Formation of Core-Shell Particles by Solid-State Dewetting of a Binary Alloy Thin Film

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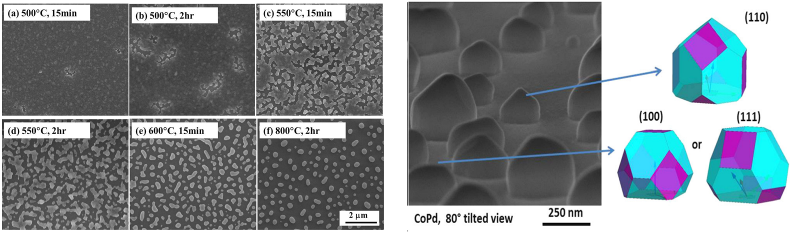
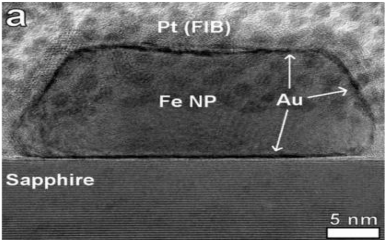
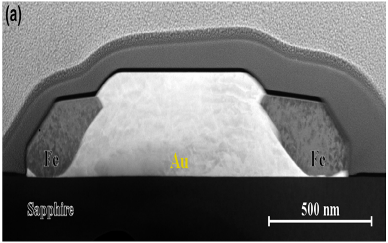
Motivations and Goals



Dewetting of CoPd alloy film, 25nm thickness, 67 at. % Co → Micron-sized alloy particles (from Esterina et al., JAP 118, 144902 (2015)).





Left photo: Dewetting of FeAu alloy film, 4nm thickness, 80 at. % Fe → Nanometer-sized alloy particles. Film annealed at 1100 C for 1 h. (from Amram & Rabkin, ACS Nano 8, 10687 (2014)). **Right photo:** Micron-scale particles.

Motivations and Goals

"Very little is known about the kinetics of phase transformations in nano- and microparticles, both in terms of experimental observations and at the level of available kinetic models" : Amram & Rabkin

The goal of research is to advance understanding of how solid alloy particles are formed through dewetting of a single-crystal films and what factors influence their compositions

We employ a novel kinetic model (based on PDEs) that accounts for the major physical mechanisms involved: the surface and bulk diffusion, bulk phase separation, and surface segregation (thermodynamic or kinetic) in the solid state

Model outline

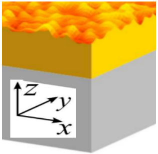
- Physics includes the bulk and surface diffusions of type A and type B atoms in a substitutional binary alloy (say, A: Fe, and B: Au), the thermodynamic and/or kinetic segregation of either A or B to the surface, the bulk phase separation (if the alloy is thermodynamically unstable), the dewetting potential (a van der Walls-type attractive-repulsive intermolecular force)
- 1D modeling to reduce complexity; thus *the film height* $h = h(x,t)$, and

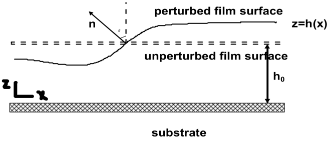
$$0 < C_A(x,t),\ C_B(x,t),\ C_A^{(b)}(x,z,t), C_B^{(b)}(x,z,t) < 1, \tag{1}$$

$$C_A(x,t) + C_B(x,t) = 1,\ C_A^{(b)}(x,z,t) + C_B^{(b)}(x,z,t) = 1. \tag{2}$$

  Notice: $C_A(x,t)$ and $C_A^{(b)}(x,z,t)$ will be eliminated from model equations.

- Assume small surface slope at all times, $|h_x| \ll 1$. The effect of this approximation (SSA) on model results is typically minor





Model formulation (based on Zhang et al., JMPS 100, 21-44 (2017))

- Surface diffusion-driven evolution of a film height $h(x,t)$:

$$h_t = -\Omega\left(\frac{\partial J_A}{\partial x} + \frac{\partial J_B}{\partial x}\right), \quad J_i = -M_i C_i(x,t)\frac{\partial \mu_i}{\partial x}, \quad i = A\,, B. \tag{3}$$

