Diffusion

- **Interstitial**
  - Fick's first law
    $$J_B = -D_B \frac{\partial C_B}{\partial x}$$
    $$D_B = D_0 e^{\frac{Q}{RT}}$$
    - Intrinsic diffusivity
  - Fick's second law

    $$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

- **Substitutional**
  - Self diffusion, vacancy diffusion
  - Lattice fixed frame of reference, drifting lattice
  - Kirkendall effect: net flow of vacancy: $J_v = -(J_A + J_B)$
  - Darken equation
    $$\tilde{J}_B = -\tilde{D} \frac{\partial C_B}{\partial x}$$
    $$\tilde{D} = x_A D_B + x_B D_A$$

Frames of reference

- **Lattice-fixed frame of reference:**
  - Defined by the inert markers, or that there is no net flow of lattice sites.

    $$\sum_{K=1}^{n} J_k = -J_{Va}$$

- **Volume-fixed frame of reference:**
  - Defined in such a way that there is no net flow of volume.

    $$\sum_{K=1}^{n} \tilde{J}_k V_k = 0$$

- **DICTRA frame of reference**
  - Volume-fixed frame, however only the substitutional components are assumed to contribute to the volume

    $$\sum_{K \in S}^{n} \tilde{J}_k = 0$$

$V_{interstice} = \emptyset$

$V_k = $ skj^{ln} pro vše dy

Frames of reference

The equation for the velocity of the markers in the diffusion zone relative to the ends of the diffusion couple, in the Kirkendall experiment, is:

$$\upsilon = \sum_{k=1}^{n} V_k J_k$$

(handwritten: Velocity of marker ; bez J_{va})

This is the velocity with which the two frames move relative to each other.

We may use this equation in order to transfer the fluxes from the volume-fixed to the lattice-fixed frame, or vise versa *(handwritten: chaopak)*

$$J_k' = J_k - c_k \left(\sum_{k=1}^{n} V_k J_k \right)$$

(handwritten annotations: lattice fixed ; Volume f/x ; $mol\ m^{-1}\ s^{-?}$; $mol\ m^{-1}\ s^{-?}$; $m^3\ s^{-1}$; $\frac{mol}{m^3}$)

(handwritten margin note: za prol pohladu ze sta li udro... rounot. houc. valoncl)

Atomistic treatment of diffusion

For crystalline phases it's usually believed that diffusion occurs through a vacancy exchange mechanism.

Assuming that threre is a random distribution of vacant sites and that the number of vacncies is everywhere adjusted to equilibrium, it's possible to derive the following expression for the flux of k in a lattice-fixed frame of reference:

$$J_k^L = -c_k y_{va} M_{kva} \nabla \mu_k$$

(handwritten: lattis fix ; $\frac{\partial \mu_k}{\partial k}$)

where M_{kva} is some kinetic factor which gives the rate of exchange if there is a vacancy adjacent to a k atom.

(handwritten margin: rchtol)

Phenomenological equations

$$J_k^L = -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} - L_{1T} \frac{\partial T}{\partial z} - L_{1P} \frac{\partial P}{\partial z} - L_{1\phi} \frac{\partial \phi}{\partial z}$$

They are called phenomenological since they steam from no model, but from the observed conditions of equilibrium.

If we choose to consider an isothermal, isobaric and isopotential system we have:

$$J_k^L = -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} \qquad \left(J_k^L = -L_{kk} \frac{\partial \mu_k}{\partial z} \right)$$

Mobility *vs* L Parameter

Assuming that the vacancy exchange mechanism is predominant, and by comparing to the expression derived earlier under this assumption, we may identify:

$$L_{kk} = c_k y_{va} M_{kva} \qquad (1)$$

$$L_{ki} = c_i y_{va} M_{iva}$$

We have now established a relation between M and L.

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Phenomenological equations

$$J_k^L = -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} - L_{1T} \frac{\partial T}{\partial z} - L_{1P} \frac{\partial P}{\partial z} - L_{1\phi} \frac{\partial \phi}{\partial z}$$

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Mobility *vs* L Parameter

Assuming that the vacancy exchange mechanism is predominant, and by comparing to the expression derived earlier under this assumption, we may identify:

$$L_{kk} = c_k y_{va} M_{kva} \qquad (A)$$

$$L_{kn} = c_i y_{va} M_{iva}$$

We have now established a relation between M and L.

