



Bundesministerium für Bildung und Forschung





Prediction of precipitation kinetics in Al alloys

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New project ClaNG⁺

- Collaboration between
 - <u>Hydro</u> (Aluminum industry)
 - <u>GTT</u> technologies



- <u>IMM</u>: Institut für Metallkunde und Metallphysik
- Extension of the use of <u>ClaNG</u> (tool for the prediction of precipitation kinetics)
 - To other alloys → extend the thermodynamic databank (input of the model)
 - To other process steps → couple precipitation with other phenomena (Deformation, RX)
- Started 01/2007...





Aluminum sheet production



- Evolution: start with a higher content of recycled products
- Goal: control the end- properties of the material
- Requirement: predict the precipitation state at each step





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ClaNG model overview



* : performed using *ChemApp* from GTT technologies





Thermodynamic calculations (I)

- At every interface, one assumes that a local equilibrium is achieved after a short time
- The equilibrium conditions are calculated using the <u>ChemApp</u> application developed by GTT technologies
- For these calculations, a thermodynamic databank is required
 - The AITT databank (Thermotech) is used for the moment
 - Light version containing 8 elements (AI, Cr, Cu, Fe, Mg, Mn, Si, Ti)



For each possible phase (Mg_2Si , Apha...), perform the <u>chemical reaction</u> corresponding the matrix decomposition occurring at the interface between the matrix and the phase





Thermodynamic calculations (II)

Use <u>ChemApp</u>:

- Set conditions (temperature, concentrations in the matrix)
- Enter 2 phases: matrix + another phase
- Perform equilibrium
- Extract information
 - > Equilibrium concentrations c_i^{α} in the AI matrix α
 - > Equilibrium concentrations c_i^{β} in the phase β
 - Chemical potentials of the elements

□ Derive the Chemical Driving Force Δg_u



Nucleation

- □ When Δg_u is known, the critical radius r_c can be derived
 - User input = interfacial energy γ

$$\mathbf{r}_{\rm c} = \frac{2\gamma \cdot \mathbf{V}_{\rm m}}{\Delta \mathbf{g}_{\rm u}}$$

- The nucleation rate is then given by the classical theory of <u>Becker & Döring</u>
- The nucleation rate is often <u>underestimated</u>
 - Reason: the thermodynamic quantities $(\Delta g_u, \gamma)$ are not precisely defined for nanoparticles
 - corrected by a "tuning" factor

$$\dot{\mathbf{N}} = \mathbf{N}^{0} \cdot \mathbf{Z} \cdot \boldsymbol{\beta} \cdot \exp\left(-\mathbf{f}^{\text{corr}} \cdot \frac{\Delta \mathbf{G}(\mathbf{r}_{\text{C}})}{\mathbf{k}_{\text{B}} \cdot \mathbf{T}}\right) \cdot \exp\left(\frac{-\tau}{\mathbf{t}}\right)$$
Usual value 1.0 $\rightarrow 0.7$





Growth & Coarsening

- Assumption: precipitate growth always <u>diffusion controlled</u> in Al alloys
- ClaNG treats growth and coarsening in a single equation
 - A particle above the critical radius grows
 - A particle below the critical radius dissolves
- The growth law used in ClaNG derives from <u>Zener</u>'s formulation
 - All particles are considered spherical



$$\mathbf{v} = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\mathbf{t}} = \frac{\mathbf{c}^{\alpha 0} - \mathbf{c}^{\alpha / \beta}(\mathbf{r})}{\mathbf{c}^{\beta} - \mathbf{c}^{\alpha / \beta}(\mathbf{r})} \cdot \frac{\mathsf{D}}{\mathsf{r}}$$

$$\mathbf{c}^{\alpha \,\prime \,\beta}(\mathbf{r}) = \mathbf{c}_{eq}^{\alpha \,\prime \,\beta} \cdot \exp\!\left(\frac{2\gamma \cdot \mathbf{V}_{m}}{\mathbf{R}_{g}\mathbf{T} \cdot \mathbf{r}}\right)$$