- Evolution of the surface concentration:

$$\delta\frac{\partial C_B}{\partial t} + C_B^{(b)} h_t = -\Omega\frac{\partial J_B}{\partial x} + \Omega F_B. \quad \text{Notice: } {}^{(b)} \equiv \text{“bulk”} \tag{4}$$

- Evolution of the bulk concentration:

$$\frac{\partial C_B^{(b)}}{\partial t} = -\Omega\nabla\cdot\mathbf{G}_B^{(b)}, \quad \mathbf{G}_B^{(b)} = -M_B^{(b)}\nabla\mu^{(b)}, \quad \nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{k}\frac{\partial}{\partial z}. \tag{5}$$

- The regular solution models for the total surface energy and the bulk energy: link

$$\gamma = \gamma_A(h)C_A + \gamma_B(h)C_B + \alpha_{int}C_AC_B + kT\nu_0\left(C_A\ln C_A + C_B\ln C_B\right), \tag{6}$$

$$g^{(b)} = g_AC_A^{(b)} + g_BC_B^{(b)} + \beta_{int}C_A^{(b)}C_B^{(b)} + kT\nu_0^{(b)}\left(C_A^{(b)}\ln C_A^{(b)} + C_B^{(b)}\ln C_B^{(b)}\right). \tag{7}$$

These energies enter the expressions for the chemical potentials μ_i and $\mu^{(b)}$ (not shown).

Model formulation

Let $\alpha_{int} = 0$ (the enthalpy) in the surface energy γ, then:

1. The model can be reduced to two PDEs (for h and $C_B^{(b)}$) through the explicit derivation of McLean's surface segregation equation (D. McLean, *Grain Boundaries in Metals*, 1957)
2. Phase separation on the surface is eliminated; however, the bulk phase separation ($\beta_{int} \neq 0$) may extend to the surface

The mass conservation provides b.c.'s at the film surface and at the substrate:

$$z = h: \quad \mathbf{n} \cdot \mathbf{G}_B^{(b)} = F_B, \quad \mathbf{G}_B^{(b)} = -M_B^{(b)} \nabla \mu^{(b)}, \tag{8}$$

$$z = 0: \quad \frac{\partial \mu^{(b)}}{\partial z} = 0. \tag{9}$$

Here F_B is the (unknown) adsorption-desorption flux of B-atoms on the bulk side of the film surface [Zhang et al. (2017)]:

$$F_B = -k_a \left[\frac{1}{\delta} \left(\frac{\partial \gamma}{\partial C_A} - \frac{\partial \gamma}{\partial C_B} \right) - \left(\frac{\partial g^{(b)}}{\partial C_A^{(b)}} - \frac{\partial g^{(b)}}{\partial C_B^{(b)}} \right) \right]. \tag{10}$$

Model reduction

- Consider F_B:

$$F_B = -k_a \left[\frac{1}{\delta} \left(\frac{\partial \gamma}{\partial C_A} - \frac{\partial \gamma}{\partial C_B} \right) - \left(\frac{\partial g^{(b)}}{\partial C_A^{(b)}} - \frac{\partial g^{(b)}}{\partial C_B^{(b)}} \right) \right]. \qquad (11)$$

- Introduce the constitutive relation that states the weights of two contributions to F_B on the RHS of Eq. (11):

$$\frac{1}{\delta} \left(\frac{\partial \gamma}{\partial C_A} - \frac{\partial \gamma}{\partial C_B} \right) = \xi \left(\frac{\partial g^{(b)}}{\partial C_A^{(b)}} - \frac{\partial g^{(b)}}{\partial C_B^{(b)}} \right), \quad \xi > 0. \qquad (12)$$

  - $\xi \approx 1 \iff F_B/k_a \approx 0$: fast adsorption-desorption kinetics. This is the McLean's condition (*Grain Boundaries in Metals*, 1957).
  - $\xi \ll 1$: F_B is primarily determined by the bulk properties
  - $\xi \gg 1$: F_B is primarily determined by the surface properties

  In computations we use $0.1 \le \xi \le 10$.

- Eq. (12) **and** the choice of vanishing surface enthalpy, $\alpha_{int} = 0$, allow to obtain $C_B = C_B\left(C_B^{(b)};\ parameters\right)$ (McLean's equation). Then only two variables, $C_B^{(b)}(x,t)$ and $h(x,t)$ remain in the mathematical formulation.

