Interdiffusion Structures and Coefficients in Ternary Systems: Research and Education at UCF

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Multicomponent - Multiphase Diffusion Workshop
April 1-2, 2004

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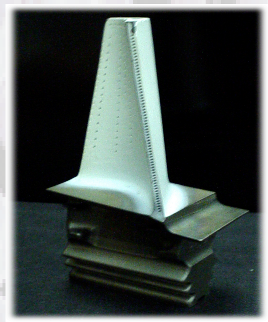
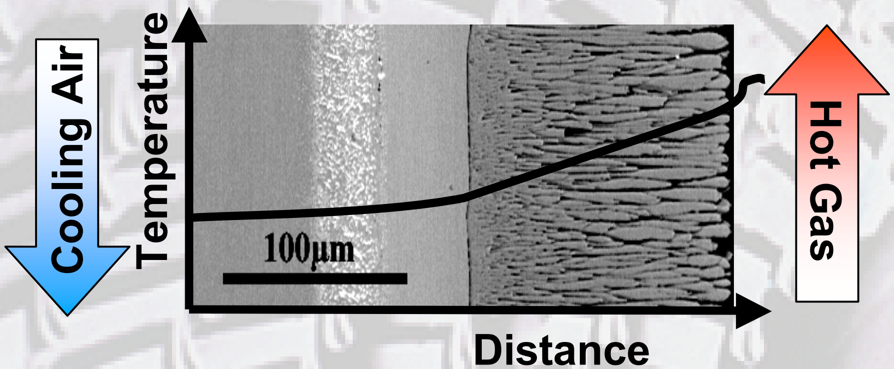
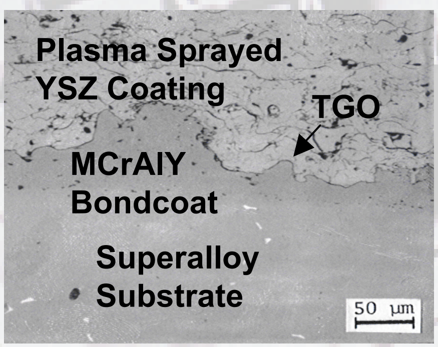
Interdiffusion Structures and Coefficients in Ternary Systems

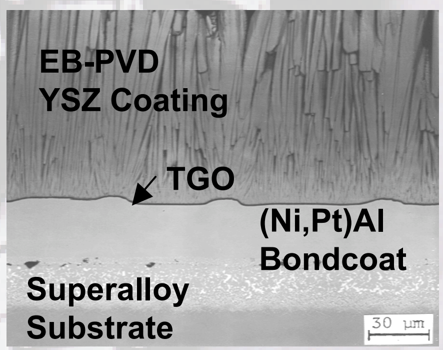
- Typical Application: High Temperature Coatings for Turbine Blades.
- Diffusion Couple Studies.
- Diffusion Structure (Microstructural Development) and Diffusion Paths.
- Compositional Analysis by EDS on TEM via Specimen Preparation by FIB-INLO.
- Determination of Ternary Interdiffusion Coefficients.

Gas Turbine Needs: Oxidation Resistant and Thermal Barrier Coatings (TBCs)









- Coatings Provide Protection of Hot Components in Advanced Gas Turbine Engines
  - Increase in Performance, Efficiency, Reliability and Maintainability.
  - Reduction in Emission and Life Cycle Costs.
- Processing, Lifetime Prediction and Failure Mechanisms of High Temperature Coatings Requires Knowledge in Multicomponent - Multiphase Diffusion.
- Coating-Substrate Interdiffusion
- External and Internal Oxidation
- Kirkendall Porosity
- Phase Transformations

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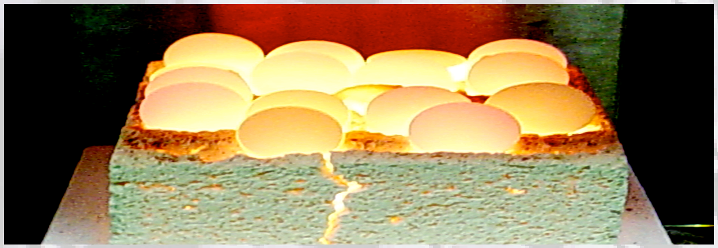
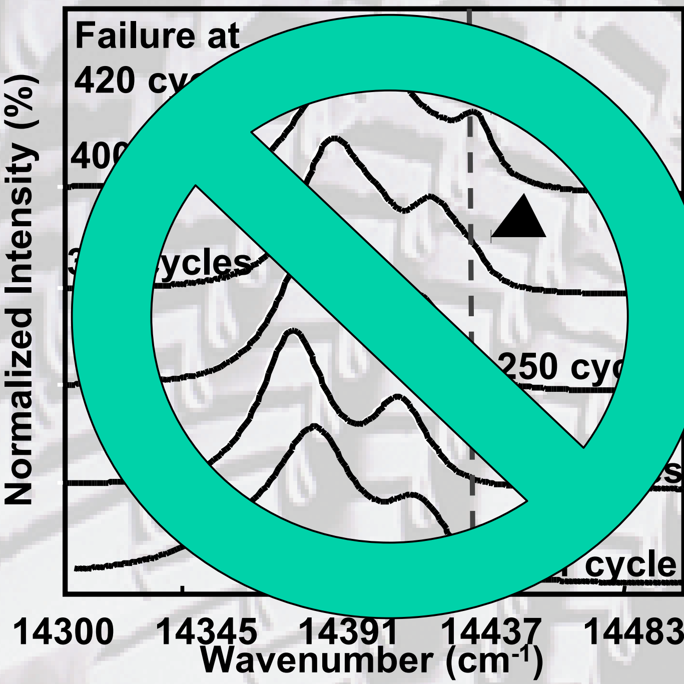
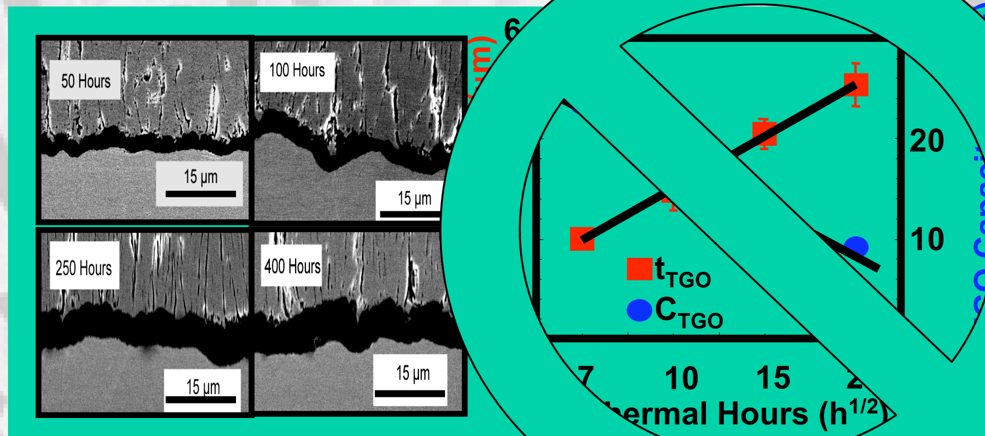
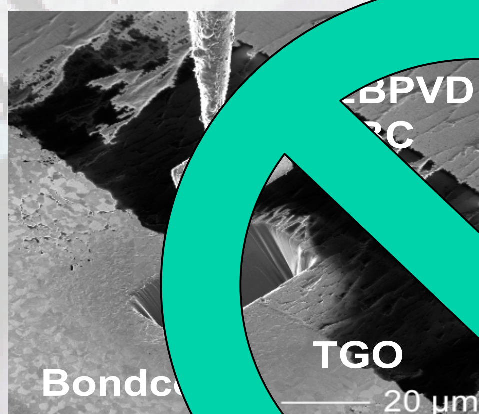
Thermal Barrier Coatings Program Overview: Assessment of Failure Mechanisms by Non-Destructive Evaluation and Advanced Microstructural A is





Damage and Stress Relief Detected Prior to Spallation at 420 Cycles.





FIB-INLO Sp men Preparation o and Subsequent TEM/STEM Analysis

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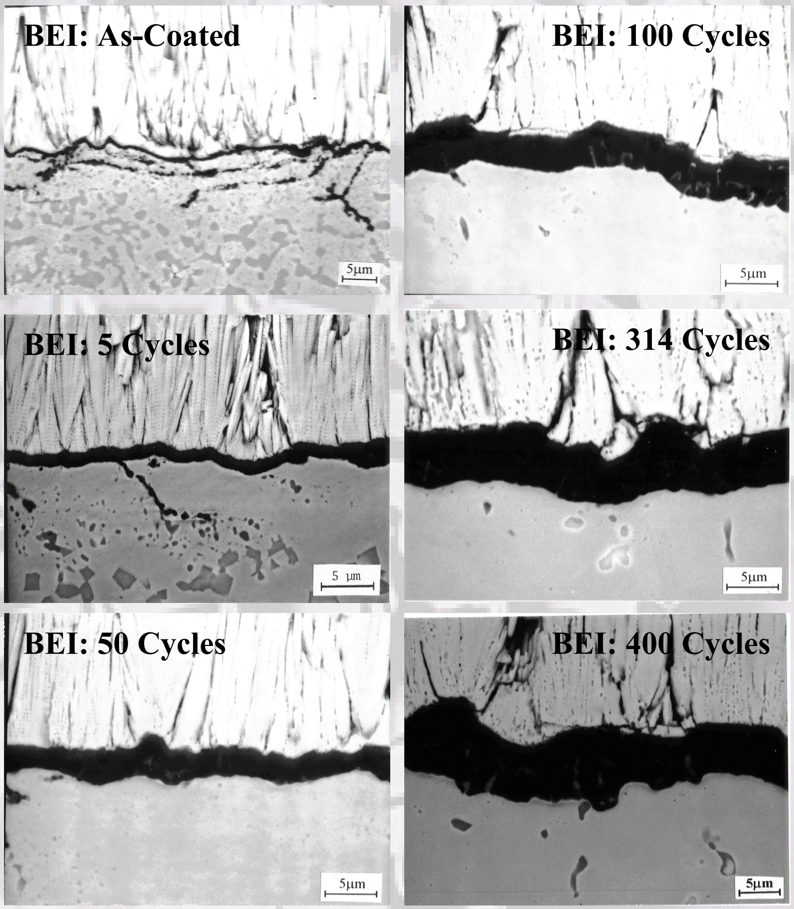
Interdiffusion and Lifetime of TBCs

Parabolic Growth of TGO

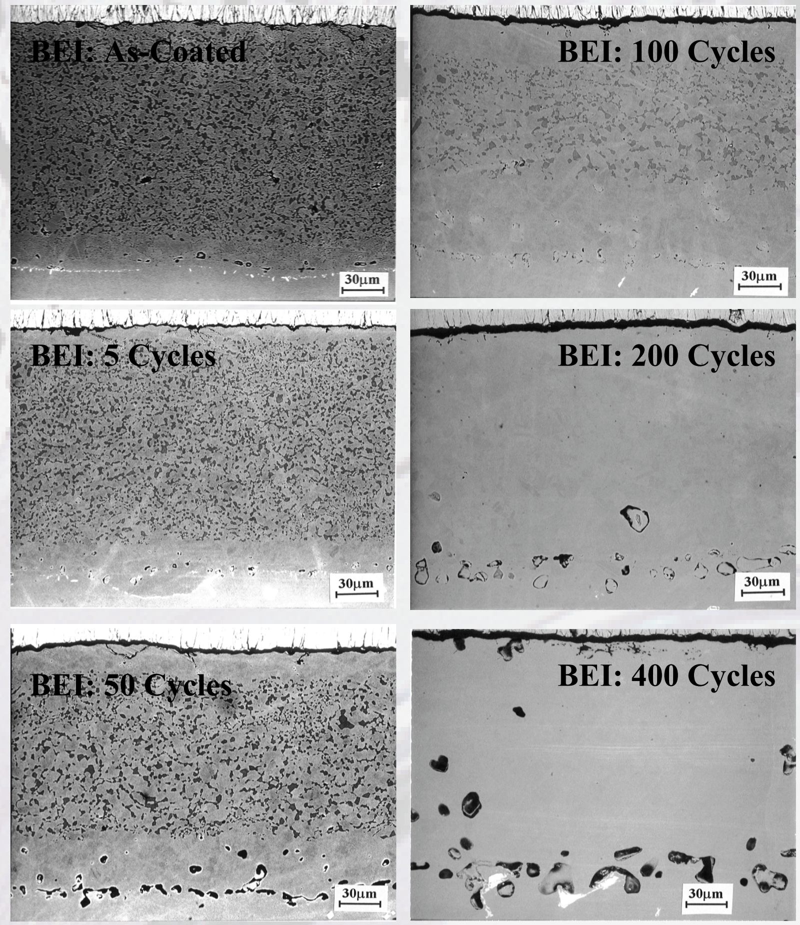
$K_p = 6.3 \times 10^{-3}\ \mu m \cdot sec^{1/2}$



Recession of (β+γ) in NiCoCrAlY

Depletion Zone: $D^{eff} = 3.4 \times 10^{-15}\ m^2/sec$

Interdiffusion Zone: $D^{eff} = 9.3 \times 10^{-15}\ m^2/sec$



Y.H. Sohn et al., Surf. Coat. Technol., 146-147 (2001) pp. 70-78.

