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Assessment of Analytical Methods for the Determination of Composition-Dependent Interdiffusion Coefficients in Ternary Alloys

Narayana Garimella, Abby Puccio, Yong-ho Sohn

Advanced Materials Processing and Analysis Center (AMPAC) and Department of Mechanical, Materials and Aerospace Engineering
University of Central Florida
Orlando, FL

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Multicomponent Diffusion in Honor of John E. Morral

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Presentation

- **Interdiffusion in Multicomponent Alloy System**
- **Approaches for the Determination of Interdiffusion coefficients**
  - **Boltzman-Matano Analysis**
  - **Square-root Diffusivity**
  - **Average (Main and cross) Interdiffusion Coefficients**
  - **Discrete (Main and cross) Interdiffusion Coefficients**
- **Assessment of Composition Dependent Ternary Interdiffusion Coefficients in α(fcc) Cu-Ni-Zn Alloy at 775°C and in β(B2) Fe-Ni-Al Alloys at 1000°C.**
- **Comparison of Ternary Interdiffusion Coefficents at Ni-9.7Cr-7.7Al (atom%) at 1100°C.**
- **Summary**

Interdiffusion in Multicomponent Alloy 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

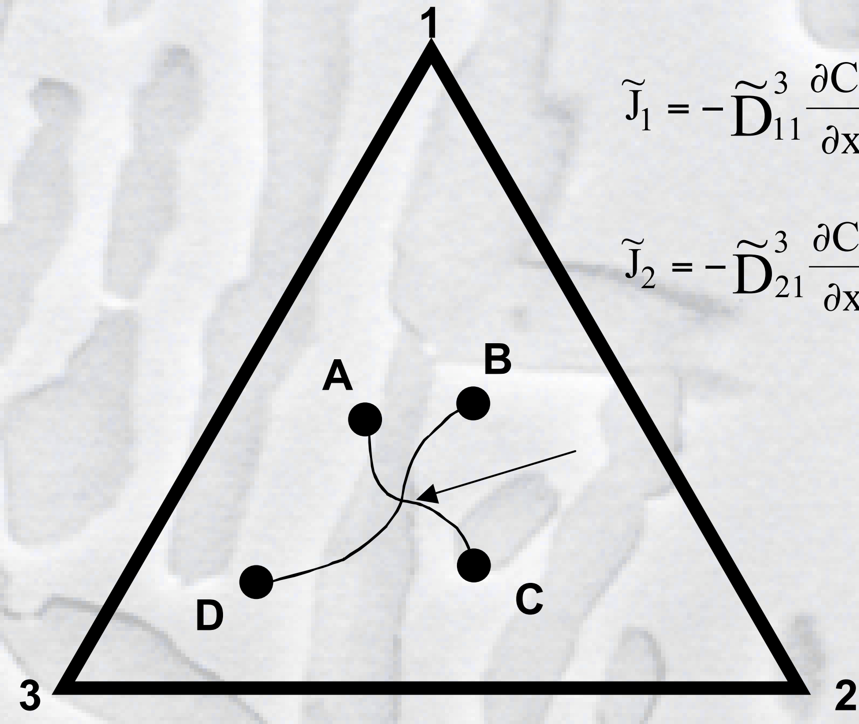
- **So, this flux equation requires the knowledge of (n-1) Independent Concentrations and $(n-1)^2$ Interdiffusion Coefficients.**

- **For a Ternary System:**

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

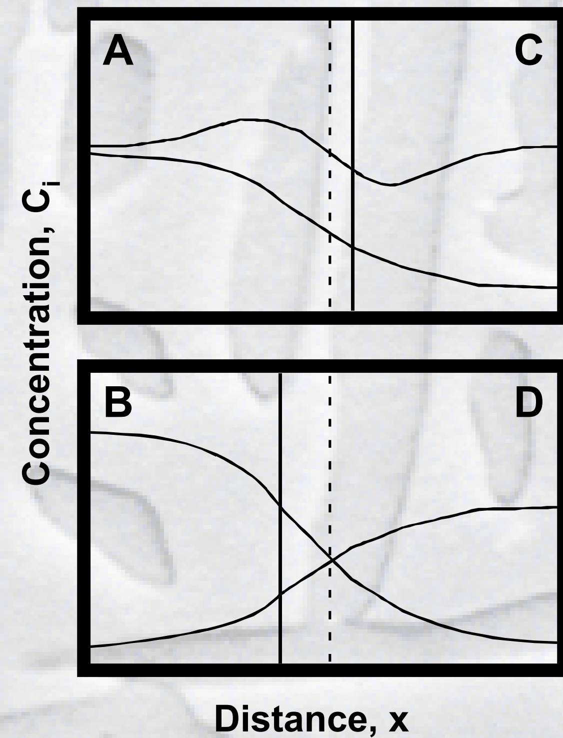
** L. Onsager, Phys. Rev., 37 (1931) 405; 38 (1932) 2265; Ann. NY Acad. Sci., 46 (1965) 241.*

Determination of Ternary Interdiffusion Coefficients based on Boltzmann-Matano Analysis



$$\tilde{J}_1 = -\tilde{D}_{11}^{3}\frac{\partial C_1}{\partial x} - \tilde{D}_{12}^{3}\frac{\partial C_2}{\partial x}$$

$$\tilde{J}_2 = -\tilde{D}_{21}^{3}\frac{\partial C_1}{\partial x} - \tilde{D}_{22}^{3}\frac{\partial C_2}{\partial x}$$



- 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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Square-Root Diffusivity

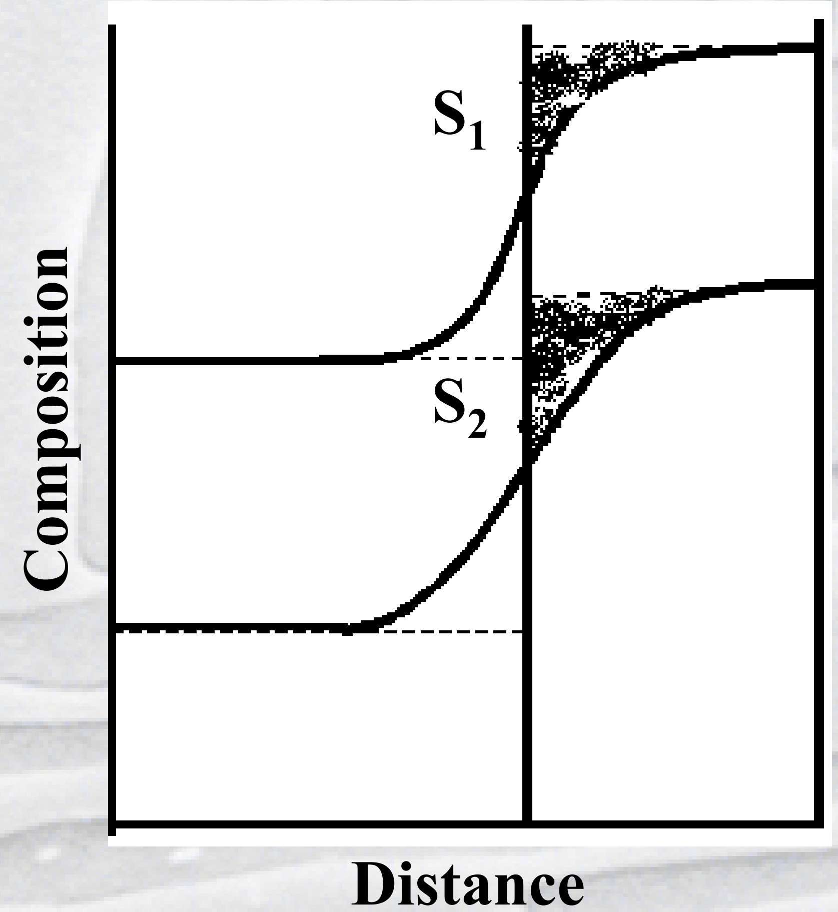
The masses accumulated on either side of the Matano-Plane are S_1 and S_2 can be expressed by:.

