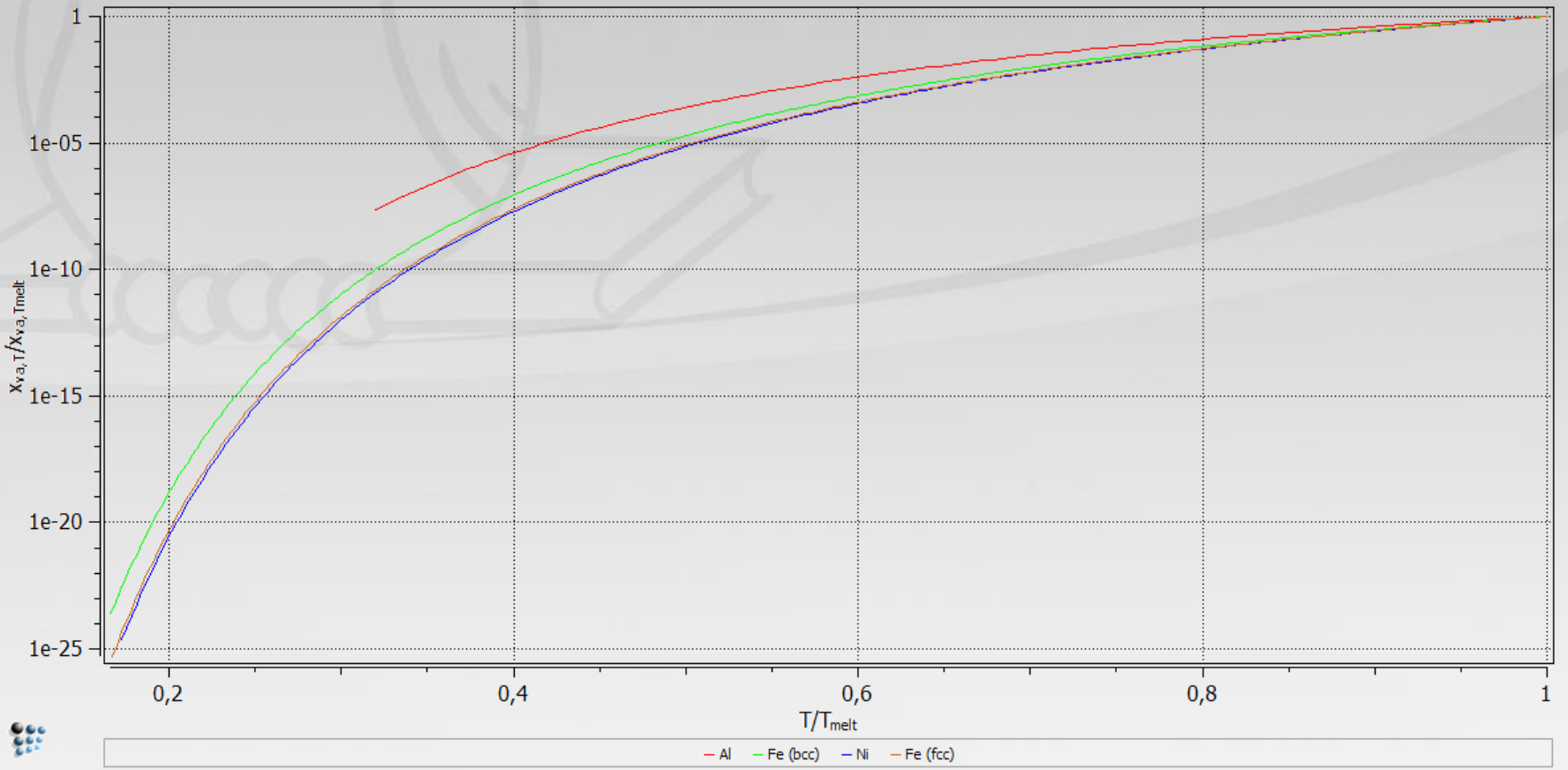
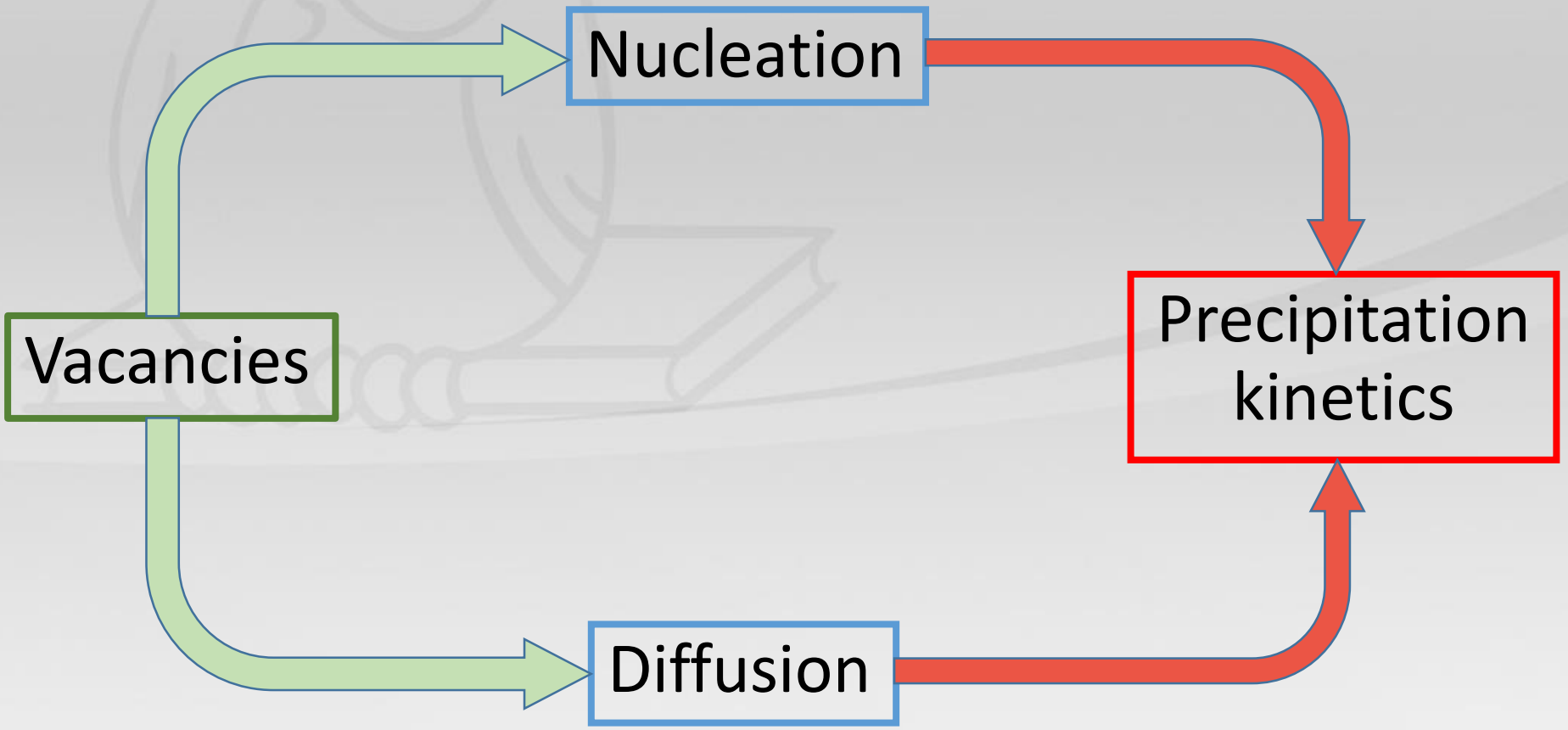


What is it all about?

- How to change the vacancy concentration?
  - New equilibrium
    - Change temperature
    - Transform to a new phase
  - Out of equilibrium
    - Deform material
    - Irradiate material

Why do we care?

MatCalc Engineering



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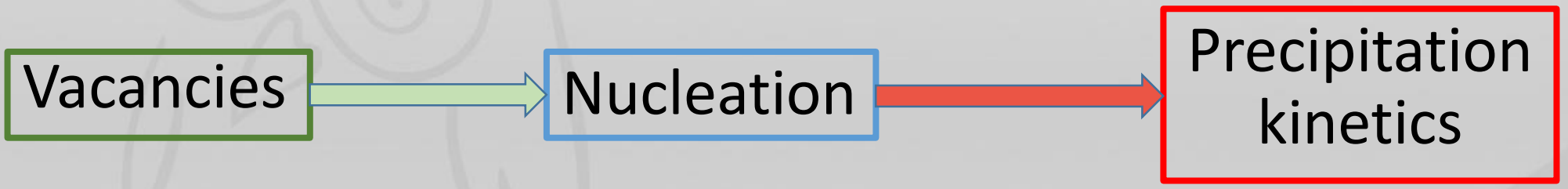


$$d_{ch}^{Va} = RTln\left(\frac{y_{Va}}{y_{Va,eq}}\right)$$

$$G^* = \frac{16\pi\gamma^3}{3\left[\underbrace{\frac{\Delta G_{chem}}{v^\alpha} - \frac{d_{ch}^{Va}}{v^\alpha}\Delta v}_{\text{Chemical part}} + \underbrace{\frac{\Delta G_{el}}{v^\alpha} + \frac{9(1-\upsilon)}{4E^\alpha}\left(\frac{d_{ch}^{Va}}{v^\alpha}\right)^2}_{\text{Elastic part}}\right]^2}$$

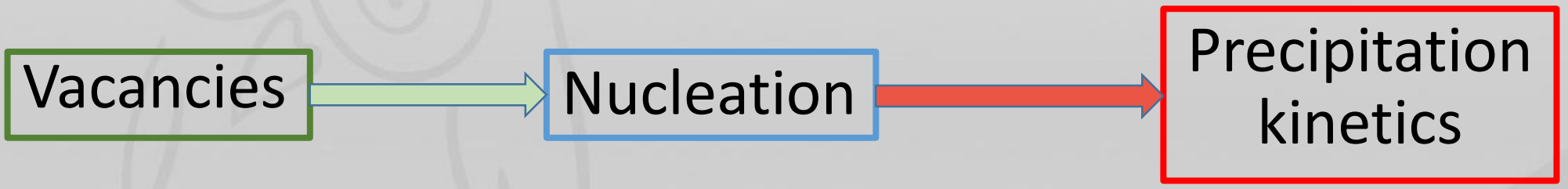
$$J \sim exp\left(-\frac{G^*}{RT}\right)$$

d_{ch}^{Va} - Vacancy contribution to driving force
R – Gas constant
T – Temperature
y_{Va} - Vacancy site fraction on subst. lattice (current)
$y_{Va,eq}$ - Vacancy site fraction on subst. lattice (equil.)
G^* - Critical nucleation energy

γ – Interfacial energy preciptate/matrix
v^α - Molar volume
Δv – volumetric misfit of precipitate
υ – Poisson‘s ratio
E^α - Young‘s modulus
J – Nucleation rate

Why do we care?

MatCalc Engineering



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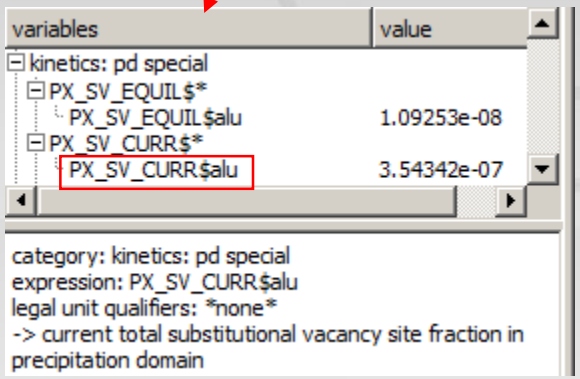
$$J \sim exp\left(-\frac{G^*}{RT}\right)$$

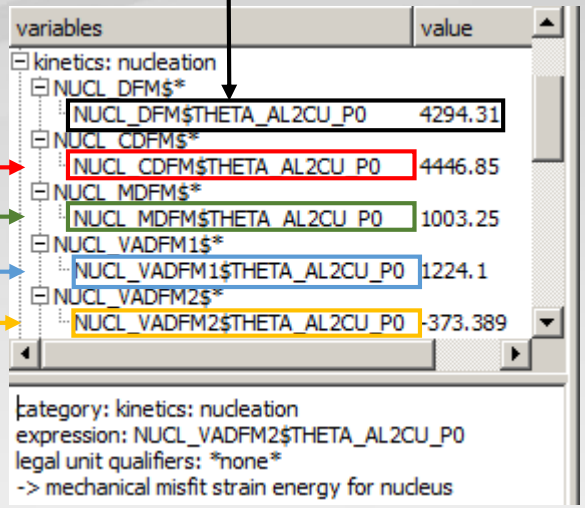
- Generation/anihilation of the excess vacancies results in a strain of the matrix (last term)
- Volumetric misfit of the precipitate may augment/decay the previous effect (second term)

Why do we care?

$$d_{ch}^{Va} = RTln\left(\frac{y_{Va}}{y_{Va,eq}}\right)$$

$$G^* = \frac{16\pi\gamma^3}{3\left[\frac{1}{v^\alpha}\left(\Delta G_{chem} + \Delta G_{el} - d_{ch}^{Va}\Delta v + \frac{9(1-\upsilon)}{4E^\alpha v^\alpha}(d_{ch}^{Va})^2\right)\right]^2}$$





Why do we care?

