Assessment of Diffusion Mobilities in the $\gamma'$ (L1$_2$-Ni$_3$Al) and B2 (NiAl) Structures

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Ordered Phase in Ni-base Superalloys

B2: CsCl structure

$\gamma'$ : L1$_2$ base

B2: Wide homogeneity range (~36 to 57 at.\% Al)

Atomic mechanism: consists of several consecutive jumps
Why add ordering to diffusion model

- Strongly composition dependent diffusion coefficients (B2-NiAl)
- Phase fractions are significant; should not ignore diffusion


Defects in Intermetallics

• 4-type of defects in $A_aB_b$ intermetallics
  – Vacancies on both sublattices: $V_A$ and $V_B$
  – Atoms on unlike sublattices $A_B$ and $B_A$
  – Structural defects: defects that are present in thermal equilibrium
  – Thermal defects

• Effect of crystal structure on the self-diffusion properties of Ni$_3$Al-L1$_2$ and NiAl-B2
  – Ni$_3$Al: metal sublattice contains a connected network for nearest neighbor jumps for vacancies
  – NiAl: metal sublattice requires jumps between different sublattices.
Diffusion Database Development: Inputs

- Thermodynamics (CALPHAD approach)
- Diffusion experiments (unary, binary, ternary systems)
  - Tracer diffusivity,
  - Intrinsic diffusivity
  - Interdiffusion coefficients
- Define Mobility Functions
  - Composition and temperature dependent

\[ M_i = \frac{M_i^\circ}{RT} \exp\left(\frac{-\Delta Q_i^\ast}{RT}\right) \quad \text{where} \quad \Delta Q_i^\ast = f(c_i, T) \]

\[ \Delta Q_i^\ast = \sum_{p=1}^{n} x_p Q_i^p + \sum_{p}^{n} \sum_{q>p}^{n} x_p x_q \left[ \sum_{r=0}^{m} A_i^{pq} (x_p - x_q)^r \right] + \sum_{p}^{n} \sum_{q>p}^{n} \sum_{v>q}^{n} x_p x_q x_v \left[ v_{pqv}^s B_i^{pqv} \right] \]

is exponentially dependent on composition

\[ M_i = \frac{1}{RT} \exp\left(\frac{\Delta Q_i}{RT}\right) \]

\[ \Delta Q_i = \Delta Q_i^\ast - RT\Theta_i \quad \text{and} \quad M_i^0 = \exp(\Theta_i) \]
Effect of chemical ordering on diffusion

\[ M_i = \frac{M_i^o}{RT} \exp\left(-\frac{\Delta Q_i}{RT}\right) \] where \( \Delta Q_i = f(c_i, T) \) and \( M_i^o = f(c_i, T) \)

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

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

\( p_A^\alpha \) is the probability of finding A atom on an \( \alpha \) site


\[ \Delta Q = \Delta Q^{\text{dis}} + \Delta Q^{\text{ord}} \]

\[ \Delta Q^{\text{ord}}_k = \sum \sum \Delta Q_{i,j}^{\text{ord}} \left[ y_i^\alpha y_j^\beta - x_i x_j \right] \]

\[ \quad + \sum \sum \sum \Delta Q_{i,j,k}^{\text{ord}} \left[ y_i^\alpha y_j^\alpha y_k^\beta - x_i x_j x_k \right] \]

\[ \quad + \sum \sum \sum \Delta Q_{k,i,j}^{\text{ord}} \left[ y_i^\beta y_j^\beta y_k^\alpha - x_i x_j x_k \right] \]

\( \Delta Q_{ij}^{\text{ord}} \) = contribution to activation energy for component \( k \) as a result of the ordering of \( i-j \) atoms

\( y_i^\alpha = \frac{N_i^\alpha}{N_{\text{tot}}^\alpha} = p_i^\alpha \)
Ni$_3$Al: Diffusion Mechanism

- Sublattice diffusion mechanism
  - Random jumps of a vacancy on a sublattice do not affect the order in the compound.
  - Diffusivities of the two components are not coupled
    - Ni diffusion is expected to be faster than Al diffusion
Experimental observations

• **Self-Diffusion**
  
  – **Ni Diffusion**
    
    • Temperature dependence
      
      – $T > 1100$ K: Arrhenius temperature on temperature
      
      – $T < 1100$ K: Some experimental results show a deviation from the linear Arrhenius dependence on temperature.
        
