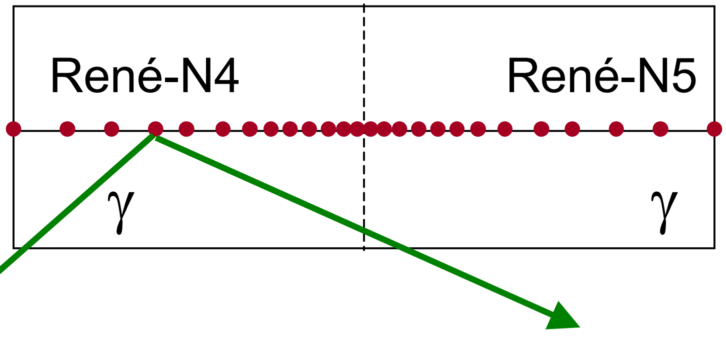
DICTRA and Diffusion Assessments

- Diffusion Mobility Assessment: Optimization
- Simulation of Diffusion Controlled Transformations

High Throughput Analysis of Multicomponent Multiphase Diffusion Data

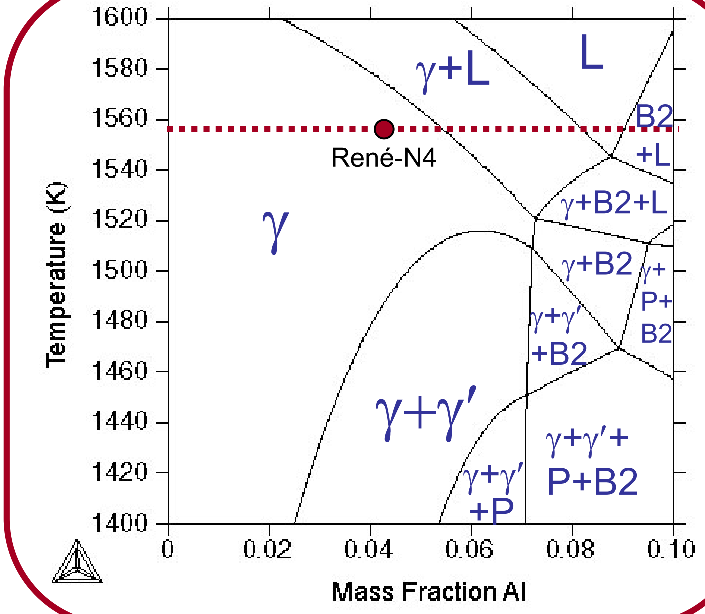
March 27-28, 2003

What is needed to simulate multicomponent diffusion?



At each grid point for each time step for a given temperature profile.

Thermodynamics



Diffusion matrix

René-N4 (x10^{-14} m^2/s) at 1293 °C

	Al	*Co*	*Cr*	*Mo*	*Nb*	*Ta*	*Ti*	*W*
Al	+119.5	+13.93	+34.83	+34.34	+42.43	+51.50	+49.51	+53.22
Co	−11.37	+17.00	−8.25	−5.67	−5.55	−1.83	−7.10	−9.69
Cr	−4.26	−5.37	+13.67	−3.21	+8.93	+9.91	+8.25	+2.49
Mo	−8.33	−0.280	−0.426	+7.57	−0.55	−0.36	−0.17	−0.45
Nb	+0.31	+0.25	+0.66	+0.27	+24.05	+0.74	+0.85	+0.31
Ta	−0.68	+0.33	+0.53	+0.24	+0.26	+0.76	+0.50	+0.23
Ti	+1.63	+1.35	+4.94	+4.94	+6.25	+6.57	+23.62	+5.41
W	−1.81	−0.62	−0.55	−0.60	−1.22	−0.83	−0.70	+3.40

➡ **Need efficient data storage**

Multicomponent Thermodynamics:
Calphad Approach

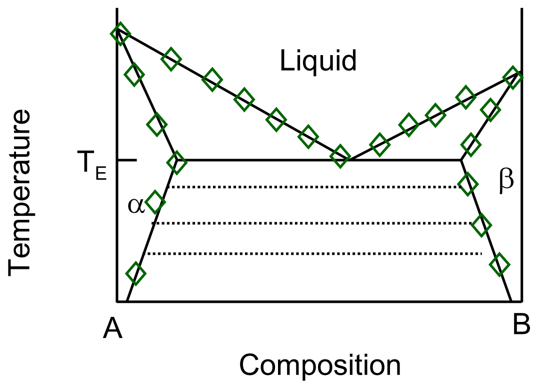
Experimental phase diagram
Thermochemical data

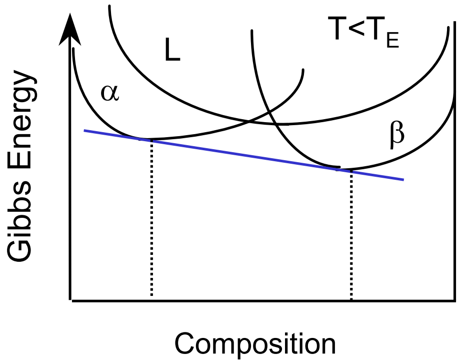
→

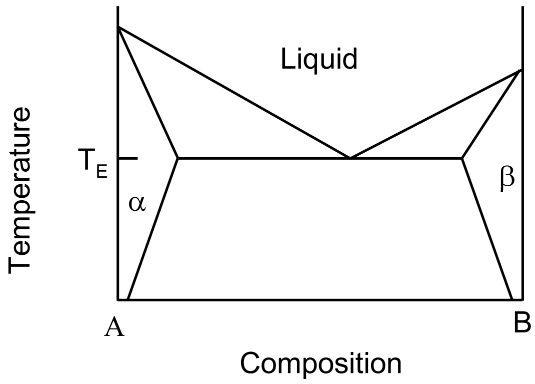
Determine Gibbs Energy
G = f(x,T,P)

→

Calculated phase
diagram







$$G^{\phi} = G^{0} + G^{ideal} + G^{excess}$$

Binaries → Ternaries → Quaternaries → nth order systems

Diffusion Database Development

- Inputs:
  - Calphad Thermodynamics
  - Diffusion experiments (unary, binary, ternary systems)
    - Tracer diffusivity,
    - Intrinsic diffusivity,
    - Interdiffusion coefficients/Marker motion

$$D_k^* = RTM_k$$

- Optimize value of mobilities, M_i, for all binaries consistent with available data
  - Composition and Temperature-dependent
  - Consistent with estimates of Metastable end members e.g., FCC W
  - Optimized using code, DICTRA (Parrot)

$$M_i = \frac{M_i^\circ}{RT}\exp\left(\frac{-\Delta Q_i}{RT}\right) \text{ where } \Delta Q_i = f\left(c_i, T\right) \text{ and } M_i^\circ = 1$$

$$\Delta Q_i = \sum_{p=1}^{n} x_p Q_i^p(T) + \sum_{p>q}^{n}\sum_{q=1}^{n} x_p x_q \; {}^0A_i^{pq}(T)$$

- Add terms $B_i^{ijk}(T)x_i x_j x_k$ if necessary to fit ternary data, etc.

Assessment of Diffusion Mobilities

Estimate Mobility

Compare experimental and calculated D

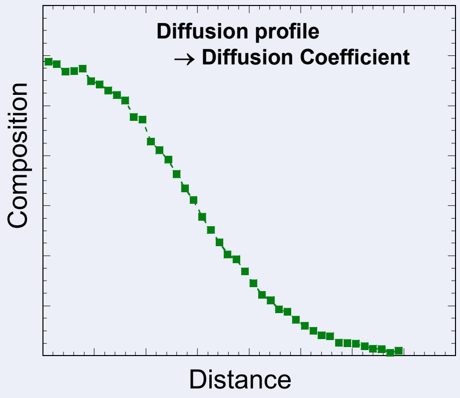
Simulate diffusion process

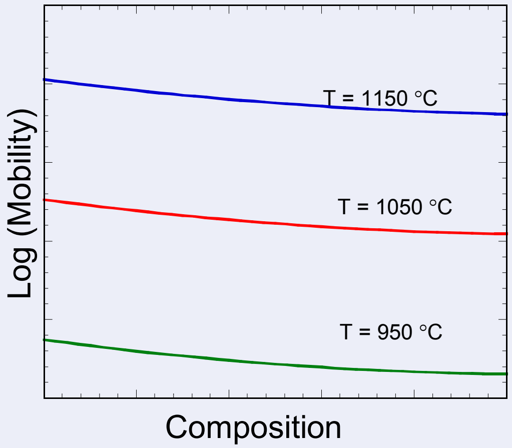
Adjust Mobility

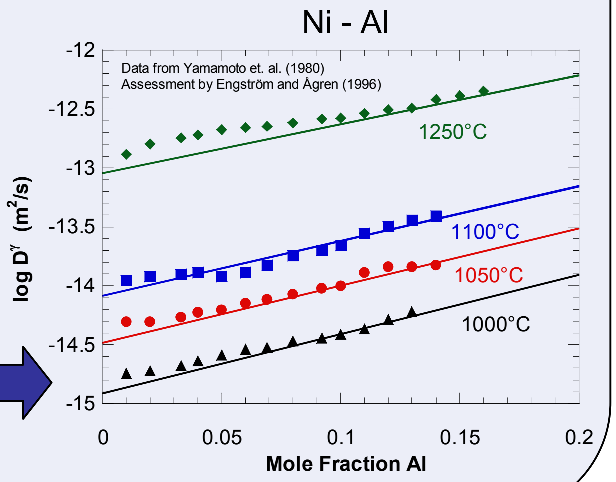
Experimental diffusion data

Mobility M=f (c,T)