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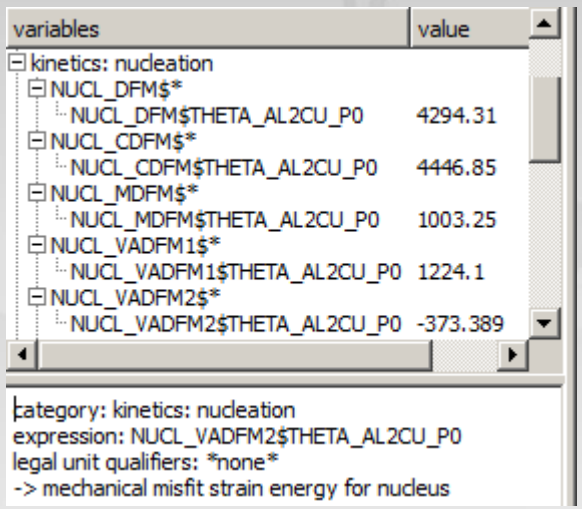
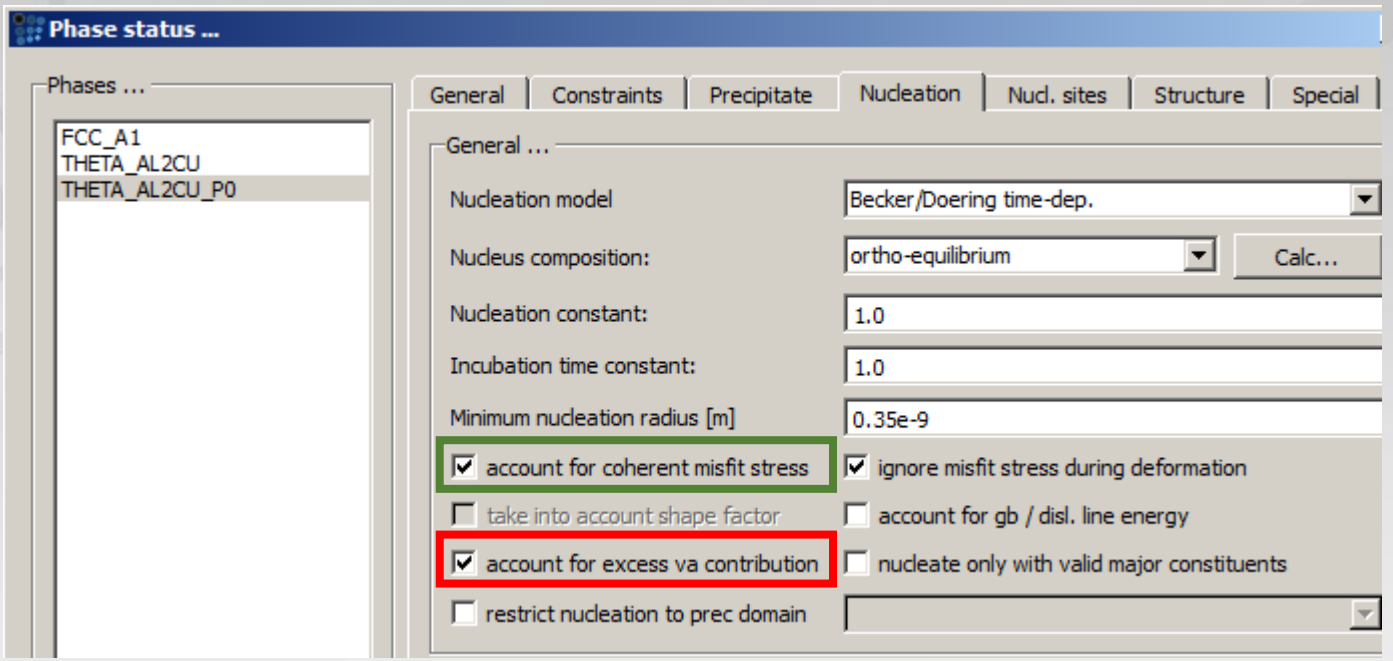
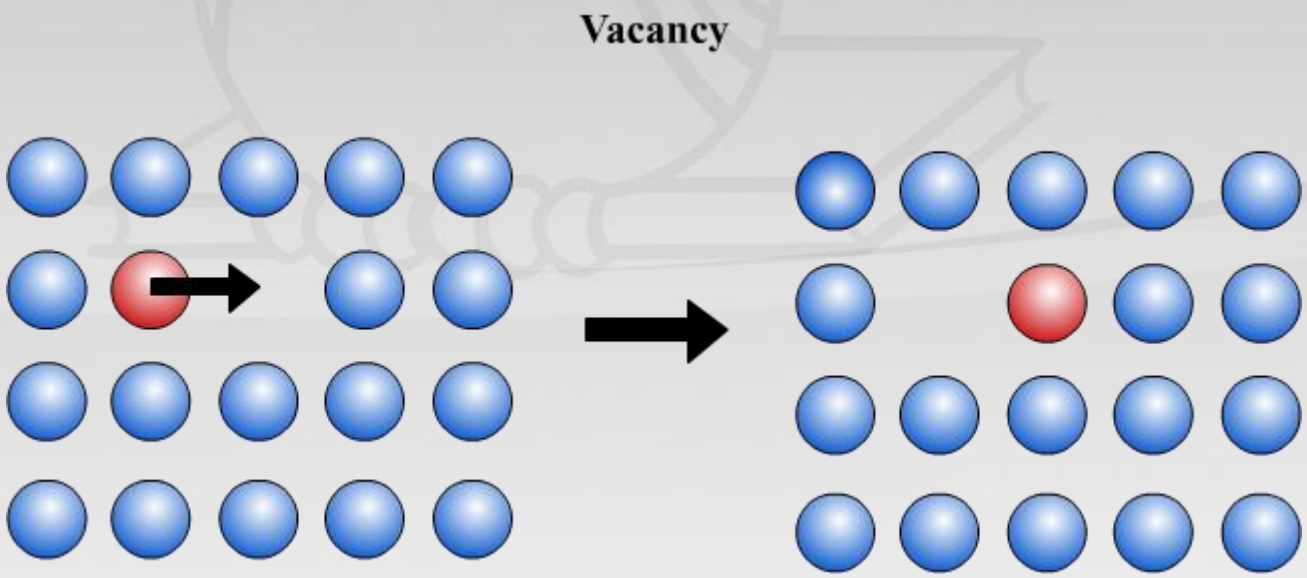




Why do we care?

MatCalc Engineering

Vacancies → Diffusion → Precipitation kinetics



http://www.doitpoms.ac.uk/tlplib/diffusion/diffusion_mechanism.php

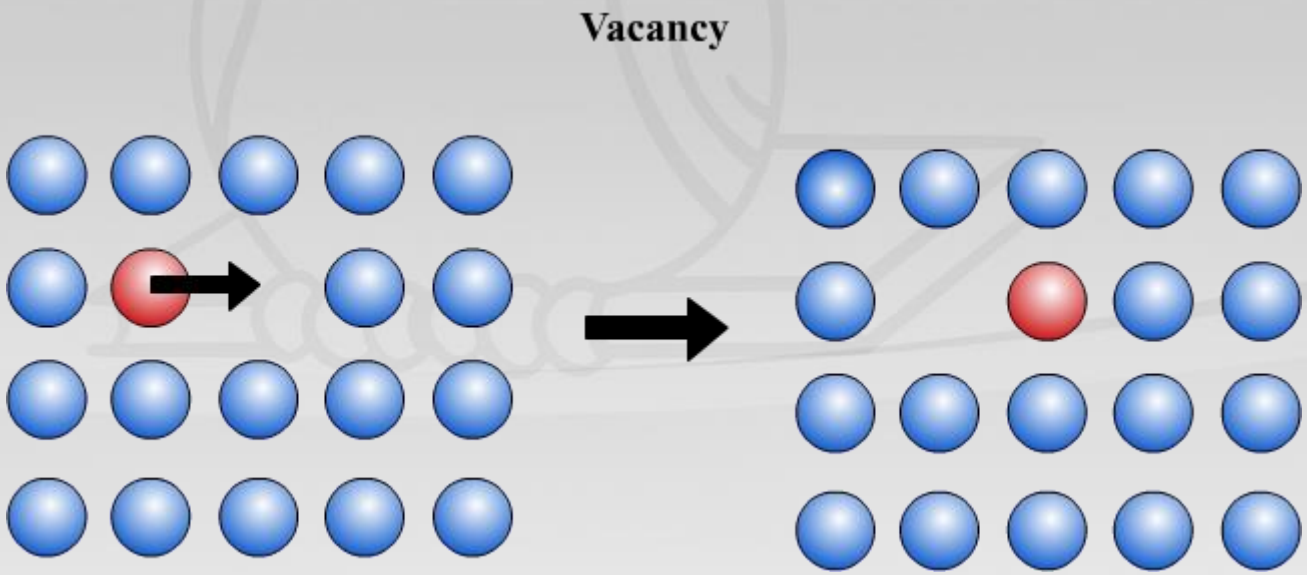
$$D_i = D_{0,i} exp\left(-\frac{Q_i}{RT}\right)\left(\frac{y_{Va}}{y_{Va,eq}}\right)$$

D_i - Diffusion coefficent
$D_{0,i}$ - Pre-exponential factor
Q_i - Activation energy of subst. diff.

Why do we care?

MatCalc Engineering

Vacancies → Diffusion → Precipitation kinetics



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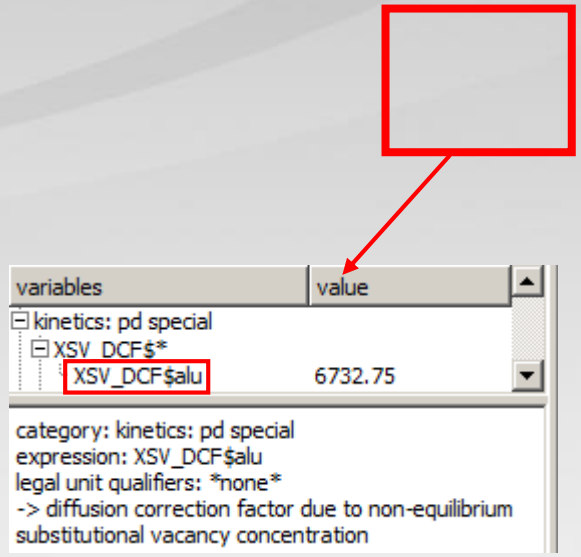

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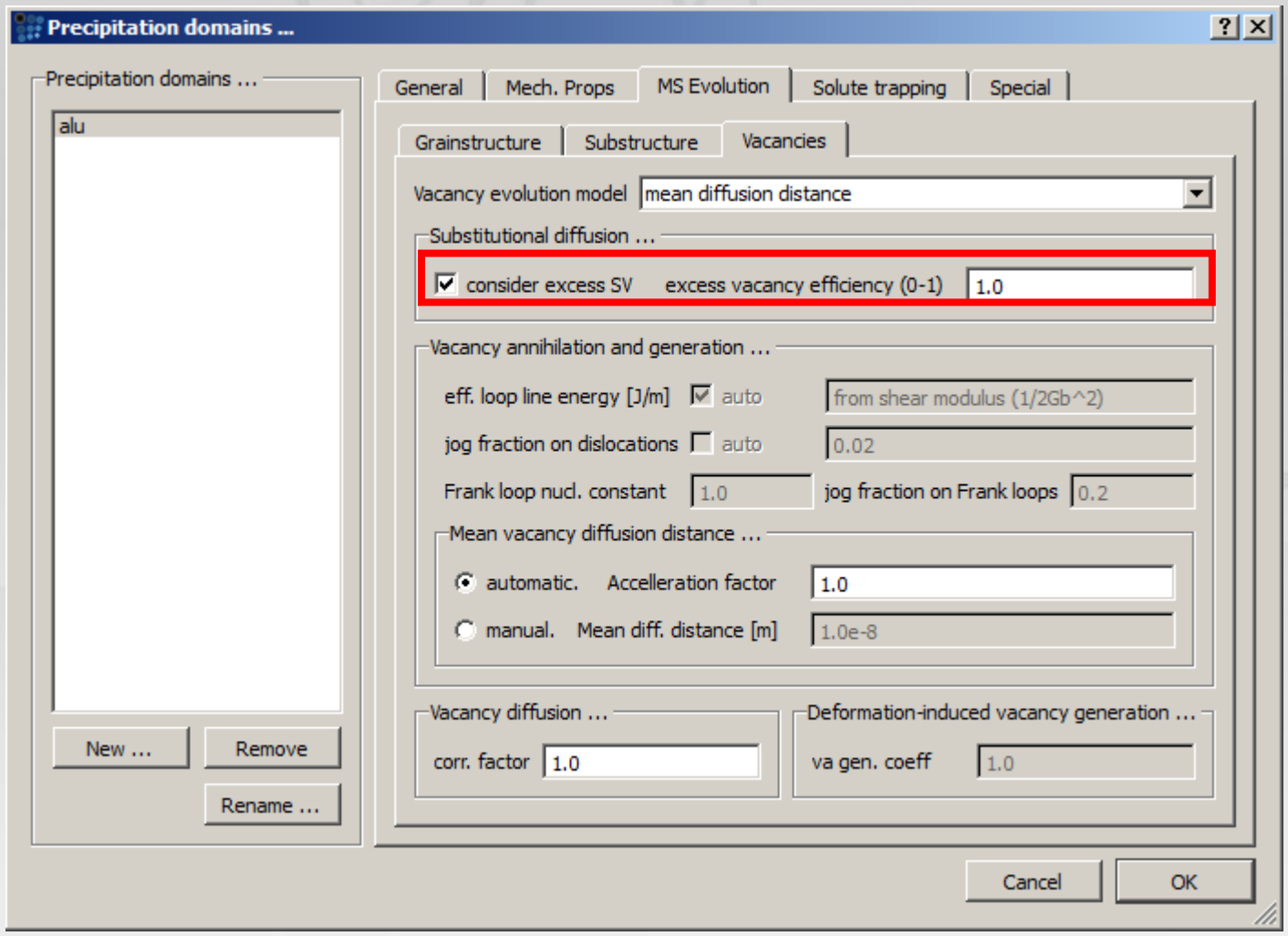

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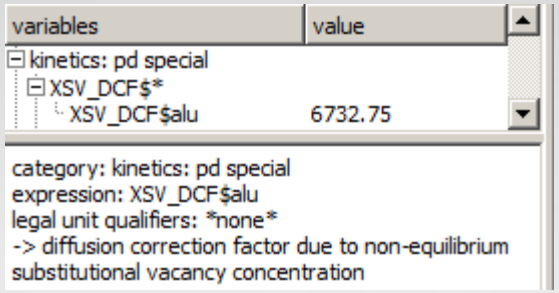
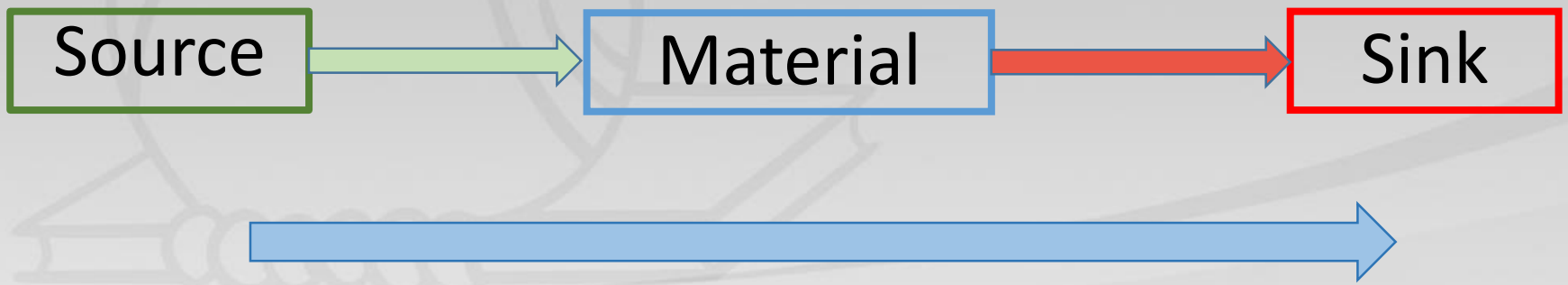


How does it evolve?

