

The Role of Diffusion in Materials

A Tutorial for Engineers

Prof. John Ågren



Copyright 2019 Thermo-Calc Software AB. All rights reserved.

Information in this document is subject to change without notice. The software described in this document is furnished under a license agreement or nondisclosure agreement. The software may be used or copied only in accordance with the terms of those agreements.

Thermo-Calc Software AB

Råsundavägen 18

Solna, Sweden

info@thermocalc.com

www.thermocalc.com

Contents

1 Introduction to Diffusion Simulations	4
1.1 About This Tutorial Guide	4
1.2 Help Resources	5
1.3 An Important Note About Terminology	6
1.4 Graphical Mode vs Console Mode	7
1.5 List of Examples	8
2 Diffusion Theory	11
2.1 What is Diffusion and When is it Important?	11
2.2 Fick's Law and the Diffusion Coefficient	13
2.3 Frame of Reference	17
2.4 Fick's Second Law: The Calculation of Concentration Profiles	18
2.5 Boundary Conditions	19
2.6 Analytical Solutions	20
2.7 Materials with Many Components	22
3 One-Phase Diffusion Problems	30
3.1 Setting Up a Simulation	30
3.2 Stationary Diffusion Through a Tube Wall	31
3.3 Example: Diffusion in a Joint Between Dissimilar Materials	45
3.4 Example: Darken's Experiment	51
3.5 Example: Carbon Diffusion in a Ni-Plated Steel	55
4 Two-Phase Diffusion Problems in Binary Alloys	64
4.1 Diffusion Controlled Growth or Shrinkage of Phases	64
4.2 Example: Fe/Fe-10mass% Ni Diffusion Couple at 850 °C	72
4.3 Example: Ferrite Formation and Dissolution in an Fe-0.2C Alloy	77
4.4 Example: Austenite Formation in a Normalized Steel	87
5 Two-Phase Diffusion Problems in Multicomponent Alloys	89
5.1 Introduction to Diffusion Problems in Multicomponent Alloys	89
5.2 Condition for Fast Reaction Controlled by a Fast Diffuser	92
5.3 Example: Isothermal Formation of Ferrite from Austenite in Steel Fe-1Mn-0.2C	94
5.4 Example: Ferrite Formation During Normalizing of Steel Fe-1Mn-0.2C	100
5.5 Example: Austenite Formation After Normalizing of Steel Fe-1Mn-0.2C	105
6 Diffusion in Dispersed Structures	108
6.1 Example: Internal Carburization of a Ni-Cr Alloy Using Homogenization	108
6.2 Example: Internal Nitriding an Fe-Ni-Cr Alloy Using Homogenization	110
6.3 Example: Carbon Transfer in a Steel Composite: A Full Scale Industrial Problem	112

1 Introduction to Diffusion Simulations

1.1 About This Tutorial Guide

This guide is an introduction to some of the concepts and practices used when you set up a diffusion simulation using the Diffusion Module (DICTRA).

The purpose of this tutorial is to make the engineer aware about the type of material issues that are related to diffusion and demonstrate how to solve them. Some problems may be tackled by very simple computations whereas others require more heavy computations based on numerical approaches. Most of the examples concern metallic systems such as steels, super alloys and light metals, but the principles can be applied to many other classes of materials, e.g. ceramics and polymers, provided that appropriate databases are available.

The guide assumes some familiarity with using the Graphical Mode interface of the Thermo-Calc software. However, if you are not familiar you can use the available help and documentation to supplement this guide. See "[Help Resources](#)" on the next page.

Except for one example at the beginning that includes details about how to recreate the simulation in both Graphical Mode and Console Mode, the exercises in this guide use the Graphical Mode interface. A brief comparison of these modes is included in "[Graphical Mode vs Console Mode](#)" on page 7. It is also useful to read "[An Important Note About Terminology](#)" on page 6.

The training material itself is available at two levels: basic and advanced. At the basic level it is assumed that you have a secondary school level (e.g. high school) understanding of mathematics, physics and chemistry. The advanced level requires a university education, often at the PhD level or higher.

Convention

Definition

Task





The task to complete for the exercise.

Note



The information can be of use to you. It is recommended that you read the text or follow the link to more information.

Convention	Definition
Tip	 This is general information that can be of use but is not required knowledge.
Examples	 Go to the example in this guide to learn more.

1.2 Help Resources

1.2.1 'Online' Help: No Internet Required


To access online help in a browser, open Thermo-Calc and press <F1> on the keyboard, or select **Help** → **Online Help**.

