

Audio test:



DICTRA – Diffusion Controlled Phase Transformation

Prof. RNDr. Jiří Sopoušek, CSc.

Brno, PS



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.

$$\sum_{K=1}^n \tilde{J}_K V_K = 0$$

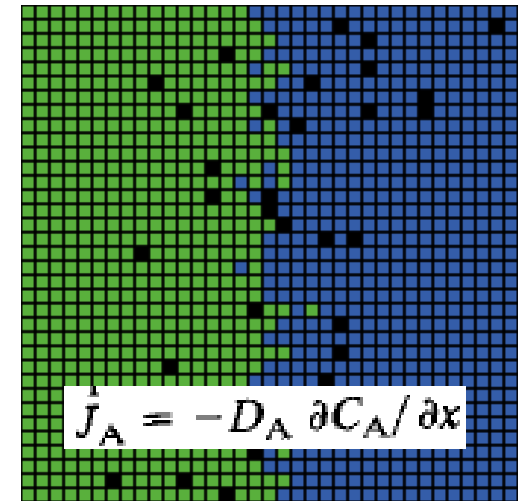
- DICTRA frame of reference**

- Volume-fixed frame, however only the substitutional components are assumed to contribute to the volume

$$\sum_{K \in S} \tilde{J}_K = 0$$

$$V_1 = V_2 = \dots V_k = \dots = V_n$$

$$V_{interstic} = 0$$



Drift mřížky

$$v = (D_A - D_B) \frac{\partial X_A}{\partial x}$$

$$J'_A = -D_A \frac{\partial C_A}{\partial x} + v C_A$$

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:

Velocity of matrix \rightarrow $V = \sum_{k=1}^n V_k J_k$ \leftarrow for Tra

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 vice versa. *hao pak*

$$J'_k = J_k - c_k \sum_{k=1}^n V_k J_k$$

Volume

(laboratory) fix. 🏠 Lattice fix.

 Lattice fix.

Atomistic treatment of diffusion

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

Assuming that there is a random distribution of vacant sites and that the number of vacancies 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:

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

(a lattice-fixed frame)

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

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 stem from no model, but from the observed conditions of equilibrium.


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

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

$$\left(J_k^L = - L_{kk} \frac{\partial \mu_k}{\partial z} \right)$$

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:


$$L_{kk} = c_k y_{va} M_{kva} \quad (1)$$
$$L_{ki} = c_i y_{va} M_{iva}$$

We have now established a relation between M and L.

Transformation to a volume-fixed frame

Volume (laboratory) fix. Lattice fix.

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

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

or,

$$J_k = - \sum_{i=1}^n L'_{ki} \frac{\partial \mu_i}{\partial z}$$

where,

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

Transformation to concentration gradients

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

$$J_k = - \sum_{i=1}^n L'_{ki} \frac{\partial \mu_i}{\partial c_k} \frac{\partial c_k}{\partial z} \quad ?$$

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

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

where,

$$D_{kj} = \sum_{i=1}^n L'_{ki} \frac{\partial \mu_i}{\partial c_j}$$

$$\mathbf{D} = \mathbf{L} \Phi$$

(3)
(3a)

Independent set of driving forces

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

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

nmajority element
(Fe in steels)

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

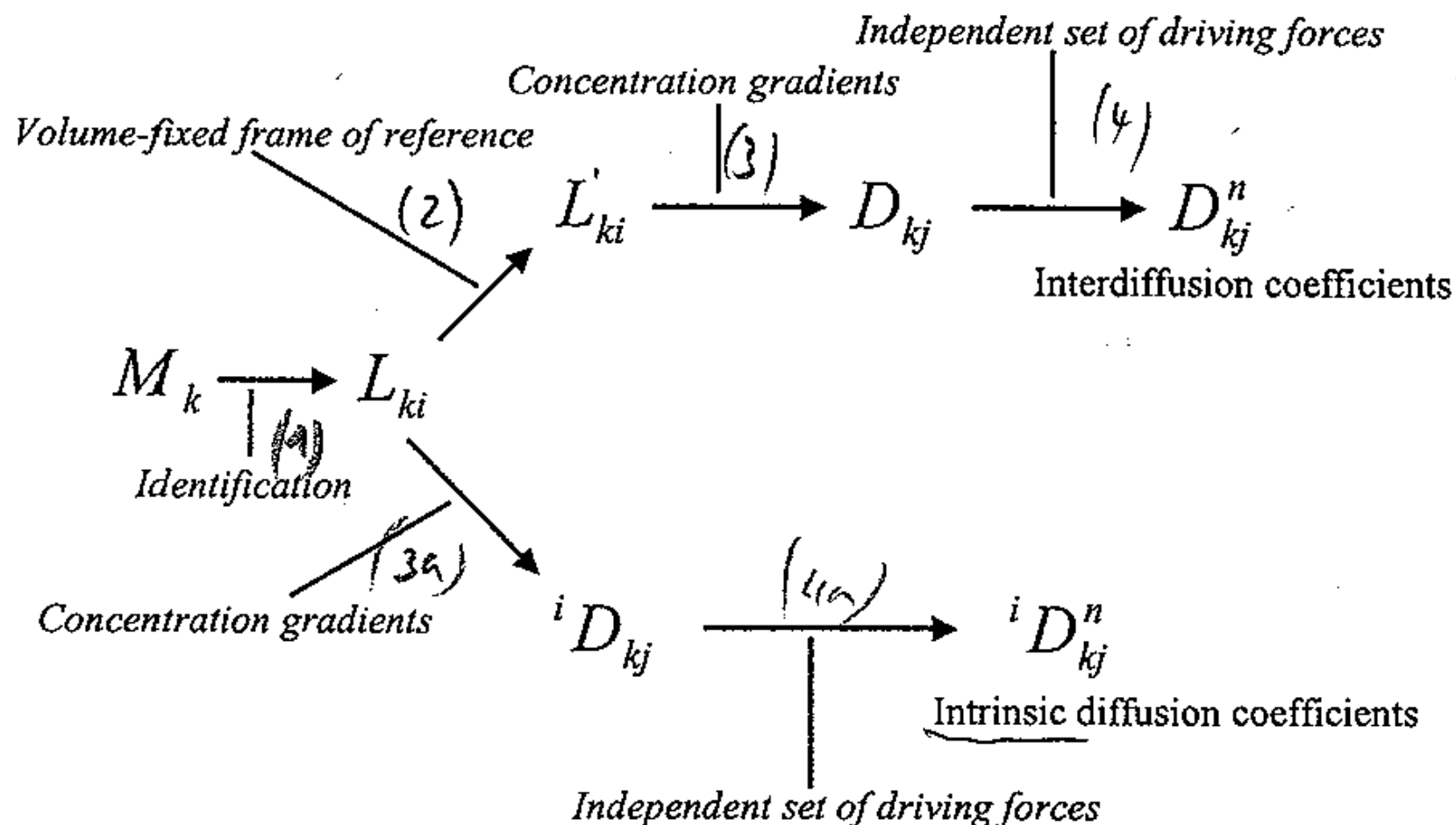
we may identify: $D_{kj}^n = D_{kj} - D_{kn}$ (4) (4a)

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

Time Dependence

$$\frac{\partial c_k}{\partial t} = -\text{div}(J_k)$$

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



Atomic mobility

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

- Tracer diffusivity $D_i^* = RTM_i$

Zjednodušení pro ideální nebo velmi zředěné roztoky $X_B \rightarrow 0$

γ_B je konstanta nebo 1. Tj.
 vztah:

$$J_B = -M_B RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\} \frac{\partial C_B}{\partial x}$$

Přejde na:

Dif. Koef stopové difúze



$$D_B^* = M_B^* RT = M_B RT$$

Výpočet atomárních mobilit v SW
 DICTRA viz další přednáška.

$$M_B = \exp\left(\frac{RT \ln M_B^0}{RT}\right) \exp\left(\frac{-Q_B}{RT}\right) \frac{1}{RT} {}^{mg} \Omega$$

M_B Mobility for element B
 M_B^0 frequency factor
 Q_B activation energy
 ${}^{mg} \Omega$ Ferromagnetic contribution

$$\Phi_B = \sum_i x_i \Phi_B^i + \sum_i \sum_{j>i} x_i x_j \left[\sum_{r=0}^m {}^r \Phi_B^{i,j} (x_i - x_j)^r \right] \\ + \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k \left[\sum_s v_{ijk}^s {}^s \Phi_B^{i,j,k} \right]; \quad (s = i, j, k)$$