MatCalc Engineering

- Sources and sinks

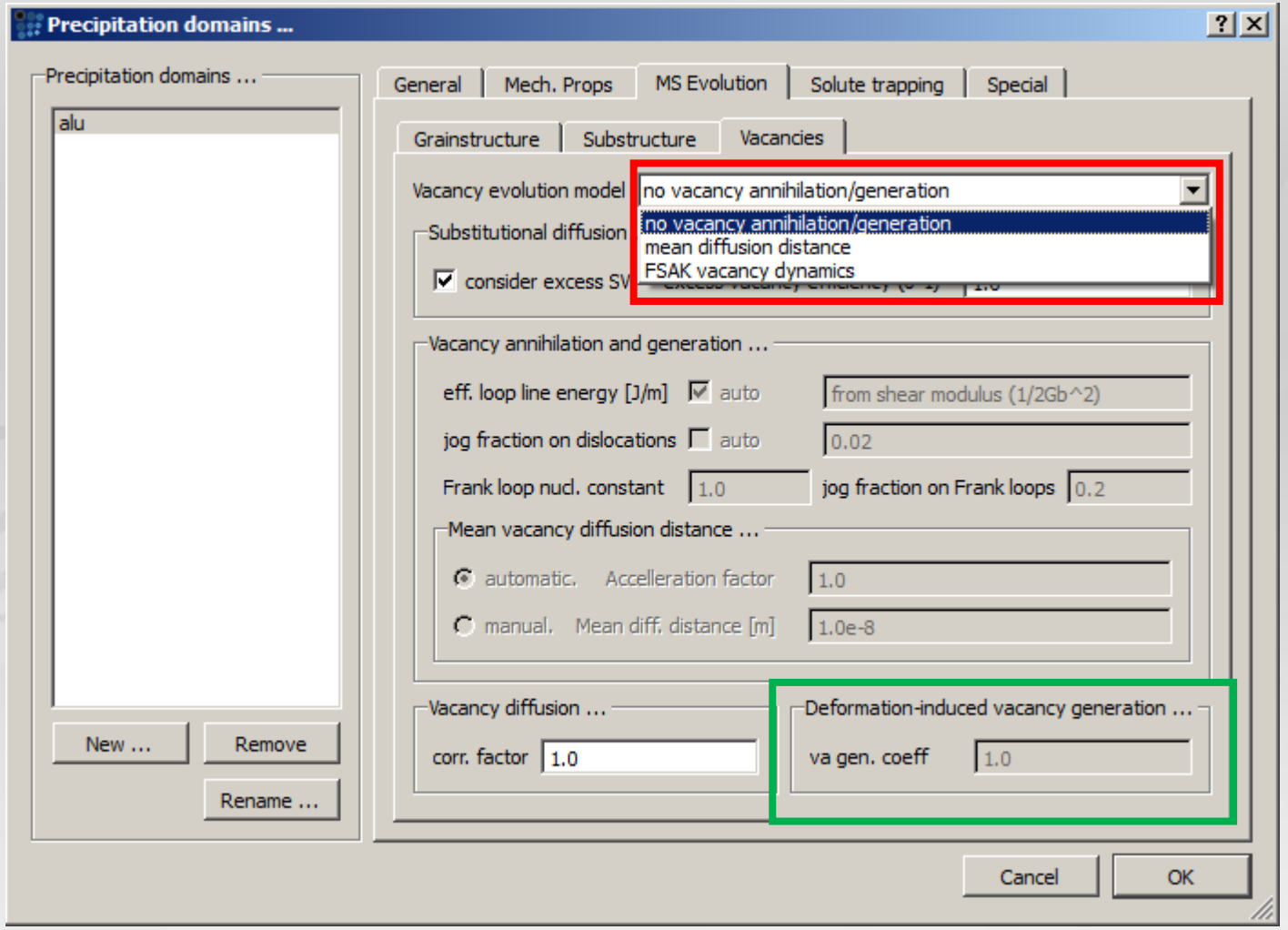


- Equilibrium → Generation rate at source = Anihilation rate at sink

How does it evolve?

MatCalc Engineering

- 3 models in MatCalc:
  - Mean diffusion distance
  - „FSAK“* model
  - Vacancy generation during the deformation (with FSAK only!)



* „Fischer-Svoboda-Appel-Kozeschnik“, Fischer et. al., Acta Mater. 59 (2011) 3463-3472

How does it evolve?

MatCalc Engineering

- Mean diffusion distance
  - Dislocations are taken as a vacancy source/sink

- Default mean diffusion distance:

$$a = 10\text{^}\left(-0.5log(\rho)\right)$$

a - Mean diffusion distance

ρ – Dislocation density

- Evolution equation:

C - Constant y_i - Element subst. site fraction

$$\Delta y_{Va}(\Delta t) = C\left[1 - exp\left(-\frac{D\Delta t}{a}\right)\right]\left(y_{Va,eq} - y_{Va}\right)$$

$$\mathrm{D} = \left(\frac{y_{Va}}{y_{Va,eq}}\right)\sum_i y_i D_i$$

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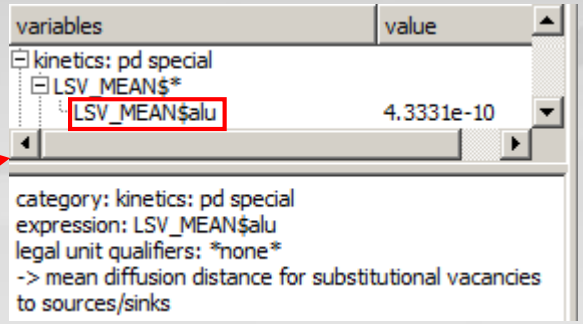

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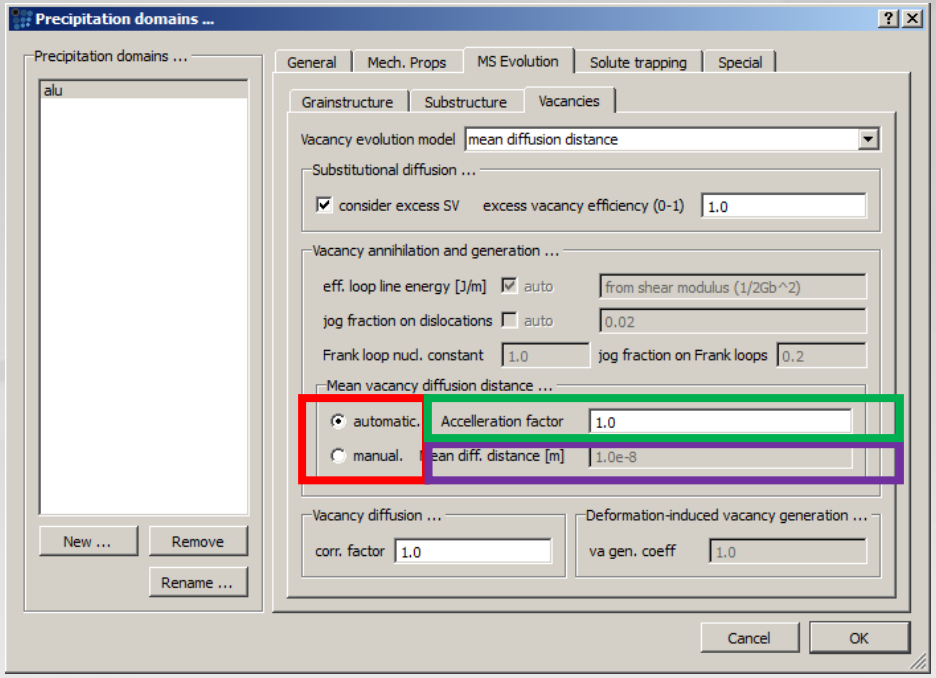

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How does it evolve?

MatCalc Engineering

- FSAK: Generation/anihilation on dislocation jogs
- Evolution equation:

$$\Delta y_{Va}^{DJ}(\Delta t) = -\frac{2\pi D}{f}\frac{y_{Va}}{y_{Va,eq}} ln\left(\frac{y_{Va}}{y_{Va,eq}}\right) bH$$

$$H = x_{jog}\rho$$

f – Diffusion correlation factor (0.75)

b – Burger‘s vector

H – Jog density

x_{jog} – Jog fraction on dislocations

How does it evolve?

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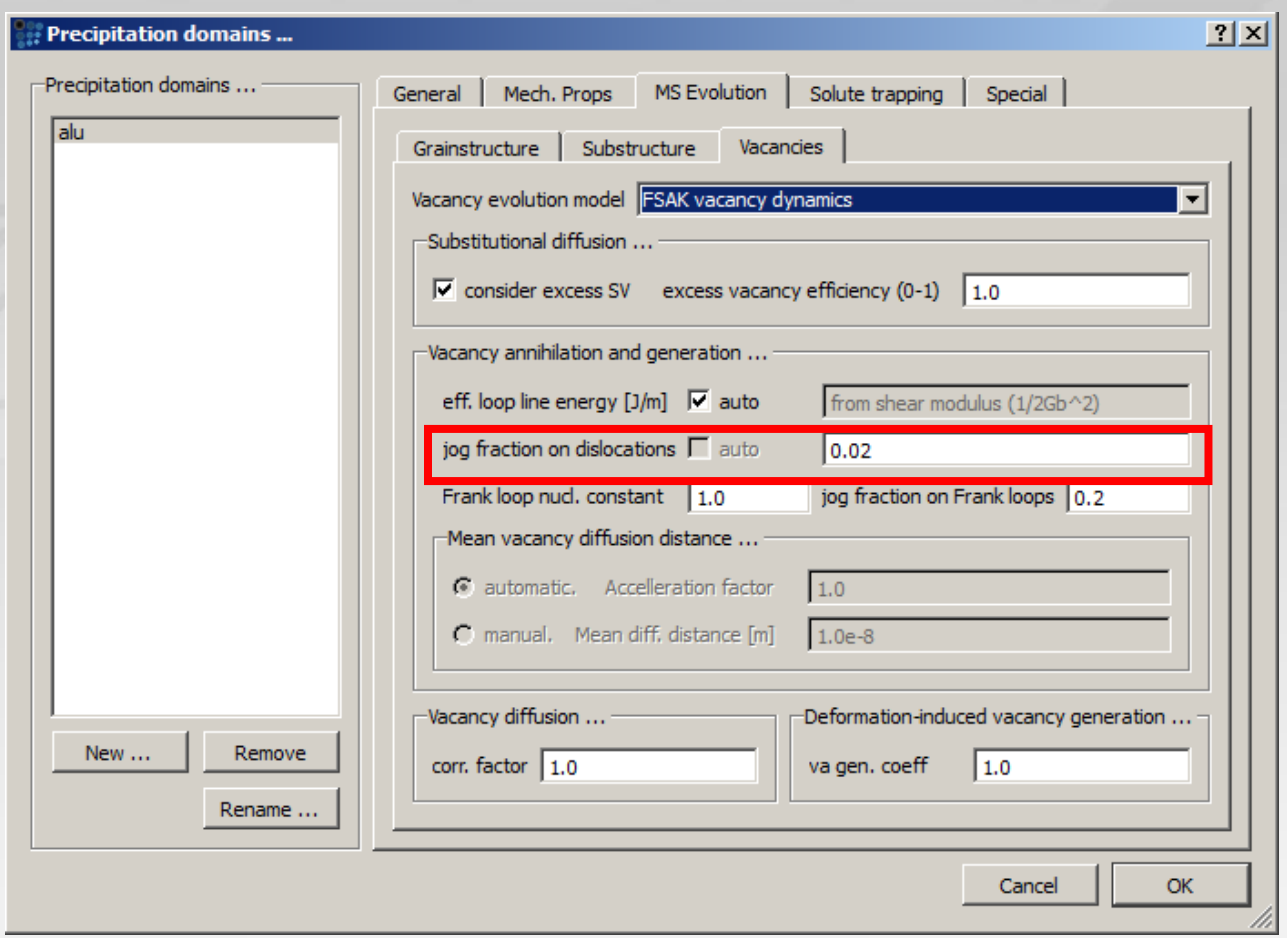

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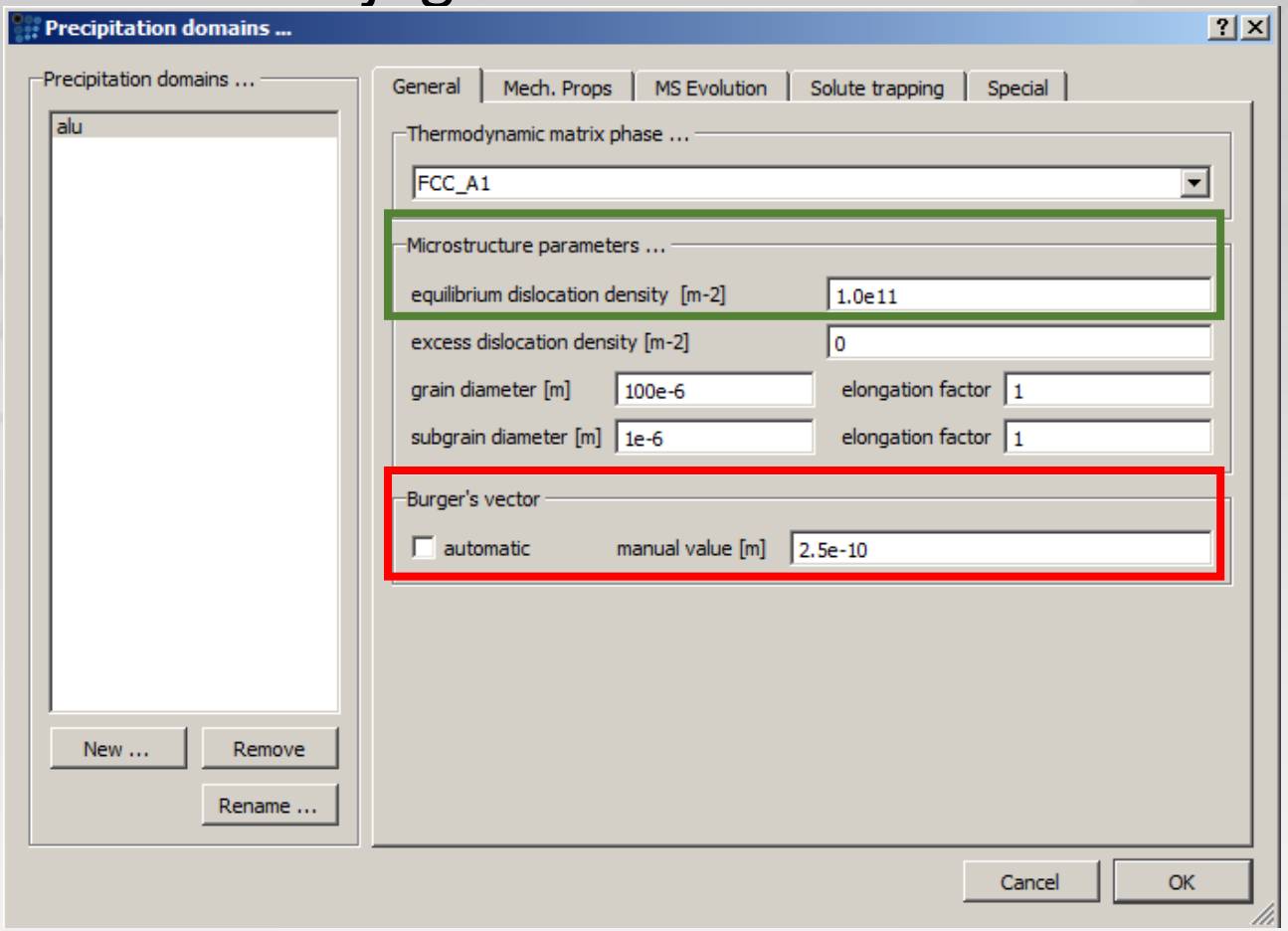

How does it evolve?

