MODELING DIFFUSION MOBILITIES IN THE L12 AND B2 PHASES

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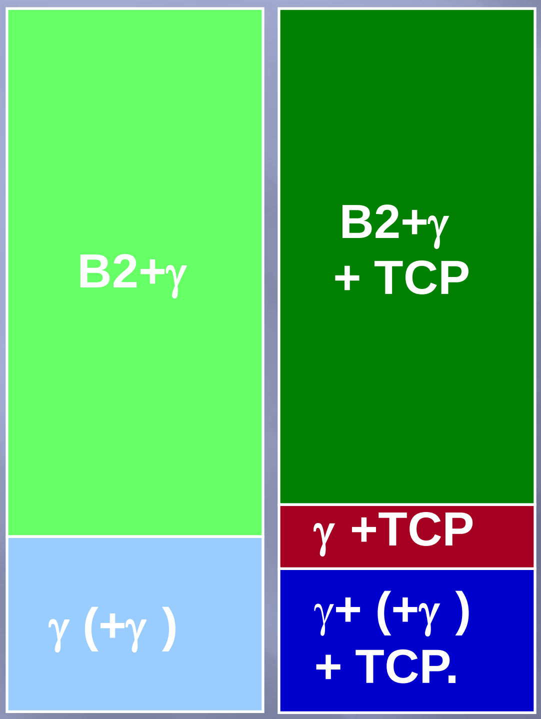
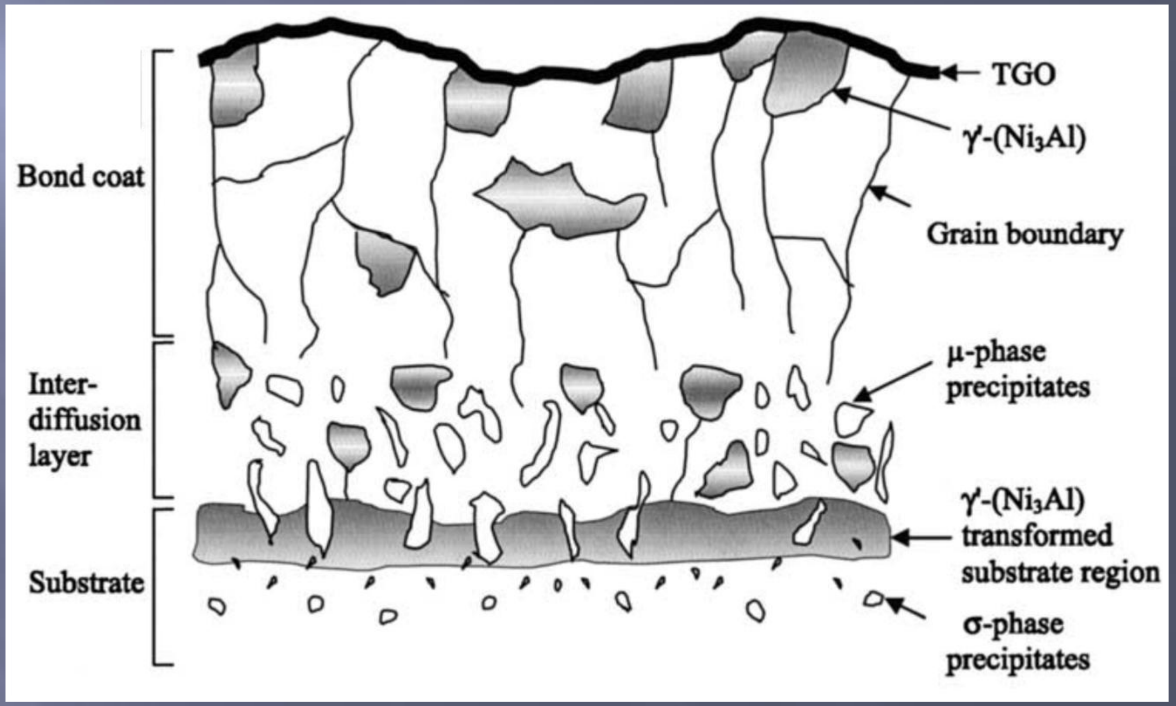
Microstructure Evolution

t = 0 s   t > 0 s



Prevent Al depletion



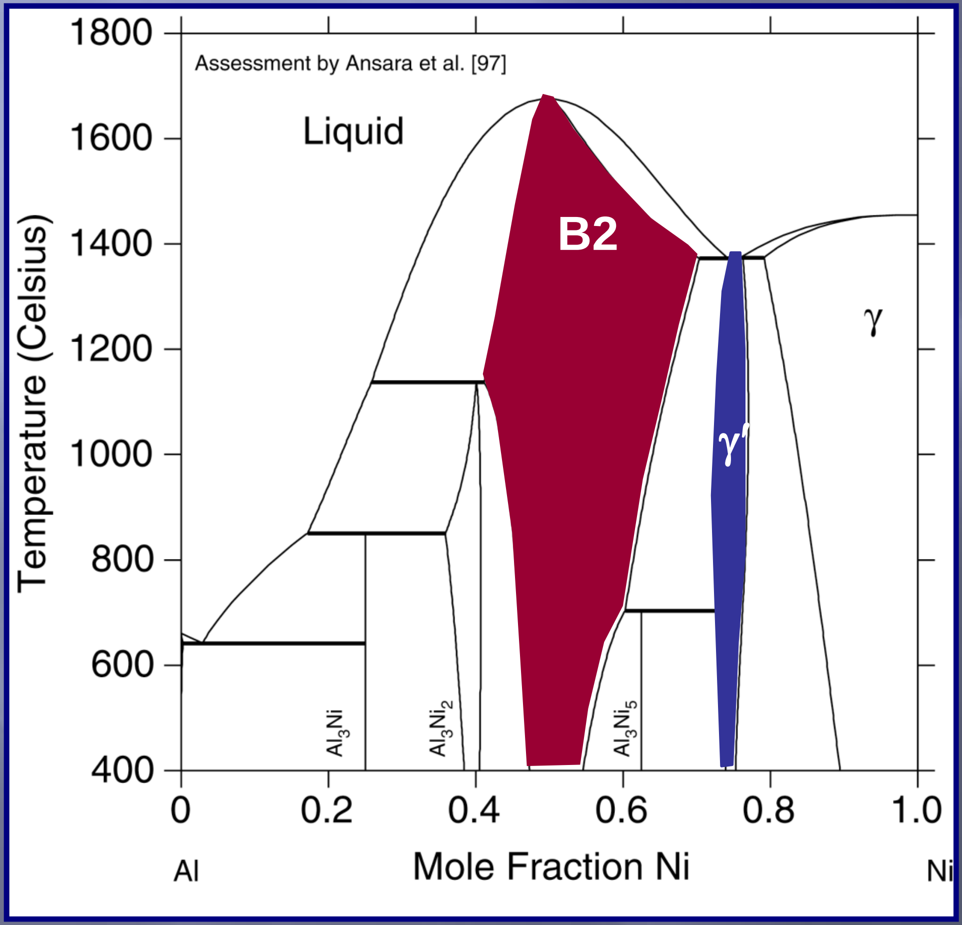
Kim and Walter, *Mater. Sci. Eng*. **A360** (2003) 7.

Need to calculate multicomponent diffusion simulations:

- γ/B2 → γ/γ /B2
- γ+γ / B2+γ → γ+γ /γ /B2+γ

Ni-Al System

- Ni-Al Assessment from Ansara et al. (1997).



γ′ (Ni_3Al): $L1_2$ base structure; metal sublattice contains a connected network for nearest neighbor jumps for vacancies

B2 (NiAl) CsCl structure: metal sublattice requires jumps between different sublattices.

Effect of chemical ordering on diffusion

$$M_i = \frac{M_i^\circ}{RT}\exp\left(\frac{-\Delta Q_i}{RT}\right) \text{ where } \Delta Q_i = f(c_i,T) \text{ and } M_i^\circ = f(c_i,T)$$

- Based on Bragg-Williams approach by Girifalco for a binary system

  (*J. Phys. Chem. Solids,* 1964, **24**, 323.)

$$\Delta Q_k = \Delta Q_k^{dis}\left[1+\alpha_k\left(S^{ord}\right)^2\right] \qquad S^{ord} = p_A^\alpha - p_A^\beta$$ = long-range order parameter

p_A^α is the probability of finding A atom on an α site

- Expansion to Multicomponent systems Helander and Ågren, (*Acta Mater.*, 1999, **47,** 1141.)