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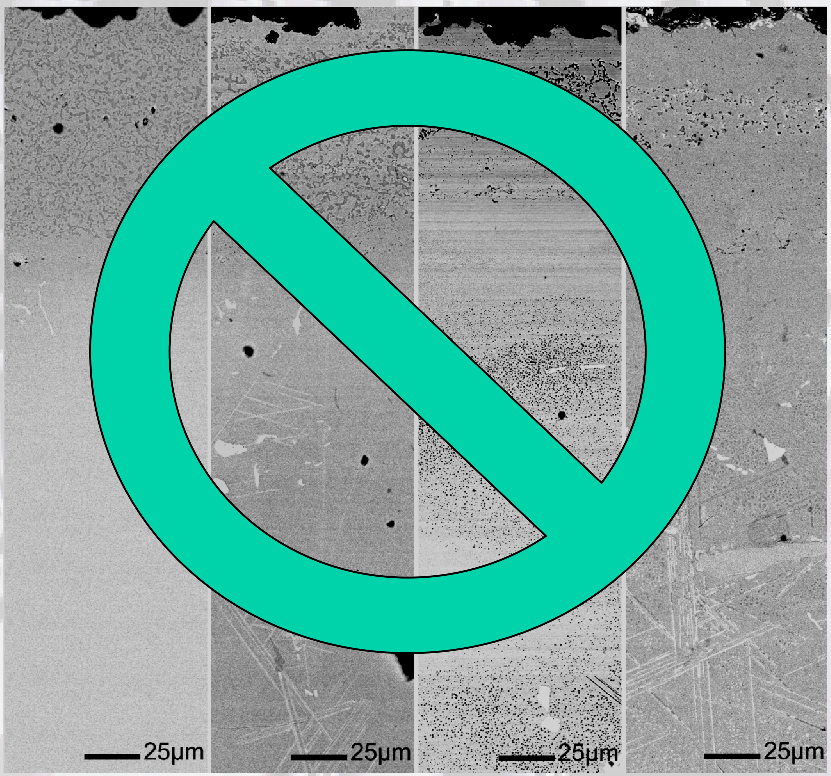
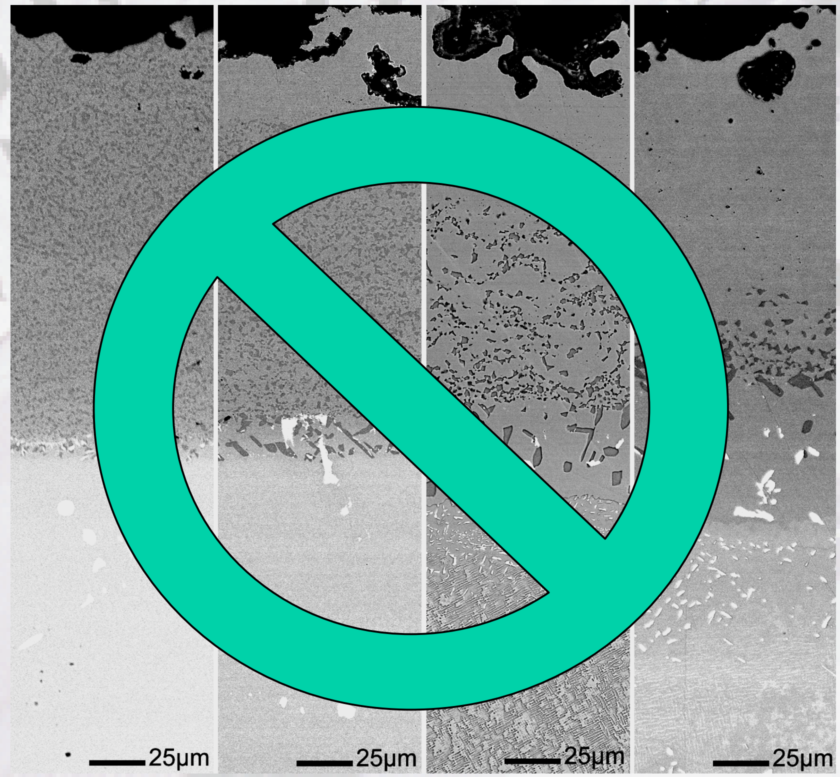
Interdiffusion and Lifetime of Oxidation Resistant Coatings

4X in Lifetime (Measured by Stability of Al-Rich β-NiAl Phase) Can be Achieved by Appropriate Selection of Substrate Composition (Given a Coating Composition).





Isothermal Exposure Time, t

4 x Isothermal Exposure Time, 4t

E. Perez, Y.H. Sohn, Unpublished Research.

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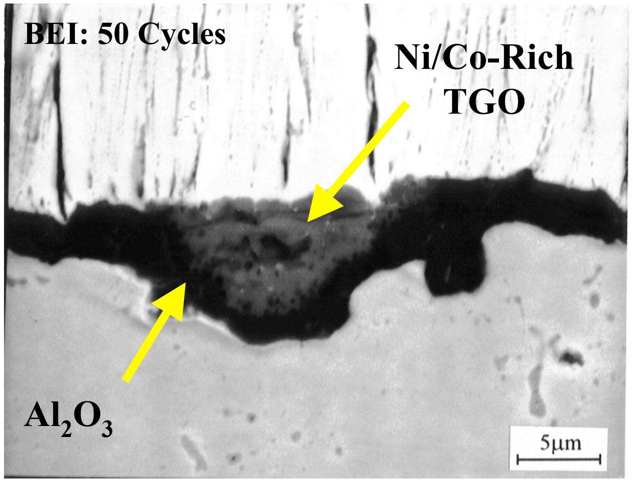
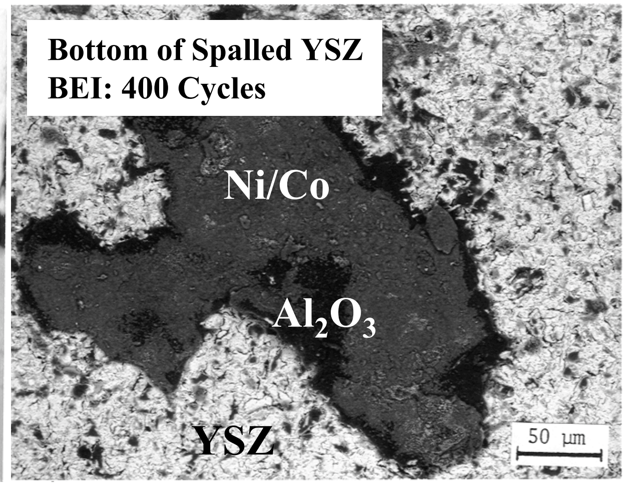
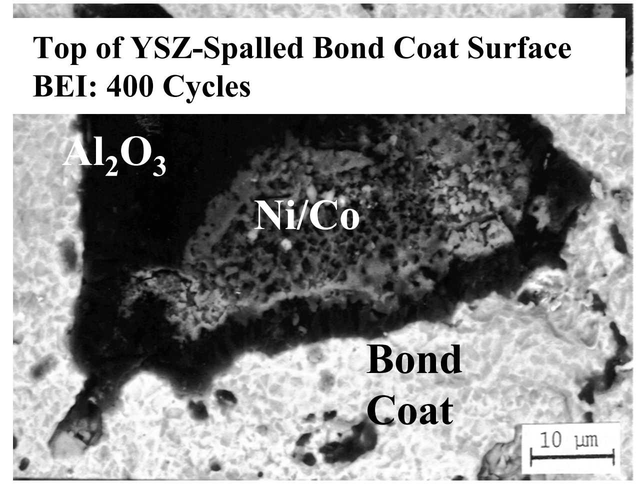
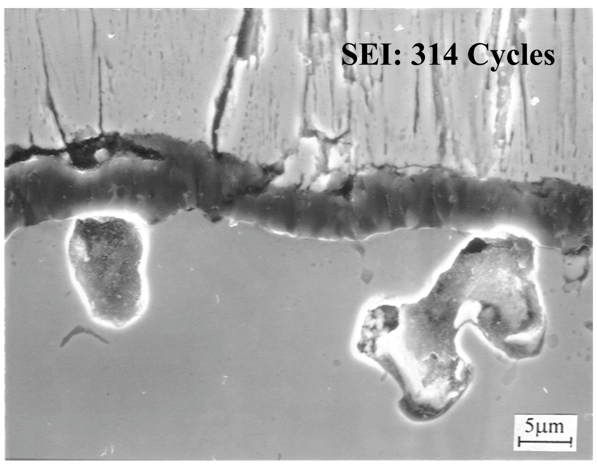
Interdiffusion and Failure of TBCs

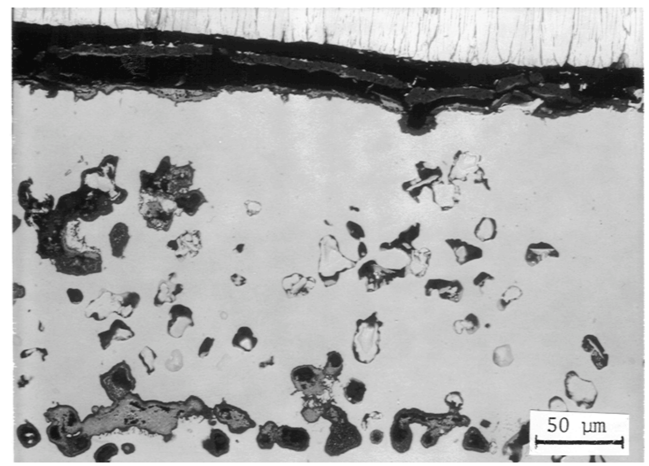






Premature Formation of Ni/Co-Rich Oxides due to Presence of Embedded Oxides.





Formation of Kirkendall Porosity Near the TGO/Bond Coat Interface and Internal Oxidation.

Y.H. Sohn et al., Surf. Coat. Technol., 146-147 (2001) pp. 70-78.

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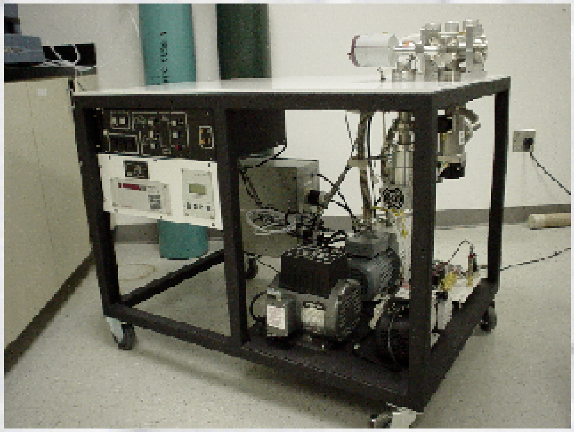
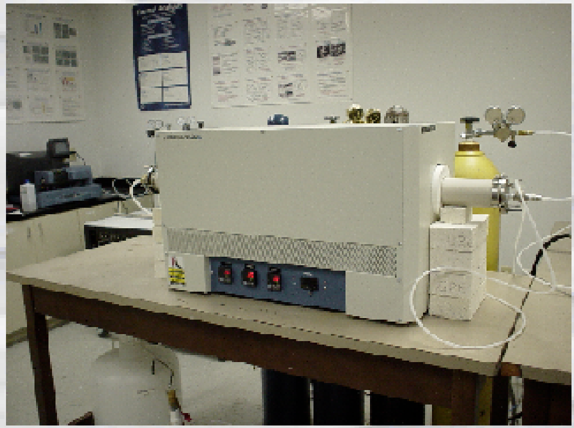
Solid-to-Solid Diffusion Couples

- Alloy Casting by Vacuum Induction Melting, Chill Casting and/or Tri-Arc Melting Furnace.
- Homogenization Heat Treatment.
- Microstructure, Phase Constituents and Compositional Analysis.
- Assembled with Kovar Steel Jigs.
- Encapsulate in Quartz Tube (Vacuum or Ar-Filled) After Several Vacuum-Hydrogen Flush.
- Diffusion Anneal Using Three-Zone Tube Furnace.
- Metallographic Preparation and Microstructural Analysis.
- Compositional Analysis by Electron Probe Microanalysis (EMPA).
- Interfacial Analysis by Transmission Electron Microscopy (TEM).