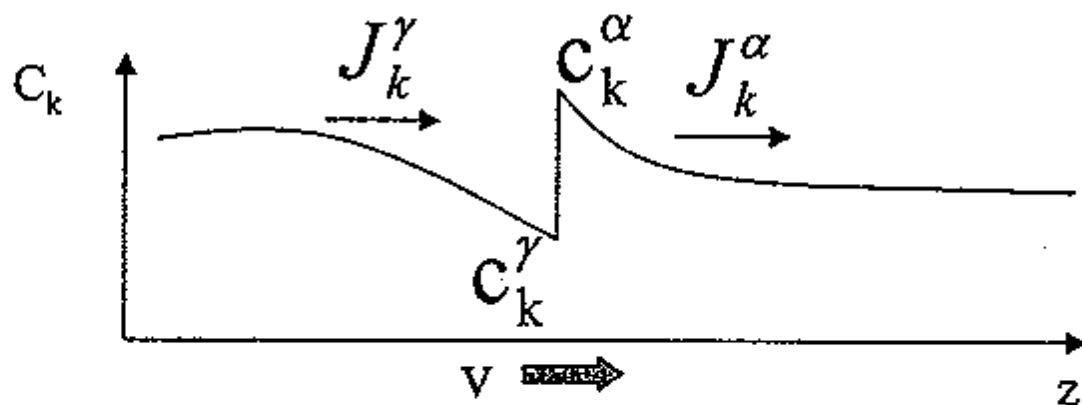
where Φ_B represents $RT \ln M_B^0 - Q_B$.

$$v_{ijk}^s = x_s + (1 - x_i - x_j - x_k)/3$$

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 Boundary



Unknowns: Tie-line, specified by $n-2$ a_i or μ_i

Velocity of phase boundary, v

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

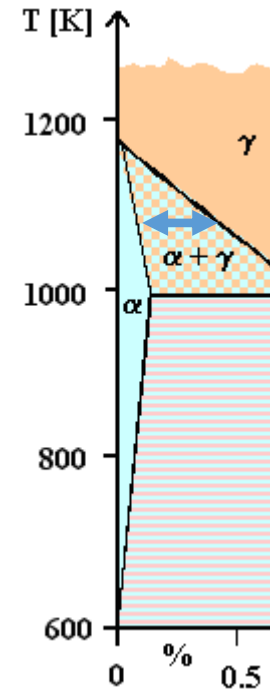
Solved as: $v(c_k^\alpha - c_k^\gamma) - (J_k^\alpha - J_k^\gamma) = 0$

$\gamma \rightarrow \alpha$ phase transformation

Fe-C: $n=2$, i.e. number of unknowns=0, $v=?$

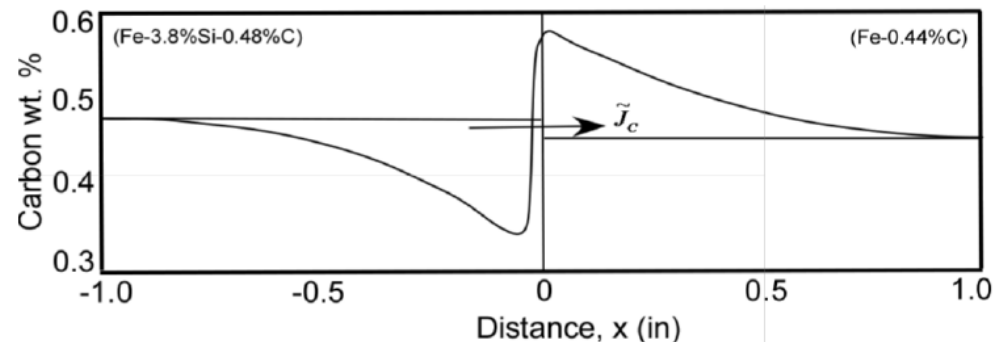
$2-1=1$ flux-balance equation for C

Working tie-line



Fe-Si-C: $n=3$, i.e. number of unknowns=1, μ_{Si} , $v=?$

$3-1=2$ flux-balance equations for C and Si



Development

Application

Thermodynamic
Data

- phase diagram data
- activity measurements
- enthalpy measurements
- cp measurements
- etc.

Parrot

Kinetic
Data

- tracer diffusivities
- chemical diffusivities
- etc.