$\Delta Q = \Delta Q^{dis} + \Delta Q^{ord}$

$$\Delta Q_l^{ord} = \sum_i\sum_j \Delta Q_{i:j}^{ord}\left[y_i^\alpha y_j^\beta - x_i x_j\right] + \sum_i\sum_j\sum_k \Delta Q_{ij:k}^{ord}\left[y_i^\alpha y_j^\alpha y_k^\beta - x_i x_j x_k\right] + \sum_i\sum_j\sum_k \Delta Q_{k:ij}^{ord}\left[y_i^\beta y_j^\beta y_k^\alpha - x_i x_j x_k\right]$$

ΔQ_{ij}^{ord} = contribution to activation energy for component *k* as a result of the ordering of *i-j* atoms

$$y_i^\alpha = \frac{N_i^\alpha}{N_{tot}^\alpha} = p_i^\alpha$$

Before assessing the diffusion mobilities need consider thermodynamics

- DICTRA

  ⇒ Thermodynamics = Diffusion

  - If one uses Ni-Data (Thermotech)

    Convert γ and B2
  - If one uses a database based Ni-Al by Dupin et. al.

    Convert B2

  ✓ Can convert phase descriptions to a MSL description (Dupin et al.)

  – only works if element does not have a stable BCC phase

- Phase Field
  - Thermodynamics do not necessarily need to match diffusion description, depends on model used

Assessment of diffusion in NiAl

- B2 (Ni,Cr)Al (Ni,Al,Cr,Va:Al,Ni,Cr,Va)
- Thermodynamics from N. Dupin, I. Ansara, B. Sundman, *CALPHAD*, **25**, (2001) 279-298
- Disorder description fixed Engstrom and Ågren assessment 1996

$$M_i = \frac{M_i^\circ}{RT}\exp\left(\frac{-\Delta Q_i^*}{RT}\right) \text{ where } \Delta Q_i^* = f\left(c_i, T\right)$$

Disorder Description

$$\Delta Q_{Ni}^* = x_{Ni}Q_{Ni}^{Ni} + x_{Al}Q_{Al}^{Ni} + x_{Cr}Q_{Cr}^{Ni} + x_{Al}x_{Ni}Q_{Al,Ni}^{Ni} + x_{Cr}x_{Ni}Q_{Cr,Ni}^{Ni}$$

$$\Delta Q_{Al}^* = x_{Ni}Q_{Ni}^{Al} + x_{Al}Q_{Al}^{Al} + x_{Cr}Q_{Cr}^{Al} + x_{Al}x_{Ni}Q_{Al,Ni}^{Al}$$

$$\Delta Q_{Cr}^* = x_{Ni}Q_{Ni}^{Cr} + x_{Al}Q_{Al}^{Cr} + x_{Cr}Q_{Cr}^{Cr} + x_{Cr}x_{Ni}Q_{Cr,Ni}^{Cr}$$

Assessment of diffusion in NiAl

- B2 (Ni,Cr)Al (Ni,Al,Cr,Va:Al,Ni,Cr,Va)
- Thermodynamics from N. Dupin, I. Ansara, B. Sundman, *CALPHAD*, **25**, (2001) 279-298
- Disorder description fixed Engstrom and Ågren assessment 1996

$$M_i = \frac{M_i^{\circ}}{RT}\exp\left(\frac{-\Delta Q_i^*}{RT}\right) \text{ where } \Delta Q_i^* = f\left(c_i, T\right)$$

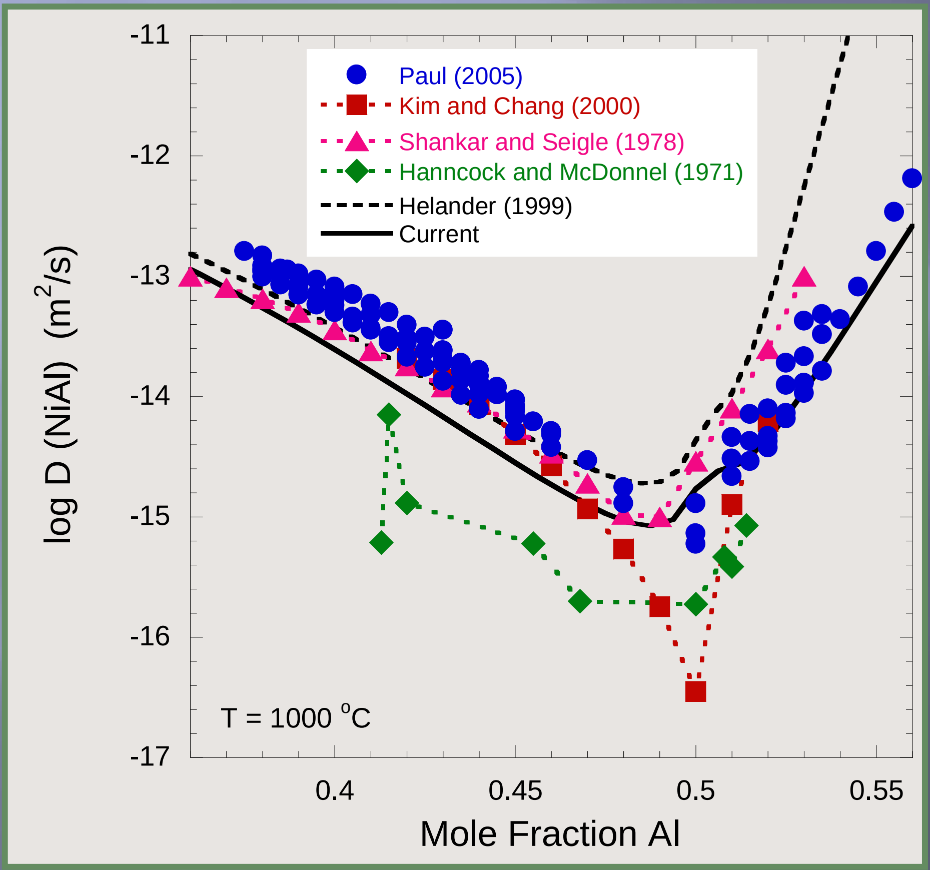
Order Description

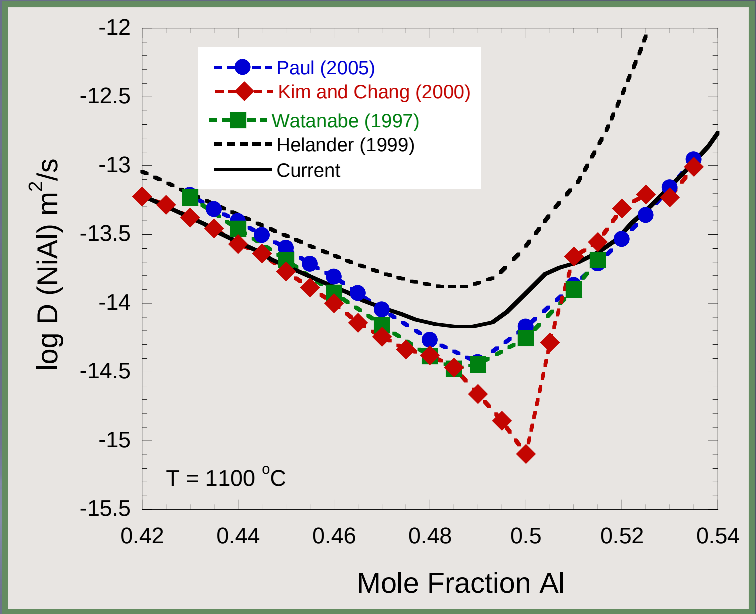
$$\begin{aligned}
\Delta Q_{Ni}^{ord} = {} & \Delta Q_{Al:Ni}^{ord}\left[y_{Al}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni}\right] + \Delta Q_{Ni:Al}^{ord}\left[y_{Ni}^{Ni} y_{Al}^{Al} - x_{Al} x_{Ni}\right] \\
& + \Delta Q_{Al:Va}^{ord}\left[y_{Al}^{Ni} y_{Va}^{Al} - x_{Al} x_{Va}\right] + \Delta Q_{Va:Al}^{ord}\left[y_{Va}^{Ni} y_{Al}^{Al} - x_{Va} x_{Al}\right] \\
& + \Delta Q_{Ni:Va}^{ord}\left[y_{Ni}^{Ni} y_{Va}^{Al} - x_{Ni} x_{Va}\right] + \Delta Q_{Va:Ni}^{ord}\left[y_{Ni}^{Ni} y_{Va}^{Al} - x_{Va} x_{Ni}\right] \\
& + \Delta Q_{Al:Cr}^{ord}\left[y_{Al}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Cr}\right] + \Delta Q_{Cr:Al}^{ord}\left[y_{Cr}^{Ni} y_{Al}^{Al} - x_{Al} x_{Cr}\right] \\
& + \Delta Q_{Cr:Va}^{ord}\left[y_{Cr}^{Ni} y_{Va}^{Al} - x_{Cr} x_{Va}\right] + \Delta Q_{Va:Cr}^{ord}\left[y_{Va}^{Ni} y_{Cr}^{Al} - x_{Va} x_{Cr}\right] \\
& + \Delta Q_{Cr:Ni}^{ord}\left[y_{Cr}^{Ni} y_{Ni}^{Al} - x_{Cr} x_{Ni}\right] + \Delta Q_{Ni:Cr}^{ord}\left[y_{Ni}^{Ni} y_{Cr}^{Al} - x_{Cr} x_{Ni}\right]
\end{aligned}$$

