RWTH AACHEN UNIVERSITY

The ALLEE project – Linking thermodynamics and diffusion with materials properties

V. Mohles

Institute of Physical Metallurgy and Metal Physics

GTT user meeting, Herzogenrath, 2. - 4. 7. 2014

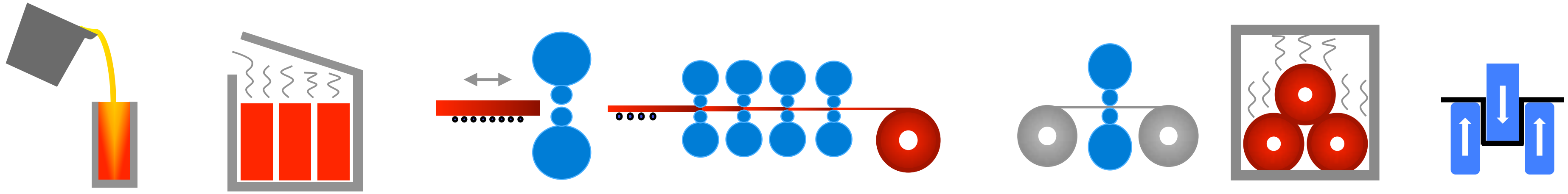
Overview

::: ClaNG model

::: ALLEE project

Through process modelling

casting | homogenisation | break-down + hot rolling | cold rolling + annealing | forming



