Multicomponent diffusion effects in joints of dissimilar materials – engineering applications

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2. Multicomponent-multiphase
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4. TBC Bond coats
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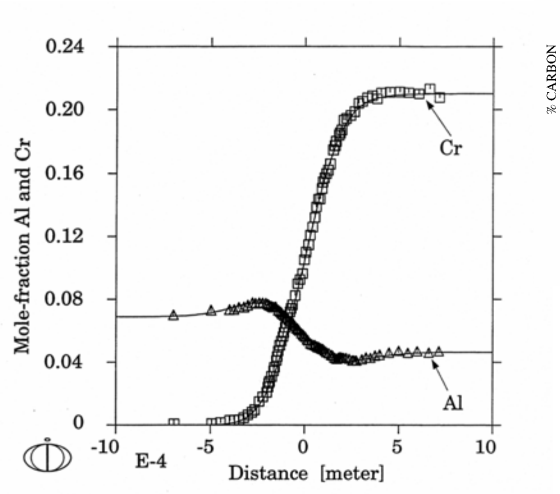
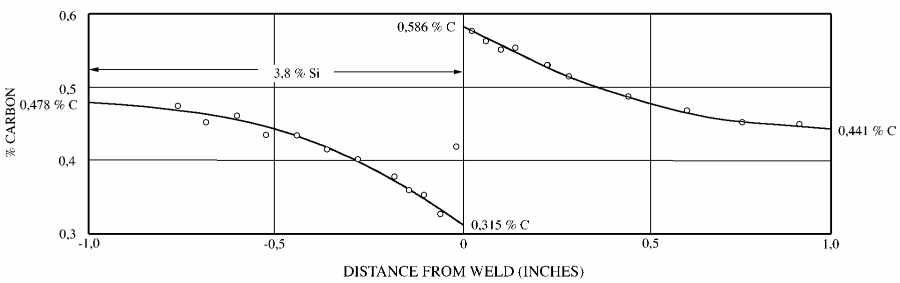
6. Mobility data

1. Background

- Engineering materials are multicomponent and often multiphase.
- Coupling effects!





$$J_k = -\sum_{j=1}^{n-1} D_{kj}^{n} \nabla c_j$$

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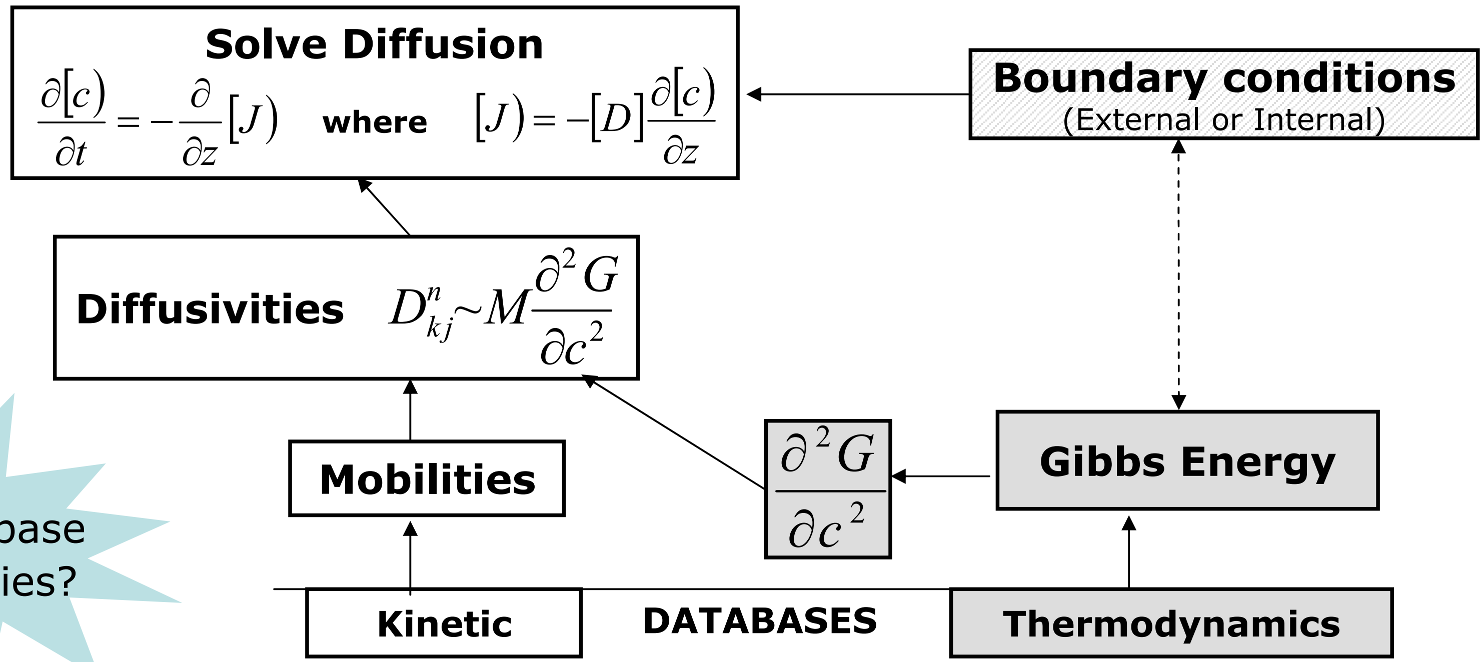
DICTRA - Basic calculation procedure

A numerical finite difference scheme is used for solving a system of coupled parabolic partial differential equations



Why a database with Mobilities?

All simulations depend on assessed kinetic and thermodynamic data, which are stored in databases

Why mobilities and not diffusion coefficients?

- Individual, intrinsic

  Lattice fixed frame of reference, in an n-component system: n-1 for each component, i.e. nx(n-1).

$$D_{kj}^{n} = u_k M_{kVa} \frac{\partial \mu_k}{\partial u_j}$$

- Self diffusion

  Diffusion of A in pure A

$$D_{AA}^{A} = RTM_{AVa}$$

- tracer diffusion $D^{*}{}_{AA}^{A} = RTM_{AVa}$
- interdiffusion, chemical diffusion

  Number-fixed frame of reference, in an n-component system: n-1 for each component, i.e. (n-1)x(n-1).

But only *n* mobilities!

One Phase diffusion along x in α:

$$J_k^\alpha = -\sum_{i=1}^{n-1} D_{ki}^{n\alpha} \frac{\partial c_i^\alpha}{\partial x}$$

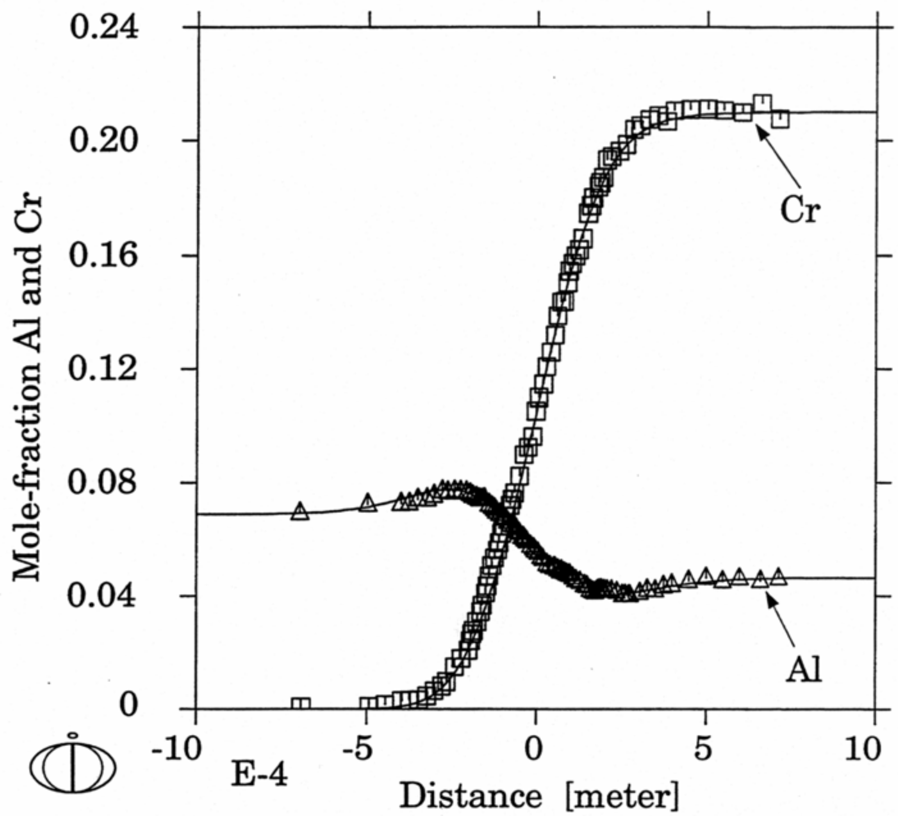
$$D_{kj}^n = u_k M_k \frac{\partial \mu_k}{\partial u_j} - u_k \sum_{i \in s}^{n} u_i M_i \frac{\partial \mu_i}{\partial u_j}$$