The content opens in a browser but uses local content so you don't need an Internet connection except for links to external websites.

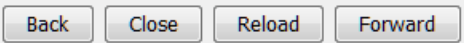
Context Help (Graphical Mode Only)



When you are in Graphical Mode, you can access feature help (also called *topic-sensitive* or *context help*) for the activity nodes in the tree.

1. In the Project window, click a node. For example, **System Definer**.
2. In the lower left corner of the **Configuration** window, click the help button .
3. The **Help** window opens to the relevant topic.

The window that opens has the same content as the help you access in the browser. There are these extra navigation buttons in this view.

- Use the buttons on the bottom of the window, , to navigate **Back** and **Forward** (these are only active once you have started using the help to load pages and create a history), to **Close** the window, and **Reload** the original content.

1.2.2 Training and Video Tutorials

Some of the Graphical Mode examples included with the Thermo-Calc installation have video tutorials available both on [our website](#) or our [YouTube channel](#).



You can go to the video tutorials when in Thermo-Calc: **Help → Video Tutorials**.

1.3 An Important Note About Terminology

DICTRA is an acronym for *Diffusion-Controlled TRAnsformations*. The software of the same name has been included in the suite of Thermo-Calc products for many years. When you are working in the original mode, called Console Mode, the terminology reflects this historical connection as does the literature that cites the use of DICTRA.

With the introduction of the Graphical Mode version of DICTRA, and to better describe what the add-on module does, the product name was changed to the *Diffusion Module (DICTRA)*. However, this means some of the terminology between the modes cannot be consistent even though the theory and concept behind the software is fundamentally the same. For example, in Graphical Mode the term "DICTRA" is not used when describing the Diffusion Calculator node.

In Console Mode there is also some terminology to be aware of as there are two submodules within the program:

- DICTRA_MONITOR: A module for running simulations of diffusion controlled transformations, and
- DIC_PARROT: A module to assess experimental data and uses this data to optimize mobilities.



Except for the first example, this training material uses Graphical Mode.

1.4 Graphical Mode vs Console Mode

There are two interfaces available in Thermo-Calc: *Graphical Mode* with a graphical user interface (GUI) and *Console Mode*, which uses a command line interface. Thermo-Calc and the Diffusion Module (DICTRA) are available in both modes.

In Graphical Mode calculations are set up, carried out, and visualized as part of a *project*. The steps in the project are performed with *activities*. There are templates and a Wizard available to guide you through the process of defining the project.

In Console Mode you work with *modules*, which are managed using commands typed at a prompt. Some modules, called *response-driven modules*, ask you a series of questions that typically take you through the process of defining your system, setting calculation conditions, performing calculations and plotting the results.

Switching Between Modes

The first time you open Thermo-Calc, it defaults to Graphical Mode. For any future instance it defaults to the last mode used.

Along the top of the GUI is the Graphical Mode Toolbar where you switch between modes. In Console Mode, except for the **Switch to Graphical Mode** button, the toolbar is not used.

File Extensions

The file extensions are different based on the mode you are in (Graphical vs. Console). In Console Mode the extensions are also based on whether you are working with Thermo-Calc or the Diffusion Module.

- In Graphical Mode, all the project files have the extension *.tcu.
- In Console Mode, the Diffusion Module (DICTRA) the file extension is *.DCM. In addition to macro files in Console Mode there are also *Log* files and *Workspace* files, which also differ.

Can I work with both modes at the same time?

The two modes can be run simultaneously, but there is no communication between them. What you do in Graphical Mode does not affect the state of the Console Mode session and

vice versa.

1.5 List of Examples

1.5.1 Diffusion Through a Tube Wall

Theory

"Fick's Law and the Diffusion Coefficient" on page 13

- "Example: Diffusion Through a Tube Wall" on page 15
- "Advanced Example: Diffusion Through a Tube Wall" on page 16

Practical Examples

"Stationary Diffusion Through a Tube Wall " on page 31

- "Graphical Mode - Diffusion Through a Tube Wall " on page 34
- "Console Mode Commands - Diffusion Through a Tube Wall" on page 40
- "Example: Carbon Diffusion in a Ni-Plated Steel" on page 55