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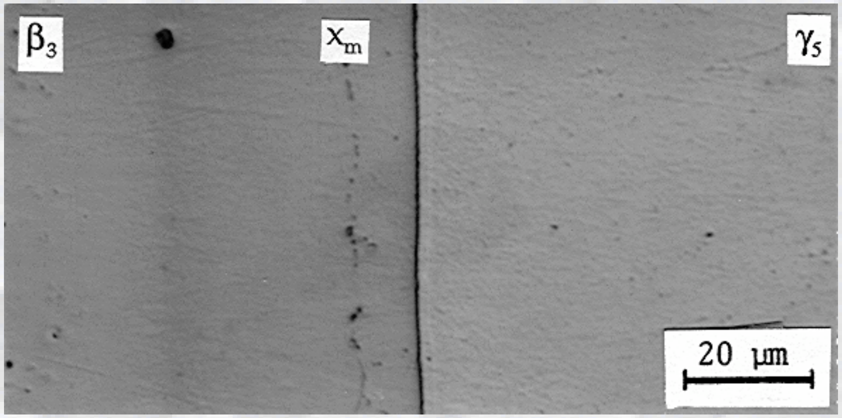
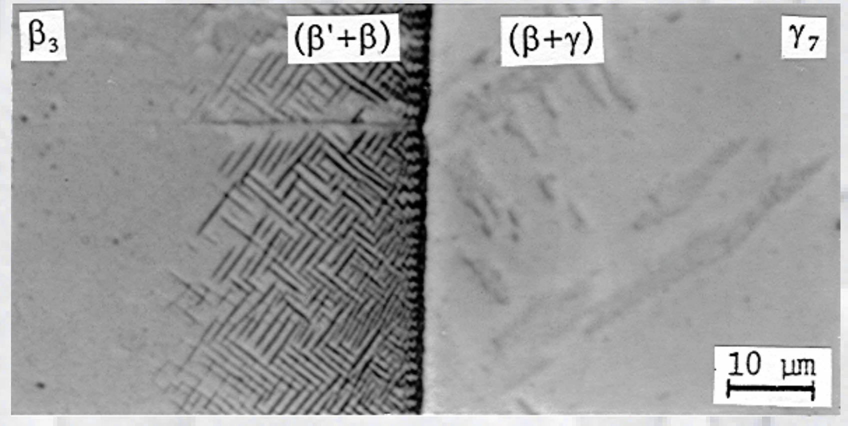
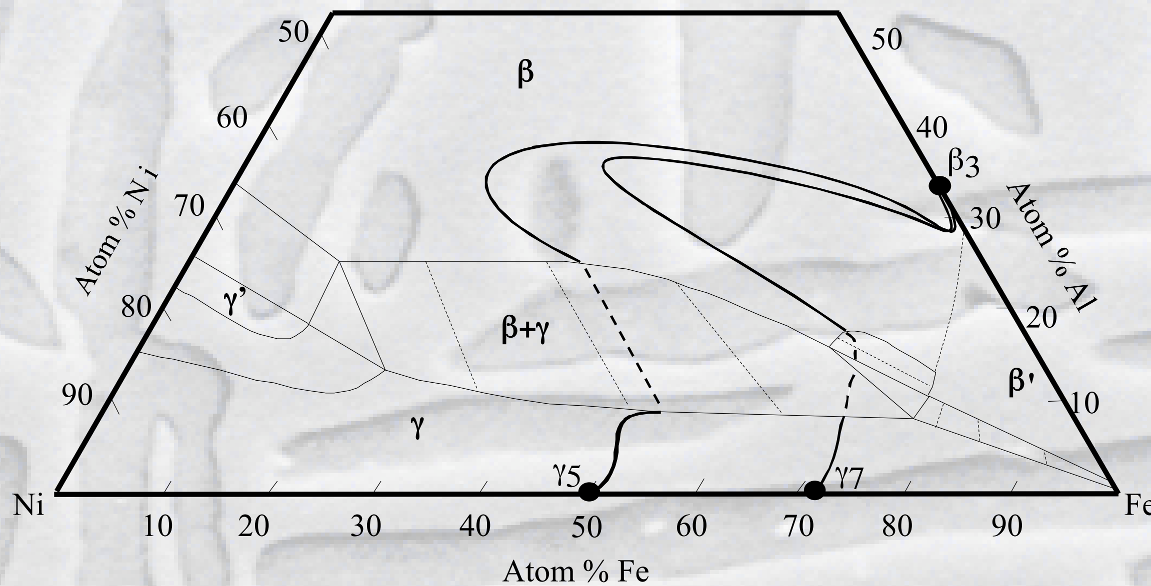
Diffusion Structures and Diffusion Paths







Y.H. Sohn and M.A. Dayananda, Metall. Mater. Trans., 48 (2000) 1427.
Y.H. Sohn, A. Puccio, M.A. Dayananda, Mater. Sci. Eng. A., in Preparation.

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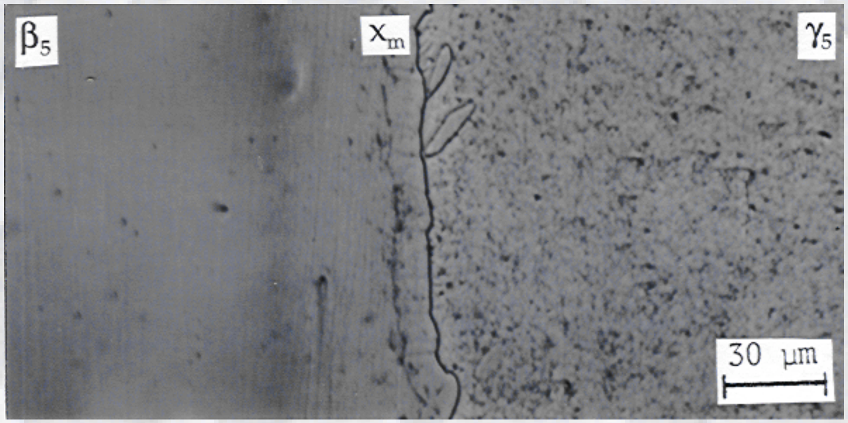

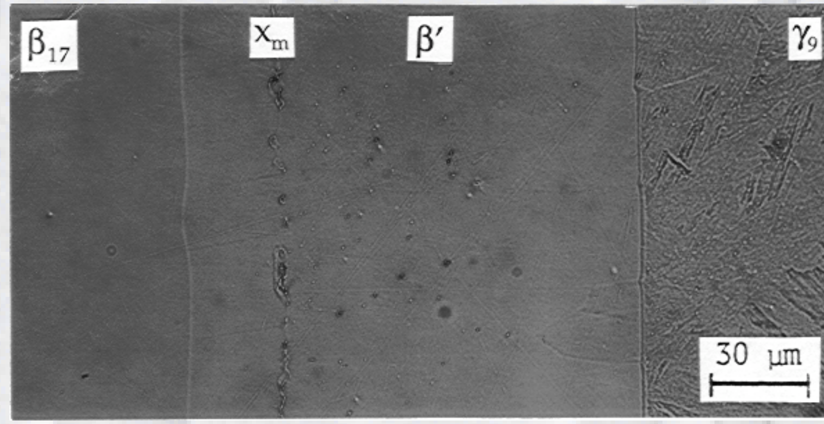

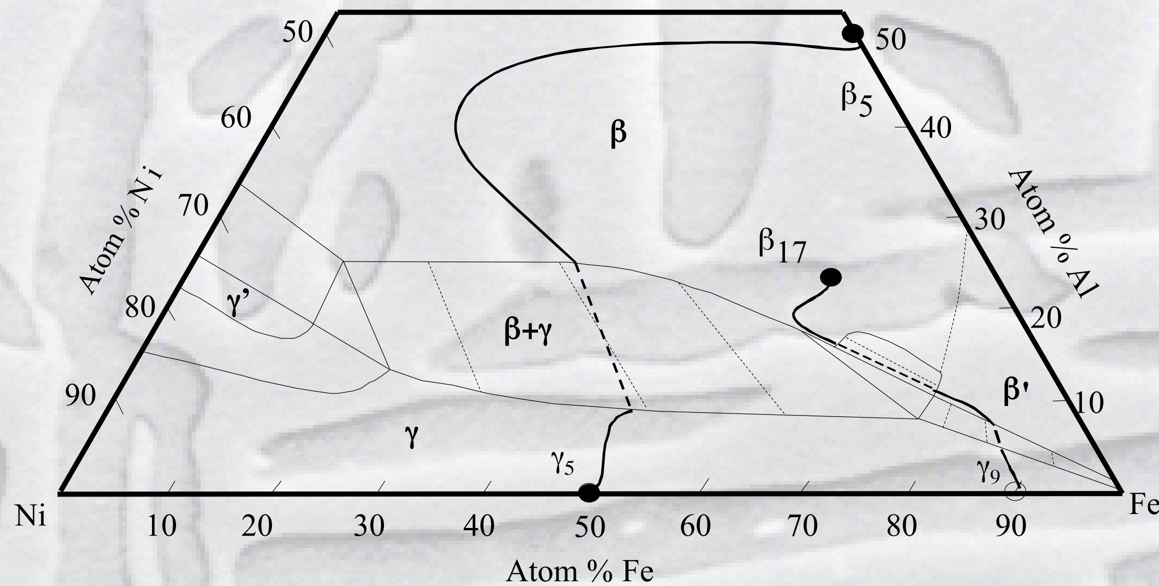

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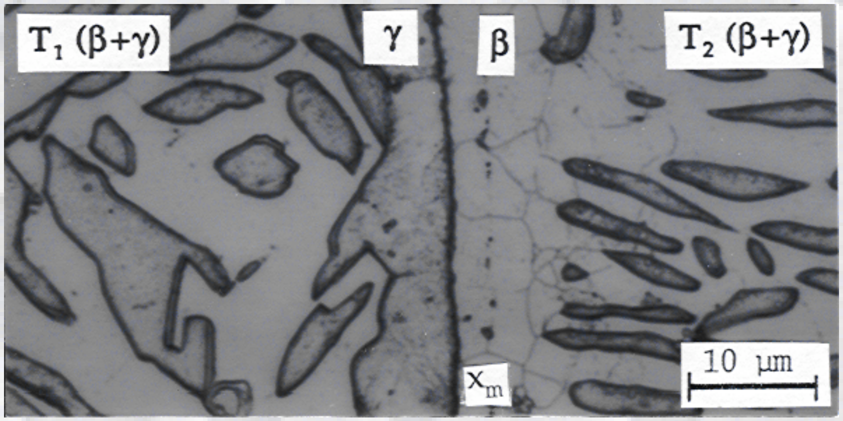

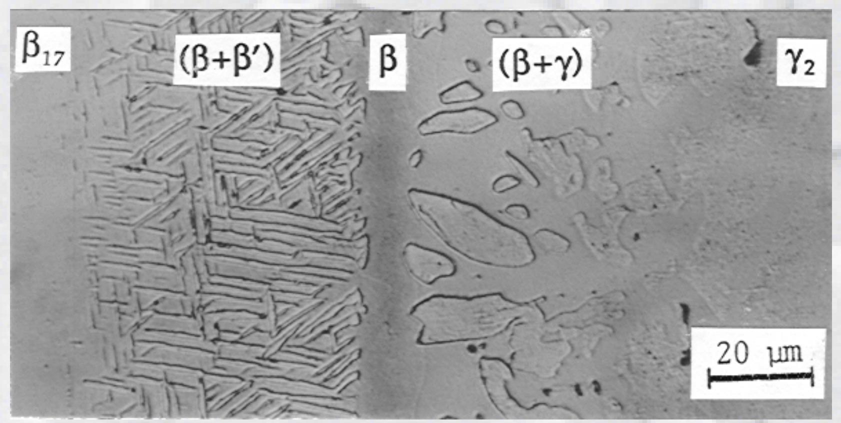

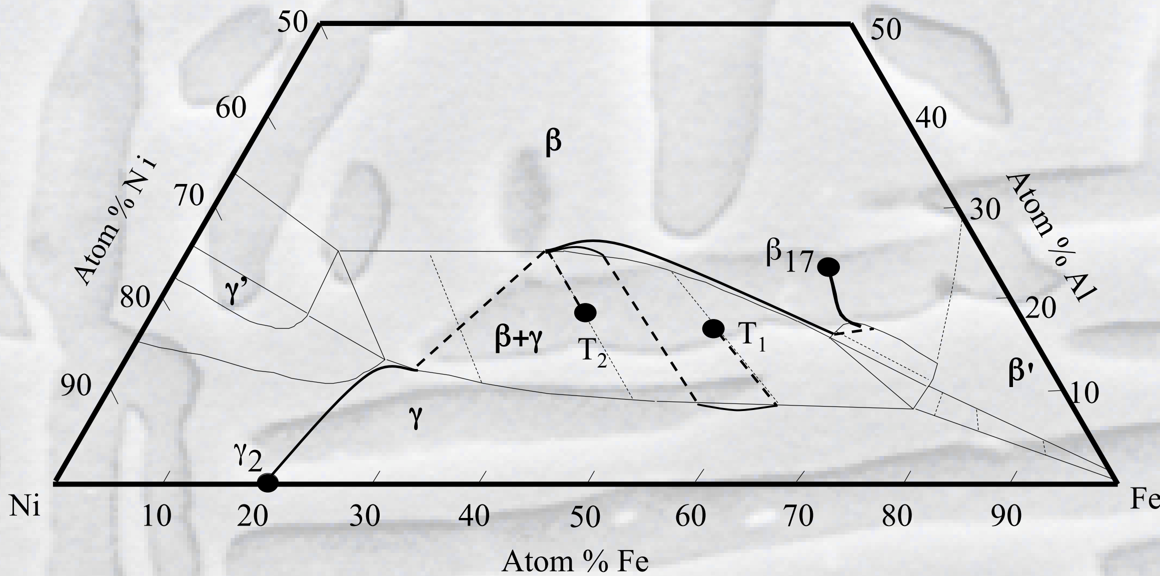

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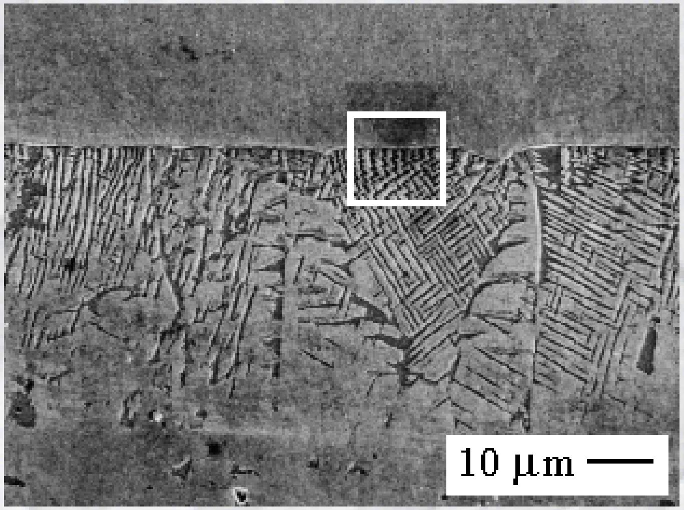

