MICROSTRUCTURE SIMULATION MODELS FOR THE GROWTH OF INTERMEDIATE PHASES WITH LOW SOLUBILITY

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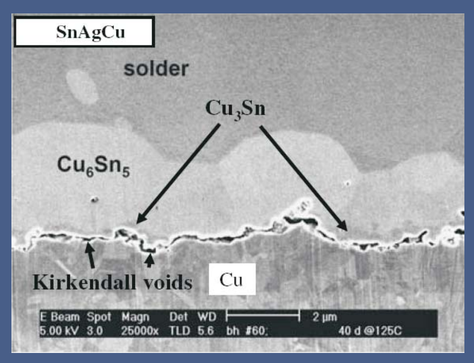
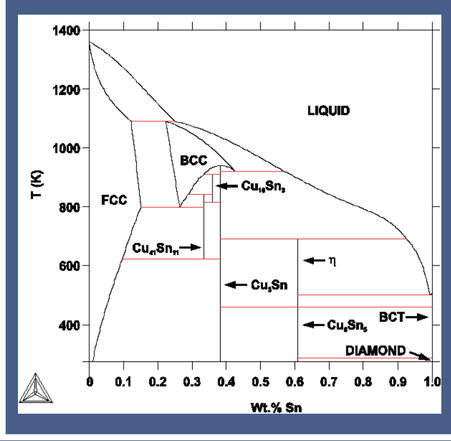
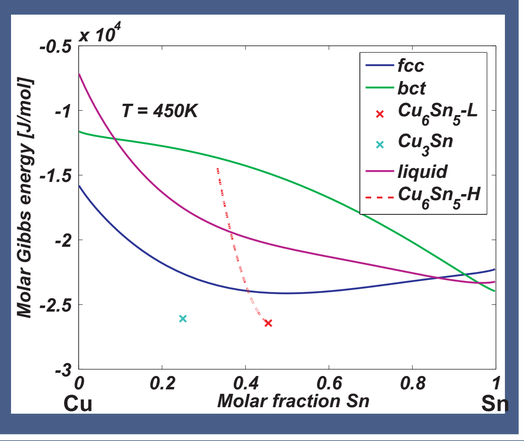
Motivation

Reactive growth of intermediate phases with low solubility is important for many applications, for example intermetallic compound (IMC) growth in solder joints, growth of silicide layers and oxidation.



In phase diagrams and CALPHAD Gibbs energy models, phases with low solubility are often treated as stoichiometric or with a very limited composition domain.
Microstructure and diffusion simulations require however information on the composition dependence of the Gibbs energy, also in metastable regions.





Phase field model for multi-phase systems[1]

Phase-field variables

Phases and grains

$$\vec{\eta} = \left(\eta_{(Cu),1}(\mathbf{r},t), \eta_{(Cu),2}, \ldots, \eta_{(Sn),1}, \ldots, \eta_{Cu6Sn5,1}, \ldots, \eta_{Cu3Sn,1}, \ldots, \eta_{\rho,i}, \ldots\right)$$

with $(\eta_{(Cu),1}, \ldots, \eta_{(Sn),1}, \ldots, \eta_{Cu6Sn5,1}, \ldots, \eta_{Cu3Sn,1}, \ldots, \ldots \eta_{\rho,i}, \ldots) =$
$(1, \ldots, 0, \ldots 0 \ldots), \ldots,$
$, \ldots, (0, \ldots, 1, \ldots, 0, \ldots), \ldots, (0, \ldots, 0, \ldots 1, \ldots), \ldots$

Composition

Binary Cu-Sn

$$\vec{x} = \left(x_{Sn}(\mathbf{r},t)\right), \quad x_{Cu}(\mathbf{r},t) = 1 - x_{Sn}(\mathbf{r},t)$$

Ternary Ag-Cu-Sn

$$\vec{x} = \left(x_{Cu}(\mathbf{r},t), x_{Sn}(\mathbf{r},t)\right),$$
$$x_{Ag}(\mathbf{r},t) = 1 - x_{Cu}(\mathbf{r},t) - x_{Sn}(\mathbf{r},t)$$

Energy functional

$$F_{tot} = \int_V [f_{int}(\eta_{\rho,i}, \nabla\eta_{\rho,i}) + f_{bulk}(\eta_{\rho,i}, x_k)]dV$$

with f_{int} from [2] and f_{bulk} of the form

$$f_{bulk} = \sum_\rho \phi_\rho f^\rho(x_k^\rho) = \sum_\rho \phi_\rho \frac{G_m^\rho(x_k^\rho)}{V_m}$$

Diffusion

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left[\sum_l \left[\left(\sum_\rho \phi_\rho M_{kl}^\rho\right) \nabla\left(\frac{\partial f^\rho}{\partial x_l^\rho}\right)\right]\right]$$

$$\nabla \cdot \left[\sum_l \left[\left(\sum_\rho \phi_\rho \frac{M_{kl}^\rho}{V_m}\right) \nabla\left(\mu_l - \mu_{dep}\right)\right]\right]$$