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vey quick

Transformation to a volume-fixed frame

$$J_k = J_k^L + c_k v = J_k^L + c_k \sum_{k=1}^{n} V_k J_k^L$$

$$= -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} - c_k \sum_{k=1}^{n} V_k \sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} \quad ✳ ✳$$

or,

$$J_k = -\sum_{i=1}^{n} L_{ki}' \frac{\partial \mu_i}{\partial z} \quad ✳ \; ?$$

where,

$$L_{ki}' = -\sum_{j=1}^{n} (\delta_{jk} - c_k V_j) L_{ji} \qquad (2)$$

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Transformation to concentration gradients

Applying the chain-rule of derivation on the previous equation:

$$J_k = -\sum_{i=1}^{n} L_{ki}' \frac{\partial \mu_i}{\partial c_j} \frac{\partial c_j}{\partial z} \qquad ?$$

Or equally if the diffusivities, D_{kj}, are introduced:

$$J_k = -\sum_{j=1}^{n} D_{kj} \frac{\partial c_j}{\partial z}$$

where,

$$D_{kj} = \sum_{i=1}^{n} L_{ki}' \frac{\partial \mu_i}{\partial c_j} \qquad \boxed{D = L \; \Phi} \quad \begin{matrix}(3) \\ (3a)\end{matrix}$$

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Independent set of driving forces

There is a relation between the n concentration gradients, and it's possible to eliminate one of them:

$$\frac{\partial c_n}{\partial z} = -\frac{\partial c_1}{\partial z} - \frac{\partial c_2}{\partial z} - \ldots\ldots\ldots - \frac{\partial c_{n-1}}{\partial z}$$

and thus, the flux is now expressed: $J_k = -\sum_{j=1}^{n-1}(D_{kj} - D_{kn})\frac{\partial c_j}{\partial z}$

we may identify: $D_{kj}^n = D_{kj} - D_{kn}$ (4) $(4a)$

and finally obtain: $J_k = -\sum_{j=1}^{n-1}D_{kj}^n\frac{\partial c_j}{\partial z}$

Time Dependence
$\dfrac{\partial c_k}{\partial t} = -\mathrm{div}(J_k)$

Summary of steps taken when transforming from M's to D's

Intrinsic diffusion coefficients

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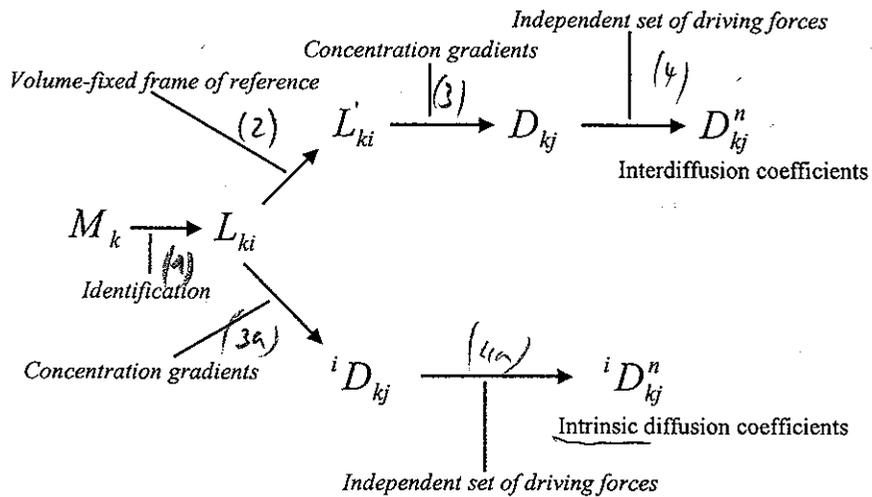
Atomic mobility

$$M_i = \frac{M_i^0}{RT} \cdot e^{-\frac{Q_i}{RT}} = \frac{1}{RT} e^{\frac{-Q_i + RT\ln\left(M_i^0\right)}{RT}}$$

- Tracer diffusivity $\quad D_i^* = RTM_i$

Moving Boundary Problems

- Sharp Interface
  - Zero thickness
  - Interface tracking
  - Interfacial energy
  - Local equilibrium and deviation from local equilibrium
  - Typically simple geometry

- Diffuse Interface (Day 2)
  - Finite interface width
  - Field variables across a boundary continuously
  - Gradient energy to represent the interfacial energy
  - Complex geometry

Moving Phase Boudary
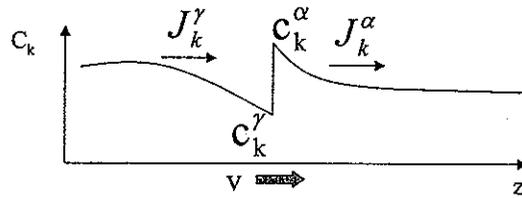
Unknowns: Tie-line, specified by n-2 a_i or μ_i

                  Velocity of phase boundary, v

Equations: n-1 flux-balance equations, $\;v(c_k^\alpha - c_k^\gamma) = J_k^\alpha - J_k^\gamma$

