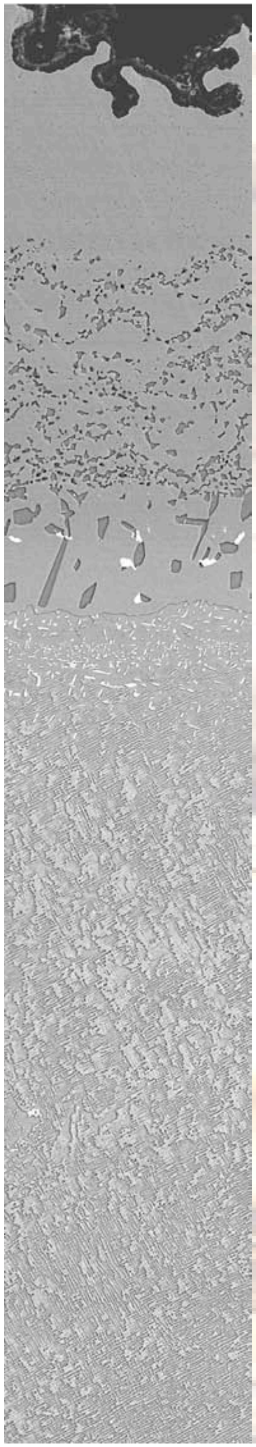

Superalloy Dependent Stability of β-NiAl Phase in NiCoCrAlY Coatings

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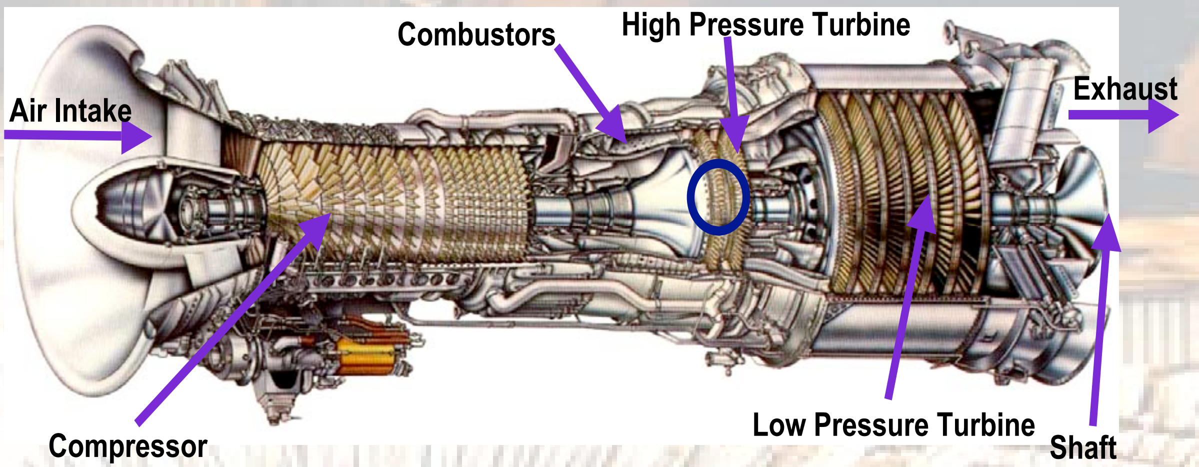
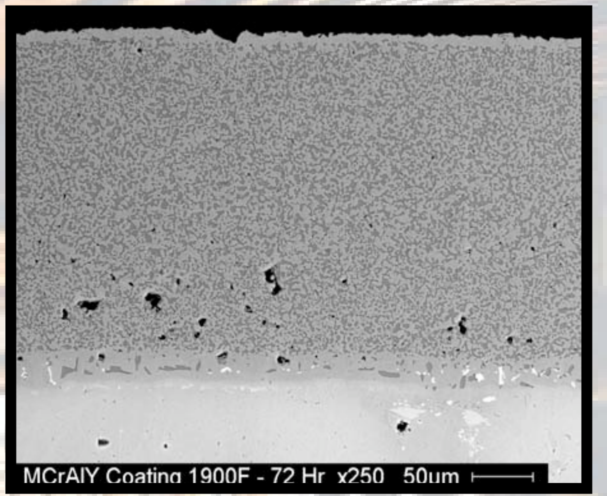
April 19, 2005
NIST Diffusion Workshop

NiCoCrAlY Coatings in Service

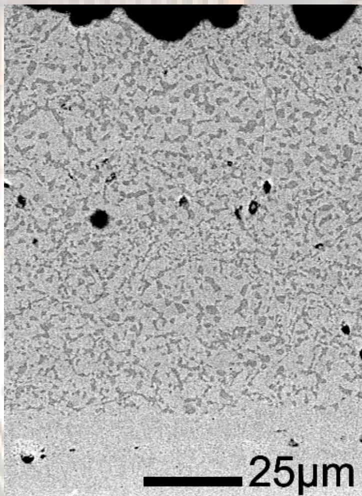




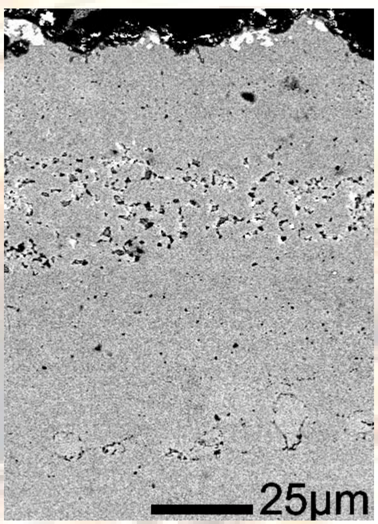
- NiCoCrAlY coatings are employed in gas turbine engines to protect hot-section components such as blades and vanes against oxidation and hot corrosion.
- These coatings possess a two-phase microstructure consisting of high Al-content β-NiAl solid solution phase and low Al-content γ-Ni solid solution phase.
- The coatings are designed to form a continuous protective Al_2O_3 oxide scale that protects the coating and in turn the substrate.