$$S_1 = -\sqrt{\frac{t}{\Pi}}(r_{11}\Delta C_1^0 + r_{12}\Delta C_2^0)$$

$$S_2 = -\sqrt{\frac{t}{\Pi}}(r_{21}\Delta C_1^0 + r_{22}\Delta C_2^0)$$

$$\nabla C_1{}^M = -\frac{1}{2\sqrt{\Pi t}}(r_{11}{}^{-1}\Delta C_1^0 + r_{12}{}^{-1}\Delta C_2^0)$$

$$\nabla C_2{}^M = -\frac{1}{2\sqrt{\Pi t}}(r_{21}{}^{-1}\Delta C_1^0 + r_{22}{}^{-1}\Delta C_2^0)$$



where r_{11}, r_{12}, r_{21}, and r_{22} are square-root diffusivities.

Morral and Coworkers

Determination of Interdiffusion Fluxes in Multicomponent Alloy System

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,

C_i^- and C_i^+ are the terminal concentrations

x_o is the Matano plane

M. A. Dayananda and C.W. Kim, Metall. Mater. Trans. A.

Determination of Average Ternary Interdiffusion Coefficients (ATIDC)

Average values of interdiffusion coefficients, treated as a characteristic constants of the diffusion path, can be defined on the basis of Onsager's formalism:

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

where $\overline{\tilde{D}}{}^3_{i1}$ and $\overline{\tilde{D}}{}^3_{i2}$ correspond to the average values of main and cross-interdiffusion coefficients,

defined by $$\overline{\tilde{D}}{}^3_{ij} = \int_{C_j(x_1)}^{C_j(x_2)} \tilde{D}^3_{ij}\,dC_j \Bigg/ \int_{C_j(x_1)}^{C_j(x_2)} dC_j \qquad (i = 1, 2)$$

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.

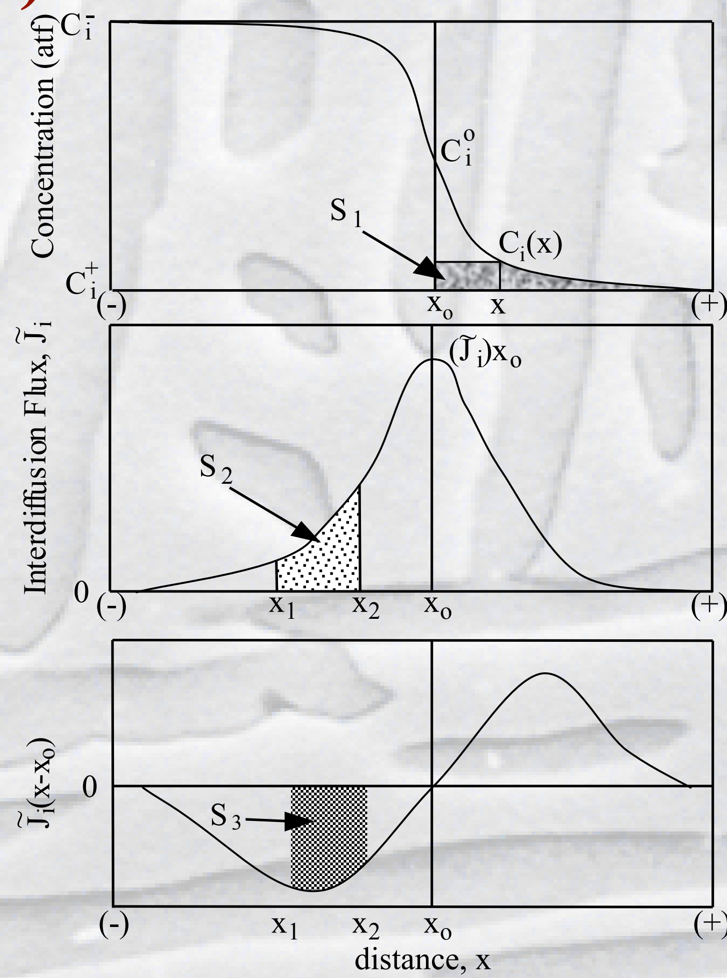
Determination of Average Ternary Interdiffusion Coefficients (ATIDC)

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

$$(i, j = 1, 2)$$

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

$$(i, j = 1, 2)$$



M. A. Dayananda and Y. H. Sohn, Metall. Mater. Trans., 30A (1999) 535.
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Salient Features of New Analytical Methods

- **Calculation of interdiffusion fluxes directly from experimental concentration profiles.**
- **Integration of interdiffusion fluxes over selected composition ranges.**
- **Determination of interdiffusion coefficients over selected composition ranges.**
- **Assessment of diffusional interactions among the components as well as contributions from the gradients of concentrations and temperature to interdiffusion fluxes of the individual components.**

Determination of Composition Dependent Discrete Ternary Interdiffusion Coefficients (DTIC)