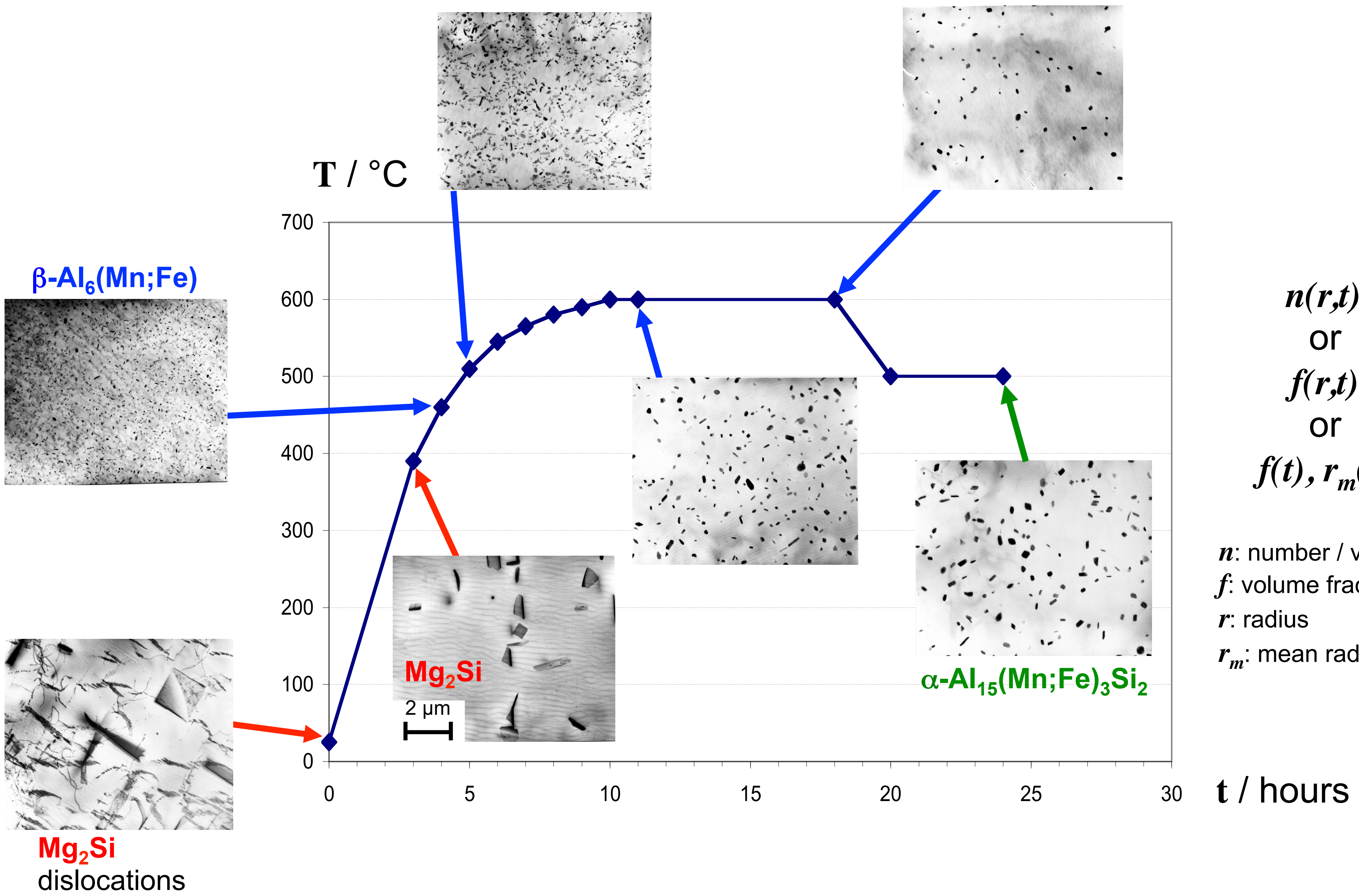
partial dissolution
of constituents

precipitation

precipitation,
dissolution
with dislocations

recrystallisation

Homogenisation AA3104



$n(r,t)$

or

$f(r,t)$

or

$f(t), r_m(t)$

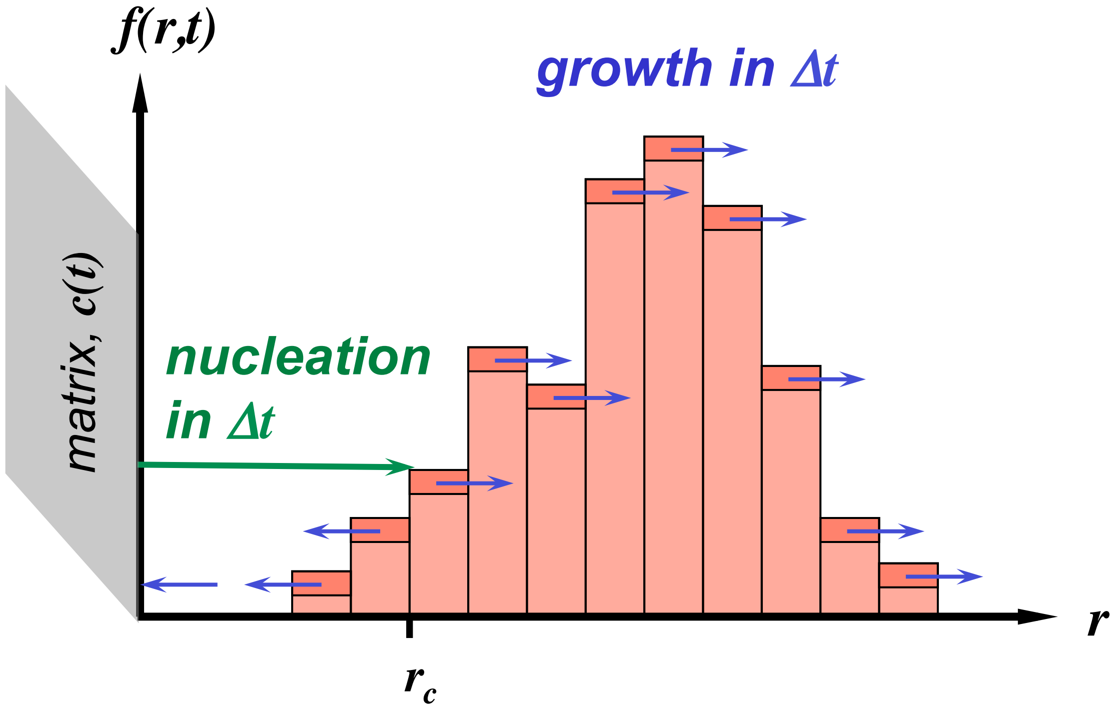
n: number / volume

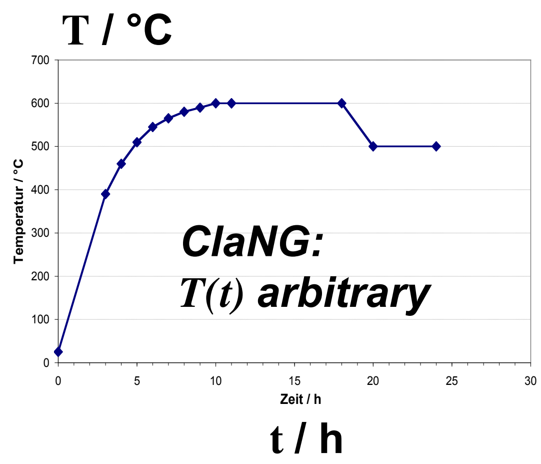
f: volume fraction

r: radius

r_m: mean radius

Statistical precipitation: ClaNG



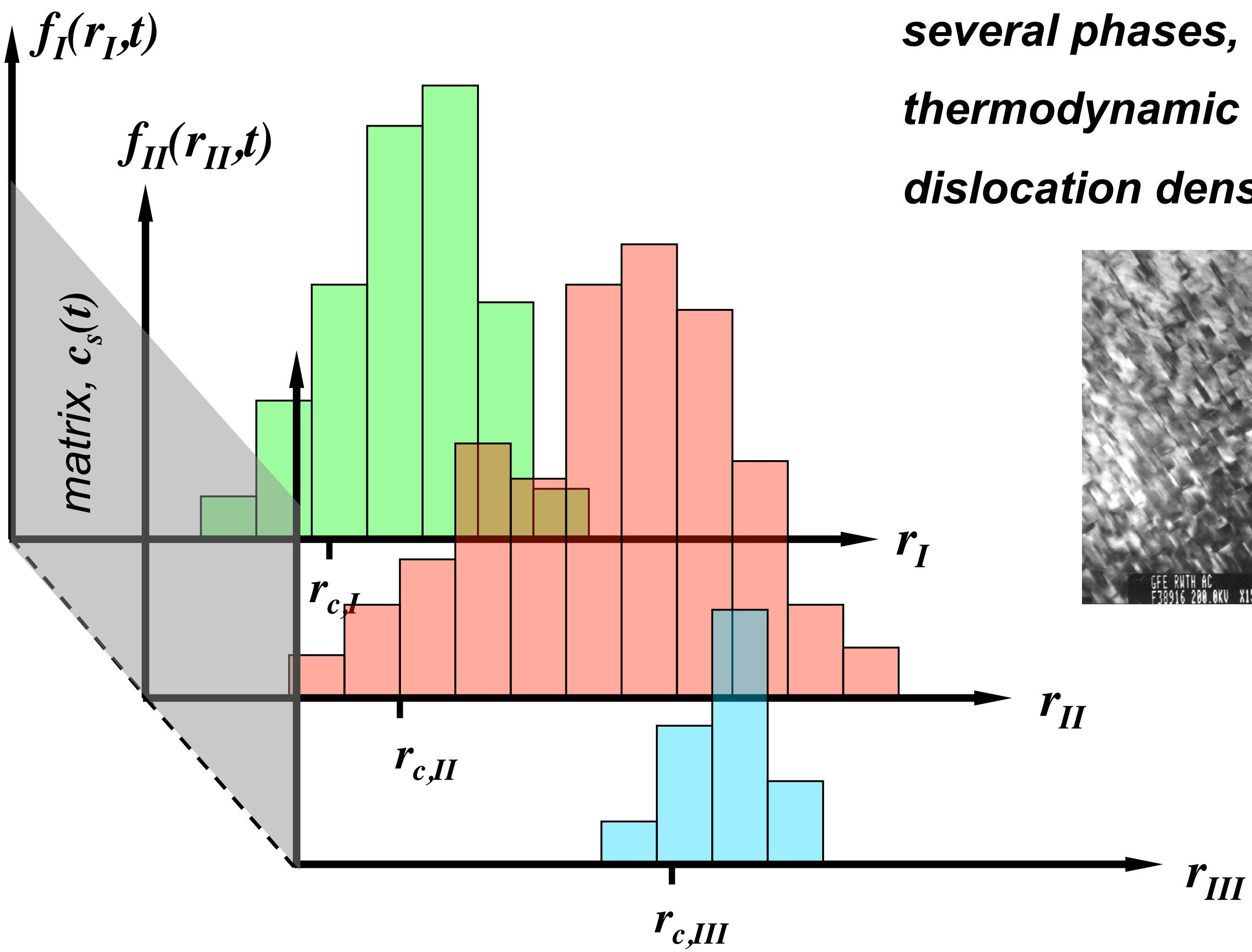


generalized ansatz of Lifshitz, Slyozov; Wagner

nucleation rate dN/dt

general temperature curve $T(t)$ relevant for application

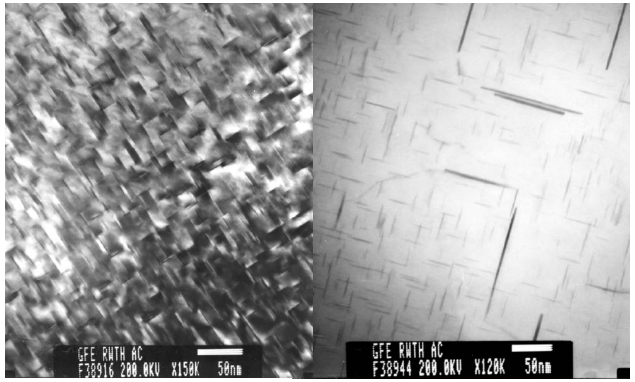
Statistical precipitation: ClaNG



several phases, e.g. α, β, Mg_2Si

thermodynamic data from database

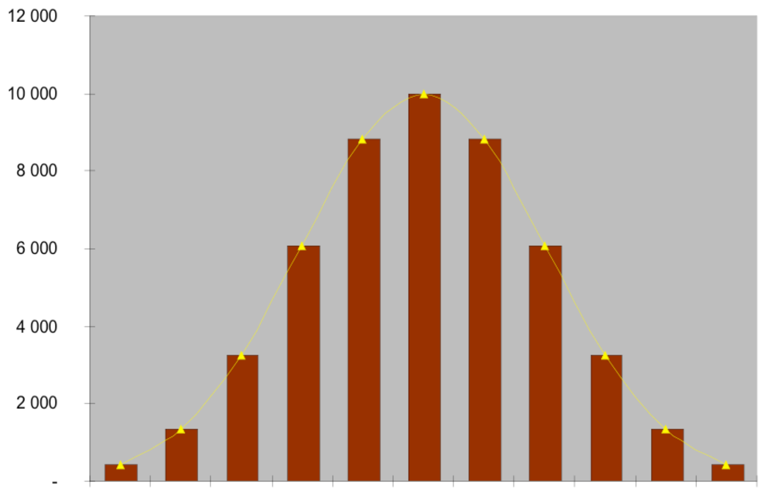
dislocation density ρ considered

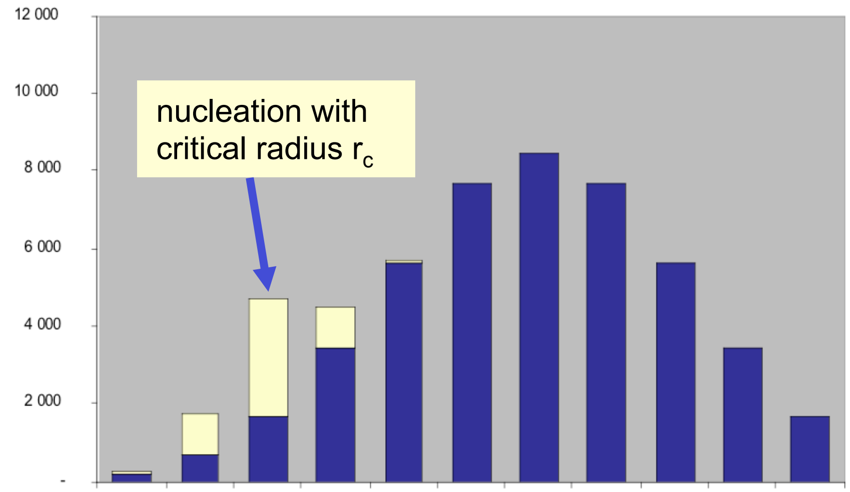


0% def. 8% def.

