Interdiffusion in Multicomponent Systems

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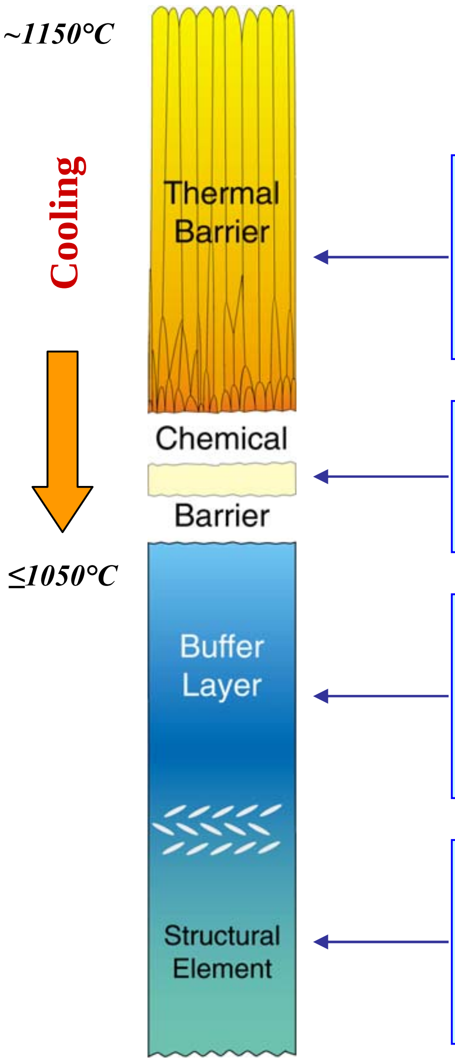
Content

1. Introduction

- Structural changes at elevated temperatures involve changes in composition.
- Such changes require diffusion.
- Thus: Diffusional processes play a major role in
  - Heat treating and processing
  - Degradation at elevated temperatures
  - ...

TBCs: Multi-functionality through Multi-layer Design



Thermal Insulation

- Low conductivity porous oxide with suitable mechanical and chemical integrity: 7YSZ

Oxidation Protection

- Adherent, thermally grown oxide: Alumina

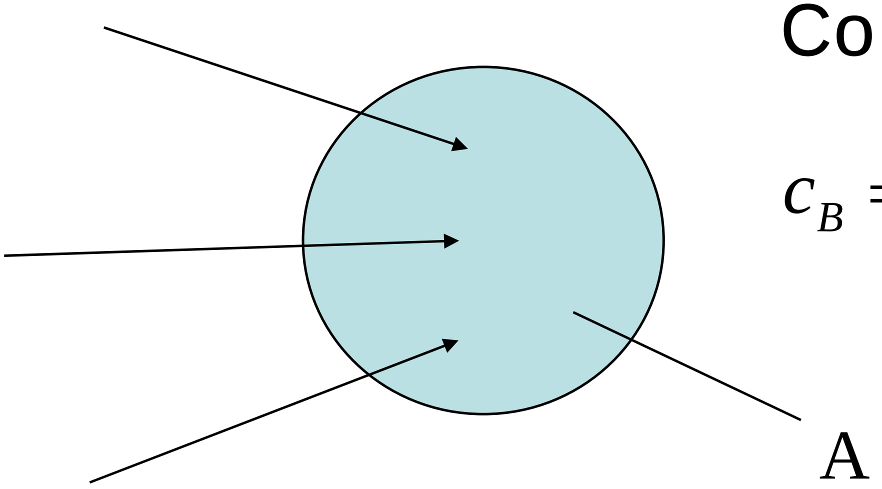
Supply Al to sustain TGO formation

- Surface alloy containing aluminide phases: β (+γ’ or γ)

Load Bearing at High Temperature

- Internally cooled superalloy optimized for structural function

2. Basics



$$\frac{dm_B}{dt}$$

Concentration:

$$c_B = \frac{m_B}{V} = \frac{x_B}{V_m} = mole/volume$$

Flux:

$$J_B = \frac{d\ m_B}{dt}\frac{1}{A} = mole/area/time$$

Fick´s (first) law:

$$J_B = -D_B \frac{\partial\ c_B}{\partial\ z} \cong -D_B \frac{1}{V_m}\frac{\partial\ x_B}{\partial\ z}$$

The value of the flux depends on frame of reference:

- Crystal lattice (lattice-fixed frame of reference)

  In a binary system *A* – *B* we can evaluate J_A and J_B.
- Net flow of atoms: $J_{tot} = J_A + J_B \neq 0$

Fick´s (first) law

$$J_A = -D_A \frac{\partial c_A}{\partial z}$$

$$J_B = -D_B \frac{\partial c_B}{\partial z}$$

Usually we prefer to write:

$$J_A = -D_{AB}^{A} \frac{\partial c_B}{\partial z}$$

$$J_B = -D_{BB}^{A} \frac{\partial c_B}{\partial z}$$

A is the dependent concentration variable

$$J_A = -D_{AB}^{A} \frac{\partial c_B}{\partial z}$$

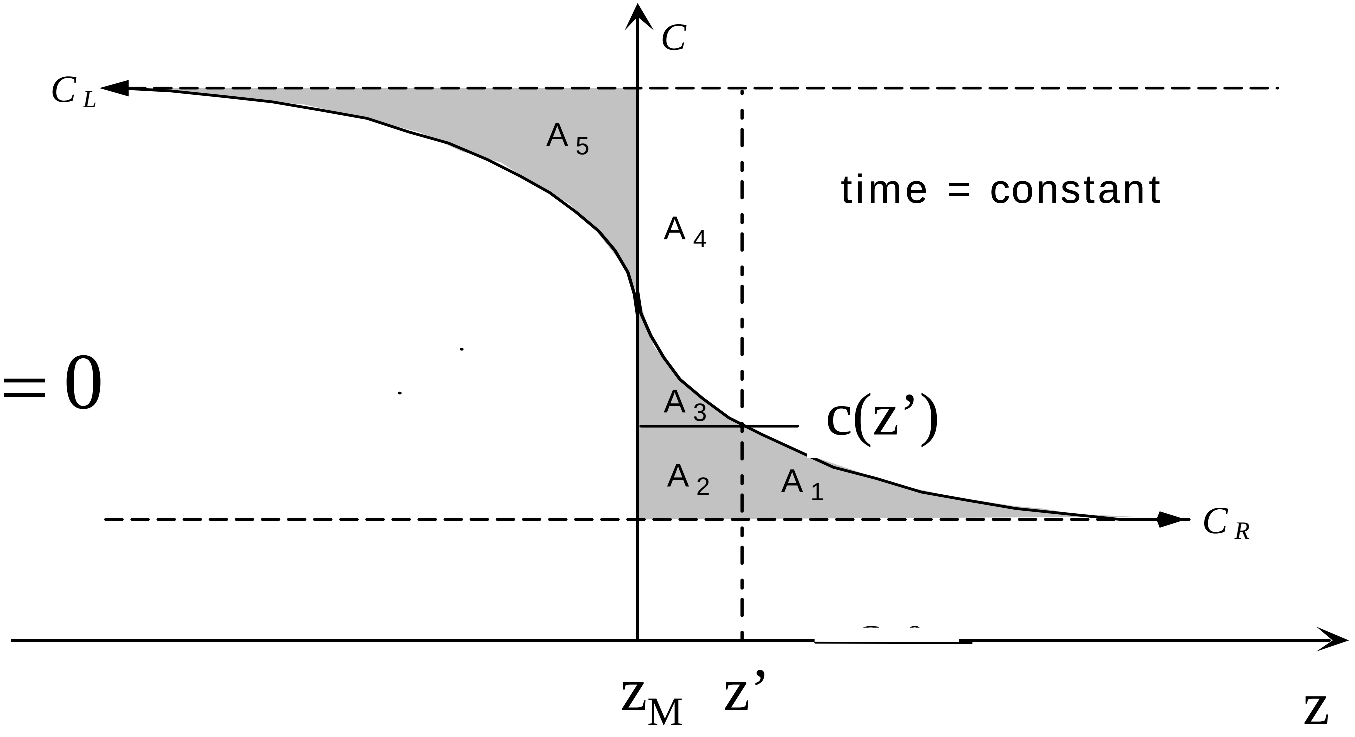
Flux of *A*

Concentration gradient of *B*

Interdiffusion (mixing of *A* and *B*)

Matano's Interface

$$\int_{c_L}^{c_R} (z - z_M)\,dc = 0$$



"Matano Interface" at z_M

Boltzmann–Matano geometry for a diffusion couple

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It appears as *A* and *B* only exchange places.

$J_A = -J_B$ or $J_{tot} = J_A + J_B = 0$

No net flow of atoms in this frame of reference:

Number-fixed frame of reference.

Fick's first law:

$$-J_A = -\left(-D_{AB}^{A} \frac{\partial c_B}{\partial z}\right) = J_B = -D_{BB}^{A} \frac{\partial c_B}{\partial z}$$

$$\Rightarrow D_{AB}^{A} = -D_{BB}^{A} = \tilde{D}_{AB}$$

Only one diffusion coefficient:

chemical diffusion coefficient

interdiffusion coefficient

...

Transformation from lattice-fixed to number-fixed:

Suppose J_A' and J_B' given in lattice-fixed frame of reference.

Transformation to number-fixed frame of reference:

$$J_A = J_A' - x_A J_{tot}'$$

$$J_B = J_B' - x_B J_{tot}'$$

$$-------------$$

$$J_A + J_B = J_A' + J_B' - (x_A + x_B) J_{tot}'$$

where

$$J_{tot}' = J_A' + J_B'$$

$$x_A + x_B = 1 \Rightarrow J_A + J_B = 0$$

We thus find:

$$D_{AB}^{A} = D_{AB}^{A}{}' - x_A (D_{AB}^{A}{}' + D_{BB}^{A}{}')$$

$$= (1 - x_A) D_{AB}^{A}{}' - x_A D_{BB}^{A}$$

$$D_{BB}^{A} = D_{BB}^{A}{}' - x_B (D_{AB}^{A}{}' + D_{BB}^{A}{}')$$

$$= (1 - x_B) D_{BB}^{A}{}' - x_B D_{AB}^{A}$$

Observe that we have:

$D_B = D_{BB}^{A}$ and $D_A = -D_{AB}^{A} \Rightarrow$

$$(1 - x_B) D_B{}' + x_B D_A{}' = \tilde{D}_{AB}$$

The *D*´ coefficients are called individual diffusion coefficients.

Change of dependent concentration variable: Binary system *A - B*

$$c_A = x_A / V_m \quad c_B = x_B / V_m \quad V_m \cong \text{const}$$

$$x_A + x_B = 1, \quad \partial x_A / \partial z = -\partial x_B / \partial z$$

$$J_A = -\frac{D_{AA}^B}{V_m}\frac{\partial x_A}{\partial z} = -\frac{D_{AA}^B}{V_m}\left(-\frac{\partial x_B}{\partial z}\right) = -\frac{D_{AB}^A}{V_m}\frac{\partial x_B}{\partial z}, \quad \text{etc}$$

$$D_{AB}^A = -D_{AA}^B$$

$$D_{BB}^A = -D_{BA}^B$$

$$D_{AA}^A = D_{BA}^A = D_{AB}^B = D_{BB}^B = 0$$

Diffusion coefficients and dependent concentration binary systems Fick´s law :

x_A dependent variable	x_B dependent variable	relations
$J_B = -\frac{D_{BB}^A}{V_m}\frac{\partial x_B}{\partial z}$	$J_B = -\frac{D_{BA}^B}{V_m}\frac{\partial x_A}{\partial z}$	$D_{BB}^A = -D_{BA}^B$
$J_A = -\frac{D_{AB}^A}{V_m}\frac{\partial x_B}{\partial z}$	$J_A = -\frac{D_{AA}^B}{V_m}\frac{\partial x_A}{\partial z}$	$D_{AB}^A = -D_{AA}^B$

$$D_{AA}^A = D_{BA}^A = D_{AB}^B = D_{BB}^B = 0$$

Chemical potential and force

All (conservative) potentials ϕ have the property that: Force $= -\mathbf{grad}\,\phi$

For chemical potential

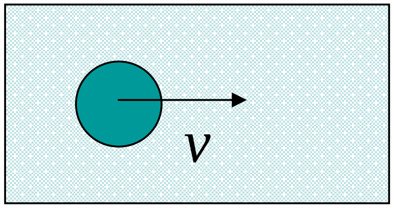
$$\mu_B = f(c_B)$$

$$\frac{\partial \mu_B}{\partial z} = \frac{d\mu_B}{dc_B}\frac{\partial c_B}{\partial z}$$

Fick's law may be written:

$$J_B = -D_B\frac{\partial c_B}{\partial z} = -\left(D_B / \frac{d\mu_B}{dc_B}\right)\frac{\partial \mu_B}{\partial z} = -L_{BB}\frac{\partial \mu_B}{\partial z}$$

Motion in system with friction:



Force

$$v_B = \boxed{M_B} F_B = -M_B \frac{\partial \mu_B}{\partial z}, \qquad J_B = c_B v_B$$

Mobility

$$J_B = -c_B M_B \frac{\partial \mu_B}{\partial z} = -c_B M_B \frac{d\mu_B}{dc_B} \frac{\partial c_B}{\partial z} = -D_B \frac{\partial c_B}{\partial z}$$

$$D_B = c_B M_B \boxed{\frac{d\mu_B}{dc_B}}$$

Thermodynamic factor

Relation between mobility and diffusivity binary system A-B

$$J_A = -M_A \frac{x_A}{V_m} \frac{\partial \mu_A}{\partial z}$$

$$J_B = -M_B \frac{x_B}{V_m} \frac{\partial \mu_B}{\partial z}$$

$$D_{AB}^{A} = M_A x_A \frac{d\mu_A}{dx_B}$$

$$D_{BB}^{A} = M_B x_B \frac{d\mu_B}{dx_B}$$

$\frac{d\mu_A}{dx_B}$ and $\frac{d\mu_B}{dx_B}$ are proportional to $\frac{d^2 G_m}{dx_B{}^2}$

Ideal solution or dilute solution:

$$\mu_B = {}^{\circ}\mu_B + RT\ln\left(x_B\right) + L_{AB}(1-x_B)^2 \approx {}^{\circ}\mu_B + RT\ln\left(x_B\right) + L_{AB}$$

$$\frac{d\mu_B}{dx_B} = RT / x_B \quad \Rightarrow \quad D_{BB}^{A} = RTM_B$$

Radioactive isotopes ”tracers” added in very low amounts fullfill this condition.

$$M_B = D_B^* / RT$$

Tracer diffusion coefficients give approximately mobilities to be used also when there is a driving force.

Summary - basics

- Fick's first law
- Value of flux depends on frame of reference – different diffusion coefficients
  - Lattice-fixed frame – individual
  - Number-fixed frame – chemical, interdiffusion
- Gradient in chemical potential a force to move species
- Relation between diffusion coefficient, mobility and thermodynamics
- $RT\,M = D^*$

3. Multicomponent systems and coupling effects

Main difference compared to binary systems:
diffusion is coupled due to several reasons

Lars Onsager
Nobel prize in Chemistry 1968

$$J_k = -D_k \frac{\partial c_k}{\partial z}$$

Works in dilute solution but not in general.

$$J_k = -\sum D_{kj} \frac{\partial c_j}{\partial z}$$

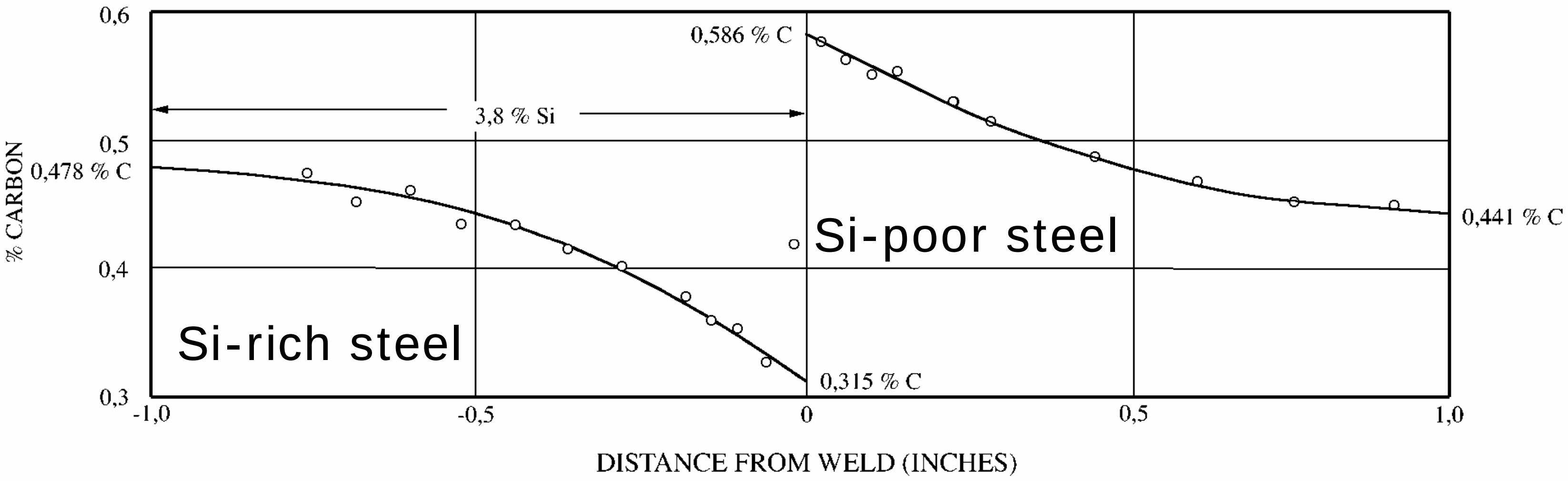
Coupled diffusion.

Reason for coupling effects

- Thermodynamic interactions
- Frame of reference
- Correlation effects

Coupling due to thermodynamic interactions

Example:Fe-Si-C ”Darken effect”



$$J_C = -D_{CC}\frac{\partial c_C}{\partial z} - D_{CSi}\frac{\partial c_{Si}}{\partial z}$$

Ternary system Fe-Si-C:

$$\left.\begin{aligned} J_C &= -M_C c_C \frac{\partial \mu_C}{\partial z} \\ \mu_C &= f(c_C, c_{Si}) \end{aligned}\right\}$$

$$J_C = -M_C c_C \left\{ \frac{\partial \mu_C}{\partial c_C} \frac{\partial c_C}{\partial z} + \frac{\partial \mu_{Si}}{\partial c_{Si}} \frac{\partial c_{Si}}{\partial z} \right\} \Rightarrow$$

$$J_C = -D_{CC} \frac{\partial c_B}{\partial z} - D_{CSi} \frac{\partial c_C}{\partial z}$$

Thermodynamic interactions predict coupling!

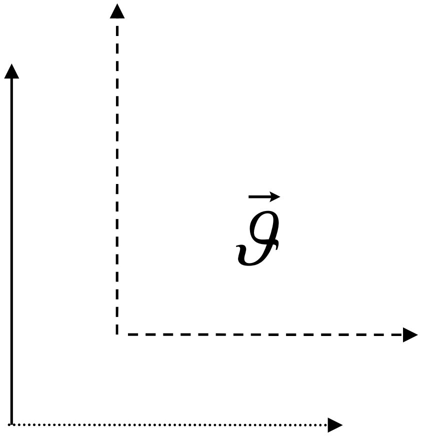
Relation between mobility and diffusivity
Ternary system A-B-C

$J_A = -M_A \frac{x_A}{V_m} \frac{\partial \mu_A}{\partial z}$	$D_{AB}^{A} = M_A x_A \frac{\partial \mu_A}{\partial x_B}$	$D_{AC}^{A} = M_A x_A \frac{\partial \mu_A}{\partial x_C}$
$J_B = -M_B \frac{x_B}{V_m} \frac{\partial \mu_B}{\partial z}$	$D_{BB}^{A} = M_B x_B \frac{\partial \mu_B}{\partial x_B}$	$D_{BC}^{A} = M_B x_B \frac{\partial \mu_B}{\partial x_C}$
$J_C = -M_C \frac{x_C}{V_m} \frac{\partial \mu_C}{\partial z}$	$D_{CB}^{A} = M_C x_C \frac{\partial \mu_C}{\partial x_B}$	$D_{CC}^{A} = M_C x_C \frac{\partial \mu_C}{\partial x_C}$

Coupling due to Frame of Reference

Measure flux relative lattice - lattice fixed frame

Change to number-fixed frame:



$$J_k = J_k' - \frac{\vartheta}{V_m} x_k$$

Defined by: $$\sum_{k=1}^{n} J_k = 0$$

$$J_k = J_k' - x_k \sum_{i=1}^{n} J_i' = \sum_{i=1}^{n} (\delta_{ik} - x_k) J_i'$$

$$1 = \sum_{i=1}^{n} x_i$$

Number fixed frame of reference:

$$J_B = -x_A J_A' + (1 - x_B) J_B' - x_C J_C' \ldots$$

I.e. the flux of B will depend on the flux of A and C!