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

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

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

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

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

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

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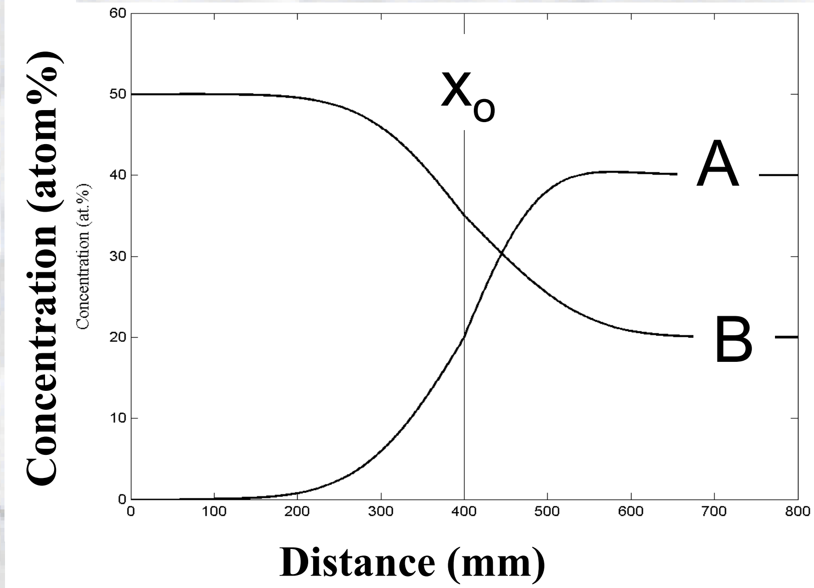
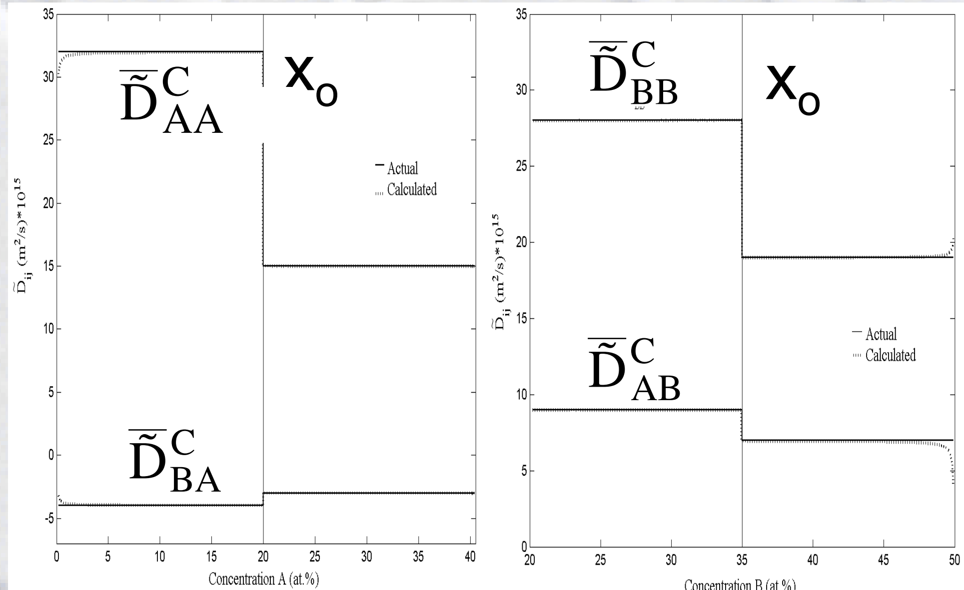
Determination of Composition Dependent Discrete Ternary Interdiffusion Coefficients (DTIC)





On the Left - hand Side of x_o :

$\tilde{\bar{D}}^{C}_{AA} = 32 \times 10^{-15}\ m^2/sec$

$\tilde{\bar{D}}^{C}_{AB} = 7 \times 10^{-15}\ m^2/sec$

$\tilde{\bar{D}}^{C}_{BA} = -4 \times 10^{-15}\ m^2/sec$

$\tilde{\bar{D}}^{C}_{BB} = 19 \times 10^{-15}\ m^2/sec$

On the Right - hand Side of x_o :

$\tilde{\bar{D}}^{C}_{AA} = 15 \times 10^{-15}\ m^2/sec$

$\tilde{\bar{D}}^{C}_{AB} = 9 \times 10^{-15}\ m^2/sec$

$\tilde{\bar{D}}^{C}_{BA} = -3 \times 10^{-15}\ m^2/sec$

$\tilde{\bar{D}}^{C}_{BB} = 28 \times 10^{-15}\ m^2/sec$

Profiles Generated Based on Ternary Error Function Solution

Input of Constant Ternary Interdiffusion Coefficients is Calculated as Constant Ternary Interdiffusion Coefficients as a Function of Composition

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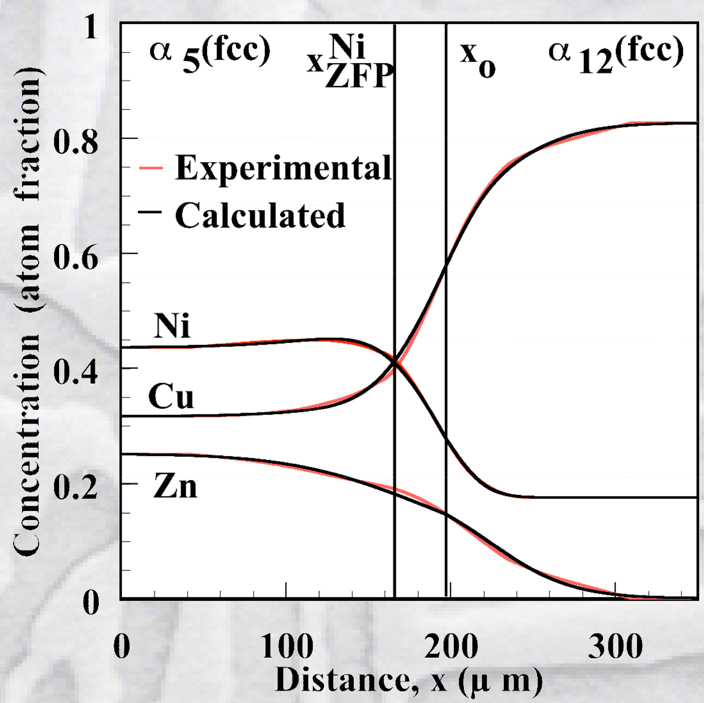
Average Ternary Interdiffusion Coefficients

