

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?



• Real materials are not perfect crystals...





• Equilibrium vacancy concentration \rightarrow thermodynamics make them appear $H_{Va}^{f} = \sum y_{i} H_{Va,i}^{f}$





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Variables & Functions		<u>? ×</u>
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Available items < <all>> Element: SE(FCC A1) HMVA(FCC A1,AL:VA;0) G(FCC_A1,AL:VA;0) G(FCC_A1,AL:VA;0) G(FCC_A1,AL;VA;0) G(FCC_A1,AL,CU:VA;0) G(FCC_A1,AL,CU:VA;0) G(FCC_A1,AL,CU:VA;0) G(FCC_A1,AL,CU:VA;1) G(FCC_A1,AL,CU:VA;1) G(FCC_A1,AL,CU:VA;2) SE(THETA_AL2CU,AL:AL;0) G(THETA_AL2CU,AL:AL;0) G(THETA_AL2CU_P0,AL:AL;0) G(THETA_AL2CU_P0,AL:AL;0) G(THETA_AL2CU_P0,AL:AL;0) G(THETA_AL2CU_P0,AL:AL,CU;0) G(THETA_AL2CU_P0,AL:AL</all>	Name H*IVA(FCC_A1,AL:VA;0) Expression 273 +64163; 6000 N Current value AktVal_T: 64163, AktVal_F: 64070.7,	Rename ,,, Set
New Remove		Close



• Equilibrium vacancy concentration \rightarrow thermodynamics make them appear $H_{Va}^{f} = \sum y_{i} H_{Va,i}^{f}$

variables	value
kinetics: pd special □PX_SV_EQUIL\$*	
PX_SV_EQUIL\$alu	9.85079e-09

category: kinetics: pd special expression: PX_SV_EQUIL\$alu legal unit qualifiers: *none* -> equilibrium substitutional vacancy site fraction in precipitation domain

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



• Equilibrium vacancy concentration \rightarrow thermodynamics make them appear





• Equilibrium vacancy concentration \rightarrow thermodynamics make them appear





• Equilibrium vacancy concentration \rightarrow thermodynamics make them appear





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







Gege Critical nucleation energy

J – Nucleation rate





- 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)

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expression: NUCL_VADFM2\$THETA_AL2CU_P0 legal unit qualifiers: *none* -> mechanical misfit strain energy for nucleus

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



category: kinetics: nucleation expression: NUCL_VADFM2\$THETA_AL2CU_P0 legal unit gualifiers: *none* -> mechanical misfit strain energy for nucleus

Phase status ...

-Phases .

Phases	General Constraints Precipitate	Nucleation Nucl. sites Structure Special
FCC_A1 THETA_AL2CU	General	
THETA_AL2CU_P0	Nucleation model	Becker/Doering time-dep.
	Nucleus composition:	ortho-equilibrium Calc
	Nucleation constant:	1.0
	Incubation time constant:	1.0
	Minimum nucleation radius [m]	0.35e-9
	account for coherent misfit stress	🔽 ignore misfit stress during deformation
	☐ take into account shape factor	account for gb / disl. line energy
	account for excess va contribution	nucleate only with valid major constituents
	restrict nucleation to prec domain	





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



Precipitation Vacancies Diffusion kinetics Vacancy variables . value inetics: pd special XSV DCF\$* XSV DCF\$alu 6732.75 Ŧ category: kinetics: pd special expression: XSV_DCF\$alu http://www.doitpoms.ac.uk/tlplib/diffusion/diffusion_mechanism.php legal unit qualifiers: *none*

-> diffusion correction factor due to non-equilibrium substitutional vacancy concentration

Precipitation domains	2.1
Precipitation domains	General Mech. Props MS Evolution Solute trapping Special
alu	Grainstructure Substructure Vacancies Vacancy evolution model mean diffusion distance Substitutional diffusion ✓ consider excess SV excess vacancy efficiency (0-1) 1.0
	Vacancy annihilation and generation eff. loop line energy [J/m] ✓ auto from shear modulus (1/2Gb^2) jog fraction on dislocations 「 auto 0.02
	Frank loop nucl. constant 1.0 jog fraction on Frank loops 0.2 Mean vacancy diffusion distance
	automatic. Accelleration factor 1.0 manual. Mean diff. distance [m] 1.0e-8
New Remove	Vacancy diffusion Deformation-induced vacancy generation corr. factor 1.0 va gen. coeff
	Cancel OK