several specific phases I, II, III, ... considered

Continuity / material conservation



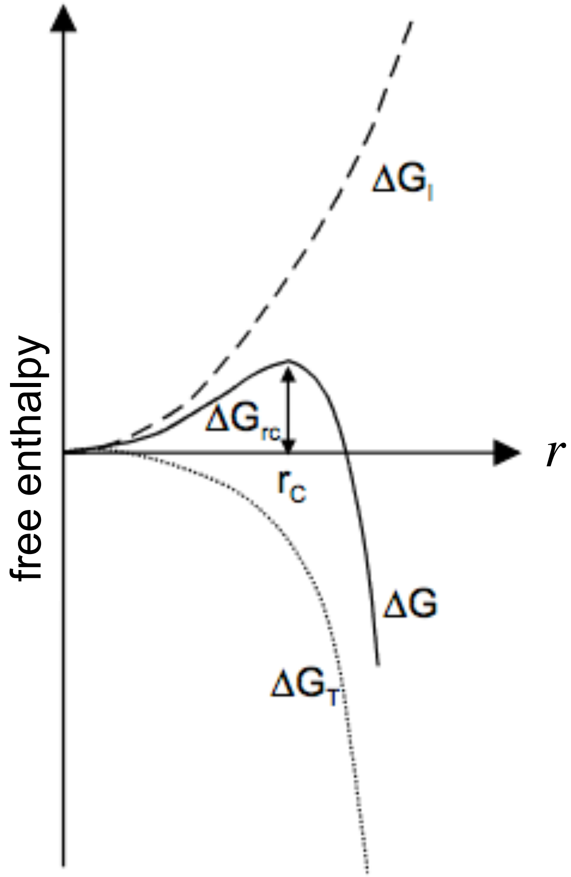


$$\frac{\partial f(r,t)}{\partial t} + \underbrace{\frac{\partial}{\partial r}\left(\dot{r} \cdot f(r,t)\right)}_{\dot{r} \cdot \frac{\partial f(r,t)}{\partial r} + \frac{\partial \dot{r}}{\partial r} \cdot f(r,t)} = \dot{N}(t)$$

solved numerically with formulations for nucleation rate $\dot{N}$
and growth law $\dot{r}$

Nucleation

nucleation radius: from $Max\left(-\Delta G_T(r) + \Delta G_i(r) + \Delta G_{elast}(r) \right)$



$$r_c = \frac{2\sigma_{nucl}}{\Delta g_T - \varepsilon_{elast}} \approx K \frac{2\sigma}{\Delta g_T}$$

ChemApp GTT

$$\Delta g_T = g_{nucl}(\underline{c}_{nucl}) - g_{matrix}(\underline{c}_{matrix})$$

σ = interface energy at $r \to \infty$

σ_{nucl} = interface energy at $r = r_c$

ε_{elast} = elastic energy

K - fit parameter accounting for σ_n / σ and ε_{el}

Nucleation

nucleation rate : $\dot{N}_{\text{total}} = \dot{N}_{\text{hom}} + \dot{N}_{\text{het}}$

$$\dot{N}(t) = N_0 \, \beta \, \exp\left(-\frac{\Delta G(r_c)}{kT}\right)$$

N_0 - site density

$N_{0,\text{hom}}$: all atoms that can form precipitates

$N_{0,\text{het}}$: $\rho^{3/2}/2$ with ρ: dislocation density

β - atomic attachment rate $\beta = Min\left(4\pi r_c^2 \, D(T) \, c(t) \, \lambda^{-4} \right)$

D - bulk/pipe diffusion coefficient

λ - lattice parameter

Nucleation

nucleation rate : $\dot{N}_{\text{total}} = \dot{N}_{\text{hom}} + \dot{N}_{\text{het}}$

$$\dot{N}(t) = N_0 \; \beta \; \exp\left(-\frac{\Delta G(r_c)}{kT} \right) \cdot Z$$

N_0 - site density

$N_{0,\text{hom}}$: all atoms that can form precipitates

$N_{0,\text{het}}$: $\rho^{3/2}/2$ with ρ: dislocation density

β - atomic attachment rate $\beta = Min\left(4\pi r_c^2 \; D(T) \; c(t) \; \lambda^{-4} \right)$

D - bulk/pipe diffusion coefficient

λ - lattice parameter

Z - Zeldovich non-equilibrium factor $Z = \sqrt{\dfrac{\Delta G(r_c)}{3\pi kT \cdot (n_{\text{in nucleus}}^{\text{atoms}})^2}}$

Nucleation

nucleation rate : $\dot{N}_{\text{total}} = \dot{N}_{\text{hom}} + \dot{N}_{\text{het}}$

$$\dot{N}(t) = N_0 \, \beta \, \exp\left(-\frac{\Delta G(r_c)}{kT}\right) \cdot Z \cdot \exp\left(-\frac{\tau}{\Delta t}\right)$$

$\tau = \beta^{-1} Z^{-2}$

N_0 - site density

$N_{0,\text{hom}}$: all atoms that can form precipitates

$N_{0,\text{het}}$: $\rho^{3/2}/2$ with ρ: dislocation density

β - atomic attachment rate $\beta = Min\left(4\pi r_c^2 \; D(T) \; c(t) \; \lambda^{-4} \right)$

D - bulk/pipe diffusion coefficient

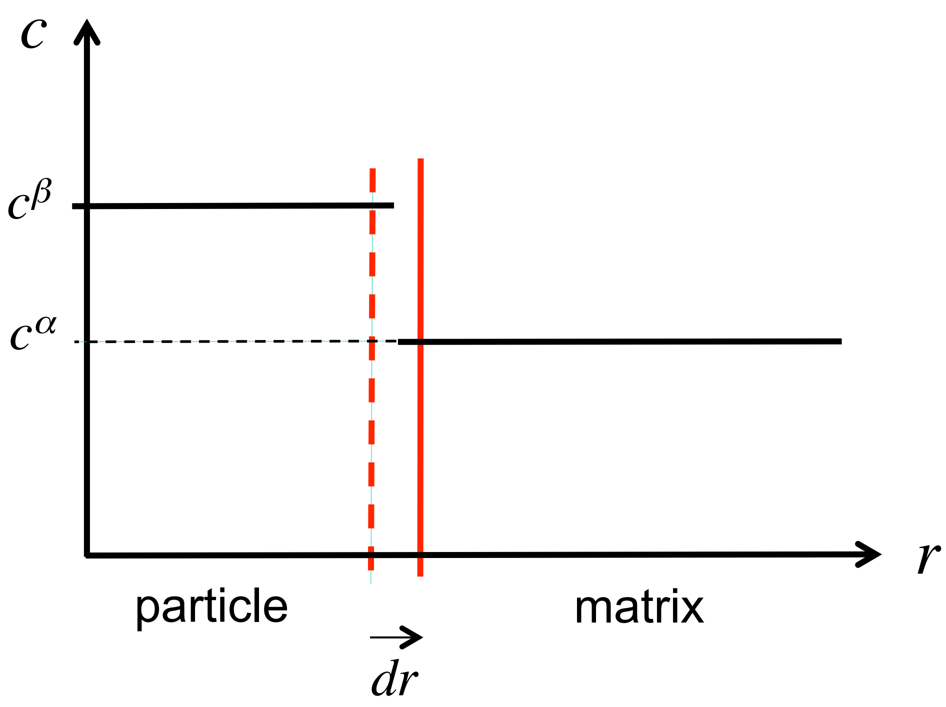
λ - lattice parameter

Z - Zeldovich non-equilibrium factor $Z = \sqrt{\dfrac{\Delta G(r_c)}{3\pi kT \cdot (n_{\text{in nucleus}}^{\text{atoms}})^2}}$