where

M_k is the mobility of k

and

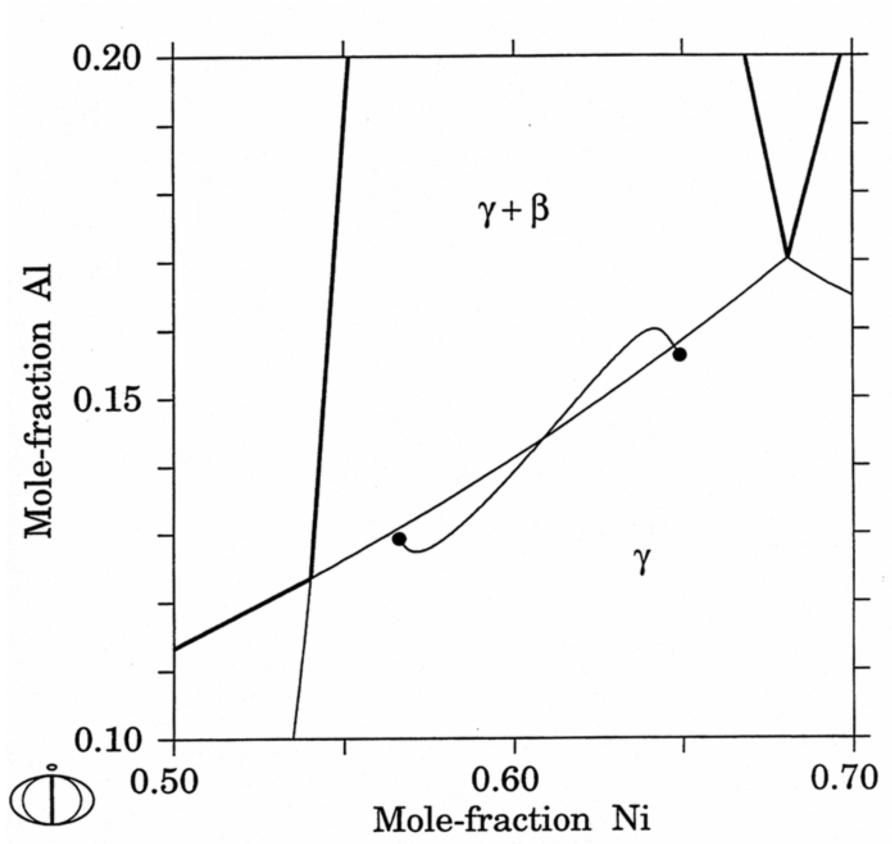
$$u_k = \frac{x_k}{1 - x_C}$$



Ni-Cr-Al diffusion couple

Engström and Ågren 1996

2. Multicomponent-multiphase

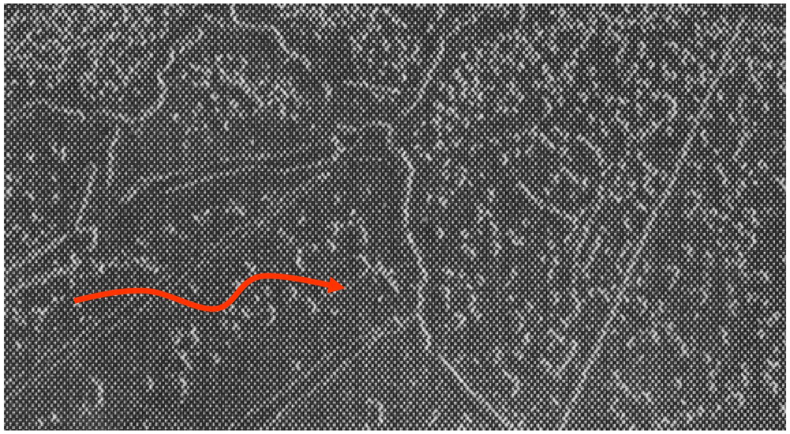


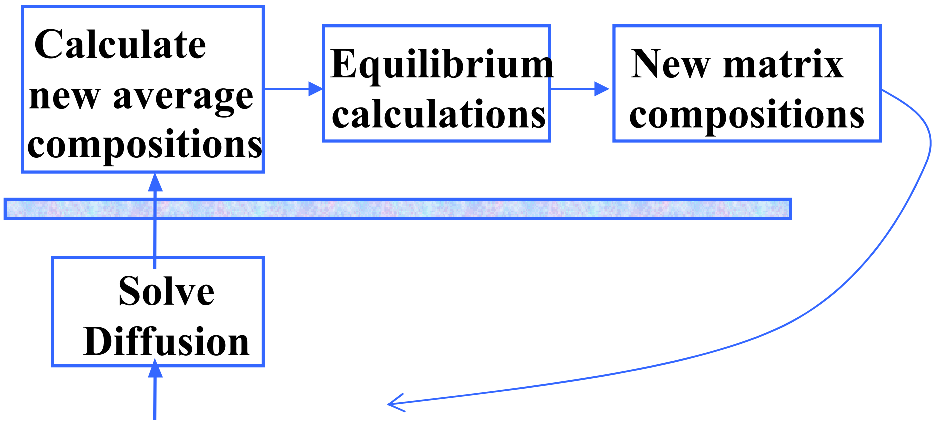
Ni-Al-Cr: Virtual diffusion path in two-phase field
(Engström and Ågren 1996)

Diffusion in dispersed systems with DICTRA

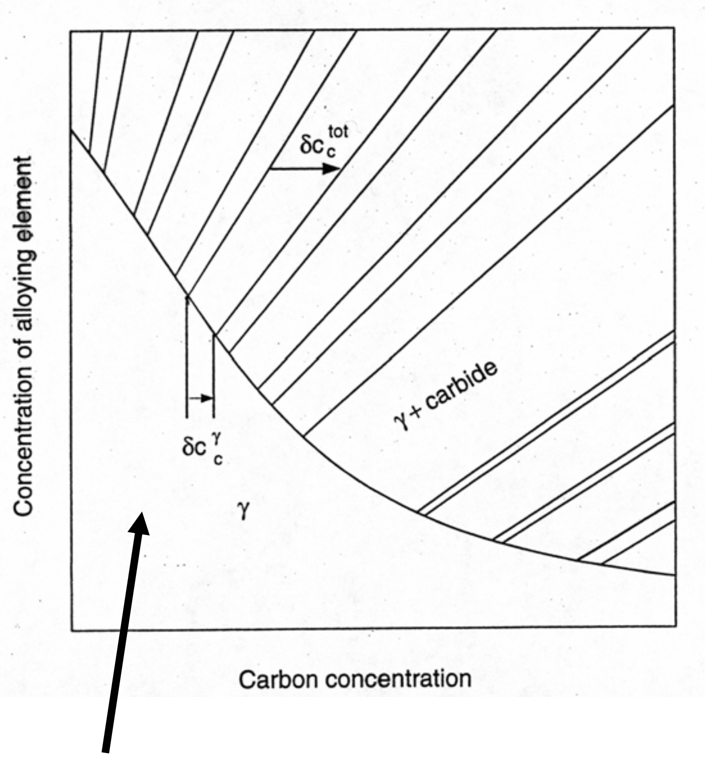
Assumptions:

- Diffusion takes place in the matrix phase only.
- Equilibrium holds locally in each node.





- Carburisation of high-temperature alloys
- Internal oxidation
- Interdiffusion in composite materials
  - coating/substrate systems
  - weldments between steels
  - joints of dissimilar steels
- Gradient sintering of cemented carbide work-tool pices



$$\frac{\partial c_i^\alpha}{\partial c_i^o}$$ Transformation Matrix

(Hopfe and Morral 1994)

One Phase diffusion along x in α :

$$J_k^\alpha = -\sum_{i=1}^{n-1} D_{ki}^{n\alpha} \frac{\partial c_i^\alpha}{\partial x}$$

Equilibrium locally in each volume element ==>

$$c_i^\alpha = c_i^\alpha (c_1^o, c_2^o, c_3^o ... c_{n-1}^o)$$

i.e.

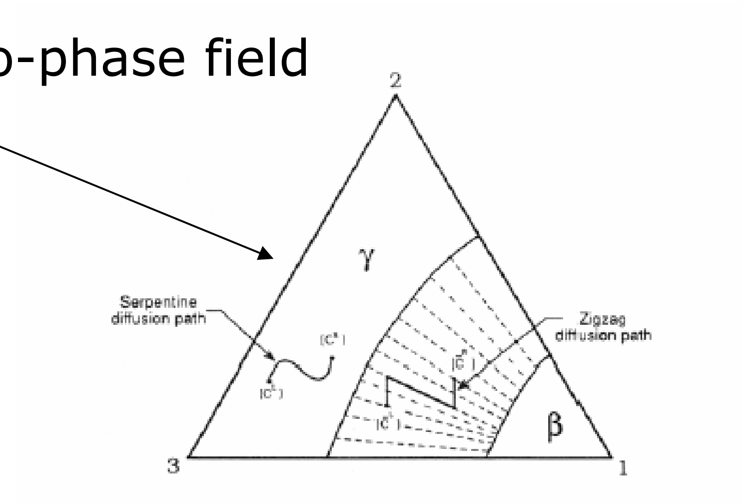
$$\frac{\partial c_i^\alpha}{\partial x} = \sum_{j=1}^{n-1} \frac{\partial c_i^\alpha}{\partial c_j^o} \frac{\partial c_j^o}{\partial x}$$

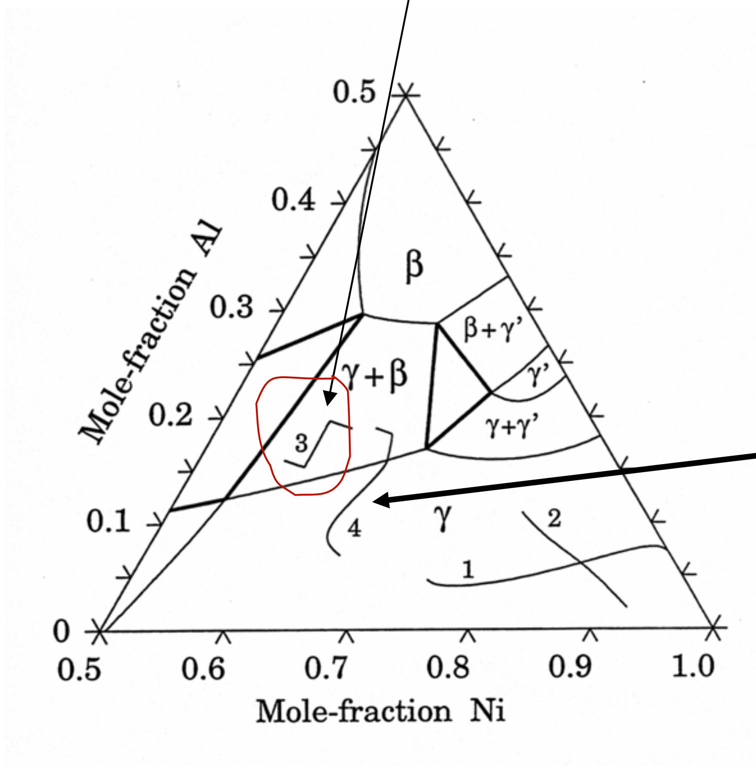
i.e.