Calculate diffusion Coefficients D = f(c,T)





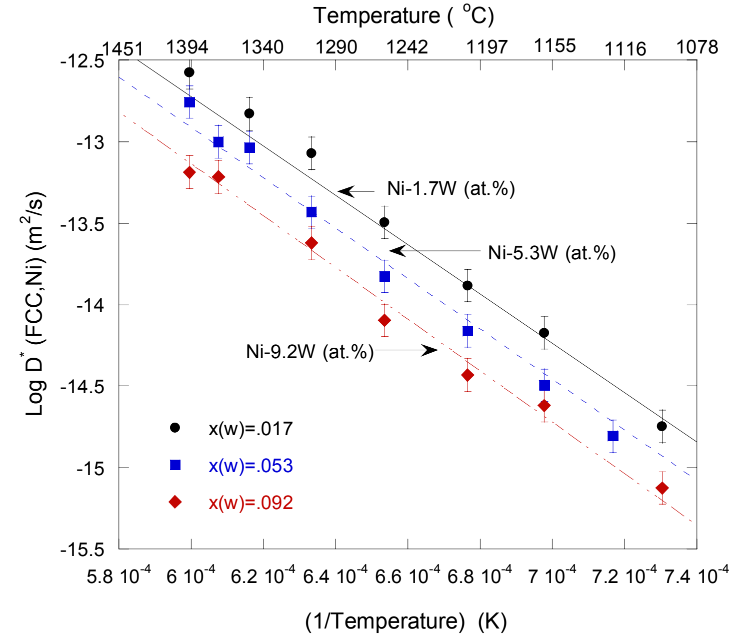


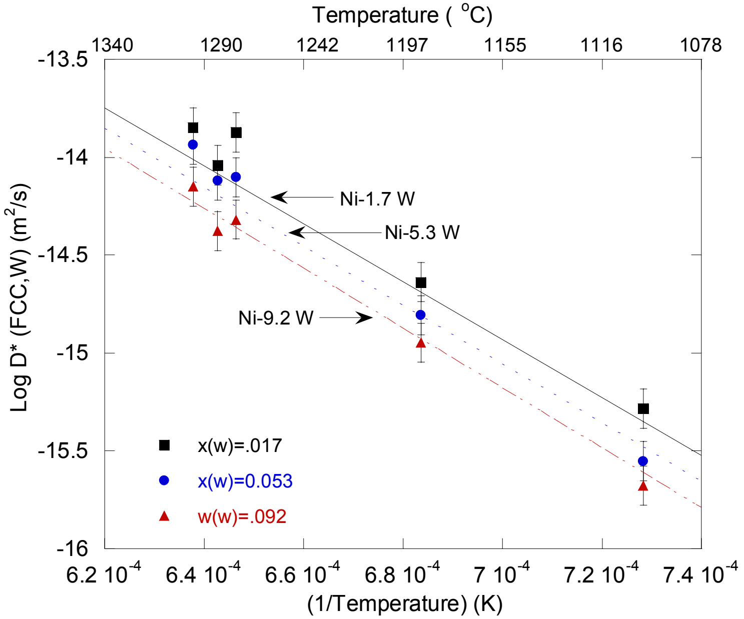
$$M_i = \frac{M_i^\circ}{RT}\exp\left(\frac{-\Delta Q_i}{RT}\right) \text{ where } \Delta Q_i = f\left(c_i, T\right) \text{ and } M_i^\circ = 1$$

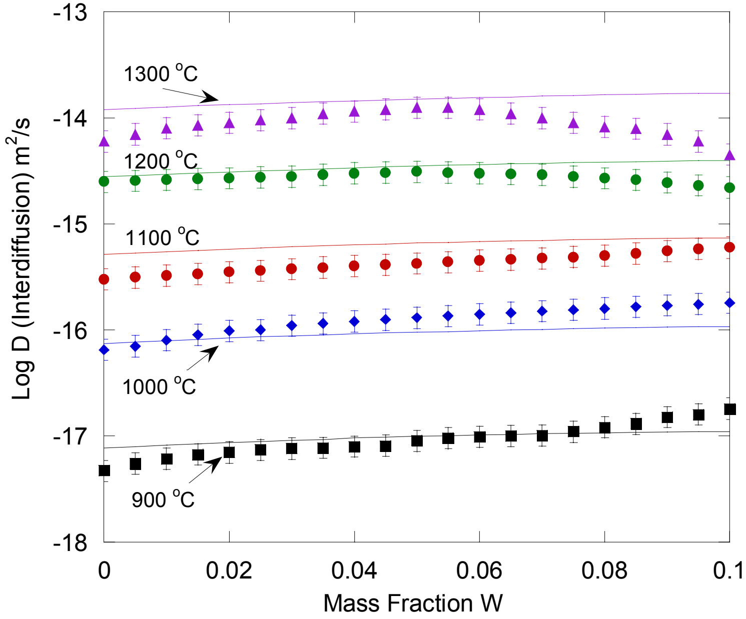
For a binary: $Q_i^\phi = c_iQ_i^i + c_jQ_i^j + c_ic_j\left(A_i^{i,j} + (c_i - c_j)B_i^{i,j} + (c_i - c_j)^2 C_i^{i,j} + \ldots\right)$

Assessment of Ni-W

Tracer diffusivity data







Interdiffusion data

Activation energies in the fcc phase

$$\Delta Q^*_{Ni} = x_{Ni}\underline{Q^{Ni}_{Ni}} + x_W\underline{Q^{W}_{Ni}} + x_{Ni}x_W\,\underline{{}^0A^{Ni,W}_{Ni}}$$

$$\Delta Q^*_{W} = x_{Ni}\underline{Q^{Ni}_{W}} + x_W\underline{Q^{W}_{W}} + x_{Ni}x_W\,\underline{{}^0A^{Ni,W}_{W}}$$

🟩 Self activation energies

🟥 Optimized parameters

Mobility Description Ni-W

- FCC_A1: Mobility of Ni
  - MQ(FCC_A1,NI:VA;0) = **-28700+69.8*T**
  - MQ(FCC_A1,W:VA;0) = **V1+R*T*LN(V2**)
  - MQ(FCC_A1,NI,W:VA;0) = **V3+V4*T**
- FCC_A1: Mobility of W
  - MQ(FCC_A1,NI:VA;0) = **V5+R*T*LN(V6)**
  - MQ(FCC_A1,W:VA;0) = **V7+R*T*LN(V8)**
  - MQ(FCC_A1,NI,W:VA;0) = **V9+V10*T**

Ni-W : DOP file

- $$ Data from Momma et al, J. Japan Inst. Metals, 28 (1964) 197-200.
- $$ Measured diffusivity in Ni-W alloys with Ni-63 and W-185

- TABLE_HEAD 655
- CREATE_NEW_EQ @@, 0
- CHANGE_STATUS COMP Ni,W=ENT
- CHANGE_STATUS PHASE FCC_A1=ENT 1
- S-COND X(W)=.017
- S-COND P=101325 N=1 T=@1
- EXPERIMENT **LOGDT(FCC,NI)=@2:.05**
- TABLE_VALUES

- $$Ni-5W
- $$ Temp(K)   Log(DT)
-   1668   -12.57675413
-   1623   -12.82973828
-   1579   -13.07058107
-   1530   -13.49485002
-   1478   -13.8827287
-   1433   -14.1739252
-   1369   -14.74714697
- TABLE_END

Ni-W Interdiffusion: DOP file

- TABLE_HEAD 325
- CREATE_NEW @@,0
- CHANGE_STATUS COMP NI,W=ENT
- CHANGE_STATUS PHASE FCC_A1=ENT 1
- S-COND w(W)=@1
- S-COND N=1 P=101325 T=1273
- EXPERIMENT **LOGDC(FCC,W,W,NI**)=@2:.1
- TABLE_VALUES

- $$ 1000 C
- $$ w(W)   logD
-   0.00E+00   -16.18708664
-   5.00E-03   -16.15490196
-   1.00E-02   -16.09691001
-   1.50E-02   -16.04575749
-   2.00E-02   -16.00877392
- :
- 9.00E-02   -15.76955108
-   9.50E-02   -15.75696195
-   1.00E-01   -15.74472749
- TABLE_END

