Modelling Multicomponent Precipitation Kinetics with CALPHAD-Based Tools

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Introduction: CALPHAD

CALPHAD method and CALPHAD-based tools play a central role in materials design.

CALPHAD-type databases where each phase is described separately using models based on physical principles and model parameters assessed from experimental and ab initio data provide fundamental inputs for predicting microstructure evolution and materials properties.
Introduction: TC-PRISMA

A general computational tool for simulating kinetics of diffusion controlled multi-particle precipitation process in multi-component and multi-phase alloy systems.

TC-PRISMA is based on Langer-Schwartz theory [1], and it adopts Kampmann-Wagner numerical (KWN) method [2] to compute the concurrent nucleation, growth, and coarsening of dispersed phase(s).

## Introduction: In and Output

### Input
- Thermodynamic data
- Kinetic data
- Alloy composition
- Temperature - Time
- Simulation time
- Property data (Interfacial energy, volume, etc.)
- Nucleation sites and related microstructure information

### Output
- Particle Size Distribution
- Number Density
- Average Particle Radius
- Volume Fraction
- Matrix composition
- Precipitate composition
- Nucleation rate
- Critical radius
- TTP

**TC-PRISMA**
Introduction: Example of results

All above simulations made under isothermal conditions.
Non-Isothermal Conditions

\(\gamma/\gamma'\) Microstructure in U720 Li

Continuous cooling at 0.0167 K/s

Influence of composition on monomodal versus multimodal $\gamma'$ precipitation in Ni–Al–Cr alloys

T. Rojhirsakool · S. Meher · J. Y. Hwang · S. Nag · J. Tiley · R. Banerjee

Abstract  This study investigates the influence of alloy composition on $\gamma'$ precipitation in Ni–8Al–8Cr and Ni–10Al–10Cr at.% during continuous cooling from a supersolvus temperature. When subjected to the same cooling rate, Ni–8Al–8Cr develops a monomodal population, whereas Ni–10Al–10Cr develops a multimodal (primarily bimodal) population of $\gamma'$ precipitates. The bimodal $\gamma'$ precipitate size distribution in Ni–10Al–10Cr alloy can be attributed to two successive nucleation bursts during continuous cooling while the monomodal $\gamma'$ size distribution in Ni–8Al–8Cr results from a single nucleation burst followed by a longer time—wider temperature window for nucleation resulting in a larger number density of precipitates. Three-dimensional atom
Ni-8Al-8Cr and Ni-10Al-10Cr

Continuous cooling from 1150 to 380 °C with a cooling rate of 14 °C/min.
Ni-8Al-8Cr and Ni-10Al-10Cr

Ni-8Al-8Cr have larger misfit between $\gamma$ and $\gamma'$ compared to Ni-10Al-10Cr. This will give an elastic energy contribution which has not been considered in the simulation.
Ni-8Al-8Cr and Ni-10Al-10Cr

Vertical Section Ni-xAl-xCr

Thermodynamic driving force
Ni-8Al-8Cr and Ni-10Al-10Cr

Thermodynamic driving force

Nucleation rate
Precipitation Kinetics during Continuous Cooling

<table>
<thead>
<tr>
<th>wt.%</th>
<th>1*</th>
<th>2**</th>
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<tbody>
<tr>
<td>Al</td>
<td>2.53</td>
<td>2.46</td>
</tr>
<tr>
<td>B</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>C</td>
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<td>0.025</td>
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<tr>
<td>Co</td>
<td>14.43</td>
<td>14.75</td>
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<tr>
<td>Cr</td>
<td>15.92</td>
<td>16.35</td>
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<tr>
<td>Fe</td>
<td>0.09</td>
<td>0.06</td>
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<tr>
<td>Mo</td>
<td>2.96</td>
<td>3.02</td>
</tr>
<tr>
<td>Ti</td>
<td>4.96</td>
<td>4.99</td>
</tr>
<tr>
<td>W</td>
<td>1.26</td>
<td>1.3</td>
</tr>
<tr>
<td>Zr</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Bal</td>
<td>Bal</td>
</tr>
</tbody>
</table>