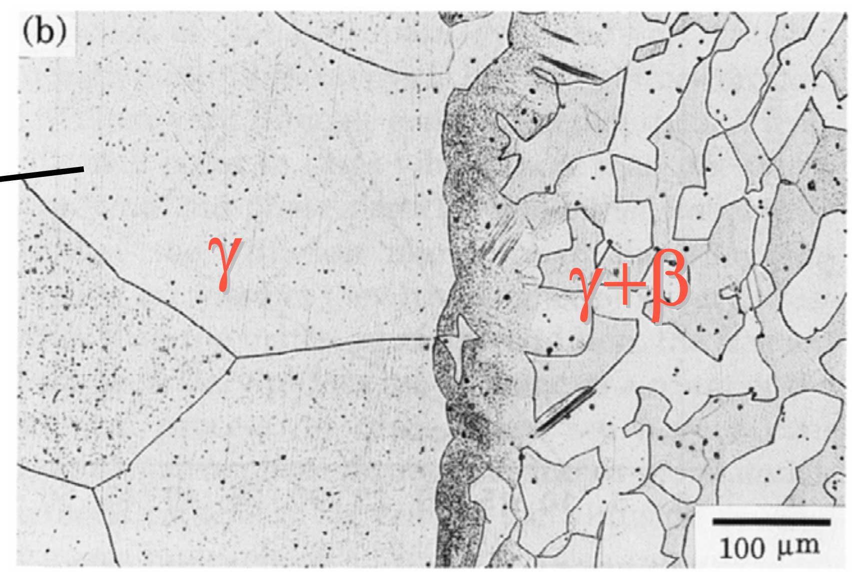
$$J_k^\alpha = -\sum_{j=1}^{n-1} D_{kj}^{n\alpha eff} \frac{\partial c_j^o}{\partial x}$$

$$D_{kj}^{n\alpha eff} = \sum_{i=1}^{n-1} \frac{\partial c_i^\alpha}{\partial c_j^o} D_{ki}^{n\alpha}$$

Zig-Zag diffusion path in two-phase field (Hopfe, Morral et al. 1994)







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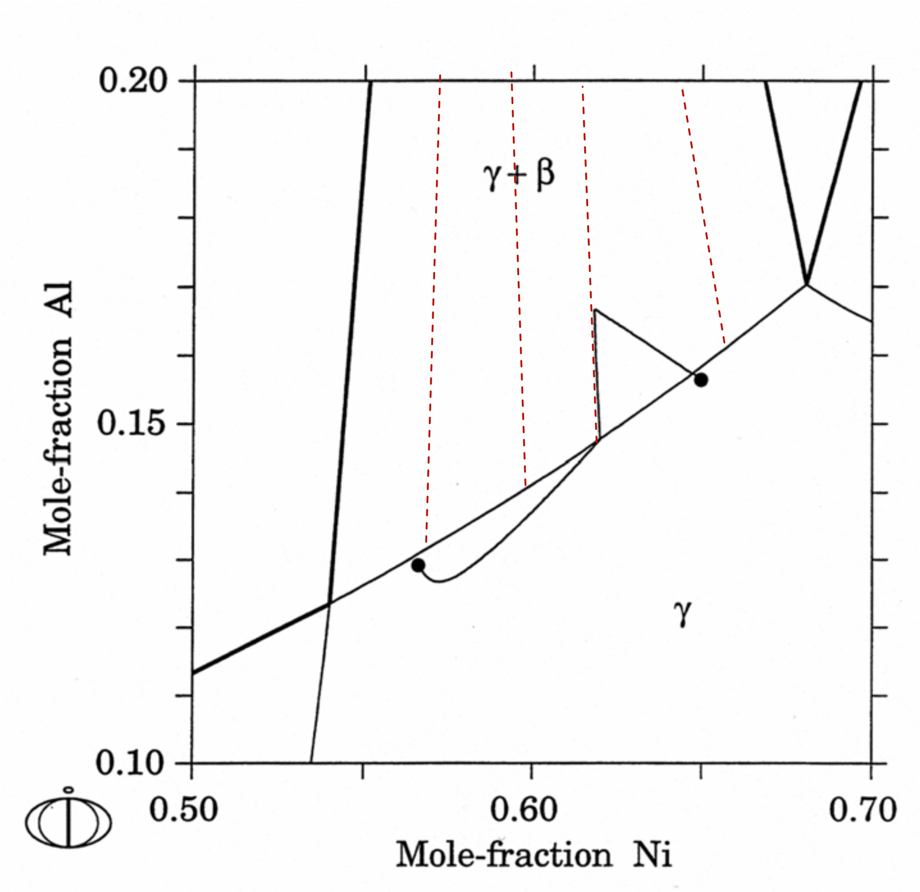
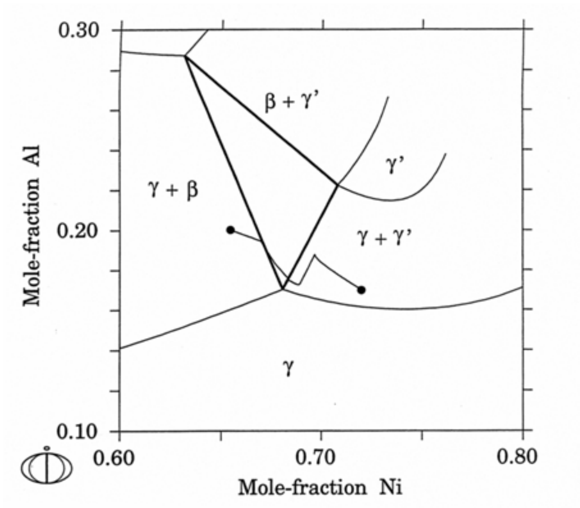
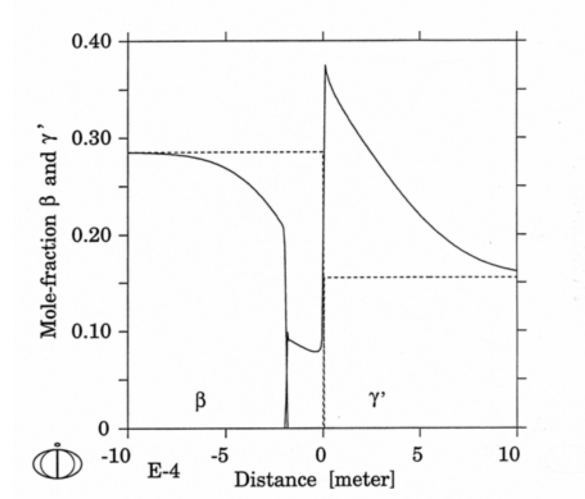
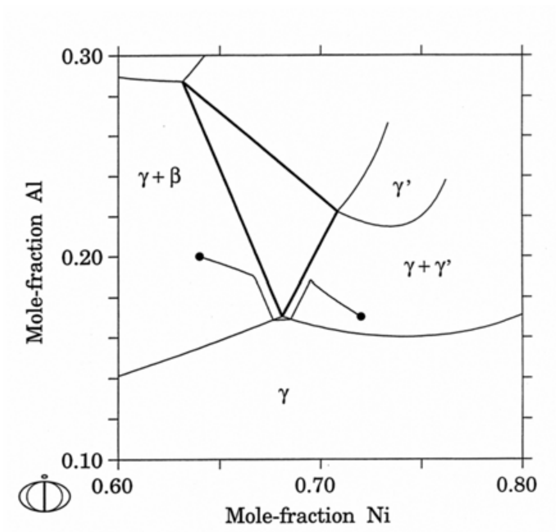
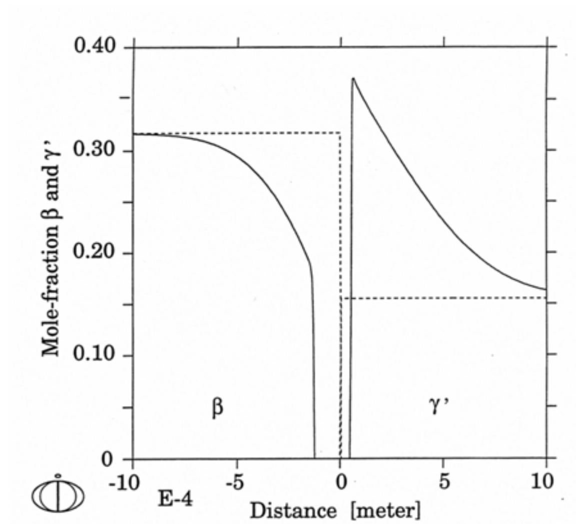