τ - incubation time to attain stable nucleation

Δt - time after phase reaches stability

Growth, ripening



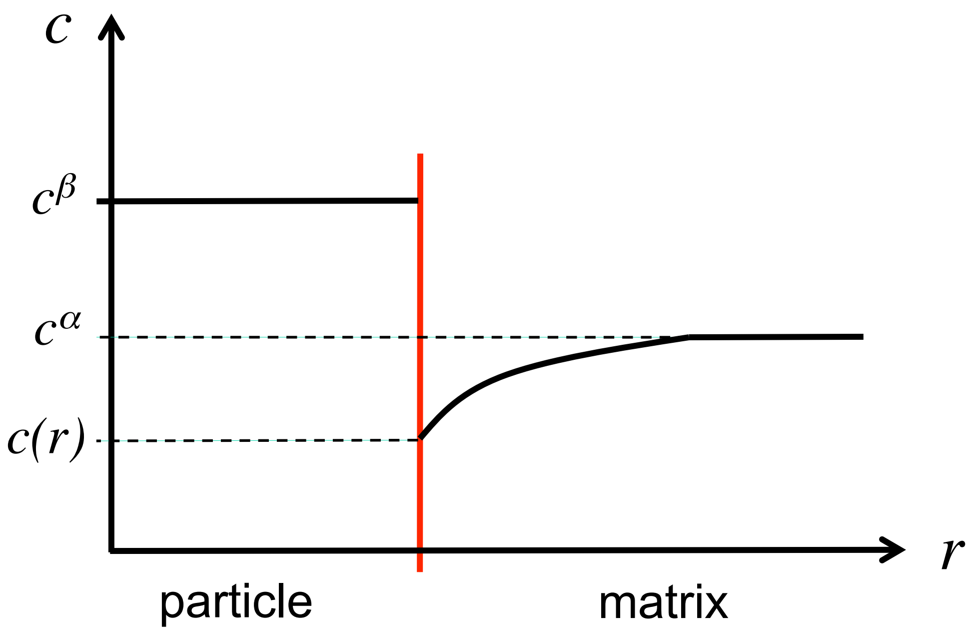
$$\left(c^\beta - c^\alpha\right) dr = j \, dt$$

c^α = atom density in matrix α

c^β = atom density in phase β

j = atoms current density

Growth, ripening



$$4\pi r^2 \left(c^\beta - c(r)\right) \frac{dr}{dt} = J$$

c^α = atom density in matrix α

c^β = atom density in phase β

J = atom current to be provided

atom current provided:

$$J = 4\pi R^2 \, D \left.\frac{dc}{dR}\right|_R \quad \Rightarrow$$

Zener's growth law for *binary* alloys:

$$\frac{dr}{dt} = \frac{D}{r} \frac{c^\alpha - c(r)}{c^\beta - c(r)}$$

Growth, ripening

Gibbs-Thomson concentration at the interface:

$$c_i^{\alpha/\beta}(r) = c_i^{\alpha/\beta}(\infty) \cdot \exp\left(\frac{2\sigma V_a}{r \cdot kT}\right)$$

$$\underbrace{\frac{2\sigma V_a}{r}}_{\text{Gibbs energy enhancement of the particle}} = \underbrace{kT \ln\left(\frac{c_i^{\alpha/\beta}(r)}{c_i^{\alpha/\beta}(r \to \infty)}\right)}_{\text{Gibbs energy enhancement in the matrix}}$$

Gibbs energy enhancement of the particle

Gibbs energy enhancement in the matrix

$$\left.\begin{aligned} \frac{2\sigma V_a}{r} &= \sum_i c_i^{\beta} \cdot kT \ln\left(\frac{c_i^{\alpha/\beta}(r)}{c_i^{\alpha/\beta}(r \to \infty)}\right) \\ c_i^{\alpha} &= (1 - f(r))\, c_i^{\alpha/\beta}(r) + f(r)\, c_i^{\beta} \end{aligned}\right\} \frac{2\sigma V_a}{r} = \sum_i c_i^{\beta} \cdot kT \ln\left(\frac{1 - f(r)\dfrac{c_i^{\beta}}{c_i^{\alpha}}}{1 - f(r)}\right)$$

Growth, ripening

$$\frac{2\sigma V_a}{r} + \Delta g_T = \sum_i c_i^\beta \cdot kT \ln\left(\frac{1-f(r)\frac{c_i^\beta}{c_i^\alpha}}{1-f(r)}\right)$$

fitted function: $h = 1-(r_c/r)^a$

numerically resolved for $f(r)$: $$f(r) = f_{\max}\cdot h(r/r_c) \qquad f_{\max} = \frac{c_i^\alpha - c_i^{\alpha/\beta}(\infty)}{c_i^\beta - c_i^{\alpha/\beta}(\infty)}$$

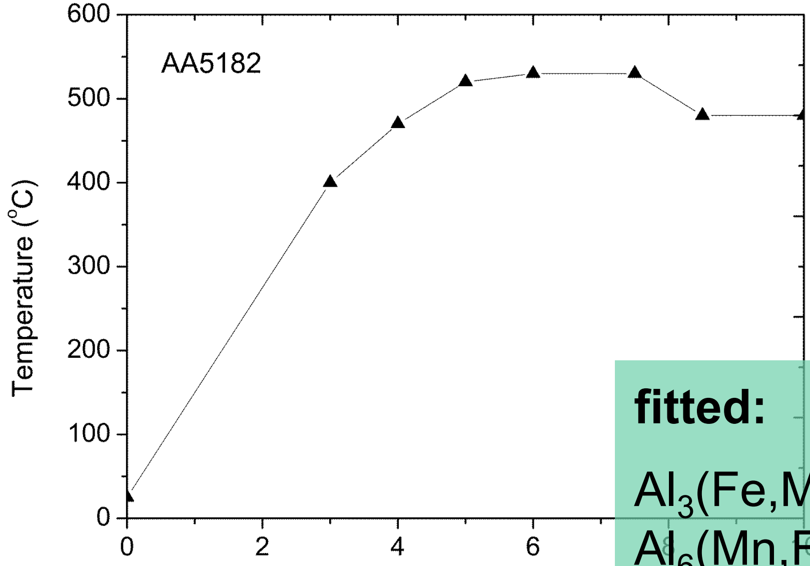
from mass conservation: $$f(r) = \frac{c_i^\alpha - c_i^{\alpha/\beta}(r)}{c_i^\beta - c_i^{\alpha/\beta}(r)}$$

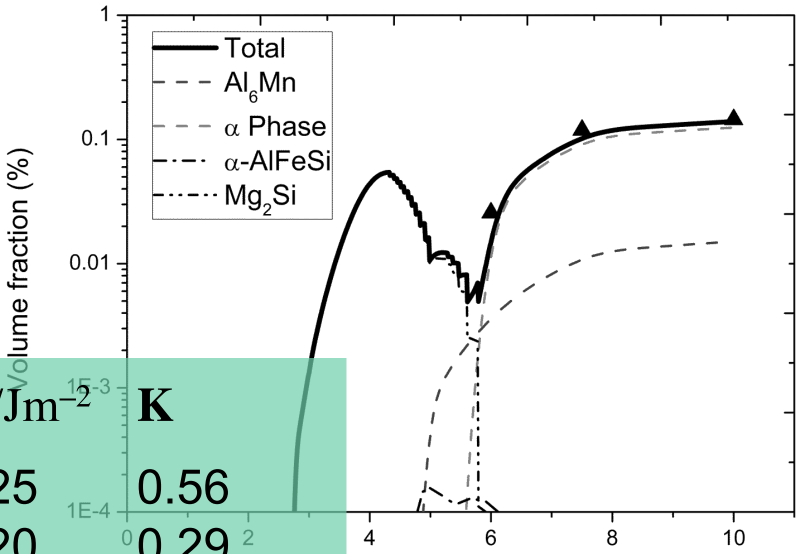
compare with Zener's law: $$\frac{dr}{dt} = \frac{c^\alpha - c^{\alpha/\beta}(r)}{c^\beta - c^{\alpha/\beta}(r)}\,\frac{D}{r}$$

