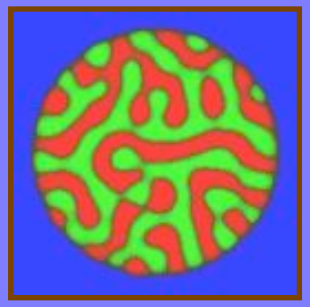

Phase Field Simulation of Thermotransport

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Collaboration with

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Laboratory of Materials and Coatings for Extreme Environment - MCEE

NIST Diffusion Workshop, May 12 & 13, 2008

Outline

- Overview of Our Research
- Introduction
- Motivation
- Mathematical Formulation
- Model Description
- Results
- Summary
- Future Work

Prime-Reliant Coatings for Gas Turbines

- Overview
- Motivation
- Introduction
- Formulation
- The Model
- Results
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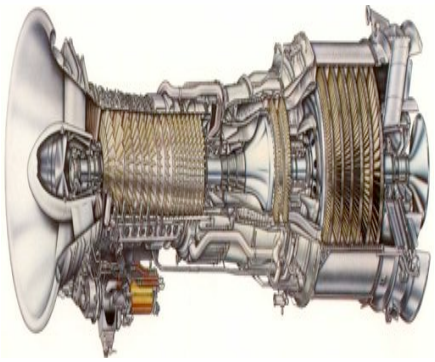
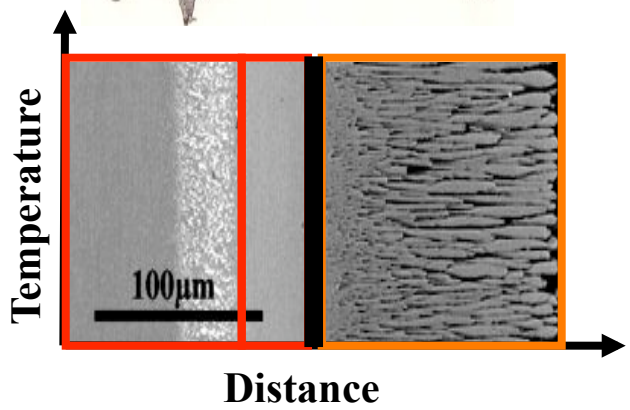
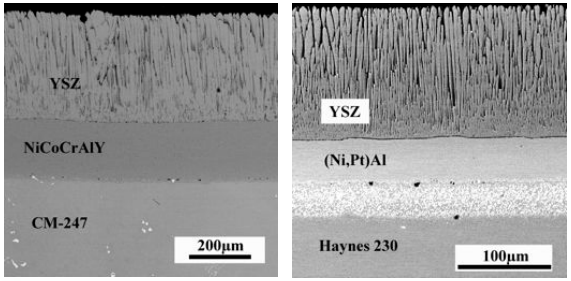
- Future Work







Topcoat: ZrO_2-8wt.%Y_2O_3

$t' \rightarrow t \rightarrow (f+m)$ Phase Transformations
Sintering, Microstructure and Strain Tolerance

Thermally Grown Oxide (TGO)

Thermal Expansion/Contraction Mismatch
Transient/Initial Oxidation
Phase Constituents (α-Al_2O_3 and Others) and Transformations

Bond coat: (Ni,Pt)Al or NiCoCrAlY

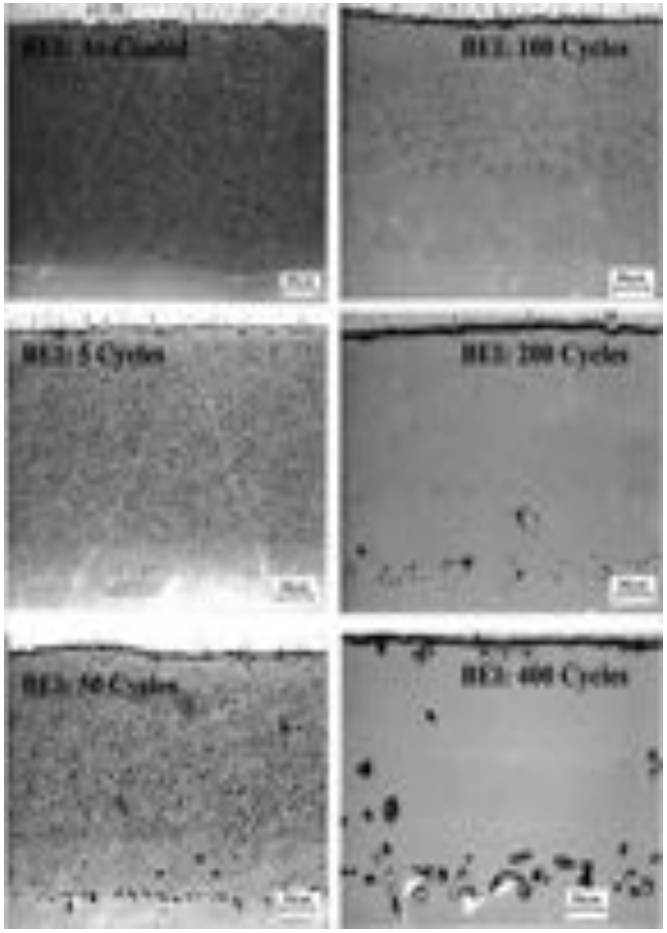
Phase Transformations and Constituents
Inward and Outward Interdiffusion
Creep Deformation/Surface Undulation

Superalloy Substrates

Phase Transformations and Constituents
Outward Interdiffusion
Creep Deformation

Isothermal Coating-Substrate Diffusion

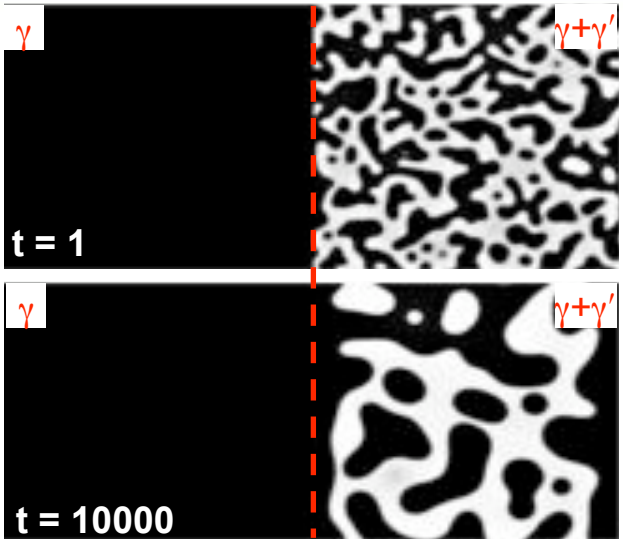
- Al Diffuses Out to Form Al_2O_3 Scale.
  - Polymorphic Transformation of Al_2O_3 Scale.
- Al Diffuses into the Substrate:
  - Dissolution of High Al β phase.
  - Formation of Oxide Scale Rich in Ni, Co and Cr.
  - Formation of Kirkendall Porosity.
- Elements Added to Substrate for High-Temperature Strengthening Diffuse into the Coating:
  - Affect Near-Surface Mechanical Properties of a Component.
  - Affect the Formation or Adherence of the Protective Oxide Scale.