"Real" diffusion path
in two-phase field
Engström and Ågren 1996





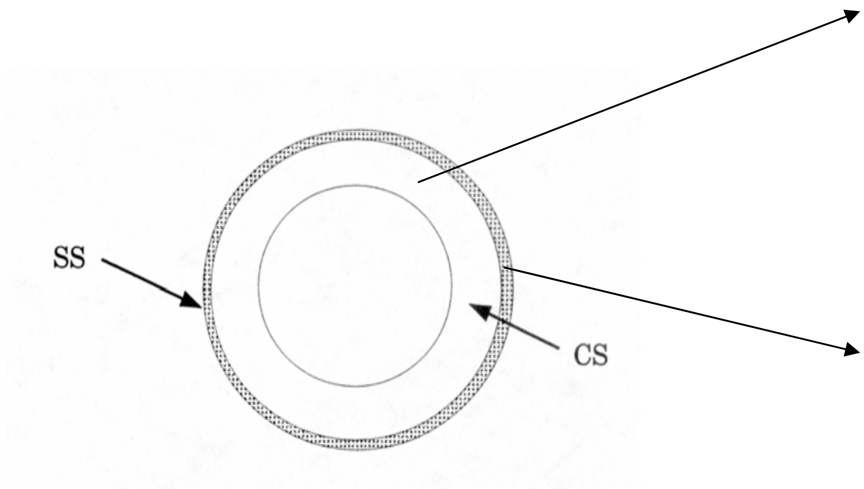


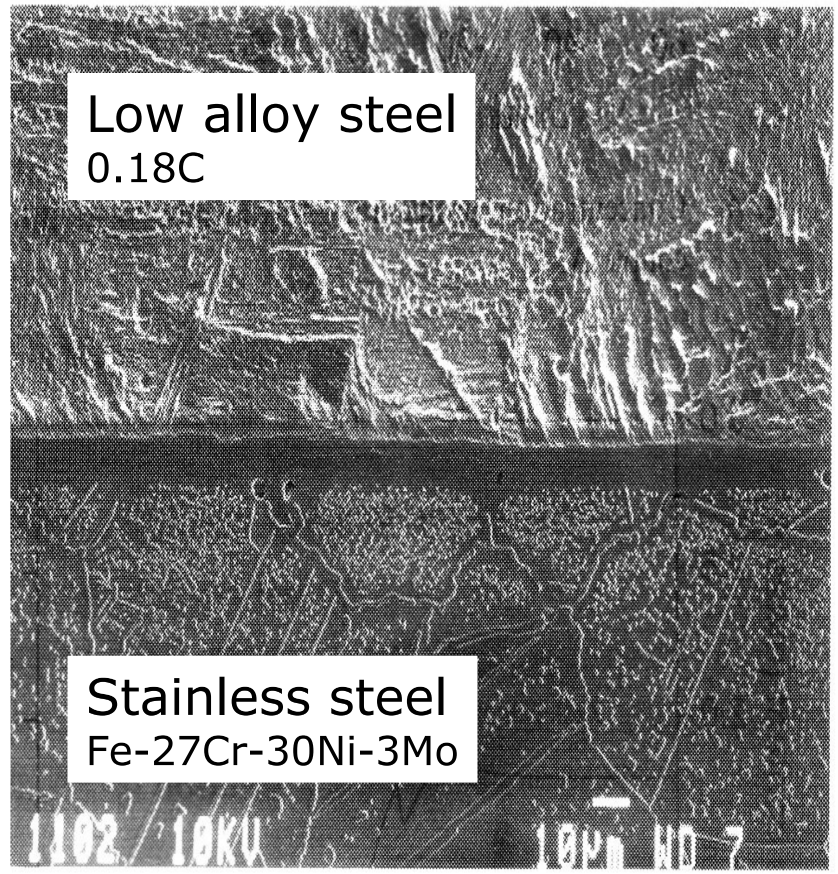


Engström et al. 1996

3. Steel composites
(Helander et al. 1997)

Tube made by coextrusion and then heat treated 1100 °C, 4h.





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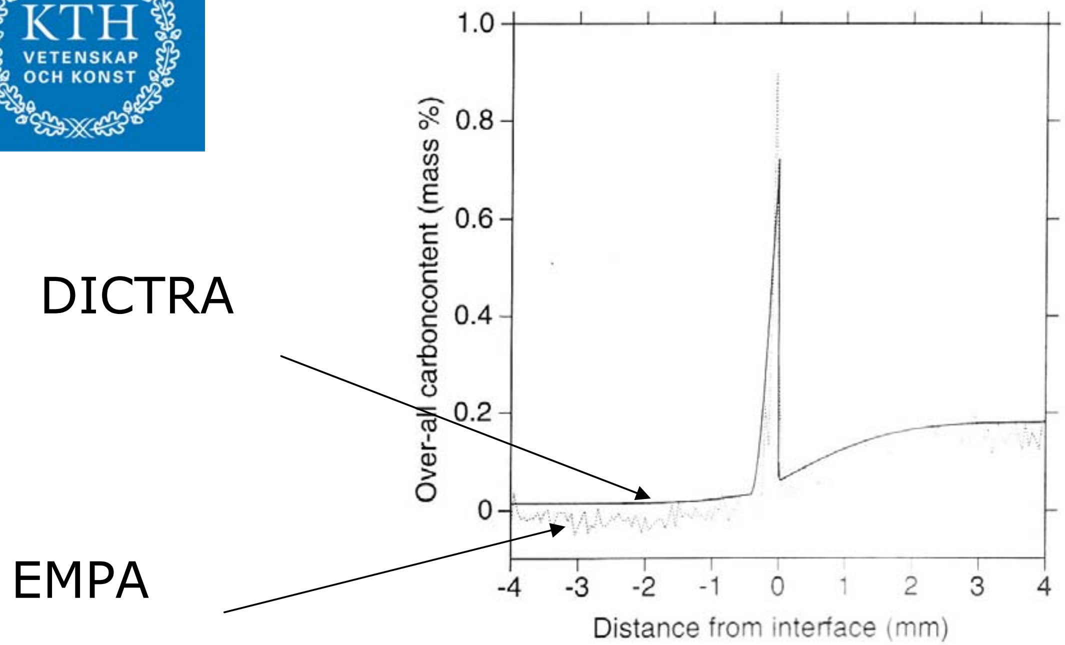

Electron diffraction pattern of particles in stainless steel close to joint: $M_{23}C_6$.

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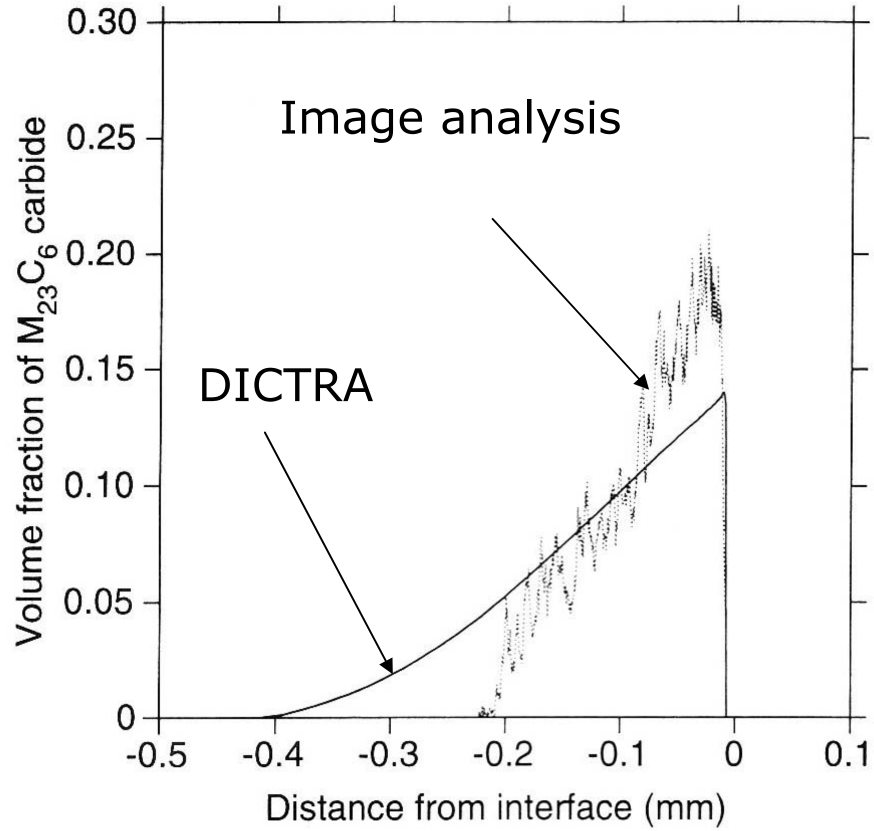


Image analysis
DICTRA
Volume fraction of $M_{23}C_6$ carbide
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
Distance from interface (mm)

4. TBC Bond coats

- The bond coat is the ”buffer” layer between super alloy and the ceramic top coat (usually YSZ).
- Al source to produce TGO layer of Al_2O_3 to protect the metal from oxidation.
- Bond coat is NiAL+...
- One should minimize interdiffusion between bond coat and super alloy.