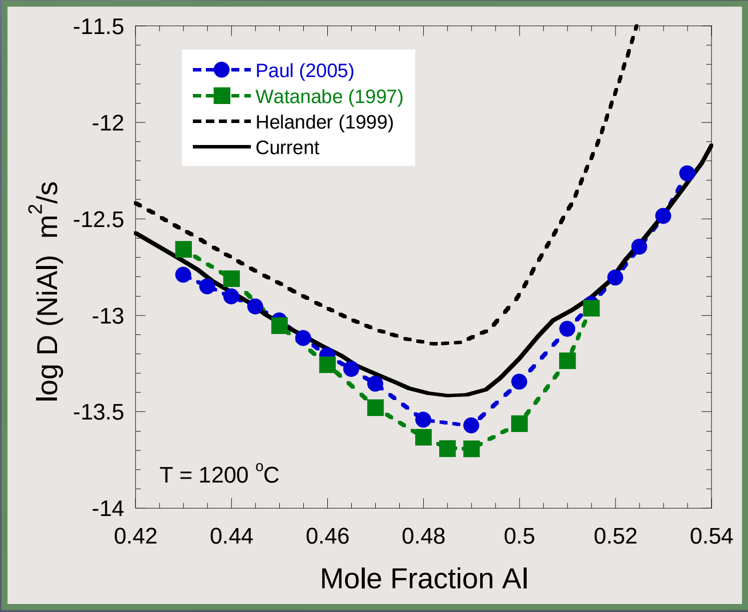
Assessed Mobility Parameters for B2 - NiAlCr

Mobility Parameters	Value
Ni	
$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al} = \Delta Q_{Cr:Al} = \Delta Q_{Cr:Al}$	-336810
$\Delta Q_{Al:Va} = \Delta Q_{Va:Al}$	-115600
$\Delta Q_{Ni:Cr} = \Delta Q_{Ni:Cr}$	-255690
Al	
$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al} = \Delta Q_{Cr:Al} = \Delta Q_{Cr:Al}$	-360140
$\Delta Q_{Al:Va} = \Delta Q_{Va:Al}$	+305900
$\Delta Q_{Ni:Cr} = \Delta Q_{Ni:Cr}$	-6220700
Cr	
$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al} = \Delta Q_{Cr:Al} = \Delta Q_{Cr:Al}$	-336810
$\Delta Q_{Al:Va} = \Delta Q_{Va:Al}$	-115600
$\Delta Q_{Ni:Cr} = \Delta Q_{Ni:Cr}$	1148100

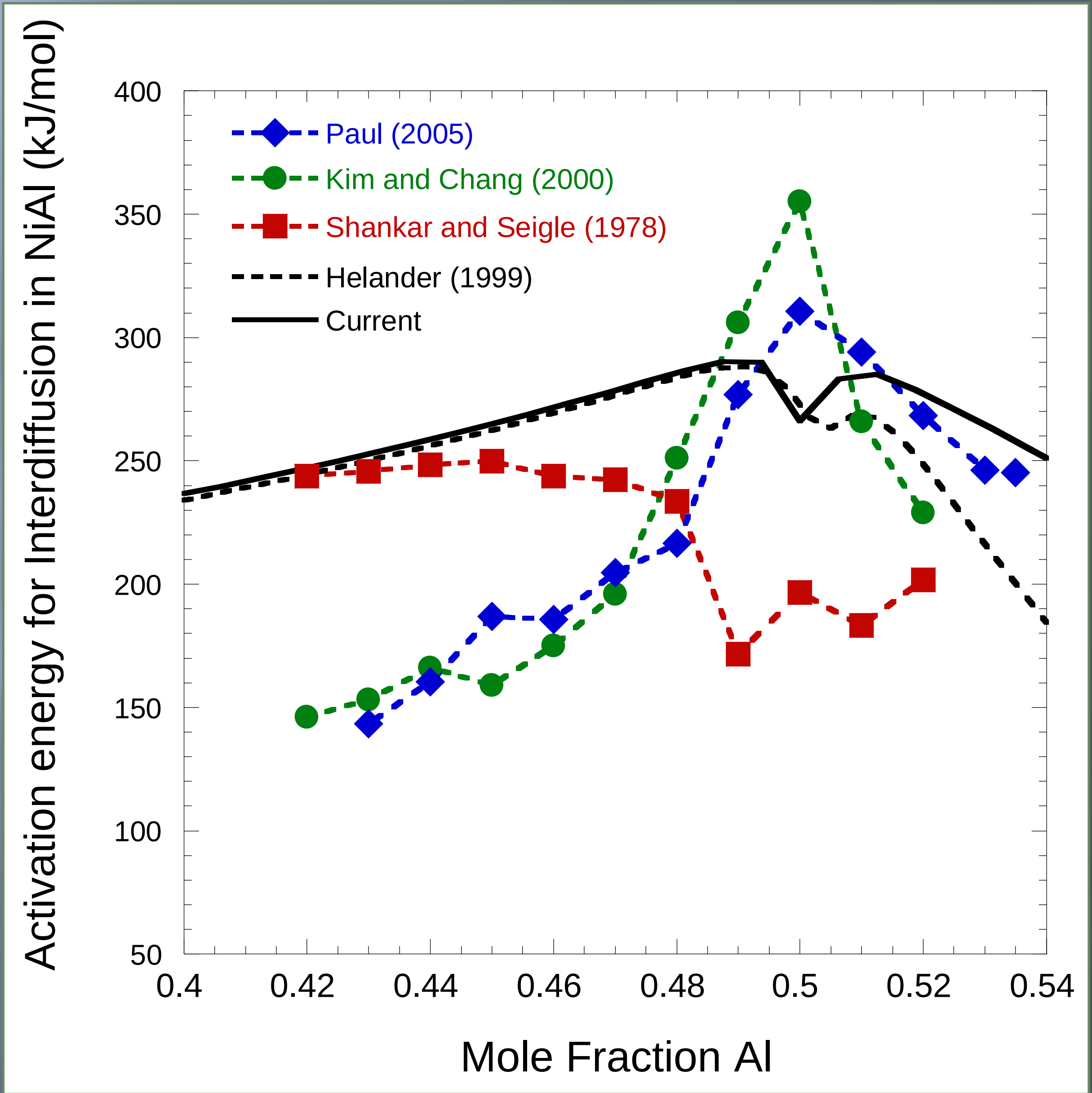
Composition and Temperature Dependence of B2 Interdiffusion Coefficient