Lifetime of NiCoCrAlY Coatings

As Coated



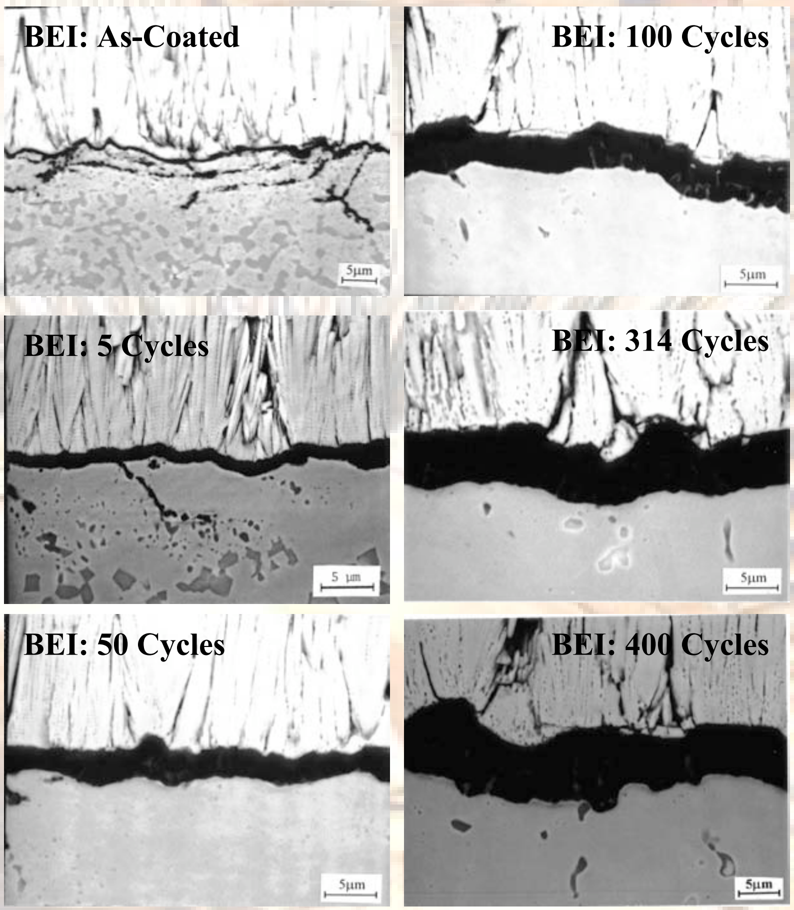
Depleted



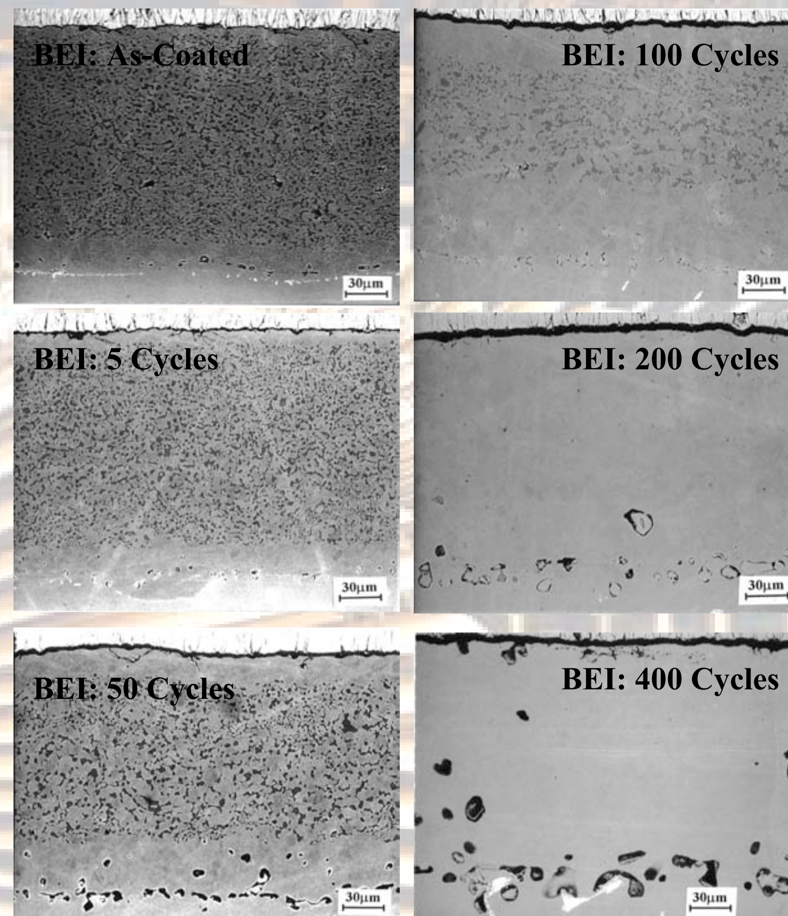
- **The Al rich β-phase in the coating is dissolved from the top and the bottom pseudo interfaces:**
  - **Al is depleted on the top by formation and maintenance of a protective oxide layer, Al_2O_3.**
  - **Al is depleted via interdiffusion with a superalloy substrate.**
- **As Al depletes, the β-phase dissolves into the γ-phase (Ni Solid Solution).**
- **The failure of NiCoCrAlY coatings may be defined by the complete dissolution of β-phase.**
  - **Al_2O_3 scale loses continuity**

Oxidation and Interdiffusion: Recession of (β+γ) in NiCoCrAlY

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



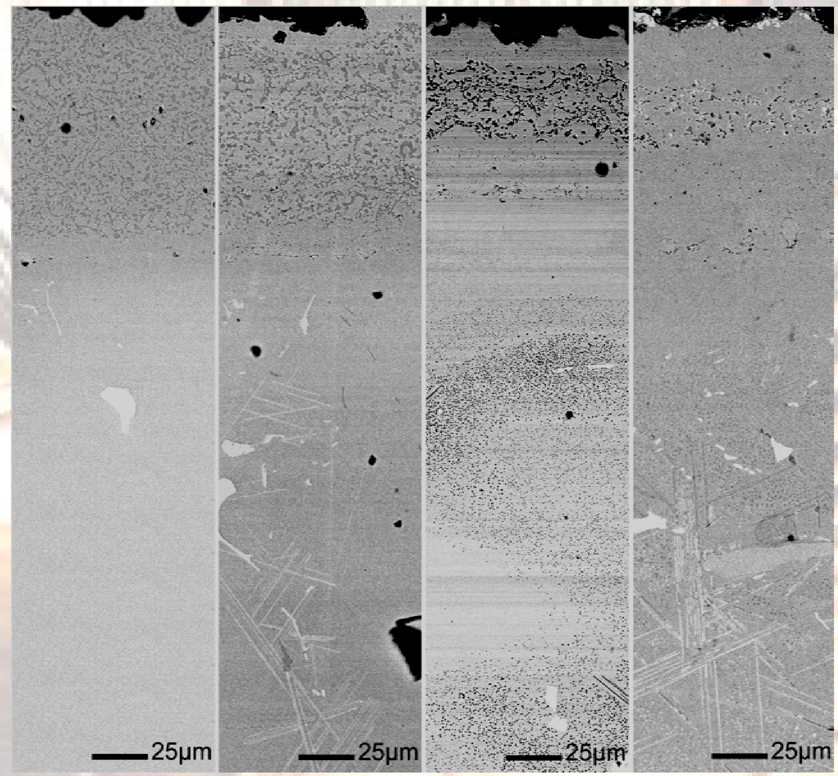
Depletion Zone: $D^{eff} = 3.4 \times 10^{-15}\ m^2/sec$
Interdiffusion Zone: $D^{eff} = 9.3 \times 10^{-15}\ m^2/sec$