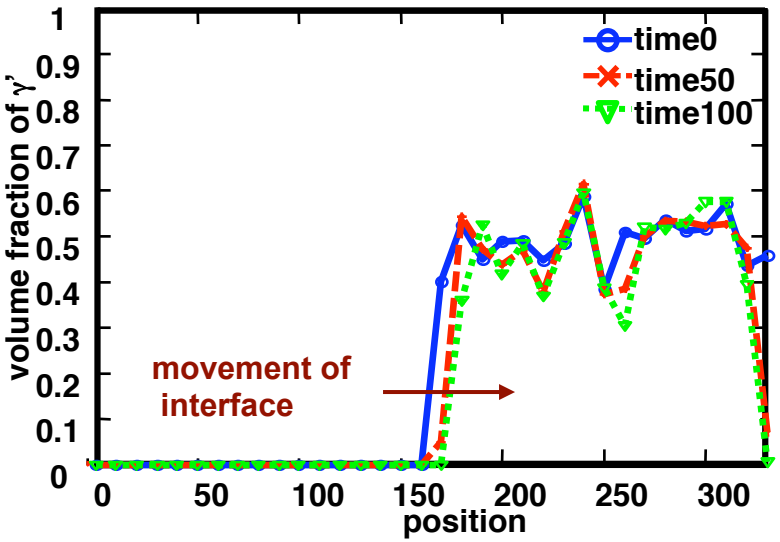


Backscatter electron micrographs of NiCoCrAlY-IN738 illustrating dissolution of β-phase as a function of thermal cyclic oxidation at 1121°C

Isothermal PFM

γ vs. γ+γ′ Diffusion Couples in Ni-Al Alloys



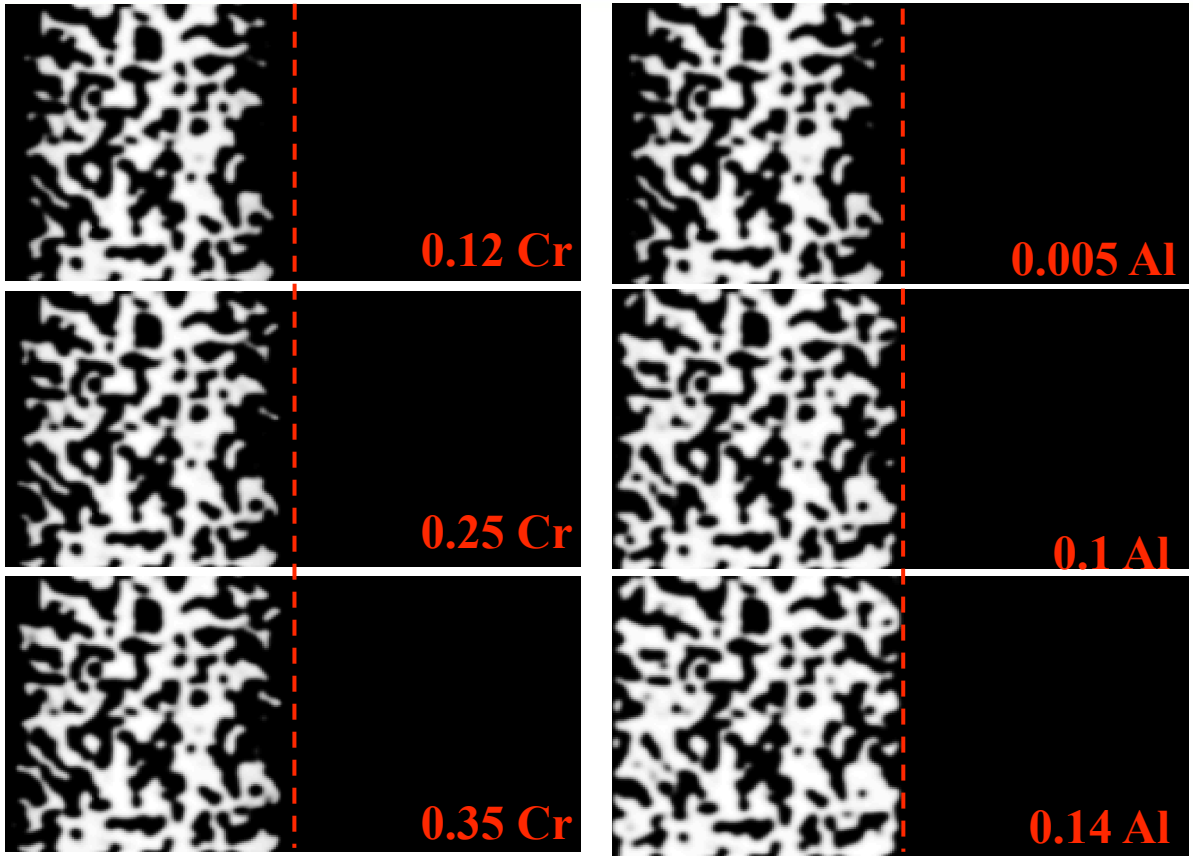


Simulated microstructure and volume fraction profile of γ vs. γ+γ′ couple.[1]

- Boundary Movement towards two-phase region: γ>γ+γ′
- Addition of γ phase at the boundary: type I boundary.
- Depletion of γ+γ′ region or increase in γ phase region was observed experimentally by Susan et al.[2]

[1] *R. R. Mohanty, A. Leon and Y. H. Sohn, Comp. Mater. Sci, in Press, 2008.*
[2] *D. F. Susan and A. R. Marder, Acta Mater. 49, 2001, 1153.*