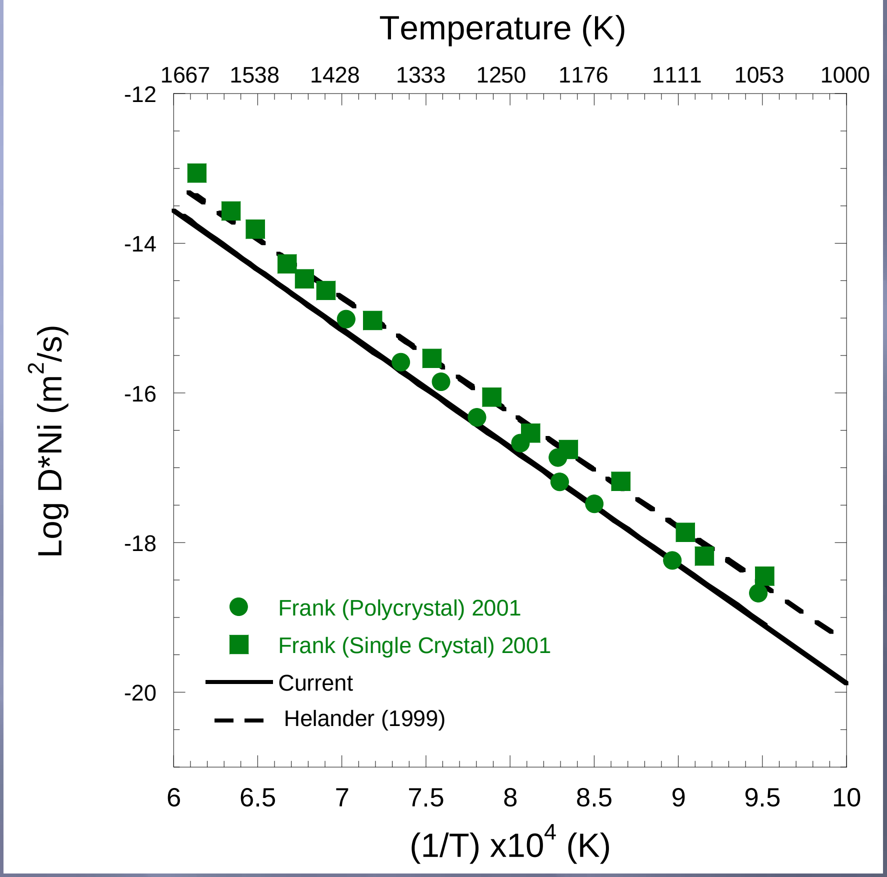


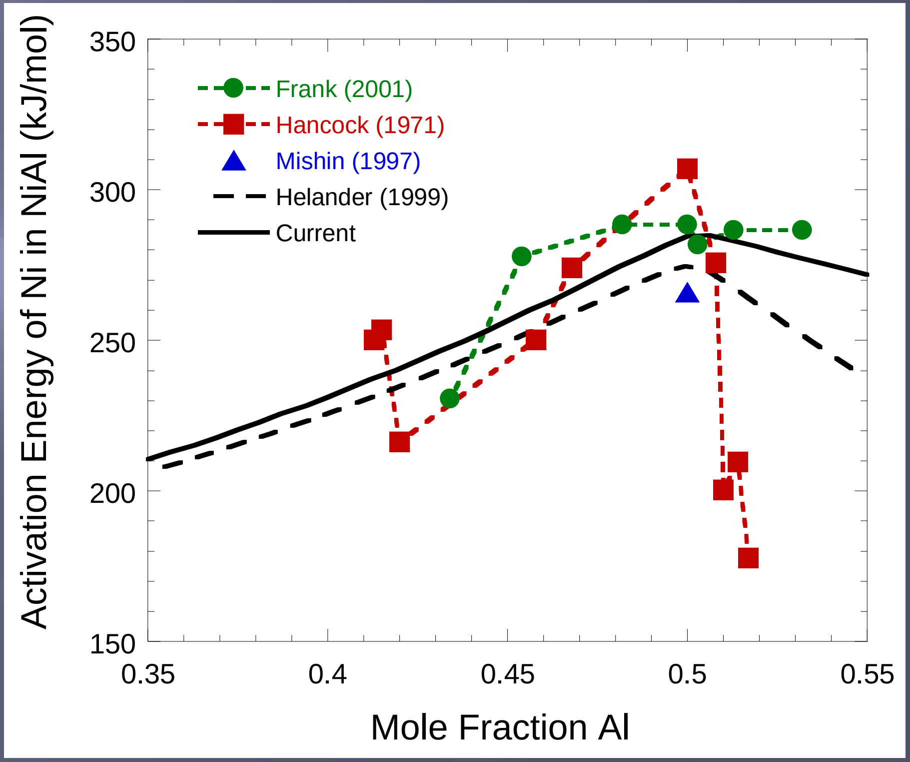


Composition Dependence of B2 Interdiffusion Activation Energy



Self Diffusion of Ni in NiAl





Assessment of diffusion mobilities in Ni_3Al

- $L1_2$ (Ni_3Al) (Ni,Al:Ni,Al)
- Disorder description fixed Engstrom and Ågren assessment 1996

$$M_i = \frac{M_i^\circ}{RT}\exp\left(\frac{-\Delta Q_i^*}{RT}\right) \text{ where } \Delta Q_i^* = f\left(c_i, T\right)$$

$$\Delta Q_{Ni}^* = x_{Ni}Q_{Ni}^{Ni} + x_{Al}Q_{Al}^{Ni} + x_{Cr}Q_{Cr}^{Ni} + x_{Al}x_{Cr}Q_{Al,Cr}^{Ni} + x_{Cr}x_{Ni}Q_{Cr,Ni}^{Ni}$$

$$\Delta Q_{Al}^* = x_{Ni}Q_{Ni}^{Al} + x_{Al}Q_{Al}^{Al} + x_{Cr}Q_{Cr}^{Al} + x_{Al}x_{Ni}Q_{Al,Ni}^{Ni} + x_{Cr}x_{Ni}Q_{Cr,Ni}^{Al}$$

$$\Delta Q_{Cr}^* = x_{Ni}Q_{Ni}^{Cr} + x_{Al}Q_{Al}^{Cr} + x_{Cr}Q_{Cr}^{Cr} + x_{Al}x_{Ni}Q_{Al,Ni}^{Cr} + x_{Al}x_{Cr}Q_{Al,Cr}^{Cr} + x_{Cr}x_{Ni}Q_{Cr,Ni}^{Cr}$$