MatCalc Engineering

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

variables	value	•
E kinetics: pd special		
L XSV_DCF\$* ∴ XSV_DCF\$alu	6732.75	-
category: kinetics: pd special expression: XSV_DCF\$alu legal unit qualifiers: *none* -> diffusion correction factor due to non-equilibrium substitutional vacancy concentration		



Sources and sinks



• Equilibrium \rightarrow Generation rate at source = Anihilation rate at sink



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	Precipitation domains	General Mech. Props MS Evolution Solute trapping Special
3 models in MatCalc:		Grainstructure Substructure Vacancies Vacancy evolution model no vacancy annihilation/generation Substitutional diffusion mean diffusion distance Set unsame Set unsame
 Mean diffusion distance "FSAK"* model 		✓ consider excess SV PSAK vacancy dynamics Vacancy annihilation and generation eff. loop line energy [J/m] ✓ auto from shear modulus (1/2Gb^2)
 Vacancy generation during the deformation (with ESAK only) 		jog fraction on dislocations 1.0 jog fraction on Frank loops 0.2 Frank loop nucl. constant 1.0 jog fraction on Frank loops 0.2 Mean vacancy diffusion distance Image: Constant fractor 1.0 Image: Constant fractor 1.0 Image: Constant fractor 1.0
deformation (with FSAK only!)	New Remove	Vacancy diffusion Deformation-induced vacancy generation va gen. coeff 1.0
	Rename	Cancel OK

Precipitation domains ...

* "Fischer-Svoboda-Appel-Kozeschnik", Fischer et. al., Acta Mater. 59 (2011) 3463-3472 Page = 19

Mean diffusion distance

• Evolution equation:

- Dislocations are taken as a vacancy source/sink
- Default mean diffusion distance:
 - $a = 10^{(-0.5log(\rho))}$

- a Mean diffusion distance
 - ρ Dislocation density

C - Constant

 y_i - Element subst. site fraction

$$\Delta y_{Va}(\Delta t) = C \left[1 - exp\left(-\frac{D\Delta t}{a}\right) \right] \left(y_{Va,eq} - y_{Va} \right)$$
Page = 20

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

$$D = \left(\frac{y_{Va}}{y_{Va} ea}\right) \sum y_i D_i$$

MatCalc Engineering

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

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



• Evolution equation:

$$\Delta y_{Va}(\Delta t) = C \left[1 - exp\left(-\frac{D\Delta t}{a}\right) \right] \left(y_{Va,eq} - y_{Va} \right)$$
Page = 21

$$\mathbf{D} = \left(\frac{y_{Va}}{y_{Va,eq}}\right) \sum_{i} y_i D_i$$





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

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

• Evolution equation

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



$$\mathbf{D} = \left(\frac{y_{Va}}{y_{Va,eq}}\right) \sum_{i} y_{i} D_{i}$$

- 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)

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- *b* Burger's vector
- H Jog density
- x_{jog} Jog fraction on dislocations



• FSAK: Generation/anihilation on dislocation jogs

Precipi Precipi

• Evolution equation:

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

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

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n domains	
lomains	General Mech. Props MS Evolution Solute transing Special
	Grainstructure Substructure Vacancies
	Vacancy evolution model ESAK vacancy dynamics
	Substitutional diffusion
	✓ consider excess SV excess vacancy efficiency (0-1) 1.0
	Vacancy annihilation and generation
	eff. loop line energy [J/m] 🔽 auto from shear modulus (1/2Gb^2)
	Frank loop nucl. constant 1.0 jog fraction on Frank loops 0.2
	Mean vacancy diffusion distance
	automatic Accelleration factor 1.0
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- FSAK: Generation/anihilation on dislocation jogs
- Evolution equation:

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

Precipitation domains General Mech. Props MS Evolution Solute trapping Special Thermodynamic matrix phase FCC A1
Microstructure parameters equilibrium dislocation density [m-2] 1.0e11 excess dislocation density [m-2] 0 grain diameter [m] 100e-6 elongation factor subgrain diameter [m] 1e-6 Burger's vector
New Remove Rename



- 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)