Thermo
database

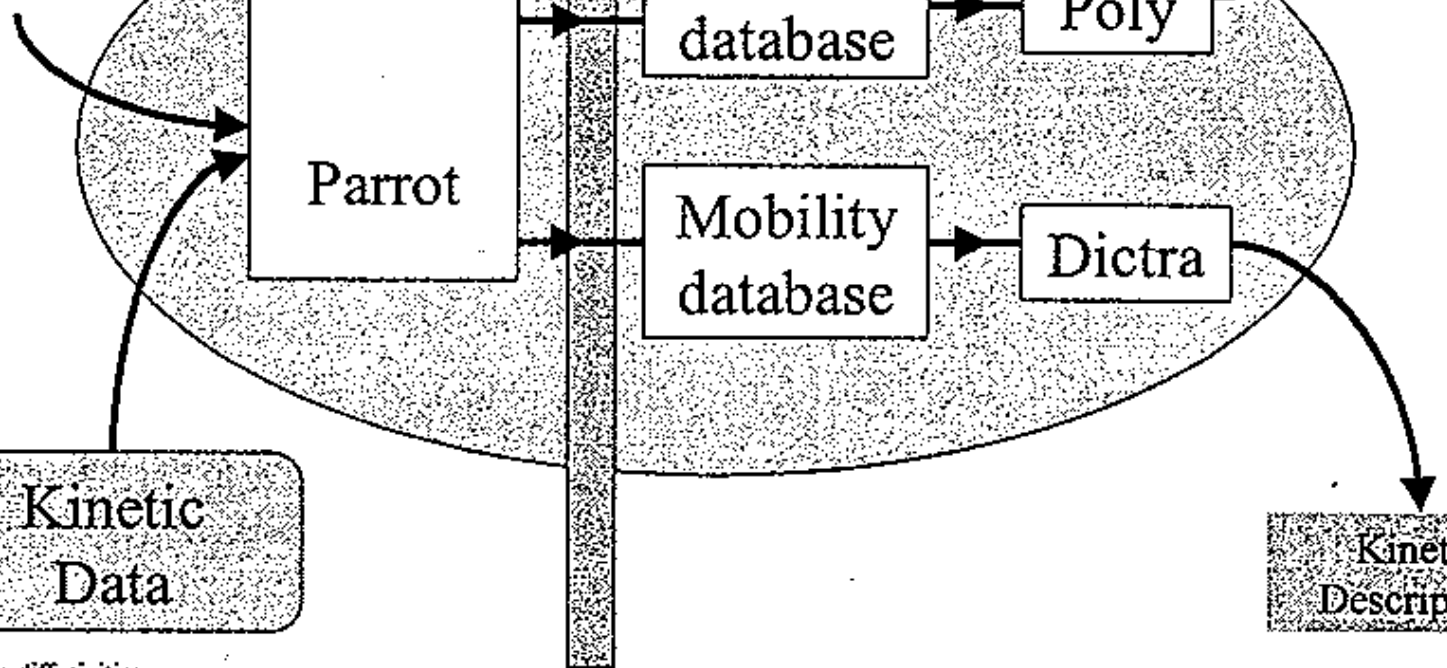
Poly

Mobility
database

Dictra

Thermodynamic
Description

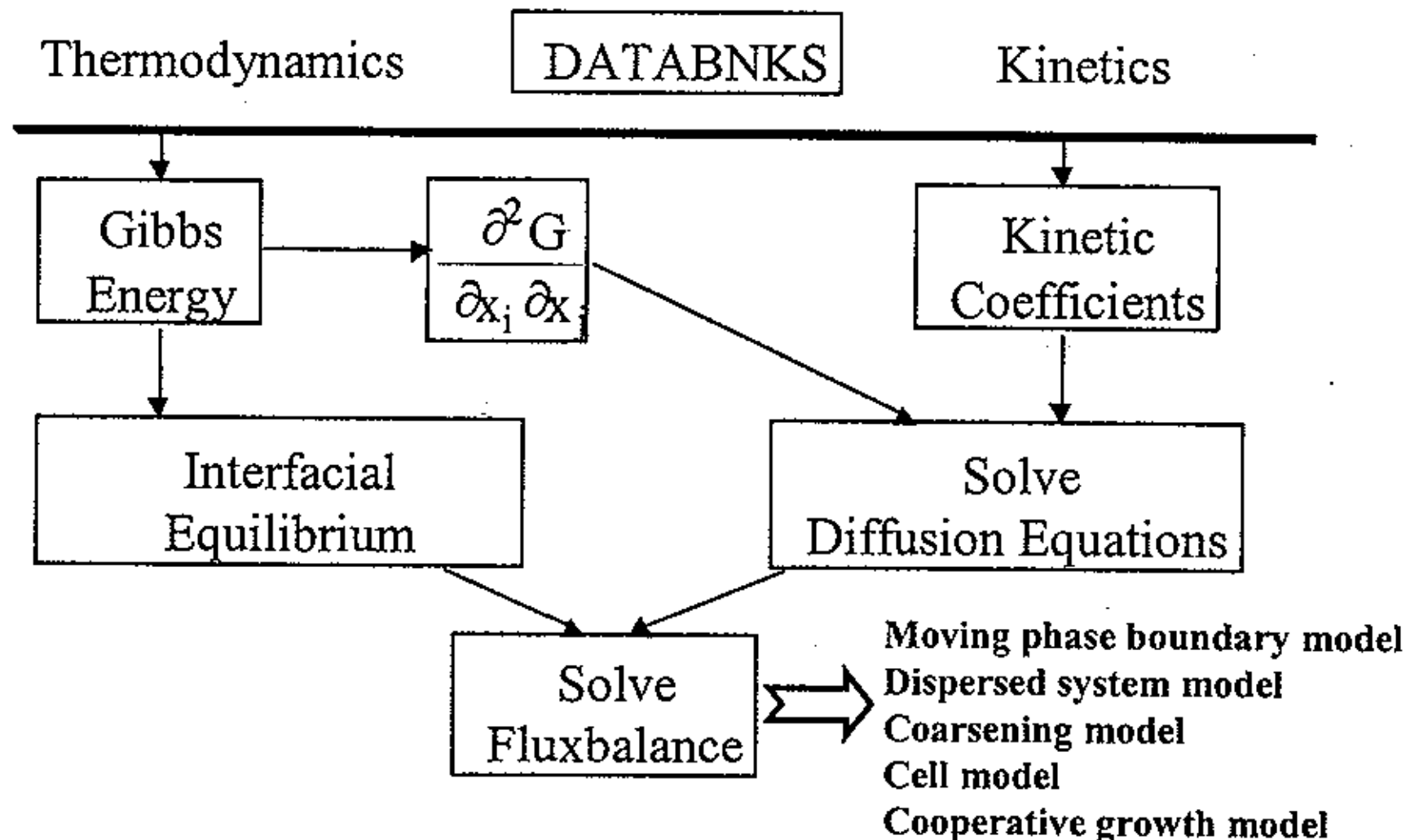
Kinetic
Description



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 platforms

Numerical Calculation of Diffusional Reaction



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

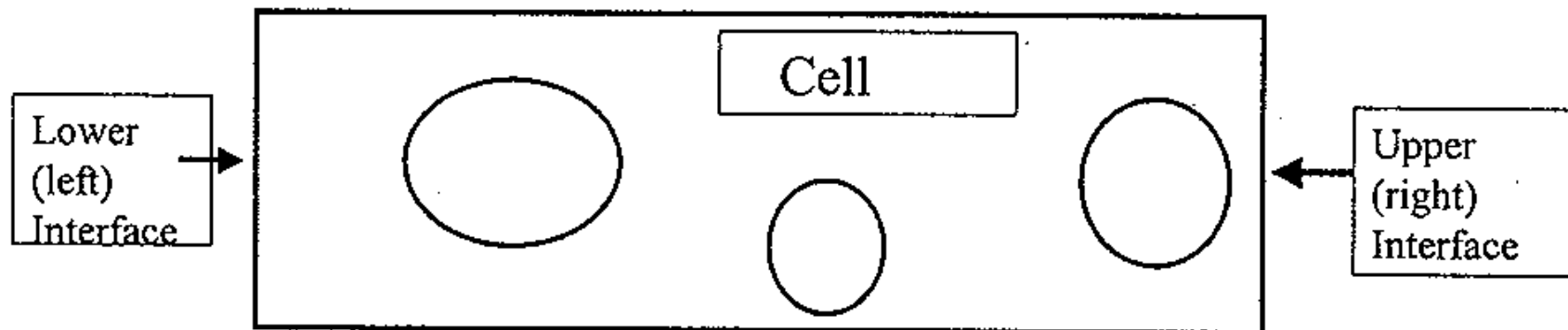
FCC_A1: Al-Cr-Ni, C-Cr-Fe, C-Fe-Ni

Assessed data for the following higher order systems

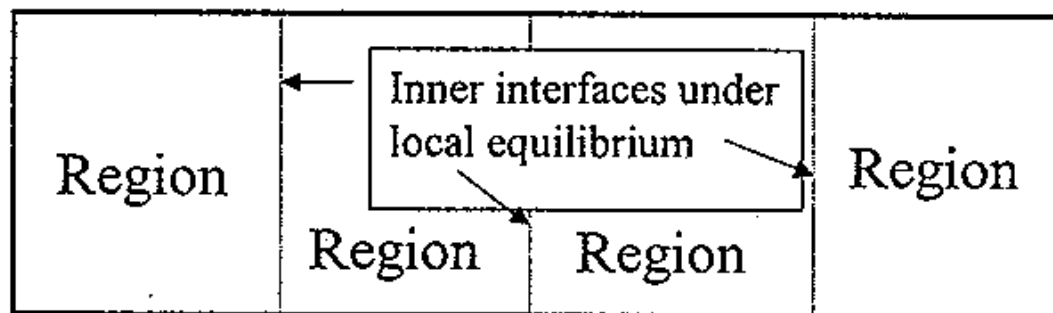
BCC_A2: C-Cr-Fe-N-Ni

FCC_A1: C-Cr-Fe-Ni

System



Cell



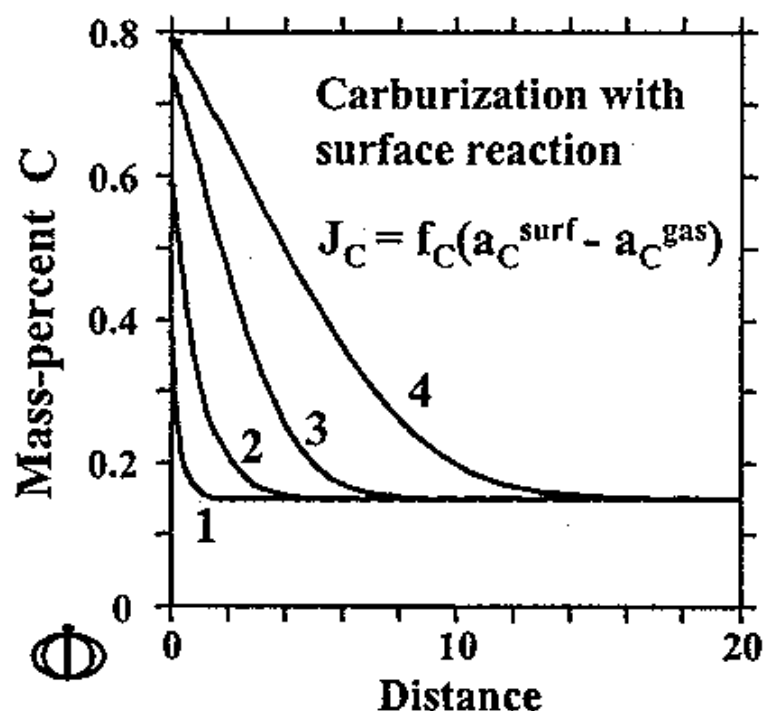
Boundary conditions in DICTRA

- **Boundary Conditions** can be specified as functions of time, temperature and pressure.
- Different functions may be used in different time intervals.

Application example:

Example of conditions are:

- Closed system (default)
- State variable expressions
- Flux conditions
- Mixed conditions



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.

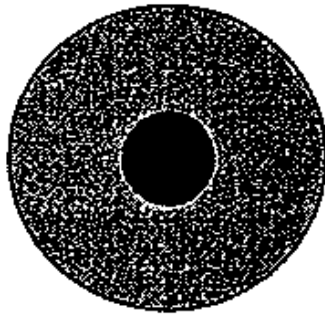
This corresponds to an infinitely long cylinder of a certain radius.



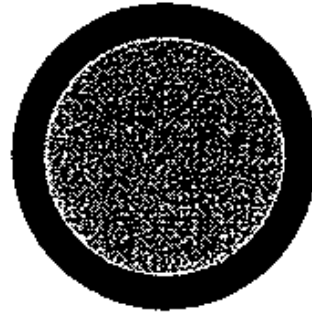
2 Spherical geometry.

A sphere with a certain radius.