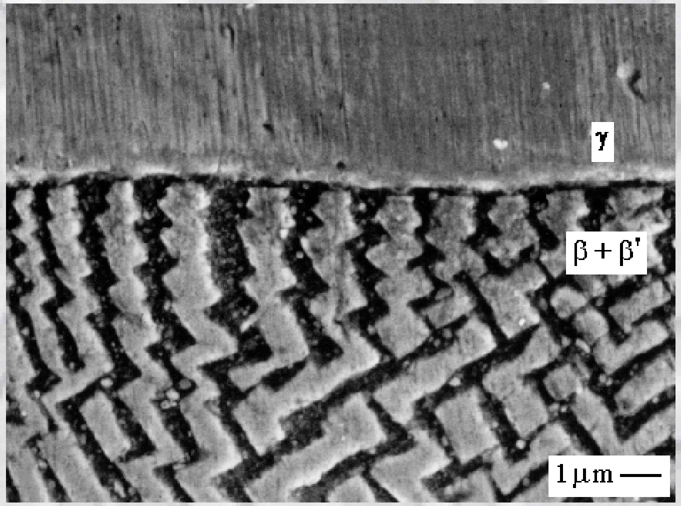

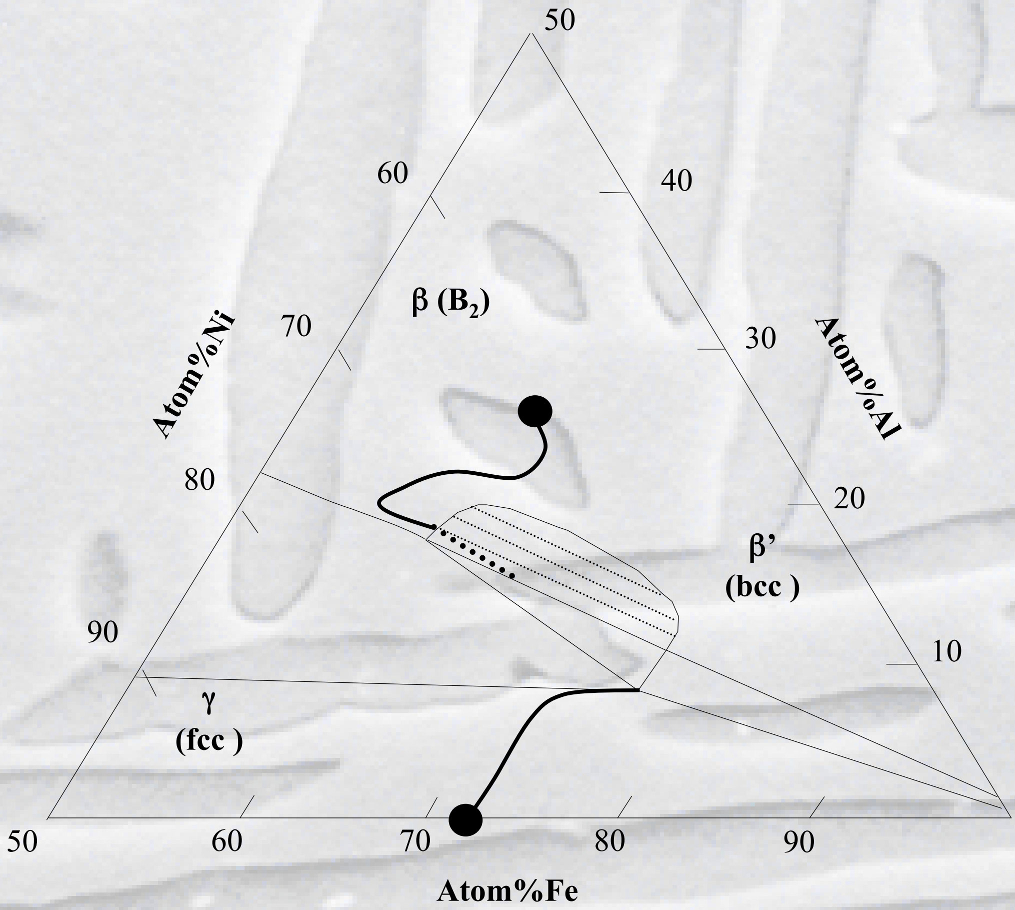

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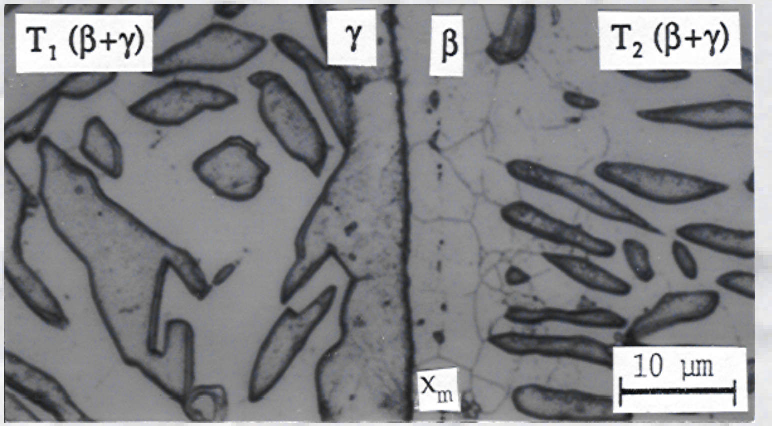

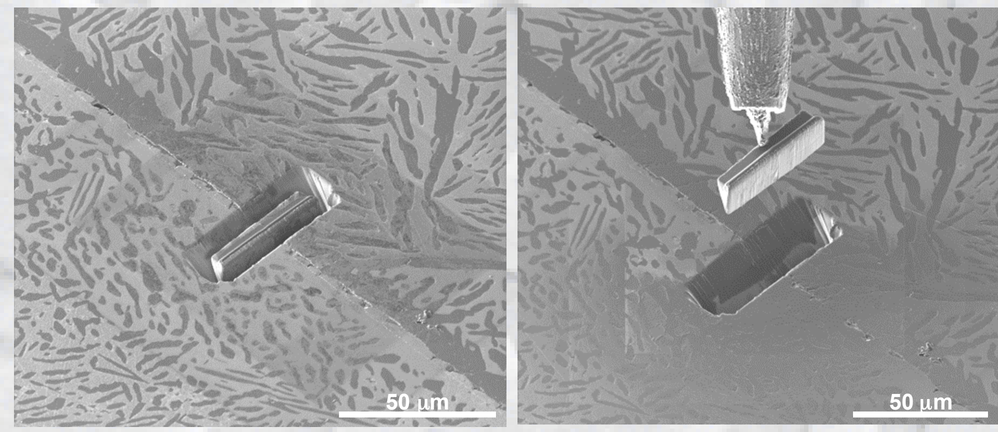

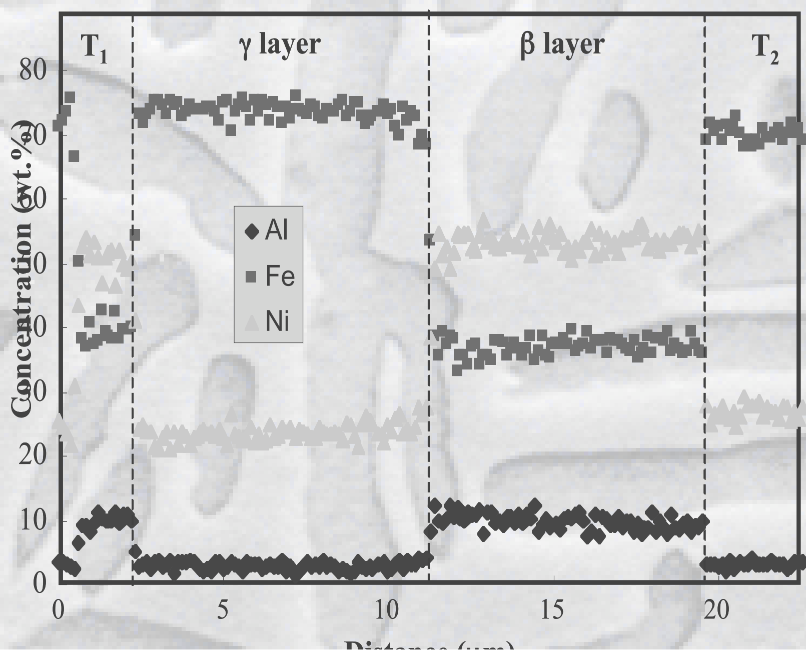

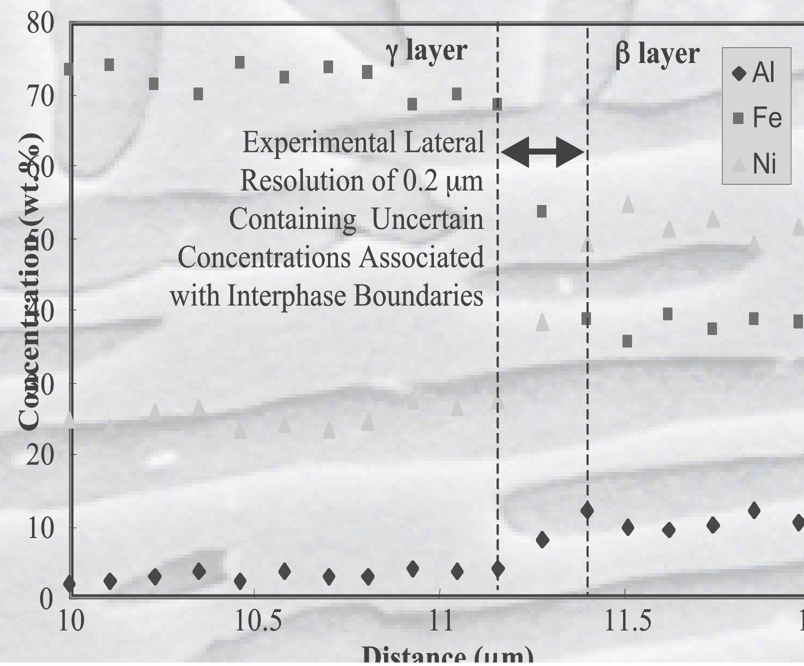

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Phenomenology of Isothermal Interdiffusion in Multicomponent System

- **Onsager's formalism* for The Interdiffusion Flux of Component i in a Multicomponent System :**

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij}^{n} \frac{\partial C_j}{\partial x} \quad (i = 1, 2, ..., n-1)$$

where $\partial C_j / \partial x$ is the $(n-1)$ independent concentration gradients

$\tilde{D}_{ij}^{n}$ is the $(n-1)^2$ interdiffusion coefficients

- **Requires Knowledge of (n-1) Independent Concentrations and $(n-1)^2$ Interdiffusion Coefficients.**

- **For a Ternary Systems:**

$$\tilde{J}_1 = -\tilde{D}_{11}^{3} \frac{\partial C_1}{\partial x} - \tilde{D}_{12}^{3} \frac{\partial C_2}{\partial x} \quad \text{and} \quad \tilde{J}_2 = -\tilde{D}_{21}^{3} \frac{\partial C_1}{\partial x} - \tilde{D}_{22}^{3} \frac{\partial C_2}{\partial x}$$

*** L. Onsager, Phys. Rev., 37 (1931) 405; 38 (1932) 2265; Ann. NY Acad. Sci., 46 (1965) 241.***

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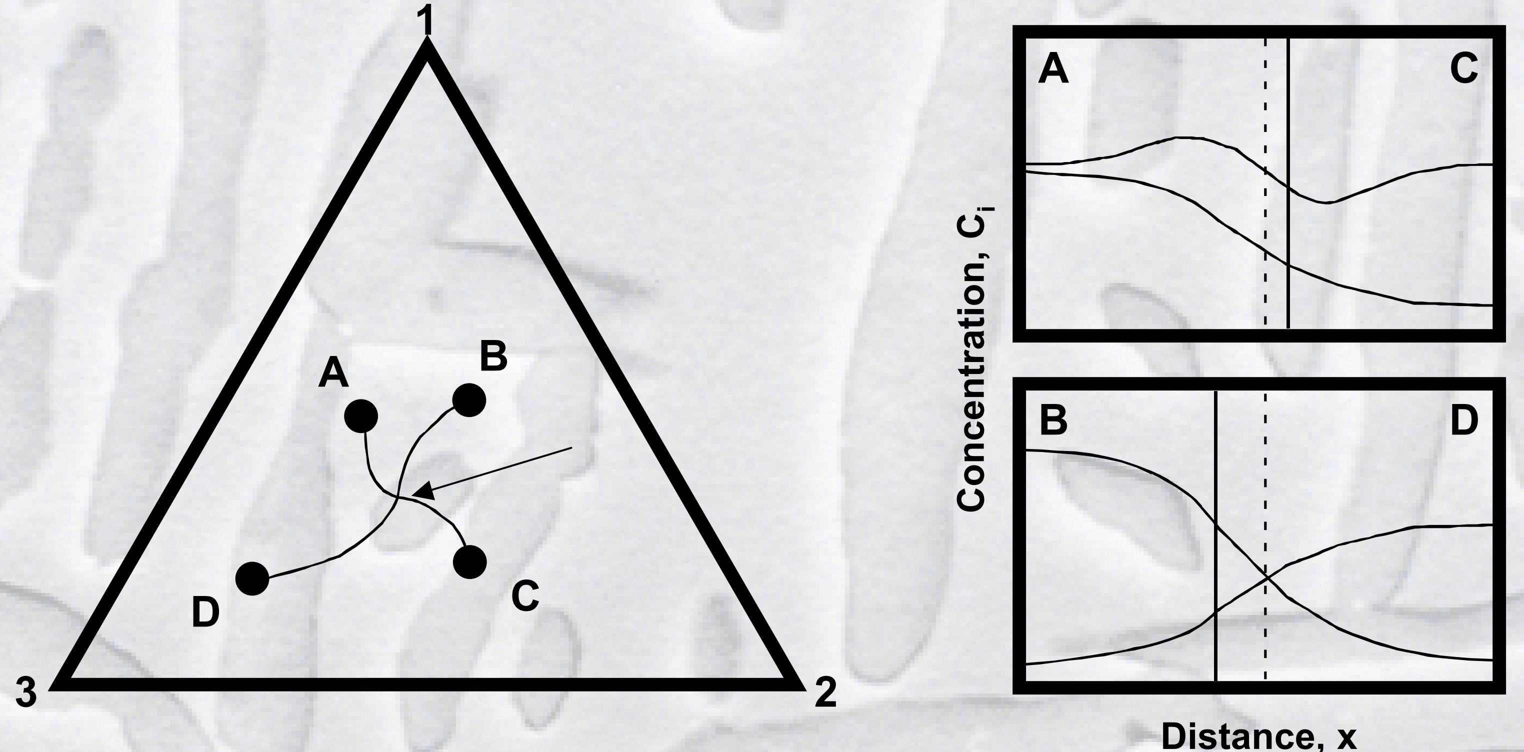
Determination of Ternary Interdiffusion Coefficients by Extension of Boltzmann-Matano Analysis*



- Requires Two Independent Diffusion Couples Intersecting at a Common Composition.
- Requires A Significant Number of Diffusion Couple Experiment to Assess Compositional Dependence of Interdiffusion Coefficients.