MatCalc Engineering

- FSAK: Generation/anihilation on grain boundaries

- Evolution equation:

$$\Delta y_{Va}^{GB}(\Delta t) = -\frac{15D}{f}\frac{y_{Va}}{y_{Va,eq}} ln\left(\frac{y_{Va}}{y_{Va,eq}}\right) R^{-2}$$

R – Radius of the spherical grain
(0.5 * grain size)

How does it evolve?

MatCalc Engineering

- FSAK: Generation/anihilation
- Evolution equation:

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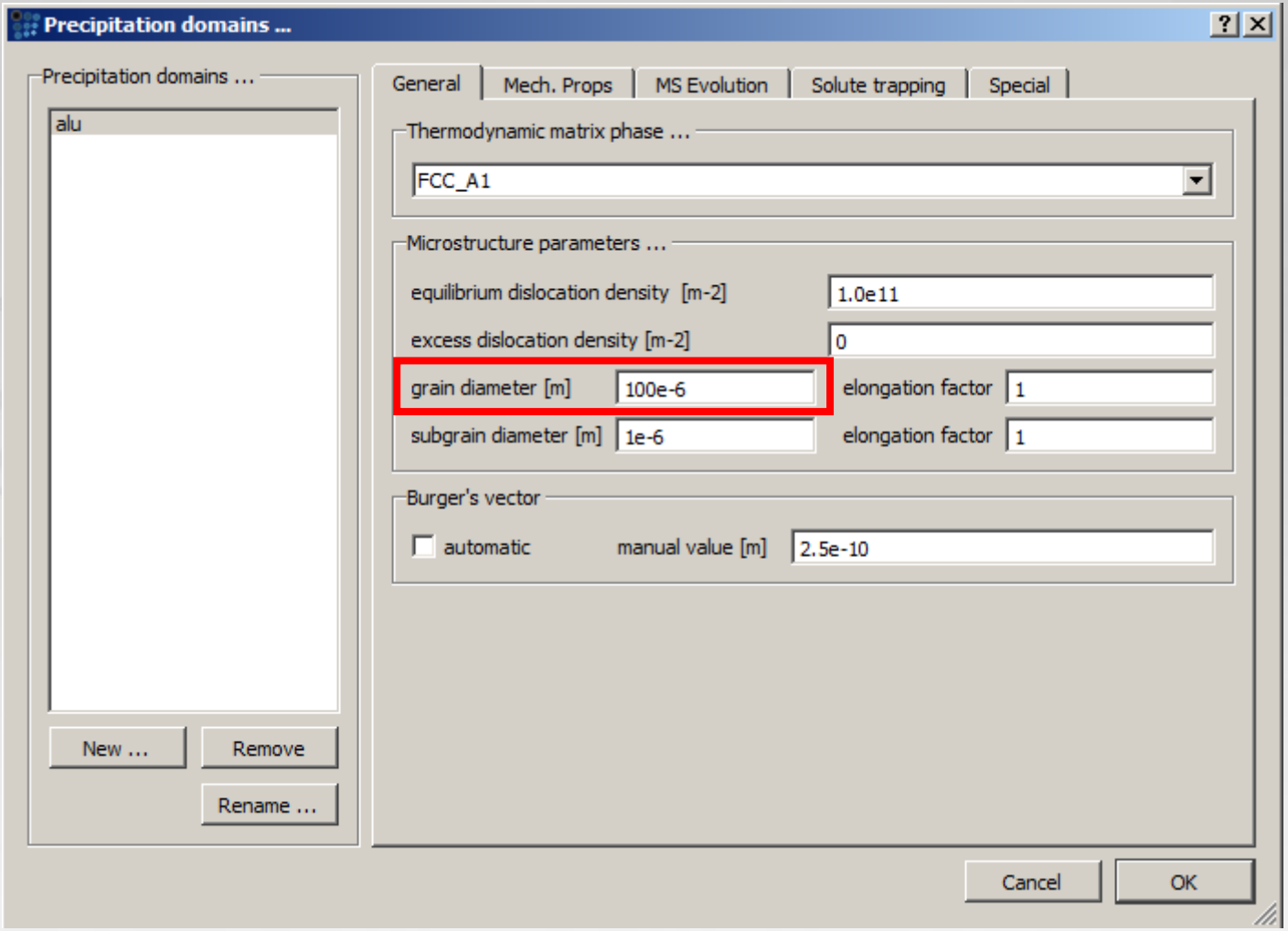

How does it evolve?

MatCalc Engineering

- FSAK: Generation/anihilation on Frank loops (test-phase?)
- Evolution equation:

$$\Delta y_{Va}^{FL}(\Delta t) = -\frac{4\pi^2 D}{f}\frac{y_{Va}}{y_{Va,eq}}\left[ln\left(\frac{y_{Va}}{y_{Va,eq}}\right) - \frac{b^2\gamma_L}{r_{FL}k_B T}\right]\frac{N_{FL}r_{FL}}{n_P}$$

$$n_P = \left(x_{jog,FL}\right)^{-1}$$

γ_L - Effective loop energy

r_{FL} - Frank loop radius (defined in the console)

N_{FL} - Frank loop density (defined in the console)

n_P - Jog spacing on Frank loops (number of atoms)

$x_{jog,FL}$ - Jog fraction on Frank loops

k_B - Boltzmann constant

How does it evolve?

MatCalc Engineering

- FSAK: Generation/anihilation on Frank loops (test-phase?)
- Evolution equation:

$$\Delta y_{Va}^{FL}(\Delta t)$$

$$= -\frac{4\pi^2 D}{f}\frac{y_{Va}}{y_{Va,eq}}\left[ln\left(\frac{y_{Va}}{y_{Va,eq}}\right) - \frac{b^2\gamma_L}{r_{FL}k_B T}\right]\frac{N_{FL}r_{FL}}{n_P}$$

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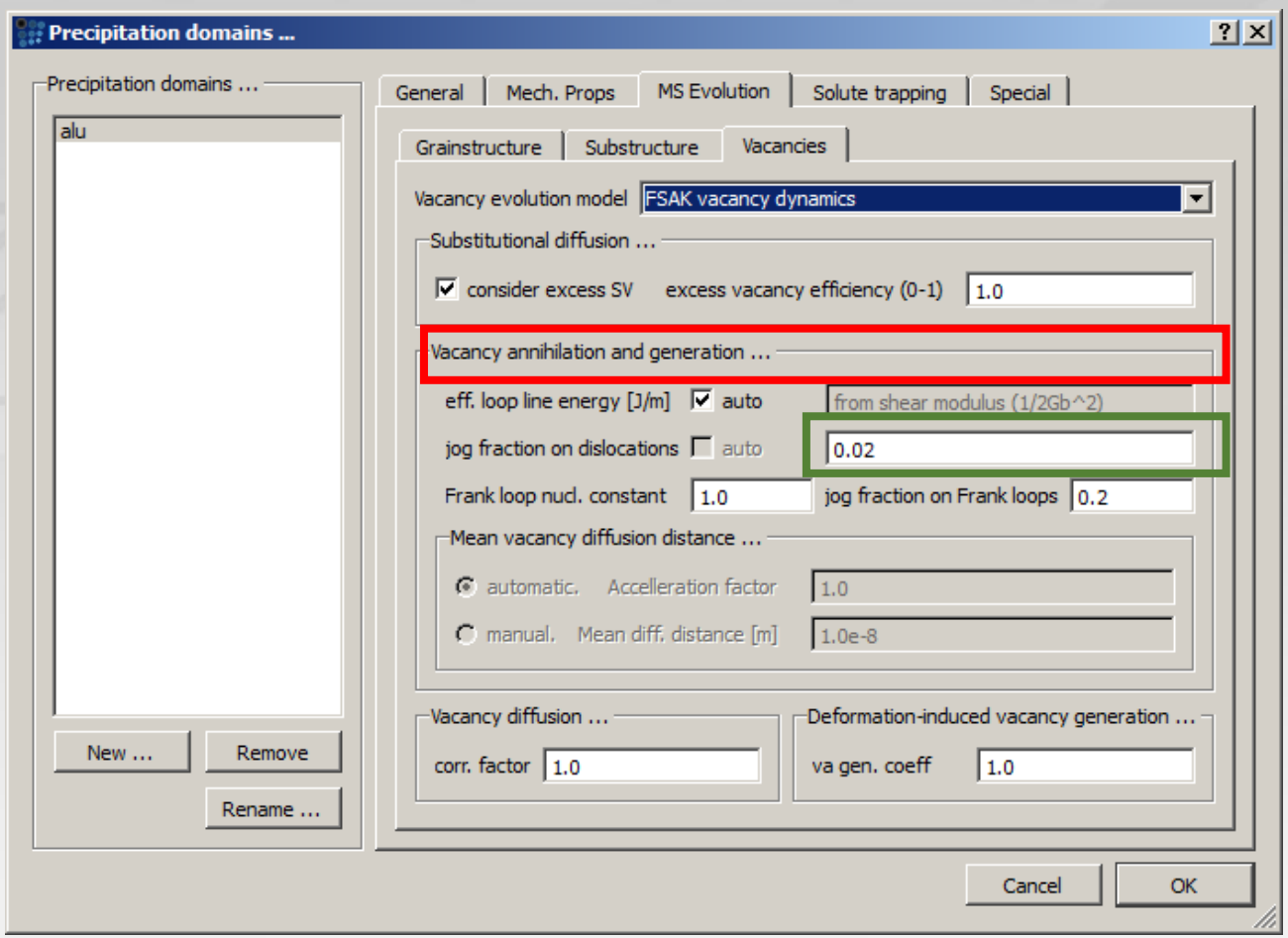


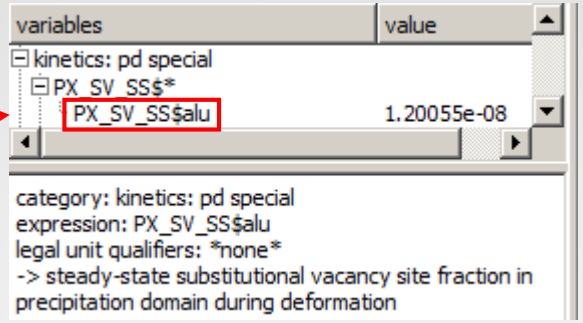
How does it evolve?

- Vacancy generation during the deformation

- Evolution equation:

$$\Delta y_{Va}^{def}(\Delta t) = \alpha M \dot{\varepsilon} \left[exp\left(-\frac{G b^3}{4\pi(1-\upsilon)k_B T} \right) - b\sqrt{\rho} \right]$$

$y_{Va,eq} + y_{Va}^{def}$



α – Constant

M – Taylor factor

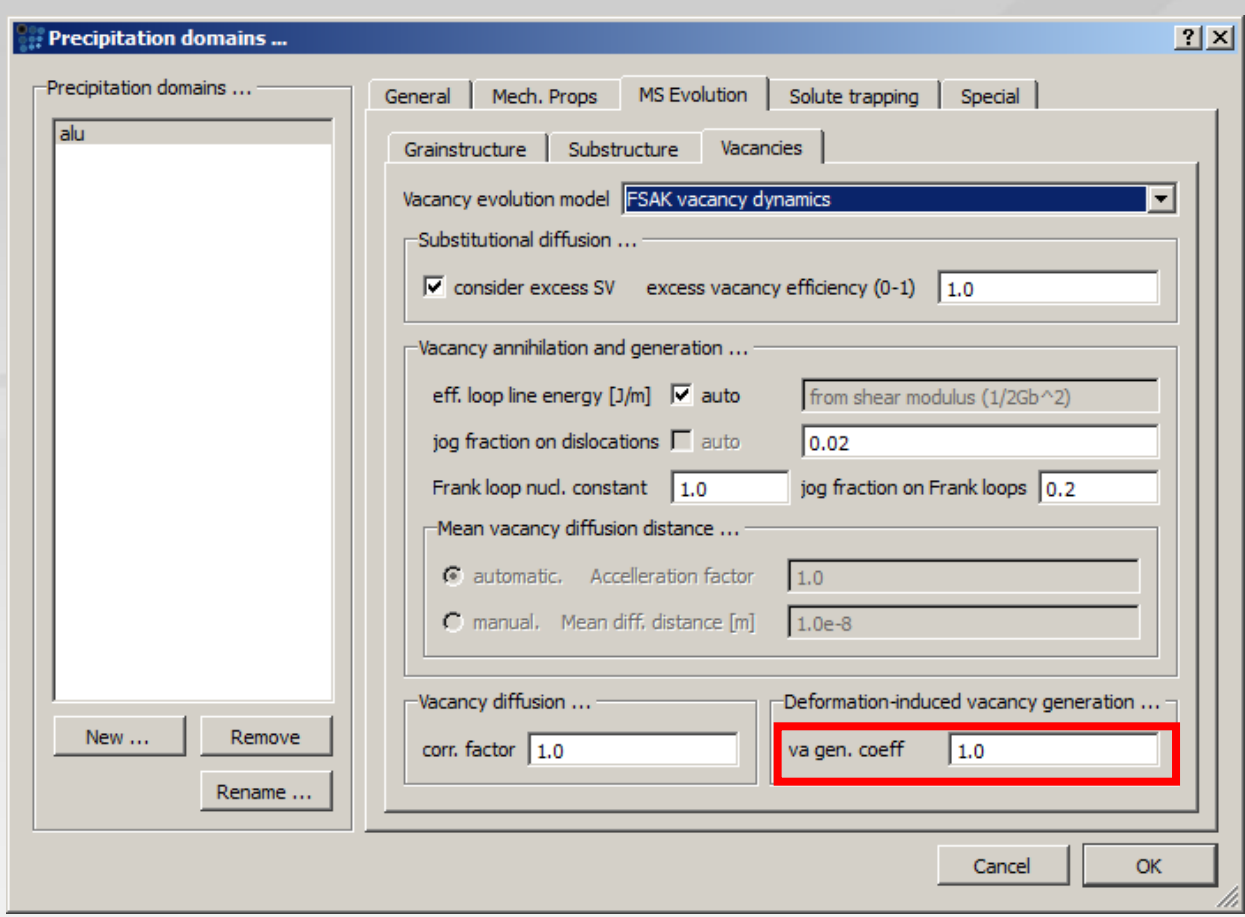
G – Shear modulus

$\dot{\varepsilon}$ - Strain rate

How does it evolve?