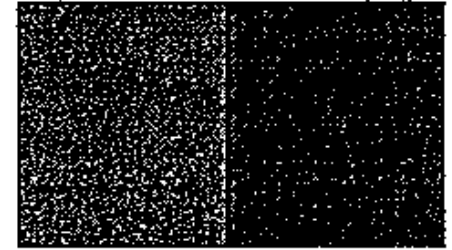
Some different possible geometries



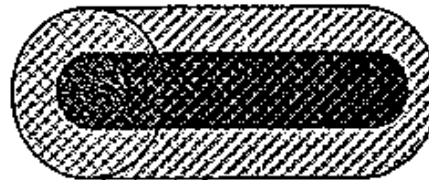
**Growth or dissolution
of spherical precipitate**



**Growth of spherical film
(Grain-boundary film)**

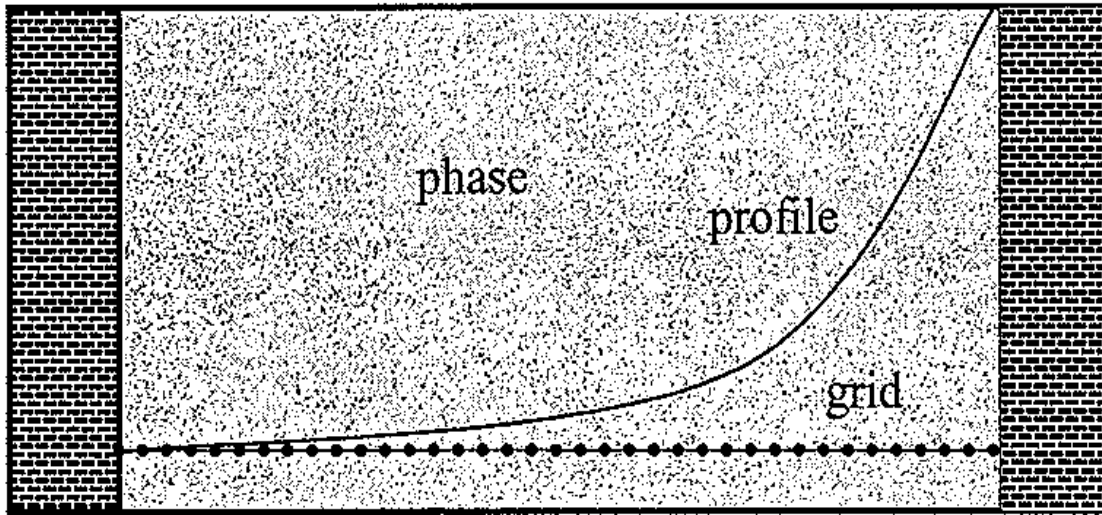


Planar growth



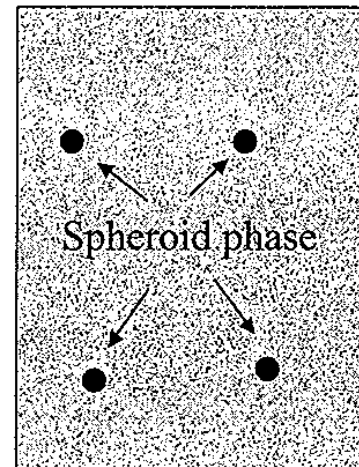
**Growth of cylindrical
precipitate**

Region

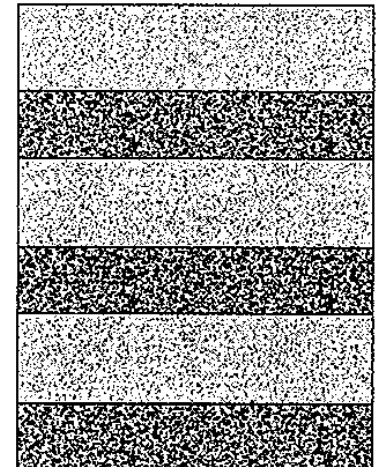


Region

Matrix phase



Lamella phase



Grid points

Lower Interface

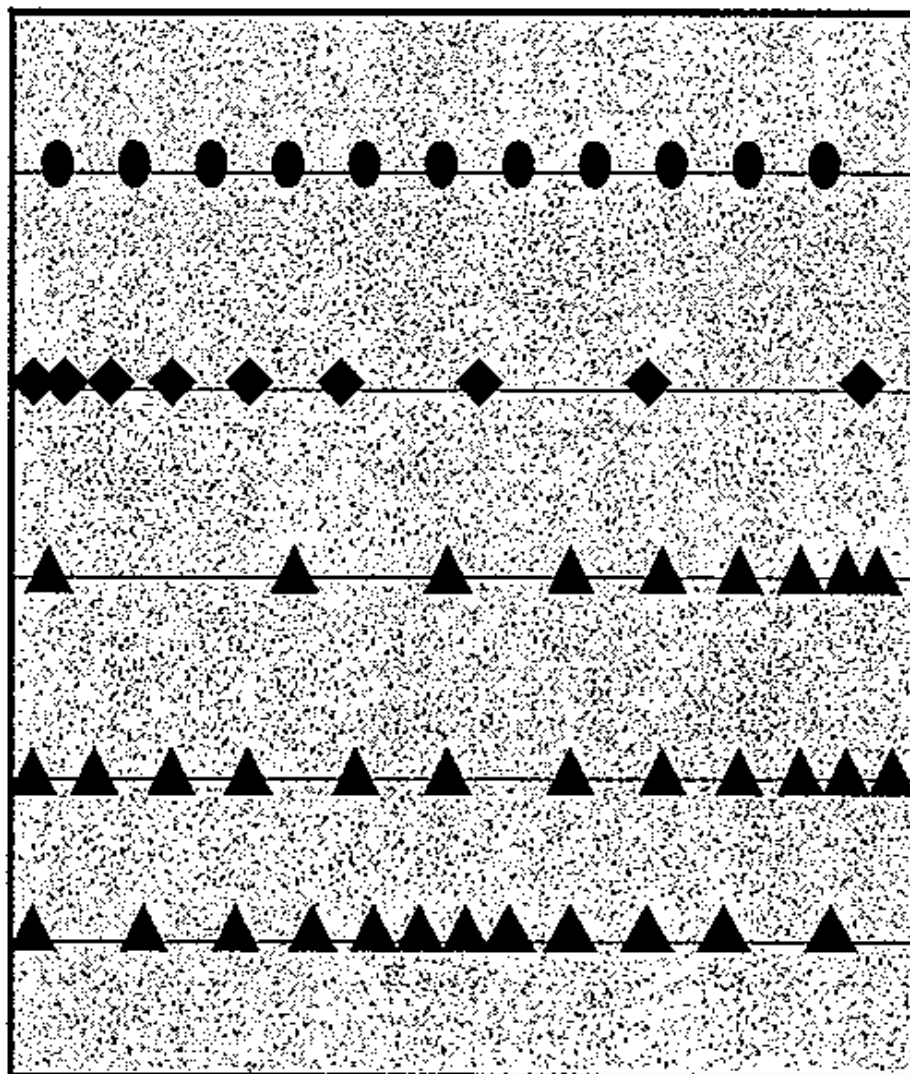
Upper Interface

Linear

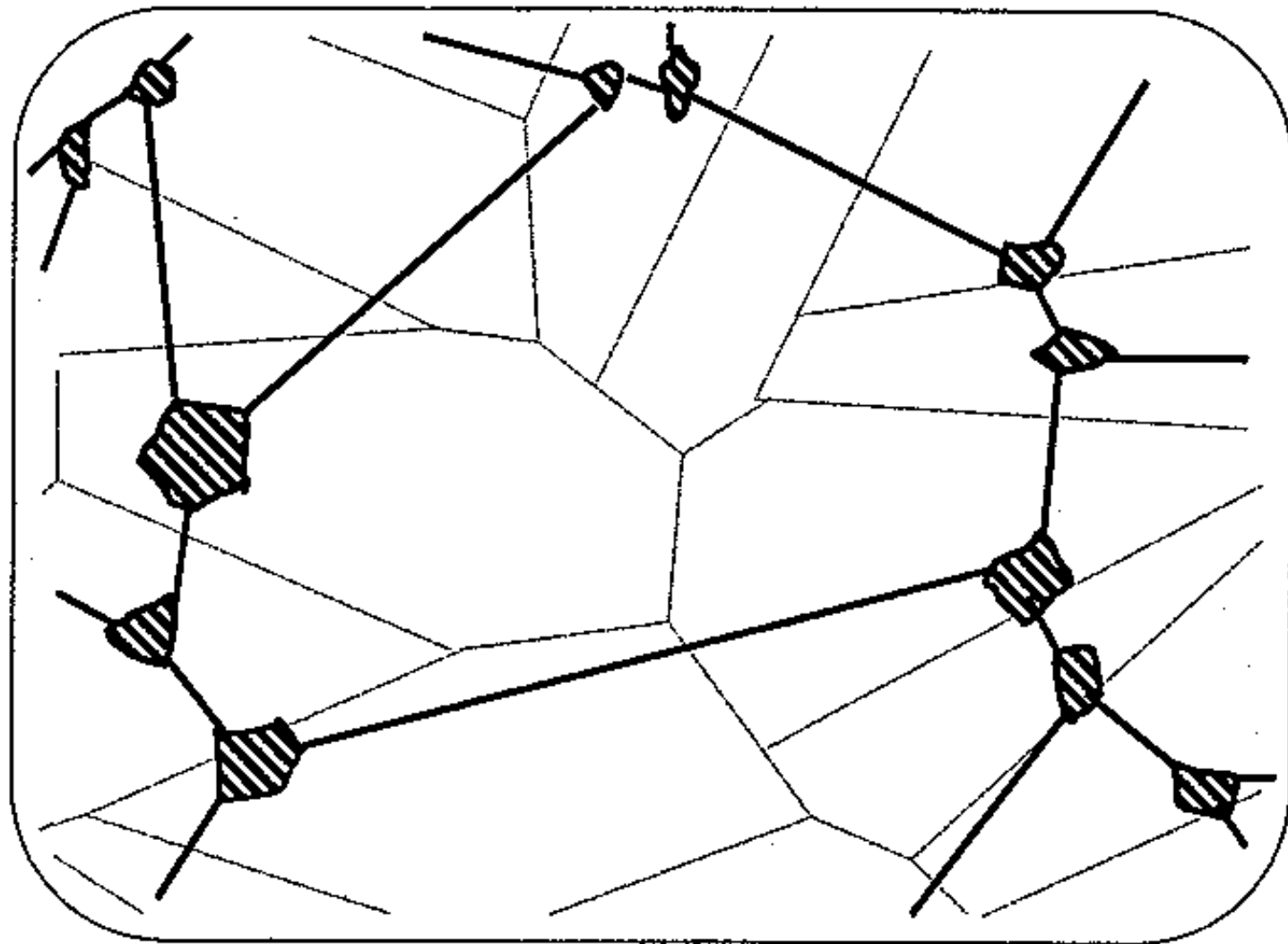
GEO >1

GEO <1

Double
GEO



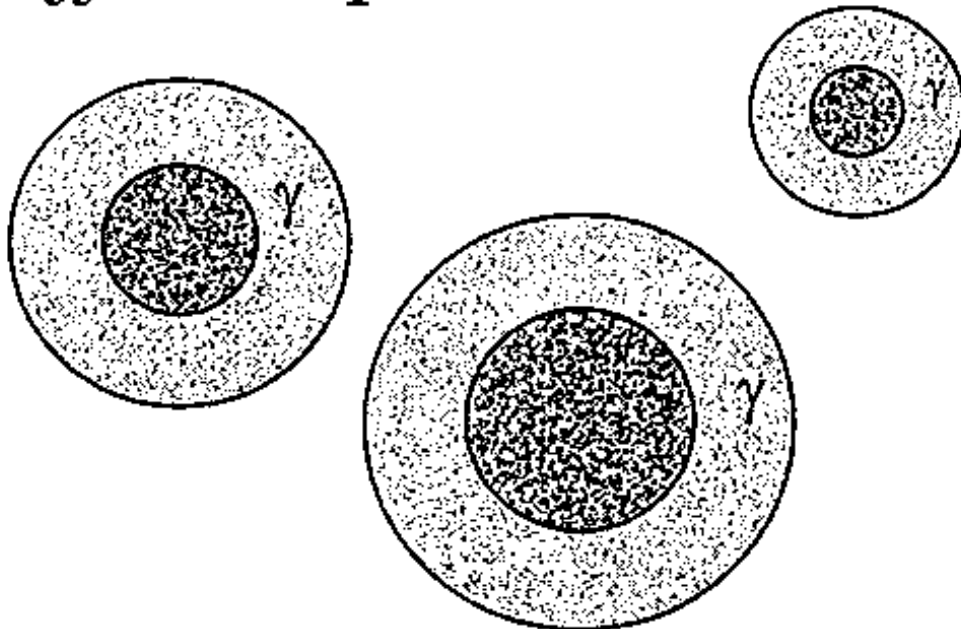
Microstructure vs Dijkstra



Multi-cell Approach

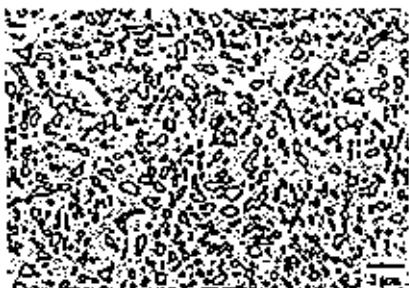
$$\sum J_i = 0$$

Diffusion potential = constant