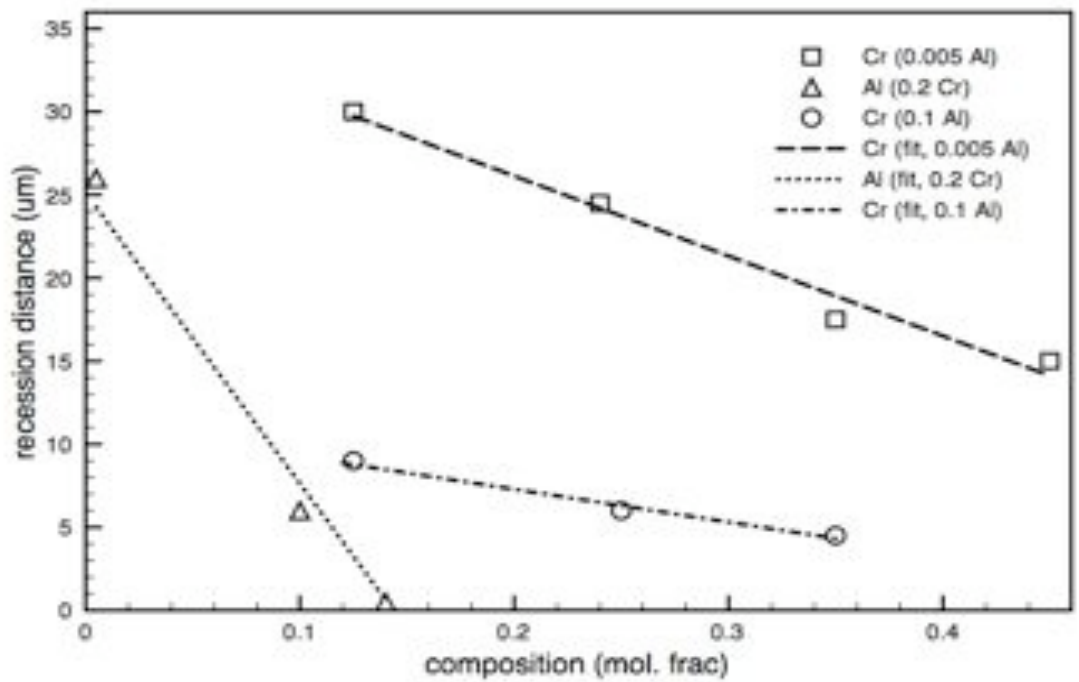
γ vs. γ+β (Ni-Cr-Al) Diffusion Couples
Composition-Dependent Microstructural Evolution



Higher concentration of Cr and Al yields lower dissolution rate of β phase and slower movement of the γ/γ+β boundary.

[1]Wu K, Chang A, Wang Y. Scripta mater. 2004; 50: 1145.

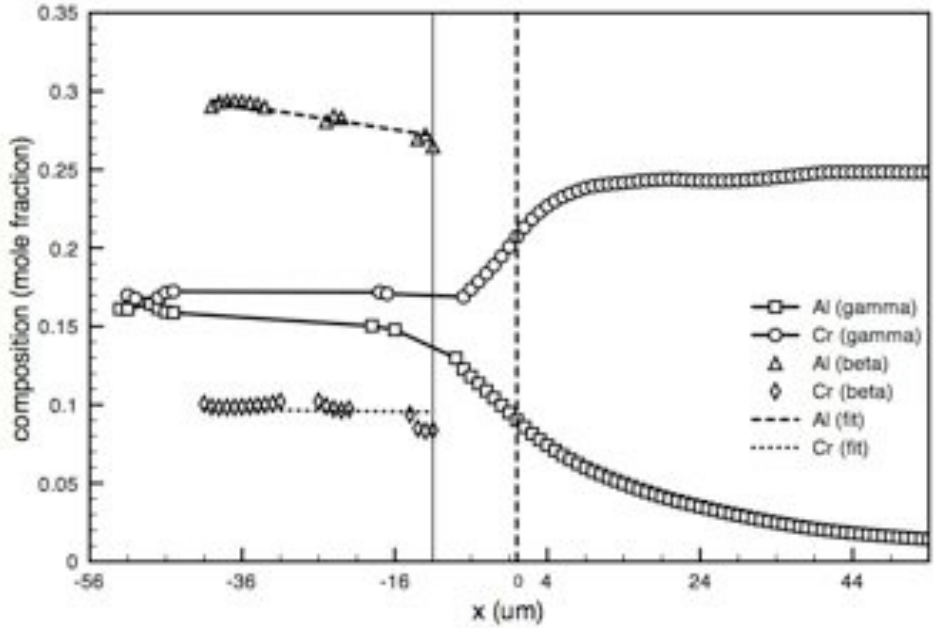
γ vs. γ+β (Ni-Cr-Al) Diffusion Couples
Composition-Dependent Microstructural Evolution



Recession Distance of γ+β region vs. Al and Cr concentration in the single phase γ alloy as predicted by phase field simulation.

Concentration of Al has greater effect on the dissolution of β phase and movement of the γ/γ+β interface.

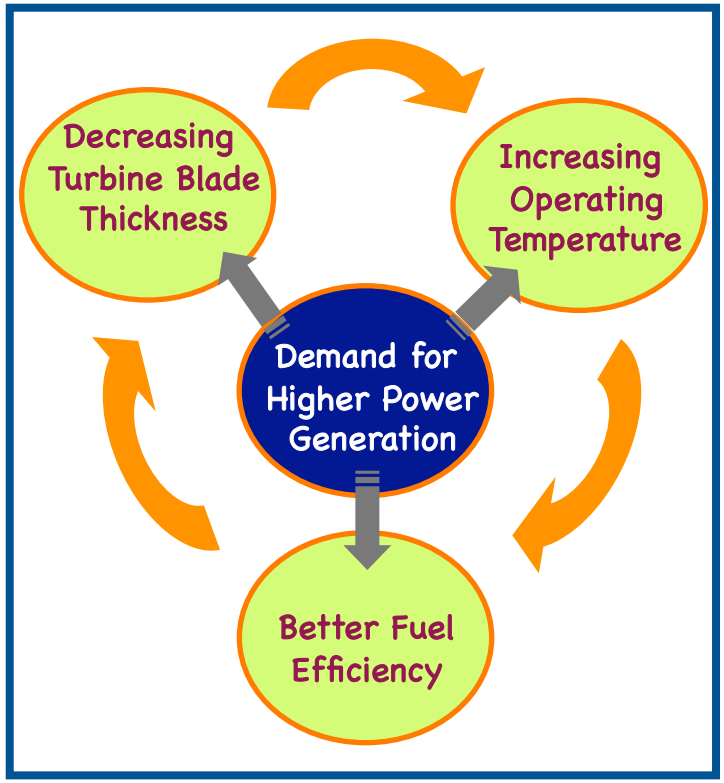
γ vs. γ+β (Ni-Cr-Al) Diffusion Couples
Concentration Profiles