Gibbs-Thomson concentration at the interface





Evolution with time

Discretization in radius classes (1 nm width)



radius of the particle

radius of the particle

For every radius r_i at $t+\Delta t$, one determines its image $g(r_i)$ at t using a Runge-Kutta method

$$N_{i}(t + \Delta t) = N_{i}(t) + \int_{g(r_{i})}^{r_{i}} f(r,t) \cdot dr - \int_{g(r_{i+1})}^{r_{i+1}} f(r,t) \cdot dr \quad \left(+\dot{N}_{i}^{nucl}\Delta t\right)$$

(Robson, Acta Mater. 51-2003)



Phase composition update

- During the heat treatment, the equilibrium phase composition changes
 - The concentration in the precipitate should be consequently updated
- Diffusion inside the precipitate does the work, but unfortunately the diffusion coefficient in the phase is generally unknown
 - Hence this phenomenon can't be accurately modeled
 - Pragmatic modeling: use of a "tuning" factor to level diffusion strength







Conclusions

- Each step is dependent on the results of an thermodynamic equilibrium calculation
- The classical nucleation and growth theory provides the frame for the precipitation kinetics calculation
- However still hard to provide a 100% physical based model
 - "Tuning" parameters still required





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Microstructure after homogenization

- AA 3104 investigated
- Still inhomogeneous after homogenization
 - Complex structure with 3 different regions



Primary phases or constituents (3%) *Phase <u>Beta</u> = AI₆(Fe,Mn)*

Precipitation free zone (30%)

Dendrites with secondary phases or dispersoides (67%)

Phase <u>Alpha</u> = $AI_{12}Mn_3Si_{1.8}$





Formation of dispersoides



HYDRO

Prediction quality





Conclusions

- The model is able to deliver good predictions of the precipitation kinetics
 - Used by Hydro since 2004
- □ <u>Acceptable sensitivity</u> to empirical factors:
 - Nucleation rates are very sensitive to their "tuning" parameters but you can't do without
 - Other factors allow simulations to 100% fit the experimental results
- Results are however very sensitive to the starting conditions
 - Model casting step...



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Problematic

- The goal of the project is to extend the use of ClaNG to different alloy systems
- Hence, you need to have a <u>robust</u> growth law which is correct for the whole range of alloys
- ClaNG uses today a growth law based on the one proposed by <u>Zener</u>
- Question: Is this law the right one?

$$\mathbf{v} = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\mathbf{t}} = \frac{\mathbf{c}^{\alpha 0} - \mathbf{c}^{\alpha / \beta}(\mathbf{r})}{\mathbf{c}^{\beta} - \mathbf{c}^{\alpha / \beta}(\mathbf{r})} \cdot \frac{\mathsf{D}}{\mathsf{r}}$$







Survey of possible growth laws

- Many groups have proposed modified versions of this growth law these last years
- **D** Robson et al. (good for AI_3Sc vs. AI_3Zr)

$$\mathbf{r'} = \frac{\mathbf{c}_{i}^{\alpha 0} - \mathbf{c}_{i}^{\alpha / \beta}(\mathbf{r})}{\mathbf{c}_{i}^{\beta} - \mathbf{c}_{i}^{\alpha / \beta}(\mathbf{r})} \cdot \frac{\mathbf{D}_{i}}{\mathbf{r}} + \frac{2\gamma \cdot \mathbf{V}_{m}}{\mathbf{r}} = \sum_{i} \mathbf{c}_{i}^{\beta} \cdot \mathbf{RT.In} \left(\frac{\mathbf{c}_{i}^{\alpha / \beta}(\mathbf{r})}{\mathbf{c}_{i}^{eq}}\right) \longrightarrow \begin{array}{c} \text{Differential equation} \\ (r, r') \text{ to solve} \end{array}$$

❑ Kozeschnik et al. (derived from the extremum principle)

$$\mathbf{r'} = \frac{\Delta \mathbf{g}_{u} - \frac{2\gamma \cdot \mathbf{V}_{m}}{\mathbf{r}}}{\mathbf{R}_{g} \mathbf{T} \cdot \mathbf{r}} \cdot \left[\sum_{i} \frac{\left(\mathbf{c}_{i}^{\beta} - \mathbf{c}_{i}^{\alpha 0}\right)^{2}}{\mathbf{c}_{i}^{\alpha 0} \cdot \mathbf{D}_{i}} \right]^{-1}$$