Coupling in one frame of reference but not in another.

Coupling due to correlation effects

- If the diffusive jumps are not independent but jumps correlated.
  - Tracer diffusion jumps are uncorrelated
  - Diffusion in chemical potential gradients jumps correlated – vacancy wind.
- Small effect – difficult to estimate.

Onsager's generalization of coupling effects:

$$J_k = -M_k \frac{x_k}{V_m} \frac{\partial \mu_k}{\partial z}$$

Assume generally:

$$J_k = \sum L_{ki} F_i$$

where

$F_i = -\nabla(\mu_i / T)$ and $F_Q / T = \nabla(1/T)$

Classical examples of cross effects

$$J_k = \sum L_{ki} F_i$$

Flux **Force**	**Heat**	**Electric**	**Diffusion**
Temperature gradient	Fourier	Seebeck	Soret Thermal migration
Voltage	Peltier	Ohm	Electro migration
Chemical potential gradient	Dufour	Volta (galvanic cell)	Fick

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Vector-matrix notation

$$\mathbf{J} = \begin{pmatrix} J_A \\ J_B \\ J_C \end{pmatrix} \qquad \mathbf{F} = \begin{pmatrix} \frac{\partial \mu_\mathbf{A}}{\partial z} \\ \frac{\partial \mu_B}{\partial z} \\ \frac{\partial \mu_C}{\partial z} \end{pmatrix} \qquad \mathbf{J}^\mathbf{T} = \begin{pmatrix} J_A & J_B & J_C \end{pmatrix} \ldots$$

$$\mathbf{D} = \begin{pmatrix} D_{AA} & D_{AB} & D_{AC} \\ D_{BA} & D_{BB} & D_{BC} \\ D_{CA} & D_{CB} & D_{CC} \end{pmatrix}$$

Fick's law may then be written:

$$\mathbf{J} = -\mathbf{D}\,\mathbf{grad\,c}$$

$$\mathbf{grad\,c} = \begin{pmatrix} \dfrac{\partial c_{\mathbf{A}}}{\partial z} \\ \dfrac{\partial c_B}{\partial z} \\ \dfrac{\partial c_C}{\partial z} \end{pmatrix} \quad \text{and} \quad \mathbf{D} = \begin{pmatrix} 0 & D_{AB}^{A} & D_{AC}^{A} \\ 0 & D_{BB}^{A} & D_{BC}^{A} \\ 0 & D_{CB}^{A} & D_{CC}^{A} \end{pmatrix}$$

and c_A is chosen as dependent concentration.

Change in frame of reference

$$J_k = J_k' - x_k \sum_{i=1}^{n} J_i' = \sum_{i=1}^{n} (\delta_{ik} - x_k) J_i'$$

may be written:

$$\mathbf{J} = \mathbf{A}\mathbf{J}'$$

$$\mathbf{A} = \begin{pmatrix} 1 - x_A & -x_A & -x_A \\ -x_B & 1 - x_B & -x_B \\ -x_C & -x_C & 1 - x_C \end{pmatrix}$$

det $\mathbf{A} = 0$

The new fluxes are dependent (as they should).

But some information has been lost!

Another interesting choice of processes

Suppose we do want to change the number of independent processes. We may then consider the processes inter-diffusion and net flow of atoms

$$J_B = -x_B J_A' + (1-x_B) J_B' - x_B J_C'$$

$$J_C = -x_C J_A' - x_B J_B' + (1-x_B) J_C'$$

$$J_{tot} = J_A' + J_B' + J_C'$$

$$\mathbf{J} = \begin{pmatrix} J_B \\ J_C \\ J_{tot} \end{pmatrix} \qquad \mathbf{A} = \begin{pmatrix} -x_B & 1-x_B & -x_B \\ -x_C & -x_C & 1-x_C \\ 1 & 1 & 1 \end{pmatrix}$$

$$\det \mathbf{A} \neq 0$$

Entropy production

Entropy production $= \sum J_i F_i = \mathbf{J}^{\mathbf{T}}\mathbf{F}$

A general expression coming from an entropy balance if the forces are properly chosen, i.e according to the combined first and second law of thermodynamics:

$$TdS = dU - VdP - \sum n_i d\mu_i$$

Onsager reciprocal relations

The fluxes J_k are linear function of n independent driving forces F_i (gradients in thermodynamic potentials):

$$J_k = \sum L_{ki} F_i \quad \Leftrightarrow \quad \mathbf{J} = \mathbf{LF}$$

If the entropy production is given by $\sum J_i F_i$ $\Leftrightarrow \mathbf{J}^{\mathrm{T}}\mathbf{F}$ then $L_{ki} = L_{ik} \Leftrightarrow \quad \mathbf{L} = \mathbf{L}^{\mathrm{T}}$

The reciprocal relations have been controversial but seem accepted.

- The relations are claimed to be very useful because:
  - Consistency check of experimental data.
  - More efficient use of experimental data.
- But: Are they true?
- If they are true, are they trivial? Do they lead to any consequences?
- Perhaps they are true but physically meaningless?

Support of reciprocal relations:

If they are valid in one frame of reference they are valid in all provided that fluxes and forces are transformed according to (leaving entropy production invariant):

$$\mathbf{J}' = \mathbf{A}\mathbf{J}$$

$$\mathbf{F}' = (\mathbf{A}^{\mathrm{T}})^{-1}\mathbf{F}$$

$$\mathbf{L}' = \mathbf{A}\mathbf{L}\mathbf{A}^{\mathrm{T}}$$

If there is a frame of reference where the processes are independent all coupling coefficients vanish $\Leftrightarrow$ symmetric in a trivial sense $\Rightarrow$ symmetric in all frames.

Experimental evidence:

- Many investigations over the years confirm reciprocal relations, e.g.
  - Diffusion in ternary aqueous solutions of salts (e.g. Miller 1960, Wendt and Shanim 1970)
  - Diffusion in ternary alloys (Ziebold and Ogilvie 1967)
  - Electro-osmosis (Beddiar et al. 2002)
- Some investigations confirm with a ”but…”
  - Diffusion in ternary alchohols and hydrocarbons (Medvedev and Shapiro 2003)

Difficult to test reciprocal relations in diffusion:

$$\mathbf{D}=\mathbf{L}\Psi \rightarrow \mathbf{L}=\mathbf{D}\,\Psi^{-1}$$

- Precise evaluation of multicomponent diffusion coefficient matrix needed.
- Good thermodynamic descriptions needed, i.e. second derivatives of the Gibbs energy as function of composition.

Summary - Multicomponent systems and coupling effects

- Fick's first law contains coupling coefficients.
- Coupling stems from
  - Thermodynamic interactions
  - Frame of reference
  - Correlation effects
- Vector matrix notation convenient
- Use gradients in thermodynamic potentials
- Entropy production
- Onsager reciprocal relations

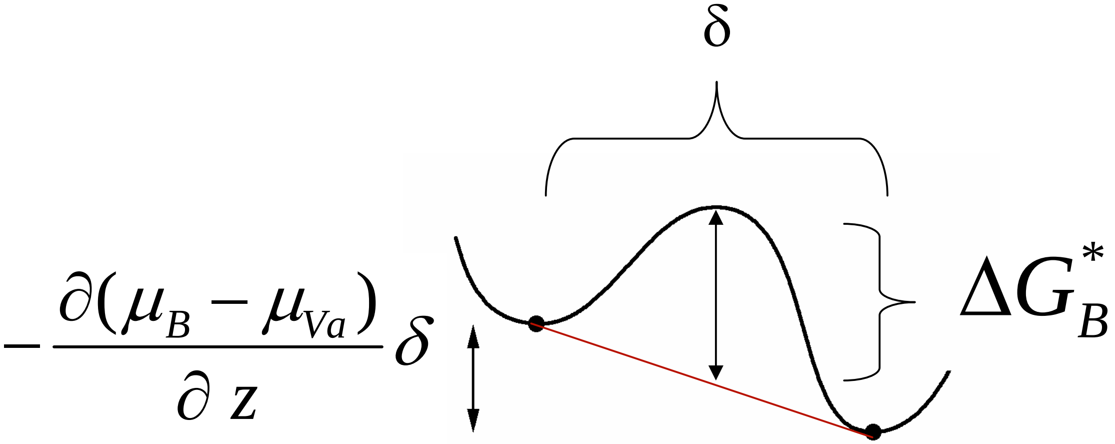
4. Diffusion models

- The dominating diffusion mechanism in metals, intermetallic and ionic crystals is an atom or ion exchanging place with a vacancy.
- The probability for a thermally activated ”jump” of an atom to neighboring vacant site is given by

$$p = \exp(-\Delta G / kT)$$

where ΔG is the change in Gibbs energy caused by jump and k is Boltzmann’s constant.

Absolute reaction rate theory



If there is a driving force ΔG will be different in the two directions.

$$\Delta\vec{G} = \Delta G_B^* + \frac{1}{2}\frac{\partial(\mu_B-\mu_{Va})}{\partial z}\delta$$

$$\Delta\overleftarrow{G} = \Delta G_B^* - \frac{1}{2}\frac{\partial(\mu_B-\mu_{Va})}{\partial z}\delta$$

Assume random mixture of vacancies in thermal equilibrium, i.e.

$$\frac{\partial G}{\partial n_{Va}} = \mu_{Va} = 0$$

The probability that a site is vacant y_{Va}

Probability for jump in forward direction:

$$\vec{p} = y_{Va} \exp\left(-\frac{1}{kT}\left(\Delta G_B^* + \frac{1}{2}\frac{\partial \mu_B}{\partial z}\delta \right)\right)$$

Probability for jump in backward direction:

$$\overleftarrow{p} = y_{Va} \exp\left(-\frac{1}{kT}\left(\Delta G_B^* - \frac{1}{2}\frac{\partial \mu_B}{\partial z}\delta \right)\right)$$

Net flux of atoms (in lattice-fixed frame):

$$J_B = c_B v(\vec{p} - \overleftarrow{p})\delta =$$

$$c_B y_{Va} \delta v \exp\left(-\frac{\Delta G_B^*}{RT}\right) *$$

$$\left[\exp\left(\frac{-1}{2RT}\frac{\partial \mu_B}{\partial z}\delta\right) - \exp\left(\frac{1}{2RT}\frac{\partial \mu_B}{\partial z}\delta\right)\right] =$$

$$= -c_B y_{Va} \delta\, v \exp\left(-\frac{\Delta G_B^*}{RT}\right) * 2\sinh\left(\frac{1}{2RT}\frac{\partial \mu_B}{\partial z}\delta\right)$$

Net flux of atoms in the limit of low Driving forces:

$$J_B \cong -\underbrace{c_B y_{Va} \delta^2 \nu \exp\left(-\frac{\Delta G_B^*}{RT}\right)\frac{1}{RT}}_{M_B} \frac{\partial \mu_B}{\partial z}$$

The mobility!

For interstitial B the fraction of vacancies is usually large and known from composition

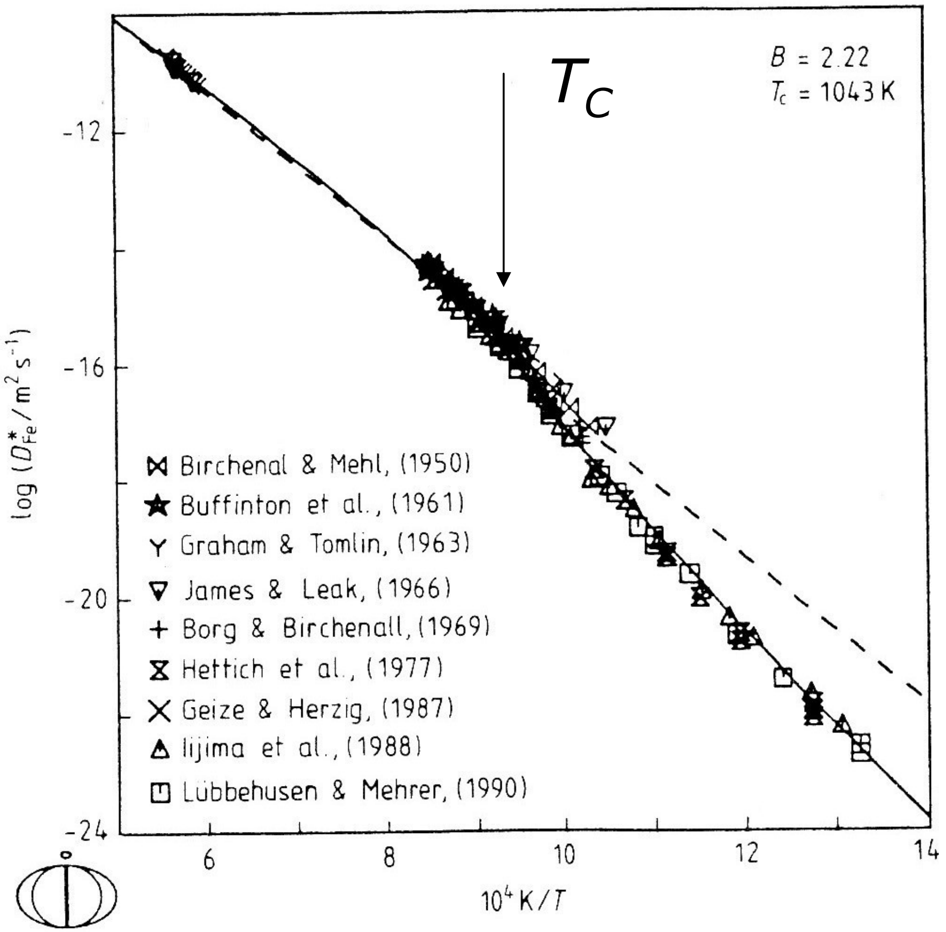
$$J_B \cong -c_B y_{Va} \underbrace{\delta^2 \nu \exp\left(-\frac{\Delta G_B^*}{RT}\right)\frac{1}{RT}}_{M_{BVa}} \frac{\partial \mu_B}{\partial z}$$

The mobility!

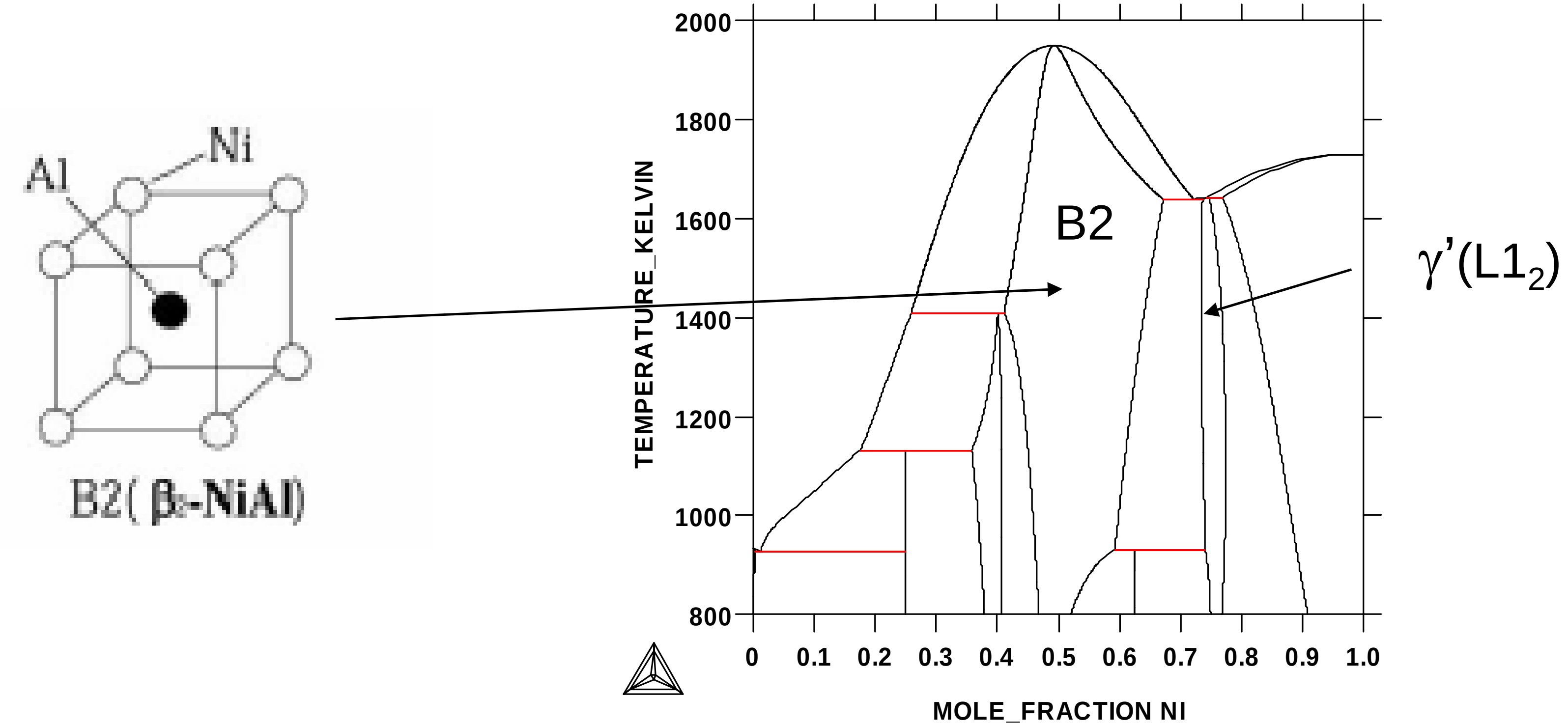
If $\delta^2\nu$ constant and ΔG_B^* has a linear temperature dependence then $RT\,M_B$ or $RT\,M_{BVa}$ have Arrhenius behaviour!

Magnetic ordering

Para-ferromagnetic transition in pure Fe at T_C. Non-Arrhenius behaviour.



Chemical ordering



Al-Ni

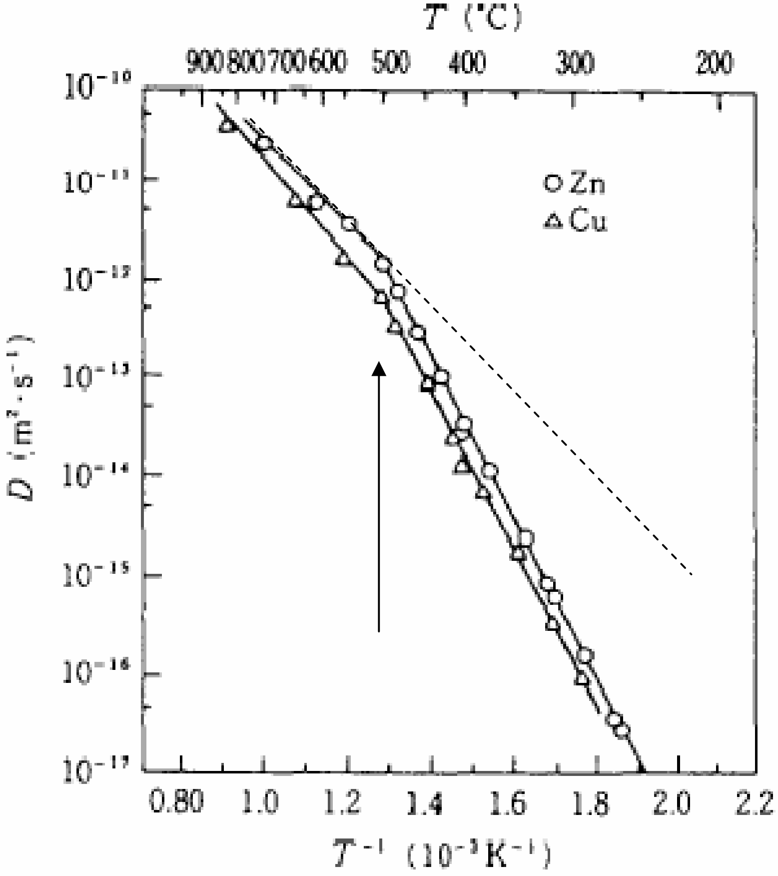


Fig. 1. Temperature dependence of self-diffusivities in B2-type CuZn intermetallic compound.[9]

Cu-Zn
(Cuper at al. 1956)

A single jump creat a defect in a highly ordered structure.