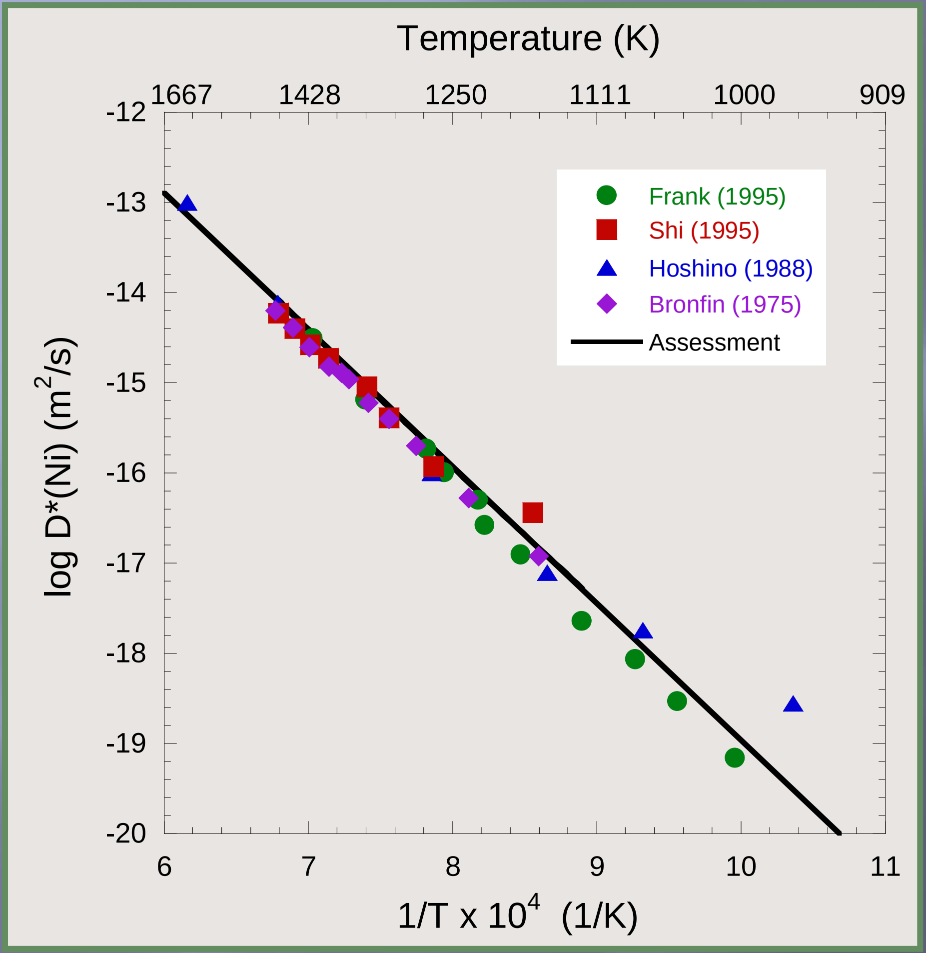
Order Description

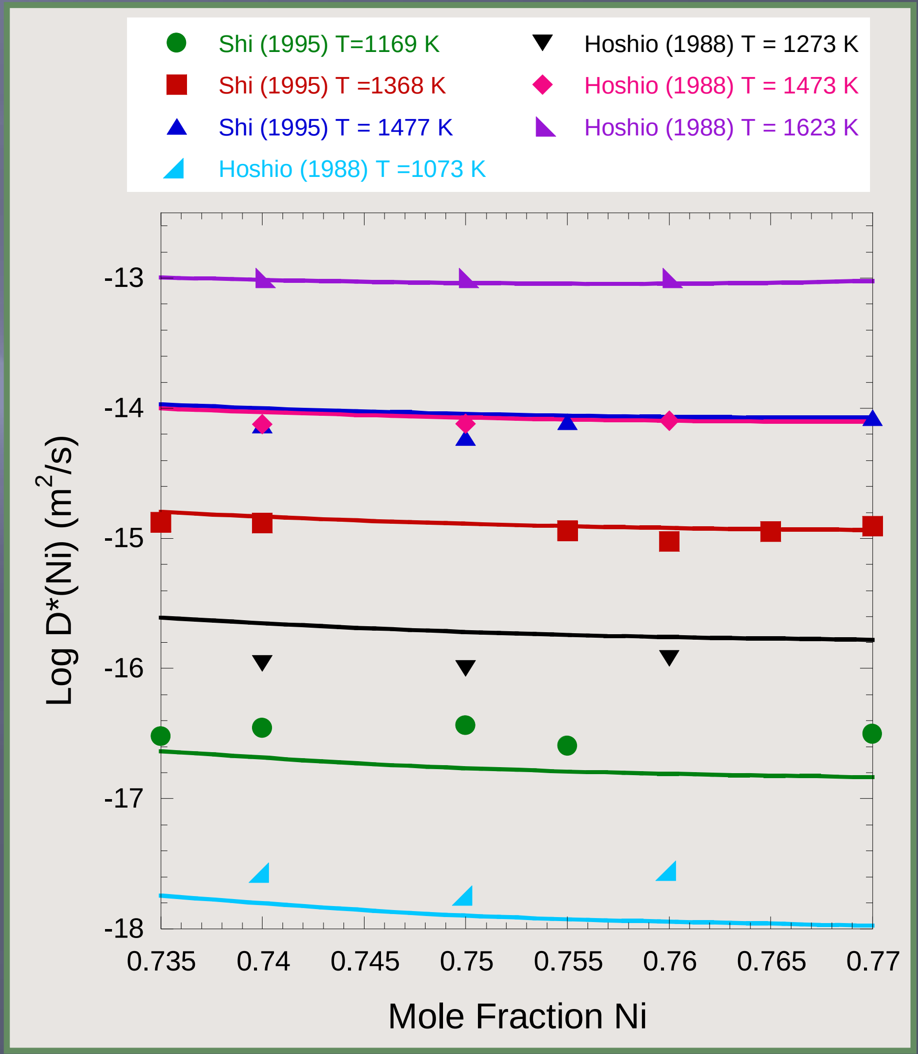
$$\begin{aligned}\Delta Q_{Ni}^{ord} = {} & \Delta Q_{Al:Ni}^{ord}\left[y_{Al}^{Ni}y_{Ni}^{Al} - x_{Al}x_{Ni}\right] + \Delta Q_{Ni:Al}^{ord}\left[y_{Ni}^{Ni}y_{Al}^{Al} - x_{Al}x_{Ni}\right] \\ & + \Delta Q_{Al:Cr}^{ord}\left[y_{Al}^{Ni}y_{Cr}^{Al} - x_{Al}x_{Cr}\right] + \Delta Q_{Cr:Al}^{ord}\left[y_{Cr}^{Ni}y_{Al}^{Al} - x_{Al}x_{Cr}\right] \\ & \Delta Q_{Cr:Ni}^{ord}\left[y_{Cr}^{Ni}y_{Ni}^{Al} - x_{Cr}x_{Ni}\right] + \Delta Q_{Ni:Cr}^{ord}\left[y_{Ni}^{Ni}y_{Cr}^{Al} - x_{Ni}x_{Cr}\right] \\ & + \Delta Q_{Al,Ni:Al}^{ord}\left[y_{Al}^{Ni}y_{Ni}^{Ni}y_{Al}^{Al} - x_{Al}x_{Ni}x_{Al}\right] + \Delta Q_{Al:Al,Ni}^{ord}\left[y_{Al}^{Ni}y_{Al}^{Al}y_{Ni}^{Al} - x_{Al}x_{Al}x_{Ni}\right] \\ & + \Delta Q_{Al,Ni:Ni}^{ord}\left[y_{Al}^{Ni}y_{Ni}^{Ni}y_{Ni}^{Al} - x_{Al}x_{Ni}x_{Ni}\right] + \Delta Q_{Ni:Al,Ni}^{ord}\left[y_{Ni}^{Ni}y_{Ni}^{Al}y_{Ni}^{Al} - x_{Ni}x_{Al}x_{Ni}\right]\end{aligned}$$

Assessed Mobility Parameters of Ni_3Al

Mobility Parameters	Value
Ni	
$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al} = \Delta Q_{Cr:Al} = \Delta Q_{Cr:Al} = \Delta Q_{Cr:Ni} = \Delta Q_{Cr:Ni}$	-101530-23.6*T
$\Delta Q^{ord}_{Al,Ni:Al} = \Delta Q^{ord}_{Al:Al,Ni}$	-311700
$\Delta Q^{ord}_{Al,Ni:Al} = \Delta Q^{ord}_{Al:Al,Ni}$	-24870
Al	
$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al} = \Delta Q_{Cr:Al} = \Delta Q_{Cr:Al} = \Delta Q_{Cr:Ni} = \Delta Q_{Cr:Ni}$	78533-59.1*T
$\Delta Q^{ord}_{Al,Ni:Al} = \Delta Q^{ord}_{Al:Al,Ni}$	869000
$\Delta Q^{ord}_{Al,Ni:Al} = \Delta Q^{ord}_{Al:Al,Ni}$	-127130
Cr	
$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al}$	-36844
$\Delta Q_{Cr:Al} = \Delta Q_{Cr:Al} = \Delta Q_{Cr:Ni} = \Delta Q_{Cr:Ni}$	-101530-23.6*T

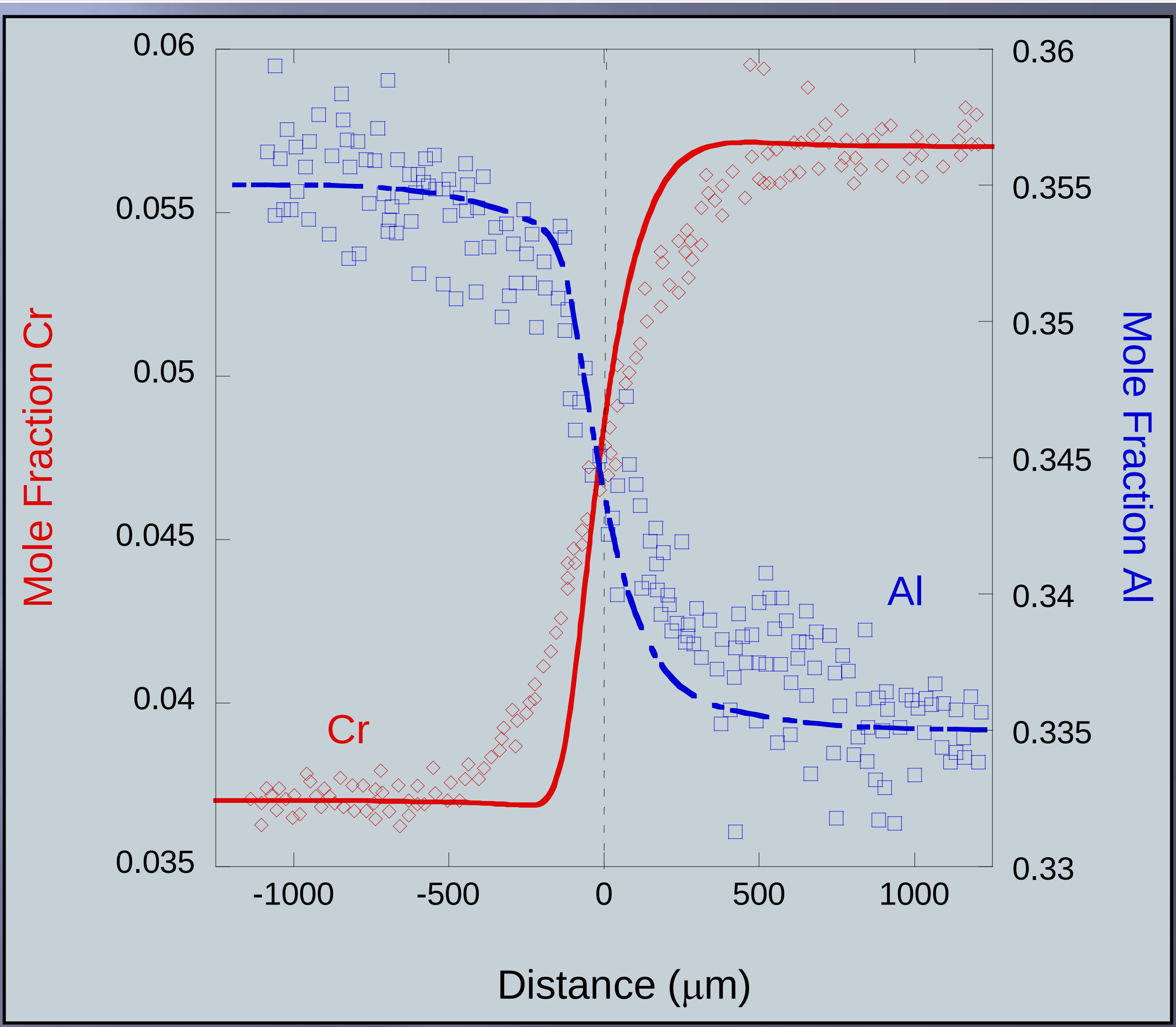
Temperature and Composition Dependence of Ni Tracer Diffusivity in γ'