$\Rightarrow$ growth law: $$\frac{dr}{dt} = \frac{D}{r} f(r) = \frac{D}{r} f_{\max}\; h(r/r_c)$$

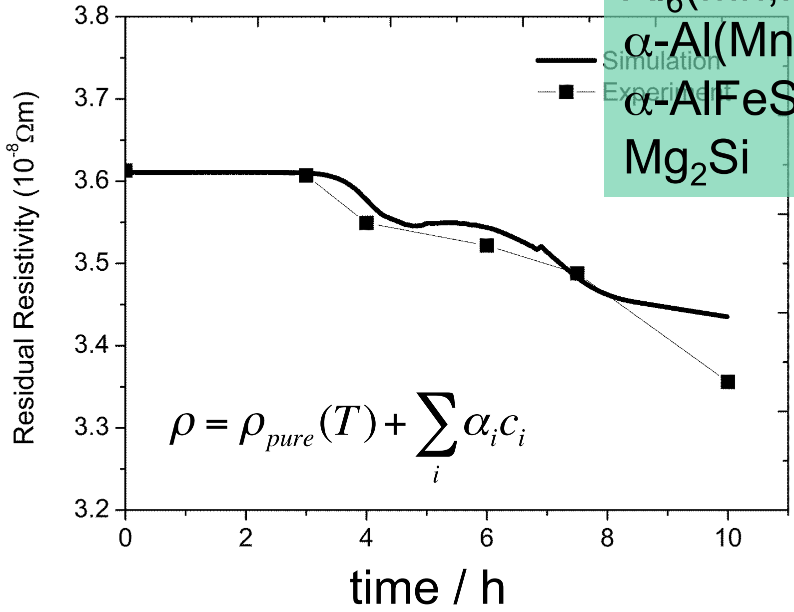
with $$D = Min\left(D_i^{bulk}(T) + (\rho/\rho_0) D_i^{pipe}(T)\right)$$

ClaNG+, AA5182: calibration

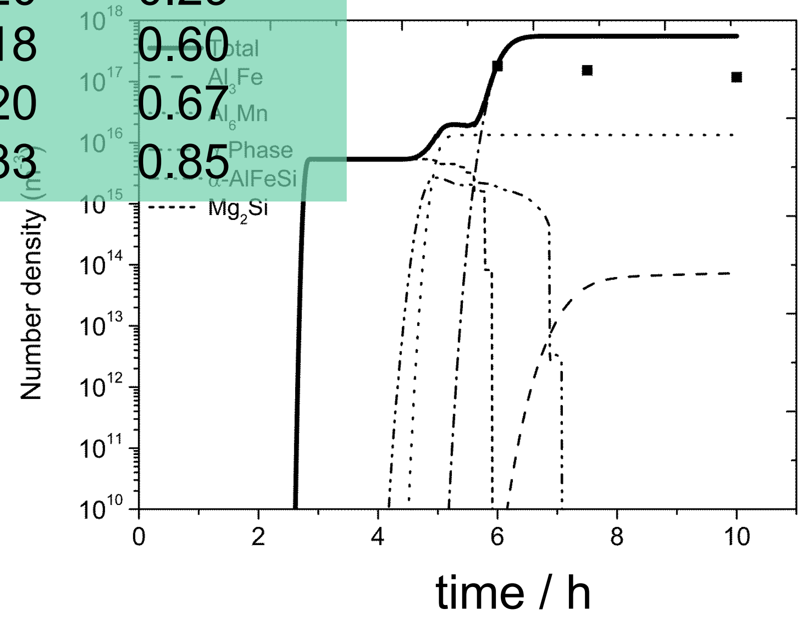




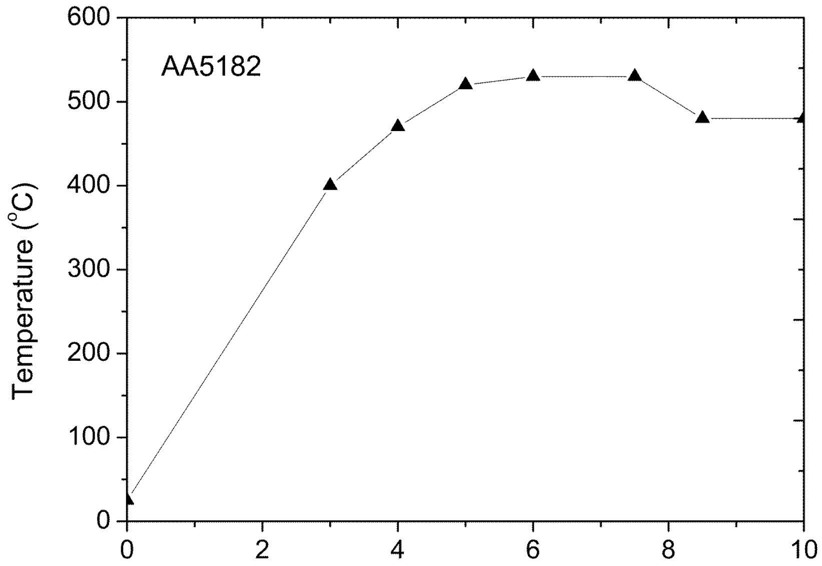
fitted:	σ /Jm^{-2}	K
$Al_3(Fe,Mn)$	0.25	0.56
$Al_6(Mn,Fe)$	0.20	0.29
α-Al(Mn,Fe)Si	0.18	0.60
α-AlFeSi	0.20	0.67
Mg_2Si	0.33	0.85

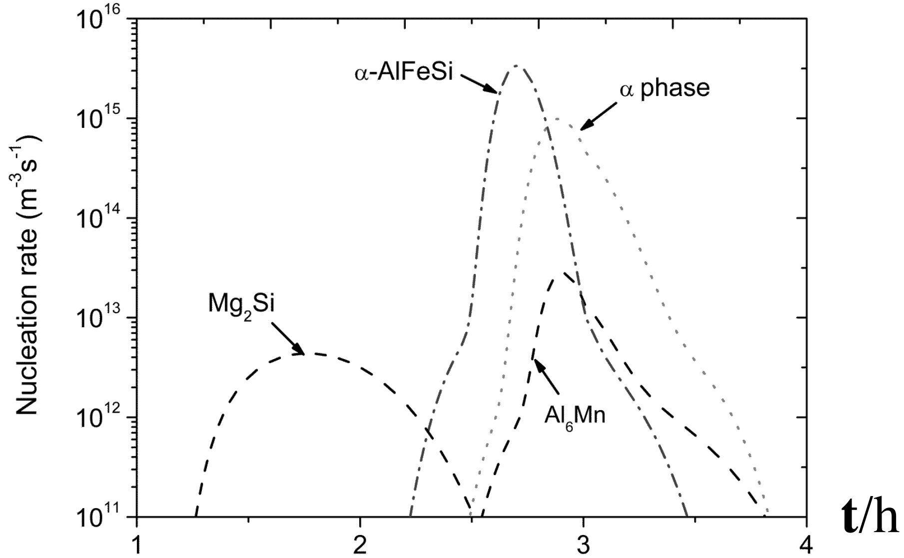


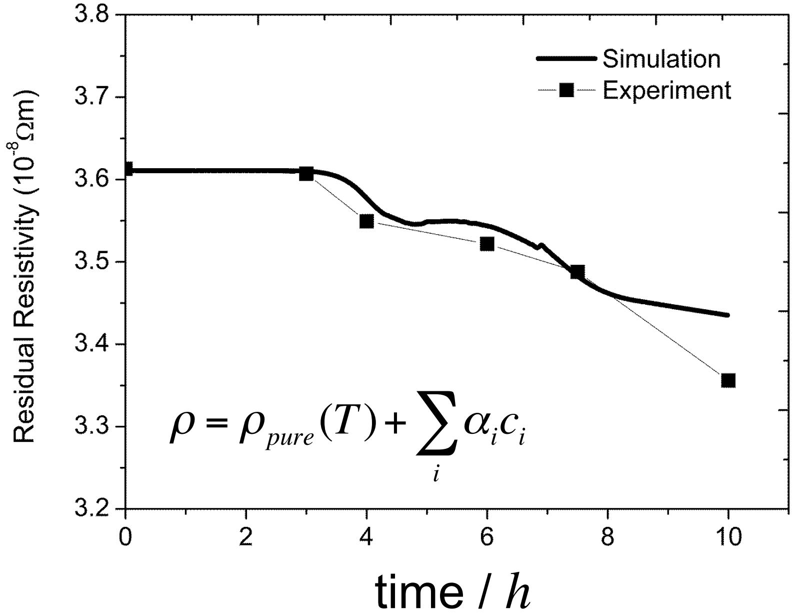
$$\rho = \rho_{pure}(T) + \sum_i \alpha_i c_i$$