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

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

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

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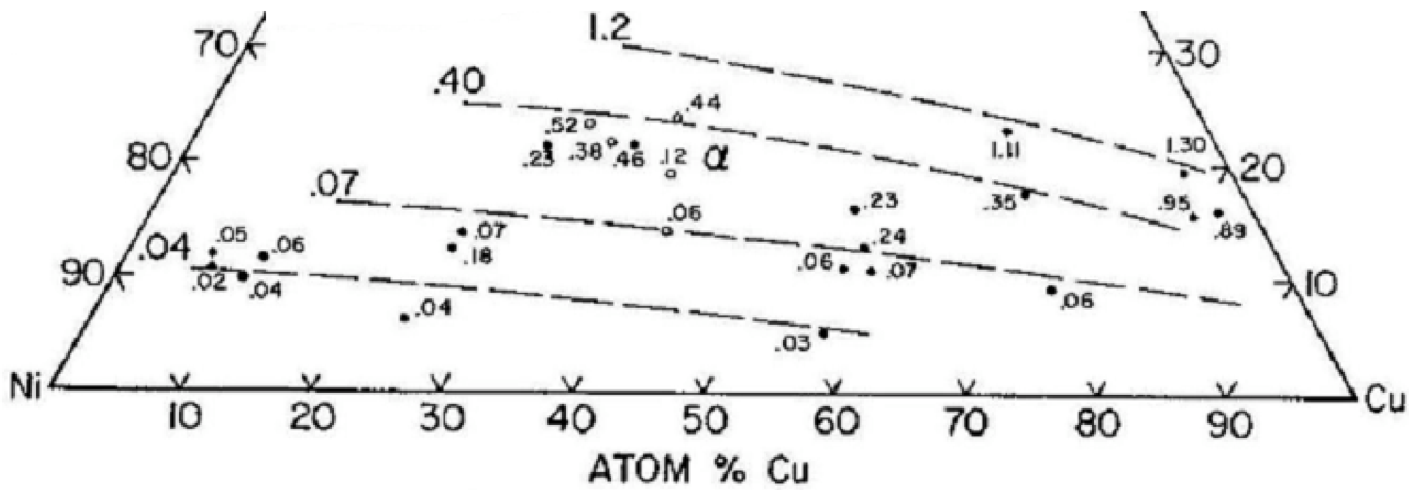
Assessment of Ternary Interdiffusion Coefficients in α(fcc) Cu-Ni-Zn Alloy at 775ºC

$$\tilde{D}^{Cu}_{NiNi}\,(10^{-10}\ cm^2/s)$$



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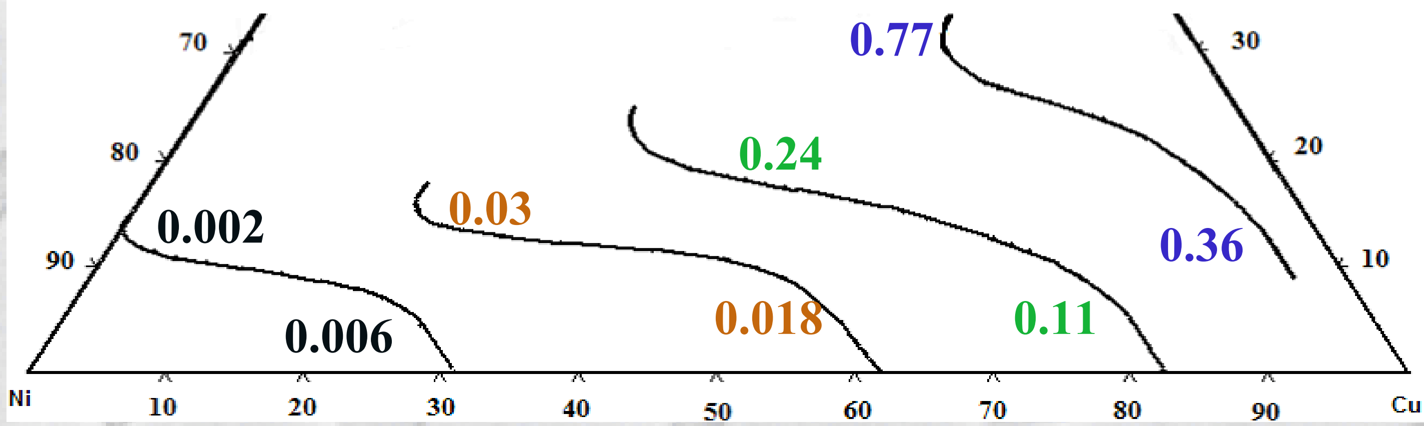
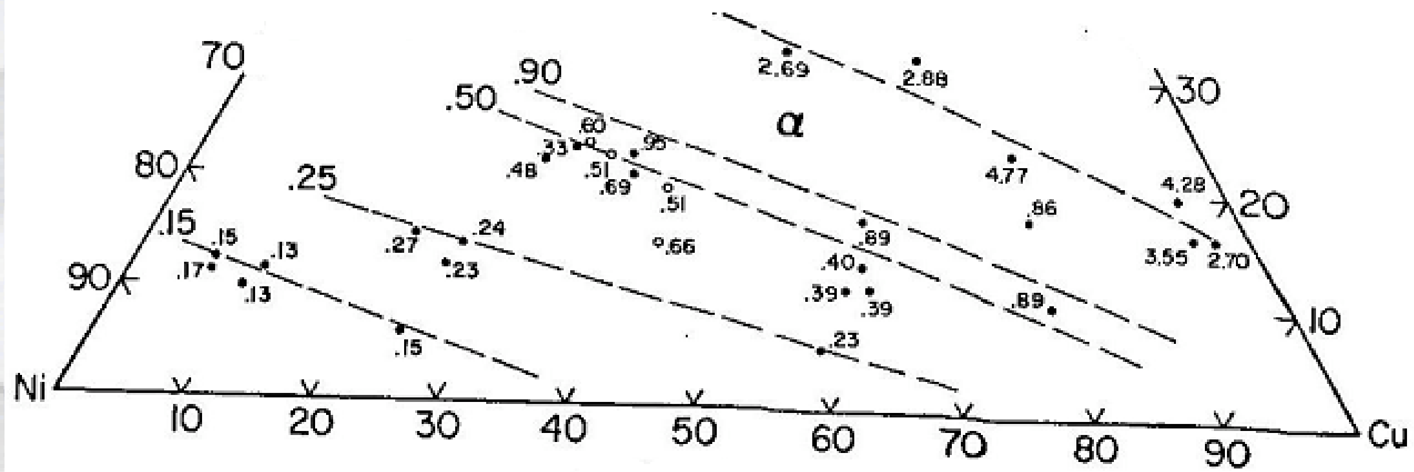


ATIDC

Assessment of Ternary Interdiffusion Coefficients in α(fcc) Cu-Ni-Zn Alloy at 775ºC

$\tilde{D}^{Cu}_{ZnZn}$ (10^{-10} cm^2/s)