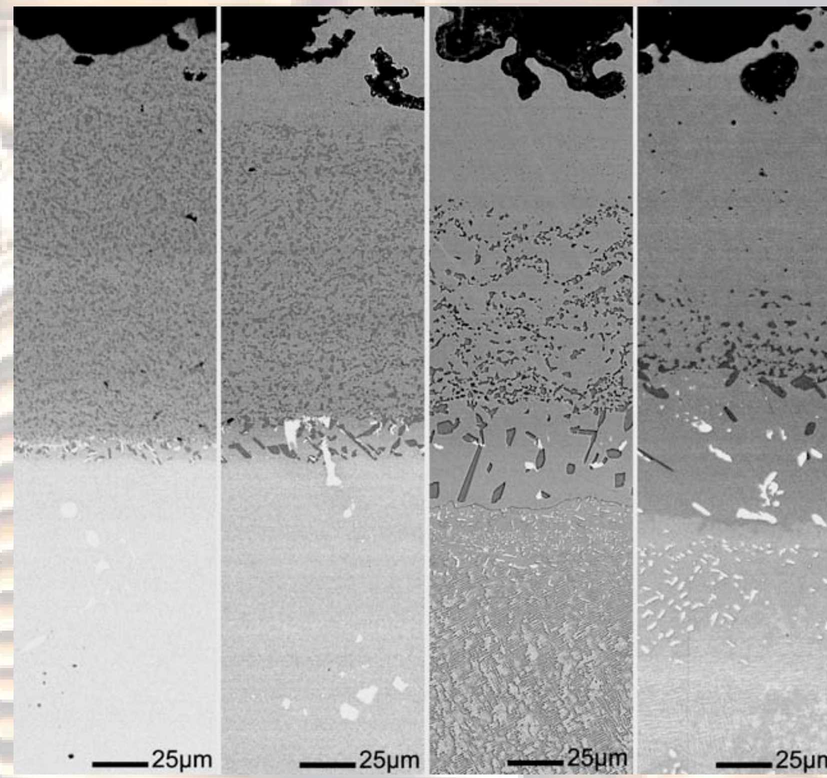


Y.H. Sohn et al., Surf. Coat. Technol., 146-147 (2001) pp. 70-78.

Interdiffusion and Lifetime of Oxidation Resistant Coatings

- **3X 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

3 x Isothermal Exposure Time, 3t

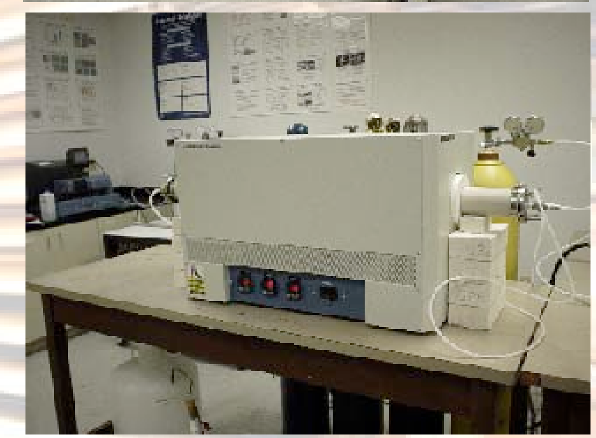
E. Perez, Y.H. Sohn, Unpublished Research.

Objectives

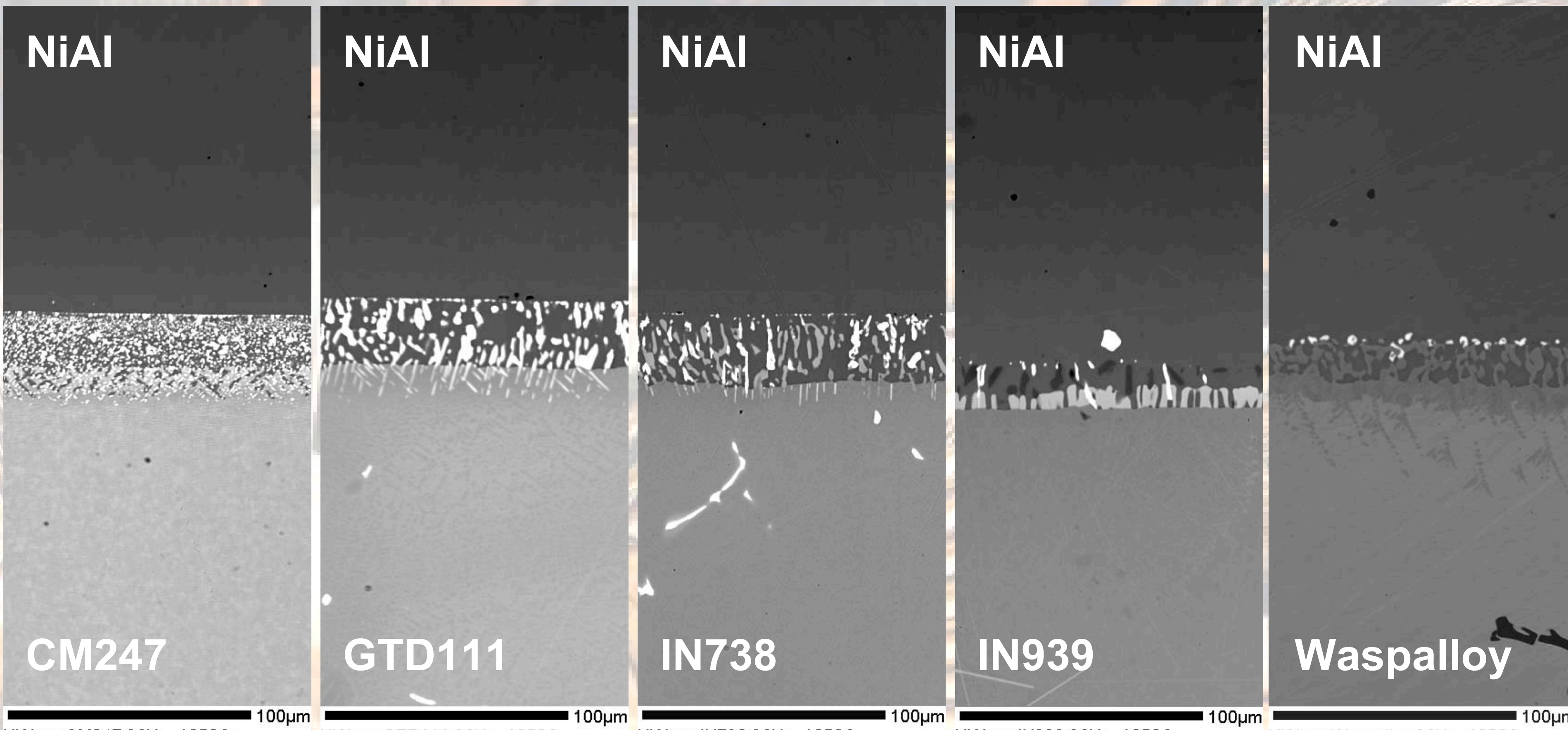
- Determine/Predict the effective interdiffusion coefficients of Al using solid-to-solid diffusion couples of β-NiAl vs. various superalloys (γ+γ'+others) by:
  - Direct determination of interdiffusion fluxes from experimental concentration profiles in single β-NiAl phase region.
  - Calculation of effective interdiffusion coefficients incorporating the multicomponent diffusional interactions.
  - Prediction of effective interdiffusion coefficients in multiphase superalloys based on mass balance.
- Examine the composition-dependence of Al interdiffusion coefficients as a function of initial superalloy compositions.