- Databases: TTN18+MOBNI1

* Radis et al., *Superalloys* 2008
U720Li : Cooling Rate Effect

Size Distribution

Mean Particle Size

σ = 0.025 J/m²
Secondary/Tertiary $\gamma'$ during Cooling + Aging

- No primary $\gamma'$ is considered, but $\gamma$ matrix concentration is adjusted due to primary $\gamma'$ formation at 1105°C (based on equilibrium calculation)
- Heat Treatment: cooling from 1105°C to 400°C, followed by aging at 700°C for 24hrs


<table>
<thead>
<tr>
<th>Elements</th>
<th>wt.%</th>
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</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.51</td>
</tr>
<tr>
<td>B</td>
<td>0.014</td>
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<tr>
<td>C</td>
<td>0.011</td>
</tr>
<tr>
<td>Co</td>
<td>14.66</td>
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<tr>
<td>Cr</td>
<td>16.14</td>
</tr>
<tr>
<td>Mo</td>
<td>2.98</td>
</tr>
<tr>
<td>Si</td>
<td>0.05</td>
</tr>
<tr>
<td>Ti</td>
<td>5.08</td>
</tr>
<tr>
<td>W</td>
<td>1.23</td>
</tr>
<tr>
<td>Ni</td>
<td>Bal</td>
</tr>
</tbody>
</table>
Simulations are good for large to intermediate cooling rate ( > 1°C/s)

Future model improvements include multiple nucleation sites, mean field deviation, loss of coherency, interfacial energy variation, interface mobility, morphology change ....

\[ \sigma = 0.025 \text{ J/m}^2 \]
Estimation of interfacial energy

- Classic or non-classic thermodynamics
- Atomistic modeling - molecular dynamics and Monte Carlo method
- First principles

Distribution of Al-Li $\alpha/\delta'$ interfacial energy value found in literature

![Graph showing the distribution of interfacial energy values](image)

Fig. 1. Values of the $\alpha/\delta'$ interfacial energy that have been measured over the period 1983–1998.

1999 Noble, Mater Sci Engr, A266, 80-85
Our first approximation

For a binary matrix and precipitate of the same structure that can be described by a regular solution model*

\[ \sigma_c = \frac{N_s Z_s}{N_A Z_l} \Delta E_{sol} \]

\[ \Delta E_{sol} = \Omega \left( X_P - X_M \right)^2 \]

- Miscibility gap of non-regular solution phase
- Matrix and precipitate of different structure
- Multicomponent system

* Based on Becker R. Ann Phys 1938;424:128
Some example results

<table>
<thead>
<tr>
<th>System</th>
<th>Phases</th>
<th>Estimation (J/m²)</th>
<th>Literature (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Li</td>
<td>α/δ’</td>
<td>0.011</td>
<td>0.004 to 0.115</td>
</tr>
<tr>
<td>Cu-Ti</td>
<td>Cu/Cu4Ti</td>
<td>0.035</td>
<td>0.067, 0.031</td>
</tr>
<tr>
<td>Ni-Al-Cr</td>
<td>γ/γ’</td>
<td>0.022</td>
<td>0.023</td>
</tr>
<tr>
<td>Co-W-C</td>
<td>Co/WC</td>
<td>0.68</td>
<td>0.44 to 1.09</td>
</tr>
</tbody>
</table>

### Used in Current Calculations

<table>
<thead>
<tr>
<th>System</th>
<th>Phases</th>
<th>Estimation (J/m²)</th>
<th>Used (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Al-Cr</td>
<td>γ/γ’</td>
<td>0.022</td>
<td>0.023</td>
</tr>
<tr>
<td>Ni-Superalloys(Bulk)</td>
<td>γ/γ’</td>
<td>0.03~ 0.06</td>
<td>0.025</td>
</tr>
<tr>
<td>Ni-Superalloys(GB)</td>
<td>γ/γ’</td>
<td>~ 0.06</td>
<td>0.06</td>
</tr>
</tbody>
</table>

