Phase-field modeling of microstructure evolution in multi-component alloys

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• Introduction: modeling of microstructure evolution

• Principles of phase field modeling

• Application examples
  • Anisotropic grain growth
  • Precipitates on grain boundaries
  • Lead-free solder joints
  • Solidification

• Summary
Role of microstructures in materials science

Chemical composition

+ Temperature, pressure, cooling rate, deformation, ...

Microstructure

Shape, size and orientation of the grains, mutual distribution of the phases

Material properties

Strength, deformability, hardness, toughness, fatigue...

Low-C steel: wt% C < 0.022
Ferrite + small carbides

Steel: wt% C = 0.4, slow cooling rate
Ferrite + cementite

Steel: wt% C = 0.4, fast cooling rate
Ferrite needles + perlite

Chemical composition

Steel: wt% C = 0.4, slow cooling rate
Steel: wt% C = 0.4, fast cooling rate
Microstructure evolution in multi-component alloys

- Connected grain structures
- Complex morphologies
- Concurrent processes
  - Solidification - grain growth - Ostwald ripening – diffusion - phase growth
- Materials’ properties are largely related to microstructure
  - Material development
  - Reliability

Low C-steel, ferritic grain structure
Microstructure evolution in multi-component alloys

- High complexity
  - Anisotropy, segregation, solute drag, second-phase precipitates, pipe diffusion, mutual distribution of phases, ...
  - Many material properties: Crystal structure, Gibbs energy, diffusion coefficient of different phases? Structure, energy, mobility of grain boundaries?

- Evolution connected grain structure?
  - → Mesoscale simulations

- Importance
  - Material development: heat treatment, alloying
  - Reliability
**Strength**

- Complex shapes
- Multi-grain, multi-phase structures
- Thermodynamic driving forces

\[ F = F_{chem} + F_{int} + F_{elast} + F_{magn} + \ldots \]

- Multi-component
- Transport equations
  - Mass and heat diffusion/convection

**Difficulties**

- Implementation for realistic length scales
- Parameter choice
Principles of phase field modeling

- Diffuse interface concept
- Phase field variables
- Thermodynamic free energy functional
- Evolution equations
- Parameter assessment
- Numerical implementation
**Diffuse-interface description**

- **Sharp interface**
  - Discontinuous variation in properties
  - Requires tracking of the interfaces
  - Simplified grain morphologies

- **Diffuse interface**
  - Continuous variation in properties
  - Interfaces implicitly given by local variations in phase-field variables
  - Complex grain morphologies

- *Diffuse interface approach* (van der Waals, Cahn-Hilliard (1958), Ginzburg-Landau (1950))
- Microstructure evolution started ± 20 years ago
Representation of microstructures

- Phase-field variables: continuous functions in space and time
  - Local composition $x_B(r,t), c_B(r,t)$
  - Local structure and orientation $\eta(r,t)$
    $\phi(r,t)$

Binary alloy A-B
- Phase $\alpha$: $\eta = 0$
- Phase $\beta$: $\eta = 1$
Thermodynamics and kinetics

- **Free energy functional**

\[
F = F_{\text{bulk}} + F_{\text{surface}} = \int_{V} f_0(x_i, \eta_k, T) + \frac{K}{2} \sum_{k=1}^{p} (\nabla \eta_k)^2 + \frac{\xi}{2} \sum_{i=1}^{c} (\nabla x_i)^2 dV
\]

Homogeneous free energy \quad Gradient free energy

(chemical, elastic, …) \quad (→ diffuse interfaces)

- **Evolution of field variables**
  - **Non-conserved field variables** (→ Interface movement)
    \[
    \frac{\partial \eta_k(r,t)}{\partial t} = -L \frac{\partial F(x_1,\ldots,x_C,\eta_1,\ldots,\eta_p)}{\partial \eta_k(r,t)} + \xi(r,t)
    \]
  - **Conserved composition fields** (→ Mass diffusion)
    \[
    \frac{1}{V_m} \frac{\partial x_i(r,t)}{\partial t} = \bar{\nabla} M \cdot \bar{\nabla} \frac{\partial F(x_1,\ldots,x_C,\eta_1,\ldots,\eta_p)}{\partial x_i(r,t)} + \xi(r,t)
    \]
Homogeneous free energy functional