Experimental Details

- **Solid-to-solid diffusion couples.**
- **Equiaxed NiAl vs various commercially available Ni-superalloys.**
- **Encapsulated in quartz capsule in Ar (1 atm at 1050°C) after several hydrogen flush.**
- **Diffusion anneal for 96 hours at 1050°C using Lindberg/Blue 3-Zone horizontal tube furnace.**
- **Diffusion structures examined by optical and scanning electron microscopy**
- **Concentration profiles determine by Electron Probe Microanalysis (EPMA) using pure standards and ZAF correction.**



Solid-to-Solid Diffusion Couples



- **Excellent Diffusion Bonding Between Alloys.**
- **Particles rich in refractory elements (e.g., Ta, W, Mo, Nb, etc) are precipitating near the interface between NiAl and superalloys.**

Phenomenology of Isothermal Interdiffusion in Multicomponent System

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

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

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

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

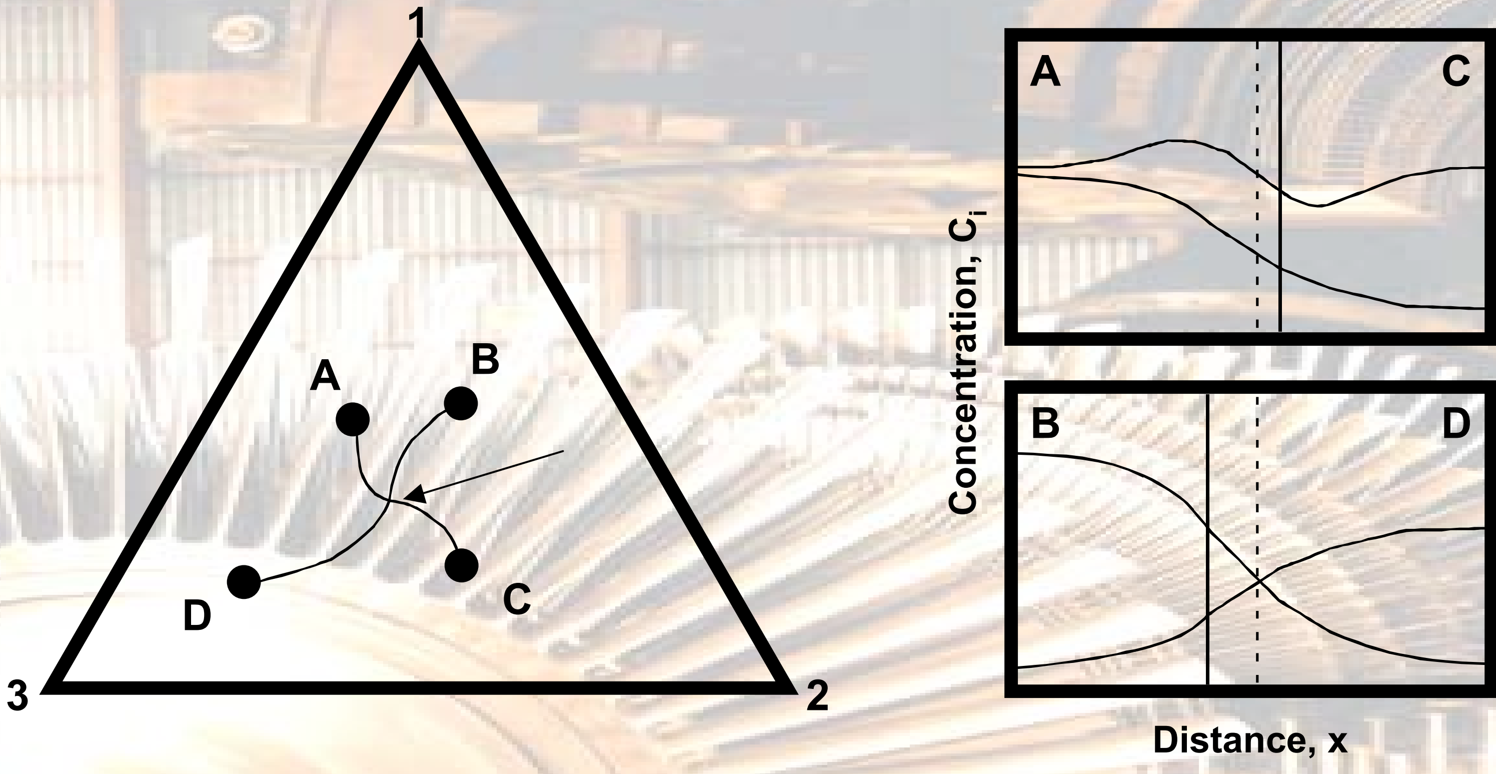
- **Requires Knowledge of (n-1) Independent Concentrations and $(n-1)^2$ Interdiffusion Coefficients.**

- **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.

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.**

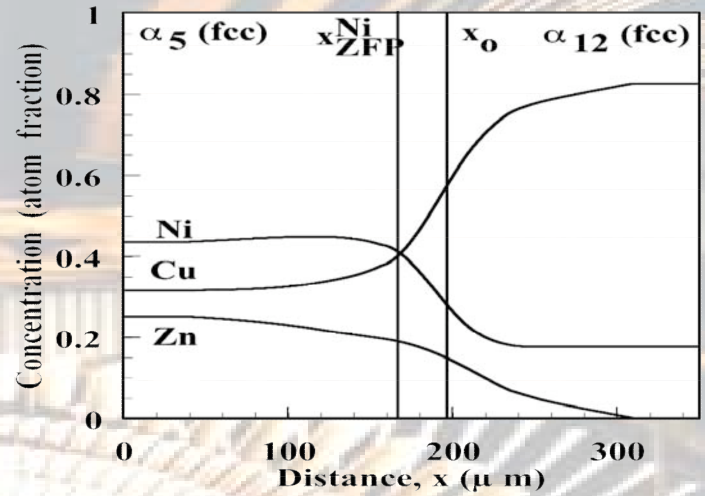
** J. Kirkaldy, Can. J. Phys., 35 (1957) 435.*

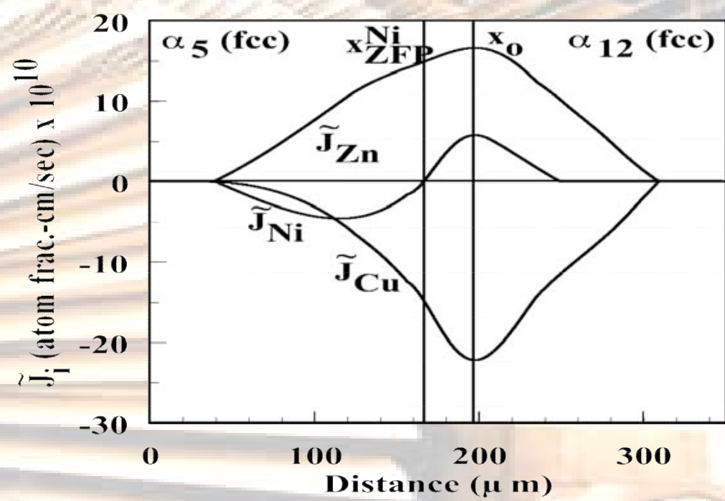
Determination of Interdiffusion Fluxes

- **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.