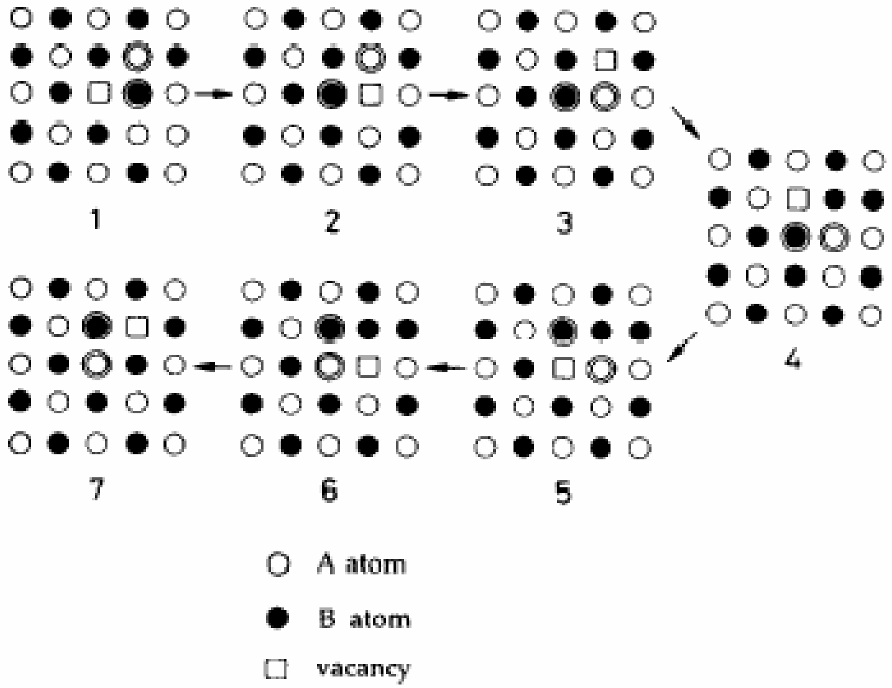


Fig. 4. Sequence (1–7) of six vacancy jumps. (○) A atom, (●) B atom, (□) vacancy. Double circles (◎,◉) are for easy identification of individual atom movements during the cycle.

Girifalco (1964)
Do not look at the microscopic behaviour.
Look at the statistical behaviour!

$$(A,B)(A,B)$$

$$Q_k = Q_k^{dis}(1+\alpha_k s^2), \quad k = A,B$$

$$s = y_B^{'} - y_B^{''}$$

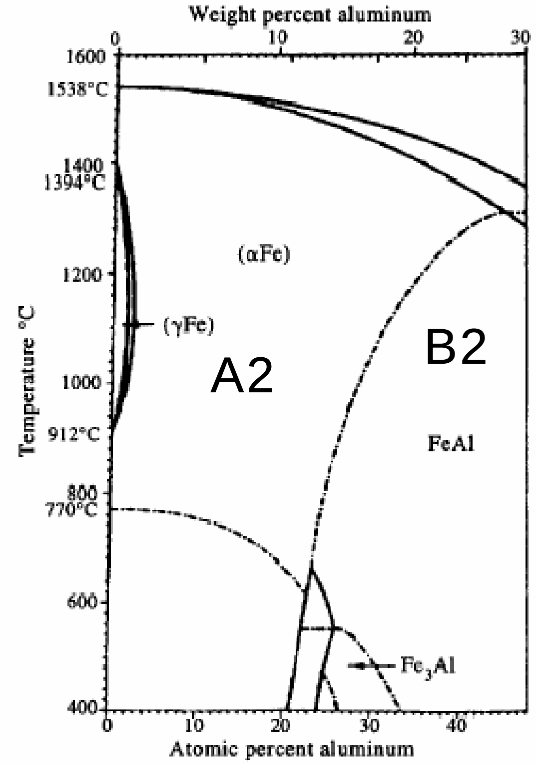


Fig. 1. Fe–Al phase diagram [1].

Fe-Al

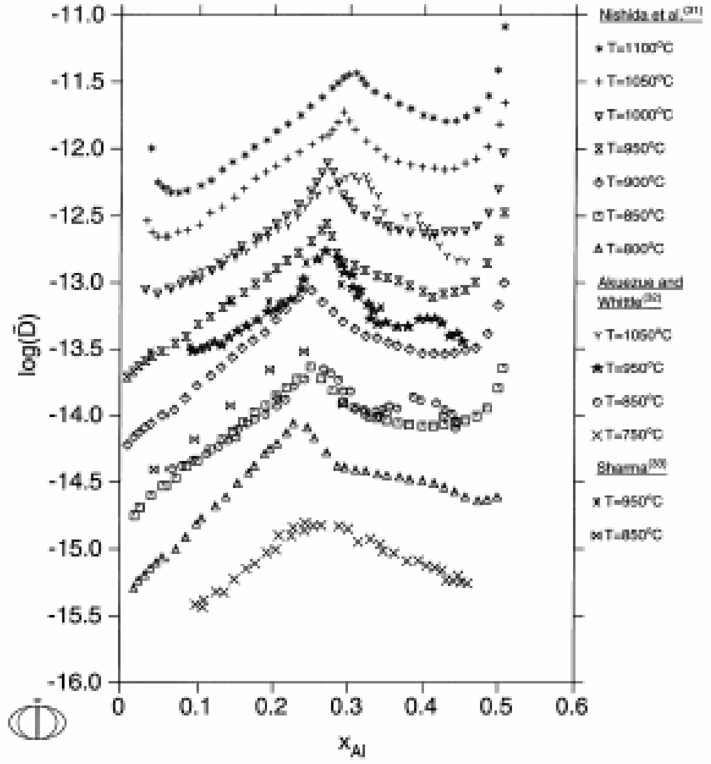


Fig. 1. Experimental information on the chemical diffusivity in the Al–Fe system.

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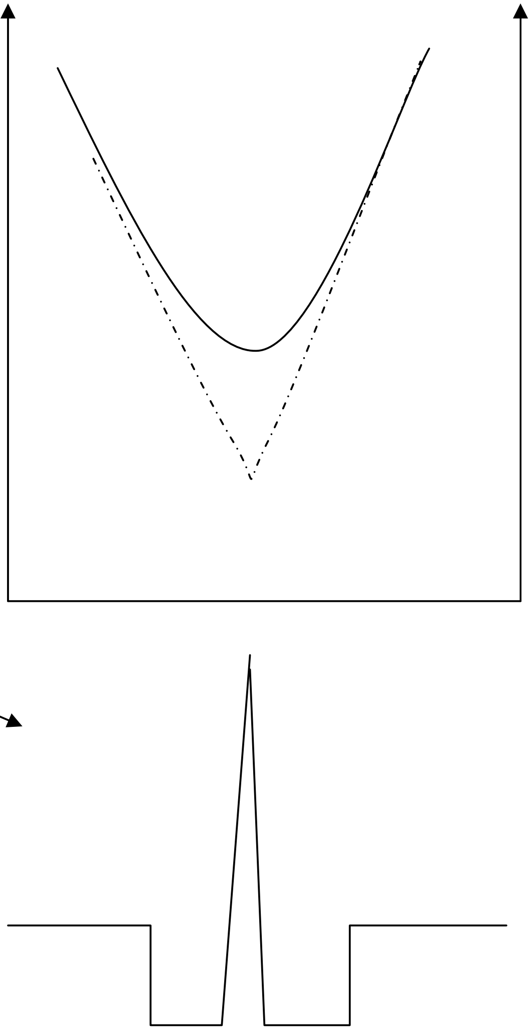
Interdiffusion

$$D^{A'}_{BB} = \left[x_A M_B + x_B M_A\right] x_B \frac{\partial \mu_B}{\partial x_B}$$

$$x_B \frac{\partial \mu_B}{\partial x_B} = x_B x_A \boxed{\frac{d^2 G_m}{d x_B^2}}$$

Two effects;
- Increased activation energy – lower mobility
- Strong variation in thermodynamic factor



(Schematic)

Multicomponent systems:

$$Q_k = Q_k^{dis}(1+\alpha_k s^2), \quad k = A, B$$

$$\left[y_A^{'} y_B^{''} + y_B^{'} y_A^{''} - 2x_A x_B \right] = \tfrac{1}{2} s^2$$

$$Q_k = Q_k^{diss} + \Delta Q_k^{order} \left[y_A^{'} y_B^{''} + y_B^{'} y_A^{''} - 2x_A x_B \right]$$

$$\Delta Q_k^{order} = 2 Q_k^{dis} \alpha_k$$

$$Q_k = Q_k^{diss} + \sum_i \sum_{i \neq j} \Delta Q_{kij}^{order} \left[y_i^{'} \; y_j^{''} - x_i x_j \right]$$

$$s_{ij} = \left[y_i^{'} \; y_j^{''} + y_j^{'} \; y_i^{''} - 2x_i x_j \right] = p_{ij}^{nn} - {}^{random}p_{ij}^{nn}$$

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Al-Fe-Ni
Helander and Ågren
1999

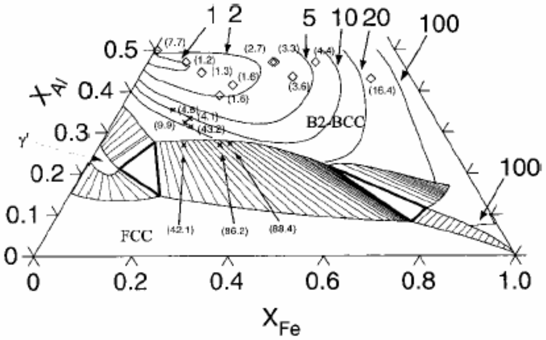


Fig. 1. An isothermal section of the Al–Fe–Ni system at 1000°C where $\tilde{D}^{Fe}_{AlAl}\times10^{-15}$ (m^2/s) is shown. The solid lines indicated by arrows are calculated iso-diffusivity lines. The symbols show experimental values from Moyer and Dayananda [12] (open squares) and Cheng and Dayananda [11] (crosses).

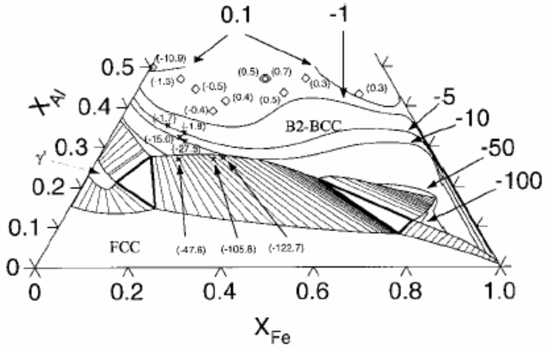


Fig. 3. An isothermal section of the Al–Fe–Ni system at 1000°C where $\tilde{D}^{Fe}_{NiAl}\times10^{-15}$ (m^2/s) is shown. The solid lines indicated by arrows are calculated iso-diffusivity lines. The symbols show experimental values from Moyer and Dayananda [12] (open squares) and Cheng and Dayananda [11] (crosses)

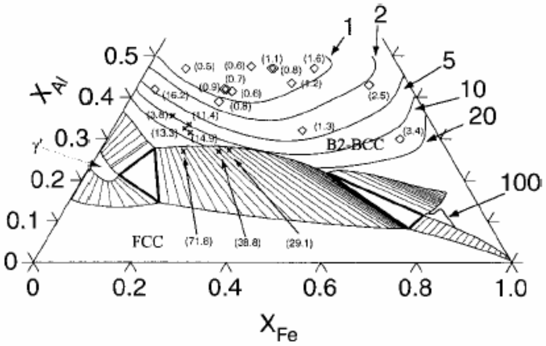


Fig. 2. An isothermal section of the Al–Fe–Ni system at 1000°C where $\tilde{D}^{Fe}_{NiNi}\times10^{-15}$ (m^2/s) is shown. The solid lines indicated by arrows are calculated iso-diffusivity lines. The symbols show experimental values from Moyer and Dayananda [12] (open squares) and Cheng and Dayananda [11] (crosses).

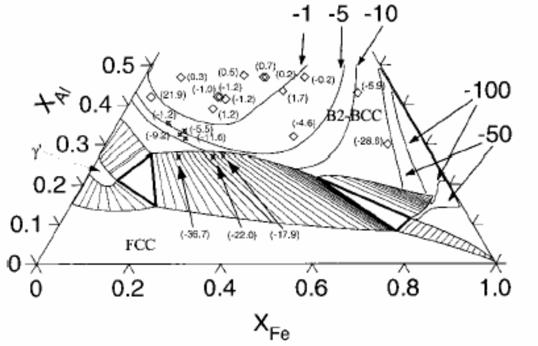


Fig. 4. An isothermal section of the Al–Fe–Ni system at 1000°C where $\tilde{D}^{Fe}_{AlNi}\times10^{-15}$ (m^2/s) is shown. The solid lines indicated by arrows are calculated iso-diffusivity lines. The symbols show experimental values from Moyer and Dayananda [12] (open squares) and Cheng and Dayananda [11] (crosses).

Al-Fe-Ni B2

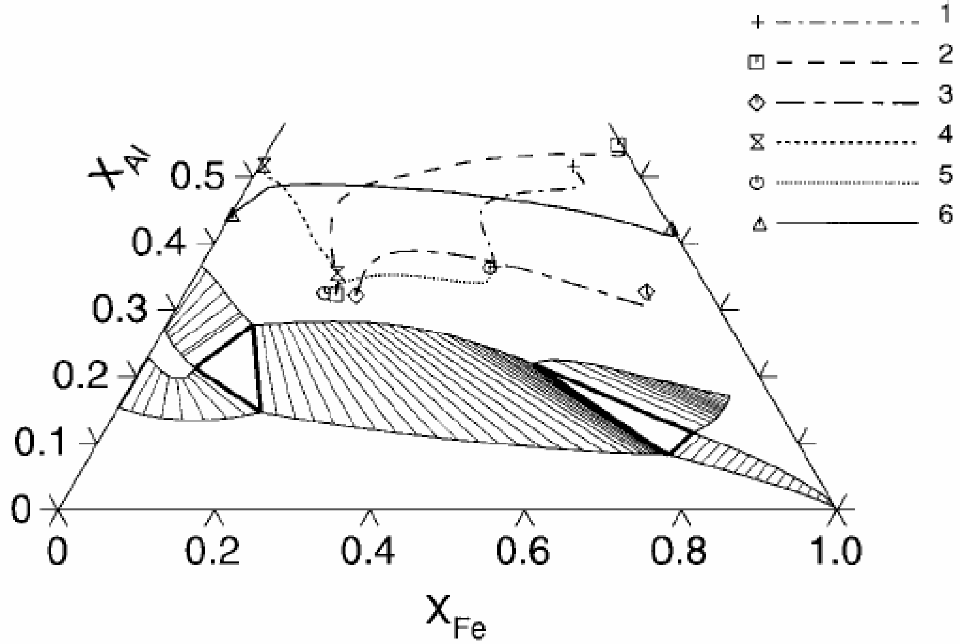
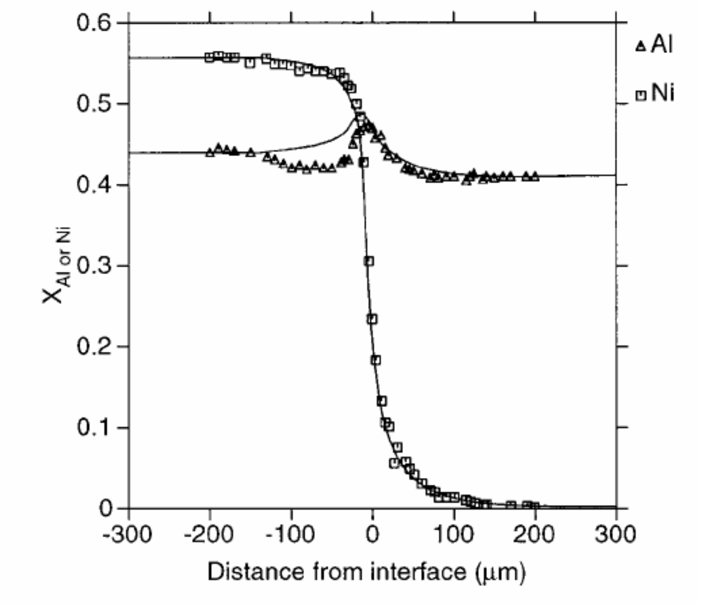
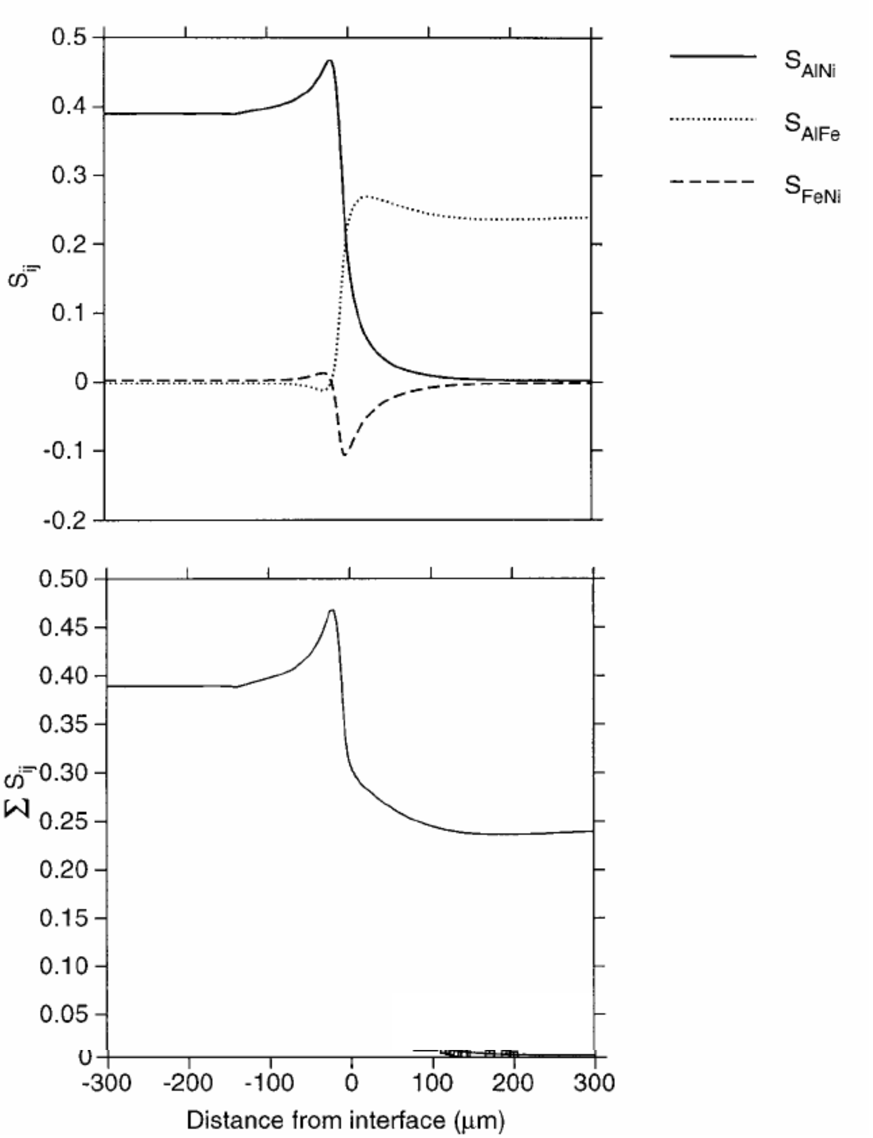


Fig. 7. Diffusion paths for the six diffusion couples superimposed on an isothermal section of the Al–Fe–Ni system at 1000°C.