Phase boundary movement

$$\frac{\partial \eta_{\rho,i}}{\partial t} = -L \frac{\delta F(\eta_{\sigma,i}, x_k)}{\eta_{\rho,i}}$$

Interpolation/phase fraction[1]

$$\phi_\rho = \sum_i \eta_{\rho,i} \Big/ \sum_\sigma \sum_i \eta_{\sigma,i}$$

Phase compositions[3]

$$\begin{cases} \dfrac{\partial f^\beta(x_k^\beta)}{\partial x_k^\beta} = \dfrac{\partial f^\alpha(x_k^\alpha)}{\partial x_k^\alpha} \\ x_k = \sum_\rho \phi_\rho x_k^\rho \end{cases}$$

Diffusion mobilities

$$M_{kl}^\rho = \frac{D_{kl}^\rho}{\partial^2 f^\rho / \partial x_k^\rho \partial x_l^\rho} = \frac{V_m D_{kl}^\rho}{\partial^2 G^\rho / \partial x_k^\rho \partial x_l^\rho}$$

4 Gibbs energy models

Stoichiometric

$$f_{bulk} = \sum_{\rho \neq stoich} \phi_\rho \frac{G_m^\rho(x_k^\rho)}{V_m} + \phi_{stoich} \frac{G_m^{stoich}}{V_m}$$

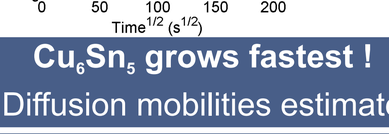
$$\frac{\partial f^\rho(x_k^\rho)}{\partial x_k^\rho} = \frac{\partial f^\sigma(x_k^\sigma)}{\partial x_k^\sigma},$$

$\forall k, \rho \neq \sigma$ solution phases

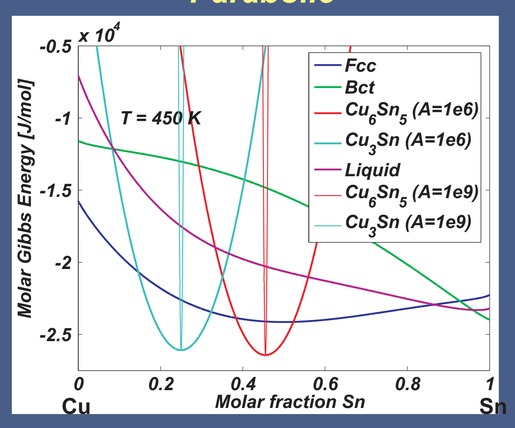
$$x_k - x_k^{stoich} = \sum_{\rho = sol} \phi_\rho (x_k^\rho - x_k^{stoich}), \forall k$$

$$D_{kl}^{stoich} = M_{kl}^{stoich} = 0$$

Diffusion through IMC phase however requires $G^\rho(x_k)$ to model grad(μ_k), the driving force for diffusion



Parabolic



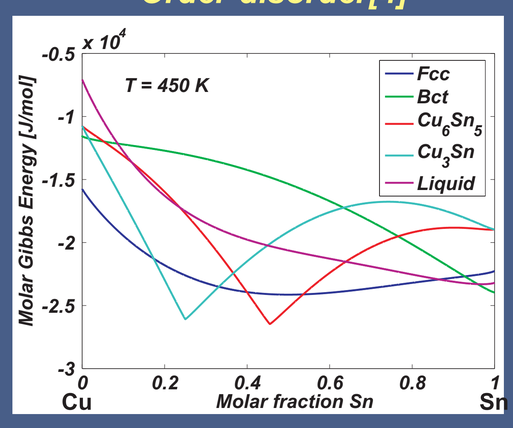
$$V_m f^{stoich} = \frac{A^{stoich}}{2}(x_{Sn} - x_{stoich})^2 + G_m^{stoich}$$

Small shift in composition depending on choice A_{stoich}

$$M^{stoich} = \frac{D^{stoich}}{A^{stoich}}$$

To optimize -- From existing optimization

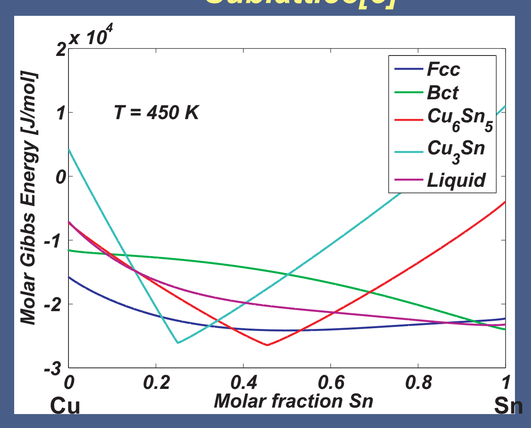
Order-disorder[4]



$$G_m^{Cu3Sn} = x_{Cu}G_{Cu}^0 + x_{Sn}G_{Sn}^0 + (y_{Cu}^1 y_{Sn}^2 - x_{Cu}x_{Sn})G_{Cu3Sn}^{ord}$$
$$+ x_{Cu}x_{Sn}L_{Cu,Sn} + RT[0.75(y_{Cu}^1 \ln(y_{Cu}^1) + y_{Sn}^1 \ln(y_{Sn}^1))$$
$$+ 0.25(y_{Cu}^2 \ln(y_{Cu}^2) + y_{Sn}^2 \ln(y_{Sn}^2))]$$

with $G_{Ag}^0 = GHSER + 5000, L_{Cu,Sn}, G_{Cu3Sn}^{ord}$ optimized

Sublattice[5]