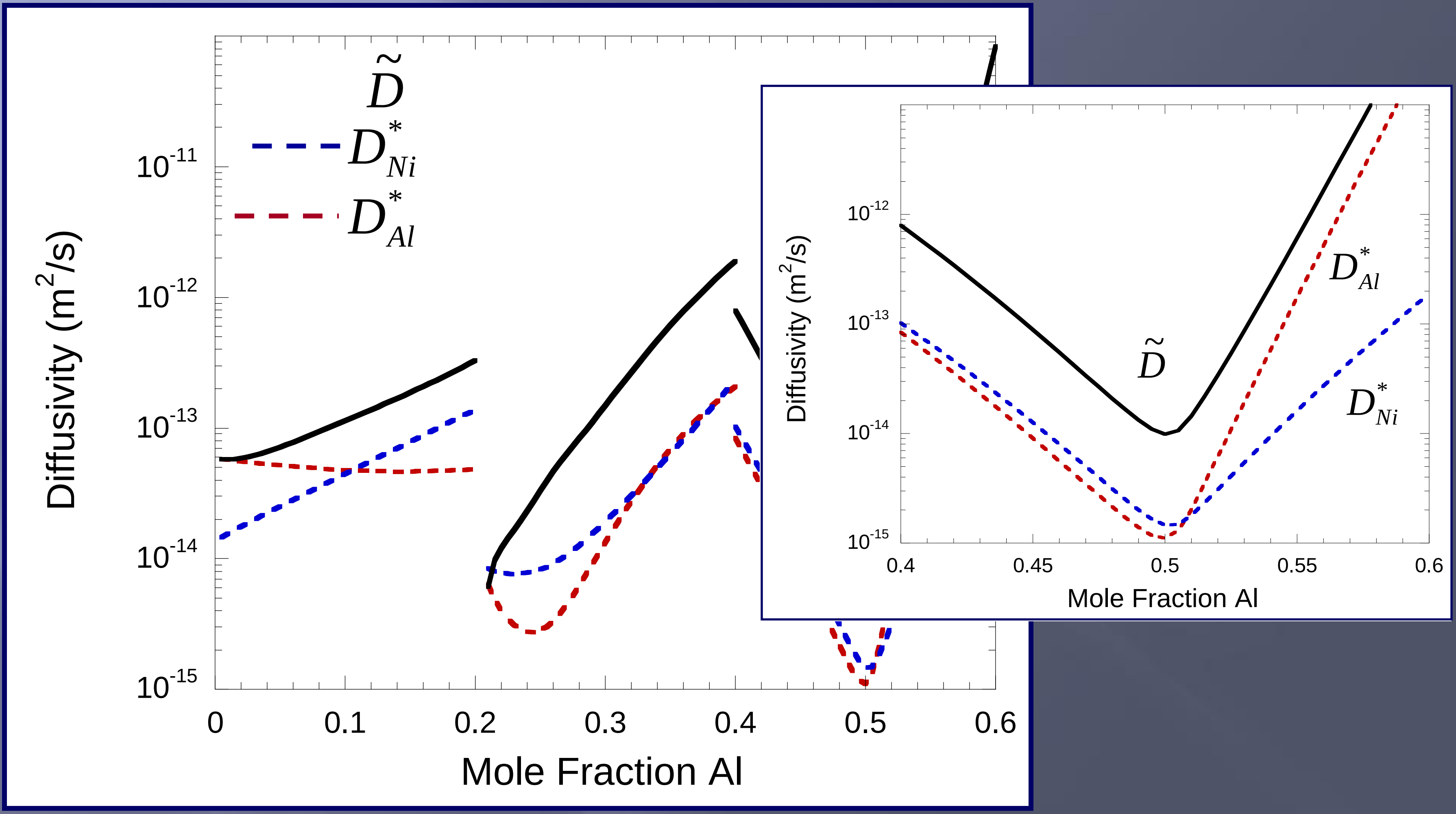
B2 Diffusion Couple at 1200 °C for 40 h

Ni-35.5Al-3.7Cr at. % / Ni-33.5Al-5.7 Cr at. %

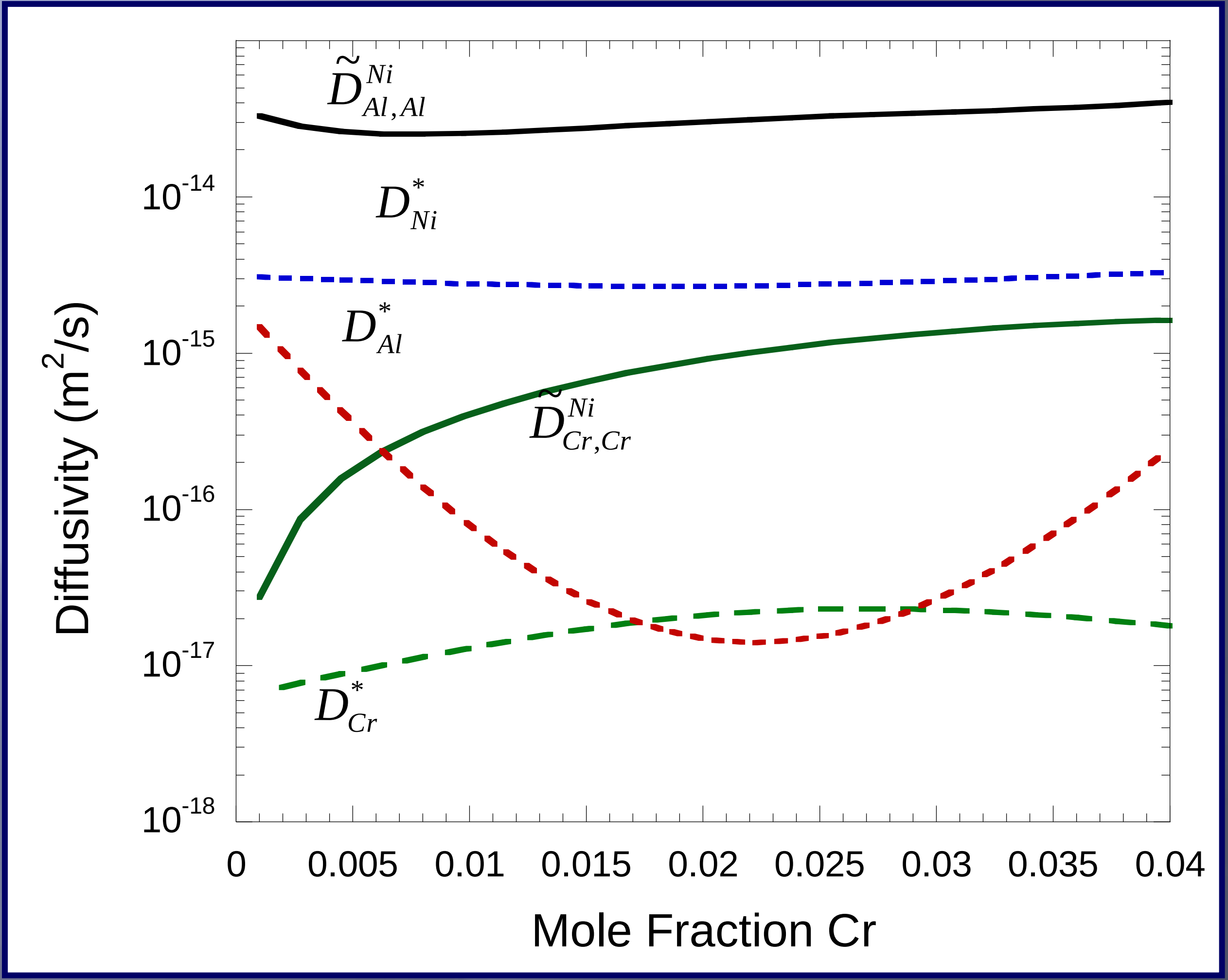


Hopfe, Son, Morral, Romig, *Diffusion in Ordered Alloys,* TMS (1993) 69.