Issues:

- Diffusion in super-alloy and bond coat
- Diffusion in ordered structures B2, $L1_2$ etc
- Phase equilibria

Diffusion in super alloy Ni–Al–Co–Cr–Hf–Mo–Re–Ta–Ti–W in FCC Campbell et al. 2002

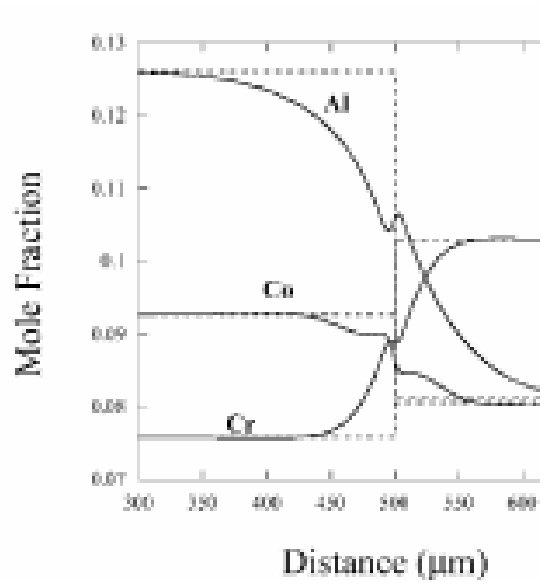
Comparison of calculated and measured diffusion coefficients for Ni–Cr–Co–Mo alloys at 1300 °C

Composition (at. %)				$\tilde{D}^{Ni}_{ij}\left(\frac{m^2}{s}\right)\times 10^{14}$		
Ni	Cr	Co	Mo	Measured	Calculated [29]*	[27]
$\tilde{D}^{Ni}_{CrCr}$						
44.3	24.2	24.1	7.4	7.5±1.5	10.2	10.7
45.3	22.7	24.5	7.4	9.7±1.9	10.1	10.6
46.8	20.8	25.0	7.4	9.9±2.0	9.85	10.3
48.8	18.4	25.6	7.2	10.1±2	9.56	10.0
51.6	15.2	25.8	7.4	8.2±1.6	9.35	9.74
55.6	10.8	26.2	7.4	6.9±1.4	8.95	9.25
58.8	6.4	27.1	7.7	6.4±1.3	8.40	8.59
61.2	3.2	47.9	7.7	6.8±1.4	4.94	5.03
$\tilde{D}^{Ni}_{CoCo}$						
64.9	26.8	1.7	6.6	8.9±1.8	10.3	10.3
62.7	26.5	4.4	6.4	6.0±1.2	9.61	9.78
59.7	26.3	7.4	6.6	4.8±1.0	8.96	9.22
47.2	25.8	19.8	7.1	3.7±0.7	7.01	7.53
45.7	25.8	21.4	7.1	4.2±0.8	6.83	7.58
50.8	25.9	16.2	7.1	3.3±0.7	7.47	7.93
50.4	24.0	24.7	0.9	3.37±0.7	8.83	7.09
$\tilde{D}^{Co}_{NiCr}$						
67.9	22.2	3.7	6.2	−2.0±0.4	−2.26	−4.69
62.0	6.5	23.9	7.6	−1.7±0.3	−2.37	−2.27
$\tilde{D}^{Ni}_{CoCr}$						
48.1	25.5	26.0	0.4	−5.7±1.1	−1.61	−2.08

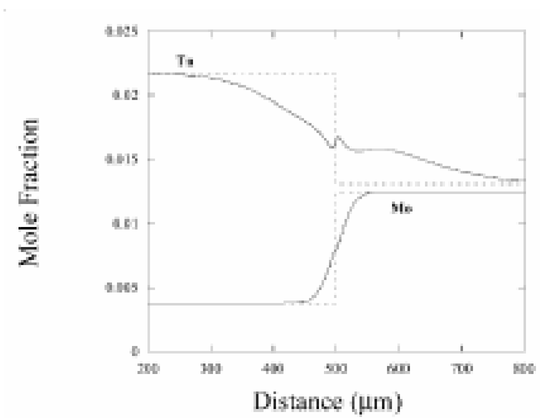
* Indicates which thermodynamic database was used to calculate the diffusivities.

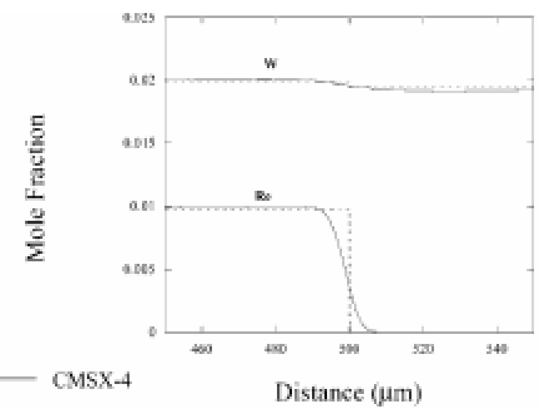
CMSX-4 René-N4

Campbell et al.
2002:
8 component system!



50°h 1050 °C





Diffusion in ordered structures (Helander and Ågren 1999)

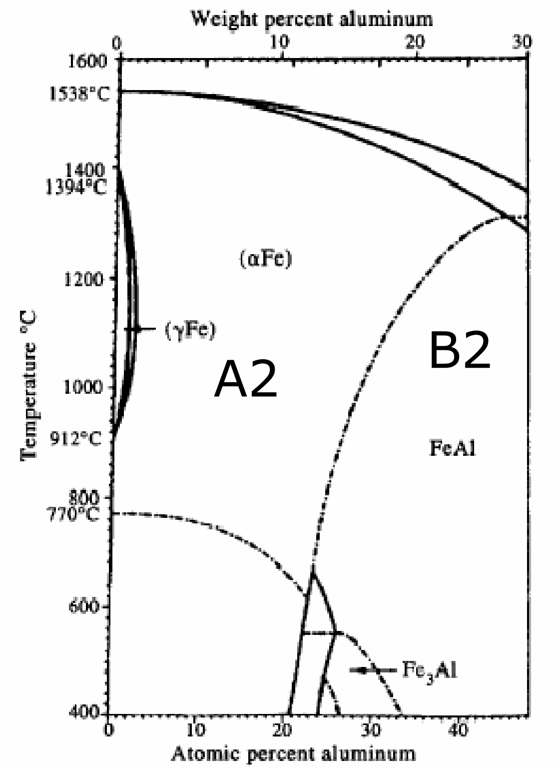
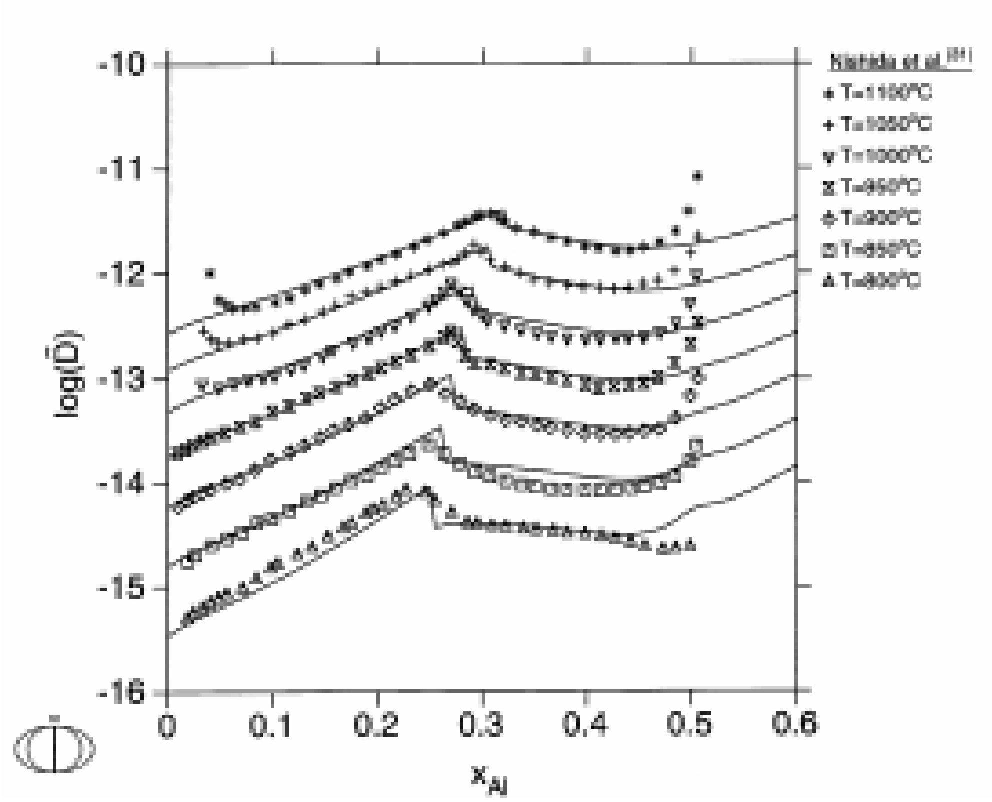
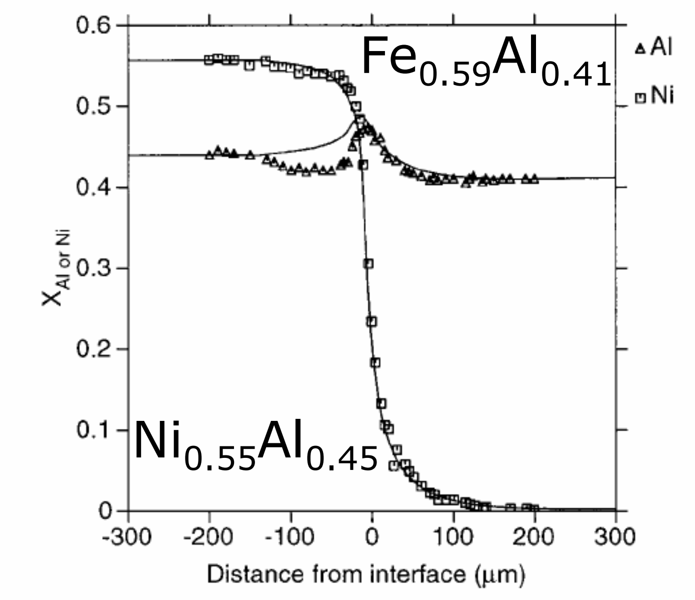


Fig. 1. Fe–Al phase diagram [1].