Sublattices: $(Cu,Sn)_{0.75}(Cu,Sn)_{0.25}$

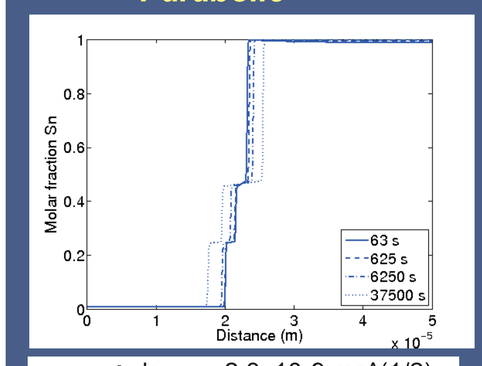
$$G_m^{Cu3Sn} = y_{Cu}^1 y_{Cu}^2 G_{Cu}^0 + y_{Sn}^1 y_{Sn}^2 G_{Sn}^0$$
$$+ y_{Cu}^1 y_{Sn}^2 G_{Cu3Sn}^0 + y_{Sn}^1 y_{Cu}^2 G_{Sn3Cu}^0$$
$$+ RT[0.75(y_{Cu}^1 \ln(y_{Cu}^1) + y_{Sn}^1 \ln(y_{Sn}^1))$$
$$+ 0.25(y_{Cu}^2 \ln(y_{Cu}^2) + y_{Sn}^2 \ln(y_{Sn}^2))]$$

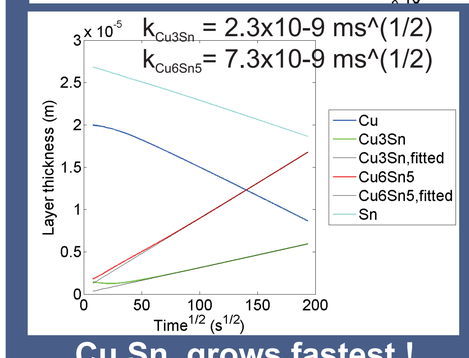
with $G_{Sn3Cu}^0 = G_{Cu}^0 + G_{Sn}^0 - G_{Cu3Sn}^0$

$$M^{Cu3Sn} = \beta^{Cu3Sn}(0.75 y_{Cu}^1 y_{Sn}^1 + 0.25 y_{Cu}^2 y_{Sn}^2)$$ [6]

Intermediate phase growth (T=450)

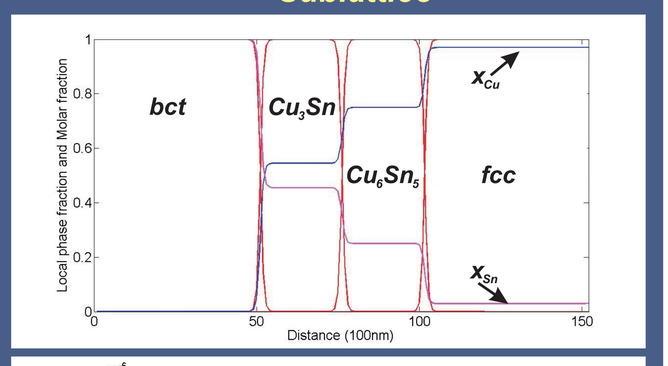
Parabolic

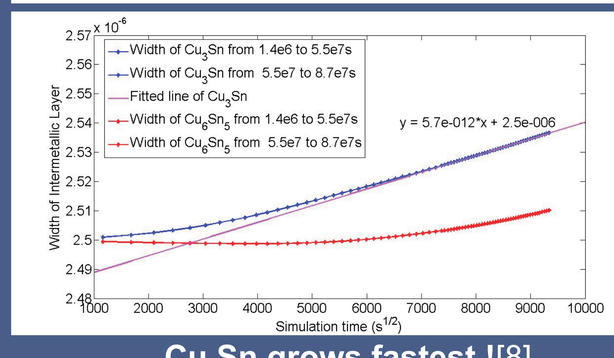




Cu_6Sn_5 grows fastest !

Sublattice





Cu_3Sn grows fastest ![8]

Diffusion mobilities estimated based on interdiffusion data from [7]

Concluding remarks

- Gibbs energy model affects IMC growth behavior and diffusion paths
- The presented approaches can be used with sharp interface models as well
- Order-disorder and sublattice model allow for extrapolation to higher order systems and iterative improvement of the model parameters
- Ab initio calculations are required to optimize the G^0 and G^{ord}

References

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