Optimization

```
= = OPTIMIZING VARIABLES = =
AVAILABLE VARIABLES ARE V1 TO V50
      Value             START Value       Scaling Factor      Rel. Stand. Dev

V1    -6.28250129E+05   -6.28250129E+05   -6.28250129E+05     3.85216307E-01

V2    4.78352423E-04    4.78304593E-04    4.78304593E-04      6.01374702E+00

V3    1.7573601E+05     1.75718445E+05    1.75718445E+05      1.44758232E+00

V5    -2.82130025E+05   -2.82130025E+05   -2.82130025E+05     1.95885497E-02

V6    2.80004792E-05    2.79975794E-05    2.79975794E-05      4.48683550E-01

V7    -4.11423418E+5    -3.11392279E+05   -3.11392279E+05     1.02636444E+01

V8    2.18664263E-04    2.18664263E-04    2.18664263E-04      1.19007328E+01

V9    -9.70248906E+4    -9.70151891E+04   -9.70151891E+04     3.15926361E+00

 NUMBER OF OPTIMIZING VARIABLES: 8
 ALL OTHER VARIABLES ARE FIX WITH THE VALUE ZERO
 THE SUM OF SQUARES HAS CHANGED FROM 5.19453290E+02 TO   5.1944291E+02
 DEGREES OF FREEDOM 109.   REDUCED SUM OF SQUARES  4.76554396E+00
```

Optimization Results: Tracer Diffusivity

Experimental Quantity	Optimized Value	Acceptable error	Difference	Difference/ Error
LOGDT(FCC_A1,NI)=-12.57	-12.72	5.0E-02	-0.1407	-2.814
LOGDT(FCC_A1,NI)=-12.83	-12.97	5.0E-02	-0.1394	-2.788
LOGDT(FCC_A1,NI)=-13.07	-13.23	5.0E-02	-0.1585	-3.170
LOGDT(FCC_A1,NI)=-13.49	-13.54	5.0E-02	-4.13E-2	-0.826
LOGDT(FCC_A1,NI)=-13.88	-13.88	5.0E-02	-1.59E-3	-3.2E-2
LOGDT(FCC_A1,NI)=-14.17	-14.21	5.0E-02	-3.2E-2	-0.642
LOGDT(FCC_A1,NI)=-14.75	-14.70	5.0E-02	4.72E-2	0.9440

Extrapolation to Higher Order Systems

Ni-Cr

$$\Delta Q_{Ni} = Q_{Ni}^{Ni} x_{Ni} + Q_{Ni}^{Cr} x_{Cr} + \boxed{A_{Ni}^{NiCr} x_{Ni} x_{Cr}}$$
$$\Delta Q_{Cr} = Q_{Cr}^{Ni} x_{Ni} + Q_{Cr}^{Cr} x_{Cr}$$

Binary

interaction

Ni-Al

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

Cr-Al

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

Ni-Cr-Al

$$\Delta Q_{Ni} = Q_{Ni}^{Ni} x_{Ni} + Q_{Ni}^{Cr} x_{Cr} + Q_{Ni}^{Al} x_{Al} + A_{Ni}^{NiCr} x_{Ni} x_{Cr} + \boxed{B_{Ni}^{NiCrAl} x_{Ni} x_{Cr} x_{Al}}$$
$$\Delta Q_{Cr} = Q_{Cr}^{Ni} x_{Ni} + Q_{Cr}^{Cr} x_{Cr} + Q_{Cr}^{Al} x_{Al}$$
$$\Delta Q_{Al} = Q_{Al}^{Ni} x_{Ni} + Q_{Al}^{Cr} x_{Cr} + Q_{Al}^{Al} x_{Al}$$

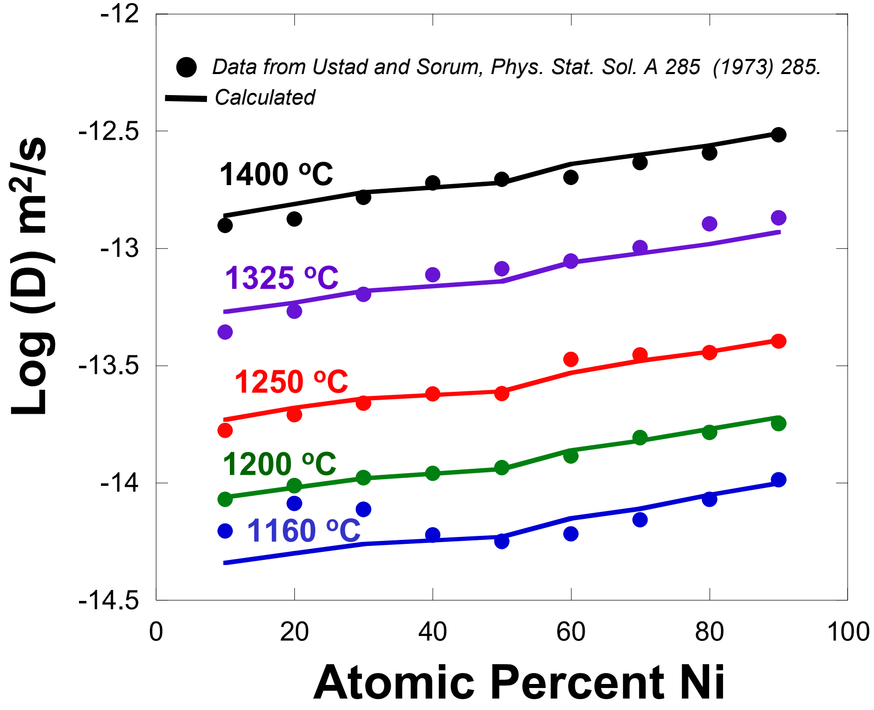
Ternary

interaction

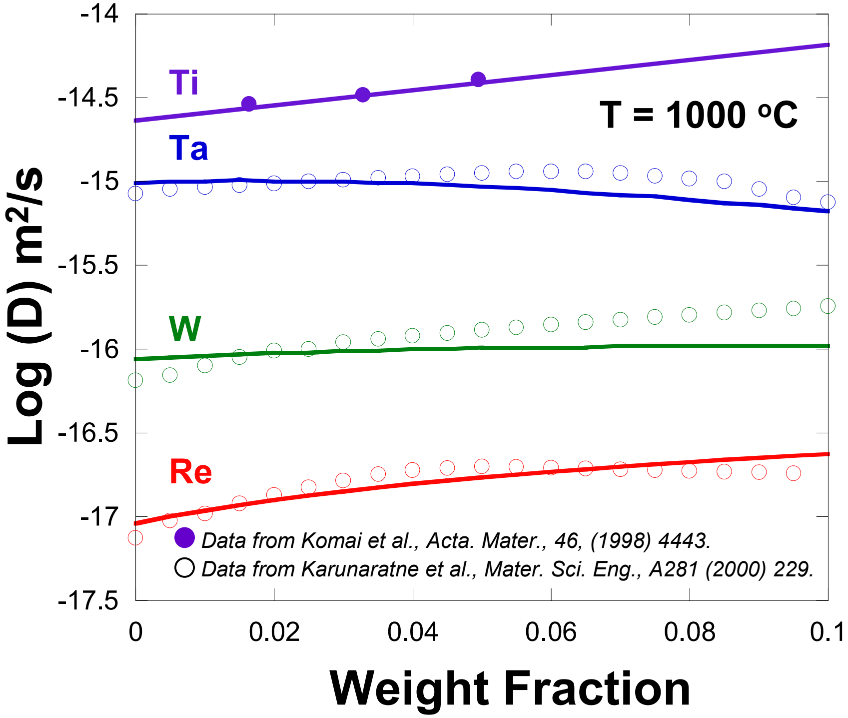
Examples of Fits for Binary Interactions

Ni-Al-Cr-Co-Hf-Nb-Mo-Re-Ta-Ti-W

Ni-Co Interdiffusion



Interdiffusion with Ni



***Previous assessments**:* **Ni-Al-Cr** Engström and Ågren, *Z. Metallkd.* 87 (1996) 92.

Ni-Al-Ti Matan et al., *Acta mater.*, 46 (1998) 4587.