Originally developed for steels

Hoyt, Morral, Purdy, Olson... (valid in case of coarsening)

$$\frac{[\mathsf{D}] \left[\Delta \overline{\mathsf{C}}^{\alpha} \right)}{\mathsf{r}} \cong -[\Delta \mathsf{C}^{\alpha\beta}) \,\mathsf{r'}$$





GT effect in multicomponent alloy (I)

Classical expression

$$\mathbf{c}^{\alpha \, \prime \, \beta}(\mathbf{r}) = \mathbf{c}_{eq}^{\alpha \, \prime \, \beta} \cdot \exp\!\left(\frac{2\gamma \cdot \mathbf{V}_{m}}{\mathbf{R}_{g} \mathbf{T} \cdot \mathbf{r}}\right)$$

- Problem: GT effect not correctly accounted when multicomponent alloy or not pure solute phase
- Solve it in the <u>"static</u>" case for a stoichiometric phase



GT effect in multicomponent alloy (II)

- □ Plotting ε as function of *r* is difficult but plotting *r* as function of ε is straightforward
- □ $r(\varepsilon)$ nearly always has the same shape and its inverse $\varepsilon(r)$ can then be extrapolated

$$\mathcal{E}(\mathbf{r}) \cong \mathcal{E}_{eq} \cdot \left(1 - \left(\frac{\mathbf{r}_c}{\mathbf{r}} \right)^a \right)$$

The parameter a is easily found by interpolation

When coarsening, a reaches the limit 1.0

$$\varepsilon_{\rm eq} = \frac{\mathbf{C}_{\rm i}^{\alpha 0} - \mathbf{C}_{\rm i}^{\rm eq}}{\mathbf{C}_{\rm i}^{\beta} - \mathbf{C}_{\rm i}^{\rm eq}}$$

Same value for all components





 <u>Assumption</u>: the slowest diffuser drives the dance (among the elements contained in the phase)

$$\dot{r} \cong v_1 = \frac{D_{\text{SlowElt}}}{r} \cdot \mathcal{E}(r) \cong \frac{D_{\text{SlowElt}}}{r} \cdot \mathcal{E}_{\text{eq}} \cdot \left(1 - \left(\frac{r_c}{r}\right)^a\right)$$

Problem: is it satisfactory?





Growth law N°2 (I)

Principle: the GT effect is a degree of freedom and the system will use it to maximize the growth rate

Generalized
1st Fick's law
$$j_i(x) = \frac{D_i c_i(x)}{R_g T} \cdot \nabla \mu_i(x)$$

 $\mu_i^{\alpha 0} - \mu_i^{\alpha / \beta}(\mathbf{r}) = -\int_r^{R_o} \frac{R_g T \cdot j_i(x)}{D_i c_i(x)} dx$

Do some calculus

$$\mu_{i}^{\alpha 0} - \mu_{i}^{\alpha / \beta}(r) = -\int_{r}^{R_{o}} \frac{4\pi x^{2}}{4\pi x^{2}} \frac{R_{g}T \cdot j_{i}(x)}{D_{i}c_{i}(x)} dx = -\frac{r^{2} \cdot R_{g}T \cdot j_{i}(r)}{D_{i}} \int_{r}^{R_{o}} \frac{1}{x^{2} \cdot c_{i}(x)} dx$$

for steady-state diffusion, $4\pi x^2 j_i(x) = cst$. for a spherical geom.