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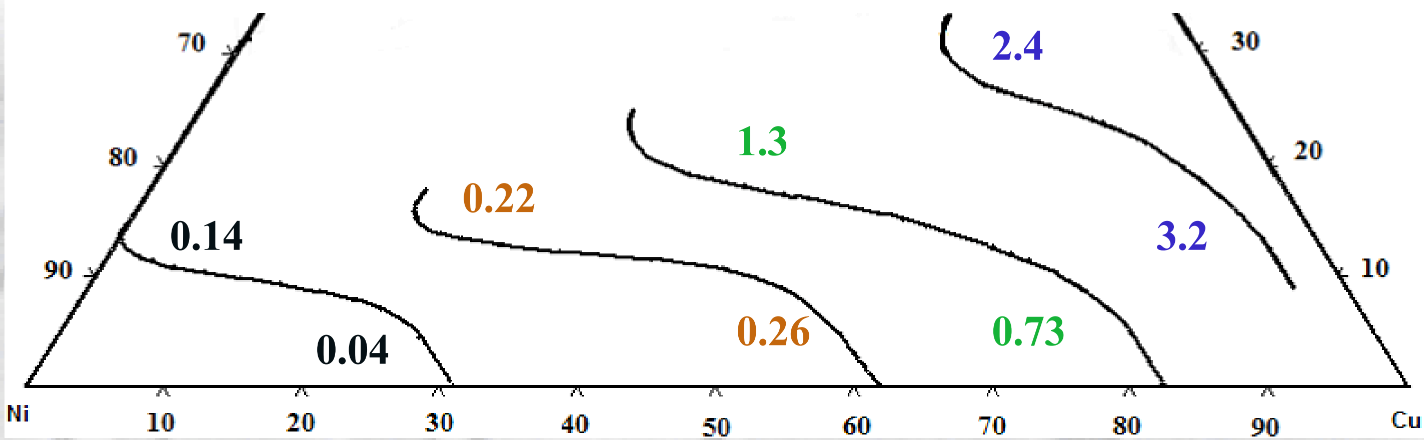
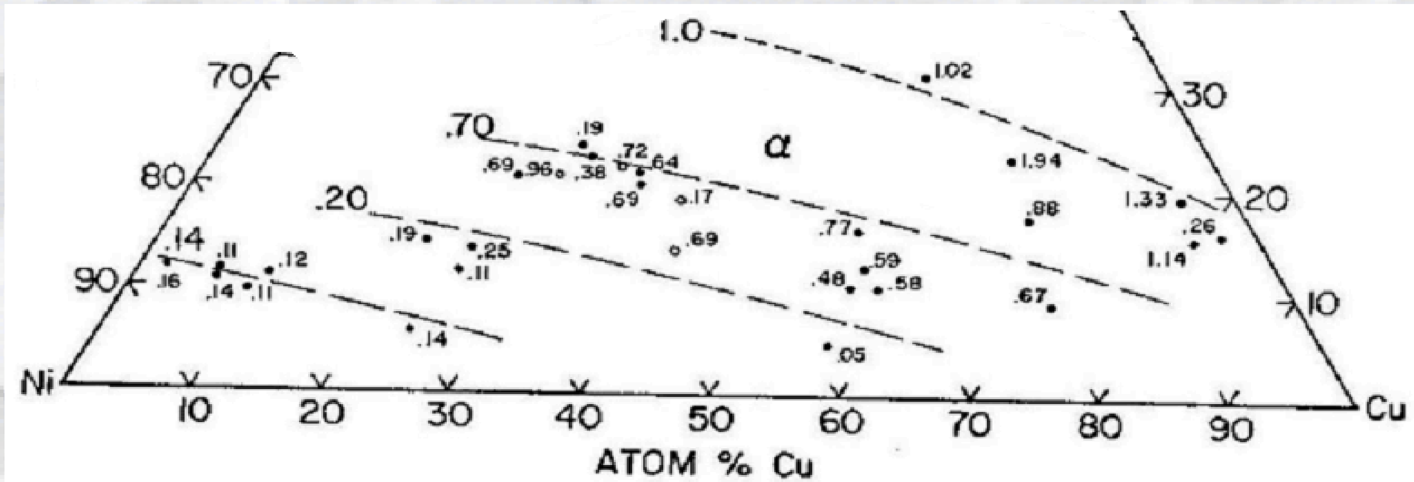


ATIDC

Assessment of Ternary Interdiffusion Coefficients in α(fcc) Cu-Ni-Zn Alloy at 775ºC

$$-\tilde{D}^{Cu}_{NiZn}(10^{-10}\ cm^2/s)$$



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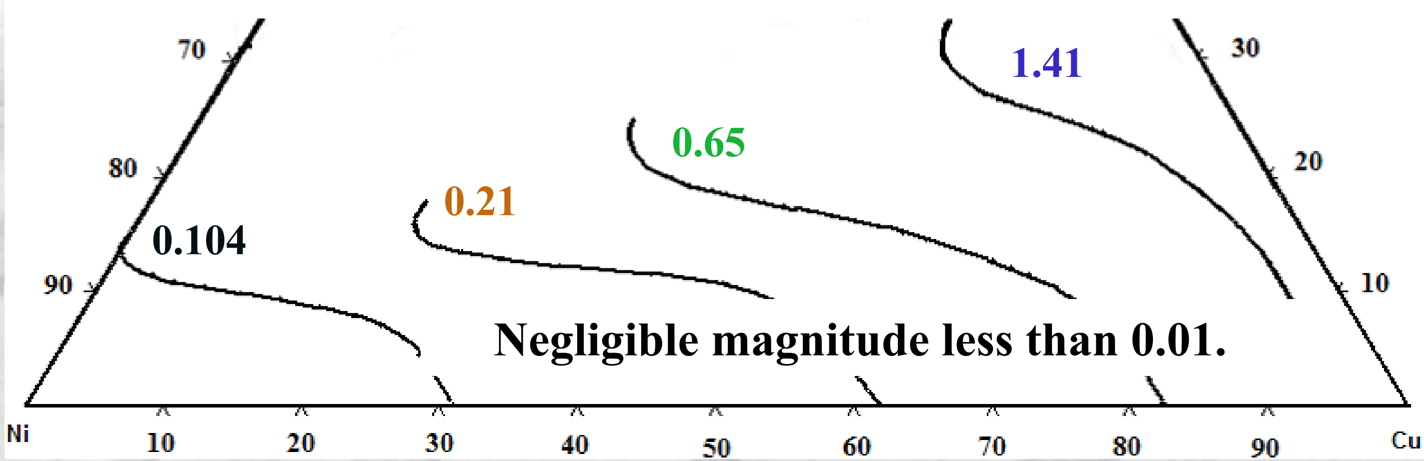
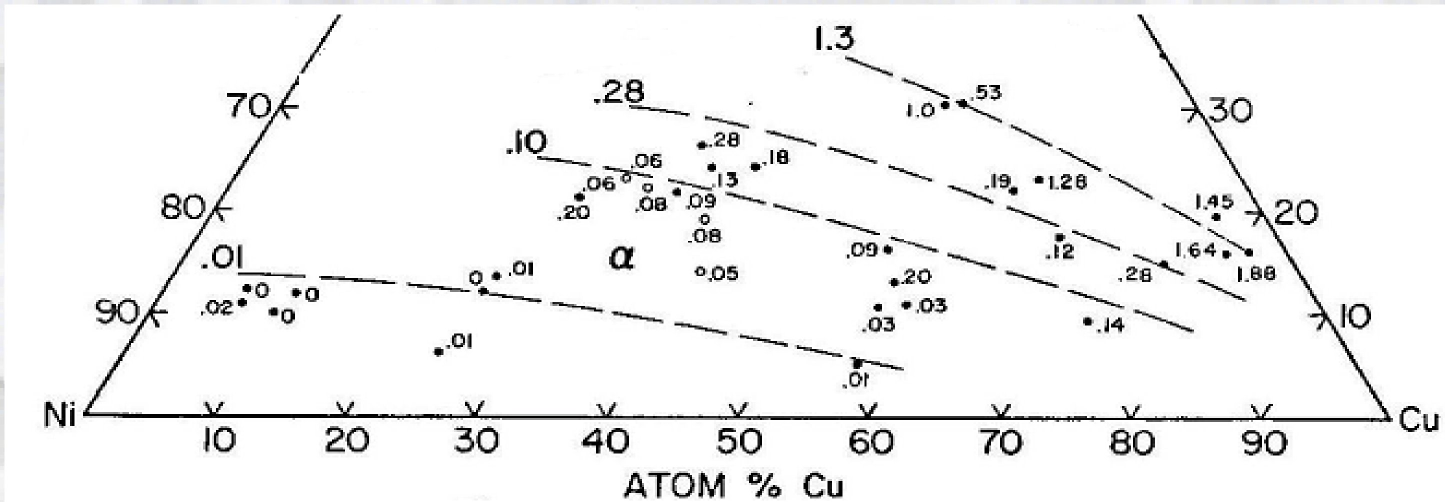