Current assessments: Ni-Co, Ni-Hf,Ni-Mo, Ni-Nb,Ni-Re, Ni-Ta, Ni-Ti,Ni-W, Co-Cr, Co-Mo

C. E. Campbell, W. J. Boettinger, U. R. Kattner, *Acta Mat,* 50 (2002) 775

Diffusion Correlation at Melting Temperature

- **For a pure metal** $\frac{-Q}{RT_M} \approx 18$

Element	Crystal Structure	T_M, K	T_M, K (fcc)	T_M, K (fcc) (Kaufman)	Activation Energy (J/mole)	-Q/RT_M (fcc) (SGTE)	-Q/RT_M (fcc) (Kaufman)
Ni	fcc	1728	1728	1725	-287000	20.0	20.0
Al	fcc	933.5	933.5	931	-142000	18.3	18.4
Cr	bcc	2133	1475	860	-235000	19.2	32.9
Co	hcp	1770	1768	1768	-286175	19.5	19.5
Hf	hcp	2504	1952	2076	-235350	14.5	13.6
Mo	bcc	2895	1740	1530	-254975	17.6	20.0
Nb	bcc	2468	1300	1170	-274328	25.4	28.2
Re	hcp	3459	3084	2830	-382950	14.9	16.3
Ta	bcc	3296	1416	1540	-268253	22.8	20.9
Ti	hcp	1946	900	1421	-256900	34.3	21.7
W	bcc	3695	2229	2230	-311420	16.8	16.8

Comparison with Ni-Co-Cr-Mo Data at 1300 °C[*]*

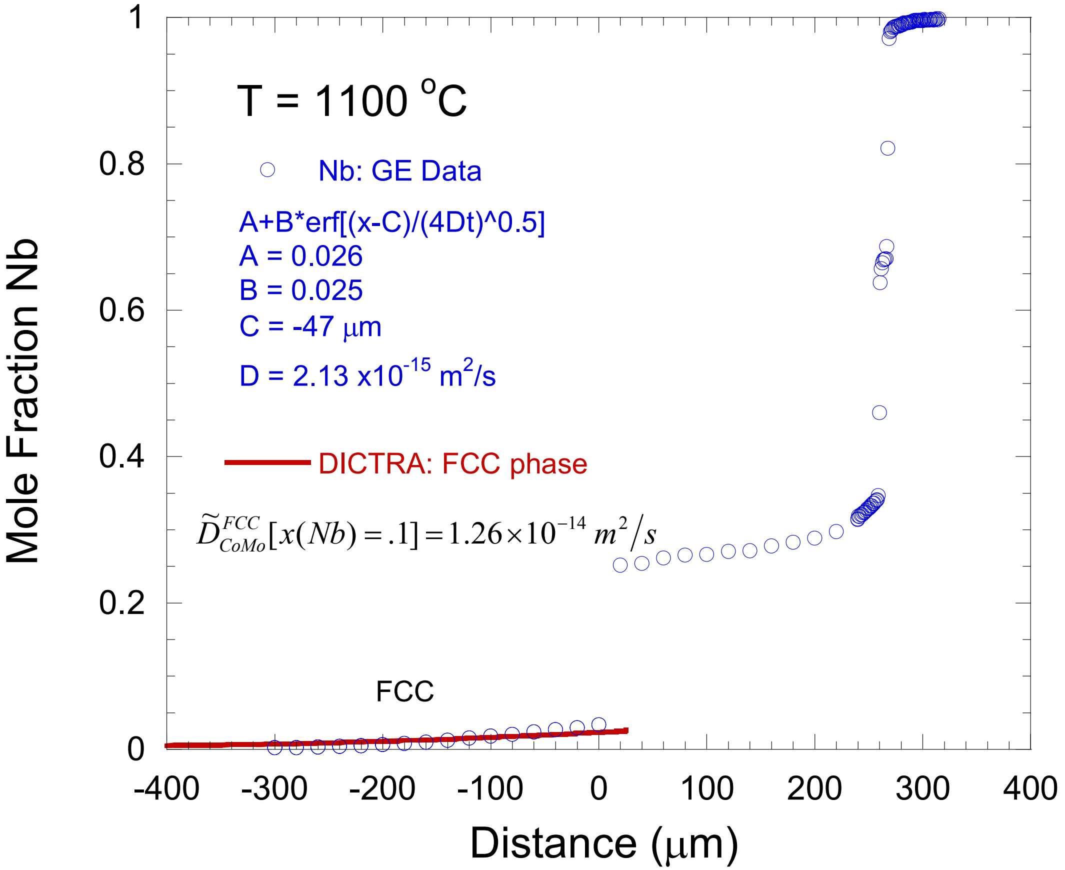
Composition (Atomic Percent) Ni = balance			$\tilde{D}_{ij}^{Ni} \times 10^{14}\ m^2/s$		
Cr	**Co**	**Mo**	**Measured**	**Calculated** NIST	 Thermotech
				$\tilde{D}_{CrCr}^{Ni}$	
24.2	24.1	7.4	7.5±1.5	10.2	10.7
22.7	24.5	7.4	9.7 ± 1.9	**10.1**	**10.6**
20.8	25.0	7.4	9.9 ± 2.0	**9.85**	**10.3**
18.4	25.6	7.2	10.1 ± 2.0	**9.56**	**10.0**
15.2	25.8	7.4	8.2 ± 1.6	9.35	9.74
10.8	26.2	7.4	6.9 ± 1.4	8.95	9.25
6.4	27.1	7.7	6.4 ± 1.3	8.4	8.59
3.2	47.9	7.7	6.8 ± 1.4	4.94	5.03
				$\tilde{D}_{CoCo}^{Ni}$	
26.8	**1.7**	6.6	8.9 ± 1.8	**10.3**	**10.3**
26.5	**4.4**	6.4	6.0 ± 1.2	9.61	9.78
26.3	**7.4**	6.6	4.8 ±1.0	8.96	9.22
25.8	**19.8**	7.1	3.7 ±0.7	7.01	7.53
25.8	**21.4**	7.1	4.2 ± 0.8	6.83	7.58
25.9	**16.2**	7.1	3.3 ± 0.7	7.47	7.93
				$\tilde{D}_{NiCr}^{Co}$	
22.2	3.7	6.2	-2.0 ± 0.4	**-2.26**	-4.69
6.5	23.9	7.6	-1.7 ± 0.3	-2.37	-2.27

Diffusion coefficients calculated using the different thermodynamic databases and a fixed diffusion mobility database.

[†] Heaney and Dayananda *Metall. Trans. A,* 1986, **17A**, 983.

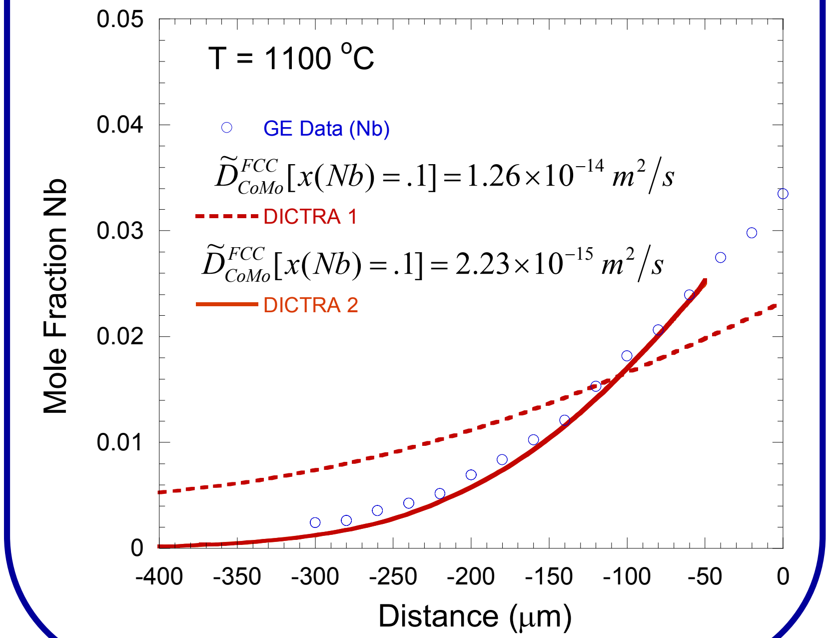
Co-Nb at 1100 C for 1000 h

Mobility of Nb in fcc Co not evaluated in diffusion database



(MQ(FCC_A1&Nb,Co:V;0) =-255333+R*T*LN(7.6071E-05)

Based on this result re-evaluate mobility parameter
(MQ(FCC_A1&Nb,Co:V;0)] =
-275333+R*T*LN(7.6071E-05)



DICTRA*

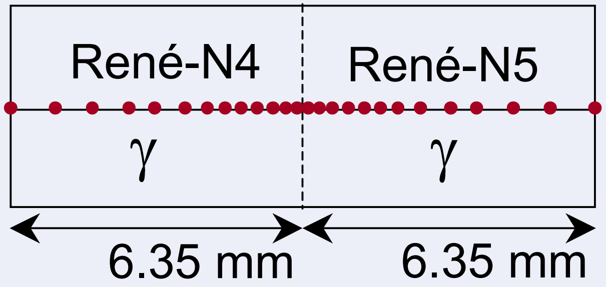
Diffusion Controlled Transformations

- 1-D finite difference solution to diffusion equations
- Variable self-adjusting mesh
- Volume fixed reference frame
- Vacancy and interstitial diffusion
- Can solve problems with planar layers of
  - single phase material
  - multiphase material (matrix and dispersed phase)
    - describes suitable average concentration of multiphase mixture
    - assumes diffusion only in the matrix phase
    - assumes phase fraction of dispersed phase is small
    - assumes the composition of the dispersed phase is given by local equilibrium for average concentration