Solved as: $v(c_k^\alpha - c_k^\gamma) - (J_k^\alpha - J_k^\gamma) = 0$
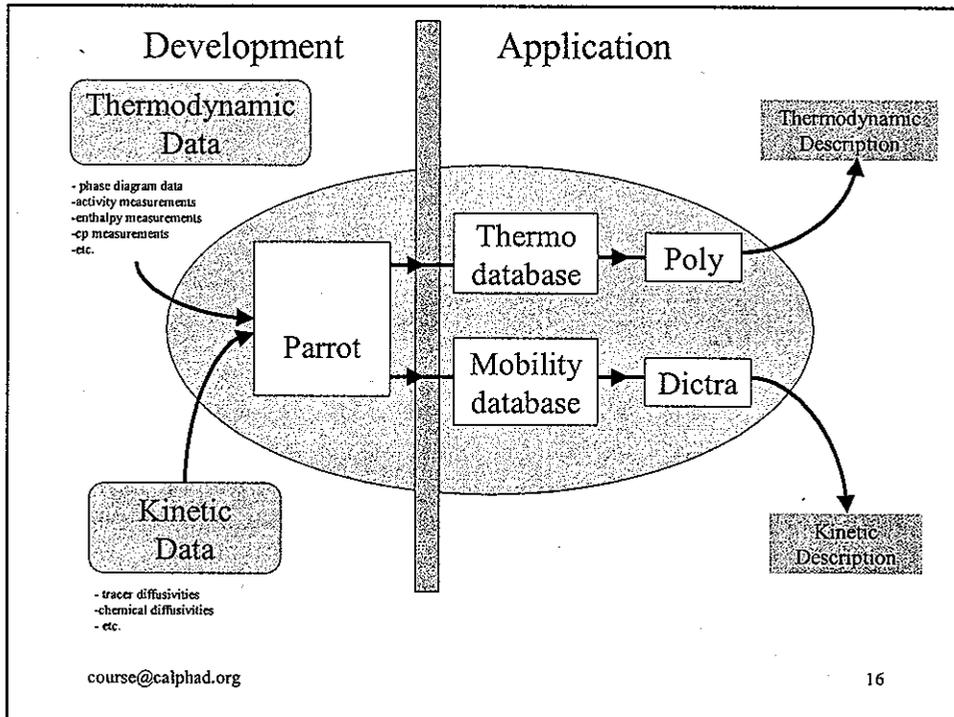
What is DICTRA?

- Software for diffusion simulations

  - One dimensional (planar,cylindrical,spherical)
  - Linked to Thermo-Calc for thermodynamics→Has all modules in Thermo-Calc plus a Dictra module.
  - Quantitative description of multicomponent diffusion
  - Simulations based on databases for thermodynamics and diffusion
  - Written in FORTRAN, runs on most plattforms

Numerical Calculation of Diffusional Reaction

Thermodynamics   DATABNKS   Kinetics

| Gibbs Energy | $\dfrac{\partial^2 G}{\partial x_i\, \partial x_j}$ | | Kinetic Coefficients |

Interfacial Equilibrium   Solve Diffusion Equations

Solve Fluxbalance

Moving phase boundary model
Dispersed system model
Coarsening model
Cell model
Cooperative growth model
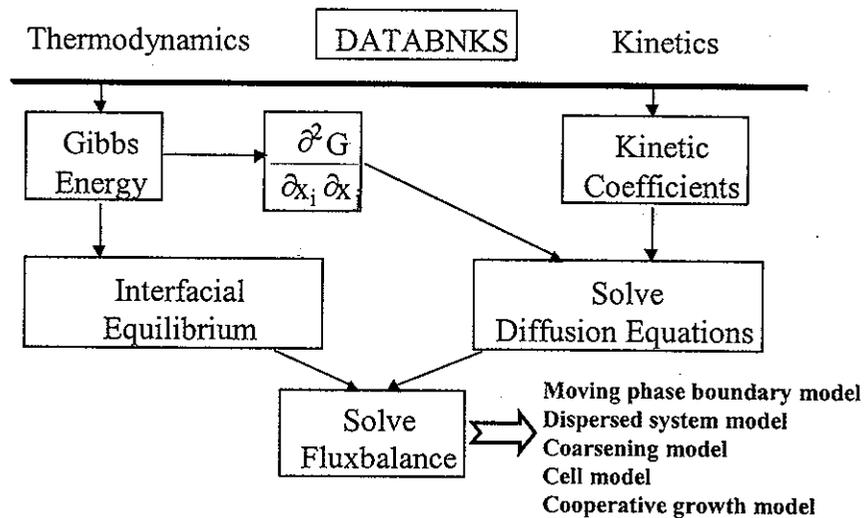
Mobility databases

MOB 2
The most general diffusion database.
Could be used for Steels, Nickel alloys, Aluminium alloys and more.