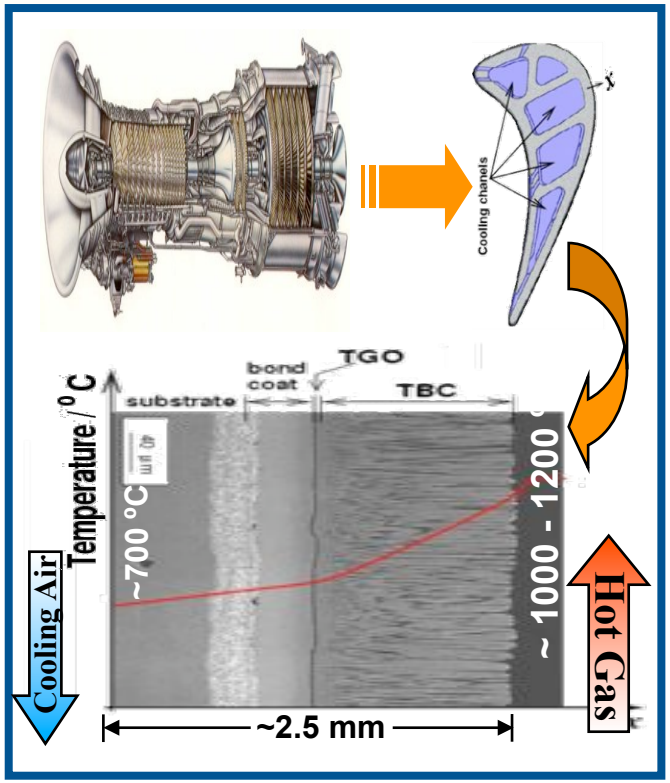


Simulated composition profiles for the γ+β /γdiffusion couple. The dashed and solid vertical lines are the location of the interface at t = 0 and t = 2.5 hour respectively.

- Interdiffusion occurs both in the γ and γ+β regions (i.e., limitation of a typical sharp interface models).
- Concentrations of γ and β phases in the γ+β region are close to the equilibrium compositions.

Motivation for The Present Work





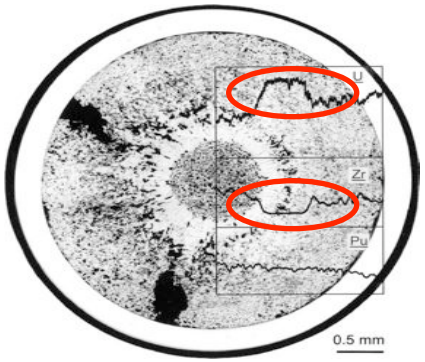
- Decreasing Thickness of Turbine Blades, Increasing Miniaturization in Electronics Industry
- Demand for More MW, Increasing Operating Temperatures and Better Efficiency in Nuclear Energy Production

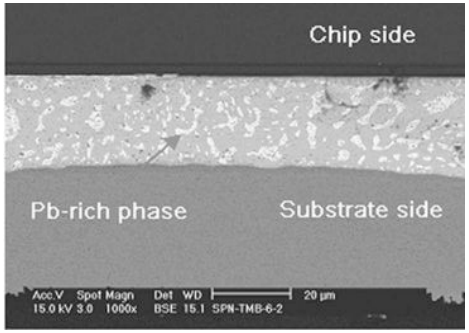
Motivation for The Present Work

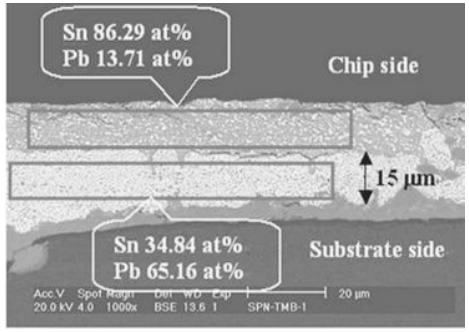
- Large magnitude of temperature gradient can exist:

  Turbine Blades ≈ 120 - 200 ºC/mm

  Nuclear Fuel ≈ 240 ºC/cm



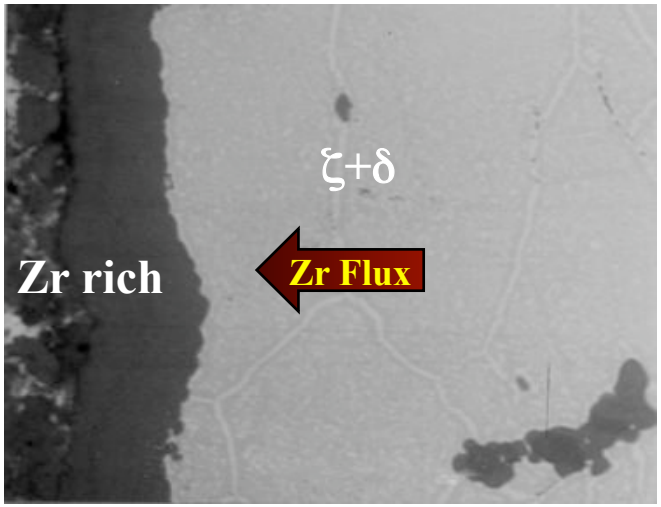


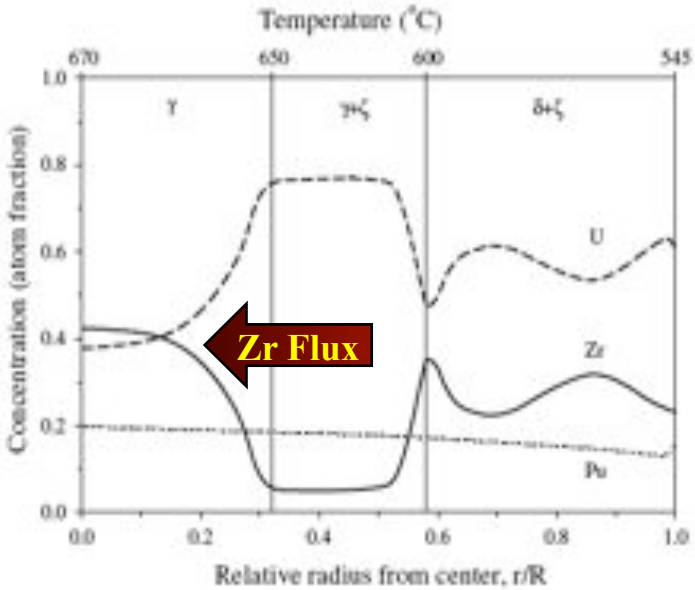


Composition and Phase Redistribution in Nuclear Fuel and Chip Interconnects

- Constituent and Phase Redistribution due to temperature gradient:
  - Change in Solidus Temperature → unwanted melting
  - Causes phase transformations
  - Change in physical and mechanical properties

Motivation for The Present Work





Composition and Phase Redistribution in U-Pu-Zr Nuclear Fuel

- Constituent redistribution in U-Pu-Zr alloy[1,2]:
  - Phase transformation occurred from the initial γ-bcc phase upon thermotransport treatment.
  - Zr flux towards the hot end forming a Zr rich layer.