Integrated and Effective Interdiffusion

Integrated interdiffusion coefficients for a component *i* in NiAl and superalloy sides can be defined as:

$$D_{i,NiAl}^{int} = \int_{-\infty}^{x_o} \tilde{J}_i(x)dx \quad \text{and} \quad D_{i,SA}^{int} = \int_{x_o}^{+\infty} \tilde{J}_i(x)dx$$

Effective interdiffusion coefficients for a component *i* in NiAl and superalloy sides can be defined as:

$$\tilde{D}_{i,NiAl}^{eff} = \frac{\tilde{D}_{i,NiAl}^{int}}{C_i^- - C_i^o} = \frac{\int_{-\infty}^{x_o} \tilde{J}_i dx}{C_i^- - C_i^o} \quad \text{and} \quad \tilde{D}_{i,SA}^{eff} = \frac{\tilde{D}_{i,SA}^{int}}{C_i^o - C_i^+} = \frac{\int_{x_o}^{+\infty} \tilde{J}_i dx}{C_i^o - C_i^+}$$

Effective interdiffusion coefficients incorporates multicomponent diffusional interactions:

$$\tilde{D}_i^{eff} = \tilde{D}_{ii}^n + \sum_j \frac{\tilde{D}_{ij}^n \, \partial C_j / \partial x}{\partial C_i / \partial x} \qquad (j \neq i)$$

M. A. Dayananda, Y.H. Sohn, Scripta Mater., 35 (1996) 683.

Correlation in Interdiffusion Coefficients with Concentrations

Effective interdiffusion coefficients on either side of the analysis can be related to compositions:

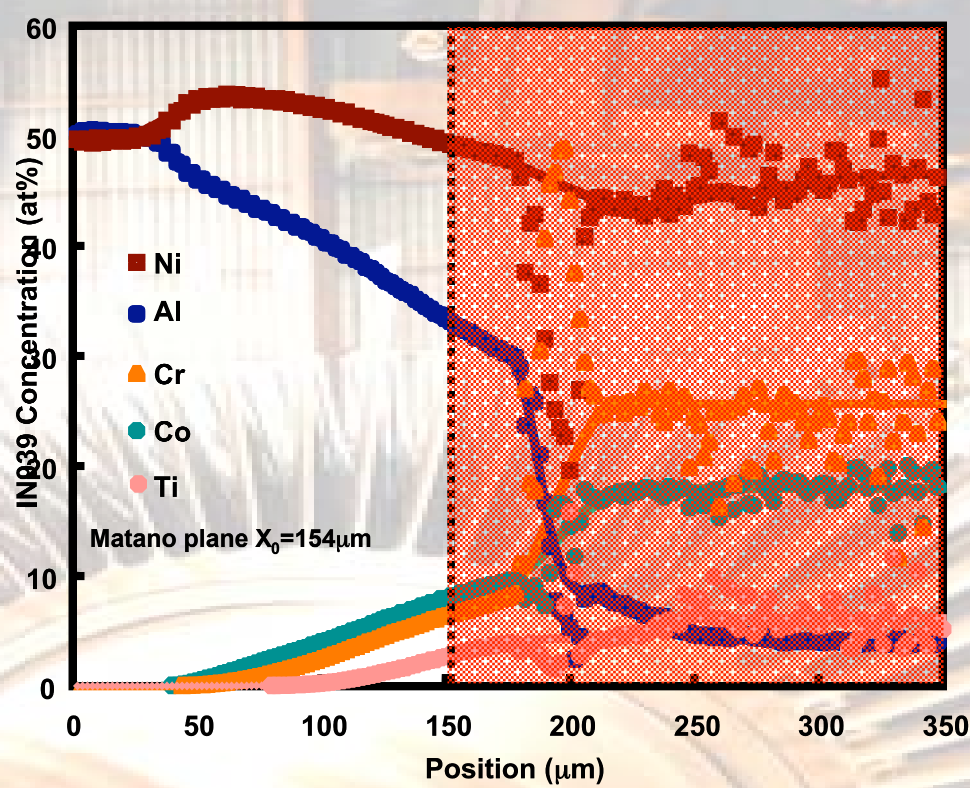
$$\frac{C_i^- - C_i^o}{C_i^o - C_i^+} = \frac{\alpha_{i,SA}}{\alpha_{i,NiAl}} \frac{\sqrt{\tilde{D}_{i,NiAl}^{eff}}}{\sqrt{\tilde{D}_{i,SA}^{eff}}}$$

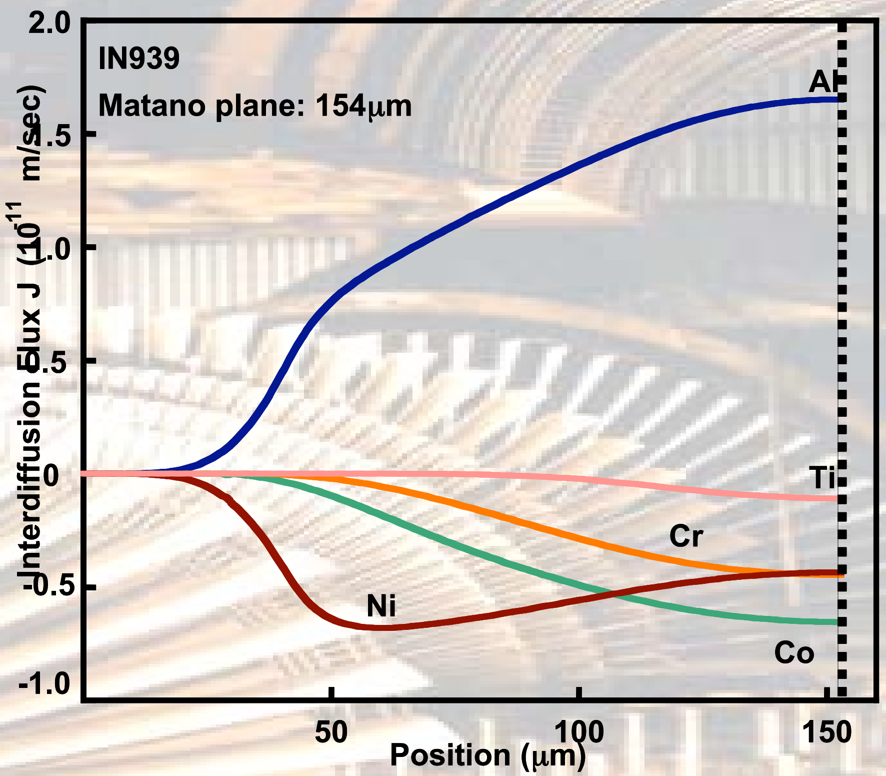
$$\text{and} \quad \frac{C_i^- - C_i^o}{C_i^o - C_i^+} = \frac{\sqrt{\tilde{D}_{i,NiAl}^{app}}}{\sqrt{\tilde{D}_{i,SA}^{app}}} \quad \text{where} \quad D_i^{app} = \frac{\sqrt{\tilde{D}_i^{eff}}}{\alpha_i}$$

Therefore, interdiffusion coefficients calculated from single-phase region (e.g., NiAl) can be employed to predict those of multiphase regions (e.g., superalloys).