75 Elements: Ag, Al, Am, As, Au, B, Ba, Be, Bi, C, Ca, Cd, Co, Cr, Cs, Cu, Dy, Er, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, N, Na, Nb, Nd, Ni, Np, Os, P, Pa, Pb, Pd, Pr, Pt, Pu, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Tc, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr

Phases with diffusion data: BCC_A2 CEMENTITE FCC_A1 FE4N HCP_A3 LIQUID

Assessed data for the following binary systems
BCC_A2: C-Fe, C-Cr, Cr-Fe, Cr-N, Cr-Ni, Fe-N, Fe-Ni
FCC_A1: Al-Cr, Al-Ni, C-Fe, C-Ni, Cr-Fe, Cr-Ni, Fe-N, Fe-Ni, Fe-Si
HCP_A3: C-Fe, Fe-N
FE4N: C-Fe, Fe-N

Assessed data for the following ternary systems
BCC_A2: C-Cr-Fe
FCC_A1: Al-Cr-Ni, C-Cr-Fe, C-Fe-Ni

Assessed data for the following higher order systems
BCC_A2: C-Cr-Fe-N-Ni
FCC_A1: C-Cr-Fe-Ni

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System

Cell

Lower (left) Interface

Upper (right) Interface

Cell

Inner interfaces under local equilibrium

Region

Region

Region

Region
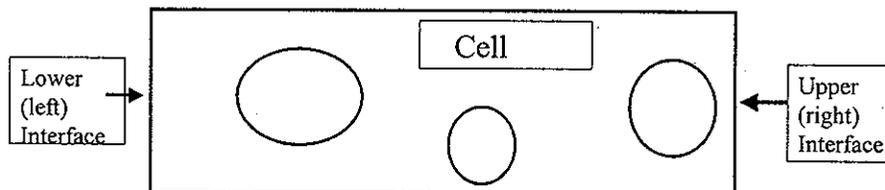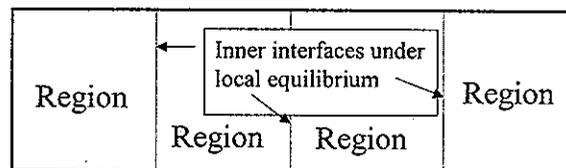
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Boundary conditions in DICTRA

- Boundary Conditions can be specified as functions of time, temperature and pressure.

- Different functions may be used in different time intervals.

Example of conditions are:

- Closed system (default)

- Sate variable expressions

- Flux conditions

- Mixed conditions

Application example:

Carburization with surface reaction

$$J_C = f_C(a_C^{surf} - a_C^{gas})$$
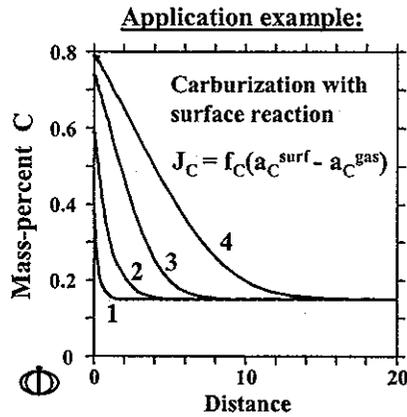
ENTER_GEOMETRICAL_EXPONENT

Command that determines the geometry of the system. The program handles problems that can be reduced to 1-dimensional geometries. Default value is zero, i.e. planar geometry.

Exponent   Geometry

0   **Planar geometry.**
This corresponds to an infinitely wide plate of a certain thickness.

1   **Cylindrical geometry.**
This corresponds to an infinitely long cylinder of a certain radius.

2   **Spherical geometry.**
A sphere with a certain radius.

Some different possible geometries
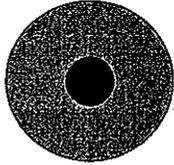
Growth or dissolution of spherical precipitate　　**Growth of spherical film (Grain-boundrary film)**　　**Planar growth**
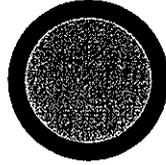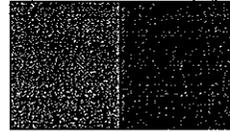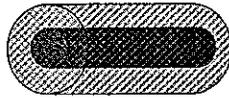
Growth of cylindrical precipitate