** J. Kirkaldy, Can. J. Phys., 35 (1957) 435.*

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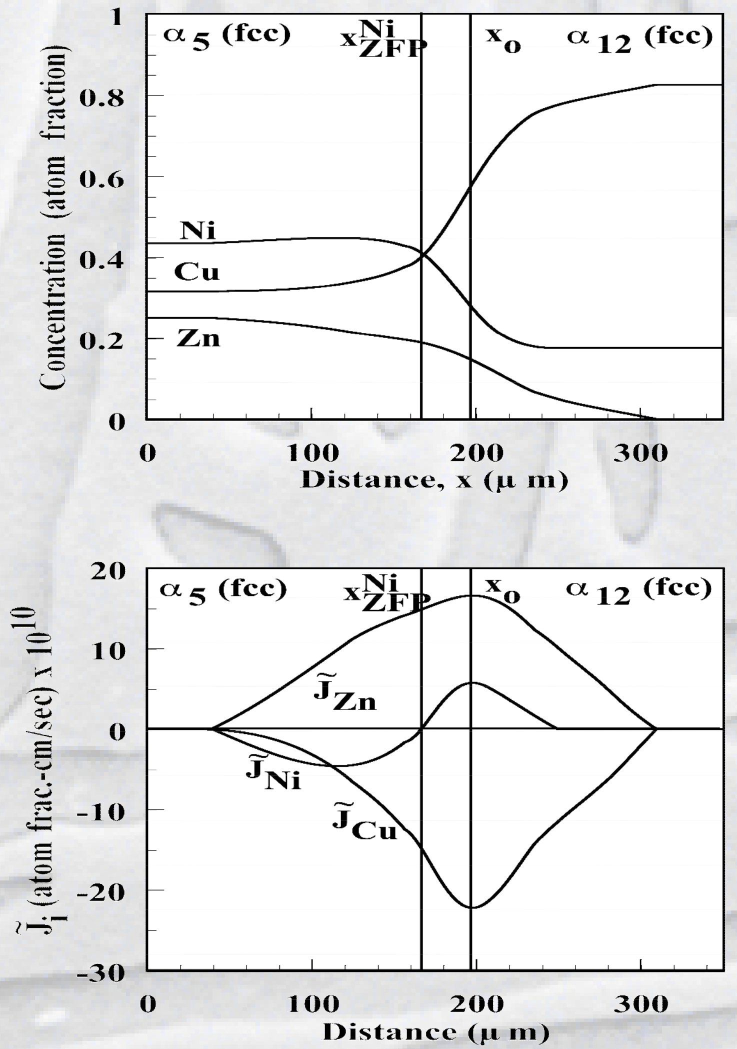
Determination of Interdiffusion Fluxes

- **Interdiffusion fluxes of all components can be determined directly from their concentration profiles without the need of the interdiffusion coefficients:**

$$\tilde{J}_i = \frac{1}{2t} \int_{C_i^- \text{ or } C_i^+}^{C_i(x)} (x - x_o)\, dC_i \quad (i = 1, 2, .., n)$$

where t is time

- **No Need for Interdiffusion Coefficient to Assess Diffusional Bahavior of Individual Components.**
- **Profiles of experimental concentration and the corresponding interdiffusion fluxes of Cu-Ni-Zn couple, α_5 (Cu-43.5at.%-25.0at.%Zn) vs. α_{12} (Cu-17.5at.%Ni), annealed at 775°C for 48 hours.**



M. A. Dayananda, C. W. Kim, Metall. Trans., 10A (1979) 1333.

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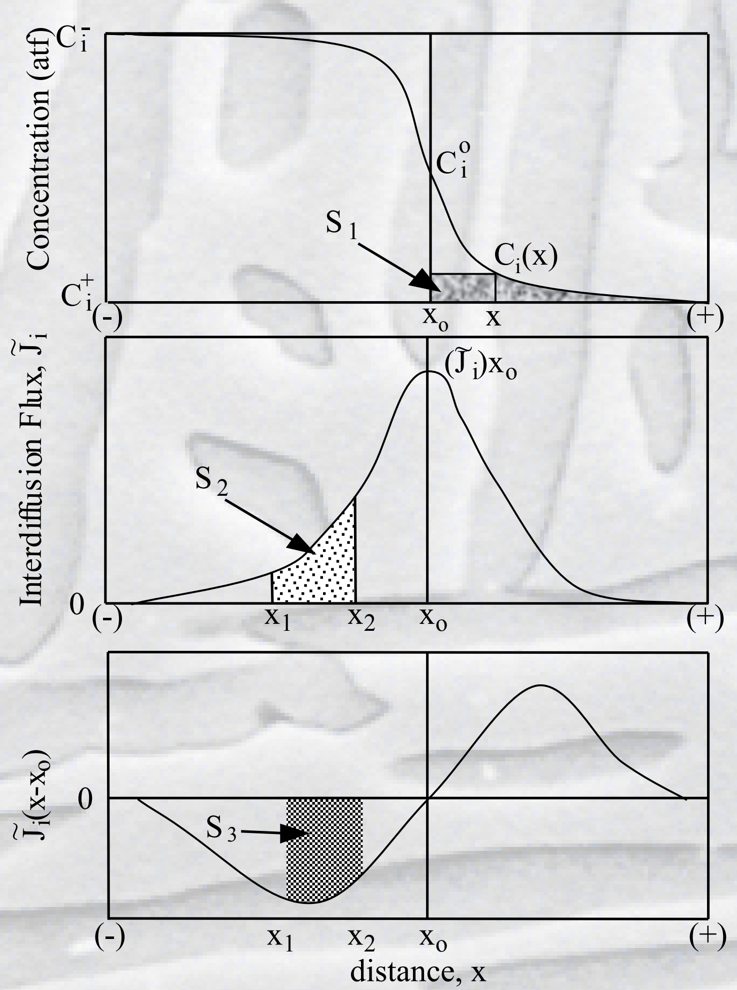
Alternative Approach for the Determination of Ternary Interdiffusion Coefficients

$$\int_{x_1}^{x_2} \tilde{J}_i dx = \overline{\tilde{D}}_{i1}^3\left[C_1(x_1) - C_1(x_2)\right] + \overline{\tilde{D}}_{i2}^3\left[C_2(x_1) - C_2(x_2)\right]$$
$$(i, j = 1, 2)$$

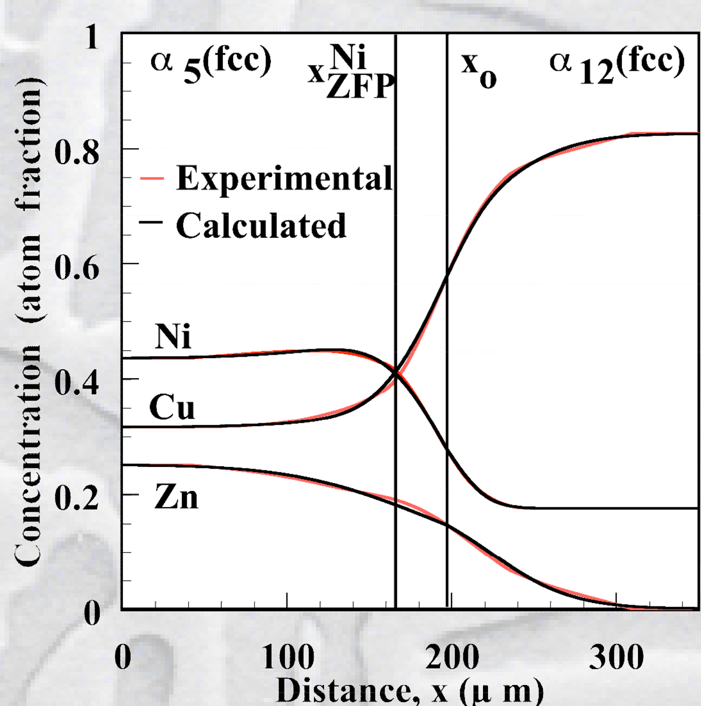
$$\int_{x_1}^{x_2} \tilde{J}_i(x - x_o)dx = 2t\left\{\overline{\tilde{D}}_{i1}^3\left[\tilde{J}_1(x_1) - \tilde{J}_1(x_2)\right] + \overline{\tilde{D}}_{i2}^3\left[\tilde{J}_2(x_1) - \tilde{J}_2(x_2)\right]\right\}$$
$$(i, j = 1, 2)$$



M. A. Dayananda and Y. H. Sohn, Metall. Mater. Trans., 30A (1999) 535.
Y.H. Sohn and M.A. Dayananda, Acta Mater., 48 (2000) 1427.

Average Ternary Interdiffusion Coefficients

Experimental and calculated concentration profiles* of Cu-Ni-Zn couple, α_5 (Cu-43.5at.%-25.0at.%Zn) vs. α_{12} (Cu-17.5at.%Ni), annealed at 775°C for 48 hours.**



Range	$\left(C_i^- \times C_i^o\right)$	$\left(C_i^o \times C_i^+\right)$
$\tilde{\bar{D}}^{Cu}_{NiNi}$	2.3	1.0
$\tilde{\bar{D}}^{Cu}_{NiZn}$	-6.1	-0.1
$\tilde{\bar{D}}^{Cu}_{ZnNi}$	1.2	2.5
$\tilde{\bar{D}}^{Cu}_{ZnZn}$	12.5	6.4

$\tilde{\bar{D}}^{Cu}_{ij}\left(10^{-15}\, m^2/sec\right)$

** M. A. Dayananda and Y. H. Sohn, Metall. Mater. Trans., 30A (1999) 535.*

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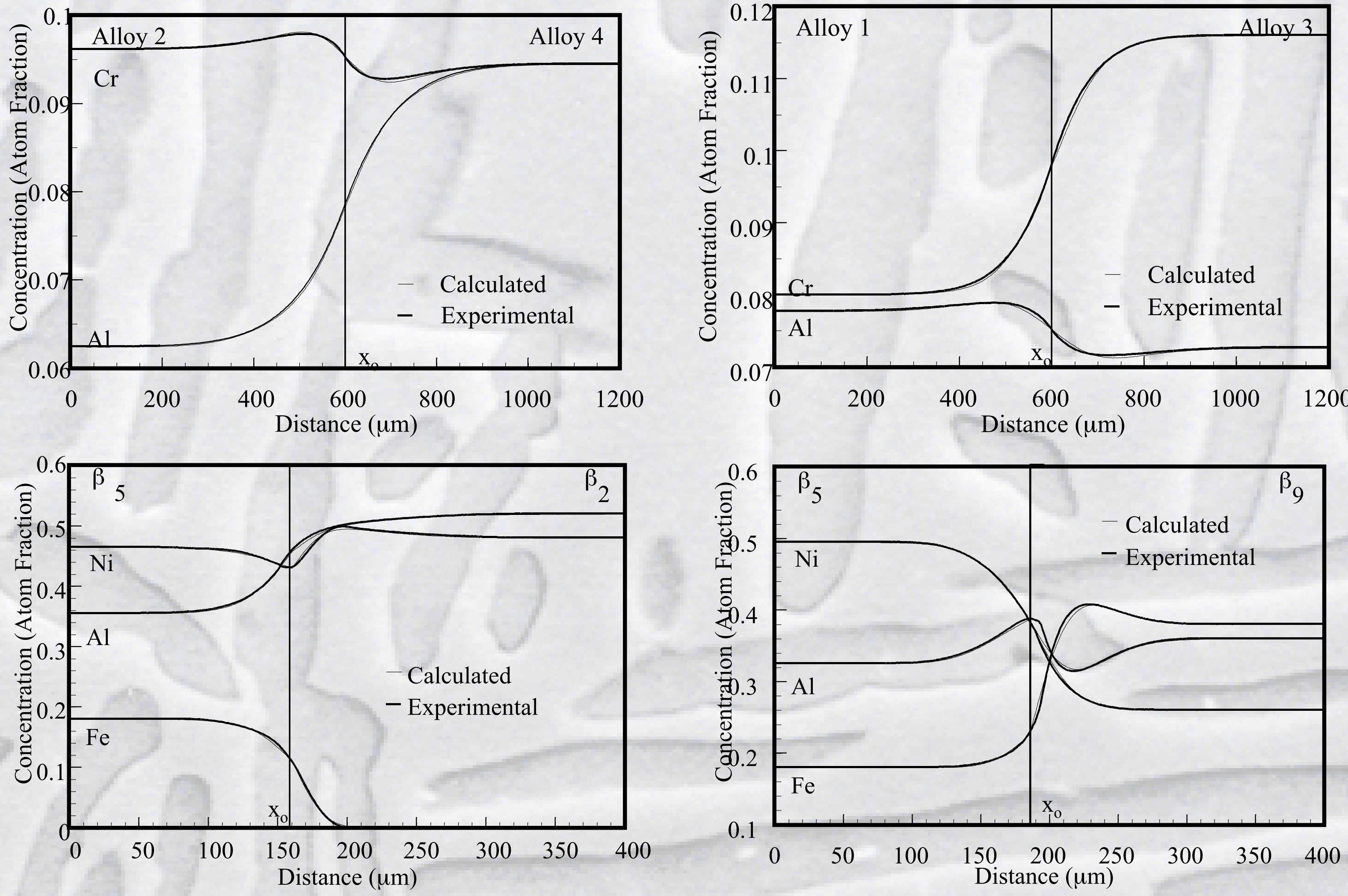
Modeling of Concentration Profiles Based on Average Ternary Interdiffusion Coefficients