- Interfacial energy shows composition and temperature independence
- Estimated value seems better for grain boundary precipitation in multi-component alloys
- Further developments include diffusiveness of interface, incoherency, size effect, grain boundary energy…
Alloy 282

Mean Particle Size (Bulk)

CCT Starting Temperature

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>1.5</td>
<td>10.0</td>
<td>19.0</td>
<td>1.5</td>
<td>8.5</td>
<td>2.1</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

➤ Databases: TCNI5+MOBNI2

* Experimental data from B. Alexandrov et al., “Continuous heating and cooling transformation diagram in Ni-base superalloy 282”, TMS 2011
Summary

- A non-isothermal model has been developed in TC-PRISMA and has been successfully applied to simulate multi-modal particle size distribution of $\gamma'$ precipitates in Ni-base superalloys.

- More GUI outputs have been provided to facilitate separate analyses of particle size distribution, mean size, volume fraction, and number density.

- A model has been implemented to estimate the interfacial energy between matrix and precipitate phases.
Thermo-Calc Software

Thank You!
Thermo-Calc Software

Theory: Conservation laws

LS (Langer-Schwartz) and KWN (Kampmann and Wagner Numerical) Approach

Continuity equation

\[ \frac{\partial f(R,t)}{\partial t} = - \frac{\partial}{\partial R} \left[ \nu(R,t) f(R,t) \right] + j(R,t) \]

Mass balance

\[ C_0^\alpha = C^\alpha + (C^\beta - C^\alpha) \int_0^\infty \frac{4\pi}{3} f(R,t) R^3 dR \]

\[ N = \int_0^\infty f(R,t) dR \quad \overline{R} = \frac{1}{N} \int_0^\infty f(R,t) R dR \]

\[ \phi = \int_0^\infty \frac{4\pi}{3} f(R,t) R^3 dR \]
Models: Multicomponent Nucleation

Classic Nucleation Theory

\[ J(t) = J_s \exp \left( -\frac{\tau}{t} \right) \]

\[ J_s = Z \beta^* N \exp \left( -\frac{\Delta G^*}{kT} \right) \]

\[ Z = \left\{ \frac{-1}{2\pi kT} \left( \frac{\partial^2 \Delta G_n}{\partial n^2} \right)_{n^*} \right\}^{1/2} \]

\[ \Delta G^* = \frac{16\pi \sigma^3 V^2_m}{3\Delta G^2_m} \]

\[ \beta^* = \frac{4\pi r^*_2}{\alpha^4} \left[ \sum_{i=1}^{n} \frac{\left( X_i^{\beta/\alpha} - X_i^{\alpha/\beta} \right)^2}{X_i^{\alpha/\beta} D_i} \right]^{-1} \]

\[ \tau = \frac{1}{2Z^2 \beta^*} \]

Grain size, dislocation density, etc

Interfacial energy, Volume
Thermo-Calc Software

Models: Multicomponent Growth Rate

Advanced – Analytical Flux-balance Approximation

\[ \mu_i^{\alpha/\beta} = \mu_i^{\beta/\alpha} + \frac{2\sigma V_m^\beta}{r} \]
\[ \nu \left( c_i^{\beta/\alpha} - c_i^{\alpha/\beta} \right) = c_i^{\alpha/\beta} M_i \left( \mu_i^{\alpha} - \mu_i^{\alpha/\beta} \right) / \xi_i r \]

Simplified – Pseudo-steady state Approximation

\[ \nu = \frac{K}{r} \left( \Delta G_m - \frac{2\sigma V_m}{r} \right) \]

Pseudo-binary dilute solution Approximation

\[ \nu = \frac{X^\alpha - X^{\alpha/\beta}}{X^\beta - X^{\alpha/\beta}} \frac{D}{r} \quad \frac{X^{\alpha/\beta}}{X_e^\alpha} = \exp \left( \frac{1 - X_e^\alpha}{X^\beta - X_e^\alpha} \frac{2\sigma V_m^\beta}{RTr} \right) \]