ATIDC

Assessment of Ternary Interdiffusion Coefficients in α(fcc) Cu-Ni-Zn Alloy at 775ºC

$-\tilde{D}^{Cu}_{ZnNi}$ (10^{-10} cm^2/s)



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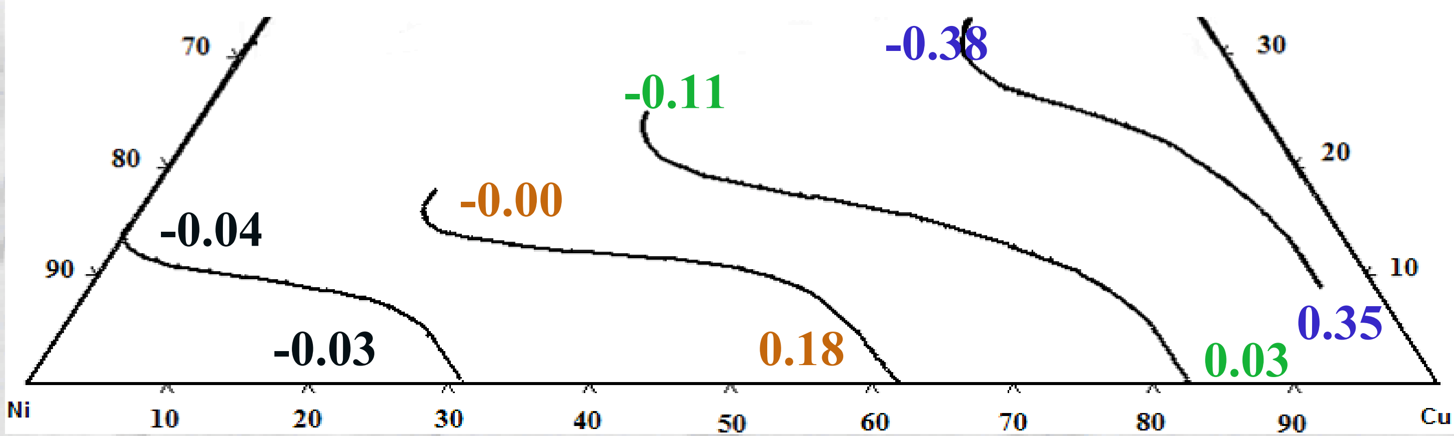