- Vacancy generation during the deformation
- Evolution equation

$$\Delta y_{Va}^{Def}(\Delta t) = \alpha M \dot{\varepsilon} \left[exp\left(-\frac{Gb^3}{4\pi(1-\upsilon)k_B T} \right) - b\sqrt{\rho} \right]$$



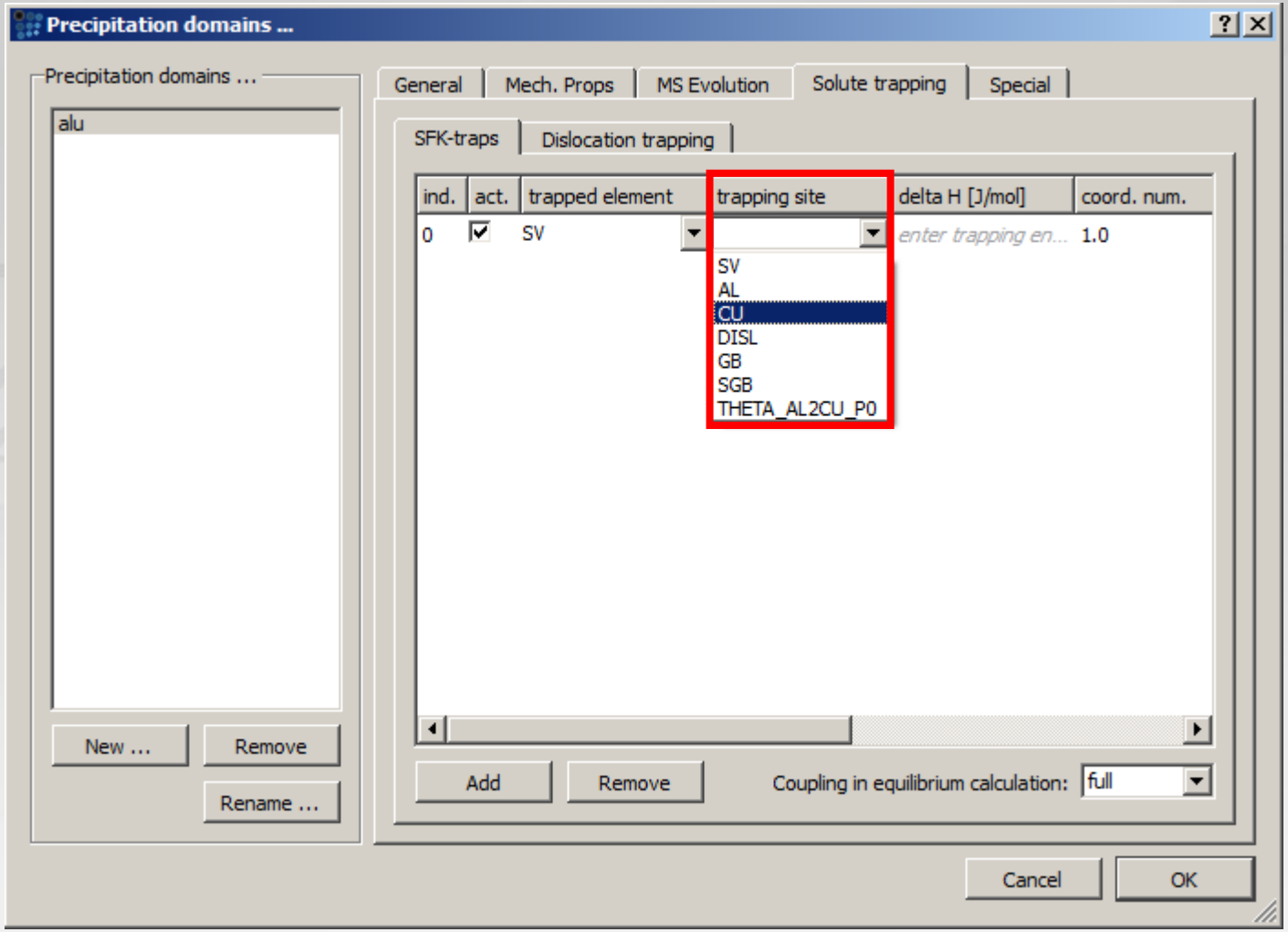
Why does it take so long to evolve?

MatCalc Engineering

- The idea:
  - Some vacancies are trapped in the material and do not proceed to the sinks.
  - Equilibrium between the trapped an „free-to-move“ vacancies
- Needed:
  - The amount of traps
  - The trapping strength
  - Relation between the amounts of trapped and free vacancies

Why does it take so long to evolve?

- Possible traps
  - Solute atoms
  - Dislocations
  - Grain- & subgrain boundaries
  - Precipitate surface



Why does it take so long to evolve?

- Possible traps

Trapping site	Fraction of trapping sites
Solute atoms	x_i
Dislocations	$\pi r_{dc}^2 \rho$
Grain boundary	N_{GB}/N_B
Subgrain boundary	N_{SGB}/N_B
Precipitate surface	$4\pi V_{at}^{\frac{1}{3}} \left(\sum_{class} N_j r_j^2 \right)$

N_B - Number of bulk sites

N_{GB} - Number of sites at grain boundary

N_{SGB} - Number of sites at subgrain boundary

r_{dc} - Dislocation core radius ($5*10^{-19}$ m)

x_i - mole fraction of component „i“

N_j - Number of precipitates in class „j“

r_j - Radius of precipitates in class „j“

V_{at} - Atomic volume

Why does it take so long to evolve?

- Trap „strength“:

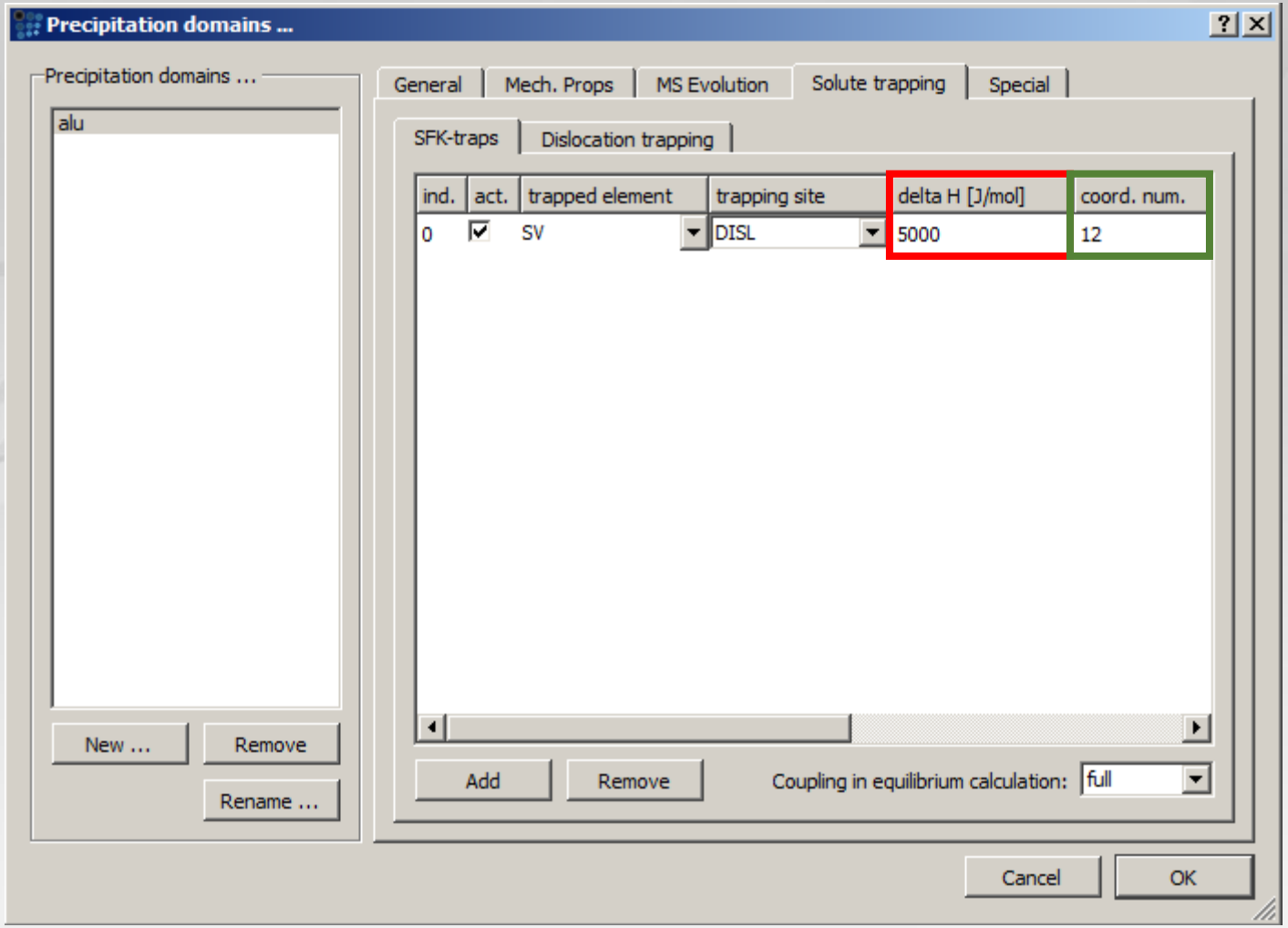
  delta H

$$K = exp\left(-\frac{\Delta H}{RT}\right)$$

ΔH - Trapping enthalpy

- Trap „range“ modifier:

coordination number



Why does it take so long to evolve?

MatCalc Engineering

- The amount of traps
  - Amount of lattice sites → expressed by molar volumes

$$n_{tot} = n_L + n_T$$

$$n_i V_{m,i} = n_{tot} V_m$$

$$x_i = \frac{n_i}{n_{tot}} = \frac{V_{m,tot}}{V_{m,i}}$$

n_{tot} - Total number of lattice sites

n_L - Number of sites on which the vacancy is free to move

n_S - Number of sites on the vacancy traps

n_i - Number of „*i*“-sites (e.g. n_L, n_T)

V_m - Molar volume (volume for n_{tot} = 1)

$V_{m,i}$ - Volume of material containing 1 mole of „*i*“-sites

x_i - Mole fraction of „*i*“-sites

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Why does it take so long to evolve?

MatCalc Engineering

- The amount of traps
  - Amount of lattice sites → e

$$n_{tot} = n_L + n_T$$

$$n_i V_{m,i} = n_{tot} V_m$$

$$x_i = \frac{n_i}{n_{tot}} = \frac{V_{m,tot}}{V_{m,i}}$$

For clarity:

- $V_{m,i}$ is the volume of the material under consideration needed to have the amount of 1 mole of „i“-sites in it. The less „i“-sites in the material, the more of it is needed.
- $V_{m,i}$ IS NOT the volume of 1 mole of „*i*“-sites! →The material does not consist of „*i*“-sites alone

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Why does it take so long to evolve?

MatCalc Engineering

- Vacancy balance

$$x_{Va,tot} = y_{Va,tot} = x_L y_{Va,L} + x_T y_{Va,T} = \frac{V_{m,T}}{V_{m,T}+V_{m,L}} y_{Va,L} + \frac{V_{m,L}}{V_{m,T}+V_{m,L}} y_{Va,T}$$

$y_{Va,i}$ - Site fraction of vacancies on „*i*“-sites (= fraction of „*i*“-sites occupied by the vacancies)

- $V_{m,T}$ ← according fraction of trapping sites*coordination number
- $V_{m,L}$ ← assumed as $V_{m,tot}$ (molar volume of system)

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Why does it take so long to evolve?

MatCalc Engineering

- Vacancy balance:

$$x_{Va,tot} = y_{Va,tot} = x_L y_{Va,L} + x_T y_{Va,T} = \frac{V_{m,T}}{V_{m,T}+V_{m,L}} y_{Va,L} + \frac{V_{m,L}}{V_{m,T}+V_{m,L}} y_{Va,T}$$

- Minimization of free energy:

$$y_{Va}^{T} = \frac{y_{Va}^{L}}{K + y_{Va}^{L}(1-K)} \qquad K = exp\left(-\frac{\Delta H}{RT}\right)$$

- Combine these two above → solve for $y_{Va,L}$ and $y_{Va,T}$
- The immobile vacancies → $x_T y_{Va,T} - x_L y_{Va,L}$

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Examples

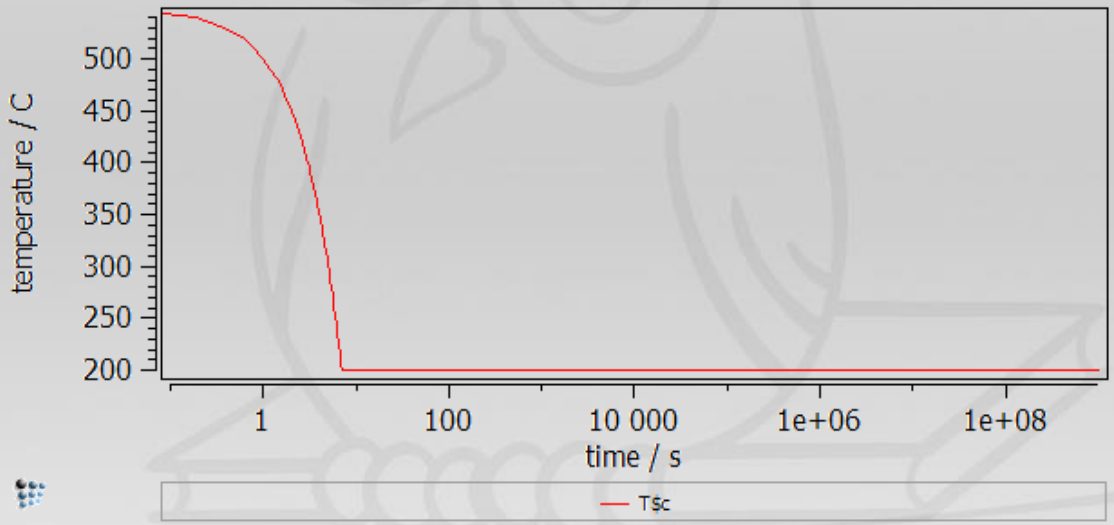
MatCalc Engineering

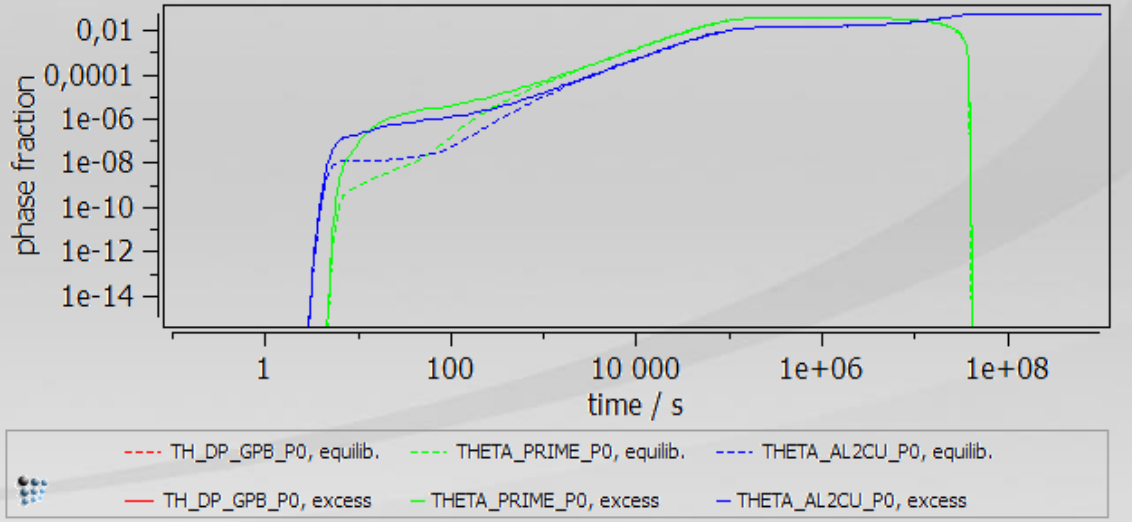
- Examples from MatCalc website (P2-1, P2-2)
  - FSAK model
  - Al-Cu system, 4.3 wt.% Cu
  - Precipitates: TH_DP_GPB- (bulk), THETA_PRIME- (disl.), THETA_AL2CU- (disl.)
  - Al-fcc domain