[1] *Y.H.Sohn, M.A.Dayananda, G.L.Hofman, R.V.Strain, S.L.Hayes, J. Nuclear Mater. (2000), 279, 317.*
[2] *Y. Kim, G. Hofman, S. Hayes and Y. H. Sohn, J. Nuclear Mater. (2004), 327, 27.*

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The Thermotransport Phenomenon

- Development of concentration gradient in a homogeneous alloy when a temperature gradient is applied - Ludwig - Soret effect.
- Fick's 1st Law must be modified to account for the effect of temperature gradient on the diffusion flux:

$$J_i = -D_i \frac{\partial c_i}{\partial x} - D_i' c_i \frac{\partial T}{\partial x}$$

where, D_i and D'_i are the isothermal and thermal diffusion coefficients[1].

- The concentration gradient can eventually reach steady state.

$$J_i = 0 \Rightarrow -D_i \frac{\partial c_i}{\partial x} = D_i' c_i \frac{\partial T}{\partial x}$$

- The concentration gradient is a characteristic of the system.

1. Allnatt AR, Chadwick AV. Chemical Rev., (1967), 67, p.681

The Thermotransport Phenomenon

- For an interstitial solute in a binary alloy, the flux equation relative to lattice can be written as:

$$J = -\frac{Dc}{RT}\left[RT\frac{d\ln c}{dx} + \frac{Q^*}{T}\frac{dT}{dx}\right]$$

where, Q^* = amount of heat carried per atom (Heat of Transport)

Steady state distribution is defined by only one Q^*

- For a substitutional alloy, relative rate of movement of solute and solvent are important:

$$J_i = -\frac{D_i c_i}{RT}\left[RT\frac{d\ln c_i}{dx} + \frac{Q_i^*}{T}\frac{dT}{dx}\right]$$

where, i denotes each element.

Condition for Validity: Vacancy mechanism of diffusion
Equilibrium vacancy concentration

Diffusivity and Q^* for both the elements necessary.

Formulation

Constant Molar Volume and Density: V_m, ρ

Concentration: n_i Mole Fraction: c_i

Mass Balance: $\sum_i n_i = \rho = \frac{1}{V_m}$, $\sum_i c_i = 1.0$

Model System

Binary Substitutional Alloy:

components A, B

- Vacancy mechanism for diffusion
- Vacancies exist everywhere in equilibrium concentration under the thermal gradient[1]

1. Howard R. E. and Lidiard A. B., "Matter Transport in Solids", Rep. Prog. Phys., 27, p.161

Formulation

Lattice Frame of Reference

- From the Onsager's linear relationship of fluxes and forces, the flux equation under thermal gradient is[1]:

$$J_k = \sum_{i=1}^{n-1} L_{ki}\left(X_i - X_n + Q_i^* X_q\right) \qquad [1]$$

where,

$X_i = -\nabla\mu_i$	: Chemical Driving Force
$X_q = -\dfrac{\nabla T}{T}$	: Thermal Driving Force
Q_i^*	: Heat of Transport

- With the vacancy mechanism for diffusion being operative, vacancy (v) is treated as the third constituent[2], so that;

$$J_A = L_{AA}\left(X_A - X_v + Q_A^* X_q\right) + L_{AB}\left(X_B - X_v + Q_B^* X_q\right) \qquad [2a]$$

$$J_B = L_{BA}\left(X_A - X_v + Q_A^* X_q\right) + L_{BB}\left(X_B - X_v + Q_B^* X_q\right) \qquad [2b]$$

where, L_{ij} are Onsager's phenomenological coefficients.

1. De Groot S. R., "Thermodynamics of Irreversible Processes", 1952
2.Howard R. E. and Lidiard A. B., "Matter Transport in Solids", Rep. Prog. Phys., 27, p.161.

Formulation

- Assuming vacancies exist everywhere in their equilibrium concentration in a dilute solution[1]:

$$X_v = -\nabla\mu_v = -kT\frac{\nabla c_v}{c_v} = -h_{fv}\frac{\nabla T}{T} = h_{fv}X_q \qquad [3]$$

where, h_{fv} is the enthalpy of formation of a vacancy.

- Substituting this in the flux equation:

$$J_A = L_{AA}\left[X_A + \left(Q_A^* - h_{fv}\right)X_q\right] + L_{AB}\left[X_B + \left(Q_B^* - h_{fv}\right)X_q\right] \qquad [4a]$$

$$J_B = L_{BA}\left[X_A + \left(Q_A^* - h_{fv}\right)X_q\right] + L_{BB}\left[X_B + \left(Q_B^* - h_{fv}\right)X_q\right] \qquad [4b]$$

- Since : $c_v << c_A, c_B$, applying Gibbs-Duhem relation:

$$c_A X_A + c_B X_B + c_v X_v \approx c_A X_A + c_B X_B \approx 0 \qquad [5]$$

1. Howard R. E. and Lidiard A. B., "Matter Transport in Solids", Rep. Prog. Phys., 27, p.161

Formulation

- Using law of mass conservation in Eq.(5) we can write:

$$L_{AA}X_A + L_{AB}X_B = \frac{cL_{AA} - (1-c)L_{AB}}{c} X_A = \rho(1-c)\beta_A X_A \qquad [6a]$$

$$L_{BB}X_B + L_{BA}X_A = \frac{(1-c)L_{BB} - cL_{BA}}{1-c} X_B = \rho c\beta_B X_B \qquad [6b]$$

where, β_i corresponds to atomic mobilities of individual elements and c is the mole fraction of B.