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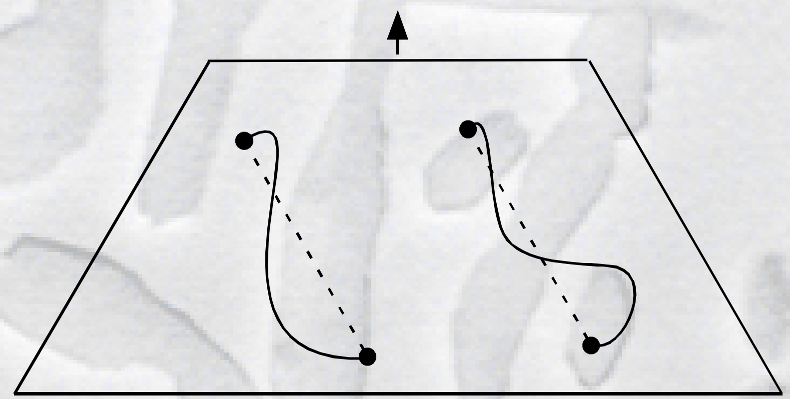
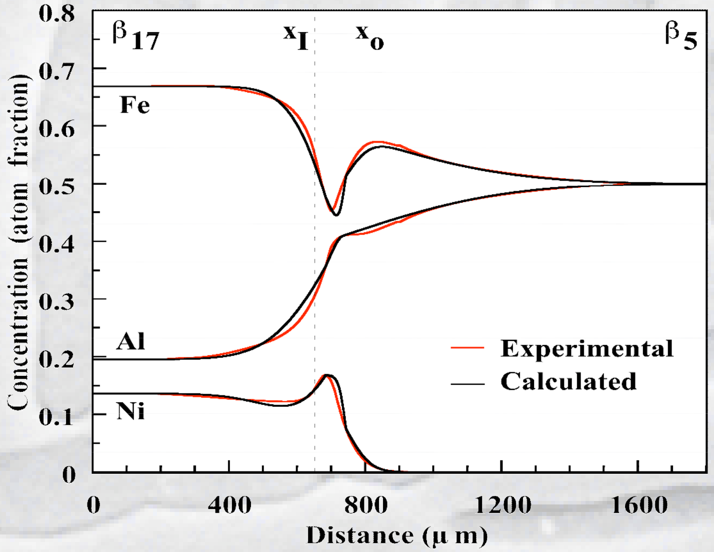
Double Serpentine Diffusion Paths in the Fe-Ni-Al System

- **Diffusion path crosses the straight line joining the terminal alloys two times for the couple β_{17} (61.8Fe-15.3Ni-22.9Al) vs. β_5 (50.7Fe-49.3Al), annealed at 1000°C for 48 hours.**





- **Double serpentine diffusion path was observed experimentally for the first time and quantitatively described using the new analysis.**

Y. H. Sohn and M. A. Dayananda, Acta Mater., 48 (2000) 1427.

Ternary Nonisothermal Thermotransport

$$\int_{x_1}^{x_2} \tilde{J}_i dx = -\overline{\beta_i \tilde{Q}_i^*} \int_{T(x_1)}^{T(x_2)} C_i \frac{\partial T}{T} - \overline{\tilde{D}}_i^{eff} \int_{C(x_1)}^{C(x_2)} dC_i \quad (i=1,2)$$

and

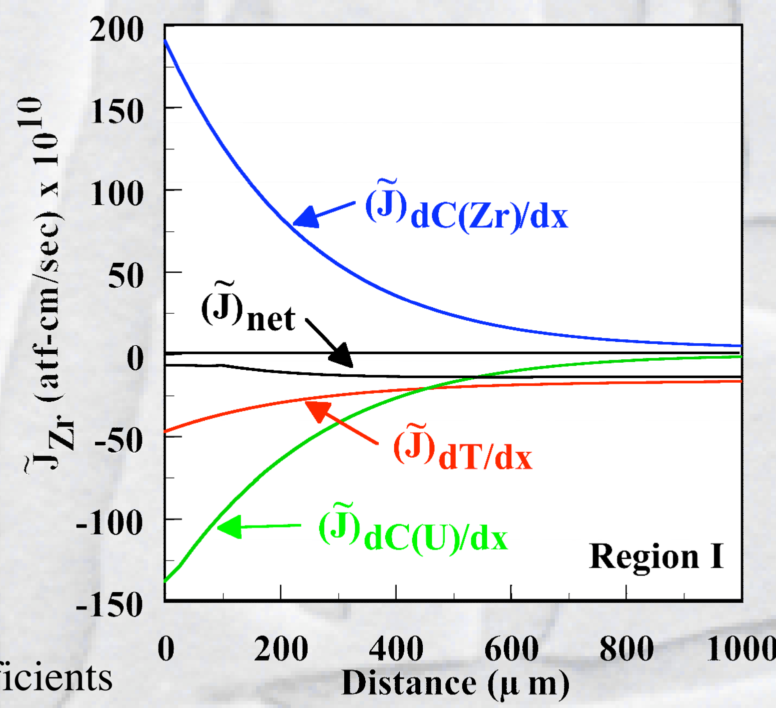
$$\int_{x_1}^{x_2} \tilde{J}_i (x - x_o) dx = -\overline{\beta_i \tilde{Q}_i^*} \int_{T(x_1)}^{T(x_2)} C_i \frac{(x - x_o)\partial T}{T}$$

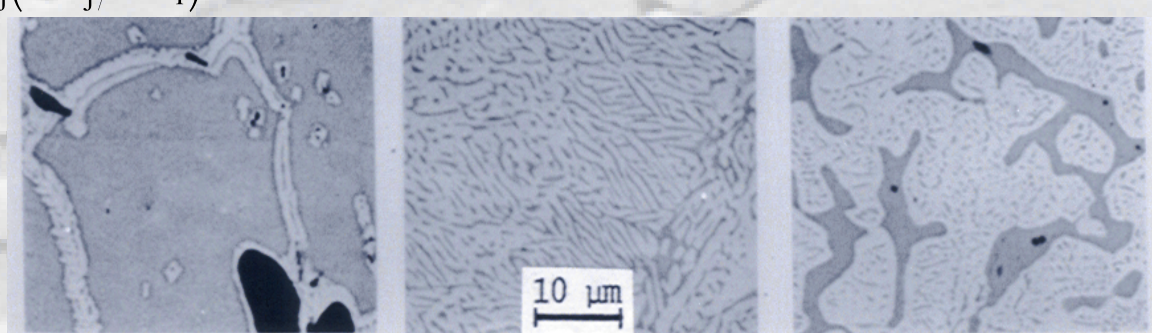
$$- \overline{\tilde{D}}_i^{eff} \int_{C(x_1)}^{C(x_2)} (x - x_o) dC_i \quad (i=1,2)$$

where $\overline{\beta_i \tilde{Q}_i^*}$ is the average thermotransport coefficient

$\overline{\tilde{D}}_i^{eff}$ is the average effective interdiffusion coefficients

Defined by $\overline{\tilde{D}}_i^{eff} = \overline{\tilde{D}}_{ii}^3 + \overline{\tilde{D}}_{ij}^3 \left(\Delta C_j / \Delta C_i\right)$





Y. H. Sohn, M.A. Dayananda, G.L. Hofman, I, J. Nucl. Mater., 279 (2000) 317.

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Determination of Composition Dependent Ternary Interdiffusion Coefficients

$$\tilde{J}_1 = -D^3_{i1}\frac{\partial C_1}{\partial x} - D^3_{i2}\frac{\partial C_2}{\partial x} \qquad (i=1,2)$$

$$\tilde{J}(x) = \frac{1}{2t}\int_{C_i^{\pm\infty}}^{C_i}(x-x_o)dC_i = \frac{1}{2t}\left[(x_o - x^{\pm\infty})C_i^{\pm\infty} - \int_{\pm\infty}^{x} C_i dx + C_i(x-x_o)\right]$$

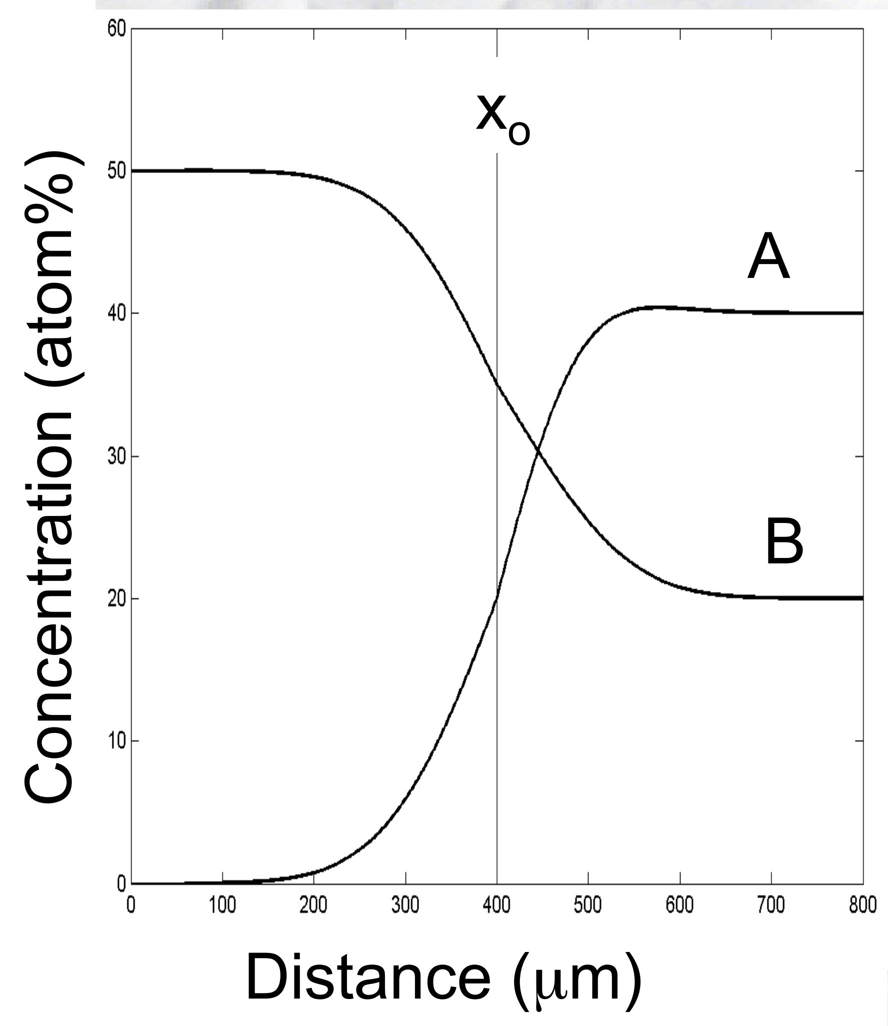
$$\tilde{J}_i(x-x_o) = -D^3_{i1}(x-x_o)\frac{\partial C_1}{\partial x} - D^3_{i2}(x-x_o)\frac{\partial C_2}{\partial x} \qquad (i=1,2)$$

$$\int_{x_1}^{x_2}\tilde{J}_i(x-x_o)dx = 2t\left\{\bar{\tilde{D}}^3_{i1}\left[\tilde{J}_1(x_1)-\tilde{J}_1(x_2)\right]+\bar{\tilde{D}}^3_{i2}\left[\tilde{J}_2(x_1)-\tilde{J}_2(x_2)\right]\right\} \qquad (i=1,2)$$

$$\frac{\partial \tilde{J}_i}{\partial x} = -\tilde{D}^3_{i1}\frac{\partial^2 C_1}{\partial x^2} - \tilde{D}^3_{i2}\frac{\partial^2 C_2}{\partial x^2} \qquad (i=1,2)$$

$$\frac{1}{2t}(x-x_o)\frac{\partial C_i}{\partial x} = -\bar{\tilde{D}}^3_{i1}\frac{\partial^2 C_1}{\partial x^2} - \bar{\tilde{D}}^3_{i2}\frac{\partial^2 C_2}{\partial x^2} \qquad (i=1,2)$$