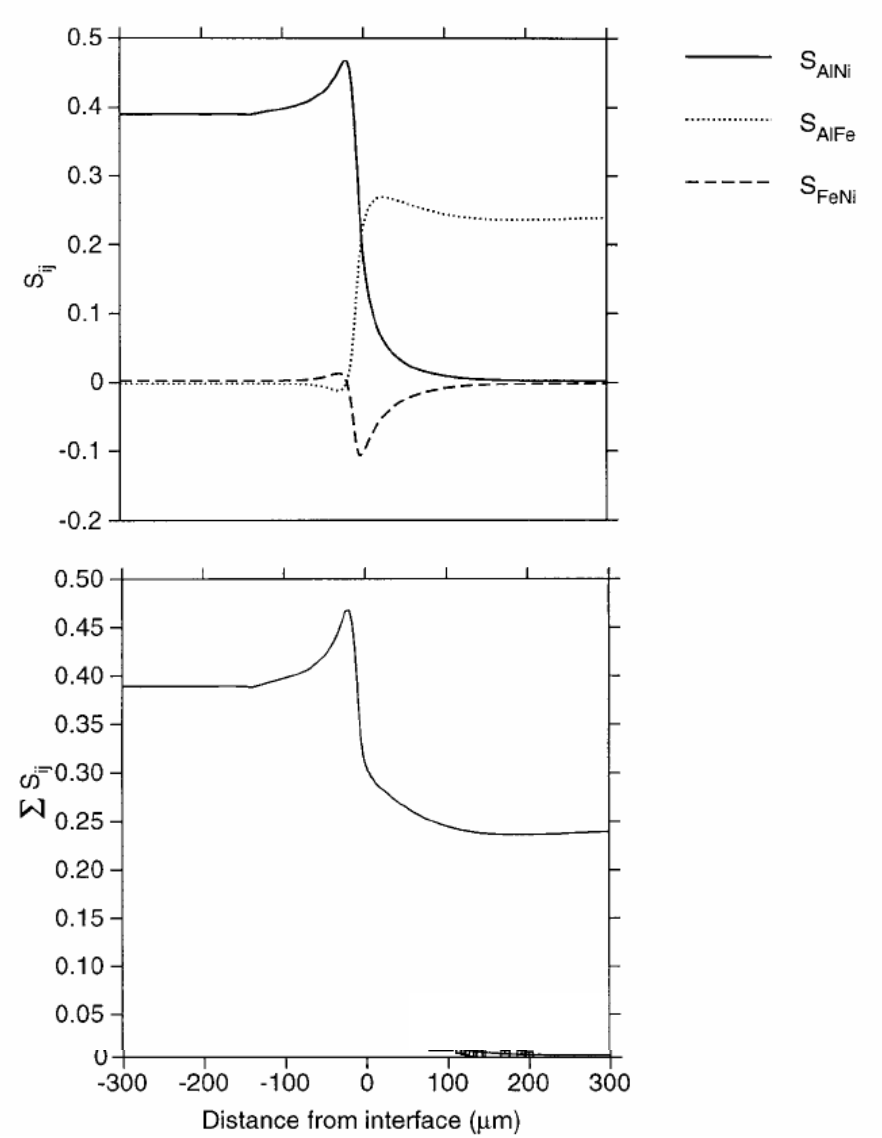


Fe-Al

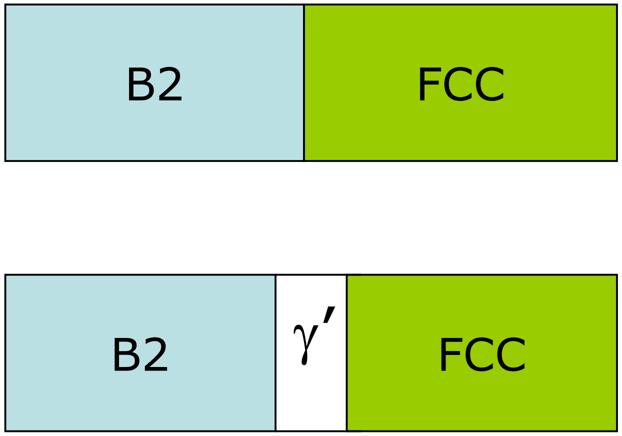
Al-Fe-Ni B2

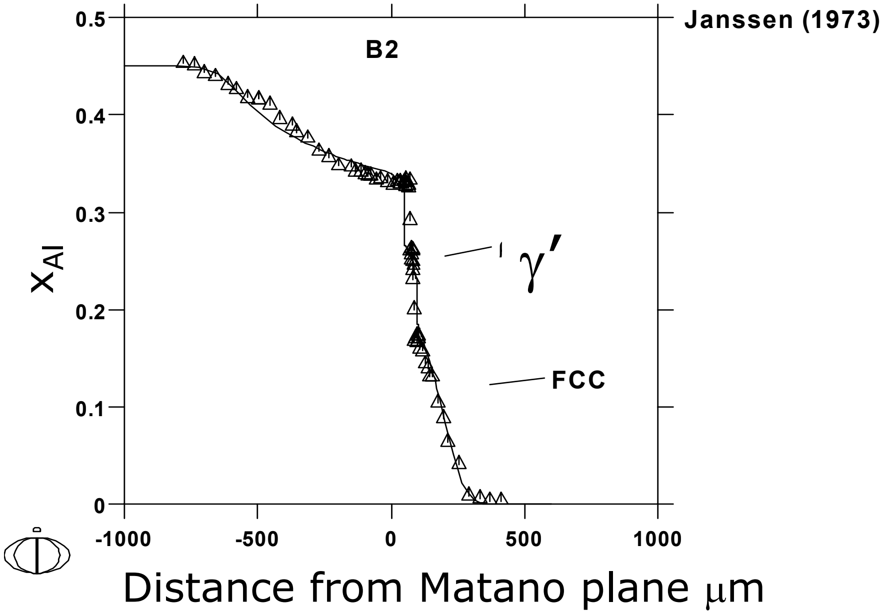


Experiments from Dayananda



AlNi-Ni diffusion couple





Simulations: Helander and Ågren 1999
Experiments: Janssen 1973

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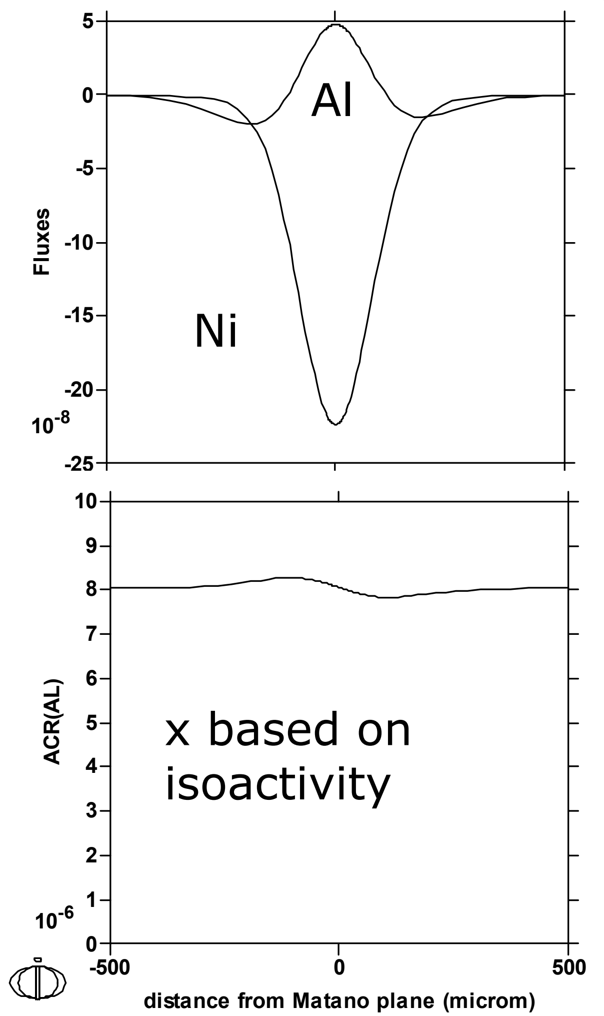
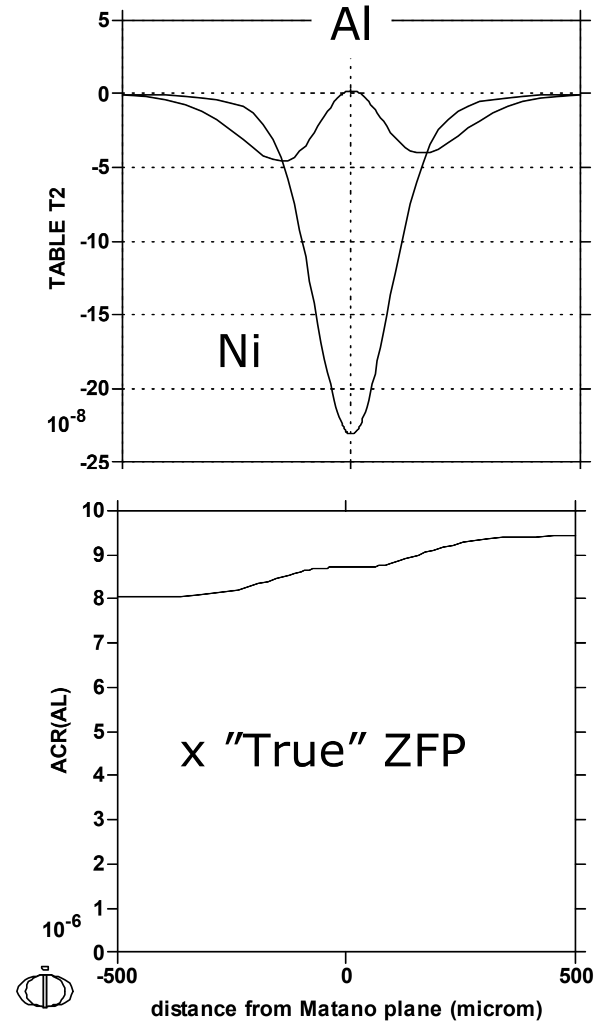
ZFP to minimize interdiffusion in Ni-Al-Cr?