Region

phase

profile
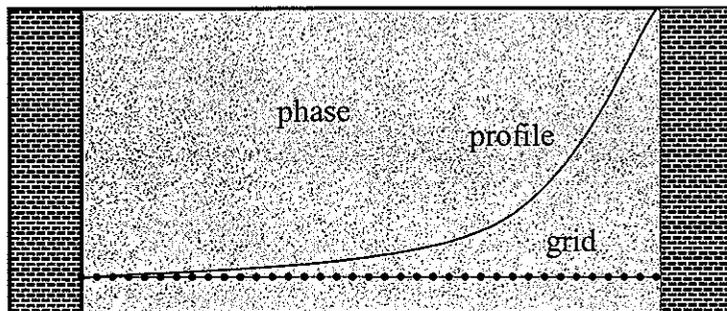
grid

Region

Matrix phase
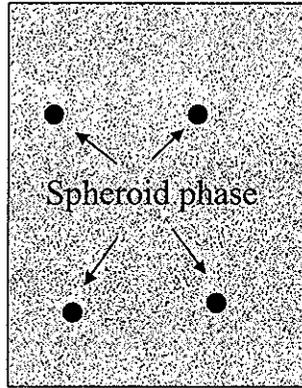
Lamella phase

Spheroid phase
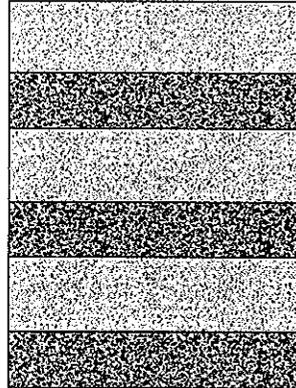
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Grid points

| Lower Interface | | Upper Interface |

Linear

GEO >1

GEO <1

Double
GEO
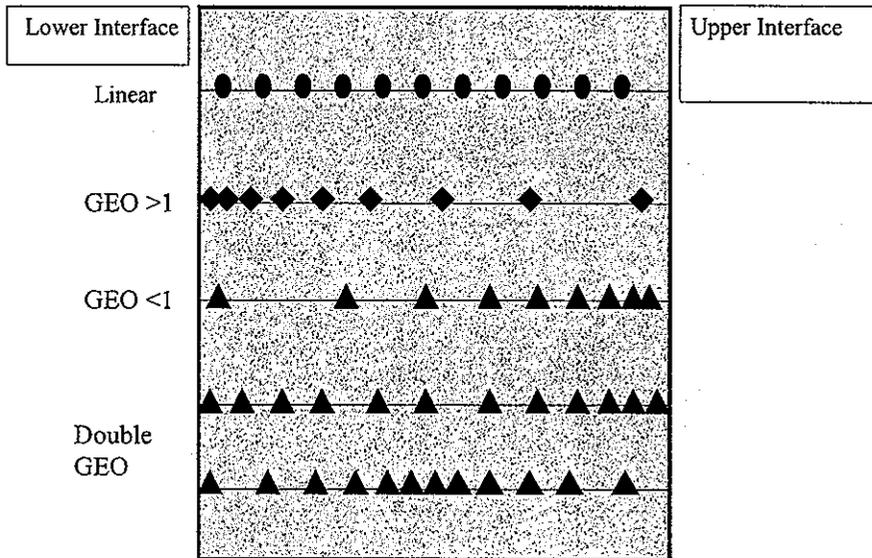
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Microstructure *vs* Dictra
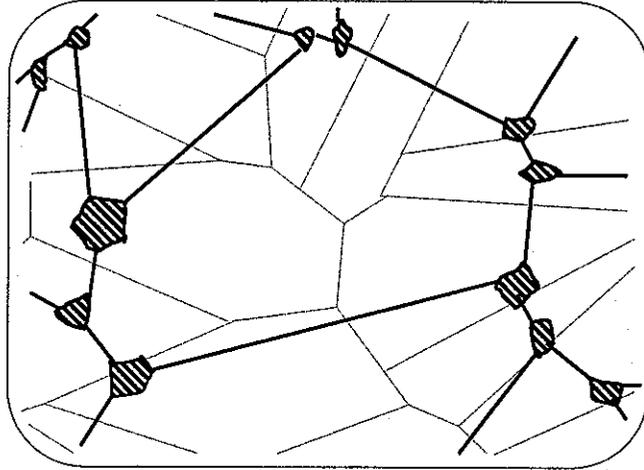
Multi-cell Approach

$$\sum J_i = 0$$

Diffusion potential = constant
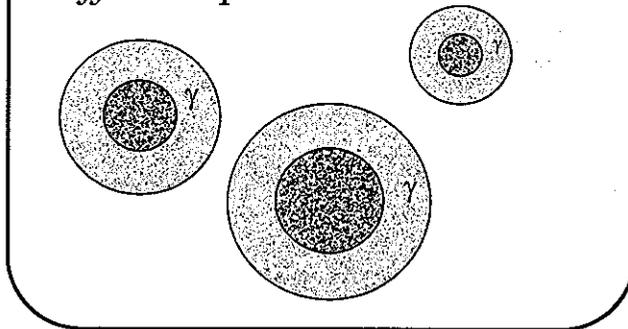
Some DICTRA applications