- Substituting Eq. 6 in the flux equation (Eq.4) :

$$J_A = -\rho(1-c)\beta_A \nabla\mu_A + \left[L_{AA}\left(Q_A^* - h_{fv}\right) + L_{AB}\left(Q_B^* - h_{fv}\right)\right]X_q \qquad [7a]$$

$$J_B = -\rho c\beta_B \nabla\mu_B + \left[L_{BA}\left(Q_A^* - h_{fv}\right) + L_{BB}\left(Q_B^* - h_{fv}\right)\right]X_q \qquad [7b]$$

Formulation

Laboratory Frame of Reference

- In the laboratory frame of reference sum of the fluxes vanishes:

$$\tilde{J}_A + \tilde{J}_B = 0 \qquad [8a]$$

$$\text{or, } \tilde{J}_A = -\tilde{J}_B = J_A - (1-c)(J_A + J_B) = cJ_A - (1-c)J_B \qquad [8a]$$

- Substituting the intrinsic fluxes from Eq. 7 and using Onsager's reciprocal relation, $L_{ij} = L_{ji}$:

$$\begin{aligned}\tilde{J}_A &= -\rho c(1-c)\beta_A \nabla\mu_A + \rho c(1-c)\beta_B \nabla\mu_B + \\ &\quad [cL_{AA} - (1-c)L_{BA}]Q_A^{*\prime} X_q + [cL_{AB} - (1-c)L_{BB}]Q_B^{*\prime} X_q \\ &= -\rho c(1-c)[\beta_A \nabla\mu_A - \beta_B \nabla\mu_B] + \rho c(1-c)\left[\beta_A Q_A^{*\prime} - \beta_B Q_B^{*\prime}\right] X_q\end{aligned} \qquad [9]$$

where, $Q_i^{*\prime} = Q_i^{*} - h_{fv}$

Formulation

- Applying Gibbs-Duhem relation:

$$\nabla\mu_A = c\nabla\mu_A^{eff}, \nabla\mu_B = -(1-c)\nabla\mu_A^{eff} \qquad [10]$$

where, $\nabla\mu_A^{eff} = -\nabla\mu_B^{eff} = \nabla(\mu_A - \mu_B)$ [11]

- Substituting Eq. 11 in the flux equation, Eq. 9, the final flux equation can be written as :

$$\tilde{J}_A = -\rho c(1-c)\left[c\beta_A + (1-c)\beta_B\right]\nabla\mu_A^{eff} + \rho c(1-c)\left[\beta_A Q_A^{*'} - \beta_B Q_B^{*'}\right]X_q$$
$$= -M_c\nabla\mu_A^{eff} + M_Q X_q \qquad [12a]$$

$$\tilde{J}_B = -\tilde{J}_A = -M_c\nabla\mu_B^{eff} + M_Q\frac{\nabla T}{T} \qquad [12b]$$

$$M_c = \rho c(1-c)\left[c\beta_A + (1-c)\beta_B\right]$$

$$M_Q = \rho c(1-c)\left[\beta_A Q_A^{*'} - \beta_B Q_B^{*'}\right]$$

The Model

- A simple regular solution model was used for the chemical free energy of the system :

$$f(c,T) = RT\left[c\ln c + (1-c)\ln(1-c)\right] + \chi c(1-c)$$

- The Cahn-Hilliard free energy functional is defined as:

$$F = N_V \int_V \left[f(c,T) + \kappa(\nabla c)^2 \right] dV$$

where, N_V is the total number of atoms in the system, V is the volume and κ corresponds to gradient energy coefficients.

- In an inhomogeneous system the effective chemical potential can be obtained as:

$$\mu_B^{eff} = \frac{\delta F}{\delta n_B} = V_m \frac{\delta F}{\delta c}$$

The Model

- Now the flux equation can be written as:

$$\tilde{J}_B = -V_m M_c \nabla\left(\frac{\partial f}{\partial c} - 2\kappa_c \nabla^2 c\right) + M_Q \frac{\nabla T}{T}$$

- The spatio-temporal evolution of composition is governed by the continuity equation:

$$\frac{\partial n_B}{\partial t} = \frac{1}{V_m}\frac{\partial c(x,t)}{\partial t} = -\nabla \cdot \tilde{J}_B$$
$$= \nabla \cdot \left[V_m M_c \nabla\left(\frac{\partial f}{\partial c} - 2\kappa_c \nabla^2 c\right) - M_Q \frac{\nabla T}{T}\right]$$

- Applied to both single phase and two phase alloys of a binary system.

Numerical Implementation

- The governing equation was made dimensionless for numerical convenience.
- Both constant and functions of temperature was used for atomic mobility and heat of transport values.
- Numerical calculations were performed using Fipy Partial Differential Equation (PDE) solver using a finite volume approach.
- Simulations of single phase (1D) and two phase (2D) were performed.

$$\beta_i = A_i \exp\left(-Q_i / RT\right) \quad \text{(Arrehenius[1])}$$

$$Q_i^* = B_i + C_i T \quad \text{(Linear[2])}$$

1.A. Engstrom, J. Agren, Z. Metallk, 87, 1996.
2.S. C. Axtell, O. N. Carlson, Metall. Trans, A21, 1990.

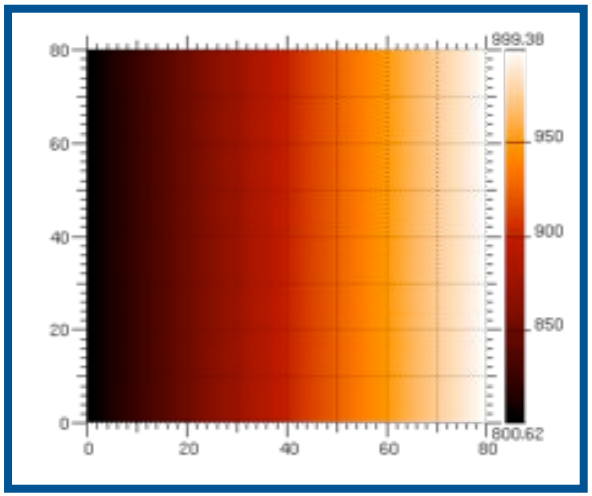
Temperature Distribution and Free Energy

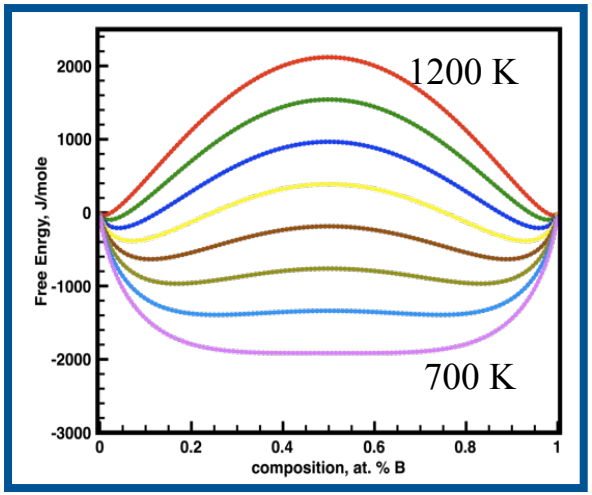
- The temperature field obeys Laplace's equation