1.5.2 Theory - Darken's Experiment

- "Example: Darken's Experiment " on page 51

1.5.3 Theory - Fick's Second Law

"Fick's Second Law: The Calculation of Concentration Profiles" on page 18

- "Advanced Example: Fick's Second Law" on page 18

1.5.4 Theory - Error Function

"Analytical Solutions" on page 20

- "Example: Carburization of Steel" on page 20

1.5.5 Theory - Sinusoidal Solution

"Analytical Solutions" on page 20

- "Example: Homogenization of an Alloy" on page 21

1.5.6 Theory - Materials with Many Components

"Materials with Many Components" on page 22

- "Example: Diffusion in a High-Entropy Alloy" on page 24
- "Advanced Example: Diffusion in a High-Entropy Alloy" on page 24

1.5.7 Two-Phase Diffusion Problems in Binary Alloys

- "Example: Diffusion in a Joint Between Dissimilar Materials" on page 45
- "Example: Fe/Fe-10mass% Ni Diffusion Couple at 850 °C" on page 72
- "Example: Ferrite Formation and Dissolution in an Fe-0.2C Alloy" on page 77
 - " Isothermal Reaction" on page 77
 - "Reaction During Cooling and Isothermal Holding" on page 81
 - "Austenite Formation During Heating" on page 84
- "Example: Austenite Formation in a Normalized Steel" on page 87

1.5.8 Two-Phase Diffusion Problems in Multicomponent Alloys

- "Example: Isothermal Formation of Ferrite from Austenite in Steel Fe-1Mn-0.2C" on page 94
- "Example: Ferrite Formation During Normalizing of Steel Fe-1Mn-0.2C" on page 100
- "Example: Austenite Formation After Normalizing of Steel Fe-1Mn-0.2C" on page 105

1.5.9 Diffusion in Dispersed Structures

- "Example: Internal Carburization of a Ni-Cr Alloy Using Homogenization " on page 108
- "Example: Internal Nitriding an Fe-Ni-Cr Alloy Using Homogenization" on page 110
- "Example: Carbon Transfer in a Steel Composite: A Full Scale Industrial Problem" on page 112

2 Diffusion Theory

2.1 What is Diffusion and When is it Important?

A material is built up by atoms. In some materials, particularly polymers and biological substances the atoms are organized in molecules and it is more convenient to regard the molecules as building blocks. We will discuss the latter type of molecular materials in a special section but here simply talk about atoms as building blocks although the principles described is also applicable to molecules.

The thermal energy causes the atoms to move. This is called thermal motion and the higher the temperature, the more extensive the motion. In a solid material thermal motion is mainly as vibrations. However, for molten material the atoms can move over longer distances. If the material, solid or molten, is in a state of equilibrium nothing happens on a more macroscopic level. At equilibrium the atomic motion is random. An atom is then as likely to move in one direction as in the opposite direction and there is no net transport of atoms.

However, often the material is not in equilibrium and the motion is not completely random, i.e. there is a bias in some direction. For example, if there is a difference in composition the average motion of the atoms are in the direction that causes the concentration difference to level out. This motion of atoms is called *atomic diffusion* or simply *diffusion*.

It is therefore obvious that diffusion occurs when there are concentration variations in the material and particularly at high temperatures. However, there is one important exception that must be kept in mind— often a material consists of different phases. A phase is a part of a material where the atoms are arranged in a certain manner, which is usually called the crystal structure of the phase. The figures below show examples of two arrangements that are common in metals, body centered cubic (*bcc*) and face centered cubic (*fcc*). In *bcc* atoms are in the corners of the unit cell as well as in the center. In *fcc* they are in the corners and on the center of each face of the cube. Each such cube is then repeated to build up a crystal. In a liquid phase the atoms are usually arranged more or less at random.

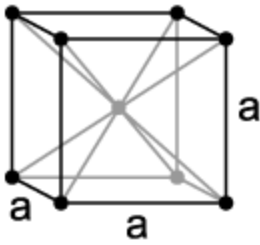


Figure 2-1: Body centered cubic arrangement (bcc).

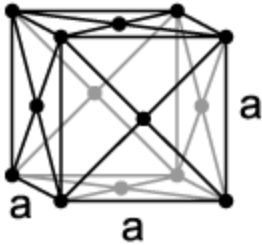


Figure 2-2: Face centered cubic arrangement (fcc).

If two phases are in equilibrium they often have different compositions but as long as equilibrium is established there will be no diffusion across the interface between them. If they are not in equilibrium there is diffusion and one phase will grow and consume the other. In fact the growth rate may then be calculated by solving a diffusion problem.

A common situation of practical importance is a joint between two dissimilar materials with different composition. This may cause problems at higher temperatures, for example during welding or usage of the material, or if there is a transport of atoms from one side to the other. Another situation is diffusion through the wall of a container, where there are different compositions on each side of the wall. This is an important problem in packing of food where oxygen molecules may be small enough to diffuse through the plastic wall and oxidize the food in the container.