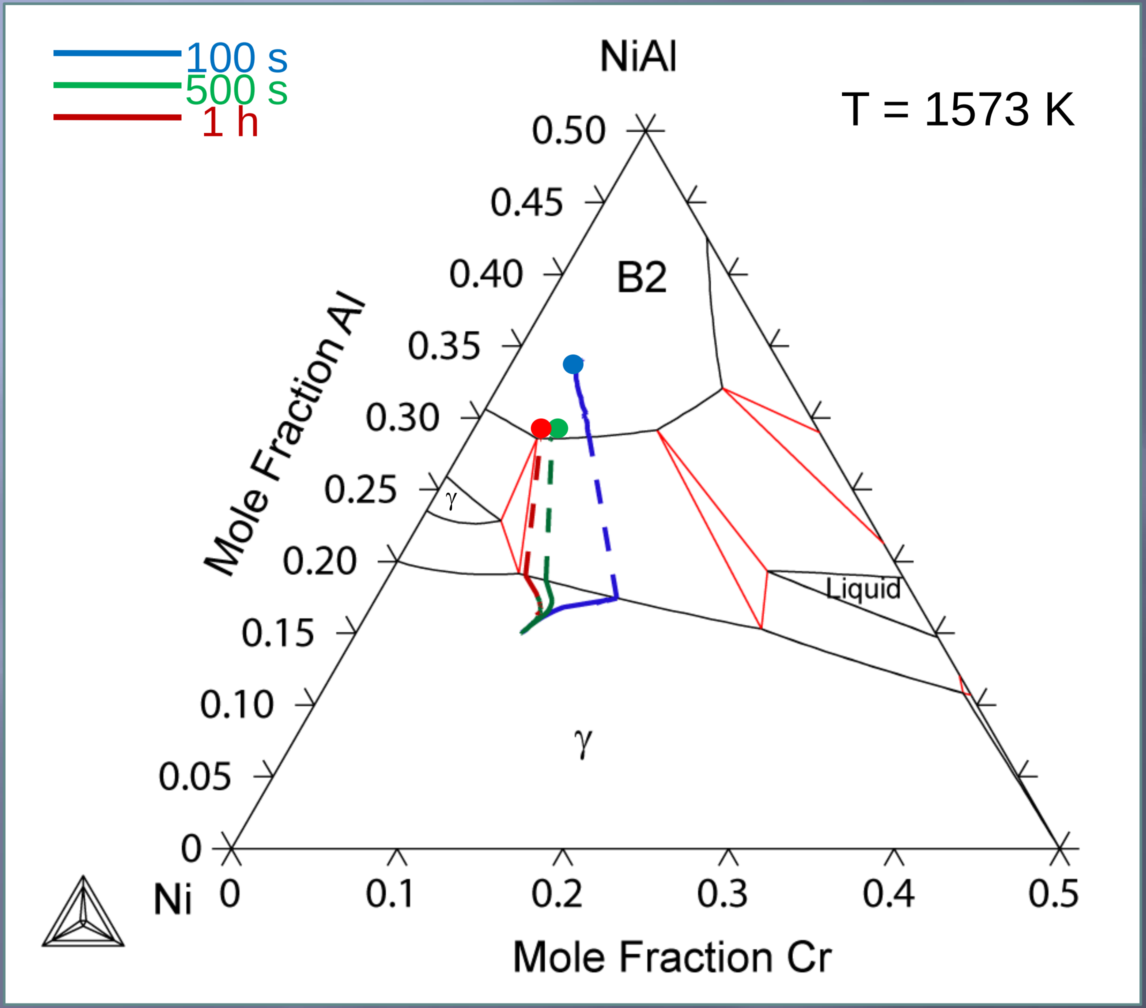
Diffusion Coefficient Composition Dependence in the Ni-Al system at 1200 ˚C

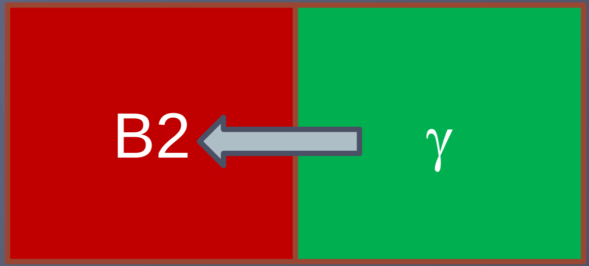


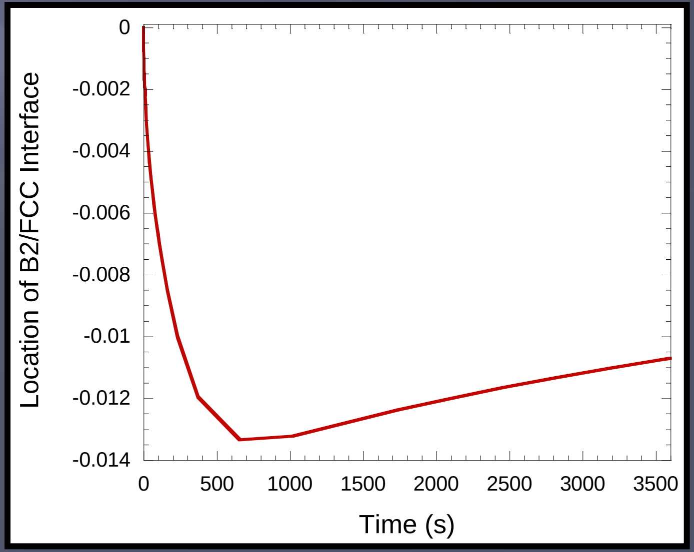
Effect of Cr addition Ni-48Al (at.%) at 1200 °C on Diffusivities in the B2 phase



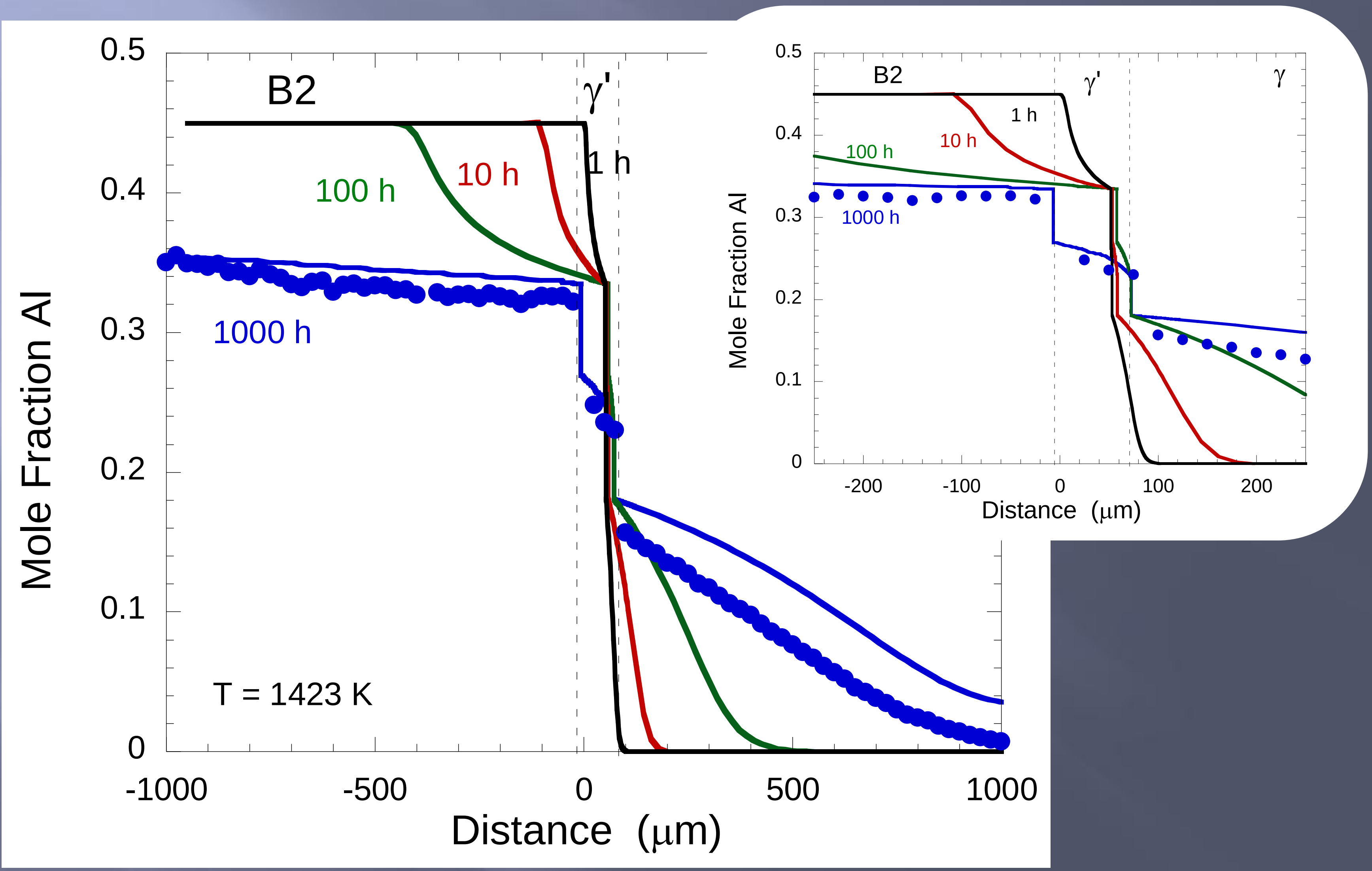
γ/B2 Diffusion Couple
Ni-40Al-5Cr/Ni-15Al-20Cr at. %