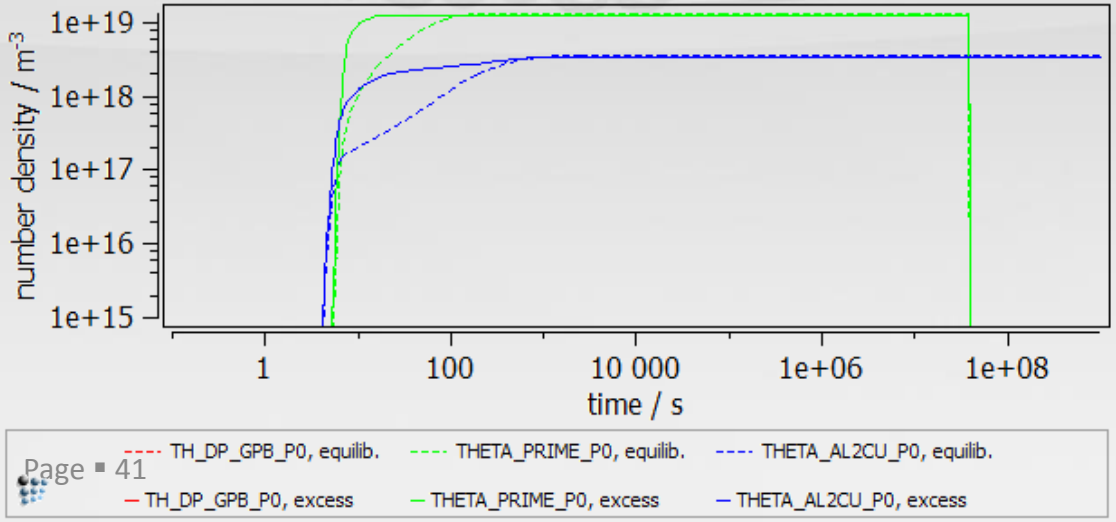
Examples

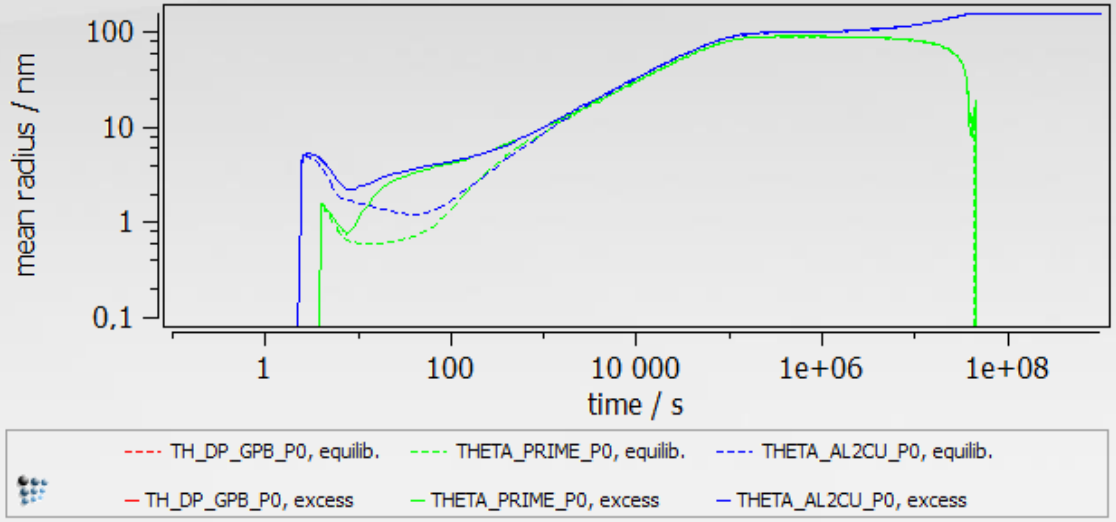
MatCalc Engineering

- Al-Cu system (Example P2-1), tempered at 200°C





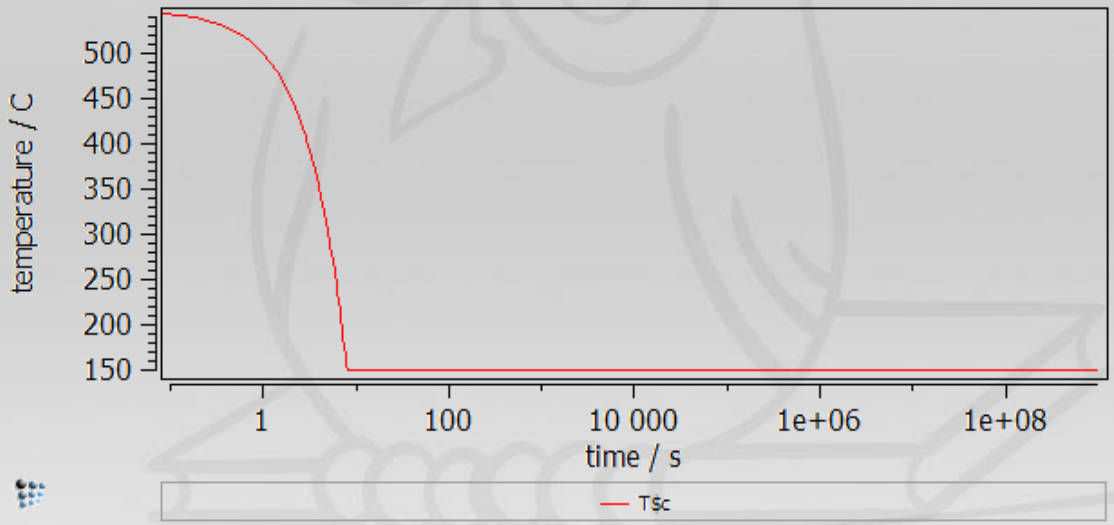


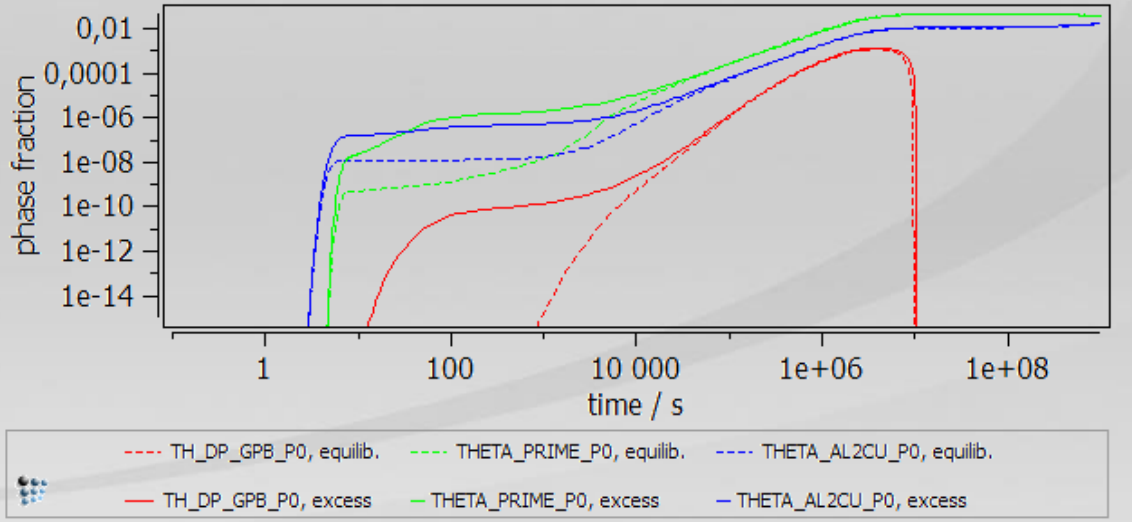


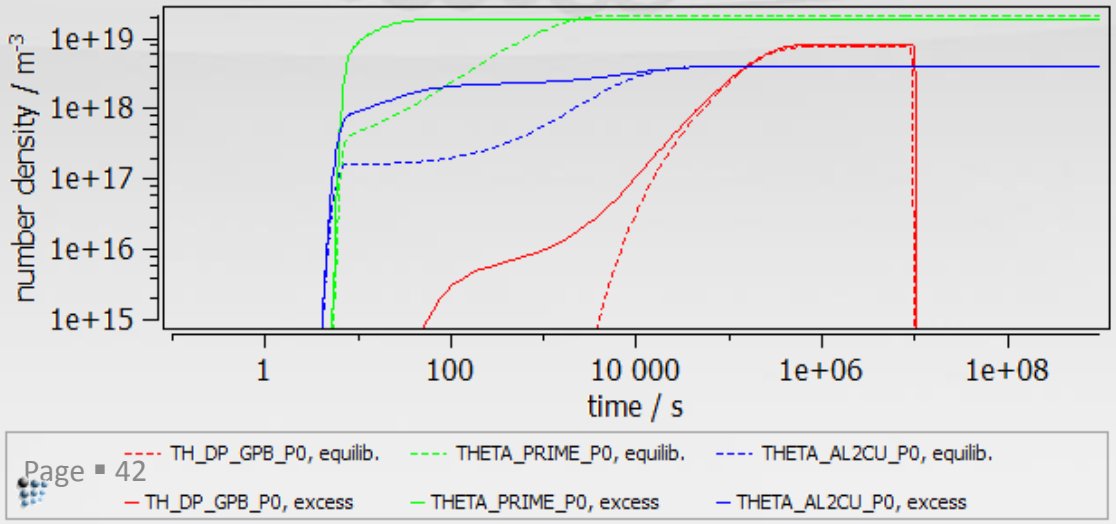
Examples

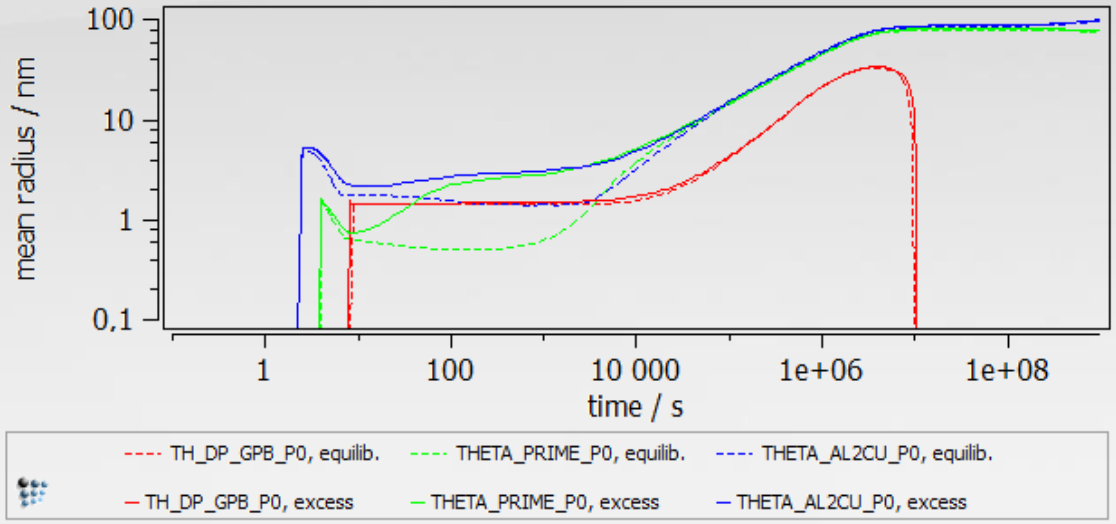
MatCalc Engineering

- Al-Cu system (Example P2-1), tempered at 150°C





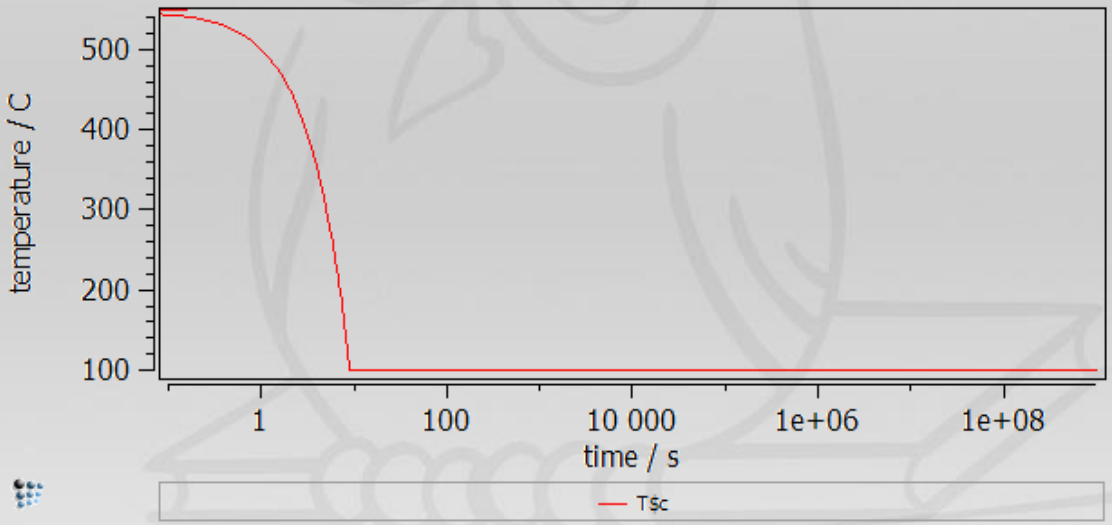