Determination of Composition Dependent Ternary Interdiffusion Coefficients



On the Left-hand Side of x_o :

$$\tilde{\bar{D}}^C_{AA} = 32 \text{ x } 10^{-15} \text{ m}^2/\text{sec}$$

$$\tilde{\bar{D}}^C_{AB} = 7 \text{ x } 10^{-15} \text{ m}^2/\text{sec}$$

$$\tilde{\bar{D}}^C_{BA} = -4 \text{ x } 10^{-15} \text{ m}^2/\text{sec}$$

$$\tilde{\bar{D}}^C_{BB} = 19 \text{ x } 10^{-15} \text{ m}^2/\text{sec}$$

On the Right-hand Side of x_o :

$$\tilde{\bar{D}}^C_{AA} = 15 \text{ x } 10^{-15} \text{ m}^2/\text{sec}$$

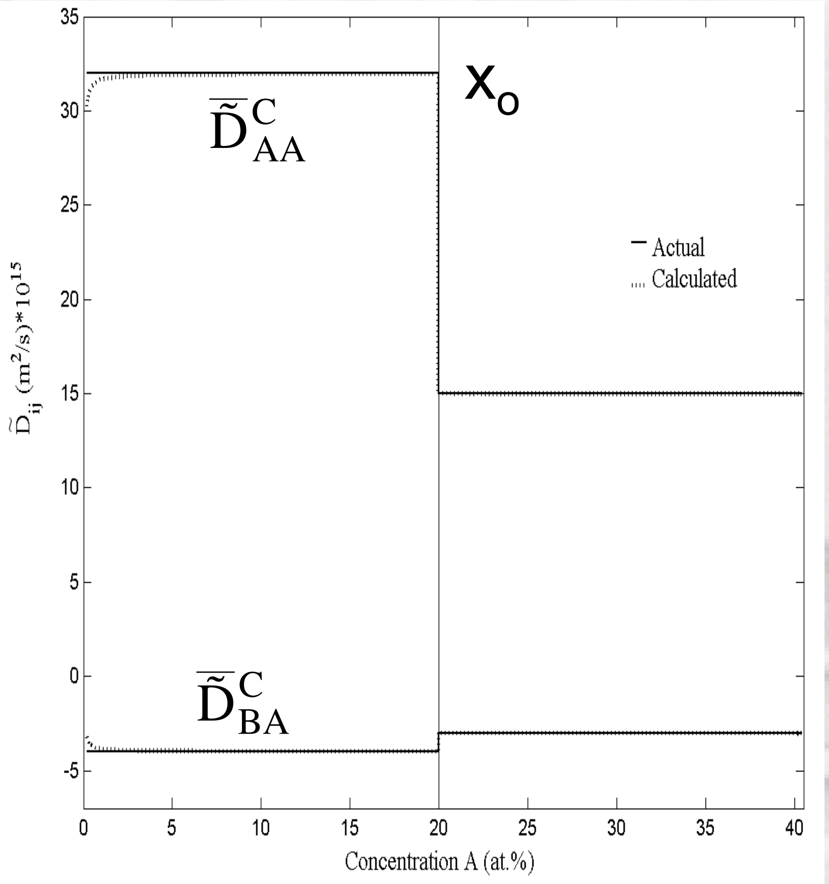
$$\tilde{\bar{D}}^C_{AB} = 9 \text{ x } 10^{-15} \text{ m}^2/\text{sec}$$

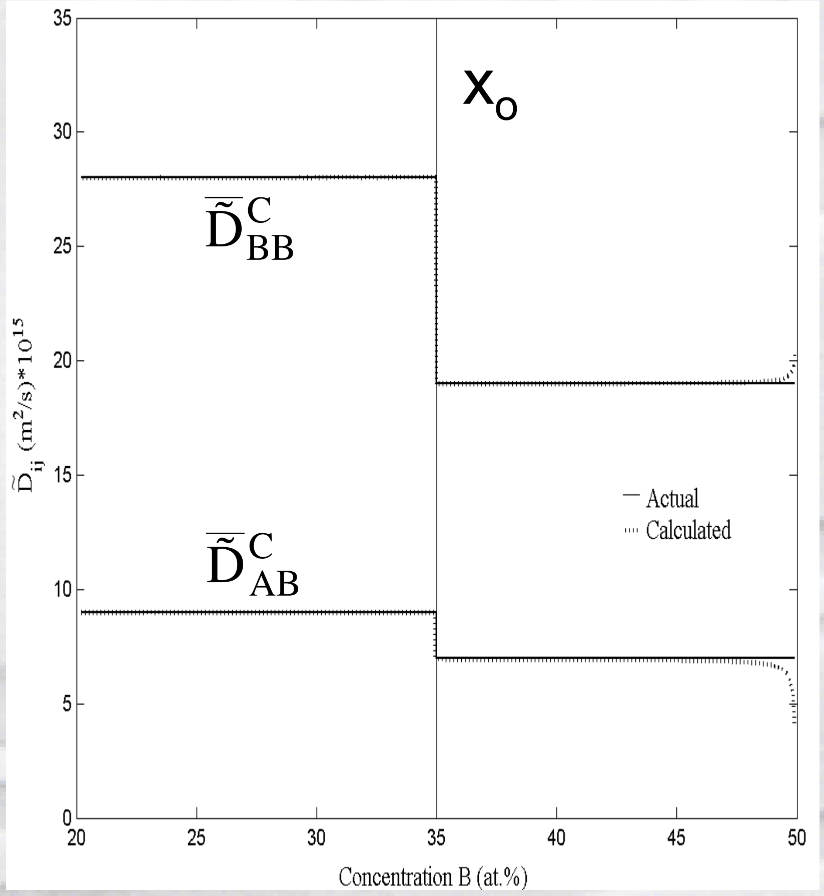
$$\tilde{\bar{D}}^C_{BA} = -3 \text{ x } 10^{-15} \text{ m}^2/\text{sec}$$

$$\tilde{\bar{D}}^C_{BB} = 28 \text{ x } 10^{-15} \text{ m}^2/\text{sec}$$

Profiles Generated Based on Ternary Error Function Solution

Determination of Composition Dependent Ternary Interdiffusion Coefficients





Input of Constant Ternary Interdiffusion Coefficients is Outputted as Constant Ternary Interdiffusion Coefficients!

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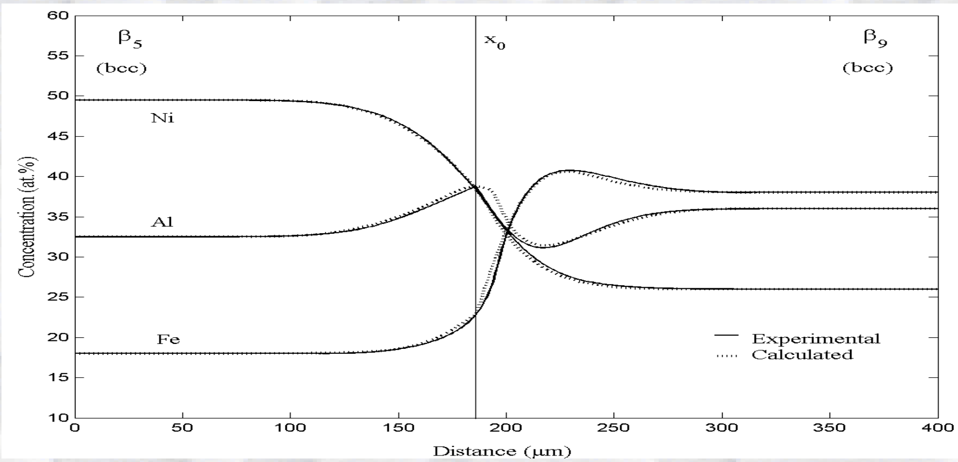
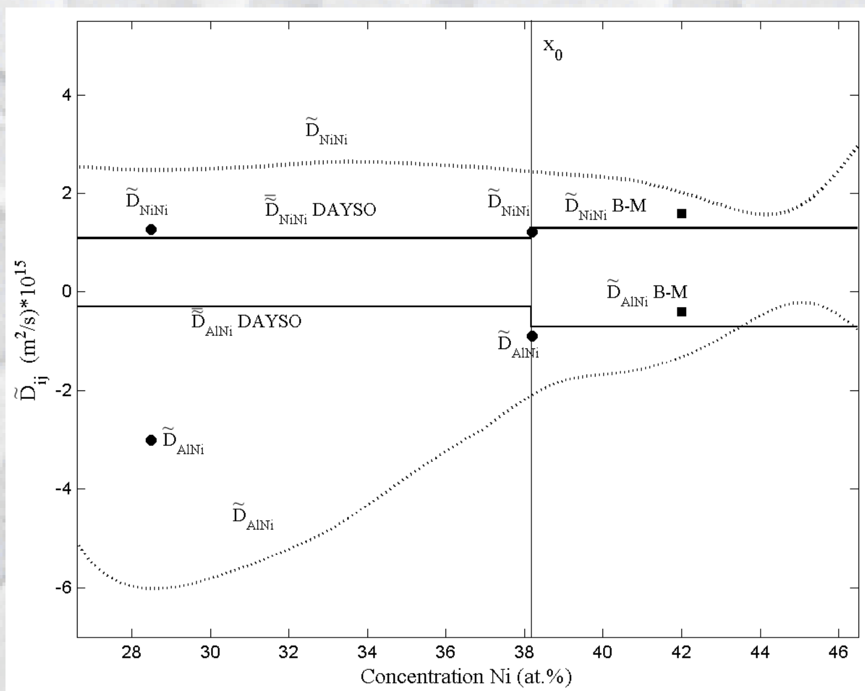
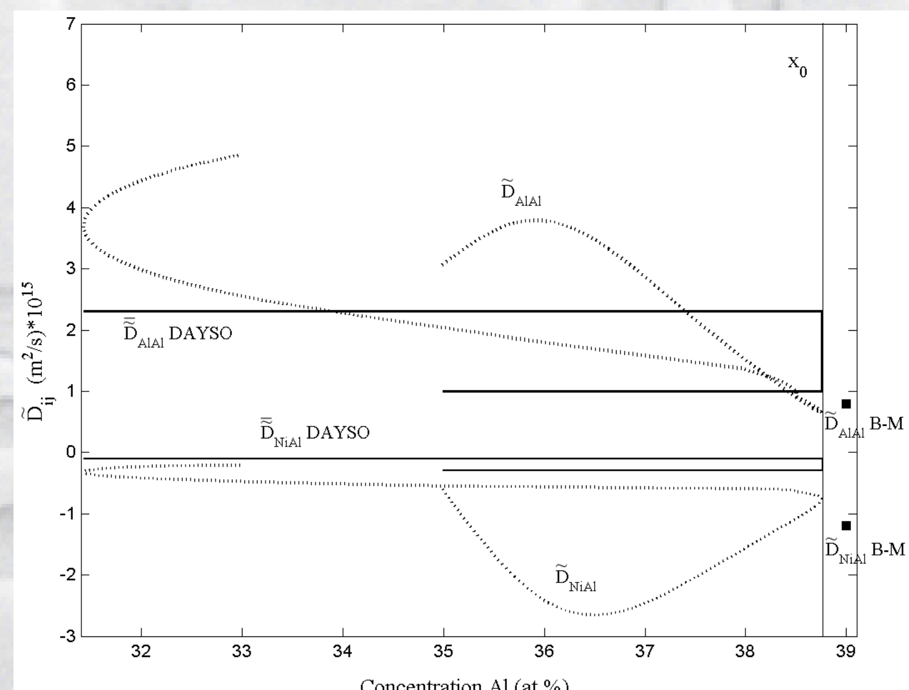
Composition Dependent Ternary Interdiffusion Coefficients



Fe-Ni-Al Alloy Diffusion at 1000ºC





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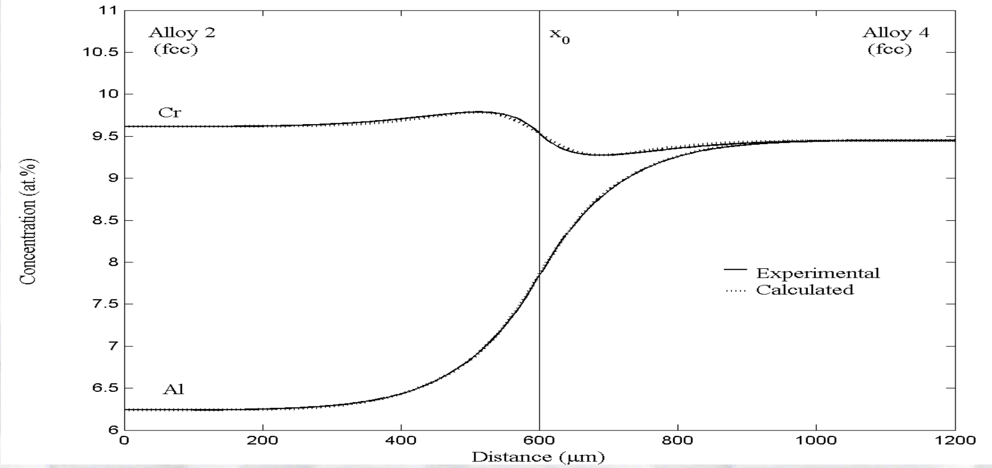
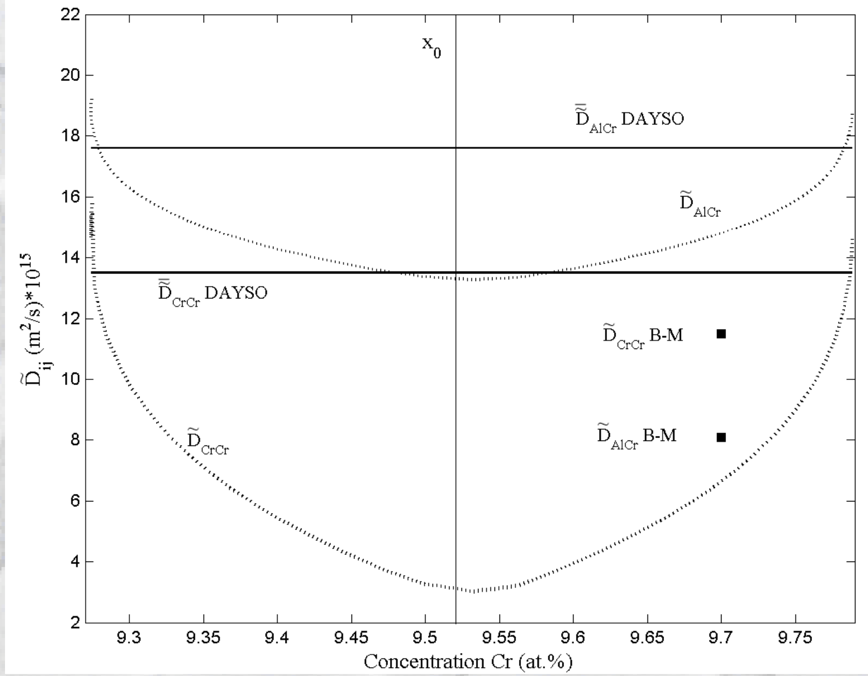
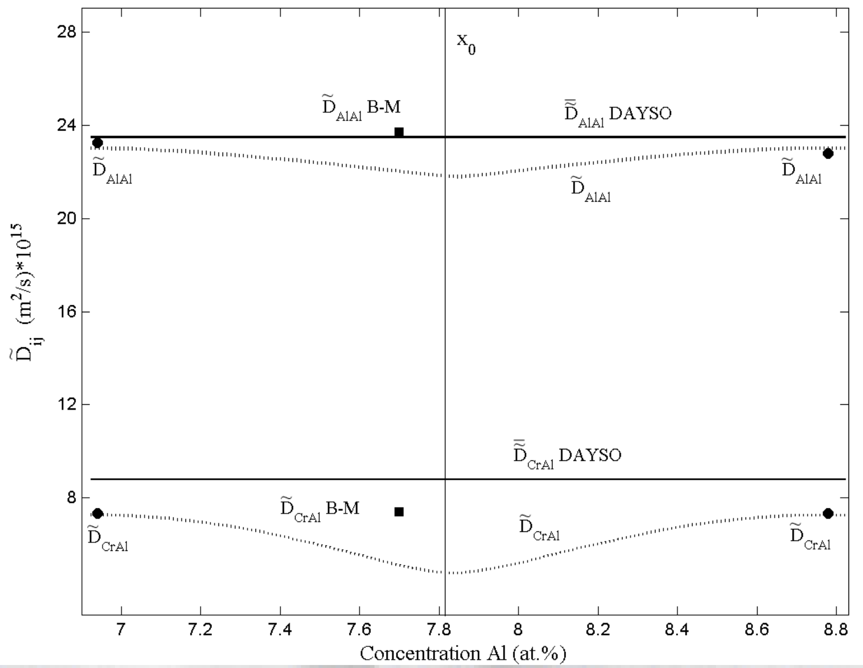
Composition Dependent Ternary Interdiffusion Coefficients