- **Anti-phase boundary**

  

  \[ \eta(r) = 1 \]
  \[ \eta(r) = -1 \]

  **Boundary energy:** \( \propto \sqrt{\kappa (\Delta f_0)_{\text{max}}} \)

  **Boundary width:** \( \propto \sqrt{\frac{\kappa}{(\Delta f_0)_{\text{max}}}} \)

  **Boundary velocity:** \( \propto \kappa L \)

  

  \[ f_0 = 4(\Delta f_0)_{\text{max}} \left( \frac{\eta^4}{4} - \frac{\eta^2}{2} \right) \]
**Homogeneous free energy**

- **Binary two-phase system**

\[ f_0 = h(\phi) f^\beta(c, T) + \left[1 - h(\phi)\right] f^\alpha(c, T) + \omega g(\phi) \]

with \( f^\alpha(c, T) = \frac{G_m^\alpha}{V_m} \), \( f^\beta(c, T) = \frac{G_m^\beta}{V_m} \) (CALPHAD)
Homogeneous free energy

- Binary two-phase system

\[ f_0 = h(\phi) f^\beta(c, T) + \left[ 1 - h(\phi) \right] f^\alpha(c, T) + \omega g(\phi) \]

Double well function
Homogeneous free energy

- Binary two-phase system

\[ f_0 = h(\phi) f^\beta(c, T) + \left[ 1 - h(\phi) \right] f^\alpha(c, T) + \omega g(\phi) \]

Interpolation function
Effect of elastic stresses and strain

- Coupling with micro-elasticity theory \( F = F_{\text{chem}} + F_{\text{int}} + F_{\text{elast}} \)
- Effect of transformation and thermal strains, applied stress/strain
- Martensitic transformation, precipitate growth
Polycrystalline structures

- Polycrystalline microstructure
  \[ \eta_1, \eta_2, ..., \eta_i(r, t), ..., \eta_p \]

- Grain \( i \) of matrix-phase
  \[ (\eta_1, \eta_2, ..., \eta_i, ..., \eta_p) = (0, 0, ..., 1, ..., 0) \]

- Free energy functional
  \[ F = F_{surface} = \int_V f_0(\eta_1, \eta_2, ..., \eta_p) + \frac{\kappa}{2} \sum_{k=1}^{p} (\nabla \eta_k)^2 dV \]
Multi-phase and multi-component alloys

- **Phase field variables:**
  - **Grains**
    \[ \eta_{\alpha_1}, \eta_{\alpha_2}, \ldots, \eta_{\alpha_i}(r, t), \ldots, \]
    \[ \eta_{\beta_1}, \eta_{\beta_2}, \ldots \eta_p \]
  - **Composition**
    \[ x_A, x_B(r, t), \ldots, x_{C-1} \]
  - **Free energy functional**
    \[ f_{\text{bulk}}(x_k, \eta_{\rho i}) = \sum_{\rho} h_\rho(\eta_{\rho i}) f_\rho(x_k^\rho) \]
    \[ = \sum_{\rho} h_\rho(\eta_{\rho i}) \frac{G_m^\rho(x_k^\rho)}{V_m} \]

*2 phase polycrystalline structure*
Parameter assessment

- Different kinds of input data (calculated and/or measured)
  - Phase stabilities, phase diagram information
    - CALPHAD ← (ab-initio, experiments)
  - Interfacial energy and mobility
    - ab-initio, (MD, MC ← ab-initio), experimental
  - Elastic properties, crystal structure, lattice parameters
    - ab-initio, experimental
  - Atomic diffusion mobilities
    - CALPHAD ← ((MC ← ab-initio), experimental)

- Orientation and composition dependence
  - Anisotropy, segregation, solute drag
Experimental characterization

Phenomenological, Empirical theories
  e.g. Read-Shockley, CALPHAD phase diagram

First principles
  Atomistic simulations
  e.g. Molecular dynamics

Thermodynamic and kinetic properties of bulk phases and interfaces

Phase-Field Simulations
  (Phenomenological models based on Thermodynamics)

Physical models
  Coarse grained models
  Multi-scale models

Microstructure evolution

Microscopy
  e.g. SEM, TEM

Reverse engineering of material properties

Microstructure analysis

Macroscopic models
  e.g. Finite-Element simulations
  Statistical models

Grain size distribution
Grain morphology
Grain boundary character distribution...