Coarsening

Carbide dissolution
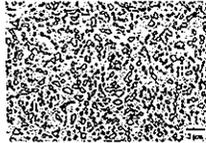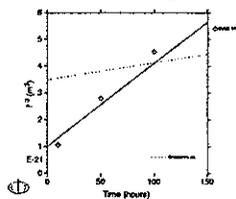
Carbon diffusion in a weld between two steels
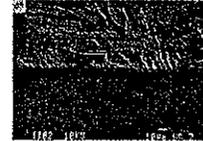
Microsegregation during solidification
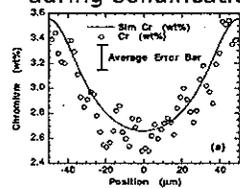
Carburizing

Lippard et al. *Metall. Mater. Trans. B* 1998
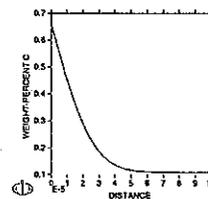
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More DICTRA applications

- Homogenisation of alloys

- Carburization and decarburization

- Carburization of alloys

- Nitriding of steels

- Diffusion during sintering of cemented carbides

- Nitrocarburizing of steels

- Austenite/ferrite diffusional transformations in steels

- Growth or dissolution of individual particles

- Transient liquid phase bonding of alloys

- Calculation of TTT-diagrams

- Interdiffusion between coating/substrate

- Coarsening of a particle distribution

- Gradient sintering of cemented carbides

- Growth of pearlite in alloyed steels

- Sigma phase precipitation in stainless steel

- Post weld heat treatment of welds between dissimilar materials

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Moving Phase Boundary

• Moving phase boundaries simulations may be setup in DICTRA in two different ways:

  • Introducing two or more adjacent regions containing different phases
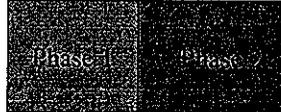
 •Entering an inactive phase (formed when thermodynamically stable)

  inactive phase ⟶
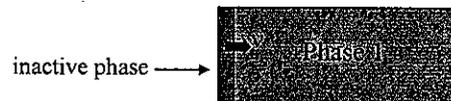
Possible Cell Calculations

• Simulation of dissolution of a size distribution of precipitates

• Simulation of diffusion at an immobile phase interface

• Coupled simulation of dissolution with precipitates of different phases

Cell#1

- - - Cell boundary
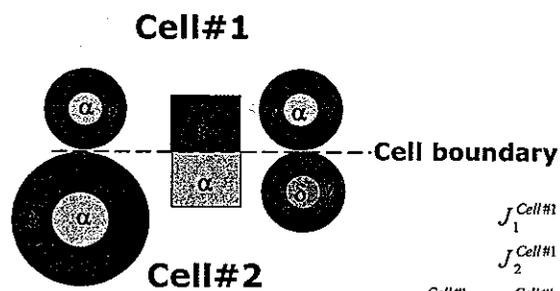
Cell#2

$$J_1^{Cell\#1} = J_1^{Cell\#2}$$

$$J_2^{Cell\#1} = J_2^{Cell\#2}$$

$$\mu_1^{Cell\#1} - \mu_n^{Cell\#1} = \mu_1^{Cell\#2} - \mu_n^{Cell\#2}$$

$$\mu_2^{Cell\#1} - \mu_n^{Cell\#1} = \mu_2^{Cell\#2} - \mu_n^{Cell\#2}$$

Cell calculations in DICTRA

• Makes it possible to couple several computational cells

• Conditions for cell boundaries:

✓ Equal diffusion potentials Φ_i for the elements

$$\Phi_i = \mu_i - \mu_n \quad \text{for subst. elements}$$

$$\Phi_i = \mu_i \quad \text{for interstitial elements}$$

✓ Flux balances to conserve the mass of the elements

$$\frac{J_i^{cell\#1}}{n^{cell\#1}} = \frac{J_i^{cell\#2}}{n^{cell\#2}}$$

n, the number of identical cells

Disperse system model

• Assumptions:
  – Diffusion takes place in the matrix phase only.
  – Equilibrium holds locally on each grid point.