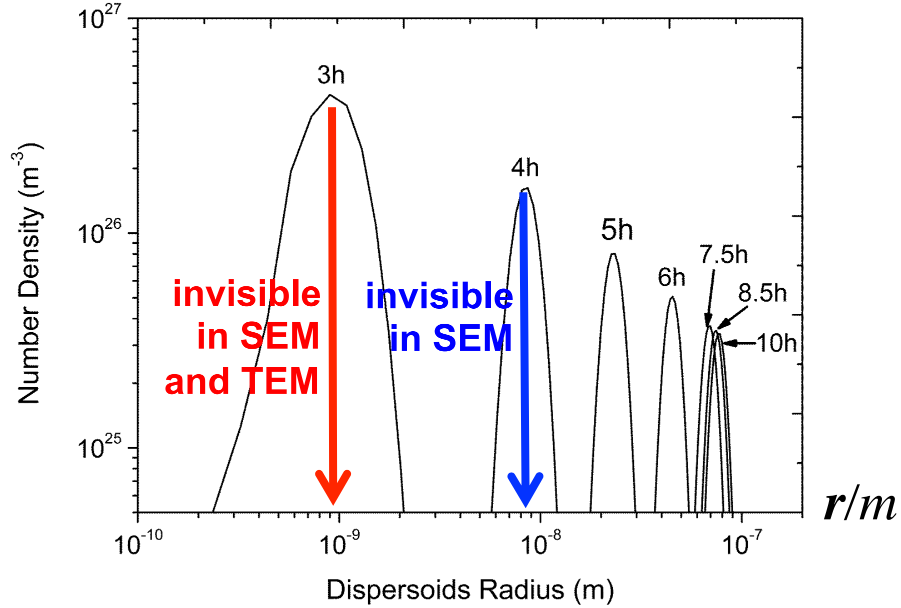


ClaNG+, AA5182: nucleation

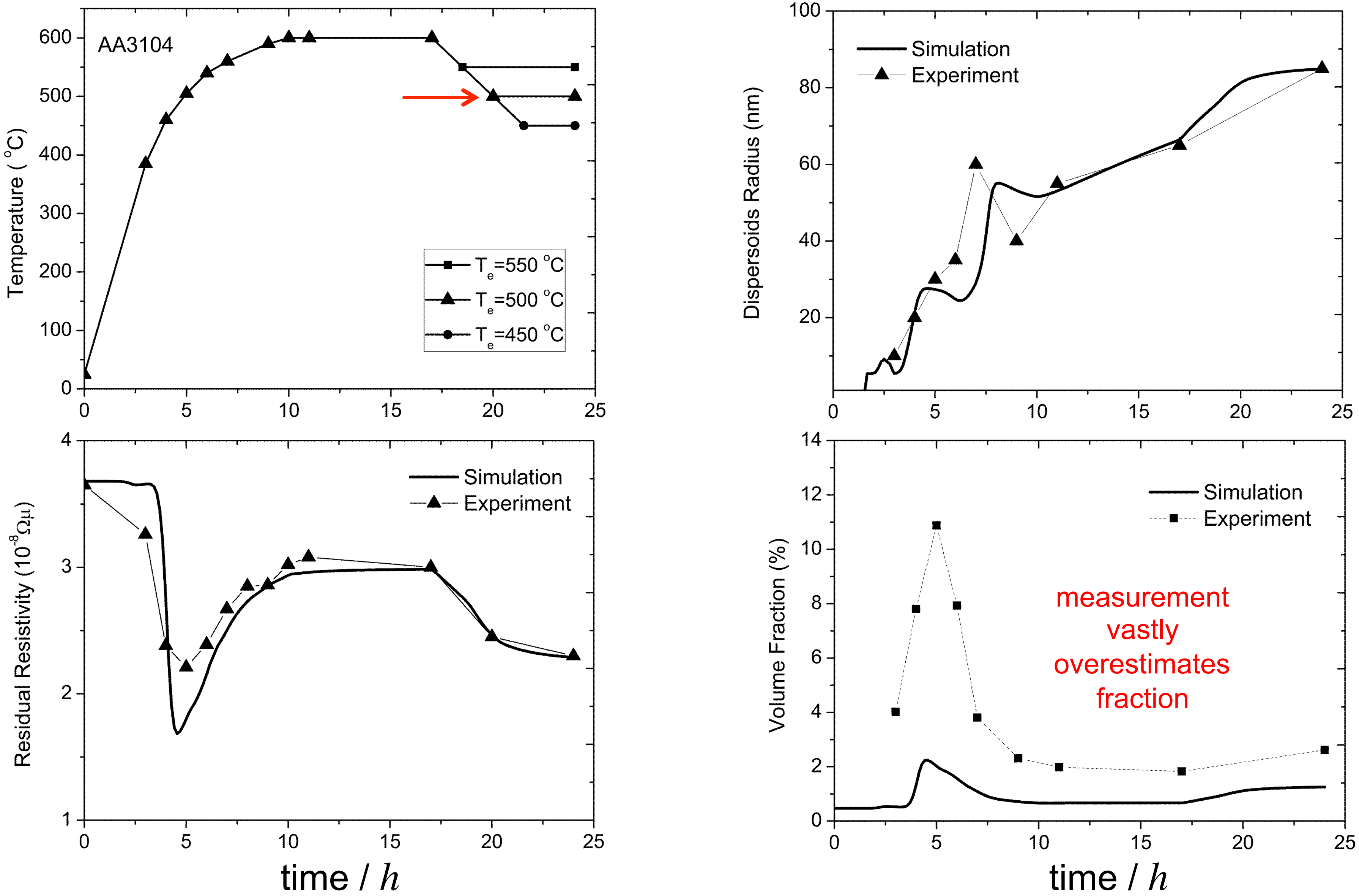








ClaNG+, AA5182 calibrated; AA3104 predictions



Overview

::: ClaNG model

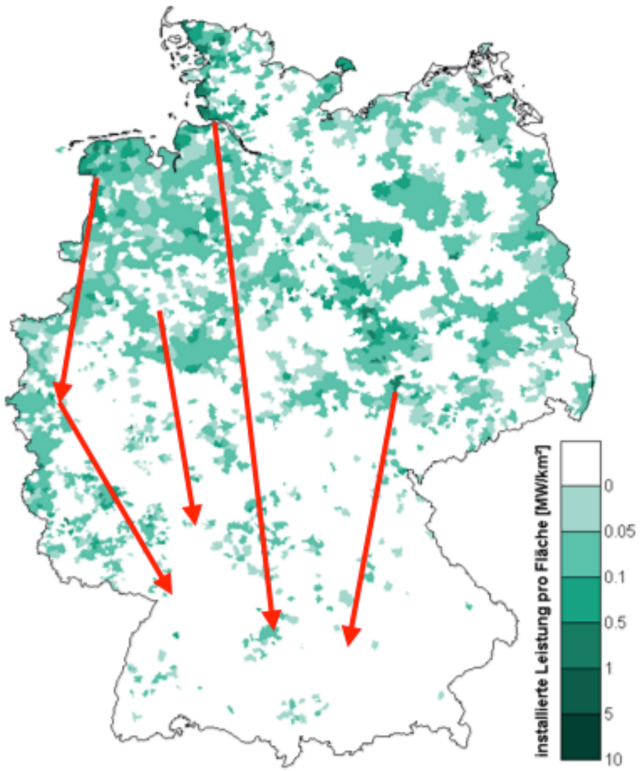
::: ALLEE project

BMBF project: ALLEE

BMBF: Support initiative „Zukunftsfähige Stromnetze“

topics: transmission and distribution techniques

⇒ **„Langzeitstabile Aluminiumlegierungen für elektrische Verbindungen“**



44 GW of wind energy produced in the north to be transferred to the energy hungry south

Copper: $16.7 \cdot 10^{-9}\ \Omega\text{m}$ (@RT)