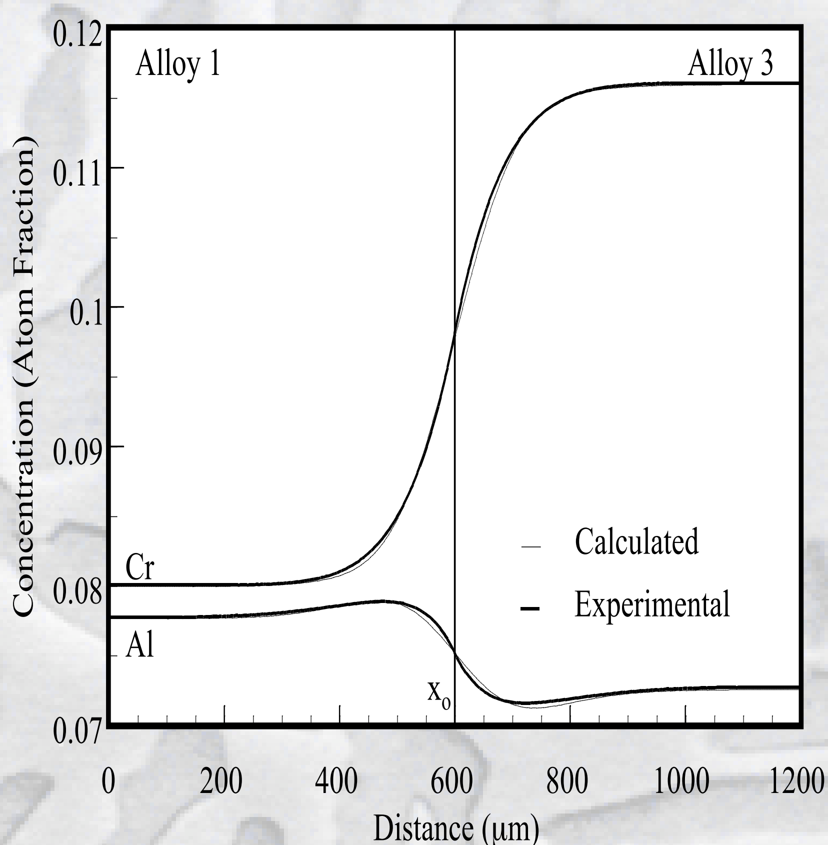
ATIDC

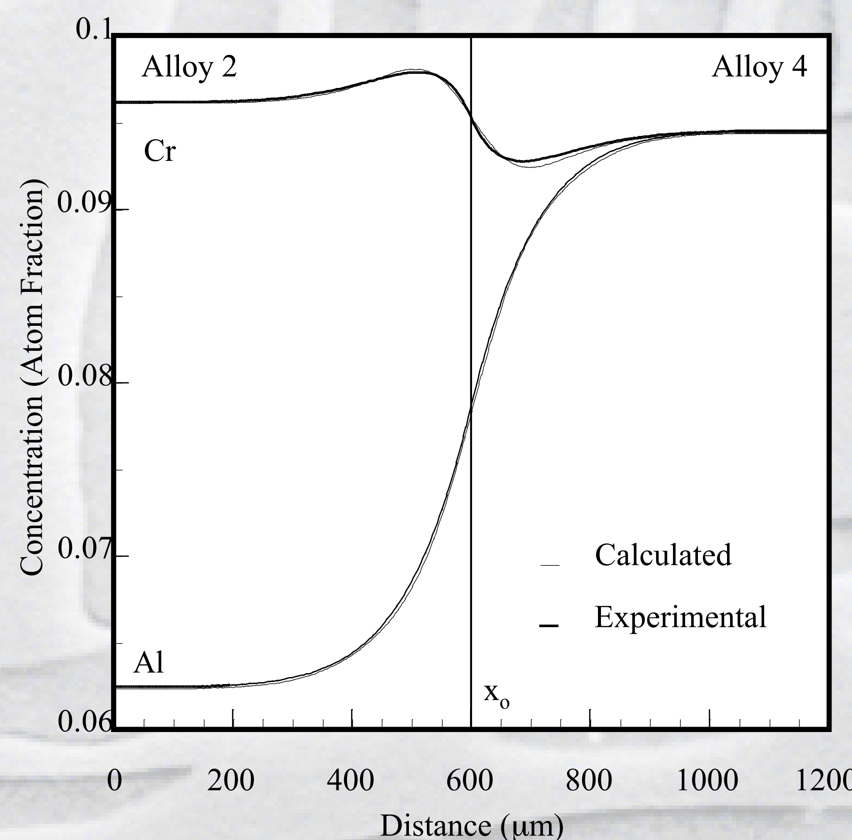
Assessment of Ternary Interdiffusion Coefficients in β(B2) Fe-Ni-Al Alloy at 1000ºC

Couple	Selected Compositions* (atom percent)	Interdiffusion Coefficients[#] $\tilde{D}^{Fe}_{ij}$ (x 10^{-15} m^2/sec)				Average Interdiff. Coefficients[+] $\bar{\tilde{D}}^{Fe}_{ij}$ (x 10^{-15} m^2/sec)			
		$\tilde{D}^{Fe}_{AlAl}$	$\tilde{D}^{Fe}_{AlNi}$	$\tilde{D}^{Fe}_{NiAl}$	$\tilde{D}^{Fe}_{NiNi}$	$\bar{\tilde{D}}^{Fe}_{AlAl}$	$\bar{\tilde{D}}^{Fe}_{AlNi}$	$\bar{\tilde{D}}^{Fe}_{NiAl}$	$\bar{\tilde{D}}^{Fe}_{NiNi}$
β_3 vs. γ_5	Fe-0.6Ni-28.8Al	-	-970.6	-	144.5	1769.	-829.8	-127.7	67.2
	Fe-0.4Ni-28.4Al	-	-810.4	-	65.3				
	Fe-45.9Ni-34.9Al	14.0	-	-5.6	-	13.0	-1.3	-6.8	2.9
	Fe-45.8Ni-34.6Al	2.8	-	-1.4	-				
	Fe-38.7Ni-35.3Al	15.1	-13.5	-4.8	5.1				
	Fe-17.8Ni-39.8Al	22.2	-0.3	-4.2	1.6				
	Fe-14.2Ni-41.0Al	-	-6.1	-	3.1				
β_{17} vs. β_5	Fe-16.5Ni-37.3Al	33.9	-	-1.1	-	88.7	-25.0	-2.0	1.4
	Fe-13.8Ni-40.1Al	48.5	-19.4	-0.9	2.1				
	Fe-12.0Ni-40.5Al	88.5	-18.8	-0.4	3.2				

* selected compositions appear in the diffusion zone of the couples.
\# ternary interdiffusion coefficients determined by the Boltzmann Matano analysis.
\+ determined for the selected composition ranges of the couples.

Concentration Profiles of Ternary Diffusion Couple: γ-Phase Ni-Cr-Al Alloys at 1100°C





Common Composition at Ni-9.7Cr-7.7Al in γ-Phase at 1100°C

J.E. Morral and Coworkers

Comparison of Interdiffusion Coefficients (10^{-11}) at Ni-9.7Cr-7.7Al in The γ-Phase Alloys at 1100°C Determined by Various Techniques

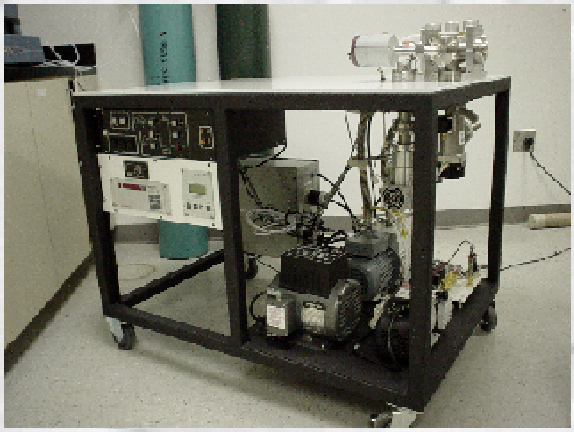
Method	AlAl (cm^2/sec)	AlCr (cm^2/sec)	CrAl (cm^2/sec)	CrCr (cm^2/sec)
BZMA	23.7	8.1	7.4	11.5
KMAZ	28.7	10.1	5.5	10.0
SQRD	22.0	7.6	7.8	12.6
NESH	23.0	7.3	6.3	9.4
ATIDC: 1/3(S)	28.5	9.8	6.8	14.2
ATIDC: 2/4(S)	23.5	17.1	8.6	14.7
DDC: 1/3(S)	13.6	5.6	19.4	17.3
DDC: 2/4(S)	23.0	17.2	7.5	10.2

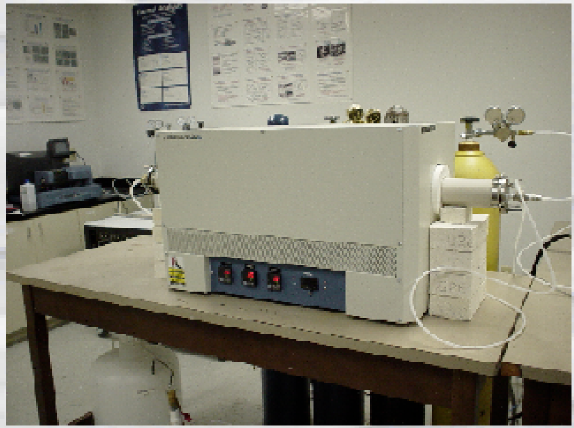
BZMA: Boltzmann-Matano analysis; KMAZ: Krishtal, Mokrov, Akimov and Zakharov analysis; SQRD: Square-Root Diffusivity; NESH: Nesbitt's Data based on BZMA, AEIDC: Average Effective Interdiffusion Coefficients; DDC: Discrete Interdiffusion Coefficients.