Al-Fe-Ni B2





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Ionic systems

More complicated because:

Complex phases

Complex defects

- defects that do not change composition
- defects that change composition

Electroneutrality

For example, consider:

$$(A^{+a},B^{+b},C^{+c},Va)(O^{-2},Va)$$

Electroneutrality: $ay_A+by_B+cy_C-2(1-y''_{Va})=0$

$$y'_{Va}=1-(y_A+y_B+y_C)=$$

$$=1-\frac{1}{a}\left(2(1-y''_{Va})-(b-a)y_B-(c-a)y_C\right)=$$

Anion fixed frame of reference:

$$J_O=0$$

No charge flux:

$$aJ_A+bJ_B+cJ_C=0$$

Consider the case $a=b=c=2$:

$$y'_{Va}=1-(y_A+y_B+y_C)=y''_{Va}$$

Only the small number of Schottky vacancies are present!

Vacancy model in lattice fixed frame:

$$J'_{k^{+2}}=-\frac{x_{k^{+2}}}{V_m}y'_{Va}M_{k^{+2}Va}\frac{\partial\mu_{k^{+2}}}{\partial z}\qquad k=A,B,C$$

$$J'_{O^{-2}}=-\frac{x_{O^{-2}}}{V_m}y''_{Va}M_{O^{-2}Va}\frac{\partial\mu_{O^{-2}}}{\partial z}$$

Transformation to anion-fixed frame:

$$J_{k^{+2}}=-\frac{x_{k^{+2}}}{V_m}y'_{Va}M_{k^{+2}Va}\frac{\partial\mu_{k^{+2}}}{\partial z}+\frac{x_{k^{+2}}}{V_m}y''_{Va}M_{O^{-2}Va}\frac{\partial\mu_{O^{-2}}}{\partial z}$$

$$J_{O^{-2}}=0$$

Requirements on driving forces:

- Should represent uncharged quantities
- be independent

Two relations: The 4 driving forces in present case may be reduced to 2 independent driving forces.

Many possibilities!

$$J_{k^{+2}} = -\frac{x_{k^{+2}}}{V_m} y^{'}_{Va} M_{k^{+2}Va} \frac{\partial \mu_{k^{+2}}}{\partial z} + \frac{x_{k^{+2}}}{V_m} y^{''}_{Va} M_{O^{-2}Va} \frac{\partial \mu_{O^{-2}}}{\partial z}$$

$$J_{O^{-2}} = 0$$

$$J_A + J_B + J_C = 0 :$$

$$\frac{\partial \mu_{O^{-2}}}{\partial z} = 2 \sum_{A,B,C} \frac{x_{k^{+2}} M_{k^{+2}Va}}{M_{O^{-2}Va}} \frac{\partial \mu_{k^{+2}}}{\partial z}$$

$$J_{k^{+2}} = -\frac{y_{Va} x_{k^{+2}}}{V_m} \left[M_{k^{+2}Va} \frac{\partial \mu_{k^{+2}}}{\partial z} - 2 \sum_{A,B,C} x_{k^{+2}} M_{k^{+2}Va} \frac{\partial \mu_{k^{+2}}}{\partial z} \right]$$

Use Gibbs Duhem to obtain two forces of the type

$\partial(\mu_B - \mu_A)/\partial z$ and $\partial(\mu_C - \mu_A)/\partial z$

No simple relation between mobility and tracer diffusivity!

Consider :

$$(A^{+2}, B^{+2}, C^{+3}, Va)(O^{-2}, Va)$$

Electroneutrality :

$$y_{Va}^{'} = y_{Va}^{''} + y_C / 2$$

The addition of C will dramtically increase the vacancy content on cation sublattice!

$$J'_A = -\frac{x_A}{V_m}(y_{Va}^{''} + y_C / 2) M_{AVa} \frac{\partial \mu_A}{\partial z} \quad \text{etc...}$$

$$J'_{O^{-2}} = -\frac{x_{O^{-2}}}{V_m} y_{Va}^{''} M_{O^{-2}Va} \frac{\partial \mu_{O^{-2}}}{\partial z}$$

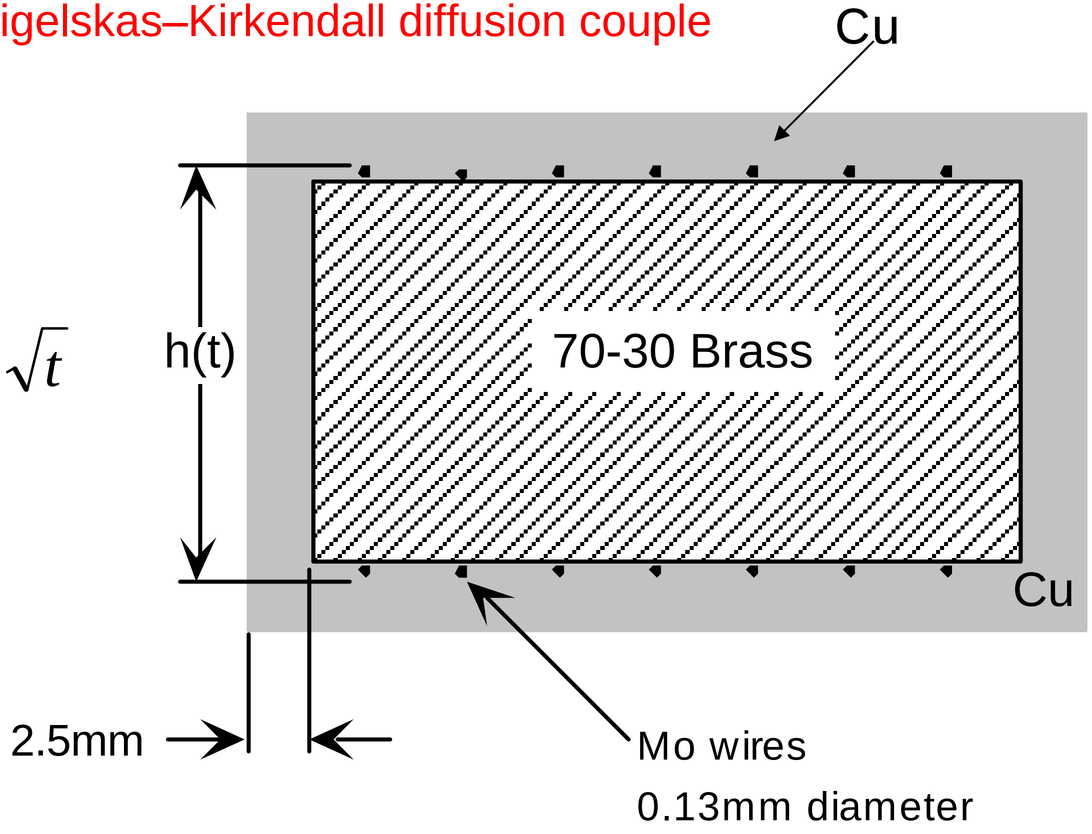
Summary - diffusion models

- Vacancy mechanism in metals, intermetallic and ionic crystals.
- Absolute reaction rate theory gives flux proportional to force and Arrhenius behaviour.
- Magnetic and chemical ordering yield a deviation from Arrhenius behaviour and increased activation energy with increased ordering.
- Ionic phases complex because complex defect structures. One needs to conisder
  - Electroneutrality
  - Charge transfer
  - Complex relation between mobility and tracer diffusivity
  - Doping of ions with different valrncy has a strong effect

5. Kirkendall effect

Schematic of the Smigelskas–Kirkendall diffusion couple

$$h(t) - h(0) = -K\sqrt{t}$$



It seems as the Mo-wire has moved!

In lattice-fixed frame of reference a net flow of atoms. In a frame of reference with no net-flow (number-fixed) the lattice points (the markers) thus appear to move.

Net-flow of atoms:

$$J_A^{'} + J_B^{'} = -\left(D_B' - D_A'\right)\frac{1}{V_m}\frac{\partial x_B}{\partial z} = -\left(D_{AB}^{A}{}' + D_{BB}^{A}{}'\right)\frac{1}{V_m}\frac{\partial x_B}{\partial z}$$

$$= -M_A \frac{x_A}{V_m}\frac{\partial \mu_A}{\partial z} - M_B \frac{x_B}{V_m}\frac{\partial \mu_B}{\partial z}$$

Gibbs-Duhem:

$$x_A \frac{\partial \mu_A}{\partial z} + x_B \frac{\partial \mu_B}{\partial z} = 0 \quad \Rightarrow \quad J_A^{'} + J_B^{'} = -(M_B - M_A)\frac{x_B}{V_m}\frac{\partial \mu_B}{\partial z}$$

Kirkendall velocity (velocity of lattice planes in number-fixed frame

$$\frac{v}{V_m} = -\left(J_A^{'} + J_B^{'}\right),$$ Rate of density ($\rho = 1/V_m$) change:

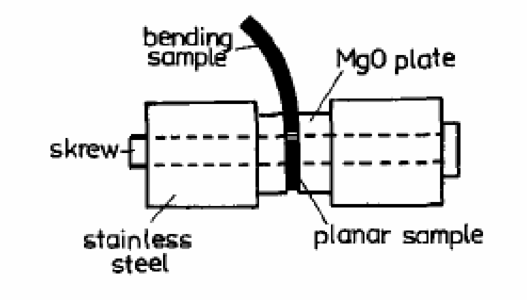
$$\frac{1}{V_m^{\ 2}}\dot{V}_m = \mathbf{div}(J_A^{'} + J_B^{'})$$

No porosity $\Rightarrow$ Strain rate:

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

Only porosity (volume fraction f_p):

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



Ti-Zr: Daruka et al. 1996

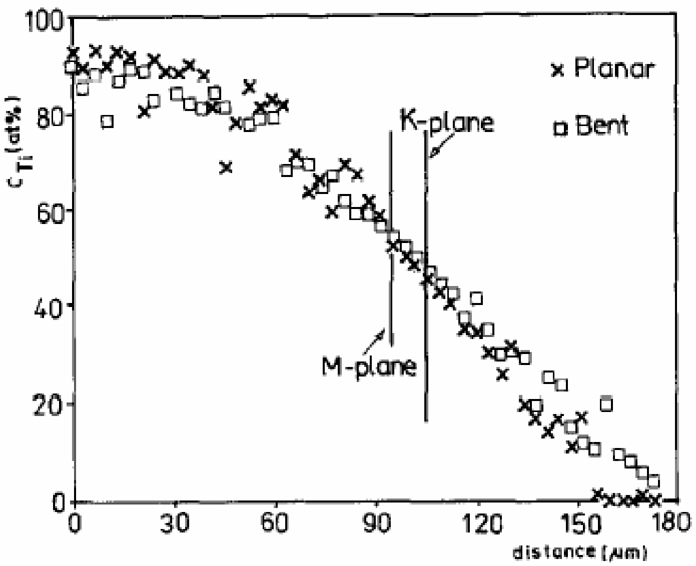


Fig. 13. Concentration profiles for planar and bent samples ($T = 1223$ K, 3 h) measured by EDAX in a SEM.

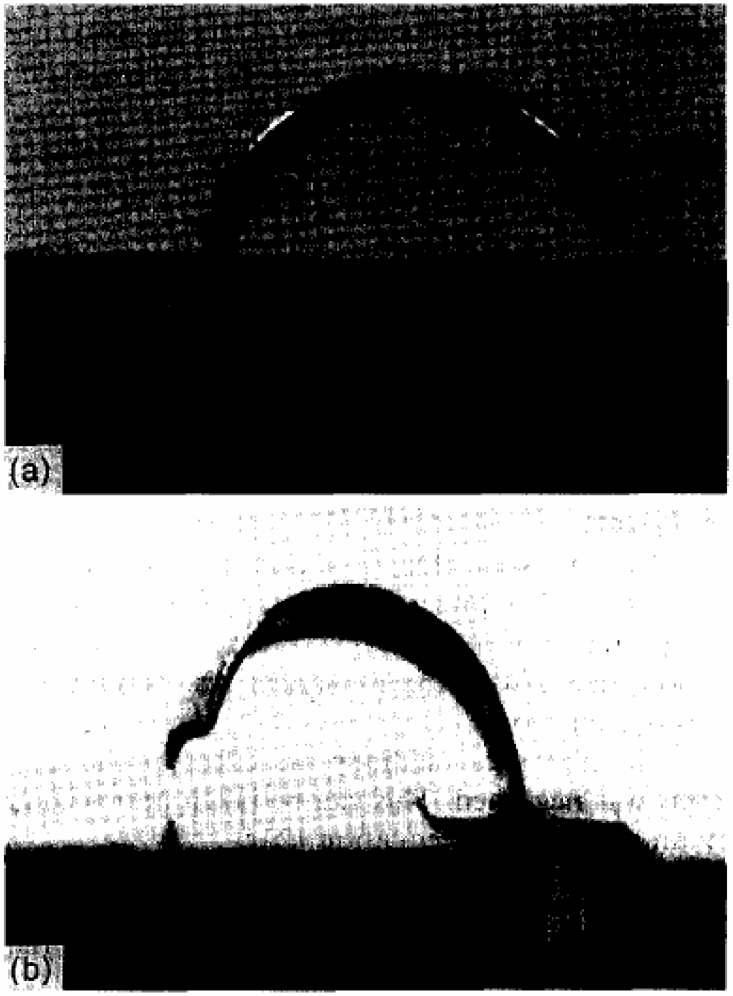
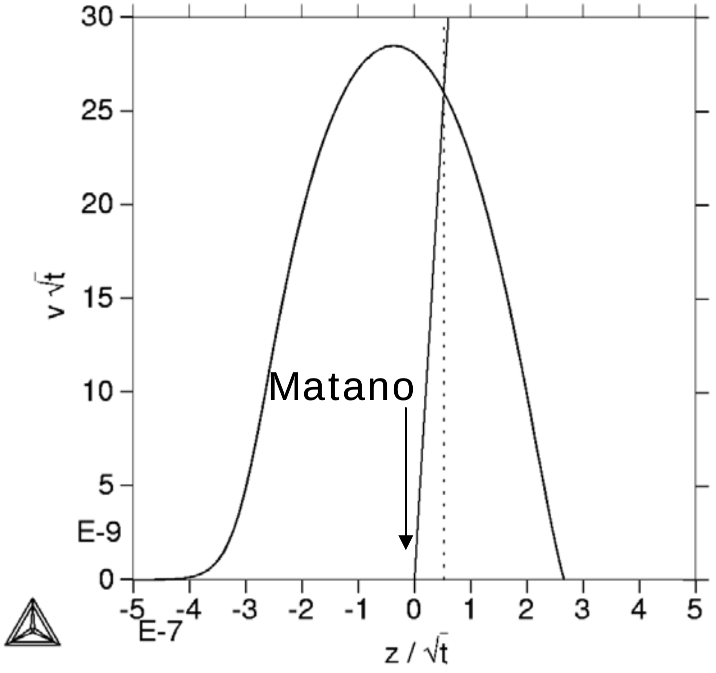


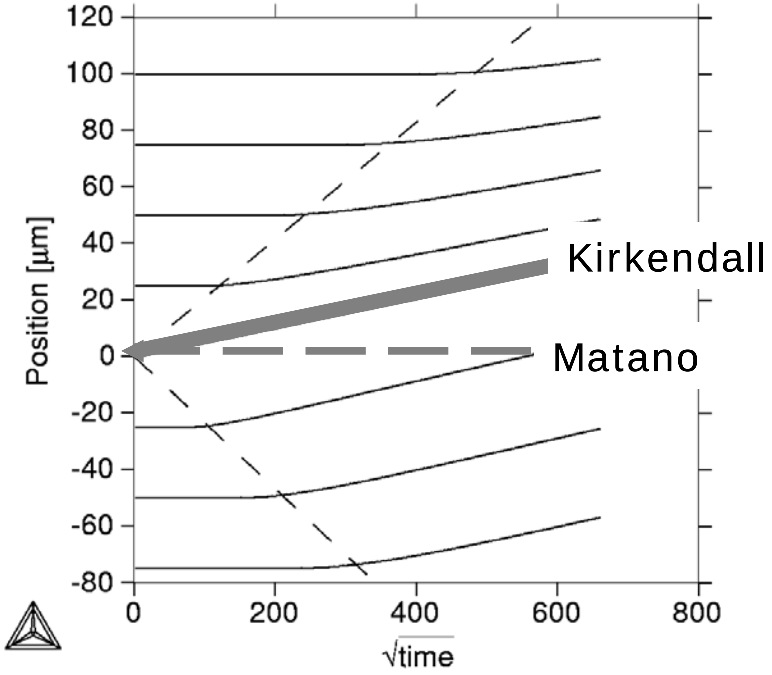
Fig. 11. Photographs of the bent samples for two samples at 1223 K. Sample (a) has ideal, cylindrical shape, while sample (b) has a screwing component as well.

Z’ position of a given lattice plane (or markers fixed to that plane) relative number-fixed frame.

$$dZ'/dt = v(Z',t) = V_m J'_{Va}(z,t) = (D'_B - D'_A)\frac{\partial x_B}{\partial z}$$



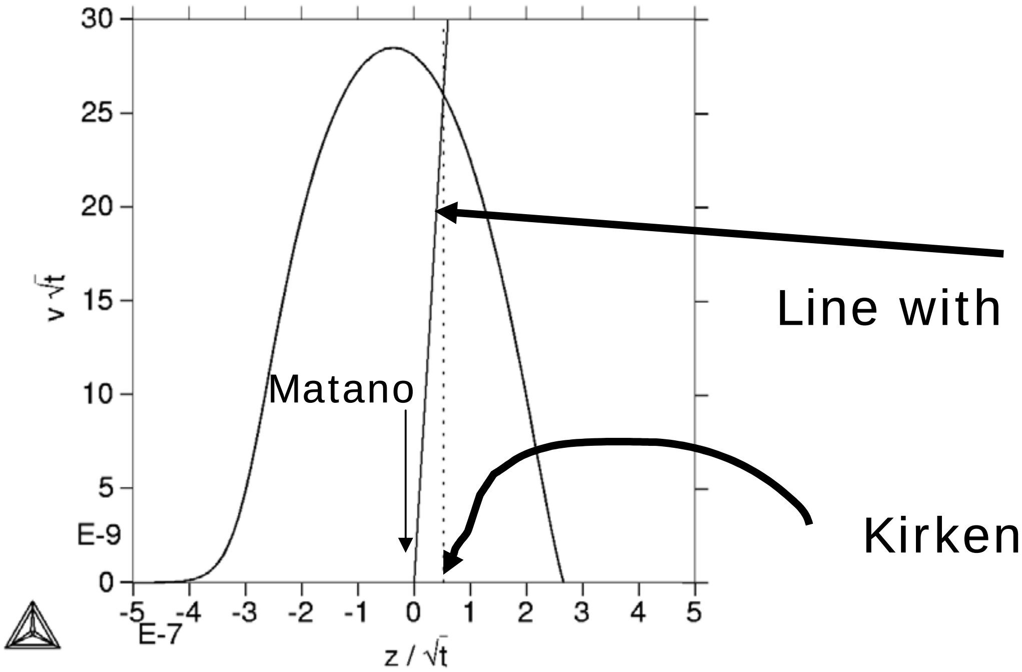
Lattice plane velocity



Lattice plane position

The Kirkendall plane is the lattice plane corresponding to the original joint.

It is the only lattice plane that moves parabolically relative the Matano plane.