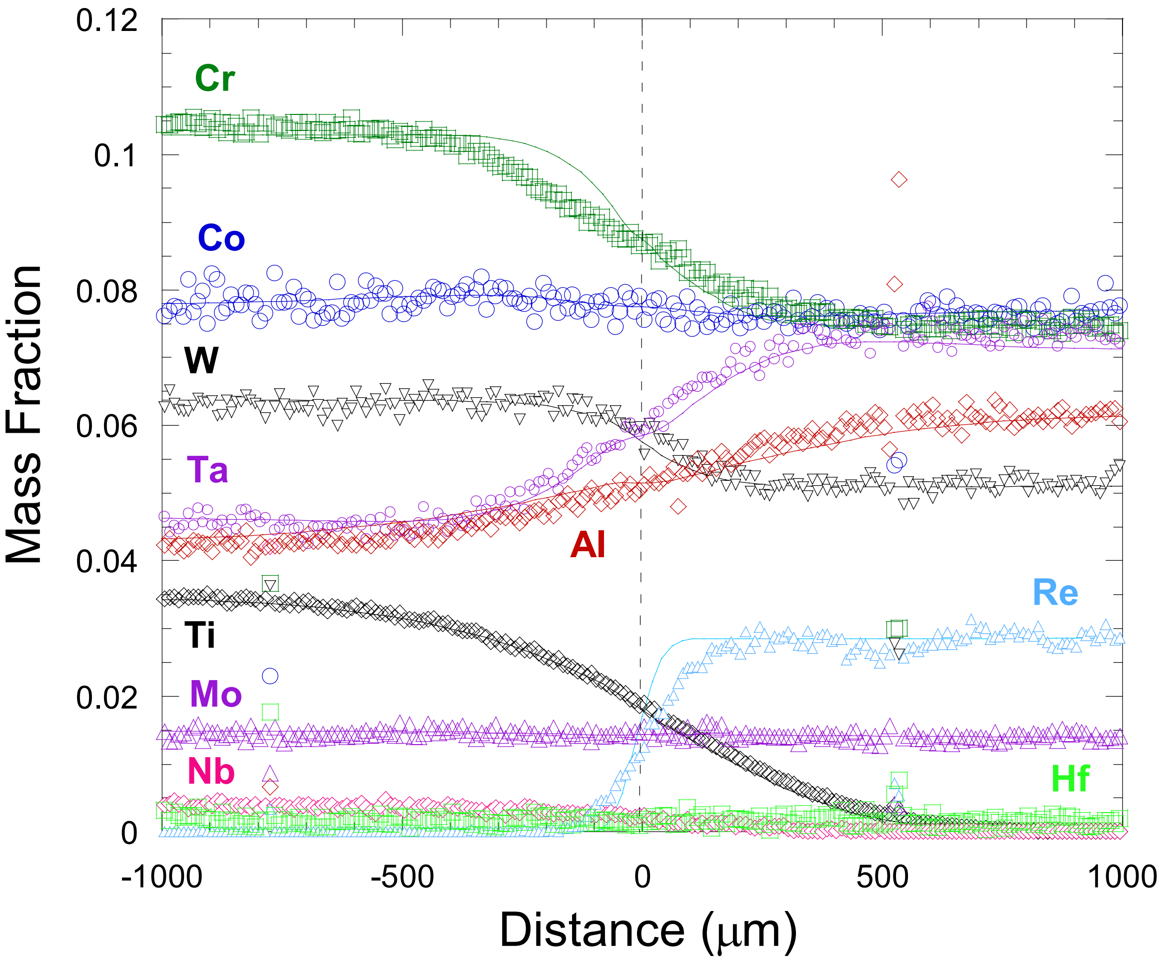
[*] *from the Division of Physical Metallurgy, The Royal Institute of Technology, Stockholm, Sweden.*

René-N4/René-N5 at 1293 °C for 100 h

- Databases used
  - Thermodynamics: Thermotech
  - Diffusion mobilities: NIST Ni-mob

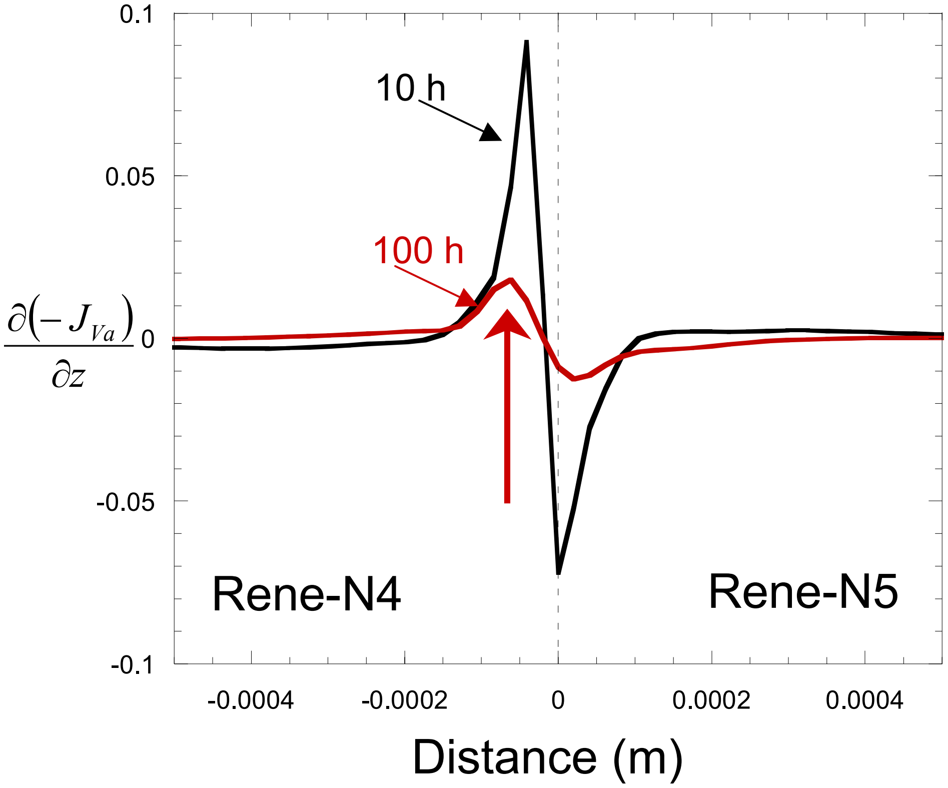


Double geometric grid: 200 points



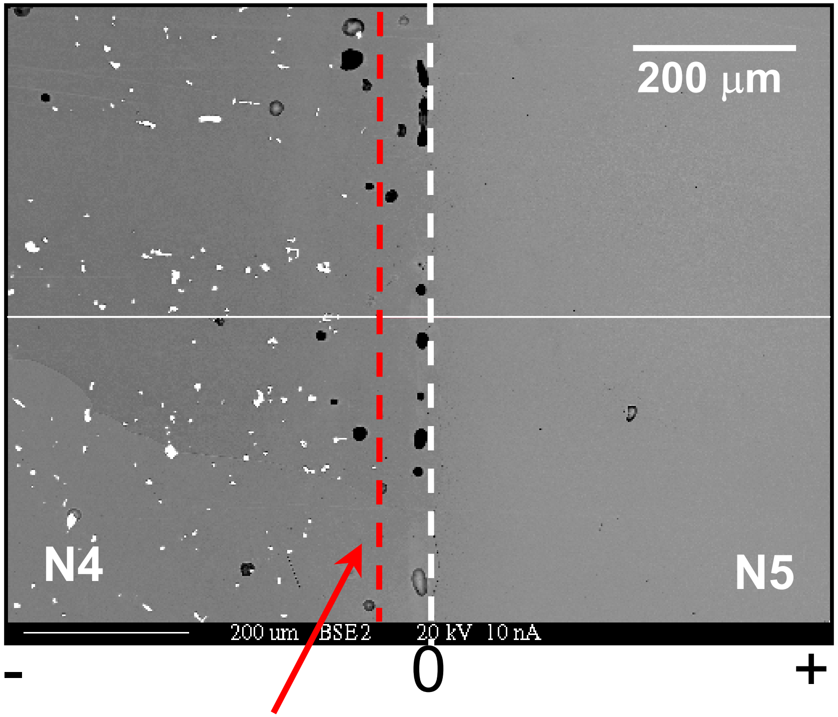
Experimental work performed by T. Hansen, P. Merewether, B. Mueller, Howmet Corporation, Whitehall, MI.