        » Frank et al. showed this deviation is due to short-circuit diffusion in polycrystalline samples
    
    • Composition dependence
      
      – Experiments indicate some minimum in $D^* \sim 76\%$ at. Ni; however, this may be due short-circuit diffusion or grain boundary diffusion effects.
      
      – Monte Carlo studies found a minimum at the stoichiometric composition due to the existence of Al and Ni antistructure atoms in Ni and Al rich alloys.
      
      – Marginal composition dependence
      
      – **Al diffusion** (limited experimental data)
        
        • Small composition dependence
        
        • $D^*_{\text{Al}}/D^* \approx 0.3$ (Ikeda 1998)
  
  • **Interdiffusion**
    
    – Marginal composition dependence
Assessment of diffusion mobilities in Ni$_3$Al

- L1$_2$ (Ni$_3$Al) (Ni,Al:Ni,Al)

- Disorder description fixed

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

\[ \Delta Q_{Ni}^* = x_{Ni} Q_{Ni}^{Ni} + x_{Al} Q_{Al}^{Ni} \]
\[ \Delta Q_{Al}^* = x_{Ni} Q_{Al}^{Al} + x_{Al} Q_{Al}^{Al} + x_{Al} x_{Ni} Q_{Al,Ni}^{Al} \]

- Order description

\[ \Delta Q_{Ni}^{ord} = \Delta Q_{Al:Ni}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni} \right] + \Delta Q_{Ni:Al}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni} \right] \]
\[ + \Delta Q_{Al:Al}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Al} \right] + \Delta Q_{Ni:Ni}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Ni} - x_{Ni} x_{Ni} \right] \]

\[ \Delta Q_{Al}^{ord} = \Delta Q_{Al:Ni}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni} \right] + \Delta Q_{Ni:Al}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni} \right] \]
\[ + \Delta Q_{Al:Al}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Al} \right] + \Delta Q_{Ni:Ni}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Ni} - x_{Ni} x_{Ni} \right] \]
\[ + \Delta Q_{Al,Ni:Al}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Ni} y_{Ni}^{Al} - x_{Al} x_{Ni} x_{Al} \right] \]
\[ + \Delta Q_{Al,Ni,Ni}^{ord} \left[ y_{Ni}^{Ni} y_{Ni}^{Ni} y_{Ni}^{Ni} - x_{Al} x_{Ni} x_{Ni} \right] \]
### Assessed Mobility Parameters

<table>
<thead>
<tr>
<th>Mobility Parameters</th>
<th>Value</th>
</tr>
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<tr>
<td><strong>Ni</strong></td>
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<td>$\Delta Q_{Ni:Al} = \Delta Q_{Ni:Al}$</td>
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<td>$\Delta Q^\text{ord}_{Ni:Ni}$</td>
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<td>$\Delta Q^\text{ord}<em>{Al,Ni:Al} = \Delta Q^\text{ord}</em>{Al,Ni:Ni}$</td>
<td>2333274</td>
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</tbody>
</table>
**Self Diffusion of Ni**

**Arrhenius temperature dependence**

**Small Composition dependence**

Temperature (K)

- 1169 K Shi
- 1368 K Shi
- 1477 K Shi
- 1073 K Hoshino
- 1273 K Hoshino
- 1473 K Hoshino
- 1623 K Hoshino

Log D*(Ni) (m²/s)

**Mole Fraction Ni**

0.0006 0.0007 0.0008 0.0009 0.001 0.0011

Frank (1995)

Hoshino (1988)

Shi (1995)

Current Assessment

Bronfin (1975)

Through the provided data, a clear Arrhenius temperature dependence is observed, indicating that the self-diffusion rate of nickel decreases exponentially with increasing temperature. Additionally, small composition dependence is observed, suggesting a slight variation in the diffusion rate with changes in mole fraction.
Self-Diffusion of Al

Experimental $D^*_{Al}$ is determined from $\tilde{D}_{Ni_3Al}$ using the Darken-Manning eqn.