Line with slope 1/2

Kirkendall plane

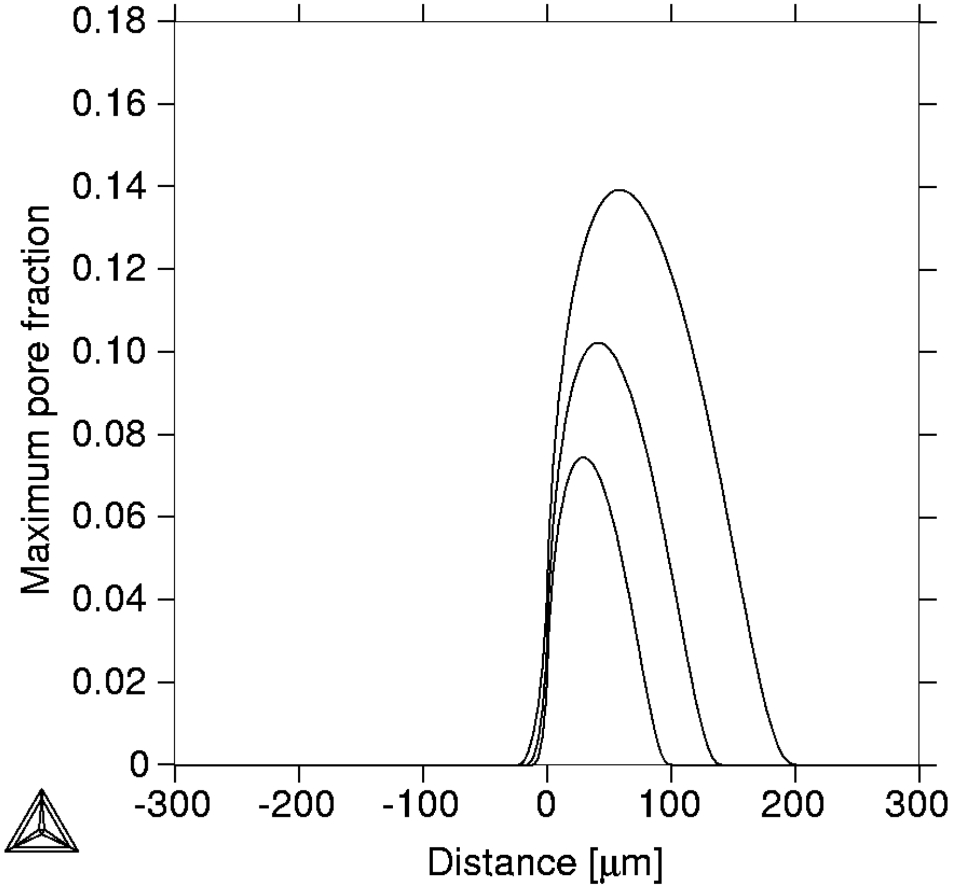
Lattice plane velocity

$\partial J'_{Va} / \partial z < 0$: Accumulation of vacancies

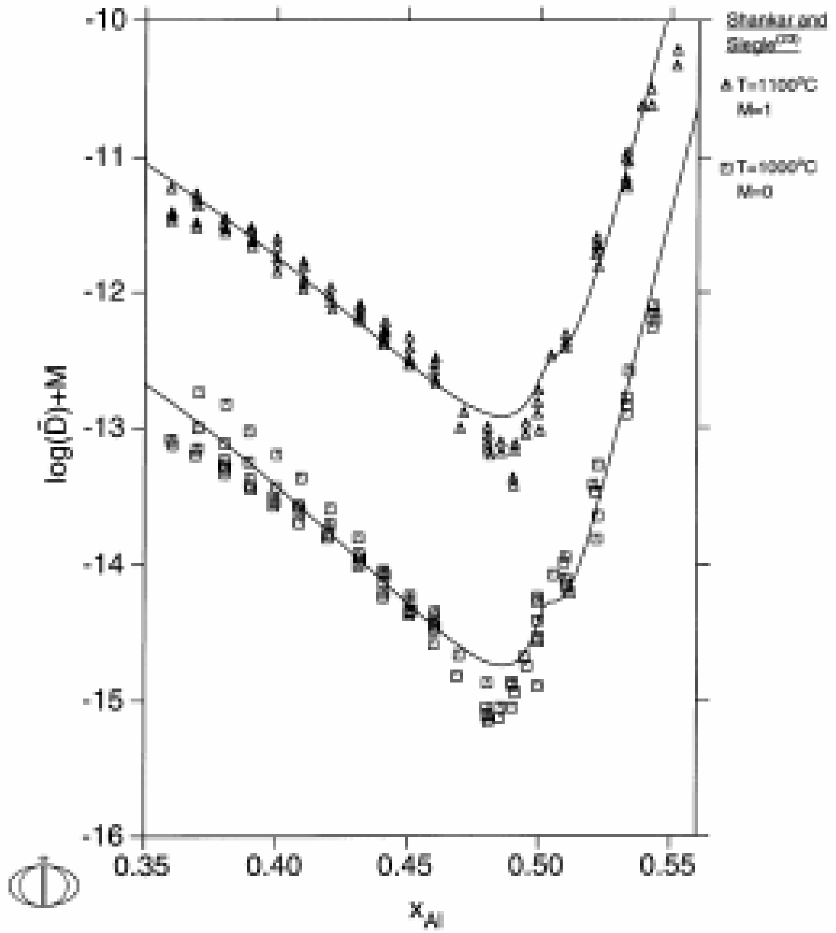
$\partial J'_{Va} / \partial z > 0$: Accumulation of atoms

Volume fraction pores if all vacancies condense to pores: $f_p = y_{Va} / (1 + y_{Va})$

$$y_{Va} = \int_0^t \partial (-J_{Va}) / \partial z \, dt$$


0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
-300
-200
-100
0
100
200
300
Maximum pore fraction
Distance [μm]

Example:
Kirkendall effect during oxidation of NiAl B2



Interdiffusion coefficient in NiAl-B2
(Helander and Ågren 1999)

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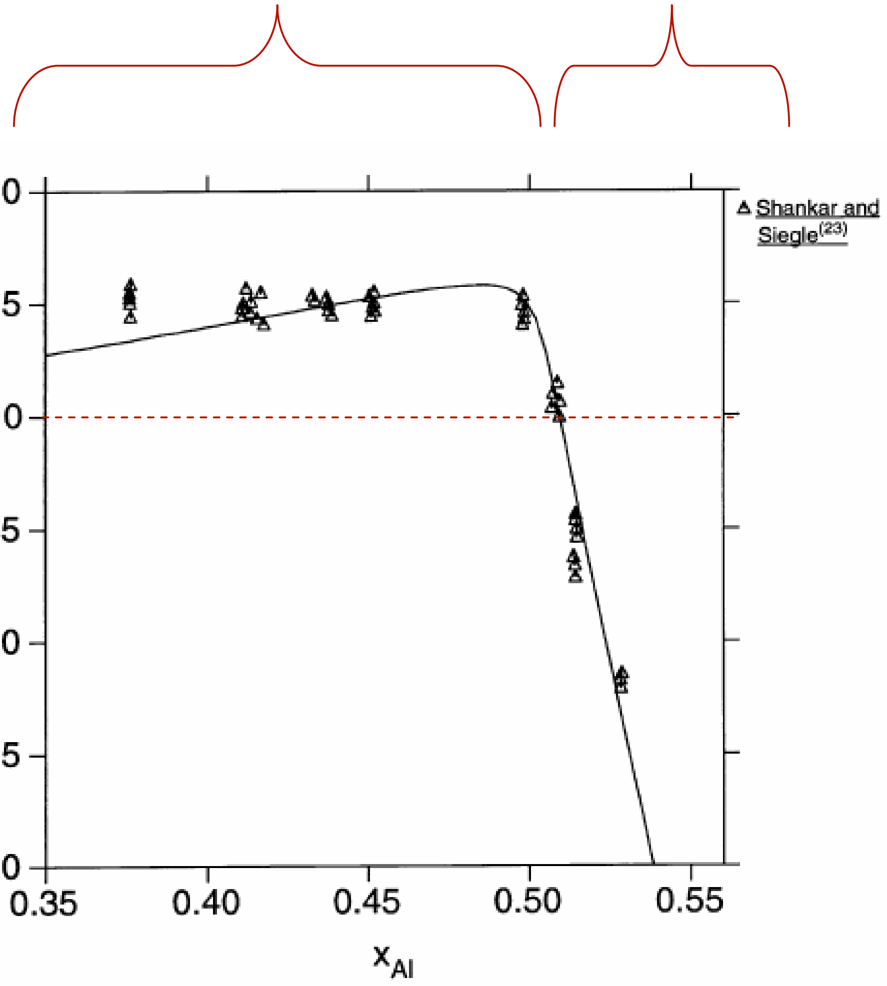
Ni diffusion faster Al diffusion faster

$$\frac{v}{V_m} = -(J_A + J_B) = J_{Va} = -\frac{1}{V_m}\left(D_B - D_A\right)\frac{\partial x_B}{\partial z}$$

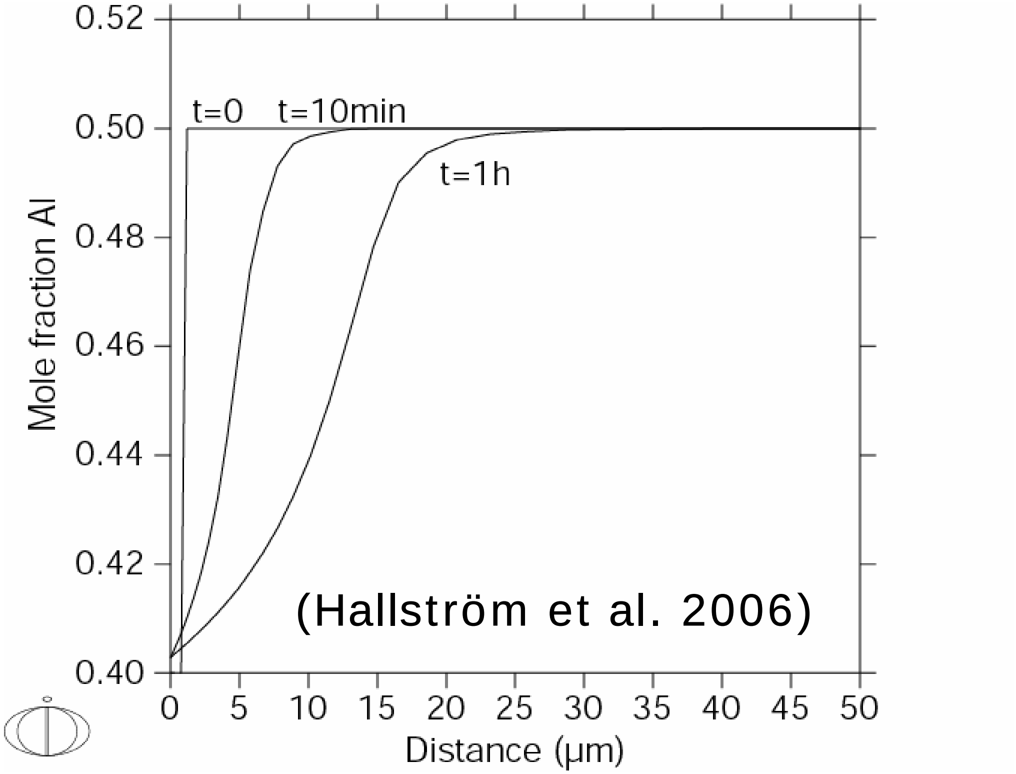
$$V_{Va}^{tot} = A\int_0^t V_m^{Va} J_{Va}\,dt$$



Ratio between tracer diffusivity of Ni and Al in Al-Ni B2

Oxidation of NiAl at 1050°C

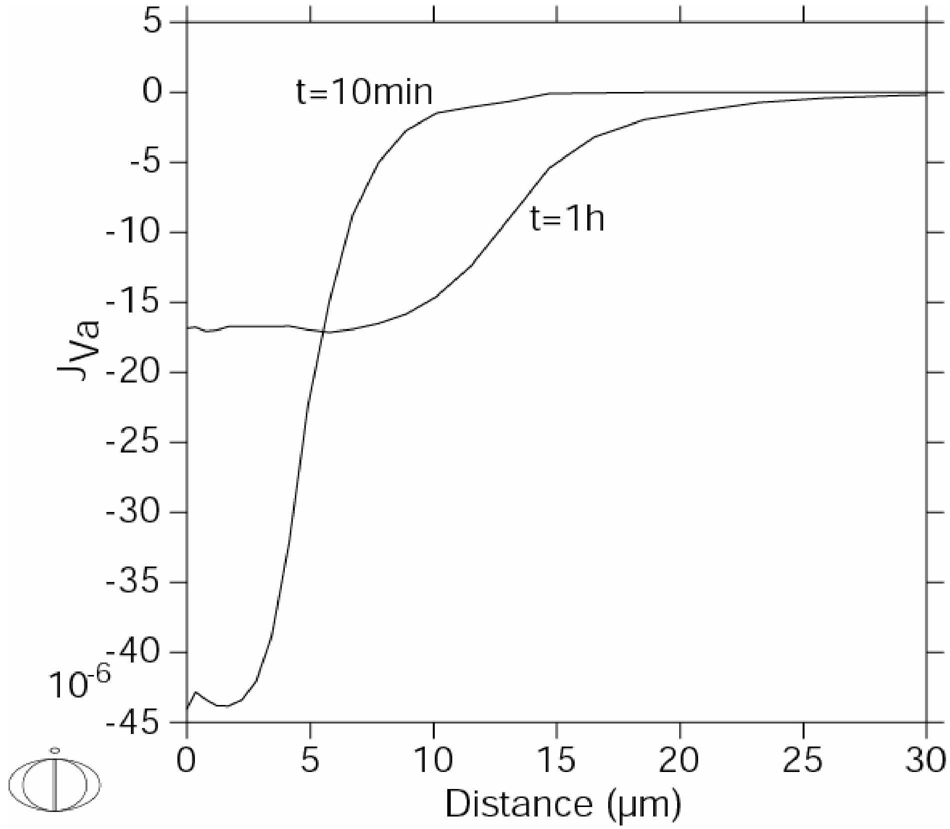
- Simplified treatment: Mole fraction Al on metal surface kept constant (~0.40, from EDS at CTH)
- No diffusion in oxide!
- Assessment of mobilities in NiAl made by Helander and Ågren.



(Hallström et al. 2006)

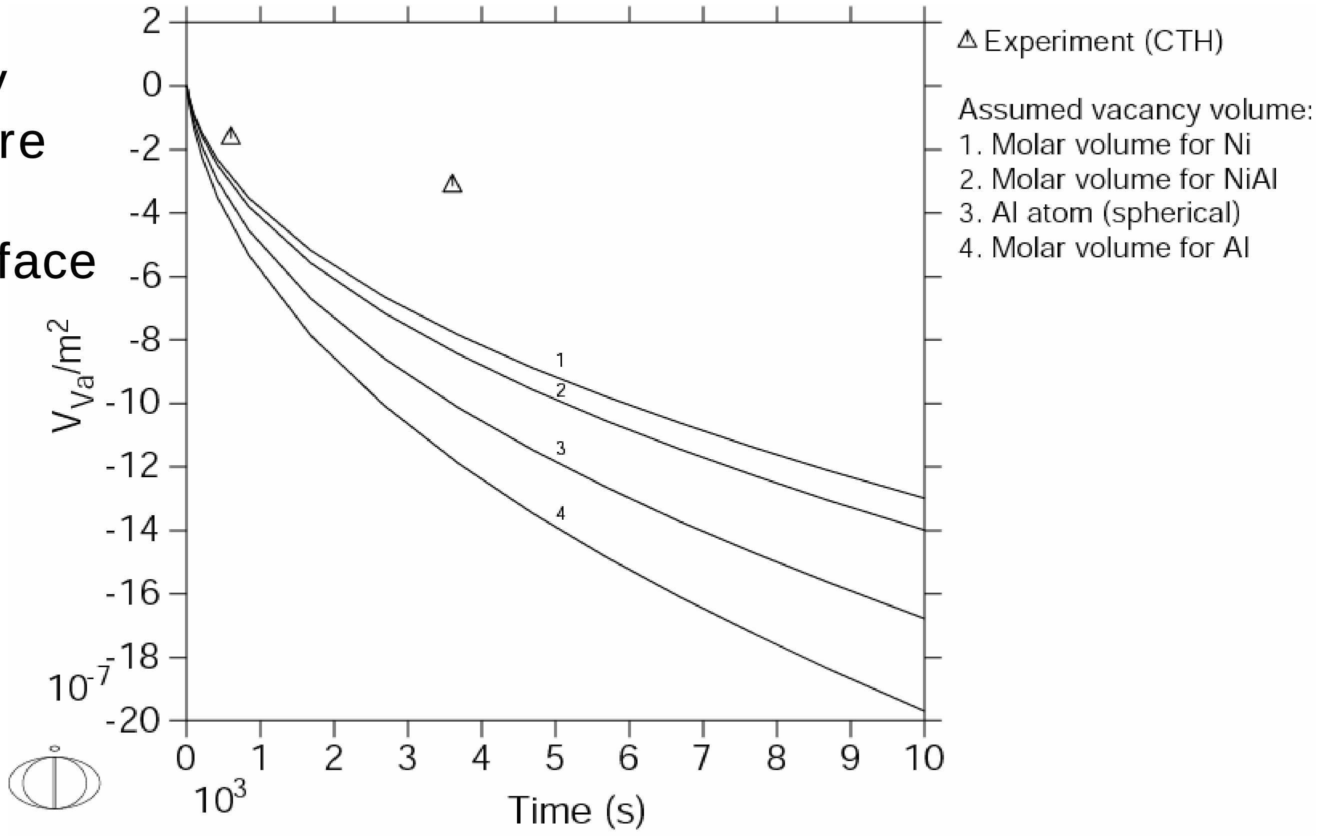
Oxidation of NiAl at 1050°C

- Vacancy flux in lattice fixed frame of reference
- Negative sign means ”toward the oxide”.
- Accumulation of vacancies towards oxide!



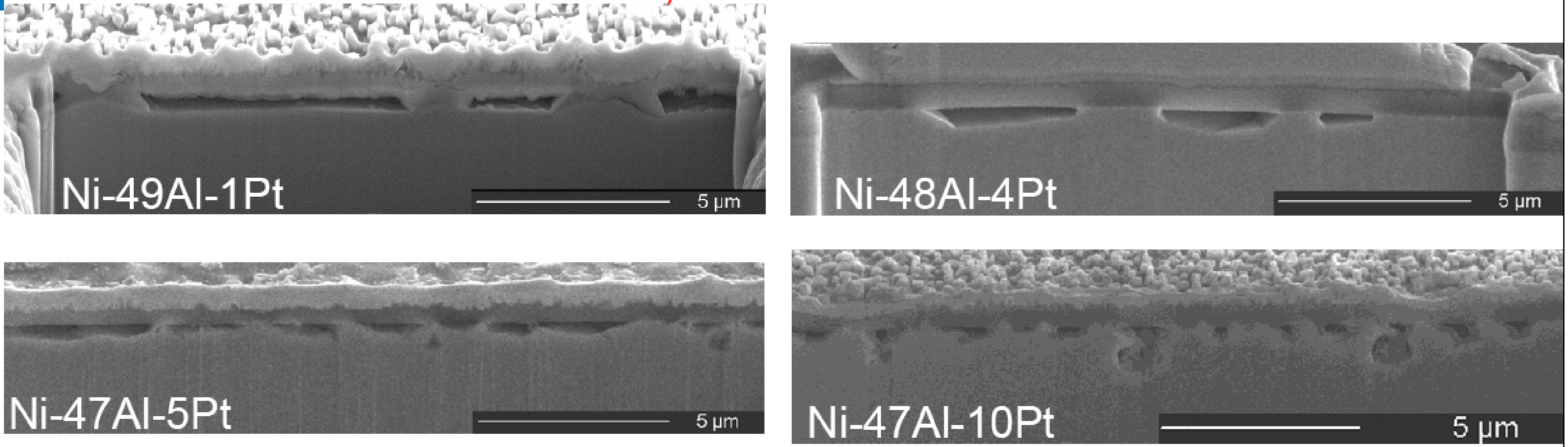
Oxidation of NiAl at 1050°C

- Integrated vacancy volume flux => pore volume per square meter of metal surface



Svensson, Petrova and Stiller 2006:

NiAlPt bulk material, oxidized in air at 1050 °C for 1h



The number and depth of the interfacial voids increase with increasing Pt content.

Voids below the metal/oxide interface are observed in high Pt materials. This indicates that Pt increases Al diffusion in the metal and prevents coalescence of interfacial voids.