Porosity Prediction



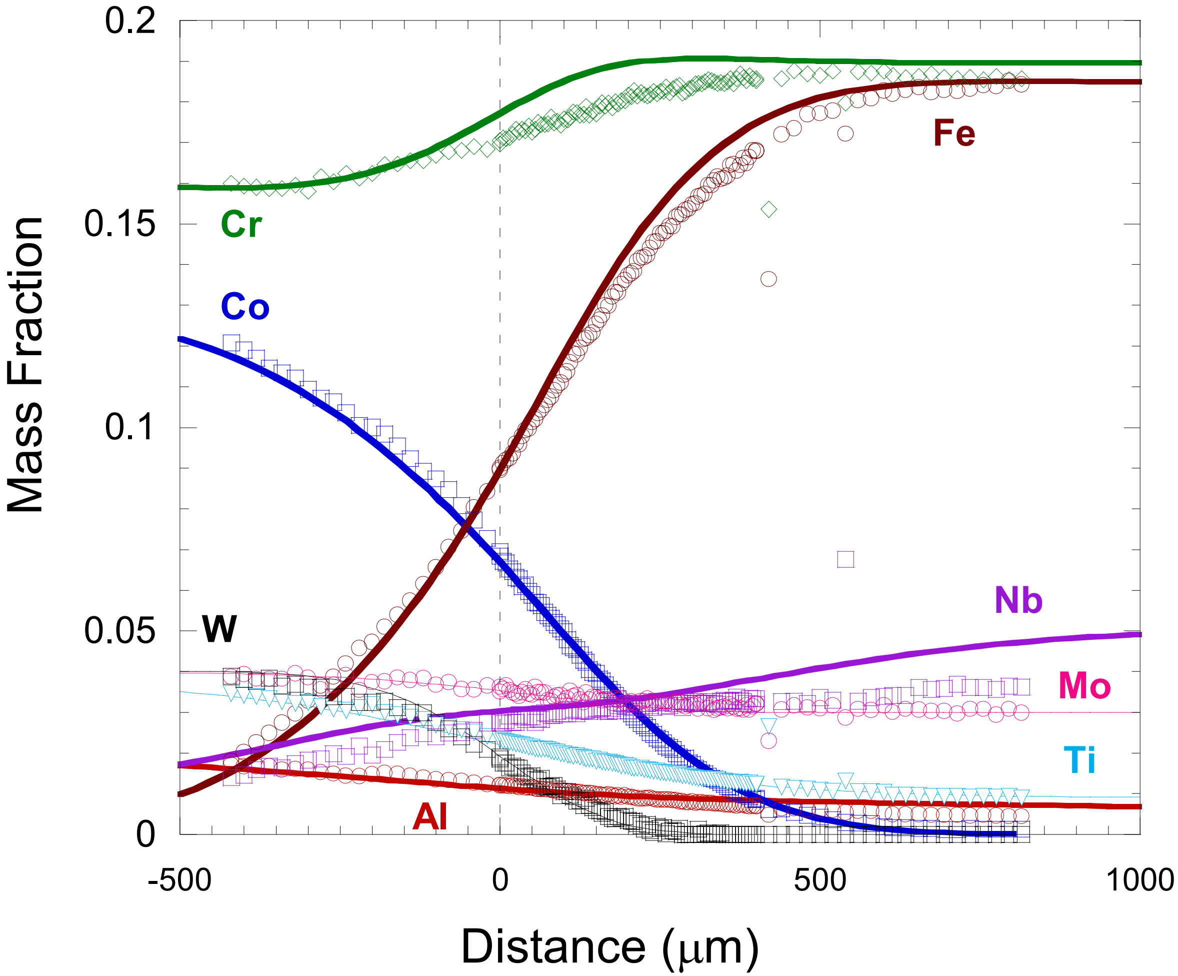
Maximum gives location of pore formation.

Back scatter image; 100 h



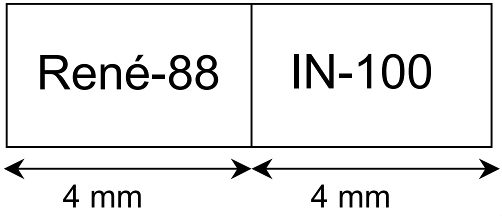
Predicted position for maximum pore formation

René-88/IN-718; 1000 h at 1150 °C



At 1150 °C equilibrium phase fractions

- René-88: $f_\gamma = 1$
- IN-718: $f_\gamma = 1$

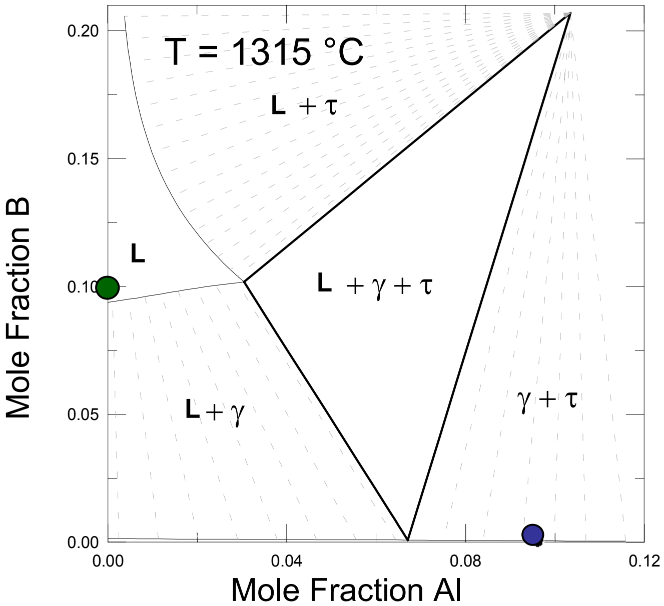


Experimental data from J. C. Zhao, GE-CRD, Schenectady, NY

Applications of Diffusion Database

- Prediction of γ' precipitation: GE-AIM program:
  - Composition and volume of γ' is key to predicting many of mechanical properties
- Back diffusion during solidification: Howmet
- Protective coatings: Howmet
  - B2/Rene-N5 diffusion simulations
    - B2 layer dissolves, forms γ' layer
- Heat treatment optimization: avoiding incipient melting.