Model reduction: the Final System

- The *surface segregation* equation (McLean's equation):

$$C_B = C_B\left(C_B^{(b)};\ parameters\right) : \quad \text{analyzed later in the talk} \tag{13}$$

- Evolution PDE for the bulk concentration:

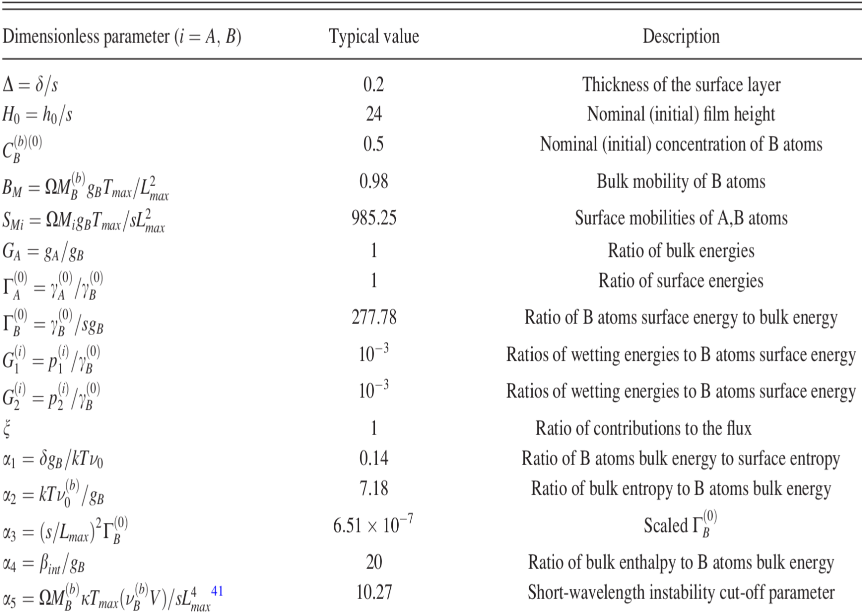
$$\begin{aligned}[h+\delta\Phi]\frac{\partial C_B^{(b)}}{\partial t} &= \Omega M_B^{(b)}\frac{\partial}{\partial x}\left(h\frac{\partial \mu^{(b)}}{\partial x}\right) - \Omega M_A C_B^{(b)}\frac{\partial}{\partial x}\left[(1-C_B)\frac{\partial \mu_A}{\partial x}\right] \\ &+ \Omega M_B\left(1-C_B^{(b)}\right)\frac{\partial}{\partial x}\left[C_B\frac{\partial \mu_B}{\partial x}\right], \qquad (14) \\ \Phi &= \Phi\left(C_B^{(b)};\ parameters\right)\end{aligned}$$

- Evolution PDE for the film height:

$$h_t = \Omega M_A\frac{\partial}{\partial x}\left[(1-C_B)\frac{\partial \mu_A}{\partial x}\right] + \Omega M_B\frac{\partial}{\partial x}\left[C_B\frac{\partial \mu_B}{\partial x}\right] \tag{15}$$

- Through Eq. (13), the evolution of h is (nonlinearly) coupled to the evolution of $C_B^{(b)}$.
- The surface concentration C_B *does not need to be computed* from a PDE, and it can be found by substitution into Eq. (13) after the entire space-time history of the bulk concentration has been determined.