Macroscopic properties
  strength, ductility, conductivity,...
Quantitative aspects

- Numerical solution of partial differential equations

- Bounding box algorithm
  - Sparse data structure
  - Object oriented C++
    (L. Vanherpe et al., K.U.Leuven)

- Discretization (Finite differences, finite elements, Fourier-spectral method)

MICRESS, commercial software for phase-field coupled with CALPHAD

- Adaptive meshing (M. Dorr et al. AMPE, LLNL)
Examples of applications

- Anisotropic grain growth
- Precipitates on grain boundaries
- Lead-free solder systems
- Solidification
Columnar films with fiber texture

- Grain boundary energy:
  - Fourfold symmetry
  - Extra cusp at \( \theta = 37.5^\circ \)
  - Read-shockley

\[
\gamma_{gb} \text{ (J/m}^2\text{)}
\]

\(\theta = 37.5^\circ\)

- Discrete orientations
  \(\eta_1, \eta_2, \ldots, \eta_i(r, t), \ldots, \eta_{60} \Rightarrow \Delta \theta = 1.5^\circ\)

- Constant mobility

- Initially random grain orientation and grain boundary type distributions

\[ q = 1.5 \]

\[ q = 3 \]

\[ q = 37.5 \]

\[ q > 3, q \neq 37.5 \]

White: \( \theta = 1.5 \)

Gray: \( \theta = 3 \)

Red: \( \theta = 37.5 \)

Black: \( \theta > 3, \theta \neq 37.5 \)

In collaboration with F. Spaepen, School of Engineering and Applied Sciences, Harvard University
3D simulations for wires with fiber texture

$\psi < 6^\circ$

$t = 40$

$t = 144$
Microstructure analysis: films

- Misorientation distribution function (MDF)

- Evolution mean grain area

- Evolution towards stead-state regime
  → Simple mean field models

\[
A - A_0 = k_{\text{eff}} t^{n_{\text{eff}}}
\]

\[
A_{\text{eff}} = \frac{kt}{A_n(0) + kt} \to 1, t \to \infty
\]

\[
k_{\text{eff}} = \frac{dA_{\text{eff}}}{dt} = \frac{k}{1 + N / N}
\]
Examples of applications

- Anisotropic grain growth
- Precipitates on grain boundaries
- Lead-free solder systems
- Solidification
**Zener pinning**

- **Mechanism for controlling grain size**
  - E.g. NbC, AlN, TiN,... in HSLA-steels
  - Nano-grain structures

- **Zener relation for limiting grain size**
  \[
  \frac{R_{\text{lim}}}{r} = K \frac{1}{f_Y^b}
  \]

- **Influence of**
  - Shape of the particle
  - Interfacial properties of particles
  - Initial distribution
  - Evolution particles

Fe-0.09 to 0.53 w%
C-0.02 w% P with Ce2O3 inclusions
(PhD. M. Guo)
Simulation results: Al thin films

- Thin films with CuAl₂ - precipitates

\[
\frac{R_{\text{lim}}}{r} = 1.28 \frac{1}{f_a^{0.5}}
\]

\[
r = 3, f_a = 0.12, l_3 = 21
\]

(exp from H.P. Longworth and C.V. Thompson)
Simulation results: effect of particle shape and coarsening

- Ellipsoid particles

- Evolving particles

\[
\frac{R_{\text{lim}}}{s} = K \frac{r_a}{1 + ar_a f_V^b} \\
K = 3.7, b = 1, a = 3.1
\]

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\[ \varepsilon = 3, f_V = 0.05 \]

\[ f_V = 0.12, L = 10M \]

\[ \text{Modified Zener relation} \]
Jerky motion during recrystallization in Al-Mn alloy