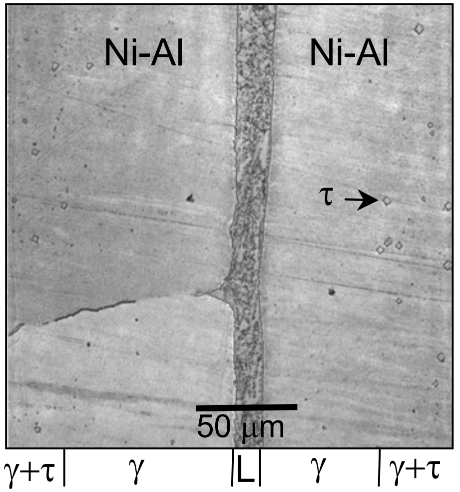
Transient Liquid Phase Bonding

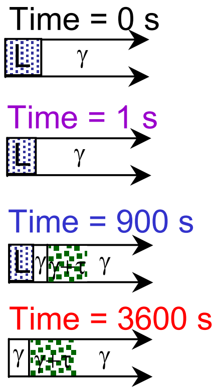


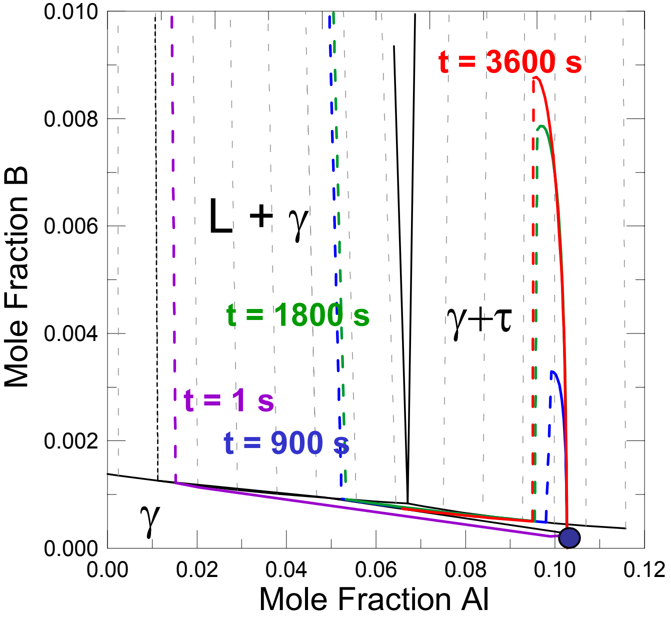
Thermodynamics & Diffusion mobilities

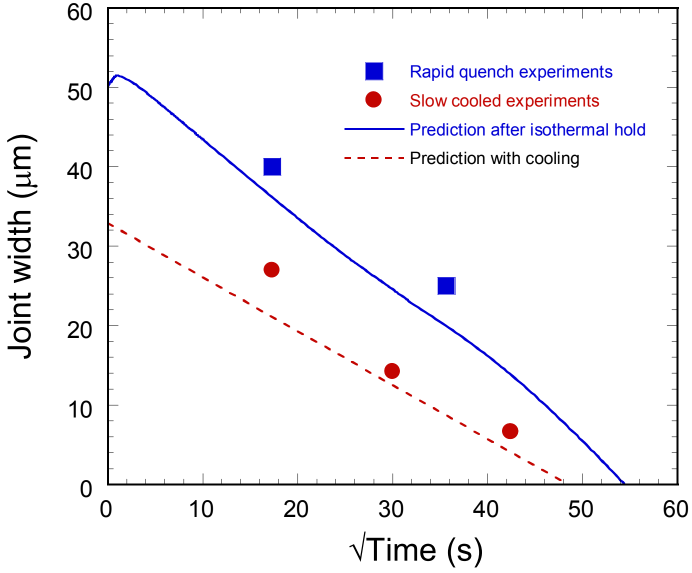
microstructure evolution

T = 1315 °C; Time 900 s
Ni-10.3Al/Ni-10B/Ni-10.3Al







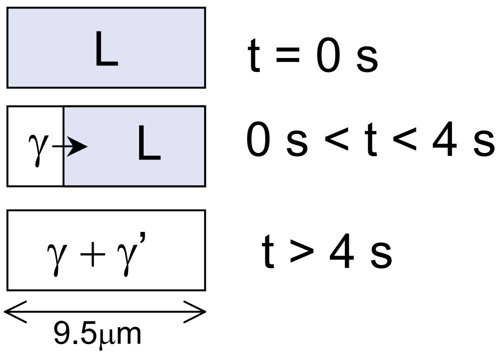


C. E. Campbell and W. J. Boettinger, Metall. Materials Trans., 31A, 2000, 2835.

Heat Treatment Optimization:
Solidification of Ni-11Al-4.5Ta (at.%)

Solidification assumptions

- Cooling rate = 8K/s;
- $\lambda/2 = 9.5\ \mu m$
- Microstructure evolution



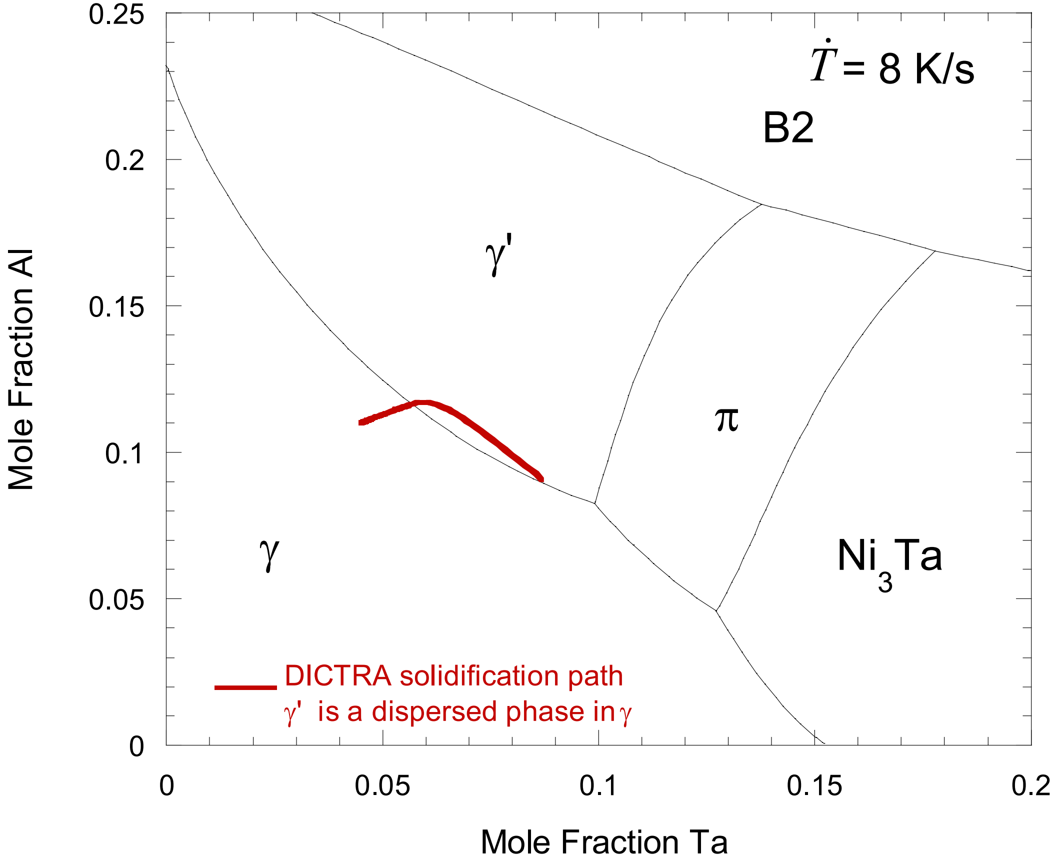
L t = 0 s

$\gamma \rightarrow$ L 0 s < t < 4 s

$\gamma + \gamma'$ t > 4 s

9.5µm

Solidification Path

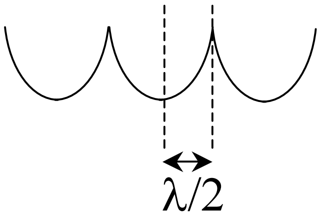


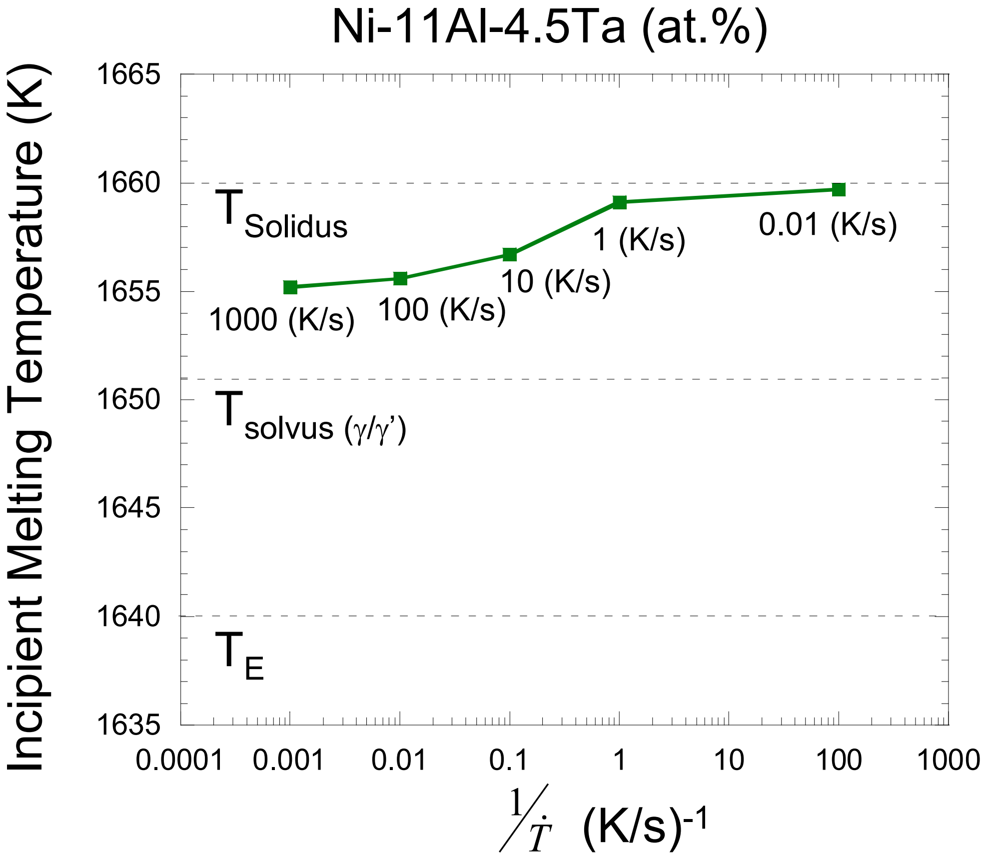
Thermodynamics: Ni-Data, Thermotech
Diffusion: Ni-Mob, NIST