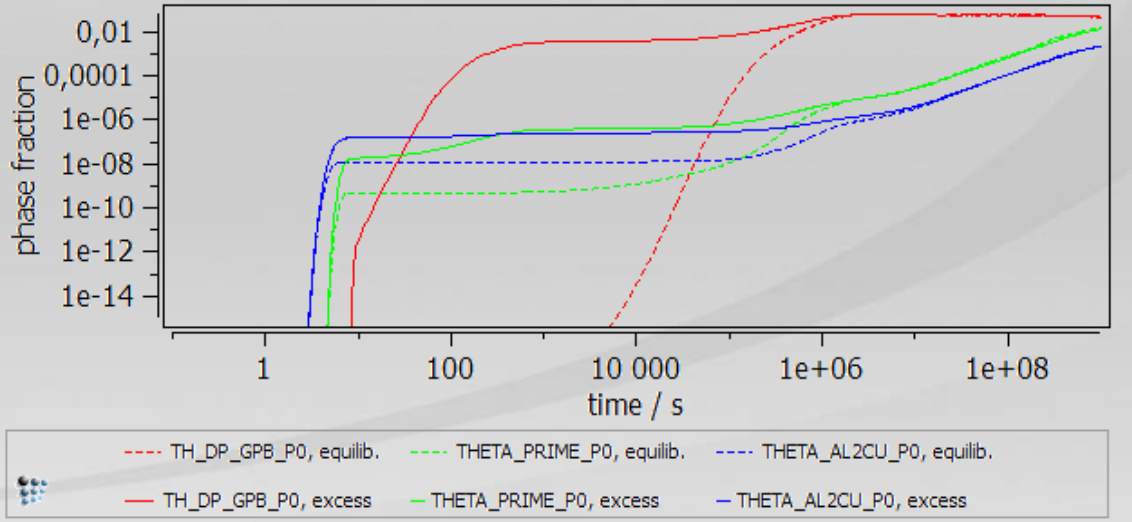


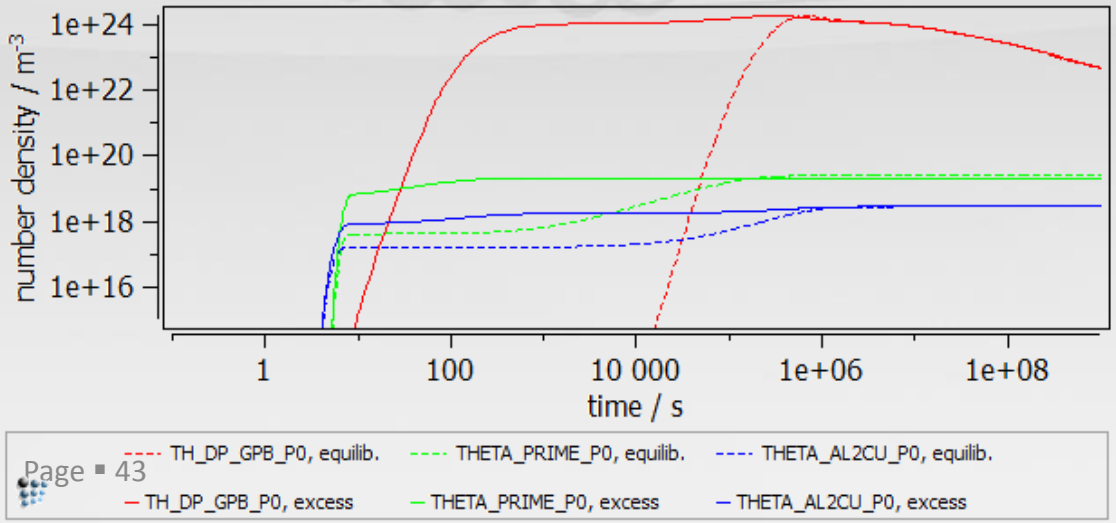
Examples

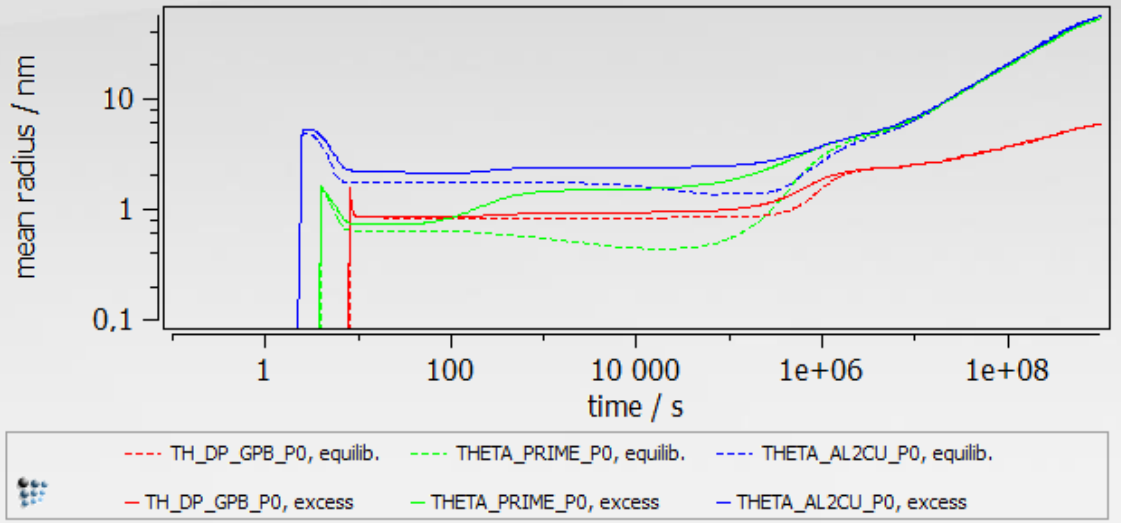
MatCalc Engineering

- Al-Cu system (Example P2-1), tempered at 100°C





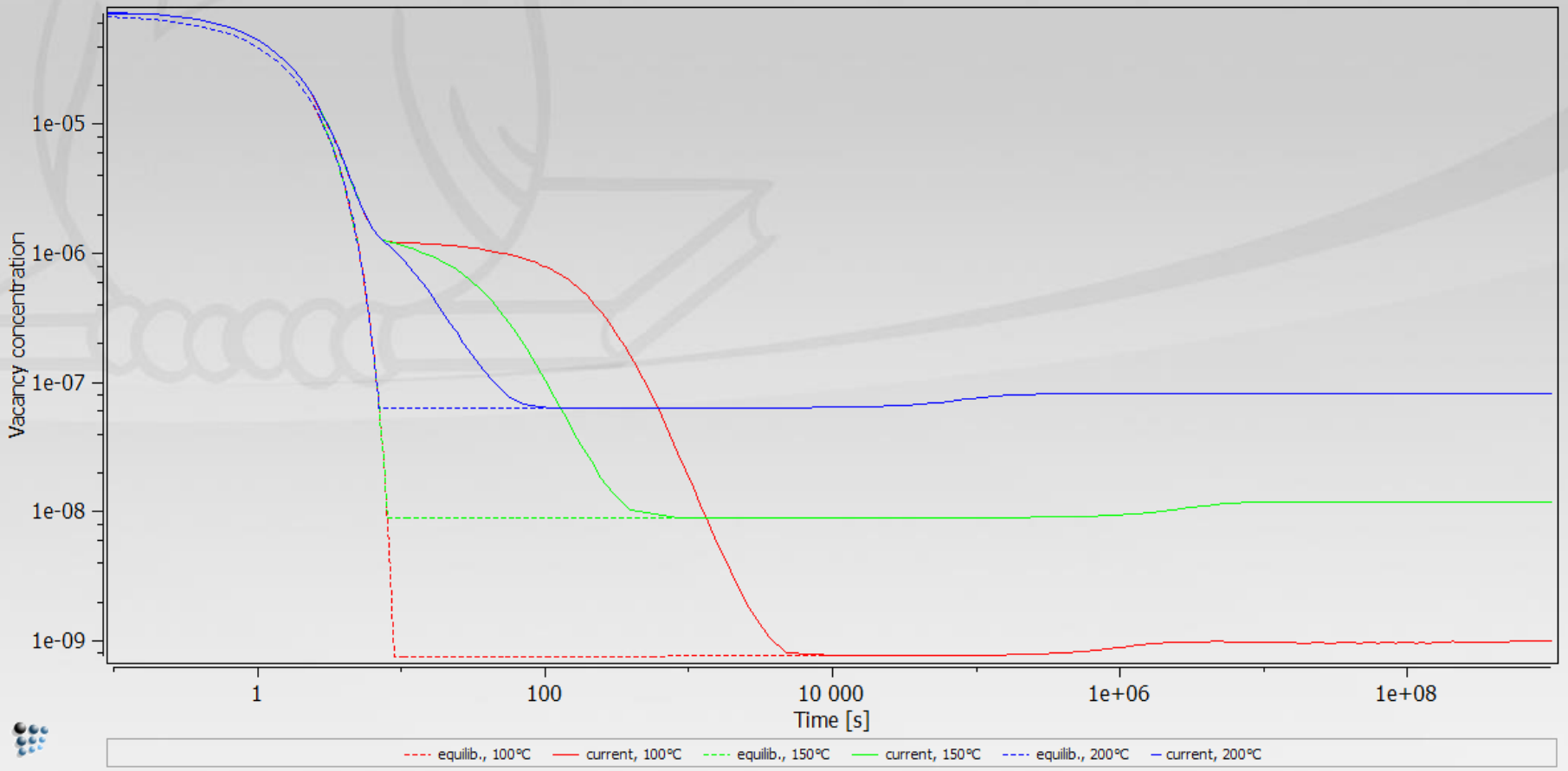




Examples

MatCalc Engineering

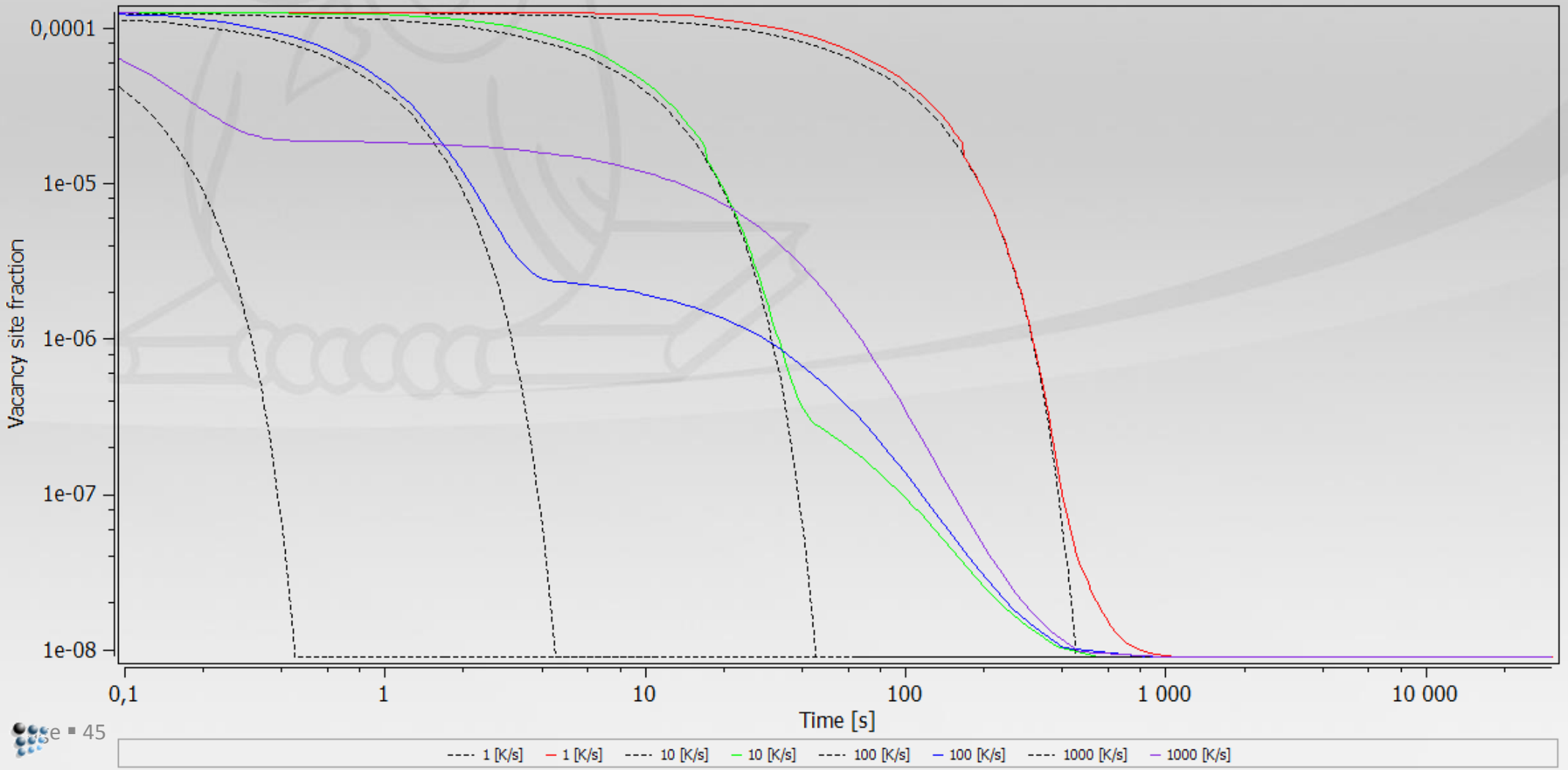
- Al-Cu system (Example P2-1)



Examples

MatCalc Engineering

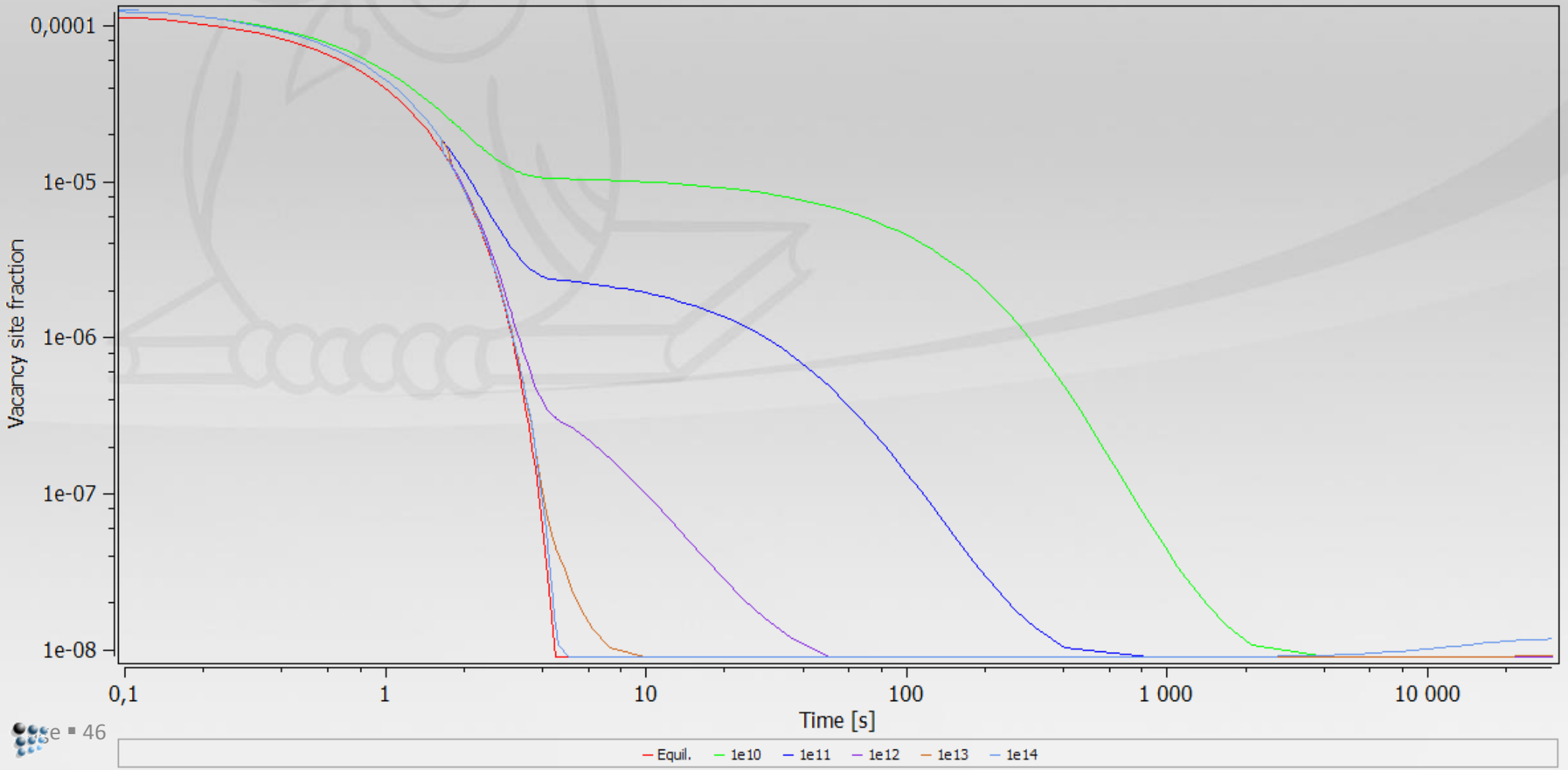
- Al-Cu system (Example P2-2), influence of cooling rate