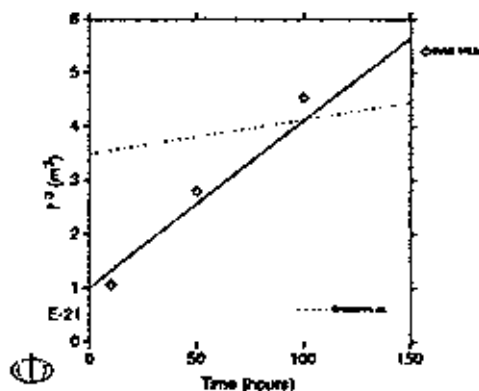


Some DICTRA applications

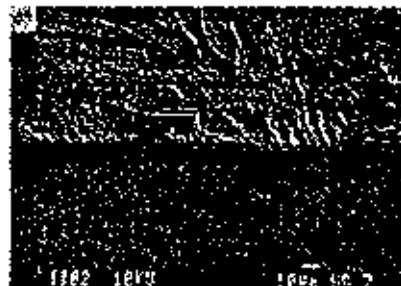
Carbide dissolution



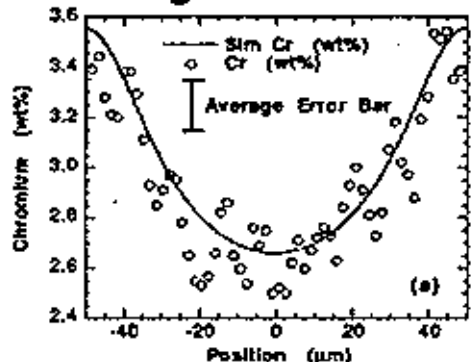
Coarsening



Carbon diffusion in a weld between two steels

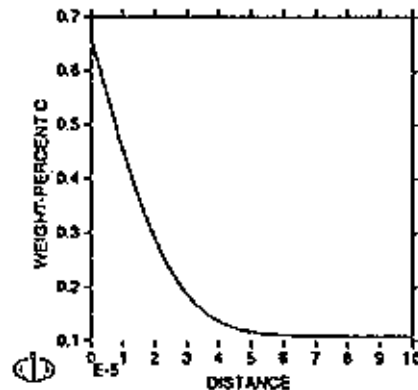


Microsegregation during solidification



Lippard et al. *Metall. Mater. Trans. B* 1998

Carburizing



More DICTRA applications

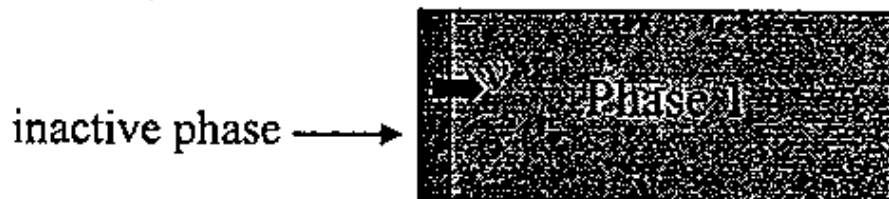
- Homogenisation of alloys
- Carburization and decarburization
- Carburization of alloys
- Nitriding of steels
- Diffusion during sintering of cemented carbides
- Nitrocarburizing of steels
- Austenite/ferrite diffusional transformations in steels
- Growth or dissolution of individual particles
- Transient 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