• Effective diffusivity
  – Diffusion matrix, Dkj, is multiplied with a labyrinth factor f(volfr), volfr being the volume fraction of the matrix phase.
  – The labyrinth factor is often taken as volfr^2.
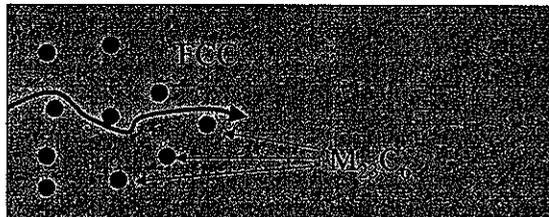
Examples

- Diffusion in one phase: Homogenization of an Fe-Ni alloy.
- Moving boundary: Dissolution of carbide in one cell and in three cells.
- Diffusion in dispersed system: Carburization of the Ni-25% Cr alloy.
- Exercise: γ to α transformation in the Fe-0.15C alloy

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Simulation Scheme

1. Get Gibbs energy and mobility
2. One cell simulation
3. Set geometry, temperature, time
4. Set boundary conditions (default: closed system)
5. Enter regions
6. Enter grid in region
7. Enter phases in regions
8. Enter concentration profiles of phases

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Dictra: Common Commands

LIST_MOBILITY_DATA
CREATE_NEW_CELL
SET_CONDITION
ENTER_REGION
ENTER_GRID_COORDINATES
ENTER_PHASE_IN_REGION
ENTER_COMPOSITIONS
ENTER_GEOMETRICAL_EXPONE
SET_SIMULATION_TIME
SIMULATE_REACTION
· POST_PROCESSOR

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Post: Common Commands

SET_DIAGRAM_AXIS

SET_INDEPENDENT_VARIABLE

SET_PLOT_CONDITION

MAKE_EXPERIMENTAL_DATAFILE

PLOT_DIAGRAM

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Variables in the Post-Processor

State variables

T, P, Amount of components (e.g. X(Cr), W(Cr), W(Fcc,Cr), etc.)

Amount of a phase, e.g. NP(Fcc)

Activity for a component: AC(Cr)

Chemical Potential for a component: MU(Cr)

Energetic properties: G, H, S, A

Variables in the Post-Processor

Integral variables (Integration in space)

Variables constructed in the following way:

First letter always I for integral variable, second letter specifies quantity

N   (number of moles)

W   (mass)

V   (volume) and many more..

Third letter (optional) specifies normalizing quantity e.g. V (total volume).

Variables in the Post-Processor

Integral variables, *Examples*

IVV(CARBIDE)

Volume of region CARBIDE divided with total volume, i.e. volume fraction of carbide

IW(CARBIDE,CEMENTITE,CR)

The mass of Cr in the cementite phase in region carbide

Variables in the Post-Processor

Auxiliary variables "Special variables" e.g.

POSITION-OF-INTERFACE

VELOCITY-OF-INTERFACE

LOGDT(phase,J)

LOGDC(phase,J,K,N)

User-defined functions

Plotting in DICTRA

- Two independent variables in a DICTRA-simulation, TIME and DISTANCE

- When plotting a diagram we need to specify one of them i.e. use it as plot condition. Command: SET-PLOT-CONDITION

- TIME can be specified as one or several values.

- When plotting integral quantities, time is automatically chosen as independent variable.

Exa1: Homogenization of an Fe-Ni alloy
# (Initially a linear concentration profile)

T = 1400 K

50% Ni

FCC

10% Ni
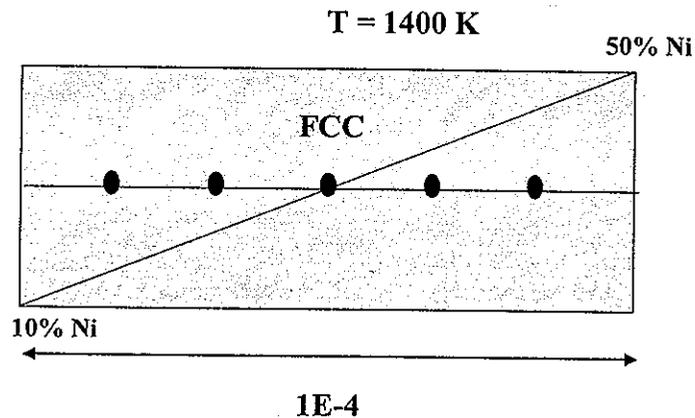
1E-4

Input of T and c

• Temperature (T) can be entered as a function of time

• Many different functions can be used (+, -, *, **, SQRT(X), EXP(X),LOG(X),SIN(X))