Ni-Cr-Al Alloy Diffusion at 1100ºC





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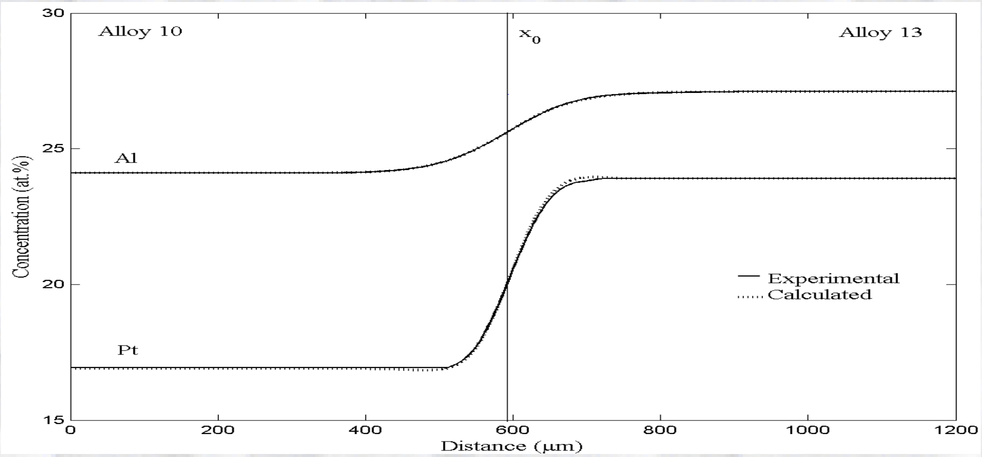
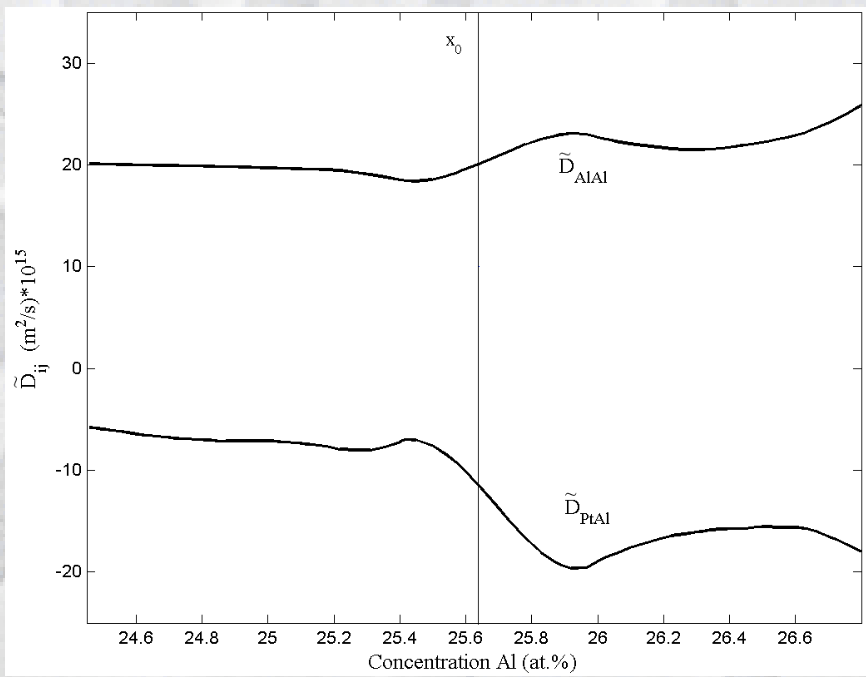
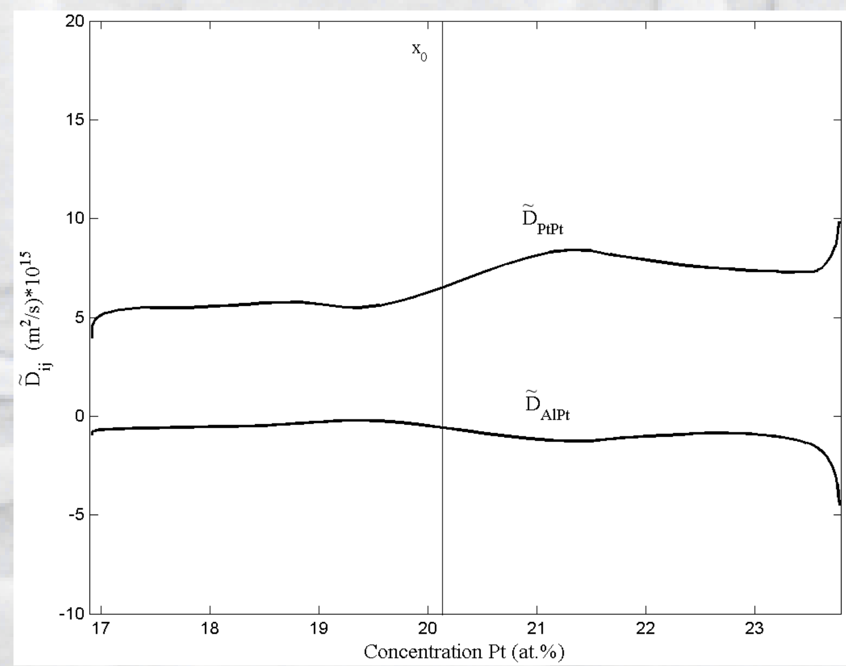
Composition Dependent Ternary Interdiffusion Coefficients



Ni-Pt-Al Alloy Diffusion at 1100ºC (Concentration Profiles Provided by B. Gleeson, ISU)





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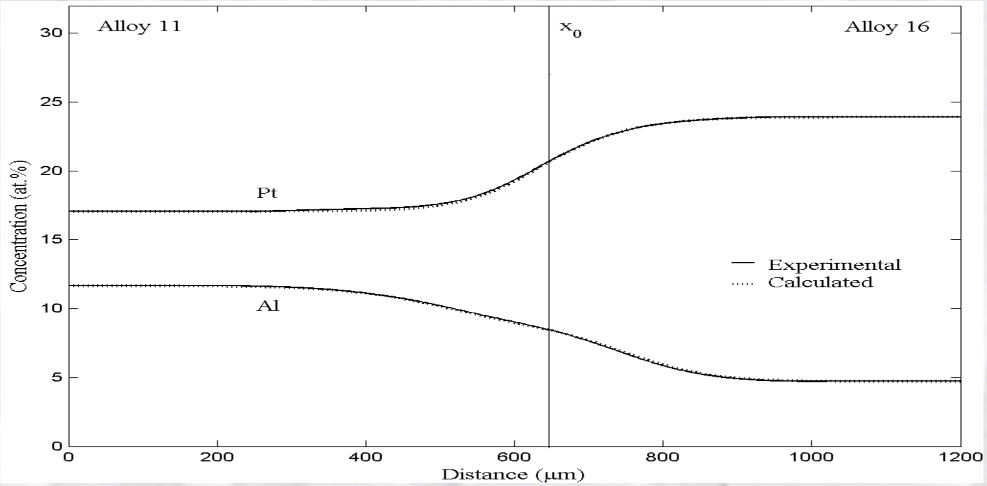
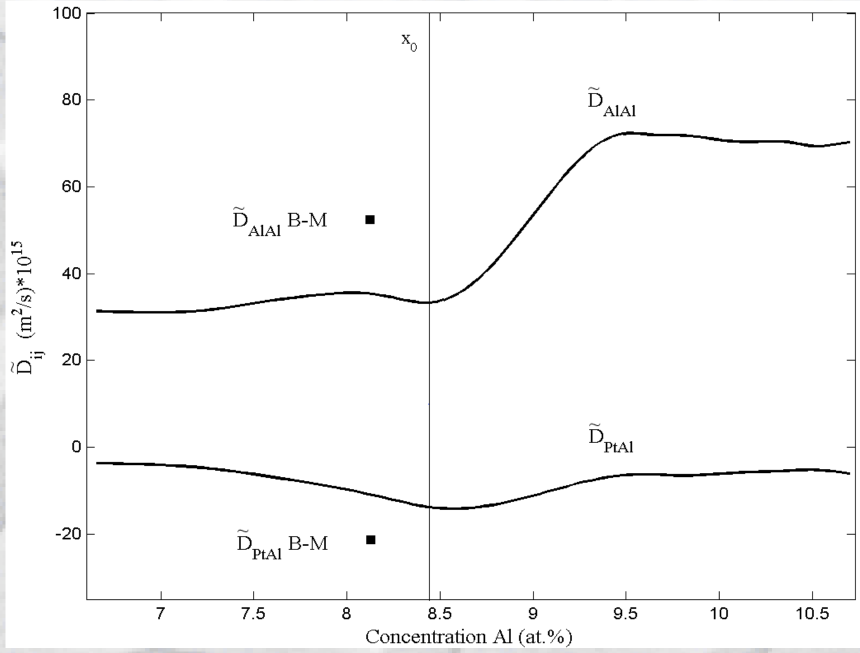
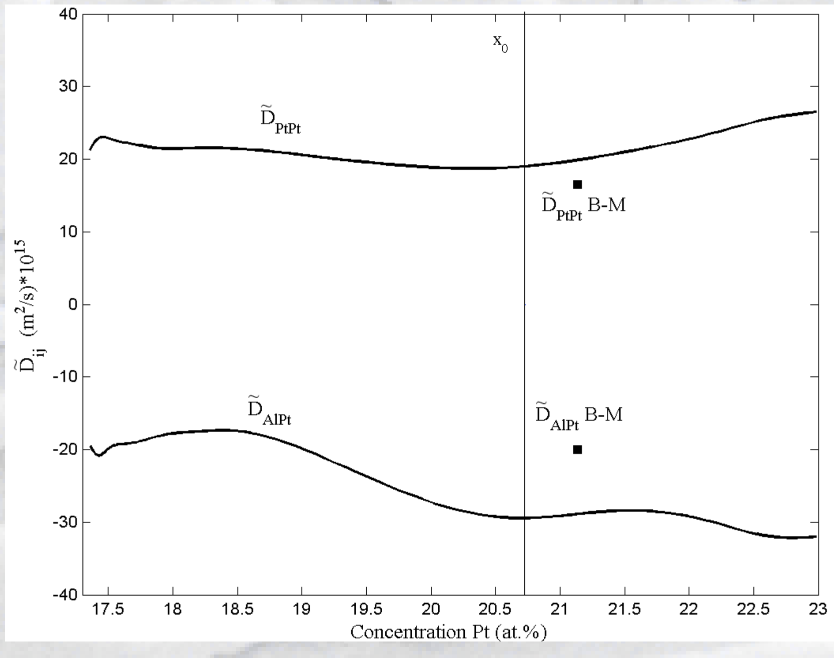
Composition Dependent Ternary Interdiffusion Coefficients



Ni-Pt-Al Alloy Diffusion at 1100ºC (Concentration Profiles Provided by B. Gleeson, ISU)





Summary

- **Multicomponent - Multiphase Diffusion Plays an Important Role in Many Materials Phenomena, Particularly Related to Coatings and Thin Films.**
- **A Complete Catalogue of Diffusion Structure in Ternary System Has Been Observed Experimentally.**
- **A New Analysis for the Determination of Composition Dependent Ternary Interdiffusion Coefficients Has Been Developed.**
- **Materials Systems with Well-Defined Boundary Condition Under Various Driving Forces of Diffusion Are Sought After.**

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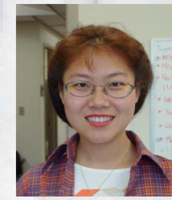
- Dr. Jaiwon Byeon (Post-Doc)





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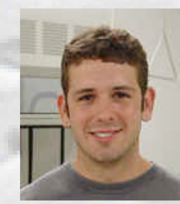
- Travis Patterson (B.S.)
- Charles O'Toole (B.S.)
- Christine Cruz (B.S.)
- Christopher Petorak (B.S., Now at Purdue University)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- Nan Mu (M.S., Now at Iowa State University)
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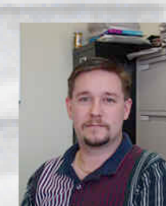

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