Aluminium: $26.5 \cdot 10^{-9}\ \Omega\text{m}$ (@RT)
but cheaper
known problem: creep resistance

requested: application temperature 140°C
period of use: 50 a

Abb. 1: Onshore-Windleistung [Fraunhofer IWES 2011] und geplante Energieautobahnen [www.netzentwicklungsplan.de]

BMBF project: ALLEE

„Langzeitstabile Aluminiumlegierungen für elektrische Verbindungen“

management:	Prof. Dr.-Ing. O. Kessler Lehrstuhl für Werkstofftechnik, Universität Rostock
partners:	Prof. Dr.-Ing. Thomas Schoenemann Lehrst. f. Hochspannungs- u. Hochstromtechnik, Universität Rostock
	Prof. Dr.-Ing. Steffen Großmann Inst. f. Elektr. Energieversorgung u. Hochspannungstechnik, TU Dresden
	PD. Dr. Volker Mohles Institut für Metallkunde und Metallphysik, RWTH Aachen University
	Prof. Dr. Jürgen Hirsch Hydro Aluminium Rolled Products GmbH, F&E, Bonn
	Prof. Dr. Klaus Hack Ges. für Technische Thermochemie und –physik mbH, Herzogenrath
start (?):	September 2014

Requirements for ALLEE alloys

low resistivity: $$\rho(T) = \rho_{Al}(T) + \sum_x c_x^{sol} \rho_x$$

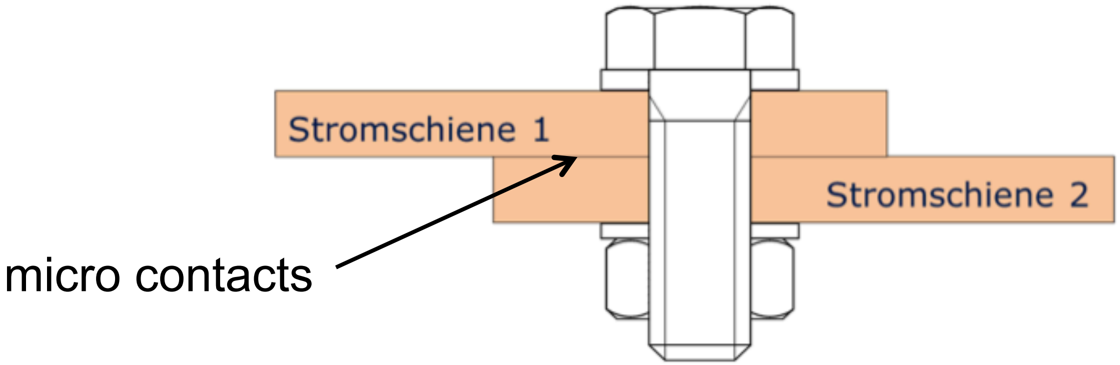
low solute concentration!

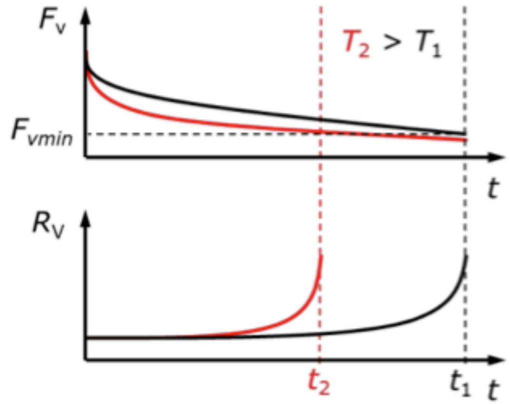
diffusion coefficient in Al, solubility at 140°C

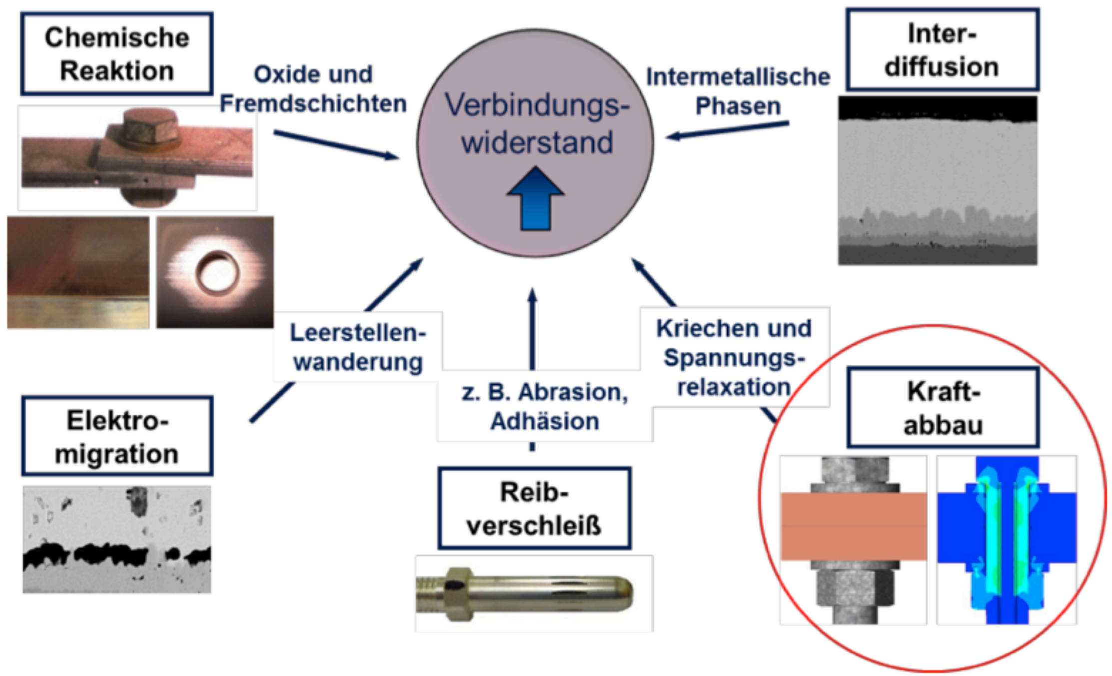
Element		D_x / m^2/s	c_{max} / wt%	ρ_x(1wt%) / ($10^{-9}\Omega m$)	$\rho_{Al}+\rho_x$(max%)
Al		$1,67 \cdot 10^{-22}$		40 (100%, 140°C)	
Cr	Dispers. bildend	$1,86 \cdot 10^{-33}$	<< 1% 0.3% übers.	42	53 (0.3wt%)
Cu		$4,12 \cdot 10^{-22}$	<< 1%	3,0	40
Fe	Dispers. bildend	$3,38 \cdot 10^{-26}$	<< 1%	32	40
Mg		$3,99 \cdot 10^{-21}$	2%	5,5	51 (2wt%)
Mn	Dispers. bildend	$1,91 \cdot 10^{-29}$	<< 1% 0.3% übers.	38 / 36	51 (0.3wt%)
Ni	Dispers. bildend	$1,51 \cdot 10^{-22}$	<< 1%		
Si		$7,48 \cdot 10^{-21}$	<< 1%	6,5	40
Ti		$1,55 \cdot 10^{-34}$	<< 1%	31	40
Zr	Dispers. bildend	$1,80 \cdot 10^{-32}$	<< 1%		