Kirkendall effect as a cross effect of interdiffusion

Consider binary system $A-B$. Suppose we want to consider the processes inter-diffusion and lattice plane (Kirkendall marker) shift:

$$-J_A = J_B = -x_B J_A' + (1-x_B) J_B'$$

$$v/V_m = -J_A' - J_B' = -J_{tot}$$

$$\mathbf{A} = \begin{pmatrix} -x_B & (1-x_B) \\ -1 & -1 \end{pmatrix}$$

$$(\mathbf{A}^{\mathrm{T}})^{-1} = \begin{pmatrix} -1 & 1 \\ -(1-x_B) & -x_B \end{pmatrix}$$

The transformation rule thus yields the new forces

$$F_1 = \partial\,(\mu_B - \mu_A)/\partial\, x$$

$$F_2 = -\left[(1-x_B)\partial\,\mu_A/\partial\, x + x_B\partial\,\mu_B/\partial\, x\right]$$

$$\mathbf{L} = \frac{y_{Va}}{V_m}\begin{pmatrix} x_B(1-x_B)\big(x_B M_A + (1-x_B)M_B\big) & x_B(1-x_B)\big(M_A - M_B\big) \\ x_B(1-x_B)\big(M_A - M_B\big) & (1-x_B)M_A + x_B M_B \end{pmatrix}$$

$F_2 = 0$ due to Gibbs Duhem:

$$J_B = -\frac{y_{Va}}{V_m} x_B(1-x_B)\big(x_B M_A + (1-x_B)M_B\big)\frac{\partial(\mu_B - \mu_A)}{\partial x}$$

$$\frac{v}{V_m} = -\frac{y_{Va}}{V_m} x_B(1-x_B)\big(M_A - M_B\big)\frac{\partial(\mu_B - \mu_A)}{\partial x}$$

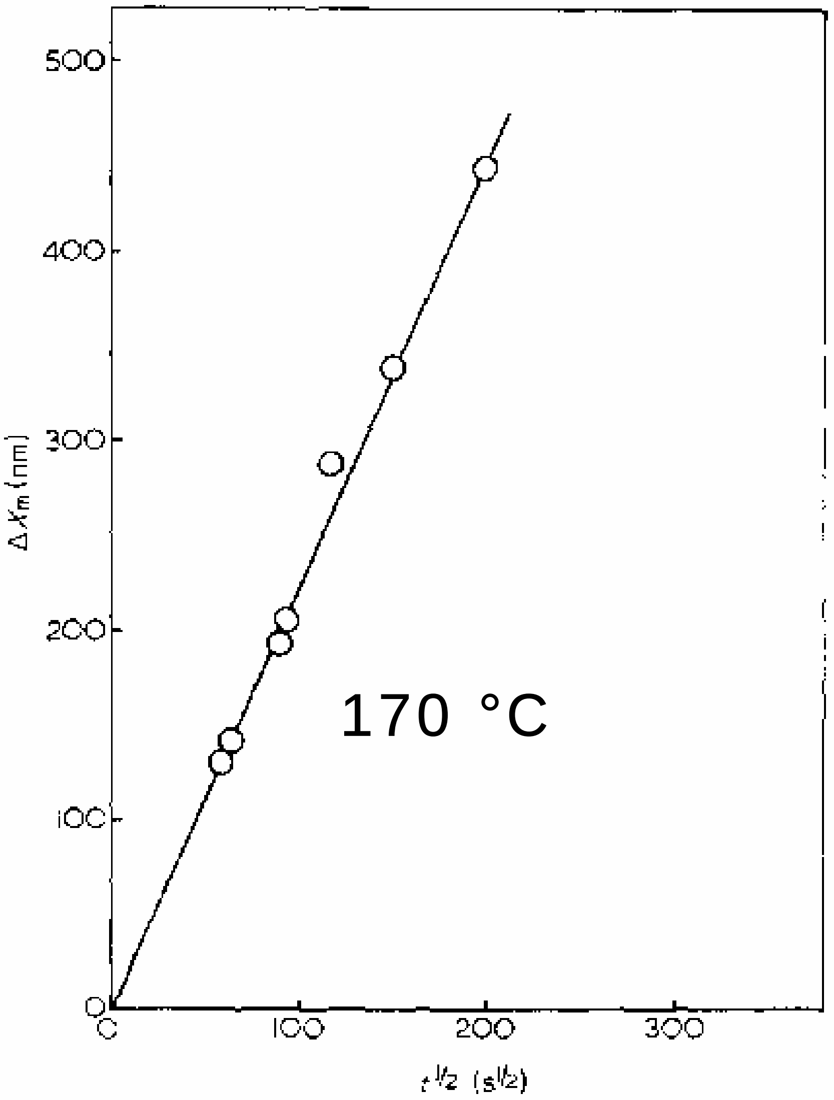
Kirkendall shift as a cross effect (Hillert 2005)

Very general effect!

Kirkendall effect during interdiffusion between two polysterene films with different chain lengths (Kramer et al. 1984).

Thermal migration: Kirkendall effect caused by heat flow?

Electromigration: Kirkendall effect caused by electric current?



Summary – Kirkendall effect

- Unequal mobilities of different elements yield a net flow of atoms.
- Net flow of atoms will give porosity, stresses or deformation.
- In a diffusion couple the Kirkendall plane of the initial joint is the only lattice plane that moves parabolically.
- Kirkendall effect may give porosity at TGO/BC interface during growth of TGO.
- Kirkendall effect is a cross effect of interdiffusion.

6. Multi-phase diffusion couples

- Gibbs phase rule and diffusion
- Virtual and real diffusion path
- Diffusion in dispersed systems – effective diffusivity
- Different types of planar interfaces
- Internal – external oxidation

Gibbs phase rule and diffusion couples

- The number of degrees freedom *f* is the number of pontials that can be varied independently:

  f = 2+c-p

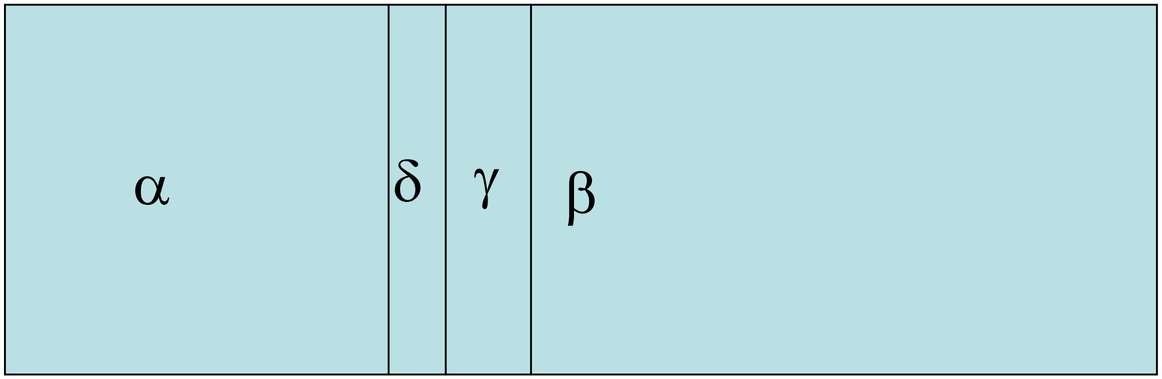
  At given P and T: f = c-p

  Binary system c = 2 and for one-phase system (p=1):

  f = 1; 1 independent chemical potentials gradient.

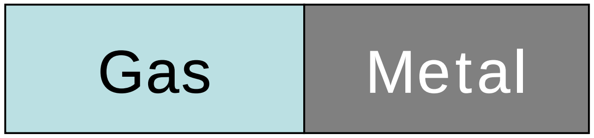
  two-phase system (p=2): f = 0, No independent chemical potential gradient. No diffusion possible.

  Diffusion only possible if supersaturation has been created at a different temperature.

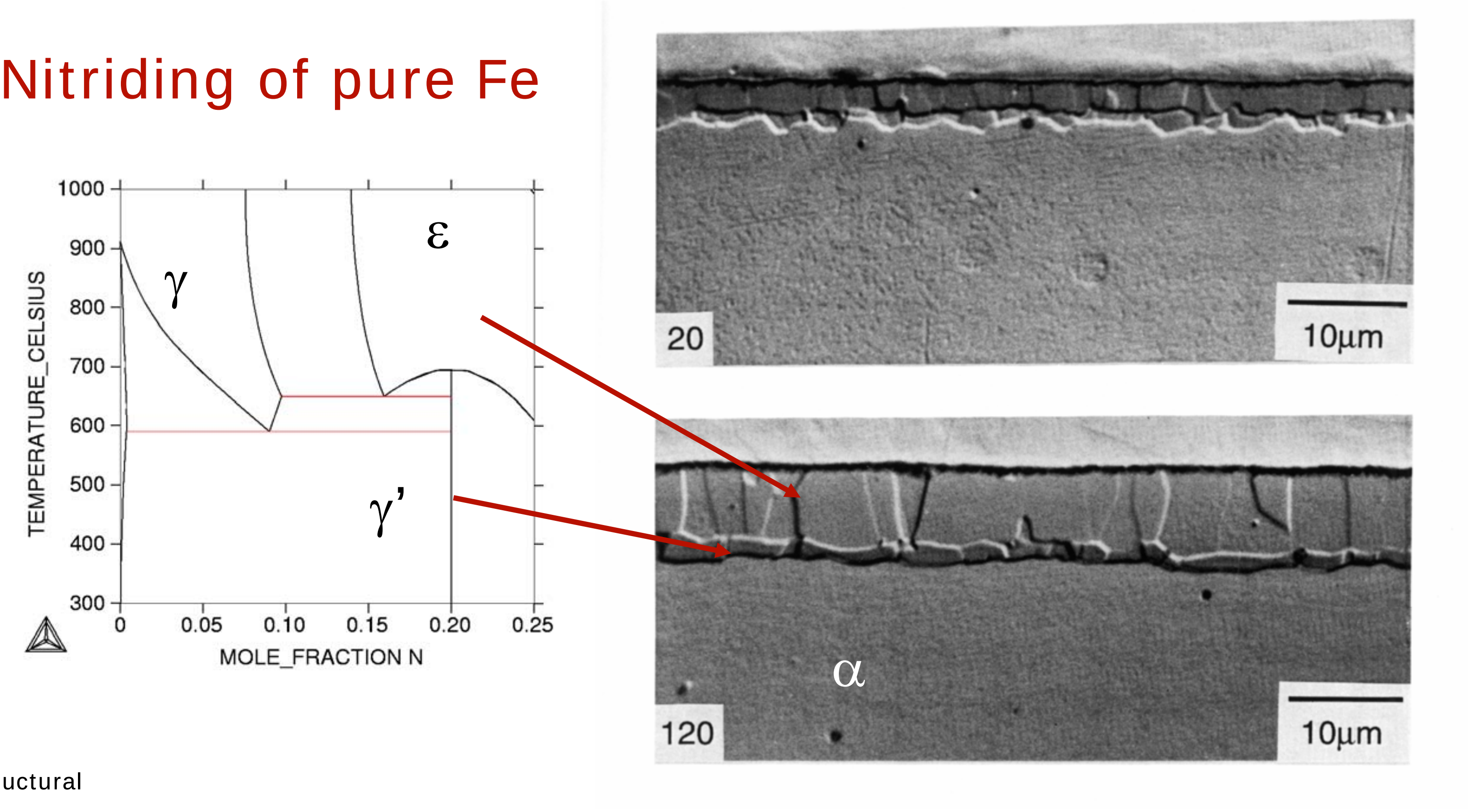


In a binary diffusion couple which is heated isothermally we can only form layers of different phases.

Example: Oxidation or nitriding of pure metal: Only external layer possible!



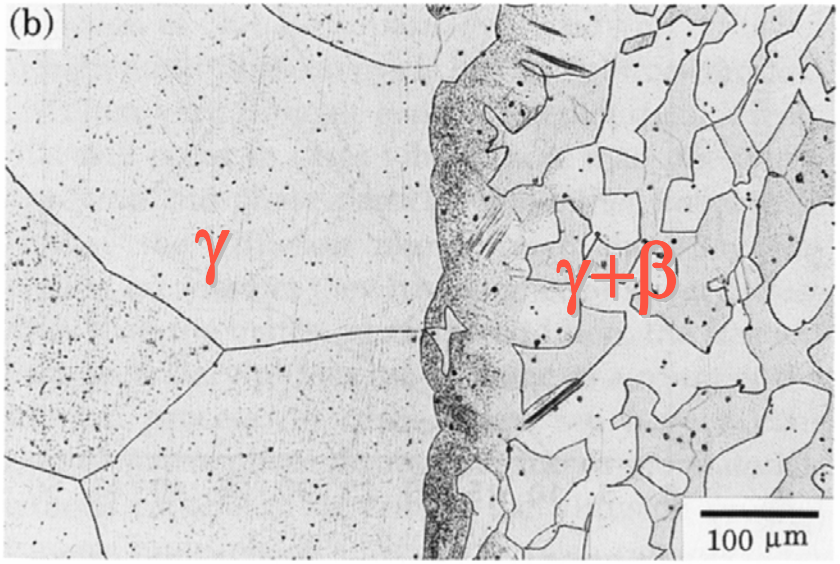
Nitriding of pure Fe



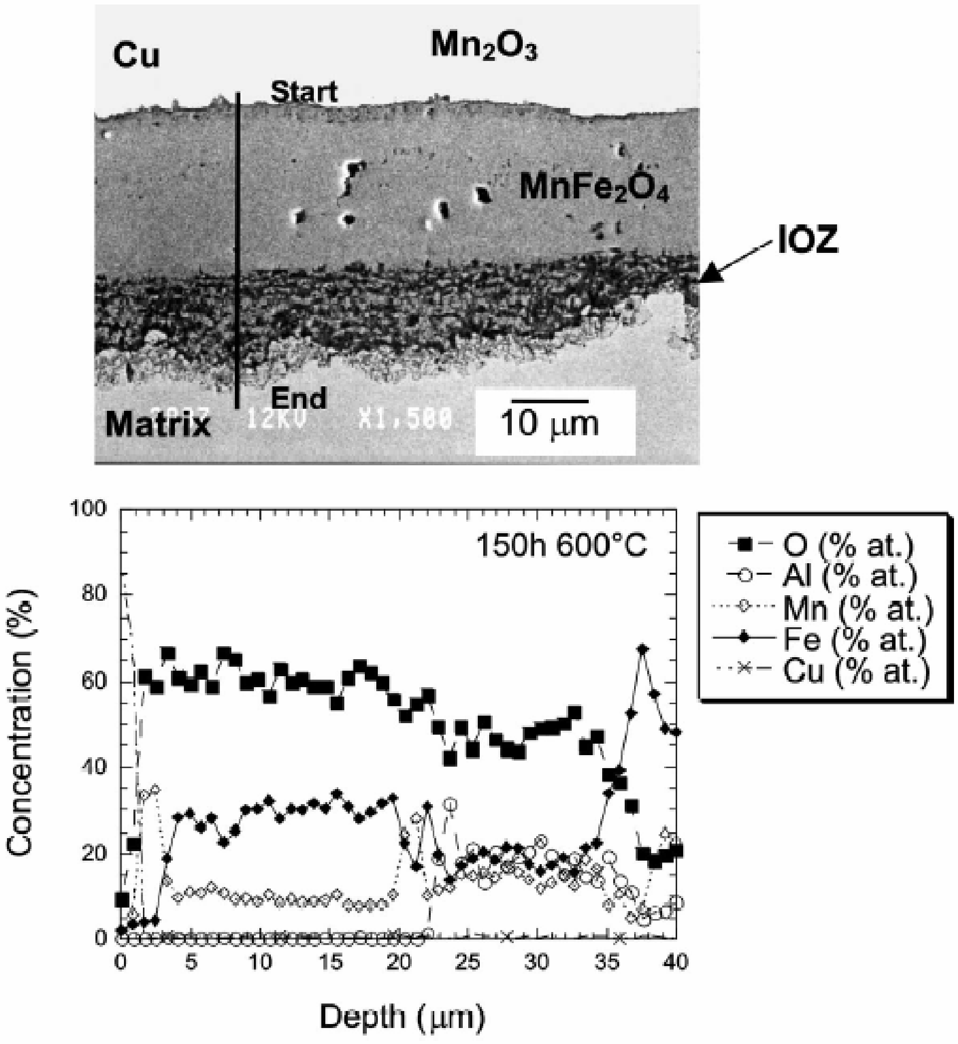
Ternary system c = 3 and for one-phase system (p=1):

f = 2; 2 independent chemical potentials gradient.

Two-phase system (p=2): f = 1, 1 independent chemical potential gradient. Diffusion possible in a two-phase mixture.

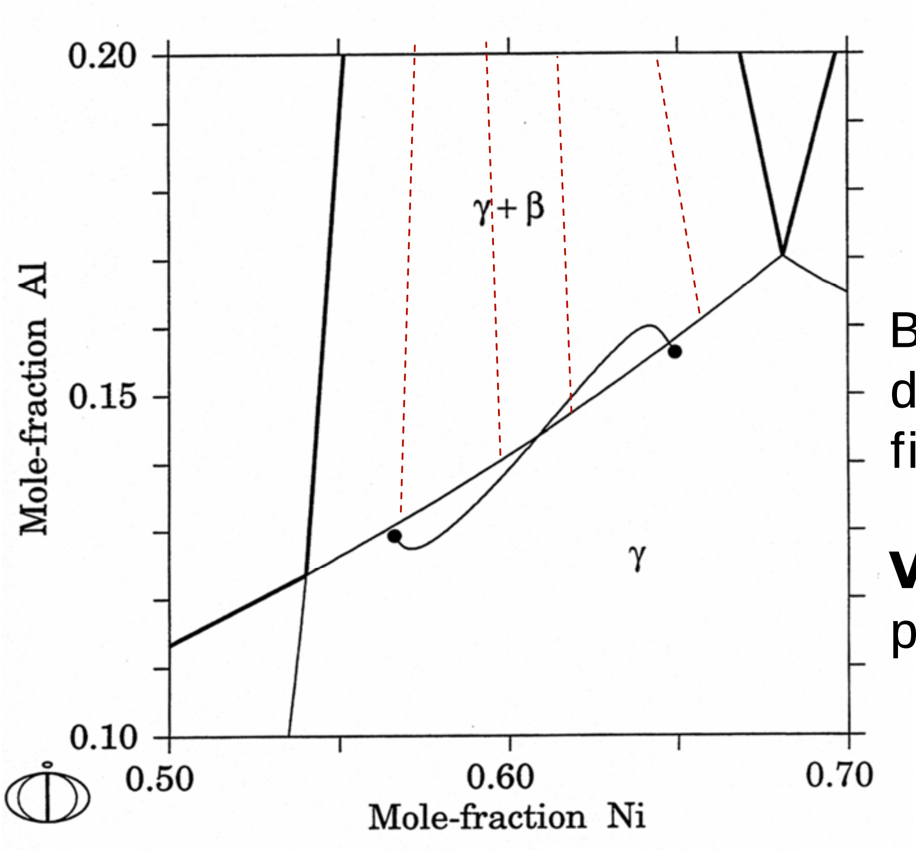


Internal oxidation of Fe-Mn-Al-C (Perez et al.)



Cross-section and the corresponding depth profile of the oxide scale after 160 h at 600°C.

Virtual and real diffusion path



Both alloys in γ phase but diffusion path in two-phase field.

Virtual path because no precipitation of β phase.