Experimental Work Currently in Progress

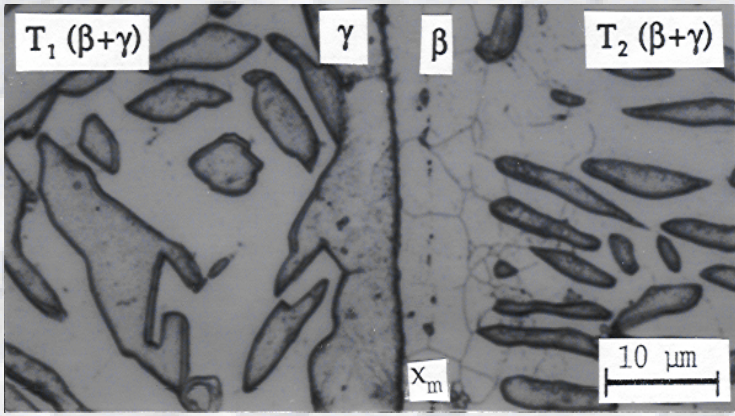
- Alloy Casting by Vacuum Induction Melting, Chill Casting and/or Tri-Arc Melting Furnace.
- Homogenization Heat Treatment.
- Microstructure, Phase Constituents and Compositional Analysis.
- Assembled with Kovar Steel Jigs.
- Encapsulate in Quartz Tube (Vacuum or Ar-Filled) After Several Vacuum-Hydrogen 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).

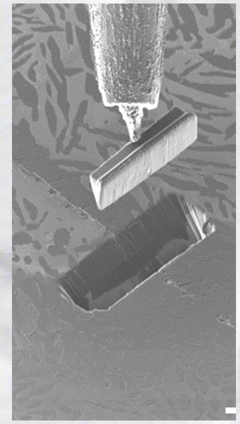
- Ni-Cr-X (X=Al, Pd, Ge, Si)

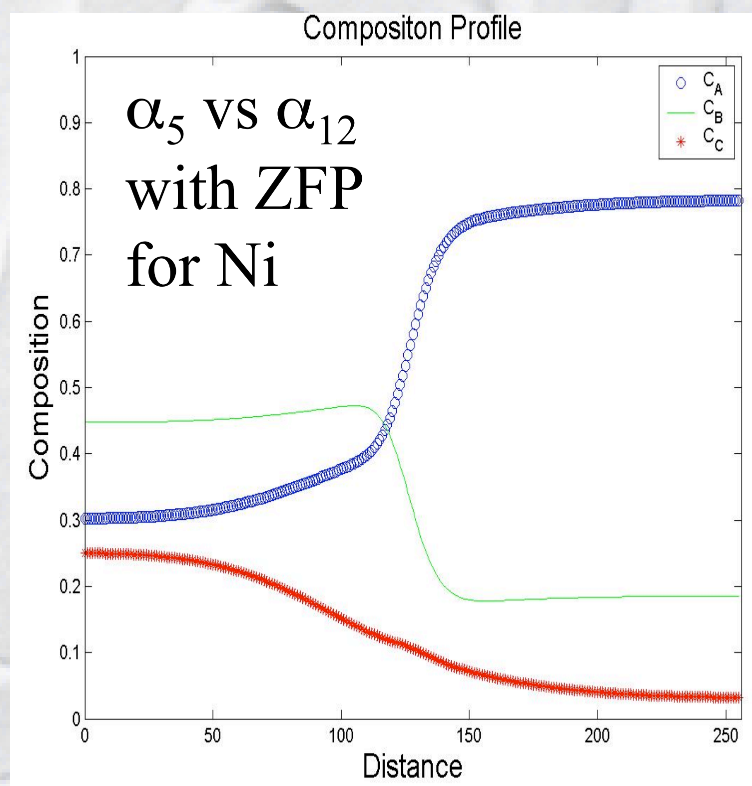


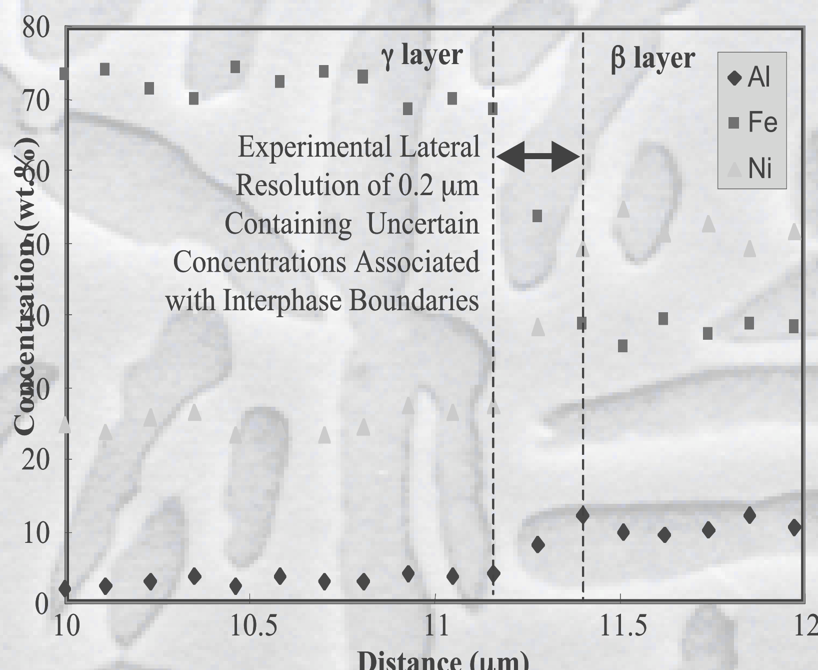


Analytical and Modeling Work Currently in Progress









Modeling Incorporating Realistic Compositional Dependent Interdiffusion Coefficients.

Summary

- **Analytical Techniques Allow Assessment of Reliable and Comparable Interdiffusion Coefficients in Ternary Systems:**
  - **Boltzmann-Matano Analysis**
  - **Square-Root Diffusivity**
  - **Average (Main and cross) Interdiffusion Coefficients**
  - **Discrete (Main and cross) Interdiffusion Coefficients**

- **Assessments of Composition Dependent Ternary Interdiffusion Coefficients in α(fcc) Cu-Ni-Zn Alloy at 775°C, β(B2) Fe-Ni-Al Alloys at 1000°C, and at Ni-9.7Cr-7.7Al (atom%) at 1100°C were Carried Out.**

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  - **General Electric Global Research Center, Schenectady, NY.**
  - **Solar Turbines Incorporated, San Diego, CA.**

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  - **General Electric Aircraft Engines, Cincinnati, OH.**
  - **General Electric Power, NC**
  - **Siemens-Westinghouse Power Corporations, Orlando, FL**
  - **Solar Turbines Incorporated, San Diego, CA.**
  - **Howmet Research Corporation, Whitehall, MI.**
  - **Pratt & Whitney, East Hartford, CT.**