Requirements for ALLEE alloys

high creep resistance

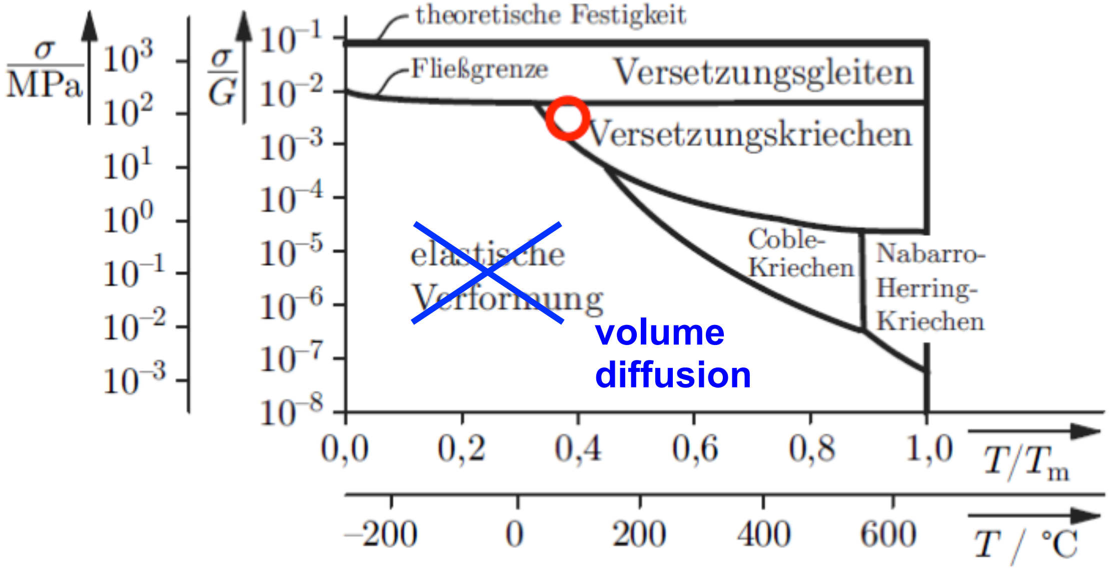






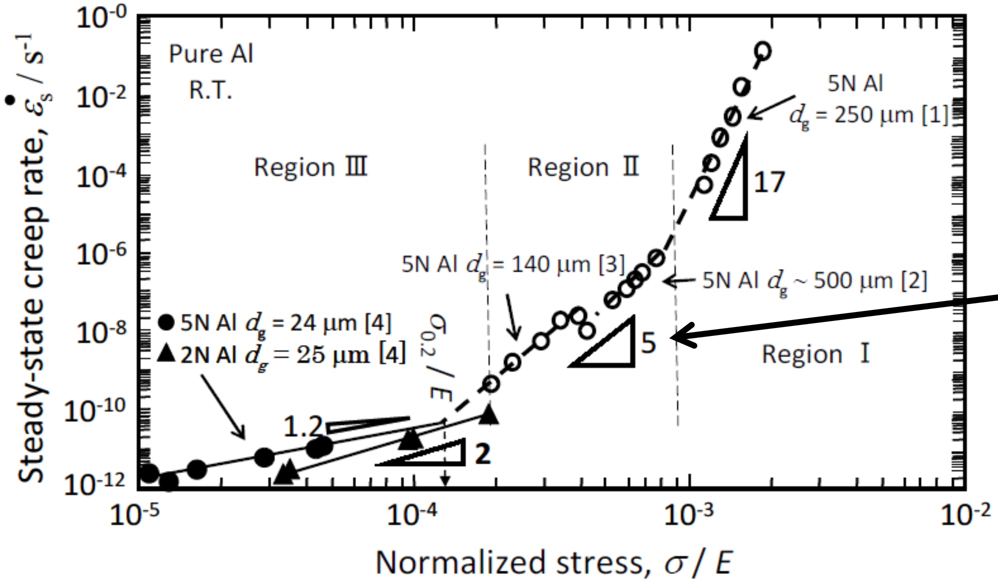
Requirements for ALLEE alloys

high creep resistance

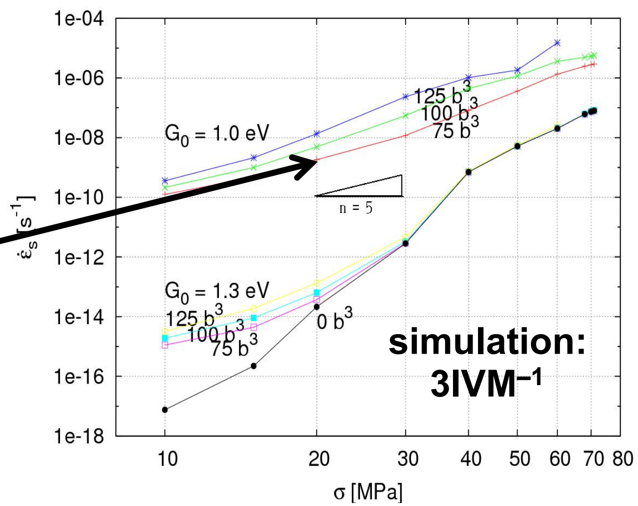


steady state creep

Materials Science Forum
747-748 (2013) pp559-563



$$\dot{\varepsilon} \sim \sigma^5$$



Requirements aggravation

applied so far:

stock alloys (AA1xxx) optimized for mechanical applications/purposes
selected for low electrical resistivity

future requirements:

increased temperature: 90°...110°C → 140°C
increased currents / higher energy/power density / compact design
increased life time / reduced down time (maintenance)
increased strength to withstand electromagnetic forces (short circuit!)
extreme environmental conditions (e.g. offshore)

potential for optimized alloys:

large grains etc. - dislocations, grain boundaries not stable
precipitates! - stable phases, aging slowly at 140°C
- but forming fast enough during production
→ selection of ideal alloying elements and contents
- production route should ensure full precipitation
→ optimization of the processing route

project structure

specification:	operating conditions, definition of test methods
alloy development:	**alloy selection** (initial and iterations) thermodynamic calculations (GTT) **precipitation modelling**: ClaNG (IMM)
alloy production:	primary shaping, homogenization, forming (Hydro)
characterization:	microstructure, calorimetry (LWT), mechanical properties electrical properties
long term experiments:	without current (HHT), with current (IEEH)
modelling an simulation:	**material model for creep** (IMM) system model (IEEH, LWT) ClaNG database extension (GTT)
evaluation:	including norming concept

Alloy selection

Element		D_x / m^2/s	c_{max} / wt%	ρ_x(1wt%) / ($10^{-9}\Omega m$)	$\rho_{Al}+\rho_x$(max%)
Al		$1{,}67 \cdot 10^{-22}$		40 (100%, 140°C)	
Cr	Dispers. bildend	$1{,}86 \cdot 10^{-33}$	<< 1% 0.3% übers.	42	53 (0.3wt%)
Cu		$4{,}12 \cdot 10^{-22}$	<< 1%	3,0	40
Fe	Dispers. bildend	$3{,}38 \cdot 10^{-26}$	<< 1%	32	40
Mg		$3{,}99 \cdot 10^{-21}$	2%	5,5	51 (2wt%)
Mn	Dispers. bildend	$1{,}91 \cdot 10^{-29}$	<< 1% 0.3% übers.	38 / 36	51 (0.3wt%)
Ni	Dispers. bildend	$1{,}51 \cdot 10^{-22}$	<< 1%		
Si		$7{,}48 \cdot 10^{-21}$	<< 1%	6,5	40
Ti		$1{,}55 \cdot 10^{-34}$	<< 1%	31	40
Zr	Dispers. bildend	$1{,}80 \cdot 10^{-32}$	<< 1%		

1) start with good element candidates within the validated database
2) look for better candidates
   - stability / resistivity
   - production feasibillity, material and production cost, ...
3) extend database (GTT)
4) ClaNG simulations for application and production conditions

Summary

::: ClaNG can deliver valuable information for other models:

- recrystallisation
- particle / solute strengthening → creep
- texture predictions
- resistivity

::: information about Δg_T and equilibrium solute concentrations from database,

- to be extended towards other elements / phases
- planned: database for interface energies

::: the ALLEE project will be a new big playground to utilize ClaNG