• Concentration can be entered as a function of distance or read from a file

• Many functions e.g. error-functions (erf(x)) and heavy-side step functions (hs(x))
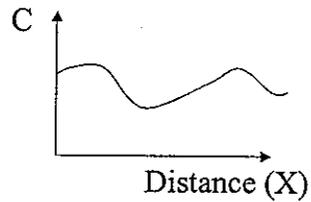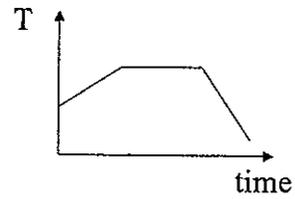

Cementite dissolution in a Fe–Cr-C alloy

Dissolution of cementite at 910C (or 1183K):
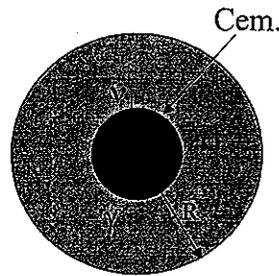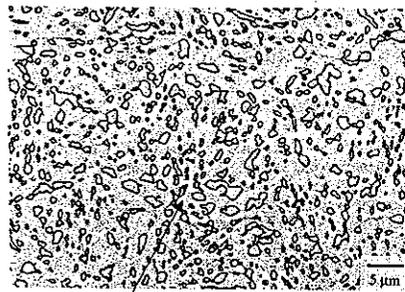
Initial particle radius is estimated to 0.5255 μm.

Cementite dissolution in a Fe–Cr-C alloy

The volume fraction of cementite and the composition in the cementite, is calculated at the normalizing temperature 735C (1008K).

The size of the γ region is calculated from:

$$\frac{R^3_{cementite}}{R^3_{tot}} = \frac{V_{cementite}}{V_{tot}} = V^f_{cementite}$$

$$\Longrightarrow \quad R_\gamma = R_{tot} - R_{cementite} = \frac{R_{cementite}}{\sqrt[3]{V^f_{cementite}}} - R_{cementite}$$

$$\left(V^f_{cementite} = \frac{n(cem, Cr) + n(cem, Fe)}{n(Cr) + n(Fe)} \right)$$

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Cementite dissolution in a Fe–Cr-C alloy
Cell calculation with size-distribution

Dissolution of cementite at 910C (or 1183K):
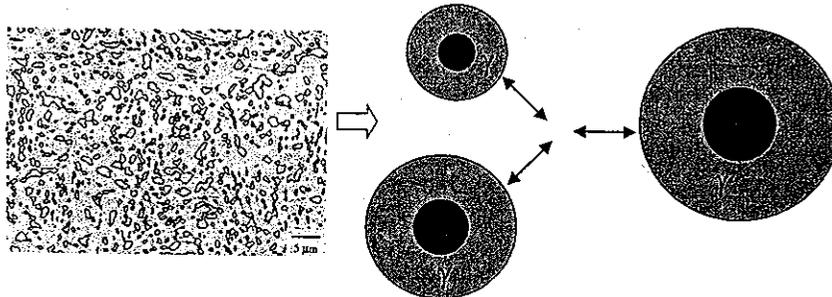
Instead of assuming an average particles size as in previous example, we will perform the simulation for a particle distribution using three cells of different sizes.

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Conditions at cell boundaries

$$\sum \frac{J_i}{n^{cell}} = 0$$

$$\mu_1^{Cell\#1} - \mu_n^{Cell\#1} = \mu_1^{Cell\#2} - \mu_n^{Cell\#2}$$

$$\mu_2^{Cell\#1} - \mu_n^{Cell\#1} = \mu_2^{Cell\#2} - \mu_n^{Cell\#2}$$

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Exd1: Carburization of a Ni-25% Cr Alloy

T=1123 K

FCC

$a_c=1$

3E-3

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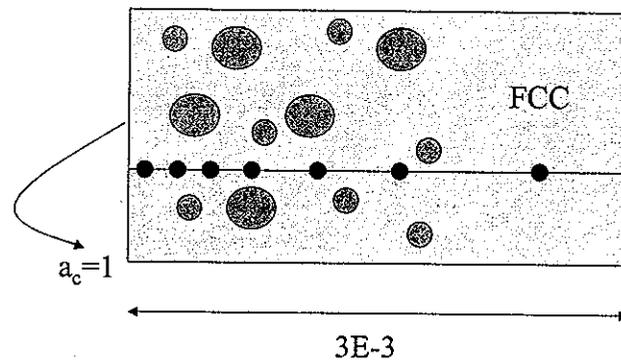
Exercise: γ to α transformation in Fe-0.15C with the following temperature variation with time

T=1173-0.1667*Time

?88 ι → bcc

T=1050K

738s

Temperature, K — Time, Second

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IUV (BCC)

Suggestions

γ   Time=0

0.15%C

Inactive α   2E-3

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