Precipitation dom • FSAK: Generation/anihilation Precipitation domains alu • Evolution equation: $\Delta y_{Va}^{GB}(\Delta t) = -\frac{15D}{f} \frac{y_{Va}}{y_{Va,eq}} ln\left(\frac{y_{Va}}{y_{Va,eq}}\right) R^{-2}$ New

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	General Mech. Props MS Evolution Solute trapping Special]
	FCC_A1	
	equilibrium dislocation density [m-2]	=
	grain diameter [m] 100e-6 elongation factor 1	=
	subgrain diameter [m] 1e-6 elongation factor 1 Burger's vector	
	automatic manual value [m] 2.5e-10	
nove		
me		
	Cancel	ок



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

$$\Delta y_{Va}^{FL}(\Delta t) = -\frac{4\pi^2 D}{f} \frac{y_{Va}}{y_{Va,eq}} \left[ln \left(\frac{y_{Va}}{y_{Va,eq}} \right) - \frac{b^2 \gamma_L}{r_{FL} k_B T} \right] \frac{N_{FL} r_{FL}}{n_P} \qquad n_P = \left(x_{jog,FL} \right)^{-1}$$

 γ_L - Effective loop energy

- r_{FL} Frank loop radius (defined in the console)
- N_{FL} Frank loop density (defined in the console) Page = 28

 n_P - Jog spacing on Frank loops (number of atoms) $x_{jog,FL}$ - Jog fraction on Frank loops k_B - Boltzmann constant



- FSAK: Generation/anihilation on Frank loops (test-phase?)
- Evolution equation: $\Delta y_{Va}^{FL}(\Delta t)$ $= -\frac{4\pi^2 D}{f} \frac{y_{Va}}{y_{Va,eq}} \left[ln \left(\frac{y_{Va}}{y_{Va,eq}} \right) - \frac{b^2 \gamma_L}{r_{FL} k_B T} \right] \frac{N_{FL} r_{FL}}{n_P}$ $n_P = \left(x_{jog,FL}\right)^{-1}$

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	Vacancy annihilation and generation	
	eff. loop line energy [J/m] 🔽 auto from shear modulus (1/2Gb^2)	
	jog fraction on dislocations auto 0.02	
	Frank loop nucl. constant 1.0 jog fraction on Frank loops 0.2 Mean vacancy diffusion distance	
	automatic. Accelleration factor 1.0 manual. Mean diff. distance [m] 1.0e-8	
New Remove	Vacancy diffusion Deformation-induced vacancy generation . corr. factor 1.0 va gen. coeff 1.0	
Rename		
	Cancel C	ж



- Vacancy generation during the deformation
- Evolution equation:

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

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



- α Constant
- *M* Taylor factor
- G Shear modulus
- $\dot{\mathcal{E}}$ Strain rate



X

- Vacancy generation during the deformation
- Evolution equation

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

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	Vacancy diffusionDeformation-induced vacancy generation	
New Remove	corr. factor 1.0 va gen. coeff 1.0	
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- 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



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





• Possible traps

Trapping site	Fraction of trapping sites
Solute atoms	x _i
Dislocations	$\pi r_{dc}^2 ho$
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_i - Number of precipitates in class "j" r_i - Radius of precipitates in class "j" V_{at} - Atomic volume

Trap "strength":

delta H

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

 ΔH - Trapping enthalpy

• Trap "range" modifier:

coordination number

recipitation domains	General	Me	ech. Props MS Ev	olution Solute tra	apping Special	
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	0	act.	sv	DISL	deita H [J/mol] 5000	coord. num. 12
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- The amount of traps
 - Amount of lattice sites \rightarrow expressed by molar volumes

 n_{tot} - Total number of lattice sites

 $n_{tot} = n_L + n_T$

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

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

- n_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

Svoboda J., Fischer F.D., Acta Mater. 60 (2012) 1211-1220



- The amount of traps
 - Amount of lattice sites \rightarrow

 $n_{tot} = n_L + n_T$

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

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

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.
- $V_{m,i}$ <u>IS NOT</u> the volume of 1 mole of *"i"*-sites! \rightarrow The material does not consist of *"i"*-sites alone

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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)

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



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:

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

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

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- 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



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





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





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



• Al-Cu system (Example P2-1)

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

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

- 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.

MatCalc

Engineering

• FSAK model

• Variation of grain size (FSAK)

• Variation of grain size (FSAK)

• Variation of trapping enthalpy (FSAK)

• Variation of trapping enthalpy (FSAK)