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



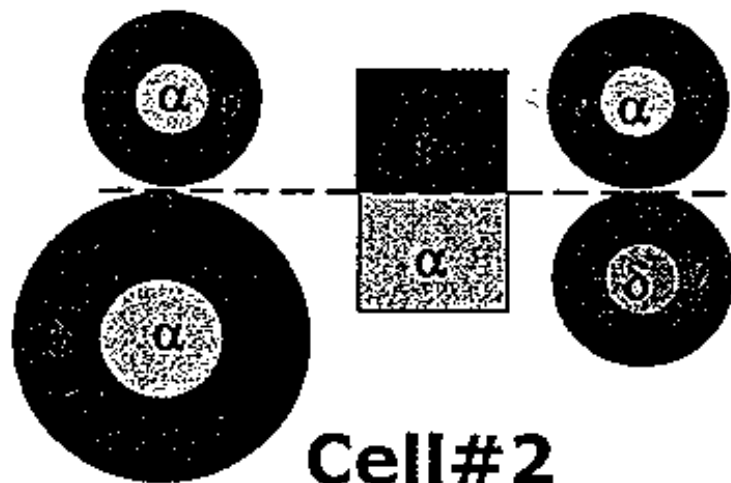
- Entering an inactive phase (formed when thermodynamically stable)



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

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

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

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

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

Cell calculations in DICTRA

- Makes it possible to couple several computational cells
- Conditions for cell boundaries:
 - ✓ Equal diffusion potentials Φ_i for the elements

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

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

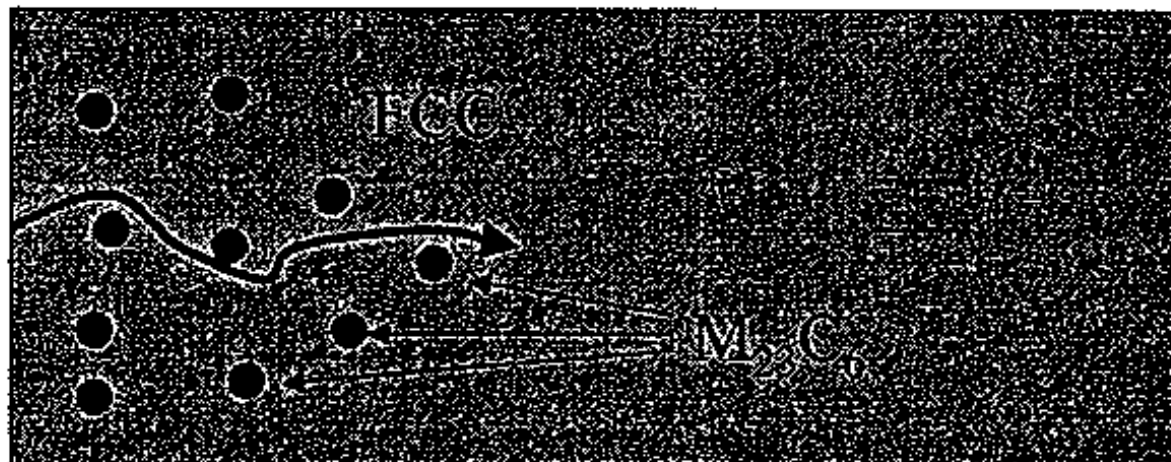
- ✓ Flux balances to conserve the mass of the elements

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

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, D_{kj} , is multiplied with a labyrinth factor $f(\text{volfr})$, 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

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

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

Post: Common Commands

SET_DIAGRAM_AXIS

SET_INDEPENDENT_VARIABLE

SET_PLOT_CONDITION

MAKE_EXPERIMENTAL_DATAFILE

PLOT_DIAGRAM

Variables in the Post-Processor

State variables

T, P, Amount of components (e.g. $X(\text{Cr})$, $W(\text{Cr})$,
 $W(\text{Fcc}, \text{Cr})$, etc.)

Amount of a phase, e.g. $NP(\text{Fcc})$

Activity for a component: $AC(\text{Cr})$

Chemical Potential for a component: $MU(\text{Cr})$

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)

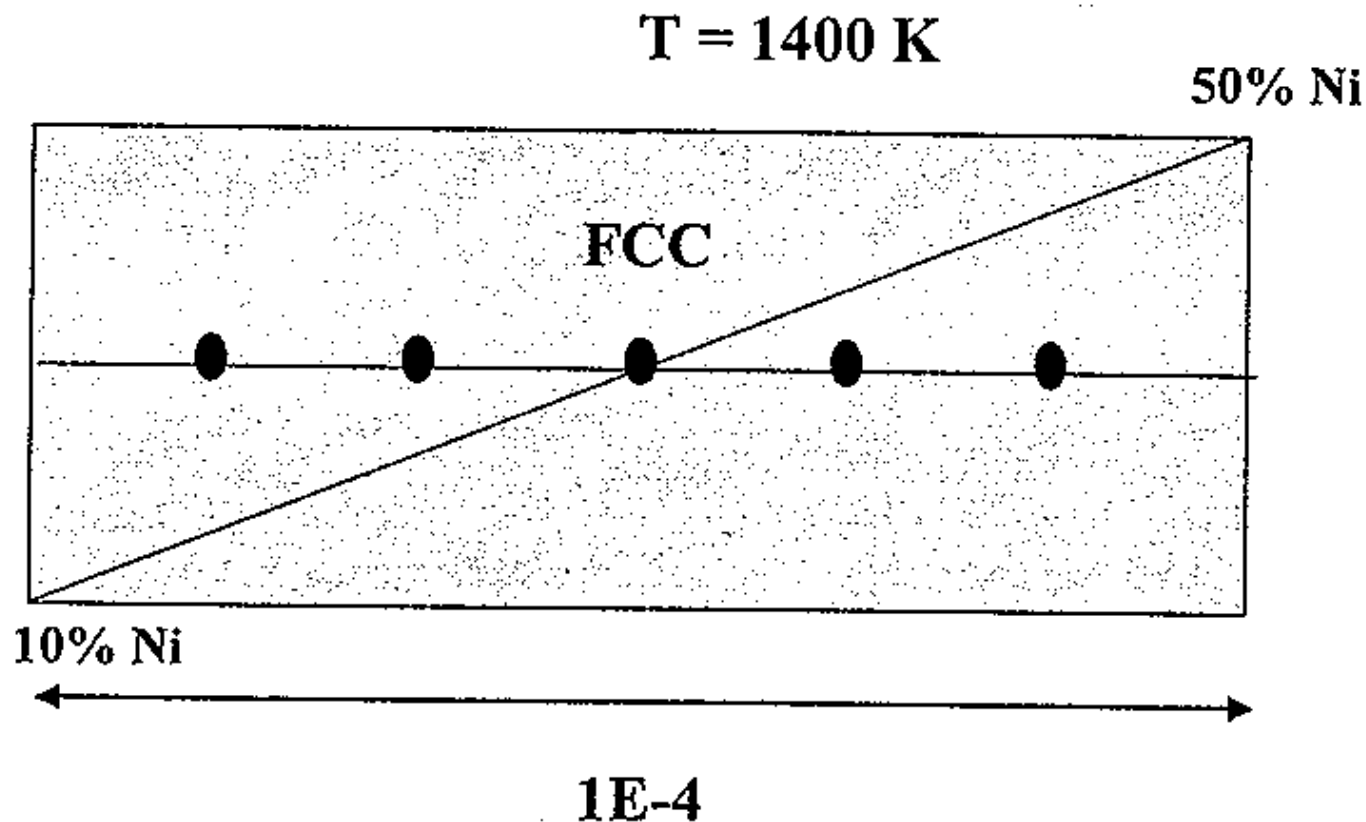
LOGDC(phase,J,K,N)

User-defined functions

Plotting in DICTRA

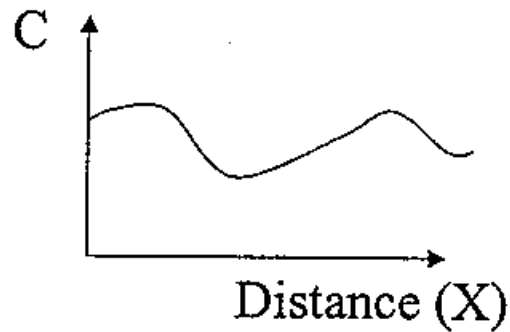
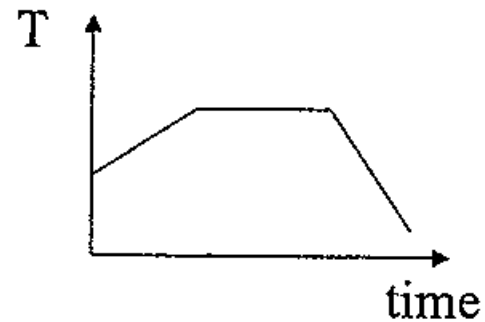
- Two independent variables in a DICTRA-simulation, TIME and DISTANCE
- When plotting a diagram we need to specify one of them i.e. use it as plot condition. Command: SET-PLOT-CONDITION
- TIME can be specified as one or several values.
- When plotting integral quantities, time is automatically chosen as independent variable.