Model reduction



Dimensionless parameter ($i = A, B$)	Typical value	Description
$\Delta = \delta/s$	0.2	Thickness of the surface layer
$H_0 = h_0/s$	24	Nominal (initial) film height
$C_B^{(b)(0)}$	0.5	Nominal (initial) concentration of B atoms
$B_M = \Omega M_B^{(b)} g_B T_{max}/L_{max}^2$	0.98	Bulk mobility of B atoms
$S_{Mi} = \Omega M_i g_B T_{max}/sL_{max}^2$	985.25	Surface mobilities of A,B atoms
$G_A = g_A/g_B$	1	Ratio of bulk energies
$\Gamma_A^{(0)} = \gamma_A^{(0)}/\gamma_B^{(0)}$	1	Ratio of surface energies
$\Gamma_B^{(0)} = \gamma_B^{(0)}/s g_B$	277.78	Ratio of B atoms surface energy to bulk energy
$G_1^{(i)} = p_1^{(i)}/\gamma_B^{(0)}$	10^{-3}	Ratios of wetting energies to B atoms surface energy
$G_2^{(i)} = p_2^{(i)}/\gamma_B^{(0)}$	10^{-3}	Ratios of wetting energies to B atoms surface energy
ξ	1	Ratio of contributions to the flux
$\alpha_1 = \delta g_B/kT\nu_0$	0.14	Ratio of B atoms bulk energy to surface entropy
$\alpha_2 = kT\nu_0^{(b)}/g_B$	7.18	Ratio of bulk entropy to B atoms bulk energy
$\alpha_3 = (s/L_{max})^2\Gamma_B^{(0)}$	6.51×10^{-7}	Scaled $\Gamma_B^{(0)}$
$\alpha_4 = \beta_{int}/g_B$	20	Ratio of bulk enthalpy to B atoms bulk energy
$\alpha_5 = \Omega M_B^{(b)} \kappa T_{max}(\nu_B^{(b)} V)/sL_{max}^4$ [41]	10.27	Short-wavelength instability cut-off parameter

Analysis of (thermodynamic) surface segregation

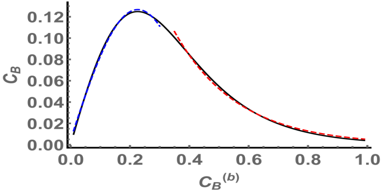
The dimensionless *surface segregation* equation (13):

$$C_B\left(C_B^{(b)}\right) = \left[\left(\frac{1}{C_B^{(b)}} - 1\right)^{\xi\alpha_1\alpha_2} + \exp\left(2\xi\alpha_1\alpha_4 C_B^{(b)}\right) + 1 + \bar{\Psi}\right]^{-1}, \qquad (16)$$

$$\bar{\Psi} = f\left(\xi, G_A, \Gamma_A^{(0)}, \Gamma_B^{(0)}, \alpha_1, \alpha_4, \Delta\right) > 0 \qquad (17)$$

- The *form* of Eq. (16) proves that this is the generalized McLean's equation, see P. Wynblatt and R.C. Ku, "Surface energy and solute strain energy effects in surface segregation", *Surf. Sci.* **65**, 511 (1977)
- $0 < C_B < 1$, as expected
- ξ: Ratio of the contributions in F_B; α_1: Ratio of B atoms bulk energy to the surface entropy; α_2: Ratio of the bulk entropy to B atoms bulk energy; α_4: Ratio of the bulk enthalpy to B atoms bulk energy; G_A: A/B ratio of the bulk energies; $\Gamma_A^{(0)}$: A/B ratio of the surface energies; $\Gamma_B^{(0)}$: Ratio of B atoms surface energy to their bulk energy; Δ: thickness of the surface layer.

Analysis of (thermodynamic) surface segregation



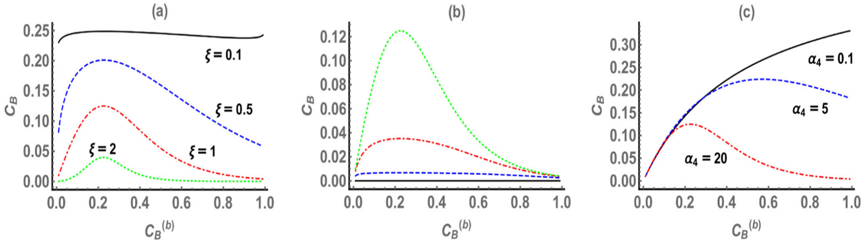
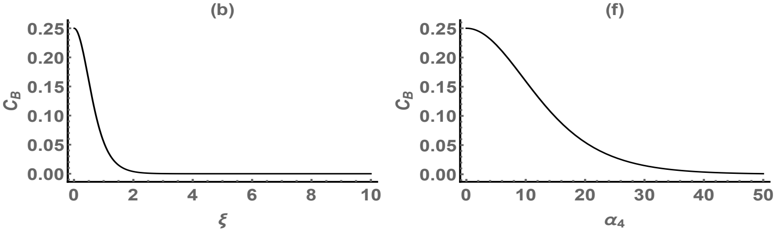


FIG. 3. C_B vs. $C_B^{(b)}$ at ξ, $\Gamma_A^{(0)}$ and α_4 varied. In (b), the solid, dashed, dashed-dotted, and dotted lines correspond to $\Gamma_A^{(0)} = 0.9, 0.96, 0.97, 1$, respectively.