M. A. Dayananda, Y.H. Sohn, Scripta Mater., 35 (1996) 683.

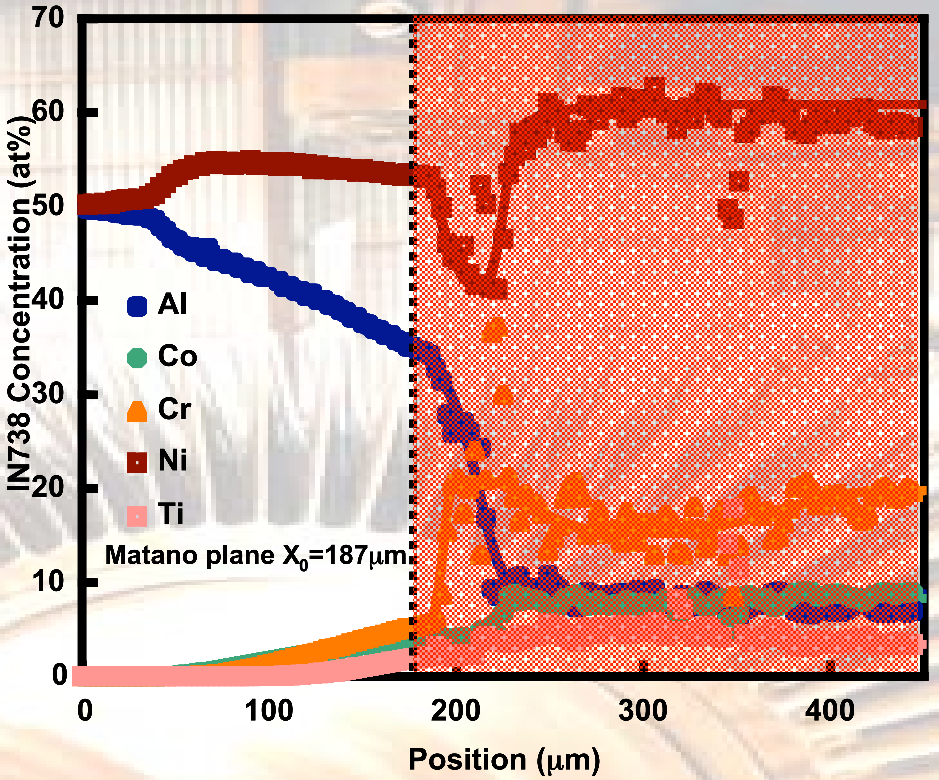
Profiles of Concentration and Interdiffusion Flux
(NiAl vs. IN939 Annealed at 1050°C for 96 Hours)

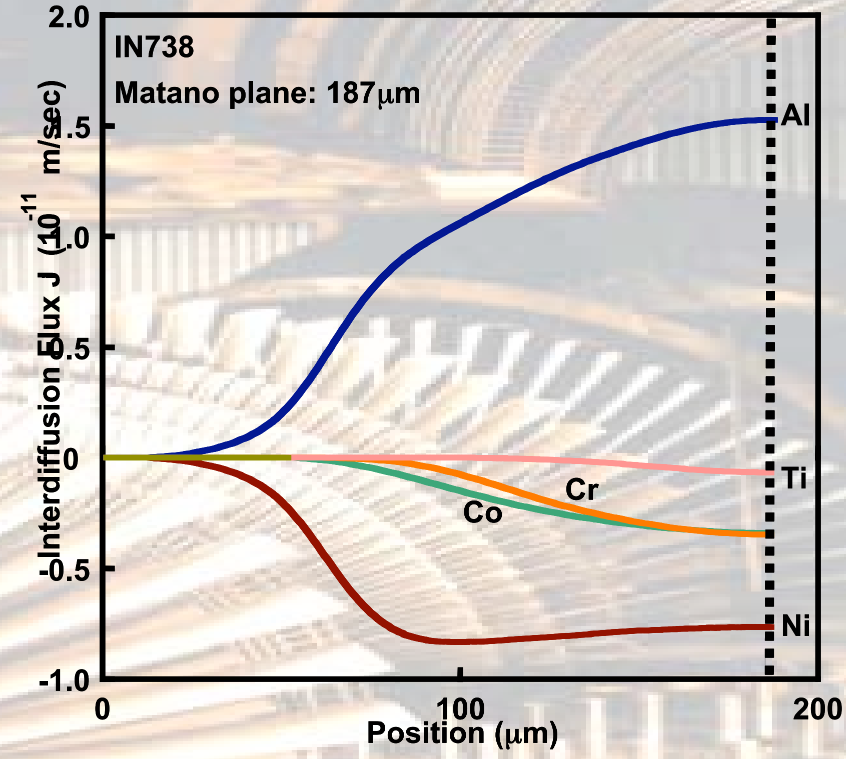




The interdiffusion flux was calculated only on the NiAl side (i.e., single-phase region) of the couple using estimated mass-balance frame of reference (e.g., Matano plane determined by concentration profiles and microscopy).

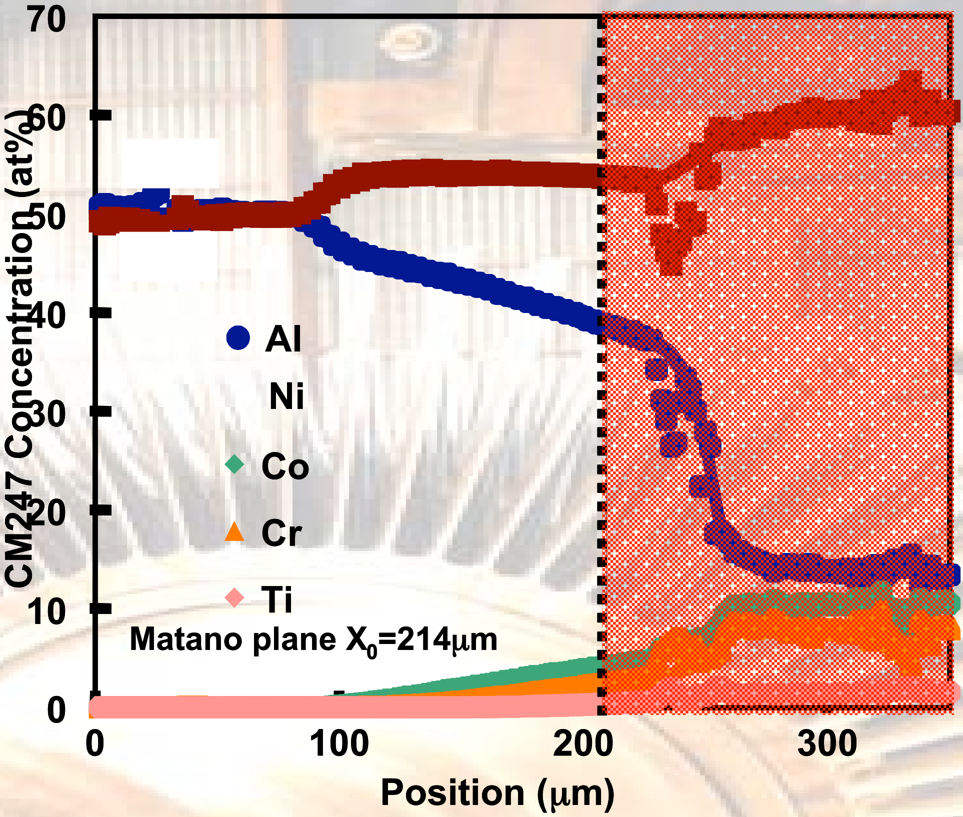
Profiles of Concentration and Interdiffusion Flux
(NiAl vs. IN738 Annealed at 1050°C for 96 Hours)