$$\nabla^2 T = 0$$

subjected to boundary conditions

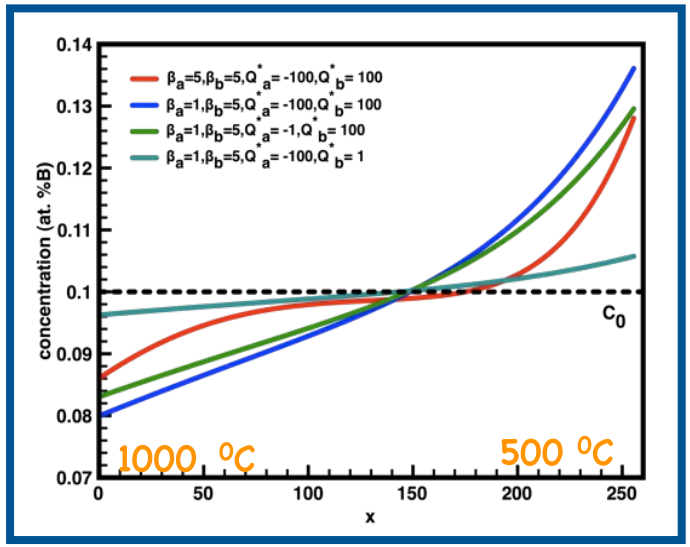
$$J_q \cdot \hat{n} = 0, T\big|_{x=0} = T_{\min}, T\big|_{x=L} = T_{\max}$$

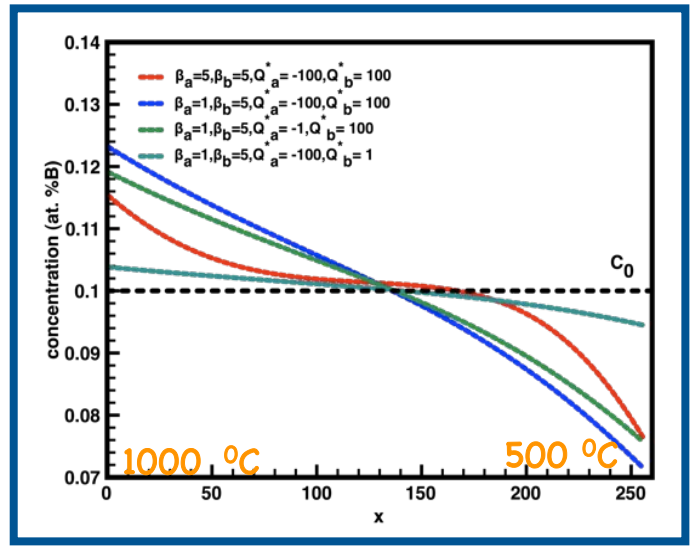




Applied temperature gradient and the free energy vs. composition curves at different temperatures.

Results
1D Simulation of Single Phase Alloy

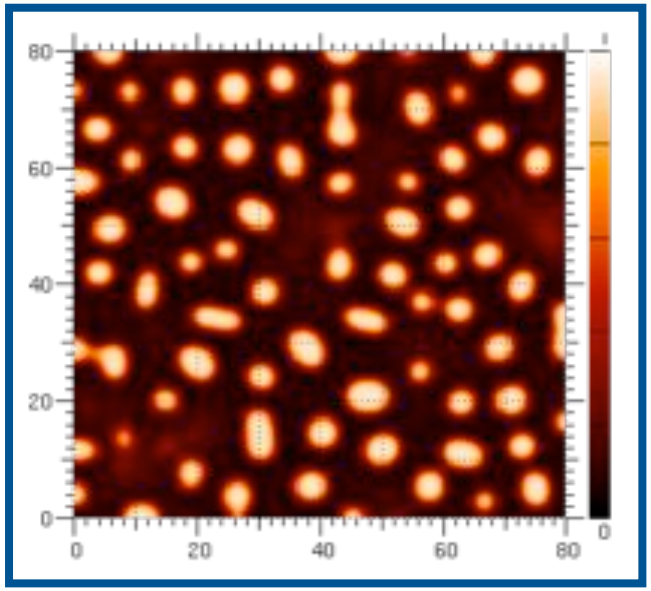


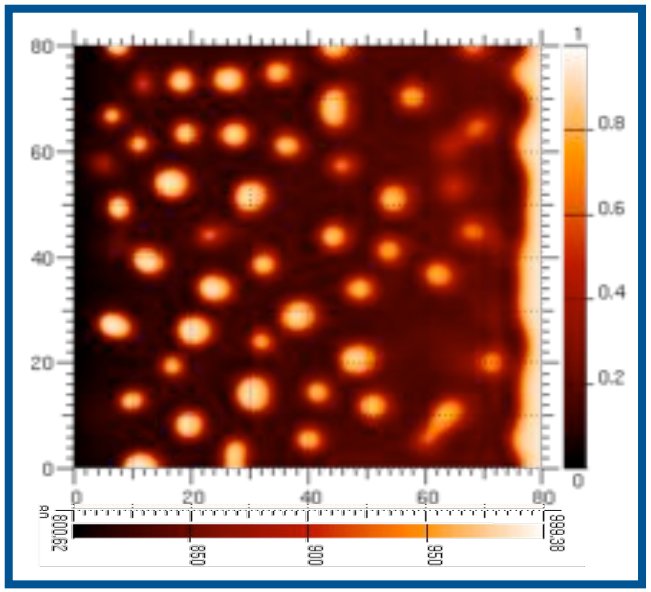


Composition Profiles of Component B developed under Temperature Gradient for various combinations of β and Q^*.

- The concentration gradient depends on the initial composition and the values of atomic mobility as well as heat of transport.
- Steady state can be reached after a long time of anneal under thermal gradient.

Results
2D Simulation of Two Phase Alloy





Phase distribution before and after the application of temperature gradient. The bright regions are B rich phase.

- Preferential movement of B atoms towards the hot end and A atoms towards the cold end.
- Phase redistribution occurs with B rich and A rich single phase regions forming at the hot and cold ends.