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



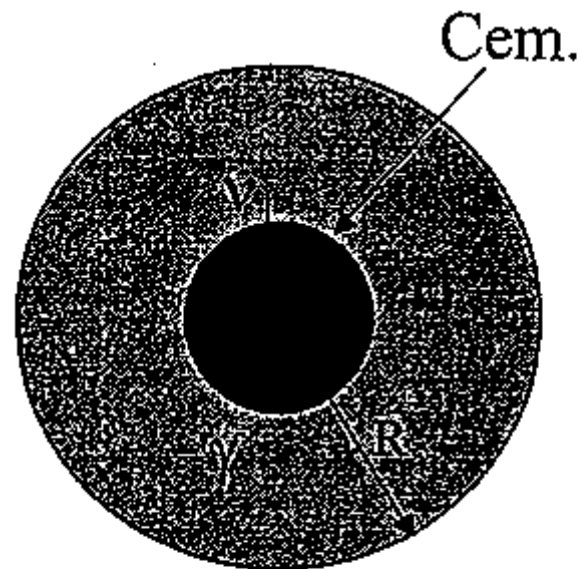
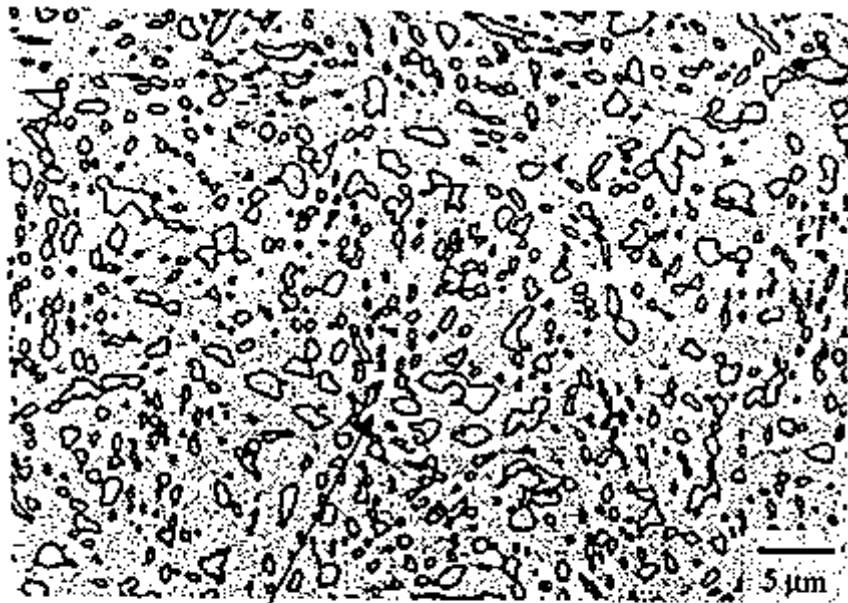
Input of T and c

- 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:

$$\frac{R_{\text{cementite}}^3}{R_{\text{tot}}^3} = \frac{V_{\text{cementite}}}{V_{\text{tot}}} = V_{\text{cementite}}^f$$

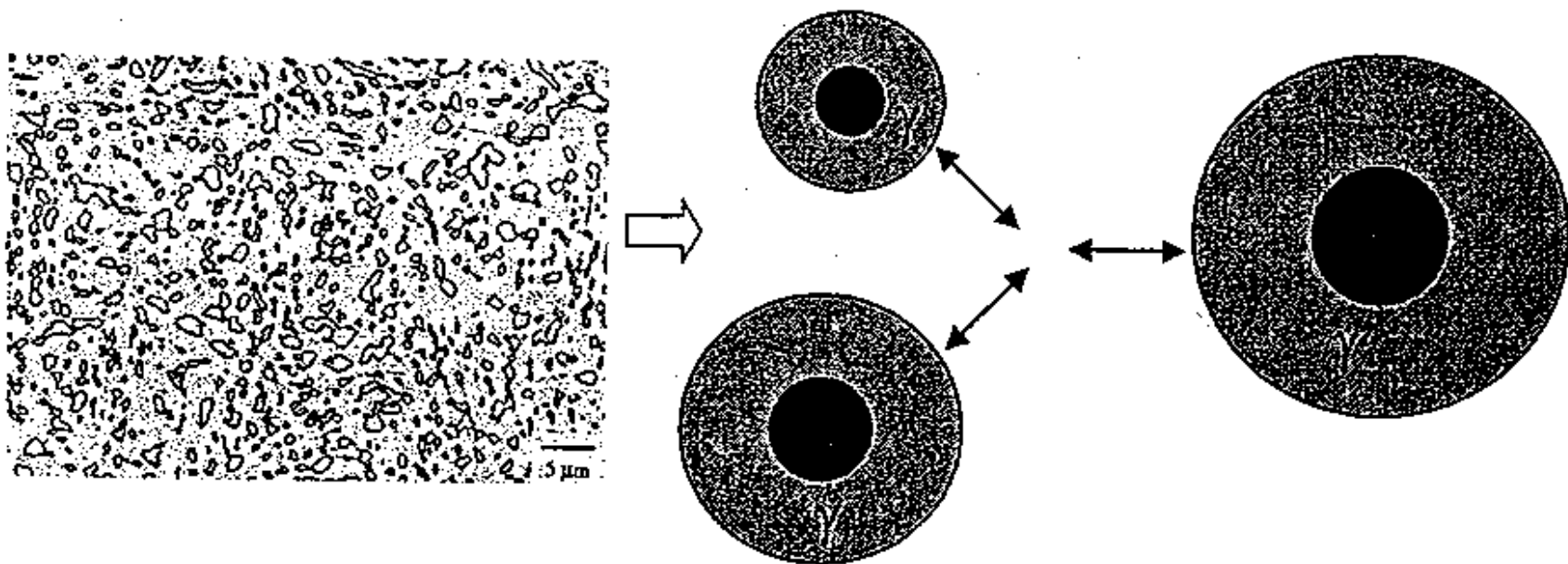
$$\Rightarrow R_{\gamma} = R_{\text{tot}} - R_{\text{cementite}} = \frac{R_{\text{cementite}}}{\sqrt[3]{V_{\text{cementite}}^f}} - R_{\text{cementite}}$$

$$\left(V_{\text{cementite}}^f = \frac{n(\text{cem}, \text{Cr}) + n(\text{cem}, \text{Fe})}{n(\text{Cr}) + n(\text{Fe})} \right)$$

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.