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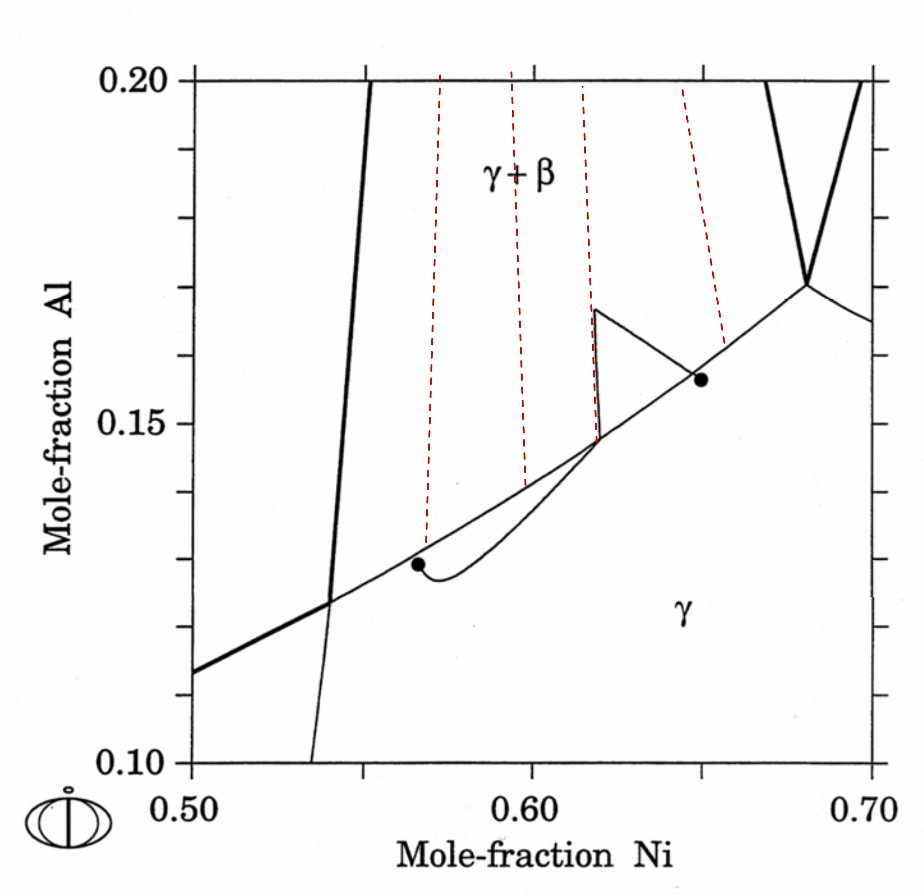
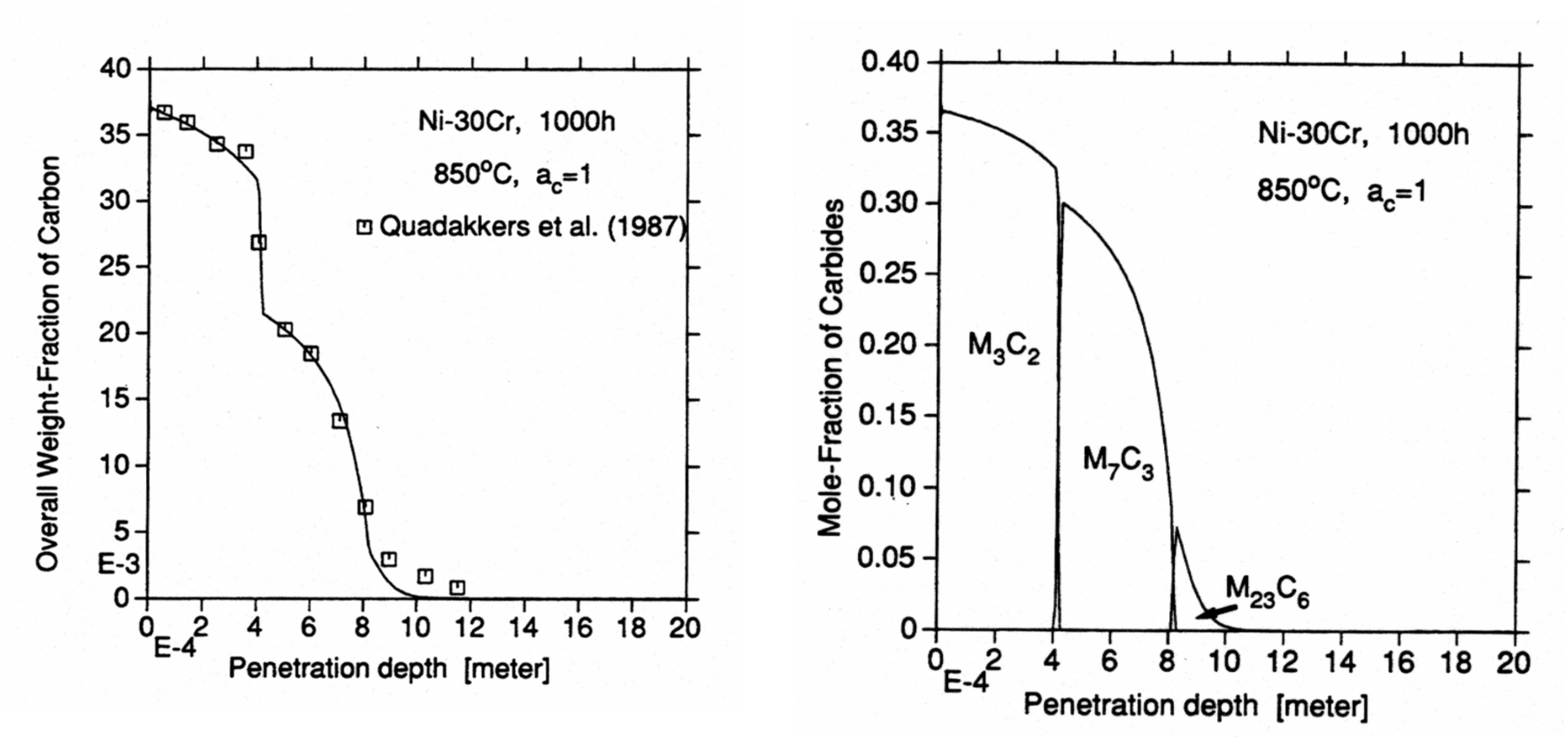


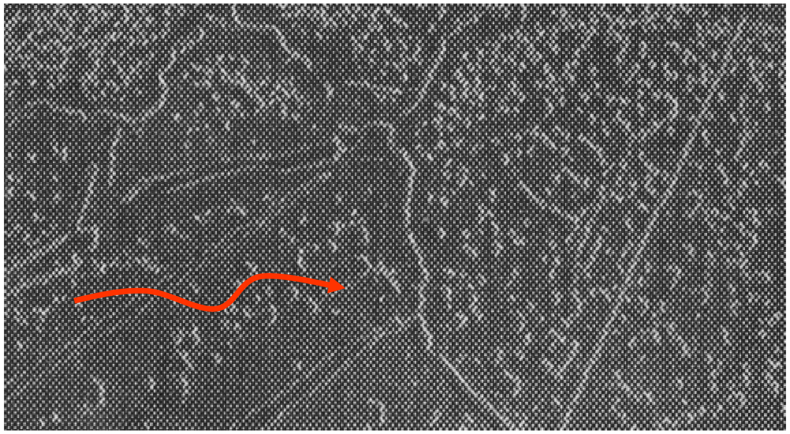
Real diffusion path
in two-phase field.

Precipitation of β taken
into account.



Carburizing of Ni-30%Cr alloy
Engström et al. 1994

Diffusion in dispersed systems – effective diffusivity



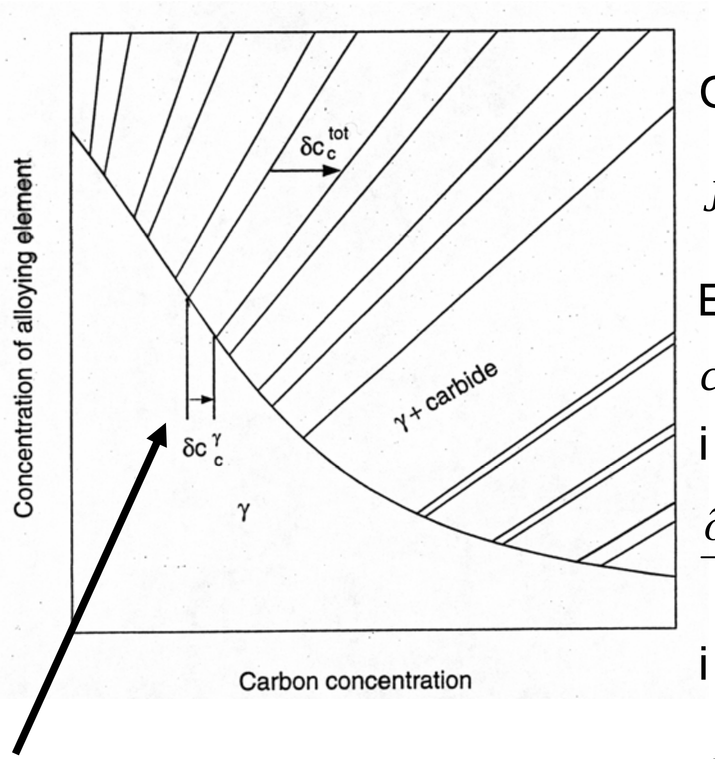
Assumptions:

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

- 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 ==>

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

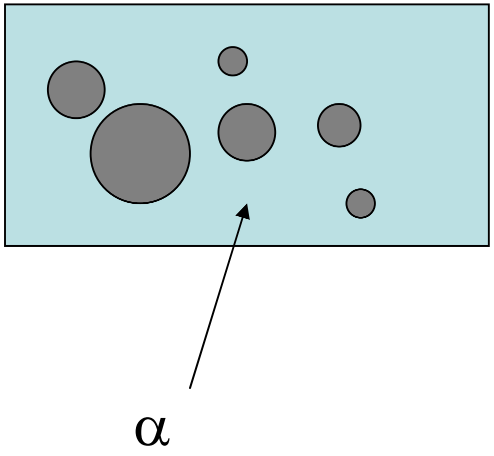
i.e.

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

i.e.

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

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



Ternary 2-phase system:

$x_B^{\alpha/\beta}, \quad x_C^{\alpha/\beta}$ not independent!

The transformation matrix is singular!

$$\begin{pmatrix} \dfrac{\partial c_B^\alpha}{\partial c_B^o} & \dfrac{\partial c_B^\alpha}{\partial c_C^o} \\ \dfrac{\partial c_C^\alpha}{\partial c_B^o} & \dfrac{\partial c_C^\alpha}{\partial c_C^o} \end{pmatrix} \quad \frac{\partial c_B^\alpha}{\partial c_C^o} = \text{const}\,\frac{\partial c_B^\alpha}{\partial c_B^o} \text{ and } \frac{\partial c_C^\alpha}{\partial c_C^o} = \text{const}\,\frac{\partial c_B^\alpha}{\partial c_B^o}$$

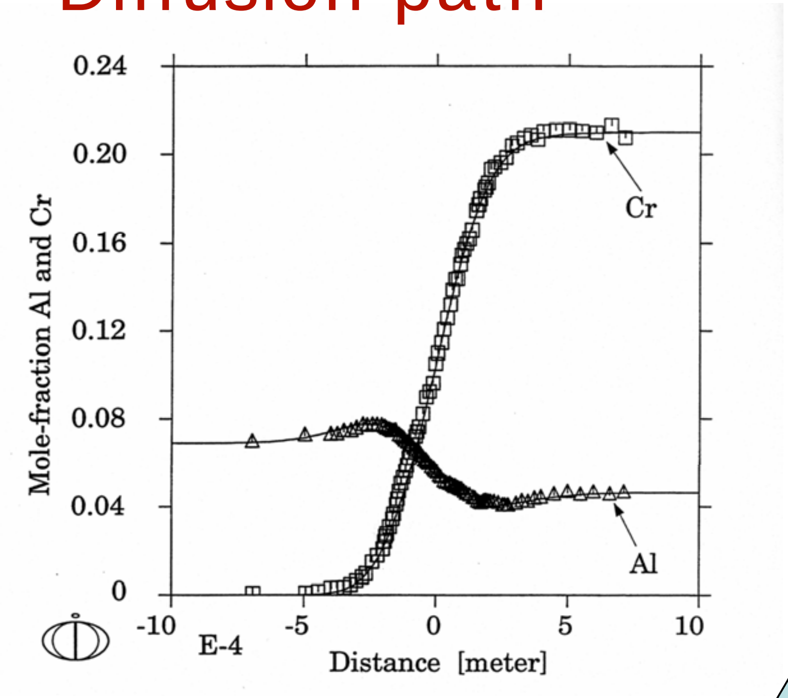
$$\det\left(\frac{\partial c_j^\alpha}{\partial c_k^o}\right) = 0$$

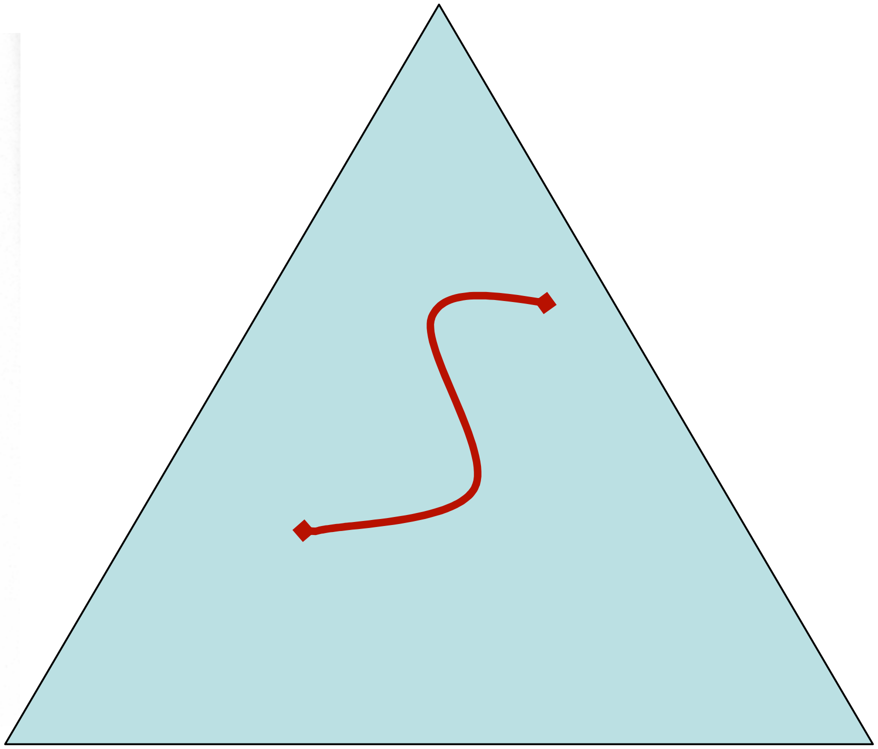
$$\det\left(\frac{\partial c_i^{\alpha}}{\partial c_j^{o}}\right) = 0 \Rightarrow$$

$$\det\left(D_{kj}^{n\alpha eff}\right) = \det\left(\sum_{i=1}^{n-1} \frac{\partial c_i^{\alpha}}{\partial c_j^{o}} D_{ki}^{n\alpha}\right) = 0$$

What does this mean for shape of diffusion path?

Diffusion path





Transformation matrix = δ_{ij}

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Zig-Zag diffusion path in two-phase field!

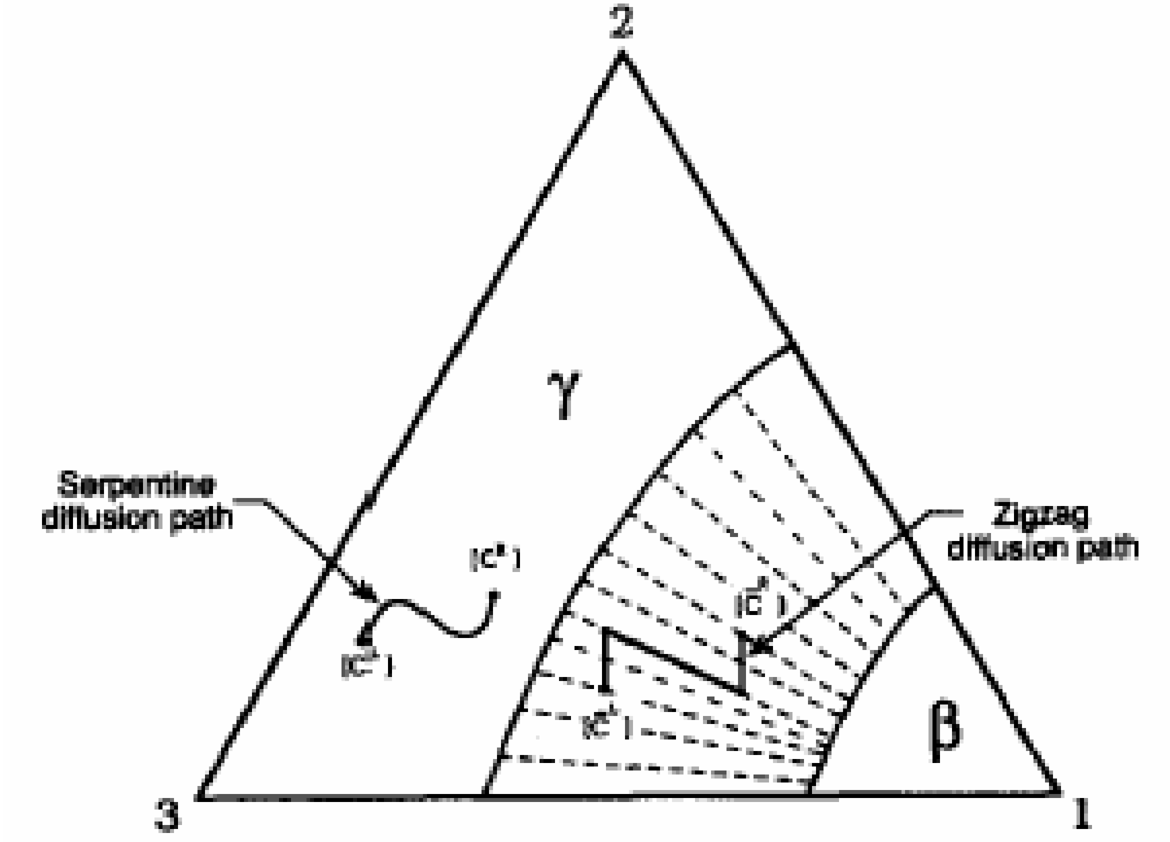
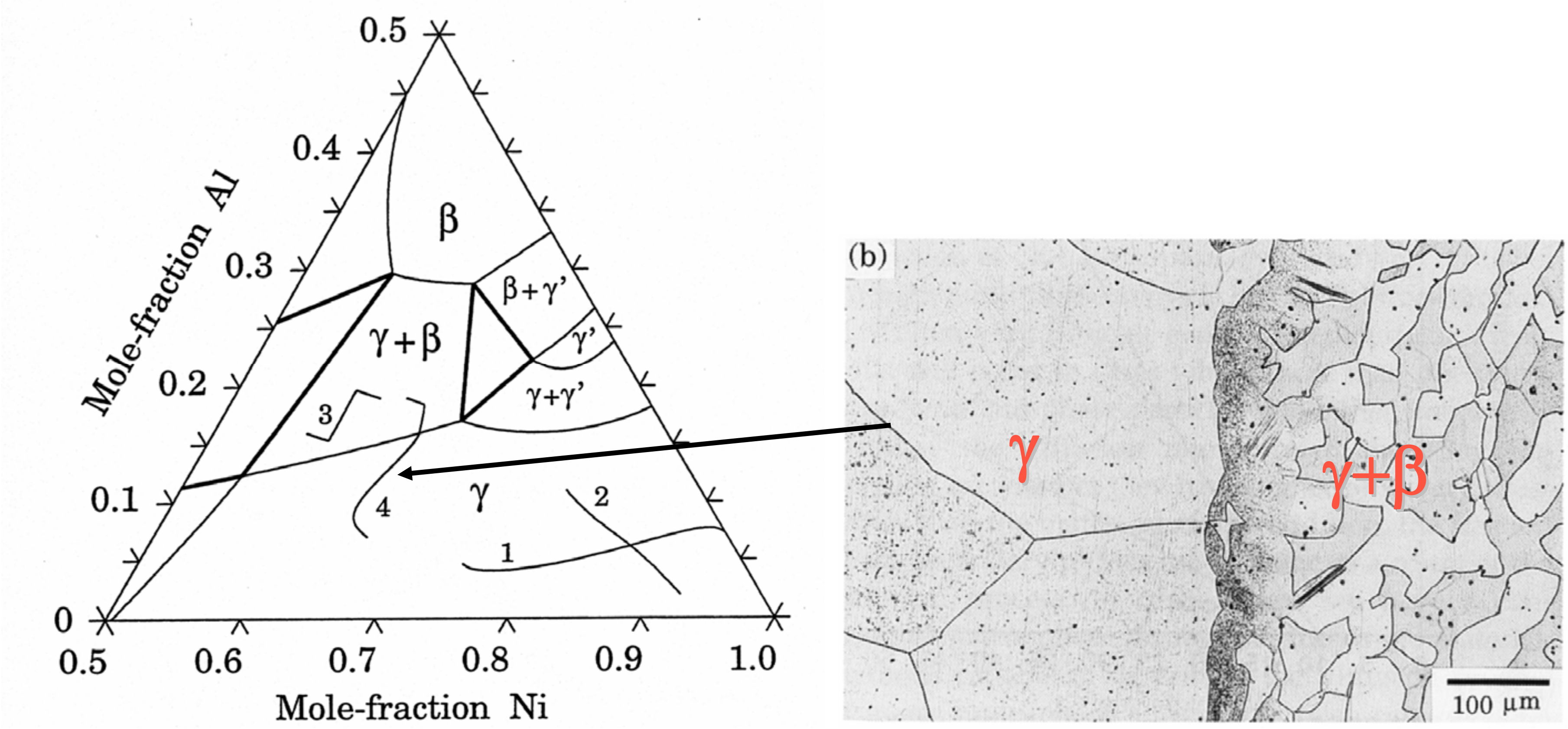


Fig. 1. A schematic ternary phase diagram illustrating a serpentine diffusion path for a single phase diffusion couple and a zigzag diffusion path for a two-phase diffusion couple. The solid circles at the ends of the paths give the compositions of the initial alloys in each couple, $[C_L)$ and $[C_R)$.