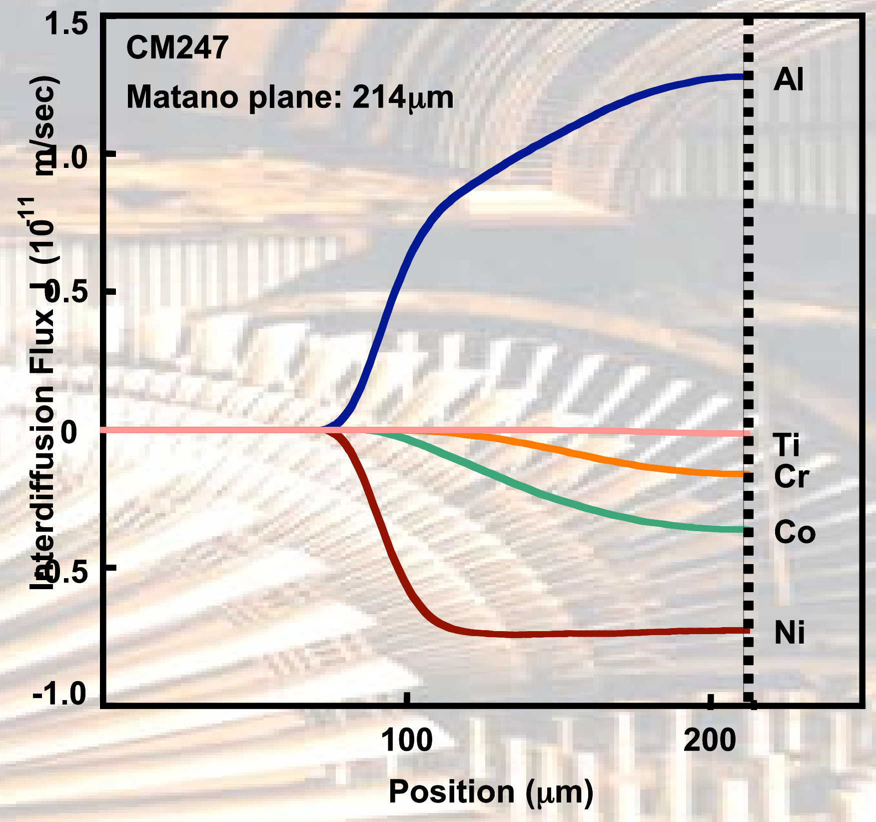




The interdiffusion flux was calculated only on the NiAl side (i.e., single-phase region) of the couple using estimated mass-balance frame of reference (e.g., Matano plane determined by concentration profiles and microscopy).

Profiles of Concentration and Interdiffusion Flux
(NiAl vs. CM247 Annealed at 1050°C for 96 Hours)





The interdiffusion flux was calculated only on the NiAl side (i.e., single-phase region) of the couple using estimated mass-balance frame of reference (e.g., Matano plane determined by concentration profiles and microscopy).

Interdiffusion Coefficients of Al
Calculated for NiAl and Predicted* for Superalloy

NiAl Side Calculated with Concentration Profiles

Aluminum	D^{Int}_{NiAl}	D^{app}_{NiAl}	D^{eff}_{NiAl}
Alloy	10^{-15}(m^2/sec)at%	10^{-15}(m^2/sec)	
CM247	1.31	4.15	11.2
GTD111	1.56	3.65	10.2
IN738	1.58	4.06	11.2
IN939	1.50	3.02	8.47
Waspalloy	2.16	5.45	14.4

Superalloy Side Predicted with Correlations* in Interdiffusion Coefficients

Aluminum	D^{Int}_{SA}	D^{app}_{SA}	D^{eff}_{SA}
Alloy	10^{-15}(m^2/sec)at%	10^{-15}(m^2/sec)	
CM247	0.62	0.92	2.89
GTD111	0.86	1.11	3.48
IN738	0.83	1.11	3.49
IN939	0.92	1.14	3.59
Waspalloy	0.98	1.13	3.54

Correlations*

$$\frac{C_i^- - C_i^o}{C_i^o - C_i^+} = \frac{\alpha_{i,SA}}{\alpha_{i,NiAl}} \frac{\sqrt{\tilde{D}^{eff}_{i,NiAl}}}{\sqrt{\tilde{D}^{eff}_{i,SA}}} \quad \text{and} \quad \frac{C_i^- - C_i^o}{C_i^o - C_i^+} = \frac{\sqrt{\tilde{D}^{app}_{i,NiAl}}}{\sqrt{\tilde{D}^{app}_{i,SA}}}$$

Integrated, apparent and effective interdiffusion coefficients for multiphase region (i.e., superalloys and precipitates) can be predicted.

D^{eff} determined based on $\alpha_i = \sqrt{\pi}$

Interdiffusion Coefficients of Al
Predicted and Estimated* for Superalloy

Predicted Interdiffusion Coefficients for Superalloys

Aluminum	D^{Int}_{SA}	D^{app}_{SA}	D^{eff}_{SA}
Alloy	10^{-15}(m^2/sec)at%	10^{-15}(m^2/sec)	
CM247	0.62	0.92	2.89
GTD111	0.86	1.11	3.48
IN738	0.83	1.11	3.49
IN939	0.92	1.14	3.59
Waspalloy	0.98	1.13	3.54

Predicted using correlations in interdiffusion coefficients.

D^{eff} determined based on $\alpha_i = \sqrt{\pi}$

Estimated* Interdiffusion Coefficients for Superalloys

Aluminum	D^{Int}_{SA}	D^{app}_{SA}	D^{eff}_{SA}
Alloy	10^{-15}(m^2/sec)at%	10^{-15}(m^2/sec)	
CM247	0.52	0.92	2.08
GTD111	0.64	1.11	2.30
IN738	0.96	2.15	3.57
IN939	0.85	1.14	2.95
Waspalloy	0.98	1.13	2.97

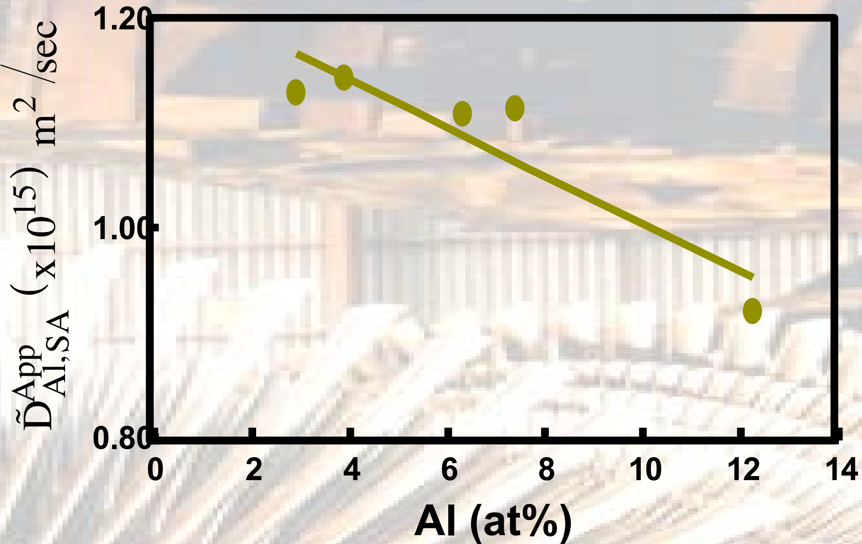
*Estimation using spline-fitted concentration profile through the scatter in multiphase region in superalloys