Incipient Melting Temperature

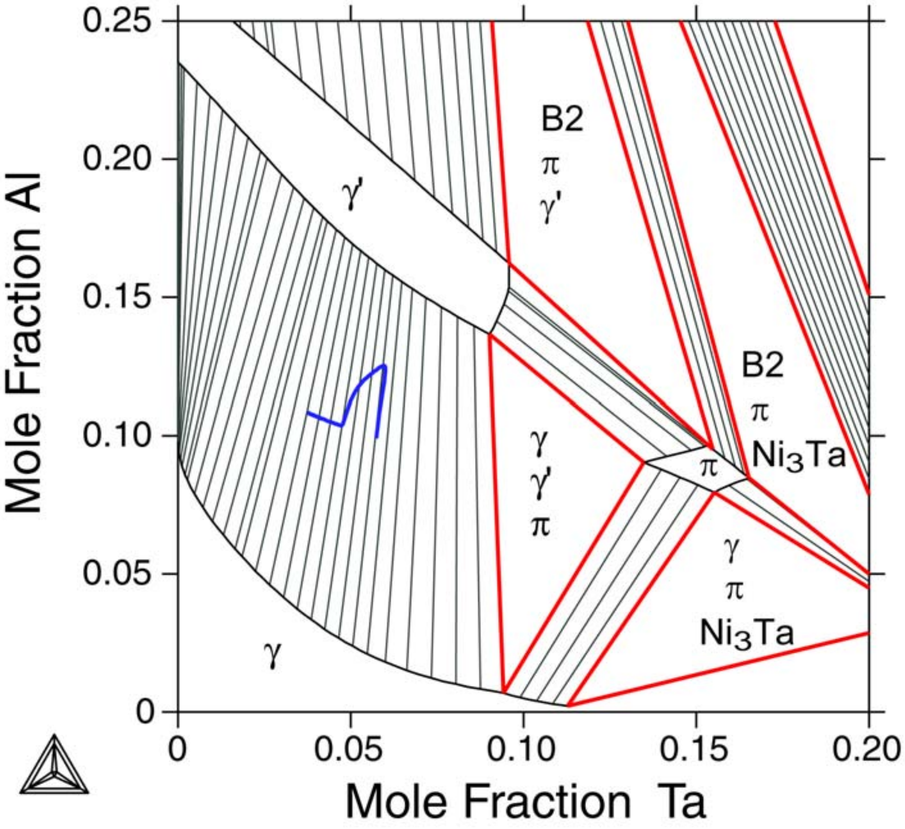
Simulation Setup

- Used composition and phase fractions from solidification calculation.
- Assume linear heating rates beginning at 800 K
- Assume γ' fraction is in equilibrium with γ matrix at each grid point.
- Assume incipient melting occurs at the center between dendrites.

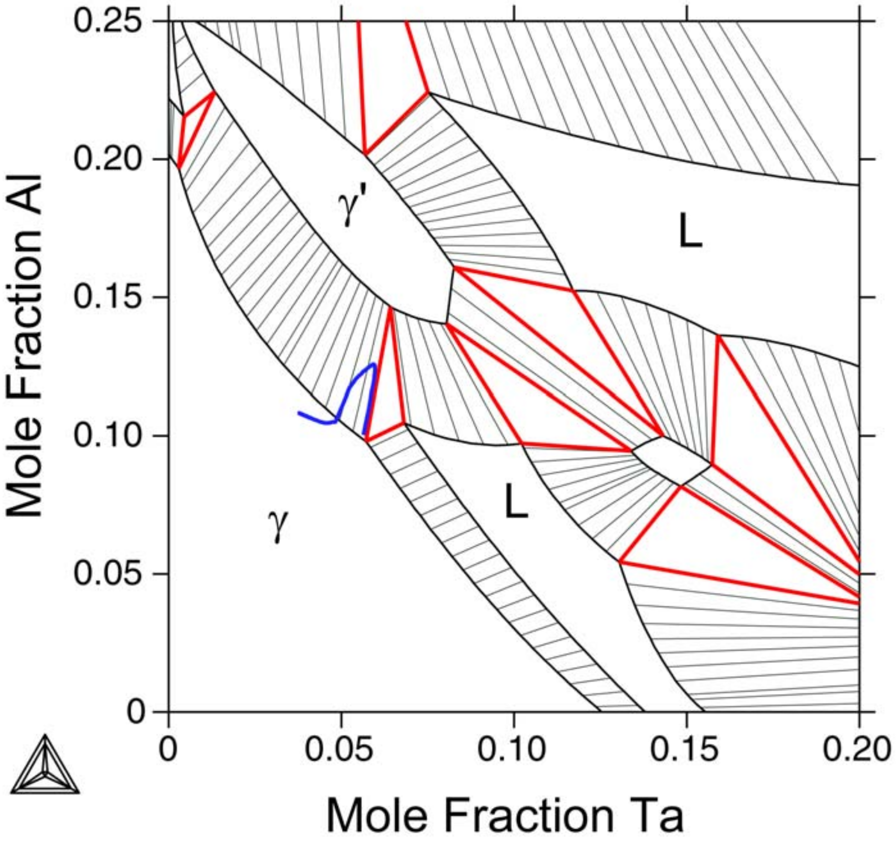




Heating Rate 100 K/s, T_{IM}= 1655 K


Ni-Al-Ta

T = 800 K; Time = 0 s

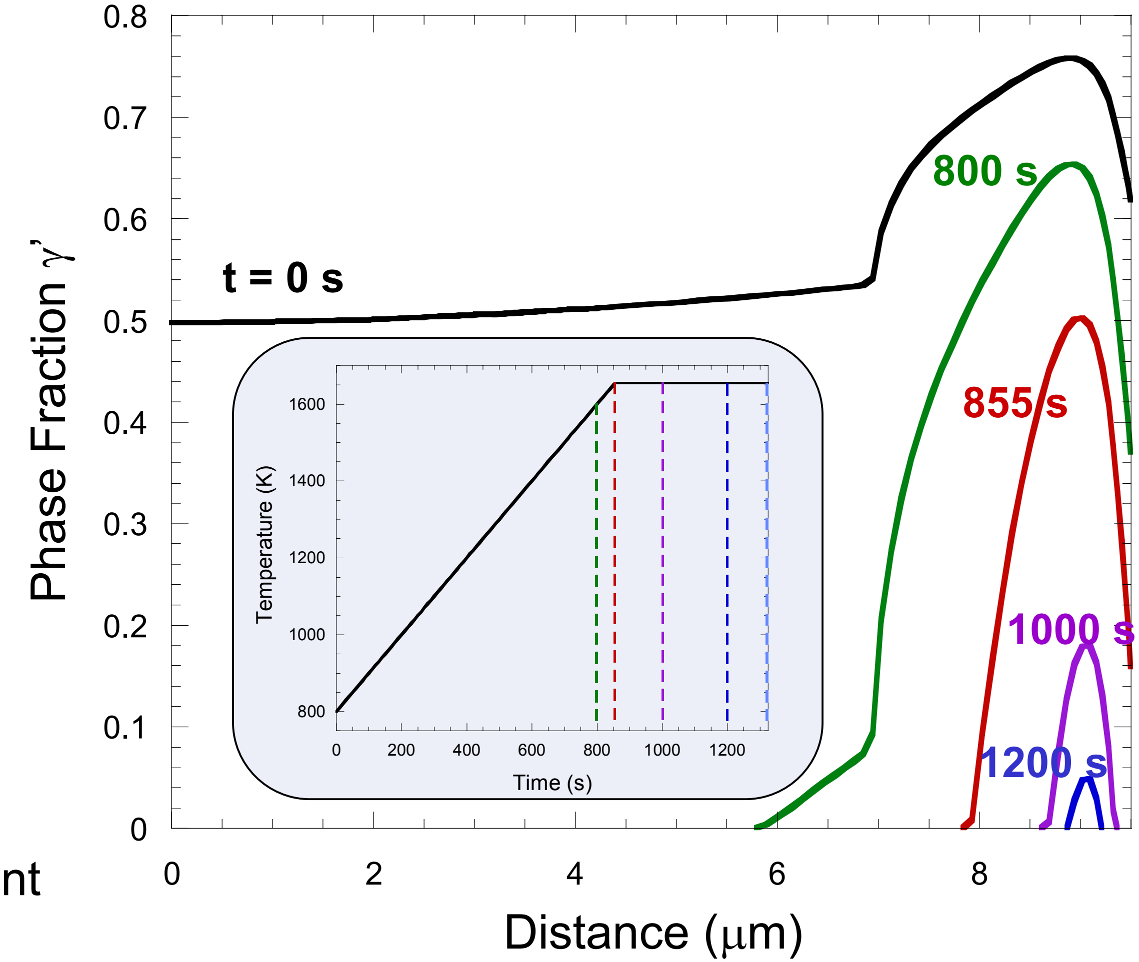

T = 1655; Heating Rate = 100 K/s

Optimized Heat Treatment

For Ni-11Al-4.5Ta alloy solidified at 8 K/s

- Heat from 800 K to 1655 K at 1 K/s
- Hold at 1655 K until t = 1325 s (Δt = 470 s)

Homogenous microstructure



Next step: Multicomponent simulation, optimization, experimental verification