- In-situ EBSD observation of recrystallization in AA3103 at 400 °C
  - CamScan X500 Crystal Probe
  - FEGSEM

- Jerky grain boundary motion
  - Stopping time: 15-25 s
  - Pinning by second-phase precipitates
    - $\text{Al}_6(\text{Fe,Mn}), \alpha\text{-Al}_{12}(\text{Fe,Mn})_3\text{Si}$

- Added to phase field model
  - Grain boundary diffusion
  - Driving force for recrystallization

In collaboration with A. Miroux, E. Anselminio, S. van der Zwaag, T. U. Delft
## Material properties at 723K

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain boundary energy high angle</td>
<td>$\gamma_h = 0.324 \text{ J/m}^2$</td>
</tr>
<tr>
<td>Interfacial energy Al$_6$Mn precipitates</td>
<td>$\gamma_{pr} = 0.3 \text{ J/m}^2$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$M_h = 2.94 \cdot 10^{-11} \text{ m}^2\text{s/kg}$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>(Mroux et al., Mater. Sci. Forum, 467-470, 393(2004))</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$c_{Mn,eq} = 0.0524 \text{ w%} (0.02456 \text{ at%})$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>(PhD thesis Lok 2005)</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$c_{Mn} = 0.3 \text{ w%} (0.1474 \text{ at%})$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>(PhD thesis Lok 2005)</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$D_{0,bulk} = 1 \cdot 10^{-2} \text{ m}^2\text{s}$, $Q_{bulk} = 211 \text{ kJ/mol}$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$\rightarrow D_{bulk} = 5.5973 \cdot 10^{-18} \text{ m}^2\text{s}$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$D_{0,p} = D_{0,bulk}$, $Q_p = 0.65Q_{bulk}$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$\rightarrow D_p = 1.2195 \cdot 10^{-12} \text{ m}^2\text{s}$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$f^p = A^p(x-x^p_0)^2$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$A^m = 6 \cdot 10^{11}$; $x^m_0 = 0.000258$</td>
</tr>
<tr>
<td>Mobility high angle grain boundary</td>
<td>$A^p = 6 \cdot 10^{12}$; $x^p_0 = 0.1429$</td>
</tr>
</tbody>
</table>
Precipitate coarsening and unpinning

- $P_D < P_{ZS} \ (P_D \approx P_{ZS})$
  - Pinning: $P_{ZS} = 3.6 \text{ MPa}$
  - Rex: $P_D = 3.1 \text{ MPa}$

- Unpinning mainly through surface diffusion around precipitates

$$J = \sqrt{J_x^2 + J_y^2}$$

| 0.002 s |
| 0.9μm x 0.375μm |

| 6 s |

$7 \cdot 10^{-10}$
Precipitate coarsening and unpinning

- $P_D << P_{ZS}$
  - Pinning: $P_{ZS} = 3.6$ MPa
  - Rex: $P_D = 1.1$ MPa

- Unpinning through grain boundary diffusion

$$J = \sqrt{J_x^2 + J_y^2}$$

0.9μm x 0.375μm
Examples of applications

- Anisotropic grain growth
- Precipitates on grain boundaries
- Lead-free solder systems
- Solidification
Coarsening in Sn(-Ag)-Cu solder joints

- COST MP-0602 (Advanced Solder Materials for High Temperature Application)
  - IMC formation and growth – precipitate growth – Kirkendal voids – stresses – grain boundary diffusion
    - CALPHAD description
    - Diffusion coefficients, growth coefficient for IMC-layers

SEM-image of Sn – 3.8Ag–0.7 Cu alloy after annealing for 200h at 150 °C

CALPHAD description
- Diffusion coefficients, growth coefficient for IMC-layers

Graph showing phase diagrams for Sn-Ag-Cu system.
**Cu-Sn system**

- **Equilibrium compositions**

- **Interdiffusion coefficients**
  
  \[
  D_{Sn}^{(Cu)} = 10^{-25} \\
  D_{Sn}^{Cu3Sn} = 5 \cdot 10^{-16} \text{ m}^2/\text{s} \\
  D_{Sn}^{Cu6Sn5} = 10^{-15} \text{ m}^2/\text{s} \\
  D_{Sn}^{(Sn)} = 10^{-12} \text{ m}^2/\text{s}
  \]