0.5
0.4
0.3
0.2
0.1
0
Mole-fraction Al
0.5
0.6
0.7
0.8
0.9
1.0
Mole-fraction Ni
β
β+γ'
γ'
γ+β
γ+γ'
γ
1
2
3
4
(b)
γ
γ+β
100 µm

Different types of planar interfaces

$\alpha+\beta|\alpha+\beta$ type 0

$\alpha>\alpha+\beta$ type 1

or

$\beta>\alpha+\beta$

$\beta>\alpha$ type 2

or

$\alpha>\beta$

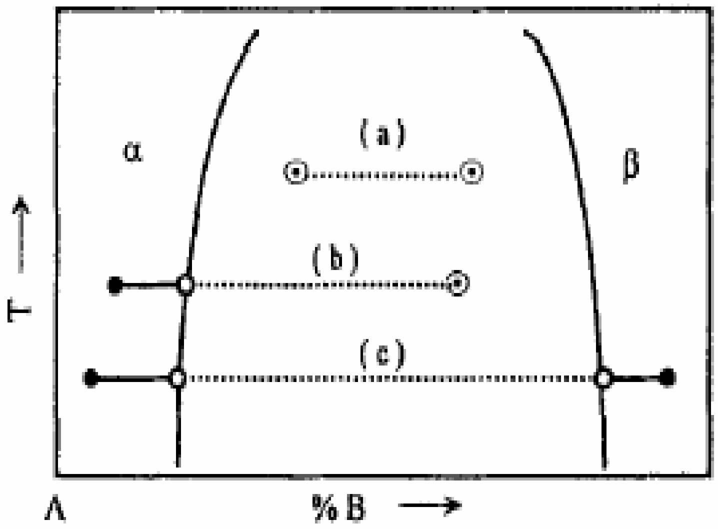


Figure 2. Diffusion paths containing (a) $\alpha+\beta \mid \alpha+\beta$ (Type 0), (b) $\alpha>\alpha+\beta$ (Type 1), and (c) $\alpha>\beta$ (Type 2) boundaries. Closed circles, ●, are initial alloys; open circles, o, are boundary compositions.

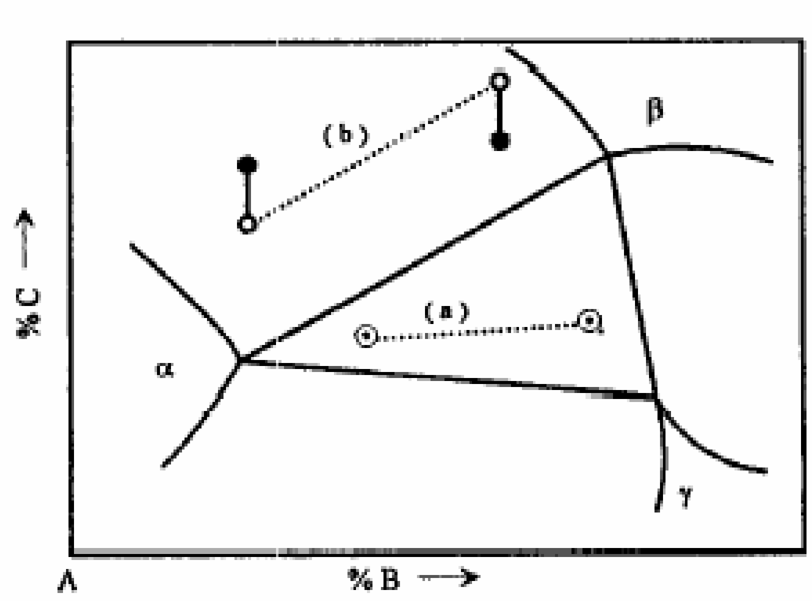


Figure 3. Diffusion paths for two kinds of Type 0 boundaries. (a) $\alpha+\beta+\gamma \mid \alpha+\beta+\gamma$ and (b) $\alpha+\beta \mid \alpha+\beta$. (b) illustrates a "zigzag" diffusion path.

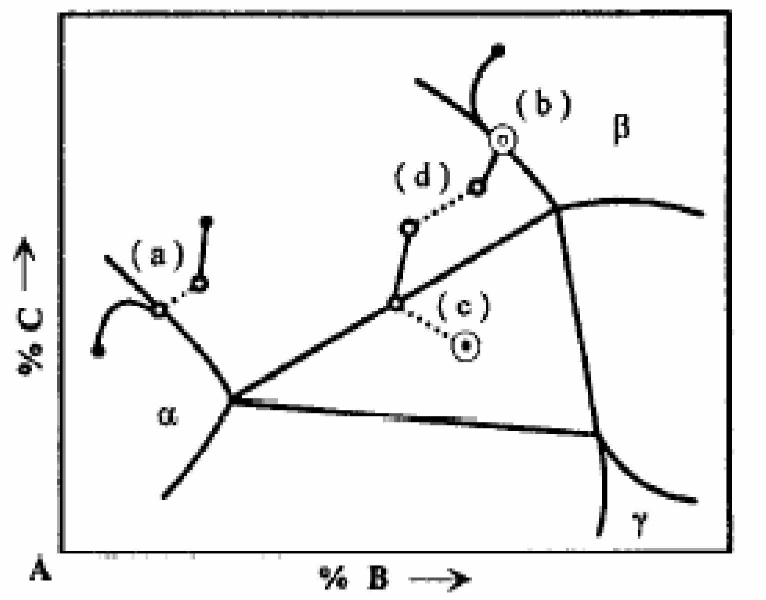
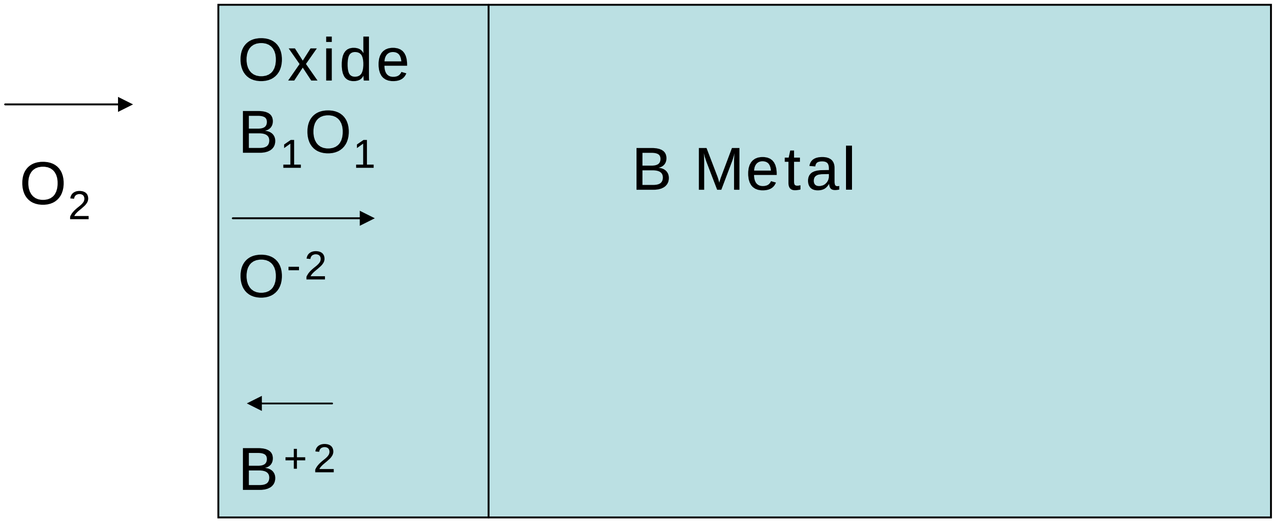


Figure 4. Diffusion paths for three kinds of Type 1 boundaries: (a) $\alpha>\alpha+\beta$, (b) $\beta<\alpha+\beta$. and (c) $\alpha+\beta>\alpha+\beta+\gamma$. (d) is a Type 0.

Internal and external oxidation



O_2

Oxide

B_1O_1

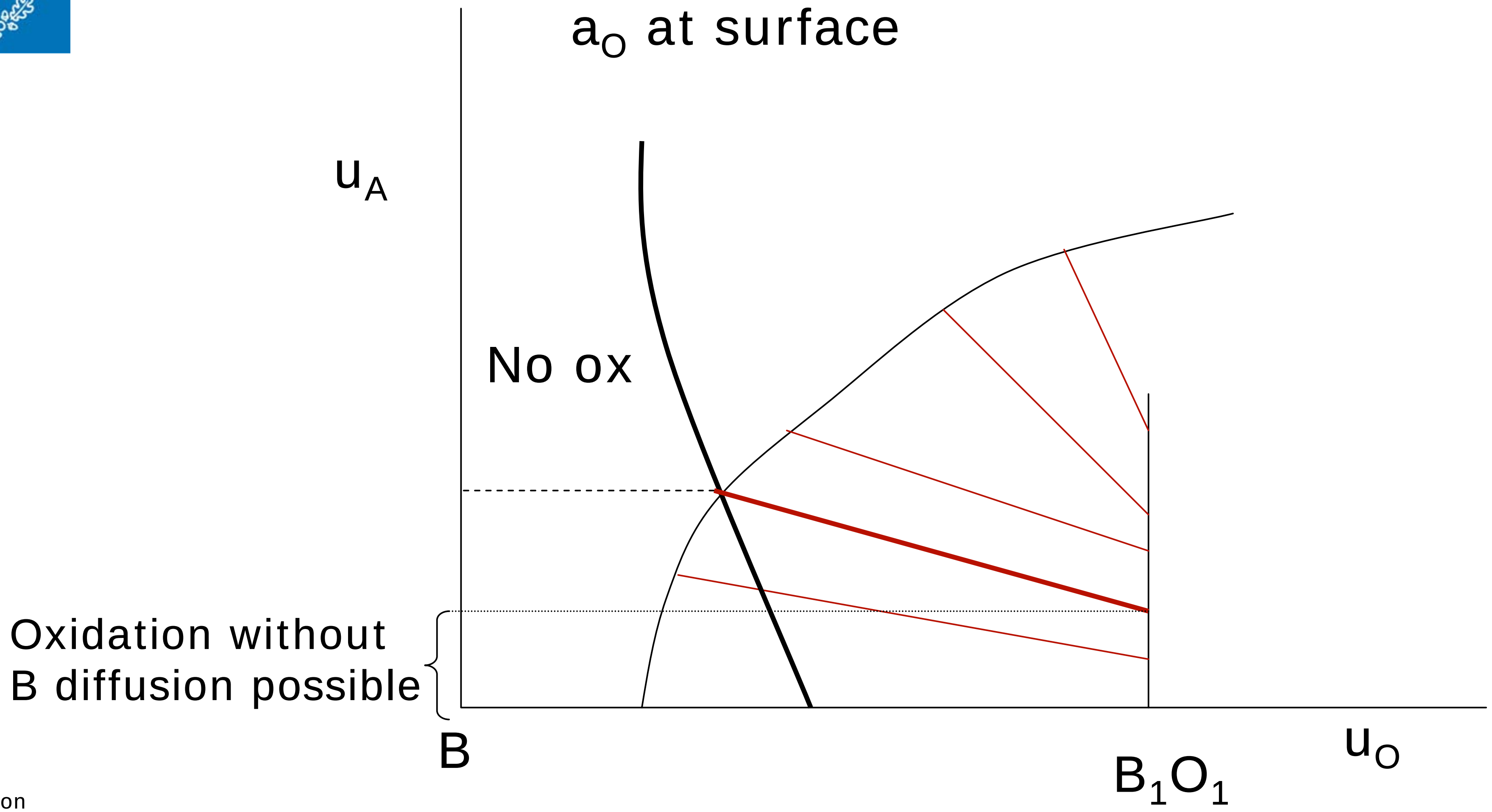
O^{-2}

B^{+2}

B Metal

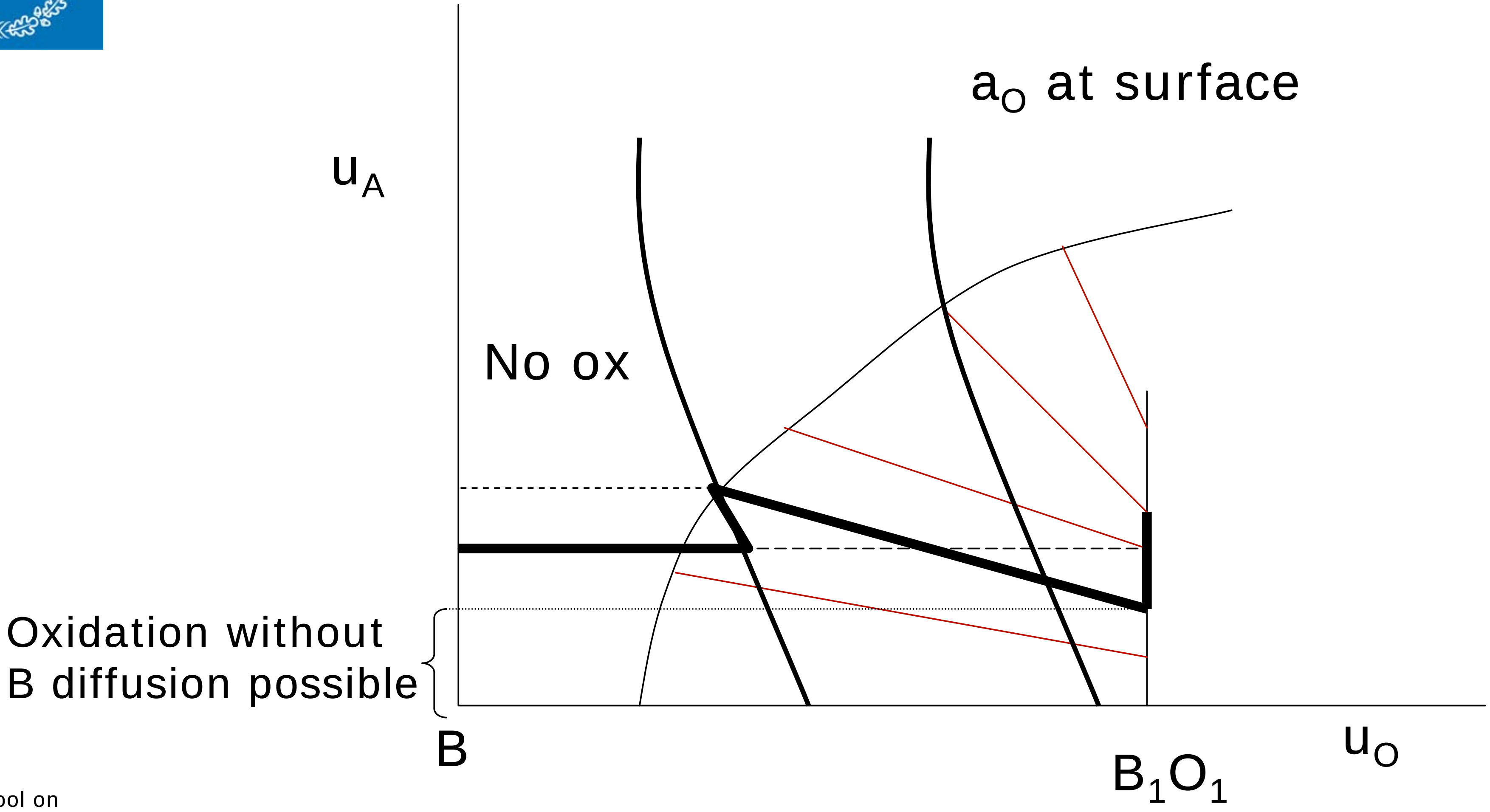
Pure B

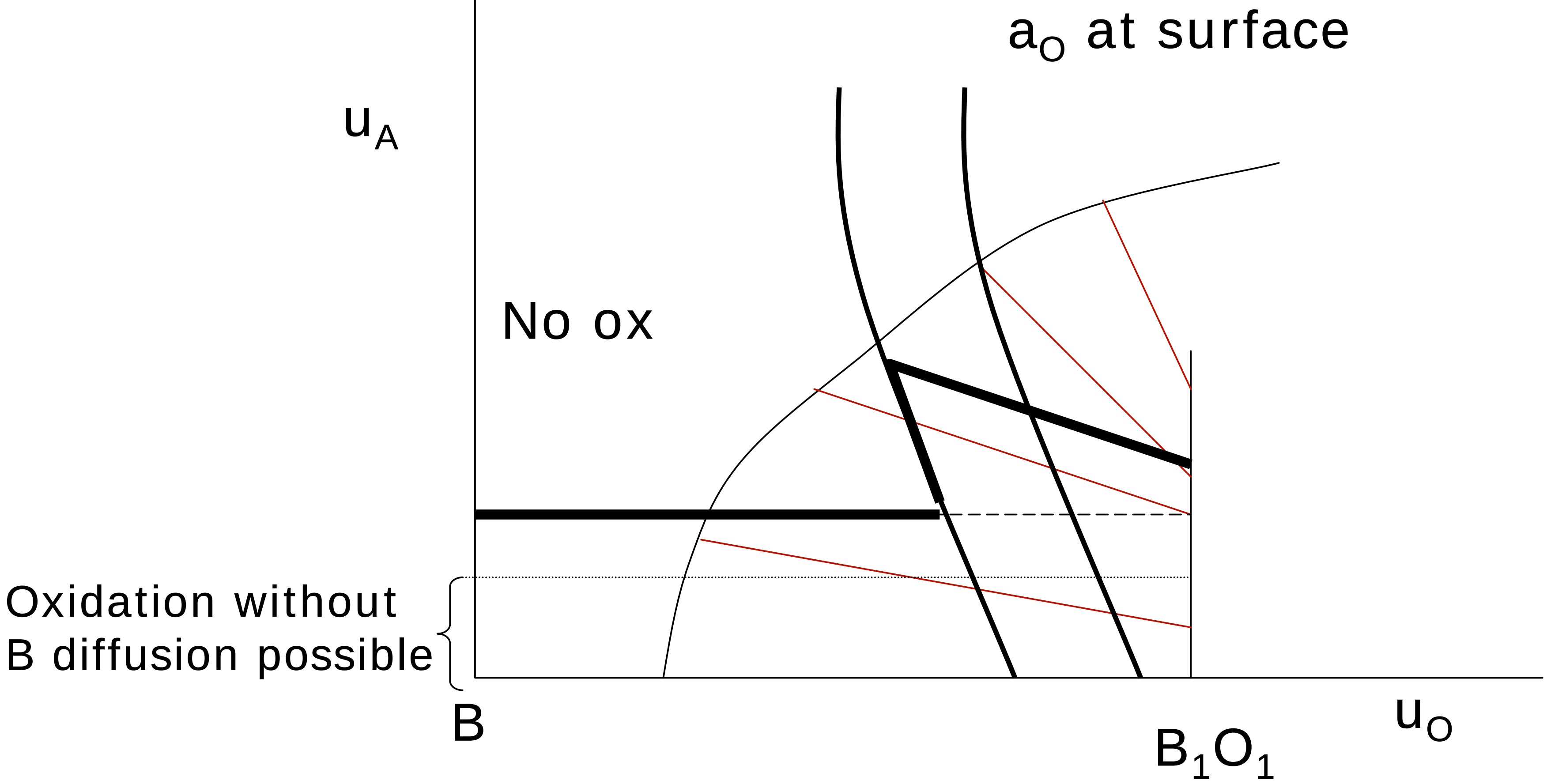
Binary alloy A-B



Oxygen diffusion in both oxide and metal stabilises the planar front (external oxidation).

B supersaturation destablizes planar front (internal oxidation).


a_O at surface
u_A
No ox
Oxidation without
B diffusion possible
B
B_1O_1
u_O


a_O at surface
u_A
No ox
Oxidation without
B diffusion possible
B
B_1O_1
u_O

Summary – multiphase diffusion couples

- In contrast to binary diffusion couples, where interdiffusion only yields new phases as layers parallell with the initial joint, multi component systems may give dispersed phases.
- Virtual and real diffusion path.
- Real diffusion path i zig-zag in a ternary two-phase system.
- Can be understood from effective model.
- Internal versus external oxidation.