$$\tilde{D} = \left( x_{Al} D^*_{Ni} + x_{Ni} D^*_{Al} \right) \cdot \Phi \cdot S$$

$D^*_{Al}$ increases by a factor of 3 for a 3 percent change in Al.
Interdiffusion Data

Temperature (K)

Log (Interdiffusion Coefficient Ni$_3$Al) (m$^2$/s)

1/T (K)

Temperature (K)

Log (Interdiffusion Coefficient Ni$_3$Al) (m$^2$/s)

Mole Fraction Al

1273 K Ikeda

1473 K Ikeda

Current Assessment

Cserhati (2003)

Shankar and Seigle (1975)

Jansen (1973)

Ikeda (1998)

Watanabe (1994)
Activation Energy for Ni Self Diffusion (J/mole) vs Mole Fraction Ni

- Shi (1995)
- Frank (1995)
- Hoshino (1998)
- Hancock (1977)
- Bronfin (1975)

Current Assessment
NiAl-B2 Crystal Structure

- 2 penetrating simple cubic lattices
  - Al atoms occupy the corners of one sublattice
  - Ni atoms occupy the corners of the other sublattice.

- Different defect structures on either side of the stoichiometric composition
  - Al-rich side: excess Ni atoms occupy Al lattice sites → anti-structure defects and structural Ni vacancies
  - Ni-rich side: structural vacancies
Experimental Observations

- **Ni-Self Diffusion**
  - Temperature dependence: \( T > 1500 \text{ K} \) upward deviation from Arrhenius dependence.
  - Composition dependence:
    - On Al-rich side, structural Ni-vacancies do not increase diffusivity (Frank et al. 2001)
    - Ni-rich side: increasing diffusivity
  - Activation energy
    - Constant from 46.5 to 53 at.% Ni
    - Decreasing for Ni>53 at.%

- **Al-Self Diffusion**
  - No direct measurements
  - Significant composition dependence deduced from interdiffusion coefficient measurements (deep minimum at stoichiometric composition)
  - Dependent on presence of \( V_{\text{Ni}} \)
**Diffusion Mechanisms in NiAl-B2**

- All nearest neighbor jumps are jumps between different sublattices
- Ni vacancies on the Al-rich side significantly affect the Ni self-diffusion

Active diffusion mechanisms:
- Triple-defect mechanism \( (2 \text{Va}_{\text{Ni}} \text{Ni}_{\text{Al}}) \)
  - Composition independent activation energy (~ 300 kJ/mol)
- Anti-structure Bridge Mechanism (ASB)
  - Percolation effect (threshold > 55.5 at.% Ni)
- Next nearest neighbor jumps of Ni atoms
  - Lower temperatures in Al-rich compositions

*From Frank et al. Acta Mater. 2001*
Activation Energy

Activation energy for Ni Self Diffusion in NiAl (kJ/mol)

Why so much disagreement?

- Grain boundary diffusion
- Annealing treatment: high temperatures may result in quenched in vacancies that are not in thermodynamic equilibrium
- Kim and Chang used lattice-mole fraction
Temperature Dependence of Ni Self-Diffusion in NiAl


NiAl-B2

Similar results on the Ni-rich and Al-rich compositions
Diffusion in B2-NiAl

*Diffusion in NiAl (B2) at 1100 °C*

*Diffusion in NiAl (B2) at 1000 °C*
Features the B2 model must reproduce

• Activation energy
  – Does not depend on composition in the range $0.46 < x_{\text{Ni}} < 0.53$: constant $\approx 290$ kJ/mol
  – Decreases with increasing Ni for $x_{\text{Ni}} > 0.53$

• Ni self diffusion
  – Ni-rich side ($0.5 < x_{\text{Ni}} < 0.53$): increases with increasing Ni composition
  – Al-rich side ($0.46 < x_{\text{Ni}} < 0.50$): remains constant with increasing Ni composition
Example: NiAl/Ni at 1150 °C
Summary

- Order diffusion model developed by Helandar and Agren successfully applied to Ni₃Al.
- Order diffusion modeling of NiAl-B2 is a greater challenge
  - Need to incorporate vacancies on sublattice model
  - *Does the Darken-Manning eq hold?*