<u>Assumption</u>: coars. & GT effect small $\rightarrow c_i(x) \approx cst. \rightarrow goes out of the integral$

$$\mu_{i}^{\alpha 0} - \mu_{i}^{\alpha / \beta}(\mathbf{r}) \cong \frac{\mathbf{r}^{2} \cdot \mathbf{R}_{g} \mathbf{T} \cdot \mathbf{j}_{i}(\mathbf{r})}{\mathbf{D}_{i} \cdot \mathbf{c}_{i}^{\alpha / \beta}(\mathbf{r})} \cdot \left(\frac{1}{\mathbf{R}_{o}} - \frac{1}{\mathbf{r}}\right) \cong -\frac{\mathbf{r} \cdot \mathbf{R}_{g} \mathbf{T} \cdot \mathbf{j}_{i}(\mathbf{r})}{\mathbf{D}_{i} \cdot \mathbf{c}_{i}^{\alpha / \beta}(\mathbf{r})}$$

If $R_0 >> r$

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Growth law N°2 (II)

Stephan's interface GT effect mass balance $\Delta g_{u} - \frac{2\gamma \cdot V_{m}}{r} = \sum_{i} c_{i}^{\beta} \left(\mu_{i}^{\alpha 0} - \mu_{i}^{\alpha'\beta}(r) \right) \qquad \mu_{i}^{\alpha' 0} - \mu_{i}^{\alpha'\beta}(r) \cong -\frac{r \cdot R_{g} T \cdot j_{i}(r)}{D_{i} \cdot c_{i}^{\alpha'\beta}(r)} \qquad j_{i}(r) = \dot{r} \cdot (c_{i}^{\alpha'\beta}(r) - c_{i}^{\alpha'\beta}(r)) = \dot{r} \cdot (c_{i}^{\alpha'$ $\mathbf{j}_{i}(\mathbf{r}) = \dot{\mathbf{r}} \cdot (\mathbf{c}_{i}^{\alpha/\beta}(\mathbf{r}) - \mathbf{c}_{i}^{\beta})$ $\dot{\mathbf{r}} \cong \mathbf{V}_2 = \frac{\Delta \mathbf{g}_u - \frac{\mathbf{Z} \mathbf{\gamma} \cdot \mathbf{v}_m}{\mathbf{r}}}{\mathbf{R} \mathbf{T} \cdot \mathbf{r}} \left(\frac{\mathbf{C}_i^{\beta}}{\mathbf{D}_i} \left(\frac{\mathbf{C}_i^{\beta}}{\mathbf{C}_i^{0}} - 1 \right) \right)^{-1} \qquad \text{Very close to Kozeschnik}$

The growth rate is only dependent on the <u>intrinsic diffusion</u> <u>coefficients</u> (interdiffusion coefficients not necessary)

□ It is valid for coarsening & small GT effect (\Leftrightarrow r > \approx 30 nm)



Prediction quality



The <u>1st law</u> provides the best results: kinetics given by the diffusion of the slowest element (Mn)...





The end

- □ Thank you for your attention,
- A version of the model is available on SimWeb
 - <u>Contact</u>: jannot@imm.rwth-aachen.de

SimWeb@IMM

□ If you have questions...







Other slides





Calculation of the nucleation rate

- Clear separation between the contributions
 - Diffusivities are type dependant: hom. or het.
- The effect on the energy of the critical radius is accounted by a separate correction factor



Dendrite flux



□ Dendrite arm focused modeling $C_i^{Arm} \neq C_i^{Nom}$

- Start with the concentrations in the arm
- The interactions between the center of the dendrite (dispersoides) and the edge (constituents) can be summarized by an exchange of solutes (j_i +···)
- Assumption: the concentrations near the constituents are linked to the concentrations in the dendrite arm by a simple proportional

$$\mathbf{C}_{i}^{\text{Edge}} = (\mathbf{1} + \theta_{i}) \cdot \mathbf{C}_{i}^{\text{Arm}}$$



 $\frac{Change of concentration in the}{dendrite arm:}$ $\Delta C_{i}^{Arm} = a_{i} \cdot D_{i} \cdot C_{i}^{Arm} \cdot \Delta t$ $a_{i}: empirical value, kept constant during the simulation$





Efficiency (I)



c [%w.] Elt. 90.10 AI 0.80 Cr 4.00 Cu Fe 0.30 1.50 Mg 1.00 Mn 0.80 Si Ti 1.50



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12

15

18

time [h]

21

24

27

30

33

1.00E+13 1.00E+12 1.00E+11 1.00E+10 1.00E+09

-

3

6

9

Efficiency (II)



Number of precipitated phases: up to 15
 Calculation takes less than a day