- **Interfacial energy**
  
  \[
  \sigma_{gb} = 0.35 \text{ J/m}^2
  \]
Effect of precipitates in Sn-2at%Cu

- **Interdiffusion coefficients:**
  \[
  D_{\text{Sn}}^{(Cu)} = 10^{-25}, 10^{-12} \text{ m}^2/\text{s} \\
  D_{\text{Sn}}^{Cu_6Sn_5} = 10^{-16}, 10^{-13}, 10^{-12} \text{ m}^2/\text{s} \\
  D_{\text{Sn}}^{(Sn)} = 10^{-12} \text{ m}^2/\text{s}
  \]

- **Interfacial energies:**
  0.35J/m^2

- **Initial volume fraction precipitates:**
  \[f_V = 0.04\]

- **Interfacial reactions are diffusion controlled**

- **Initial compositions**
  - **Solder:**
    \[x_{\text{Sn}, 0} = 0.98\]
    \[(\text{Sn})\text{-matrix} \]
    \[x_{\text{Sn}} = 0.999\]
    \[\text{Cu}_6\text{Sn}_5\text{-precipitates} \]
    \[x_{\text{Sn}} = 0.4545\]
  - **IMC layer**
    \[\text{Cu}_6\text{Sn}_5 \]
    \[x_{\text{Sn}} = 0.4545\]
  - **(Cu)-substrate**
    \[x_{\text{Sn}} = 0.001\]

- **System size:** 0.1\(\mu\)m x 0.5\(\mu\)m
Effect of grain boundary diffusion

\[ D_{\text{CuSn}}^{(\text{Cu})} = 2 \cdot 10^{-25} \times 2 \cdot 10^{-25} \text{ m}^2/\text{s} \]
\[ D_{\text{CuSn}}^{(\text{Cu3Sn})} = 2 \cdot 10^{-15} \times 2 \cdot 10^{-13} \text{ m}^2/\text{s} \]
\[ D_{\text{CuSn}}^{(\text{Cu6Sn5})} = 2 \cdot 10^{-15} \times 2 \cdot 10^{-13} \text{ m}^2/\text{s} \]
\[ D_{\text{Sn}}^{(\text{Sn})} = 2 \cdot 10^{-12} \times 2 \cdot 10^{-12} \text{ m}^2/\text{s} \]
Growth behavior $\text{Cu}_3\text{Sn}$

\[ D^{(\text{Cu})}_\text{Sn} = 2 \cdot 10^{-25} \text{ m}^2/\text{s} \]
\[ D^{\text{Cu}_3\text{Sn}}_\text{Sn} = 2 \cdot 10^{-15} \text{ m}^2/\text{s} \]
\[ D^{\text{Cu}_6\text{Sn}_5}_\text{Sn} = 2 \cdot 10^{-15} \text{ m}^2/\text{s} \]
\[ D^{(\text{Sn})}_\text{Sn} = 2 \cdot 10^{-12} \text{ m}^2/\text{s} \]
\[ D^{\text{surf}}_\text{Sn} = 2 \cdot 10^{-12} \text{ m}^2/\text{s} \]
Examples of applications

- Anisotropic grain growth
- Zener pinning
- Coarsening of precipitates on grain boundaries
- Lead-free solder systems
- Solidification
Solidification

- **Dendritic growth**

- **Eutectic growth**

- **Faceted growth (strong anisotropy)**

4-fold weak anisotropy in interface energy, Cu-Ni

4-fold anisotropy in interface energy

4-fold anisotropy in interface mobility

J. Heulens, K.U. Leuven
Summary

- Understanding microstructure evolution is important for material science, but processes can be very complex
  - Phase-field technique + other models and experimental input

- Principles phase-field modeling
  - Diffuse interface concept, conserved and non-conserved field variables
  - Evolution equations derived from a free energy functional
  - Quantitative aspects: Parameter choice + advanced implementation techniques

- Applications
  - Grain growth, recrystallization, coarsening, solidification, growth intermetallic phases, …