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Results
2D Simulation of Two Phase Alloy

- Elements in a substitutional alloy can have similar mobilities.
- β and Q^* values of all the elements are important and needs to be considered.
- Combination of β and Q^* decide the magnitude and sign of M_Q
- Four cases were considered:

  Case - I: $Q_A^* = Q_B^*$ and $M_Q < 0$

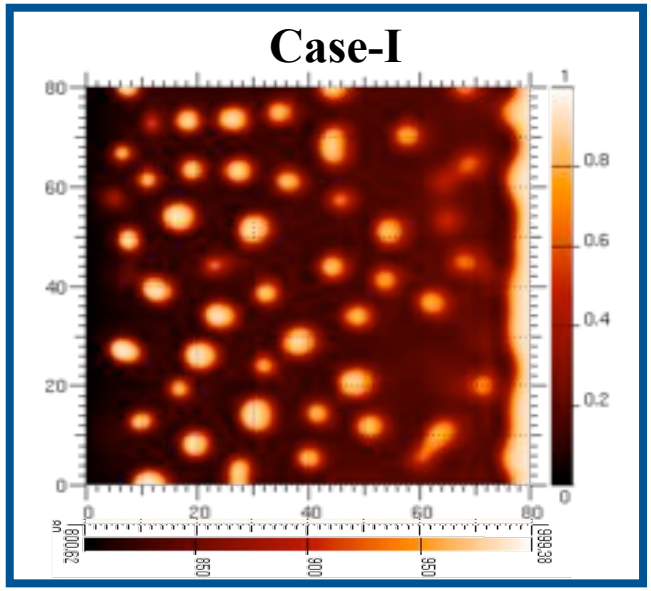
  Case - II: $Q_B^* >> Q_A^*$ and $M_Q < 0$, $|M_Q|$ is large

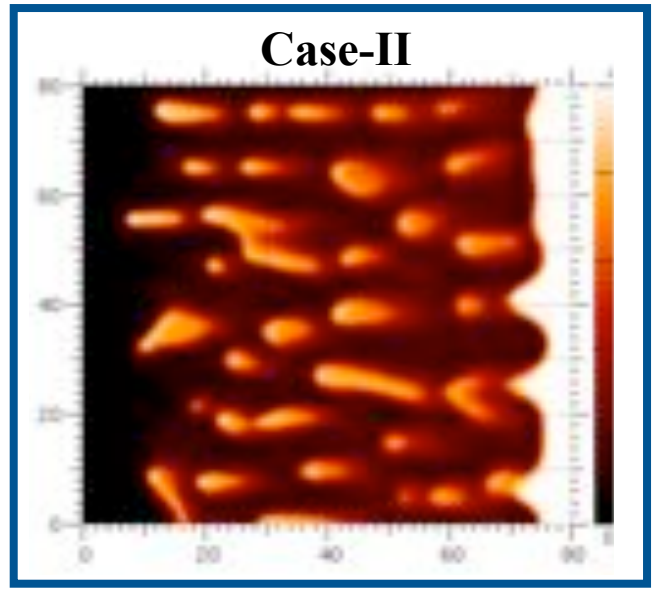
  Case - III: $Q_B^* << Q_A^*$ and $M_Q > 0$, $|M_Q|$ is large

  Case - IV: $Q_B^* < Q_A^*$ and $M_Q > 0$, $|M_Q| \approx 0$

In all the four cases $\beta_B > \beta_A$ and $Q_A^*, Q_B^* > 0$.

2D Simulation of Two Phase Alloy

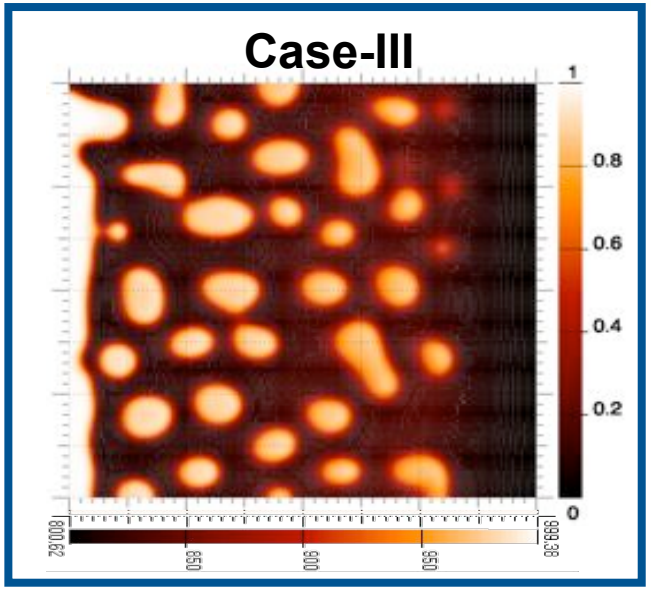


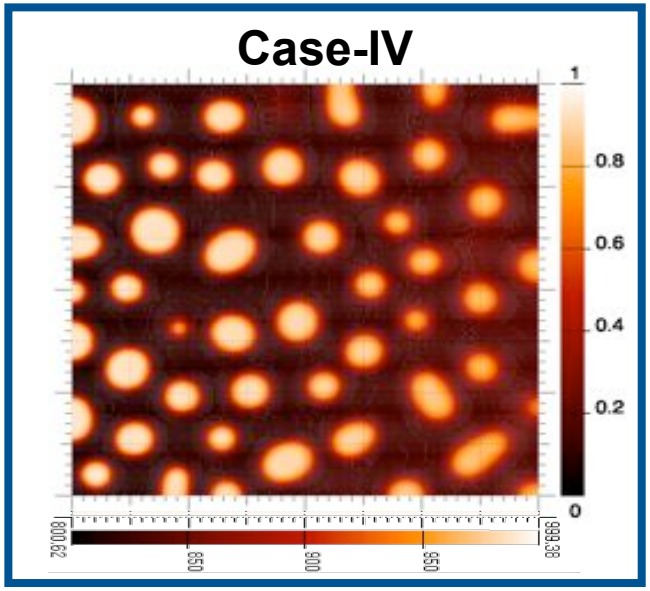


Phase distribution in a two phase alloy with different M_Q values subjected to temperature gradient.

- Both in Case - I and Case - II, $M_Q < 0$ and the contribution of temperature gradient to the flux is in the same direction to that of the concentration gradient.
- Stronger effect is evident in Case - II with a large M_Q.

2D Simulation of Two Phase Alloy





Phase distribution in a two phase alloy with different M_Q values subjected to temperature gradient.

- Both in Case - III and Case - IV, $M_Q > 0$ and the contribution of temperature gradient to the flux is in the opposite direction to that of the concentration gradient.
- Effect is negligible in Case - IV with $M_Q \approx 0$.

Summary

- A phase field model was devised to simulate Thermotransport phenomenon in binary alloys.
- Constituent and phase redistribution in single and two phase alloys were studied utilizing the model.
  - Concentration gradient developed in an initially homogeneous single phase alloy when subjected to temperature gradient.
  - A and B rich layer formed due to the preferential movement of atoms towards the hot or cold end.
  - The redistribution is dependent on the sign and magnitude of heat of transport and values of atomic mobilities.
- The model can use real thermodynamic and kinetic data.

Future Work

- Extension of the model to simulate real alloy systems using thermodynamic and kinetic database.
- Extension of the model to study ternary systems.

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