ξ: Ratio of the contributions in F_B; $\Gamma_A^{(0)}$: A/B ratio of the surface energies; α_4: Ratio of the bulk enthalpy to B atoms bulk energy; other parameters fixed to values in the Table

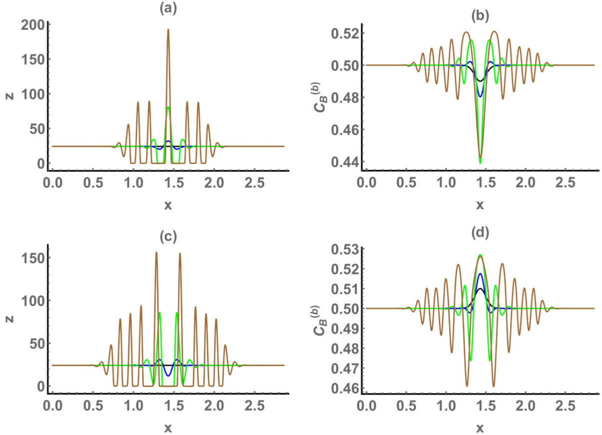
Analysis of (thermodynamic) surface segregation



$C_B^{(b)} = 0.5$;
ξ: Ratio of the contributions in F_B;
α_4: Ratio of the bulk enthalpy to B atoms bulk energy;
Other parameters fixed to values in the Table

Conclusion: In all scenarios, *B*-atoms are severely depleted at the surface; they segregate from the surface into the bulk, while *A*-atoms segregate from the bulk to the surface

Computations of surface morphology and bulk concentration



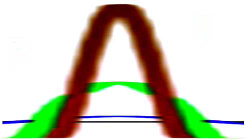
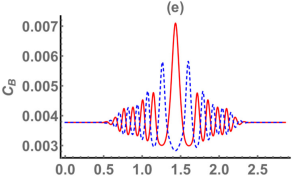
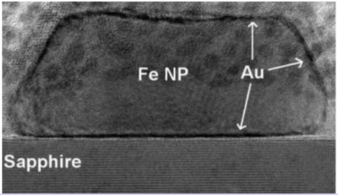


FIG. 6. Evolution of the small Gaussian spike of the bulk concentration (b) and (d) and the corresponding film morphology (a) and (c) (initially the planar surface). The parameters in the Gaussian are $W = 0.1$, $L = 2.86$ and (b) $\eta = -0.01$ and (d) $\eta = 0.01$. The final profiles of the surface concentration for these cases are shown in (e), with the solid (dashed) line corresponding to $\eta = -0.01$ ($\eta = 0.01$).





Computations of surface morphology and bulk concentration

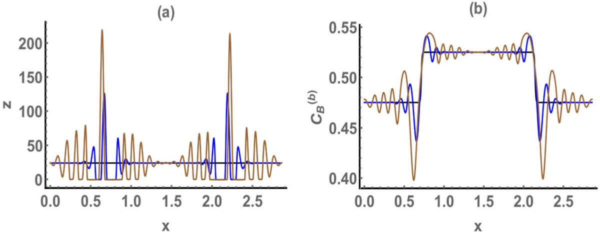


FIG. 8. (b) Evolution of the step-like profile of the bulk concentration and (a) the corresponding film morphology (initially the planar surface).

Conclusions:

- Particle size 0.5μm - 8μm (from LSA); agreement with the FeAu experiment by Amram & Rabkin at $h \sim 12$ nm and $T = 650$ C
- Particles: core-shell, as per analysis of segregation and computations; shell: the nanometric segregated *A*-layer, core: *A*-rich alloy. The wetting layer: *B*-rich alloy. (Partial agreement with the experiment, as the model yet does not predict a single-metal particle core)
- Let $\beta_{int} = 0$, then the bulk phase separation is turned off→ evolution time scale increases; the core-shell particles still form. **Bulk/surface diffusion and thermodynamic surface segregation are the most important mechanisms in the formation of core-shell particles**

THANKS!

Paper: Journal of Applied Physics 123, 034302 (2018)

Preprint: arxiv.org/abs/1801.00764