Examples

MatCalc Engineering

- Al-Cu system (Example P2-2), influence of dislocation density



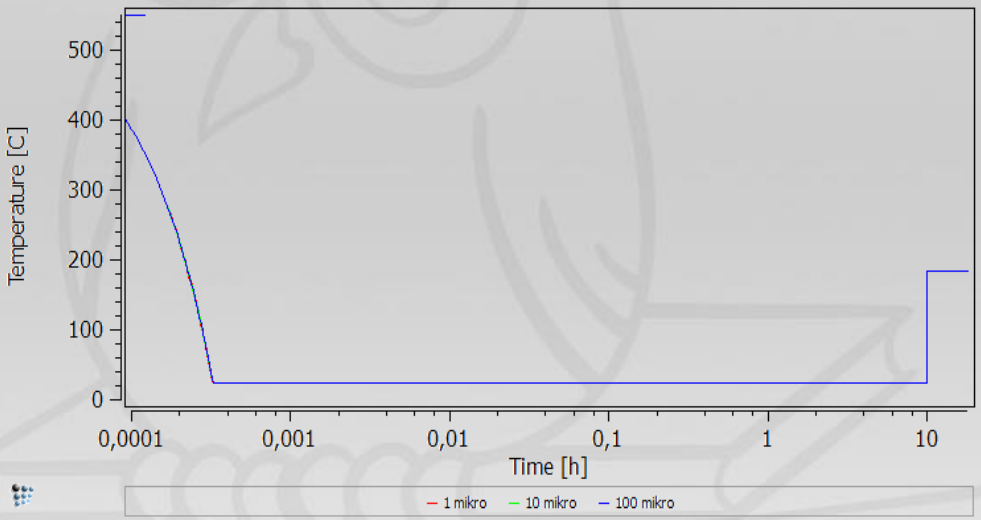
Examples

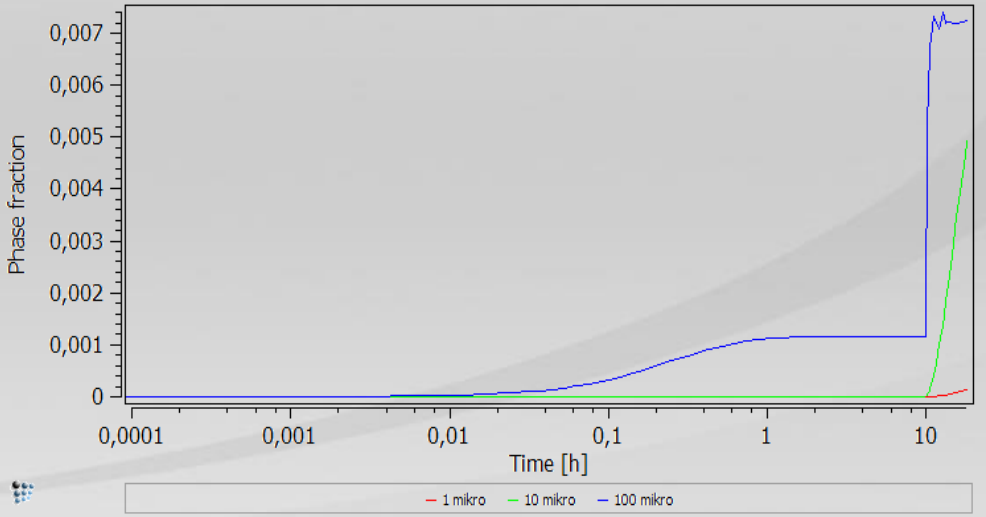
MatCalc Engineering

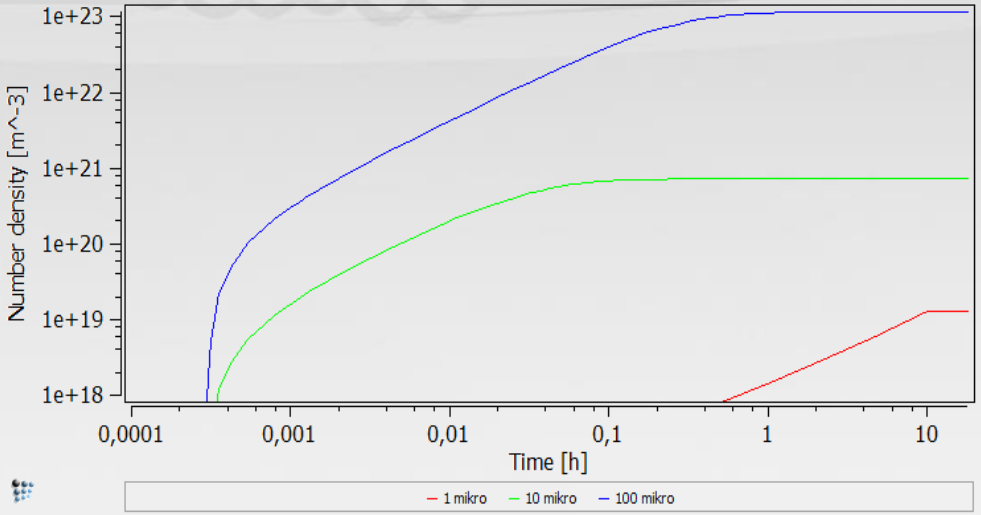
- System Al-Mg-Si
- Mg = 0,4 wt.%, Si = 1,1 wt.%
- Mg5Si6_B_DP-precipiate. Nucleates at bulk sites
- Al-fcc domain
- Trapping sites: Mg (2600 J/mol) and Si (3500 J/mol) solute atoms.
- FSAK model

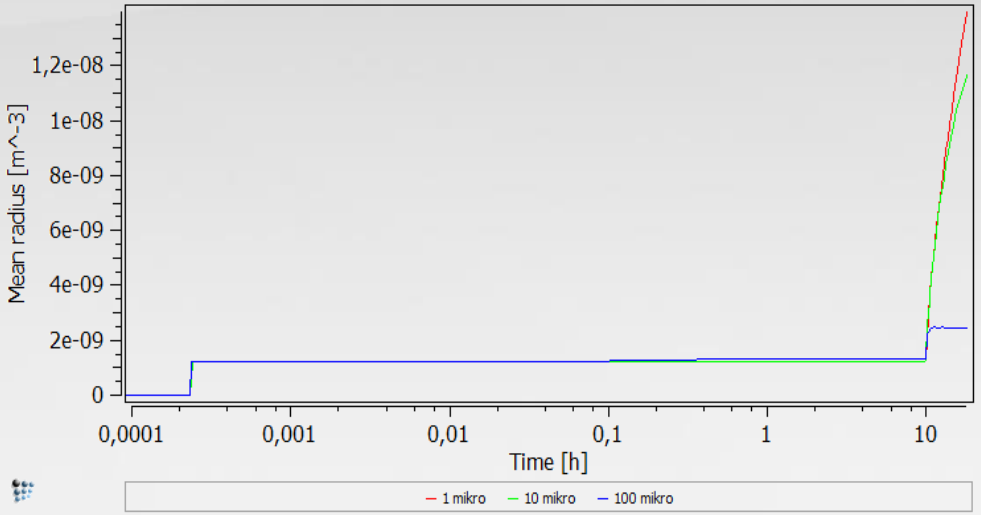
Examples

- Variation of grain size (FSAK)





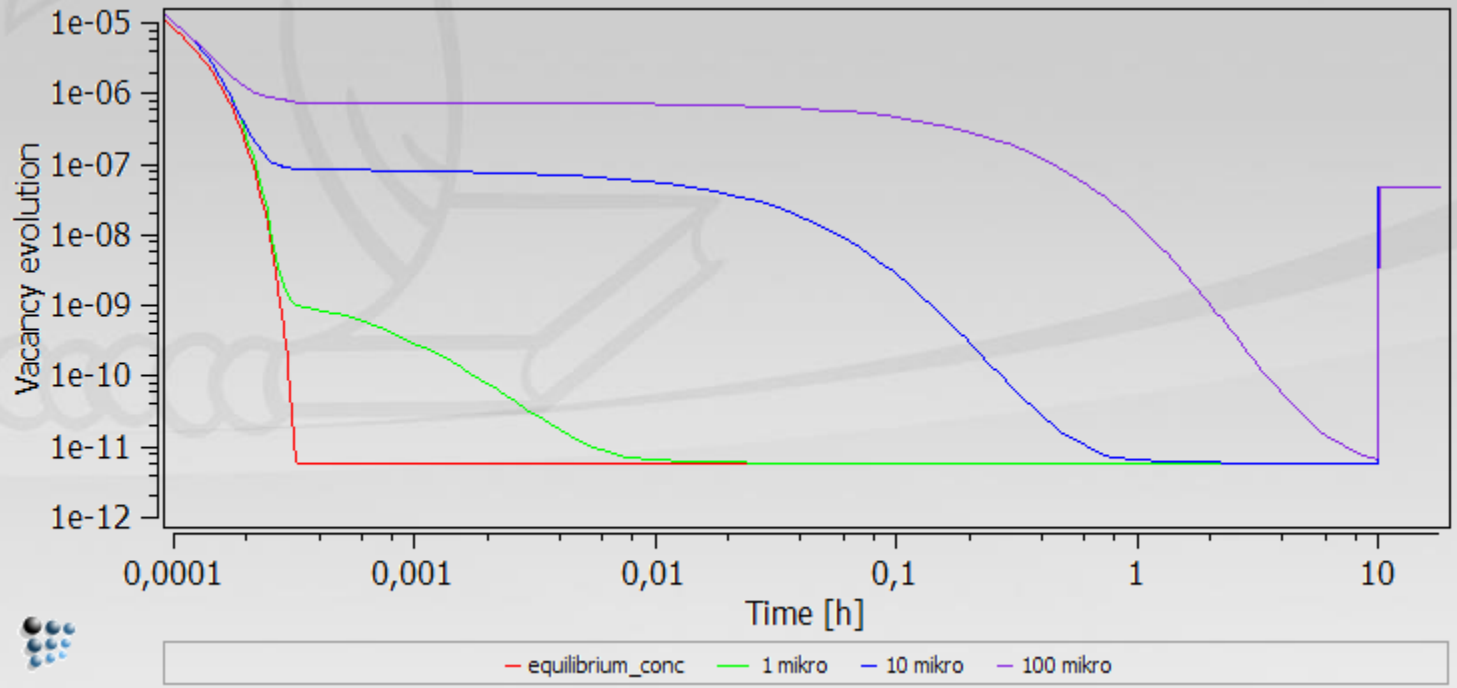




Examples

MatCalc Engineering

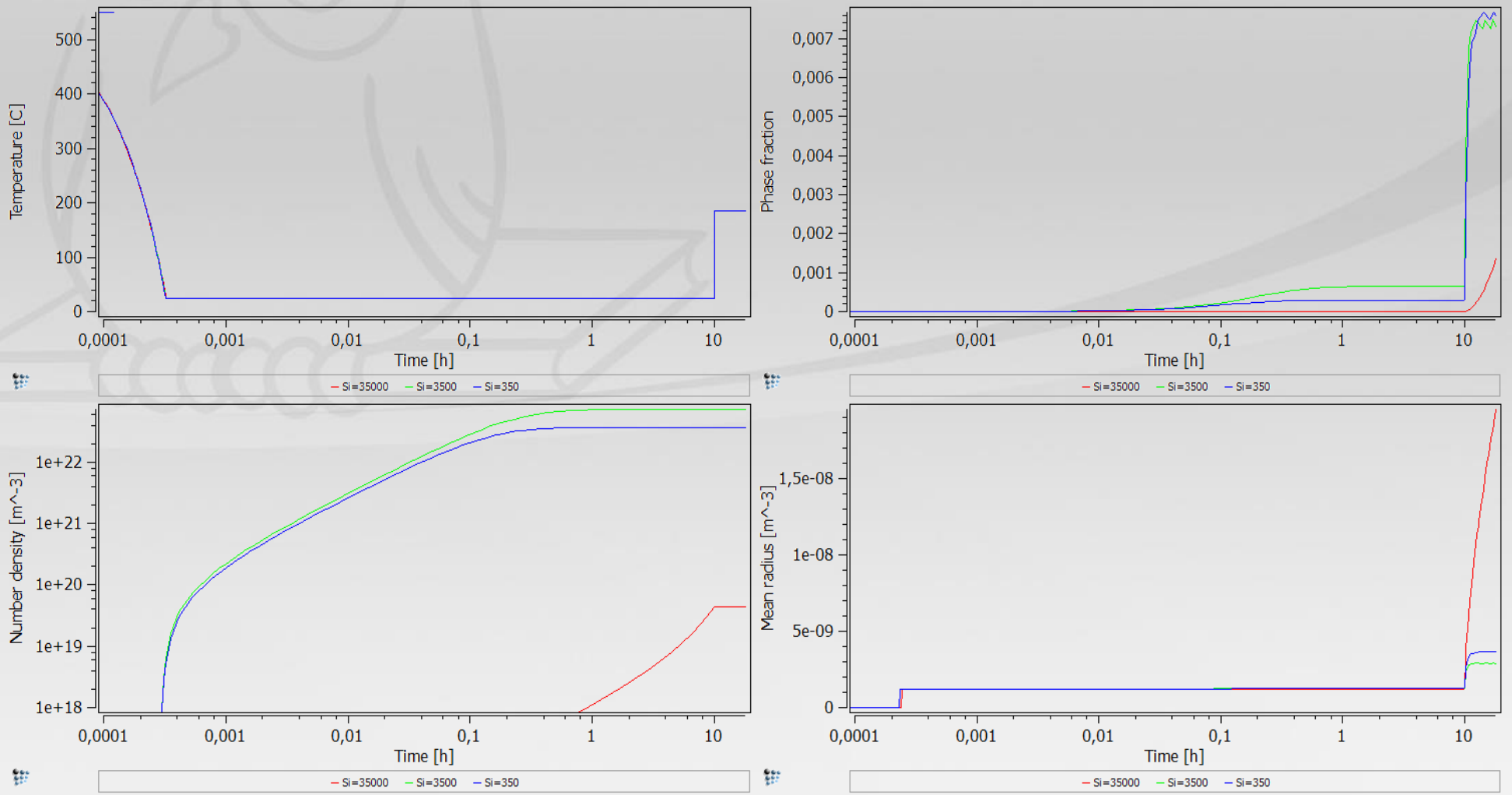
- Variation of grain size (FSAK)



Examples

MatCalc Engineering

- Variation of trapping enthalpy (FSAK)



Examples

MatCalc Engineering

- Variation of trapping enthalpy (FSAK)