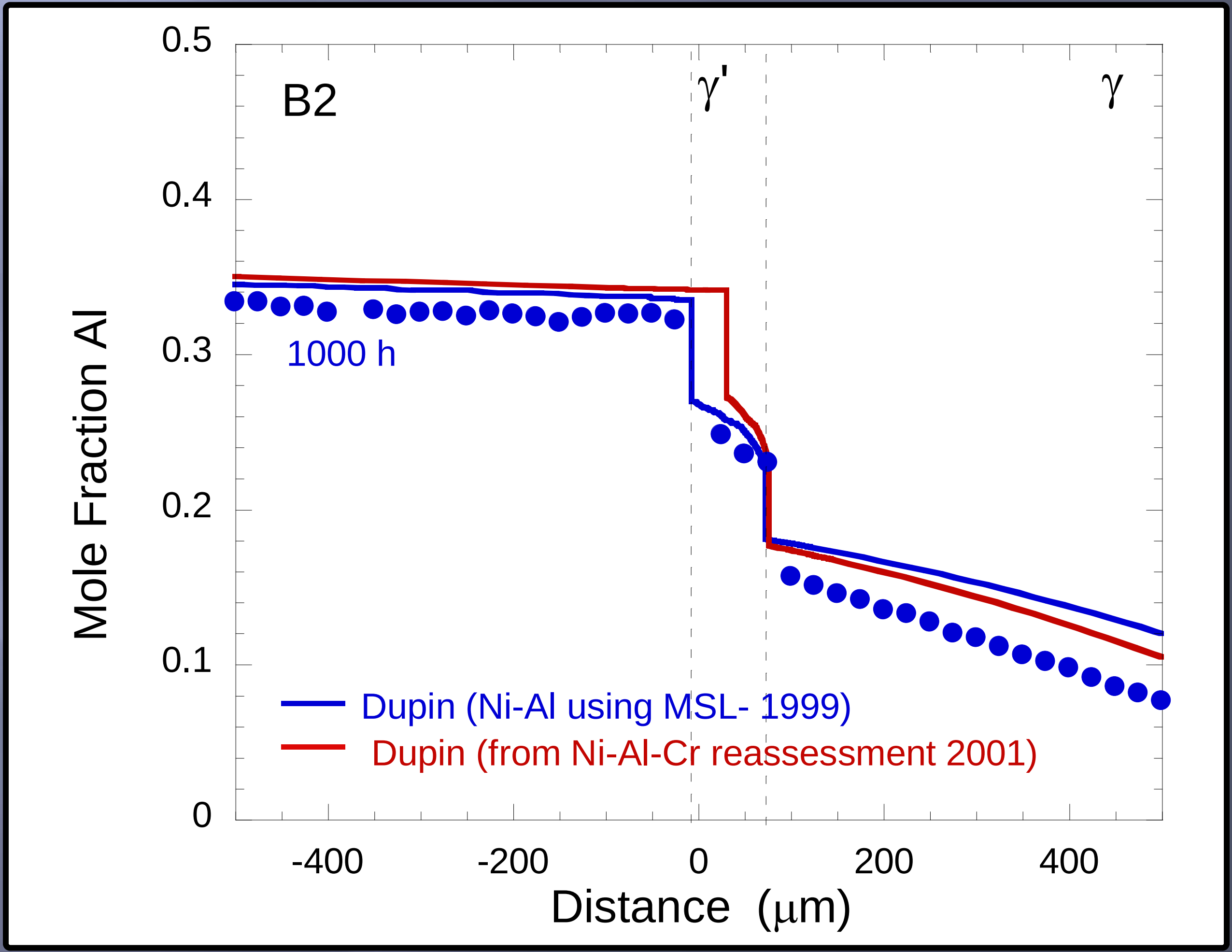


Test: B2/Ni Simulation

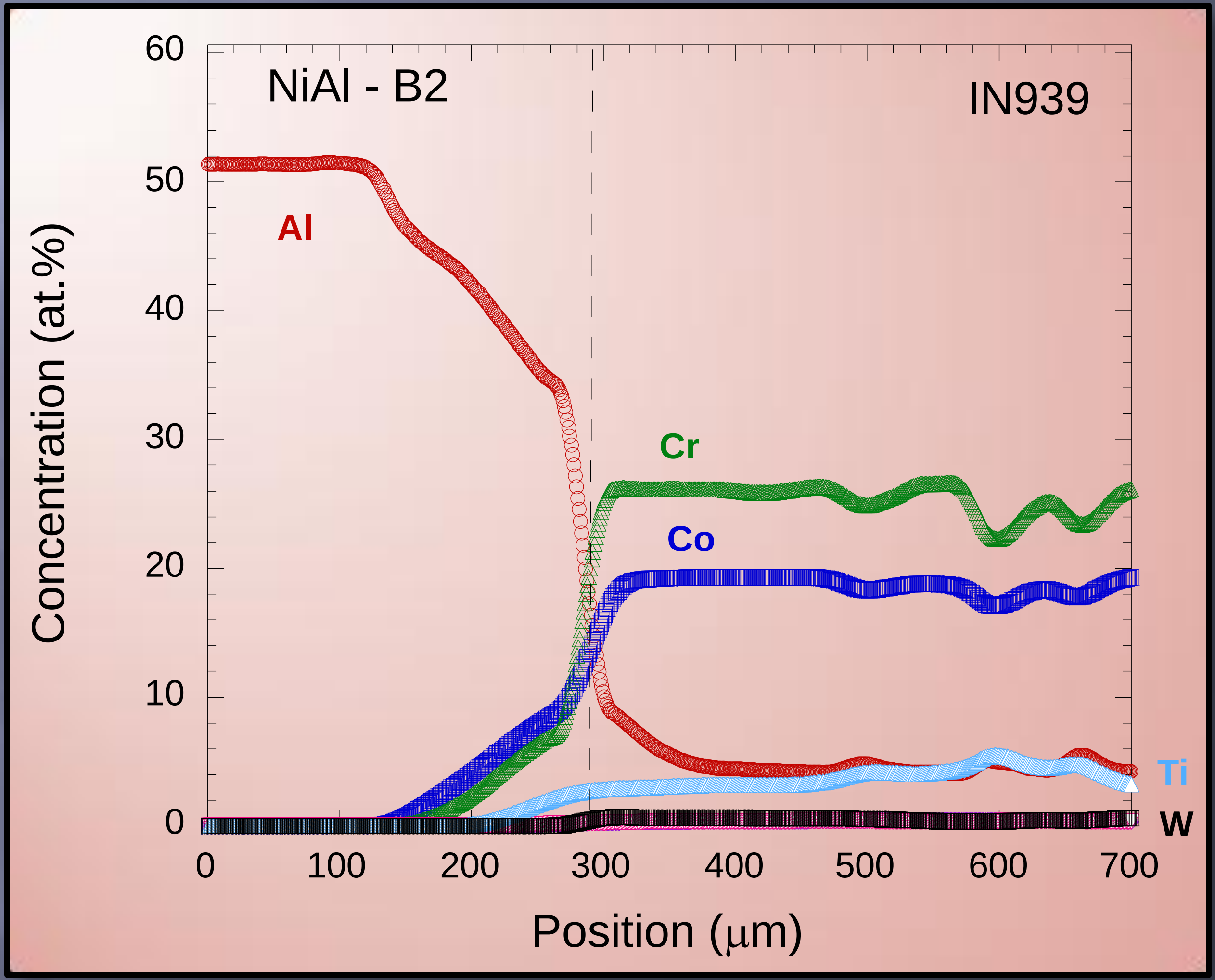


Experimental data from J-C Zhao,GE-CRD

Does the Thermodynamic Database Make a Difference?



Ultimate Goal



1050 C for 96 h.

E. Perez, T. Patterson, Y. Sohn, *J. Phase Equil. Diff.*, **27** (2006) 659.