$Ni\text{-}Al_{0.10}Cr_{0.10}$ // $Ni\text{-}Al_xCr_{0.15}$





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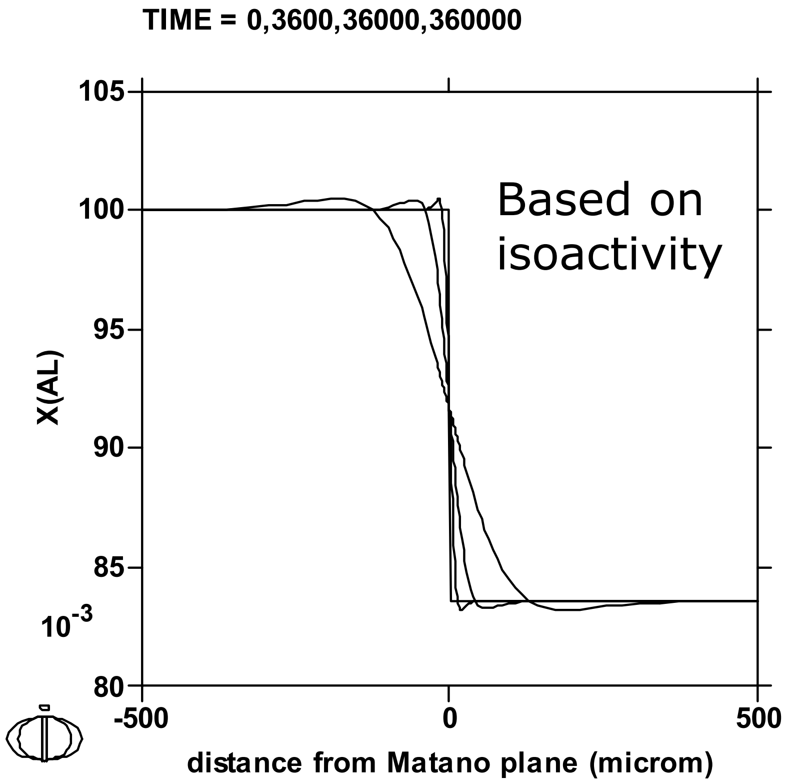

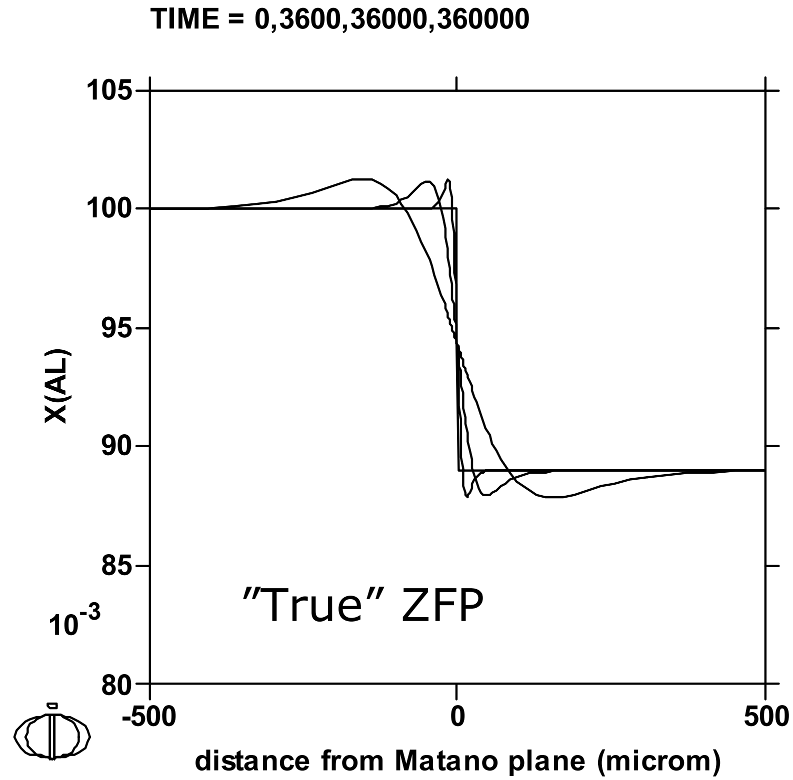

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5. Kirkendall Effect

When diffusion occurs by a vacancy mechanism opposes the net flux of atoms is opposed by a net flux of vacancies (as regarded in a lattice-fixed frame of reference).

$$J'_A + J'_B + ... + J'_{Va} = 0$$

In binary system: Net-flow of atoms:

$$J'_A + J'_B = -(M_B - M_A)\frac{x_A x_B}{V_m}\frac{\partial(\mu_B - \mu_A)}{\partial z}$$

Two extremes of the Kirkendall effect:

Rate of density ($\rho = 1/V_m$) change:

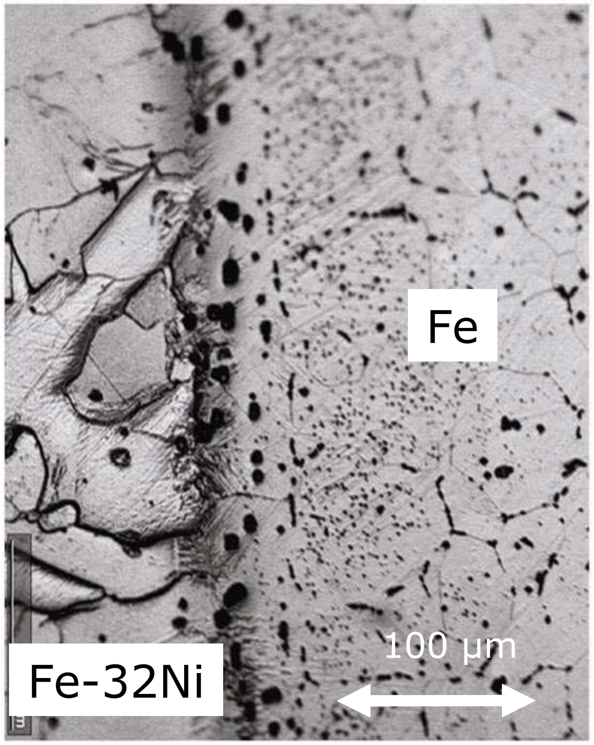
$$-\dot{\rho} = \frac{1}{V_m^{\ 2}}\dot{V}_m = \mathbf{div}(J_A^{'} + J_B^{'})$$

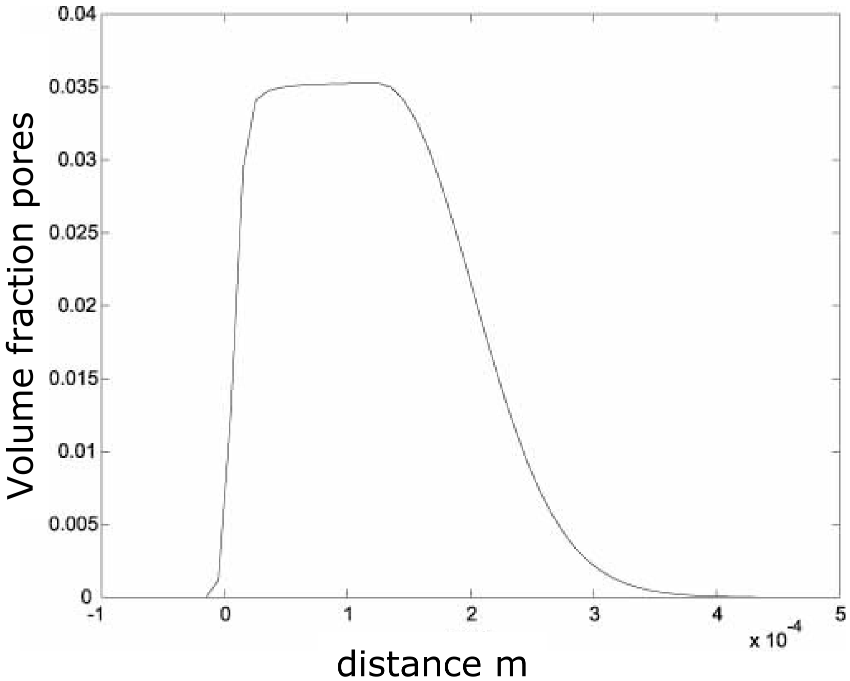
1. No porosity $\Rightarrow$ Strain rate:

$$\dot{\varepsilon}_{11} + \dot{\varepsilon}_{22} + \dot{\varepsilon}_{33} = \frac{1}{V_m}\dot{V}_m = V_m \mathbf{div}(J_A^{'} + J_B^{'})$$