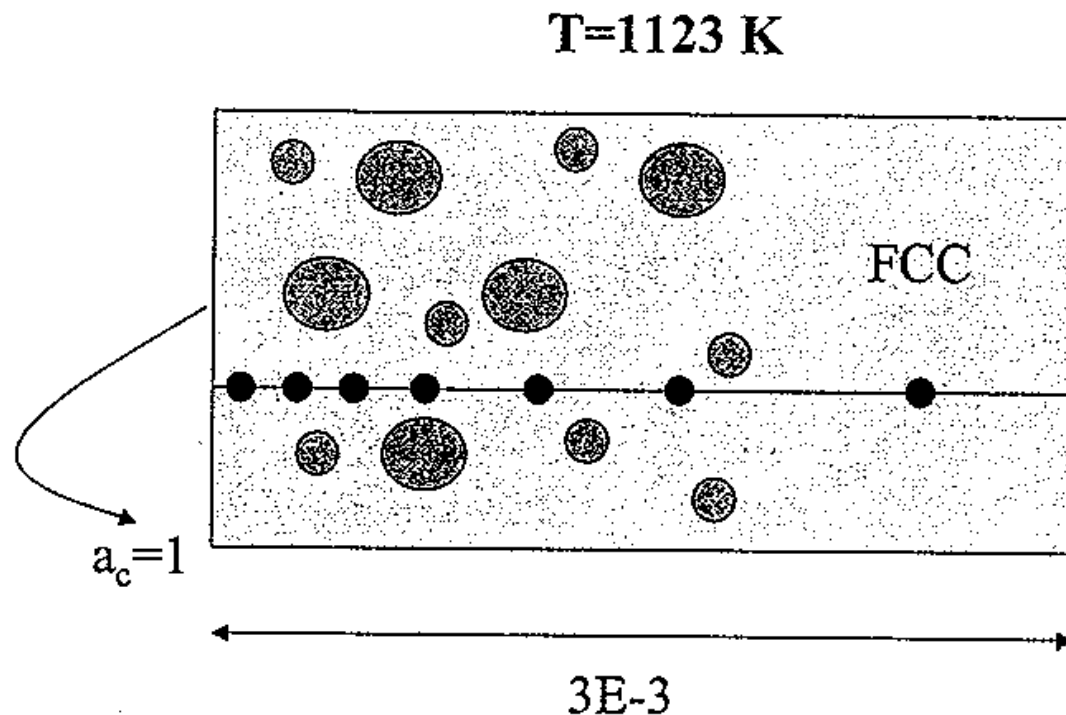
Conditions at cell boundaries

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

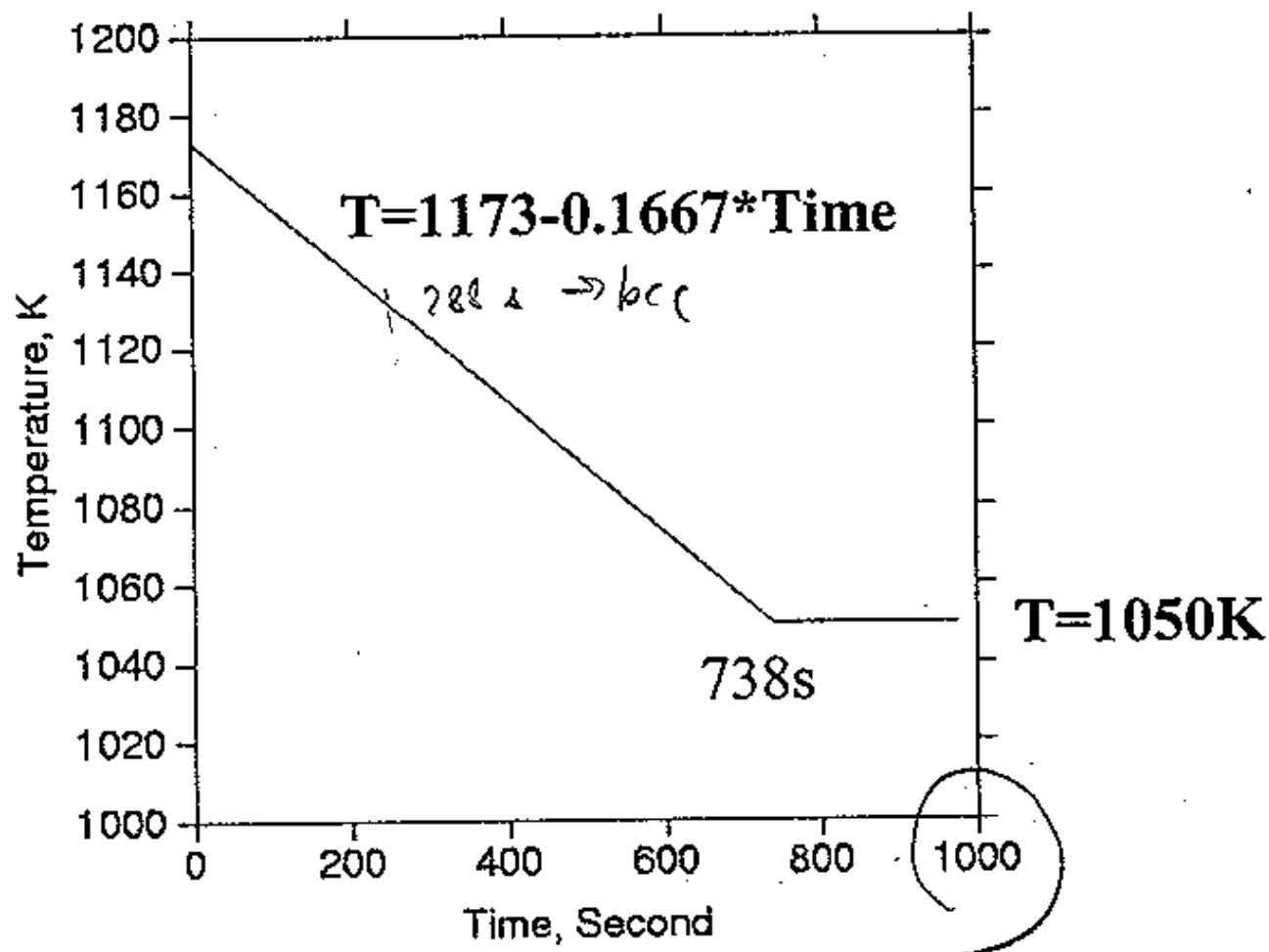
$$\mu_1^{Cell\#1} - \mu_n^{Cell\#1} = \mu_1^{Cell\#2} - \mu_n^{Cell\#2}$$

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

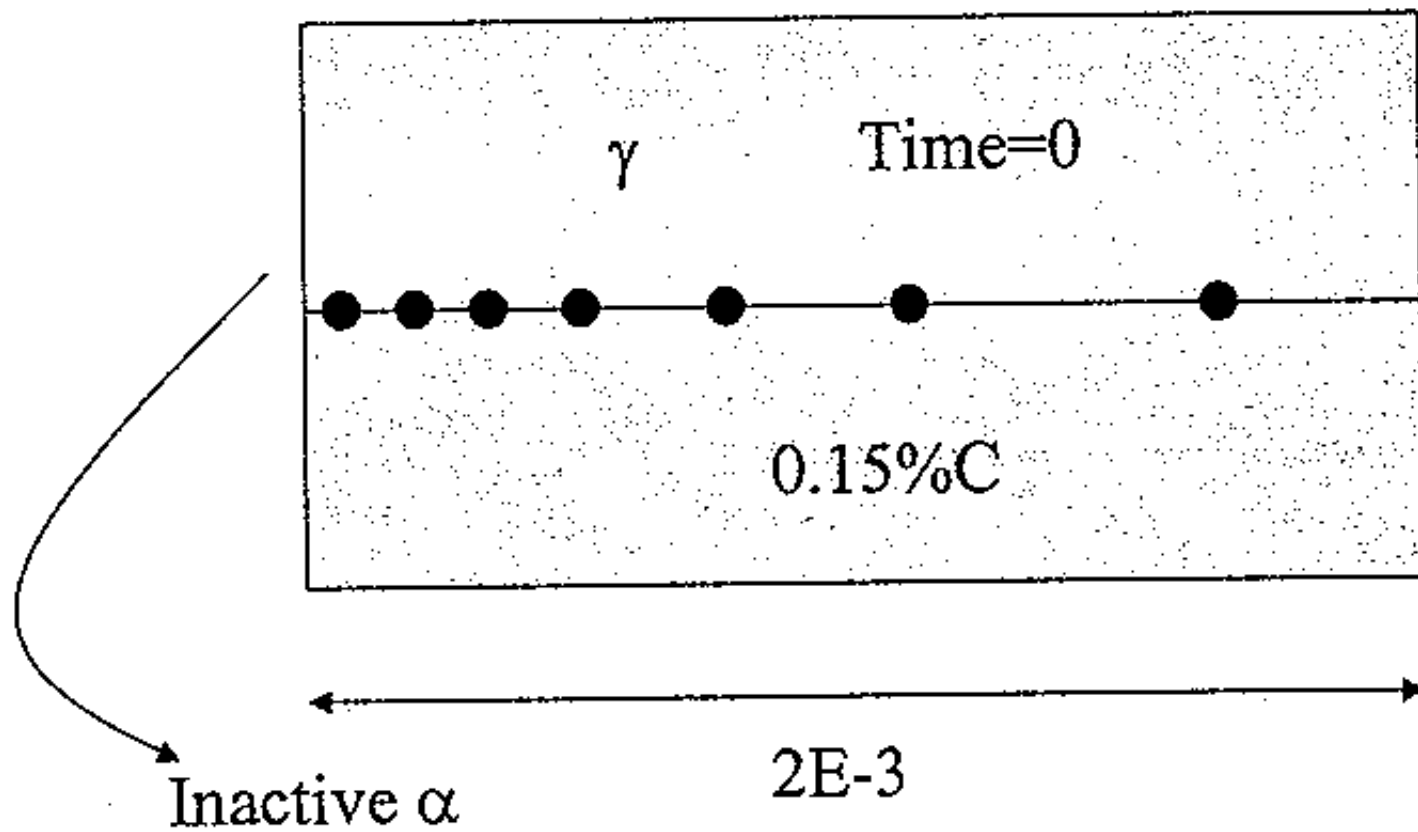
Exd1: Carburization of a Ni-25% Cr Alloy



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



Suggestions



Discussion and practical simulations using DICTRA