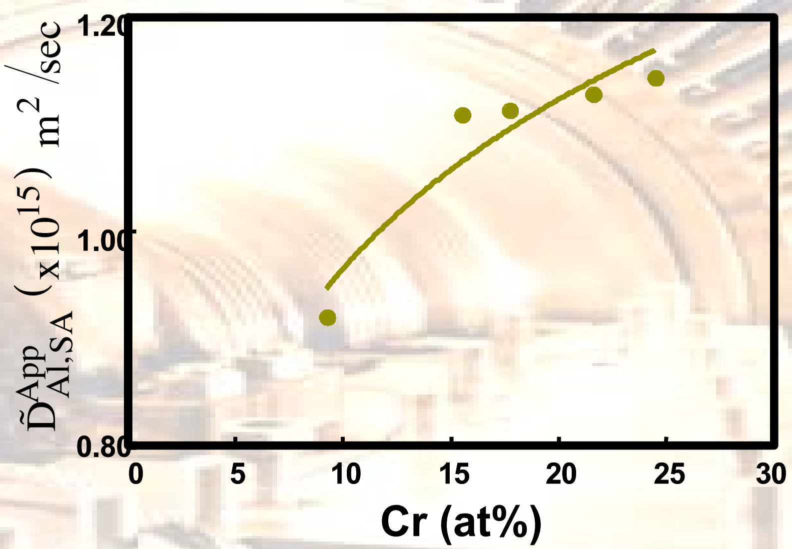
Integrated Diffusion Coefficient (i.e., Total Interdiffusion Flux) of Al in Various Superalloys

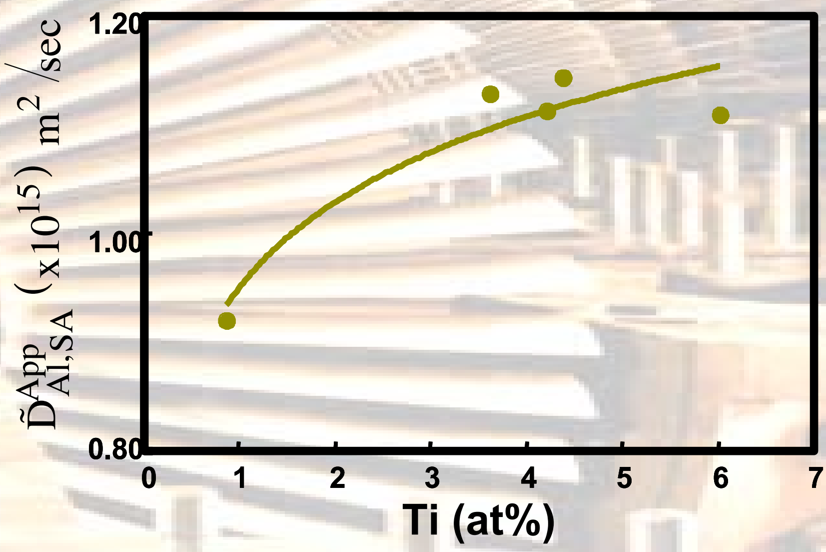
Aluminum	$\tilde{D}^{Int}_{Al,\ Total}$
Alloy	10^{-15}(m^2/sec)at%
CM247	1.83
GTD111	2.20
IN738	2.54
IN939	2.34
Waspalloy	3.14

- The integrated interdiffusion coefficient for the entire profile employs that calculated from the NiAl side (i.e., single-phase region) of the couple and that predicted for the superalloy side (i.e., multiphase-region).
- The integrated interdiffusion coefficient indicates the overall interdiffusion flux for each diffusion couples.

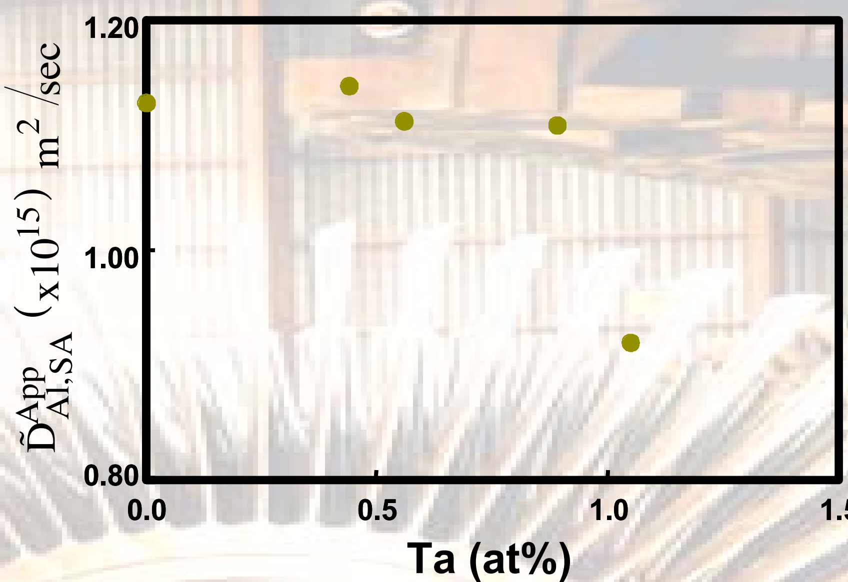
Variation of Apparent Diffusion Coefficients with Initial Superalloy Composition

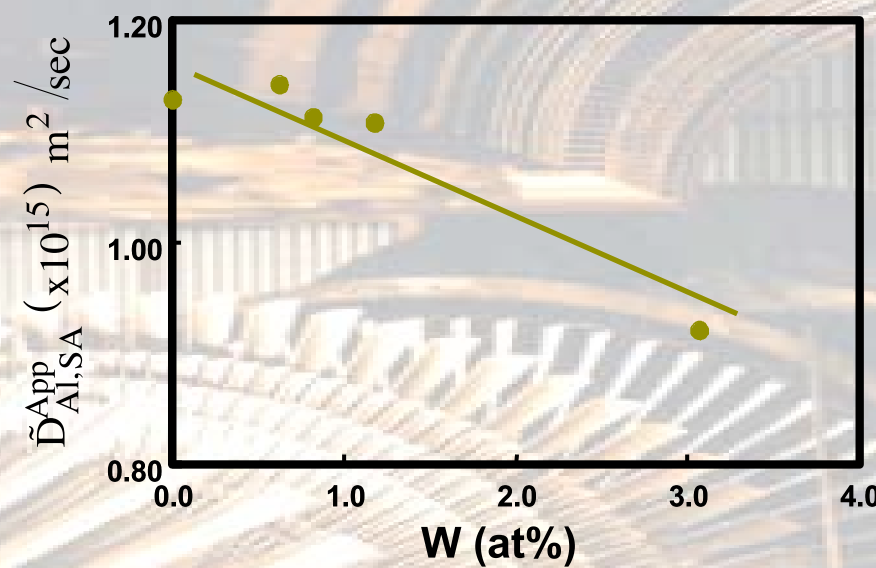






Variation of Apparent Diffusion Coefficients with Initial Superalloy Composition





Apparent Al interdiffusion coefficients in superalloys increased with increases in Cr and Ti concentrations, but decreased with increases in Al, Ta and W concentrations in the superalloys.

Summary

- Solid-to-solid diffusion couples studies using β-NiAl vs. CM247, GTD111, IN738, IN939 and Waspalloy were carried out.
- Integrated, effective and apparent interdiffusion coefficients from single-phase region (β-NiAl) were calculated based on concentration profiles determined by EPMA.
- Integrated, effective and apparent interdiffusion coefficients in the multiphase phase region (superalloys) were predicted.
- Apparent Al interdiffusion coefficients in superalloys increased with increases in Cr and Ti concentrations, but decreased with increases in Al, Ta and W concentrations in superalloys.
- Experimental work is in progress to determine the magnitude of compositional dependence (I.e., cross interdiffusion coefficients).