2. Only porosity (volume fraction f_p):

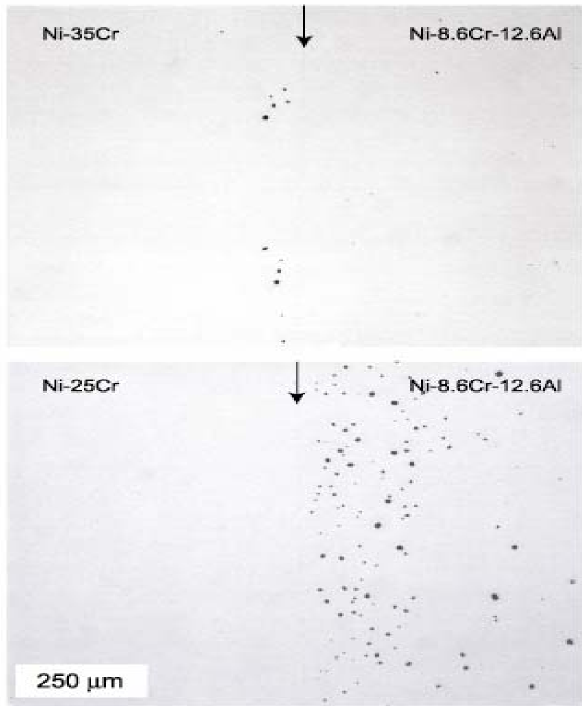
$$\frac{\dot{f}_p}{(1 - f_p)^2} = -V_m \mathbf{div}(J_A^{'} + J_B^{'})$$



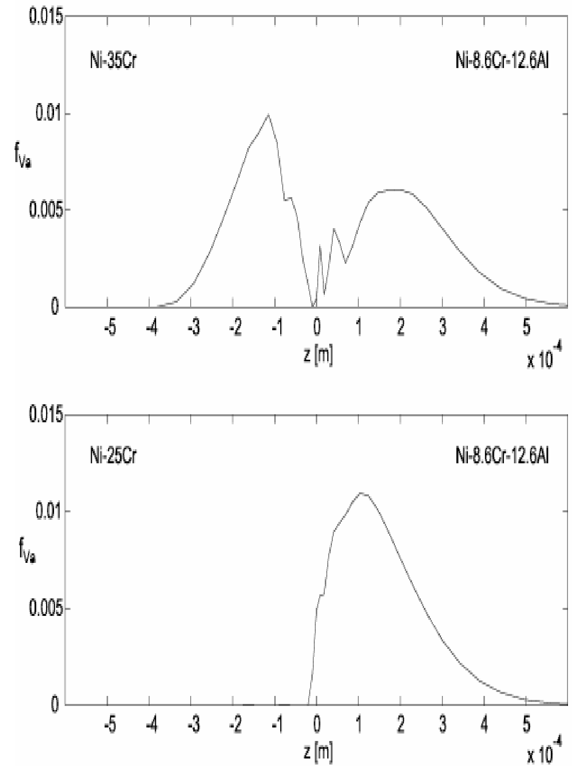


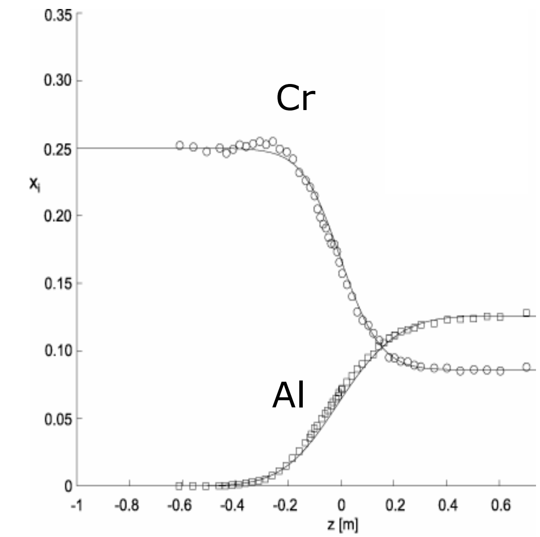
Borgenstam and Hillert 2000 experiments

Strandlund and Larsson 2004 simulations



Nesbitt and Heckel 1987





Strandlund and Larsson, 2004

6. Mobility data

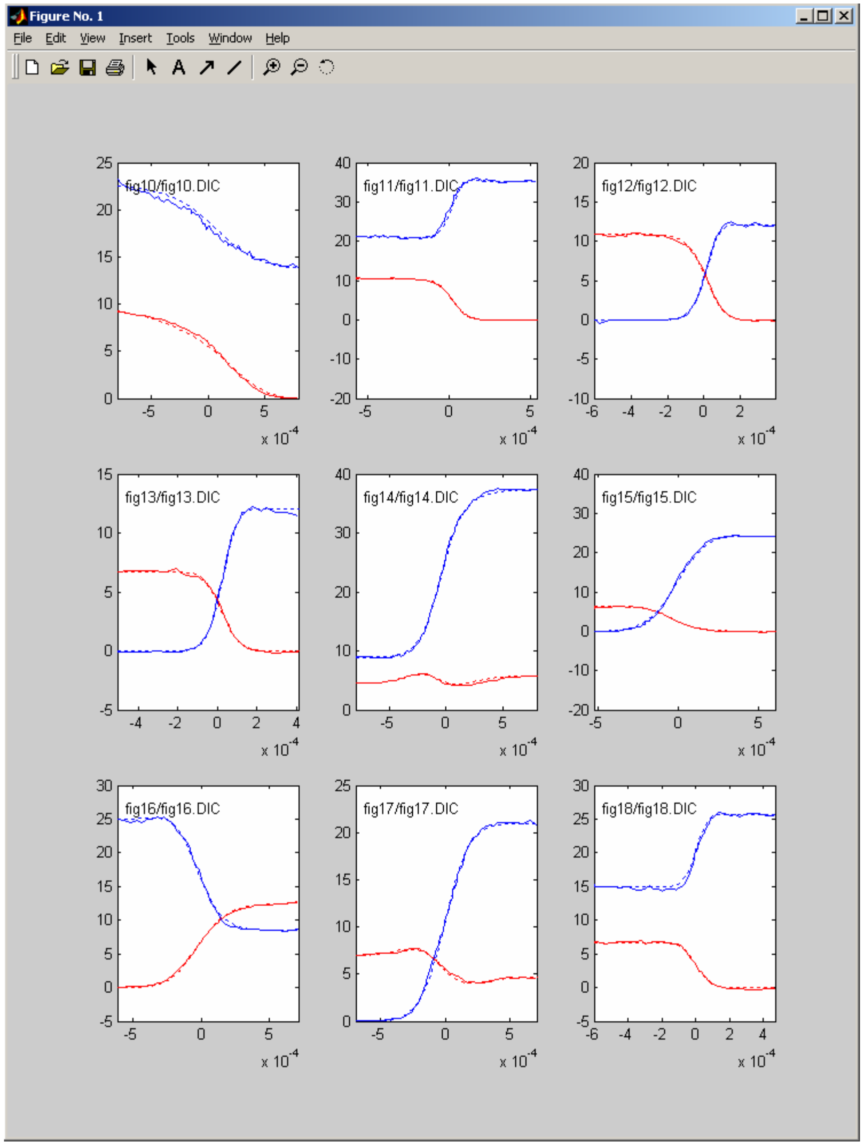
Al-Cr-Ni

Simultaneous optimization directly to concentration profiles in ternary system with 9 different

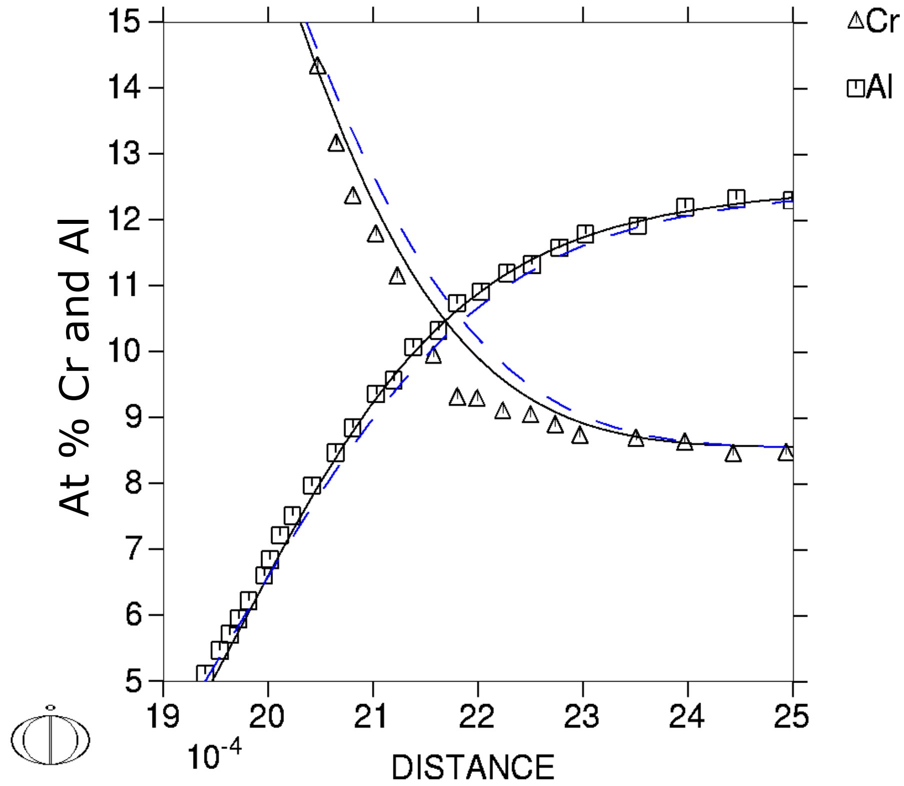
diffusion couples as well as and other pieces of information.

Experimental information from Nesbitt et. al. 1987.

Höglund 2004



Example of fit to data



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Conclusions

- Multicomponent diffusion theory is a valuable tool in engineering design.
- Databases much needed.
- Fundamental issues:
  - Kirkendall effect
  - Thermal migration
  - Electro migration
  - ...