Different atoms have different mobility and problems caused by diffusion are particularly important for fast diffusing elements, such as carbon and nitrogen in metals. It should also be emphasized that diffusion is not always problematic but in processing can often provide an opportunity to improve the properties of a material.

In summary diffusion is important when:

- there are concentration differences within the same phase,
- a material is not in equilibrium, and
- temperature is high and diffusion becomes rapid.

2.2 Fick's Law and the Diffusion Coefficient

Diffusion is described mathematically by Fick's law. For the one-dimensional situation with diffusion along an x -axis it reads

$$\text{Eq. 2-1} \quad J_k = -D_k \frac{d c_k}{d x}$$

The diffusional transport of the species k is represented by its flux J_k , i.e. the amount of k that crosses a unit area perpendicular to the direction of diffusion per time unit. If the amount of k atoms is counted in moles (1 mole $\approx 6,022 \cdot 10^{23}$ atoms) the dimension of the flux in SI units is $\text{mol m}^{-2} \text{s}^{-1}$. c_k is the concentration of k , i.e. the amount of k per unit volume, i.e. the number of moles per unit volume. The quantity $d c_k / d x$ is called the concentration gradient and measures how strongly the concentration varies in the x direction. D_k is the diffusion coefficient of k and expresses how mobile k is. A high value means that k moves easily and a low value that it is sluggish. In SI units the diffusivity has the dimension $\text{m}^2 \text{s}^{-1}$. The diffusion coefficient has a strong temperature dependence and it usually varies with composition as well. The temperature dependence is expressed by the Arrhenius equation:

$$\text{Eq. 2-2} \quad D_k = D_k^0 \exp\left(-\frac{Q_k}{RT}\right)$$

where Q_k is the so-called activation energy and expressed in J mol^{-1} and D_k^0 the frequency factor with the same dimension as the diffusion coefficient. R is the gas constant $R \cong 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T is the temperature in Kelvin (K). In scientific calculations the temperature is usually expressed in K and the relation to the Celsius temperature scale is

$$\text{Eq. 2-3} \quad T(K) = 273.15 + ^\circ C$$

In steels carbon (C) diffuses rapidly and at 900 °C its diffusion coefficient is $6 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$. As a comparison manganese (Mn) is slow diffusing with a diffusion coefficient $3 \cdot 10^{-17} \text{ m}^2 \text{ s}^{-1}$ at the same temperature. Thus Mn diffuses 200 000 times slower than C if the two elements were exposed for the same concentration gradient.

In chemistry and metallurgy it is common to express the composition in terms of the mole fraction. The mole fraction x_k is related to the concentration of k by means of

$$\text{Eq. 2-4} \quad x_k = c_k V_m$$

V_m is the molar volume, i.e. the volume of one mole of atoms. For example, for pure iron at room temperature and atmospheric pressure it is $V_m = 7.1 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. In practical calculations one often represents the composition in mass %. If the content of alloying elements is low (in the order of a few percent) one may use the approximation

$$x_k \cong w_k M_{\text{solvent}} / M_k$$

where w_k is the mass fraction of k , i.e. the mass% divided by 100. M_k and M_{solvent} are the molar mass for k and the major alloy element, respectively. In steels the major element is iron (Fe) and its molar mass is roughly 55.85 g/mol and the molar mass of carbon (C) is 12 g/mol.

From a practical point of view one often would like to make a quick estimate whether diffusion is important or not in a certain situation. Then it is convenient to apply the Einstein's formula. It can be used to estimate the average distance ℓ in a certain direction that an atom is able to diffuse in time t ;

$$\text{Eq. 2-5} \quad \ell = \sqrt{2D_k t}$$

If all quantities are expressed in SI units ℓ is obtained in m. In the above example of C and Mn at 900 °C we find that during 1 hour (3600 s) C diffuses an average 0.2 mm and Mn 0.0004 mm. The C diffusion is certainly important in this case but if the Mn diffusion is important or not depends on the special application. If we are interested in a certain distance and want to know when to expect the effect of diffusion we can rephrase [Eq. 2-5](#) into

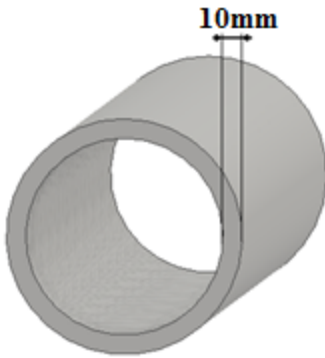
$$\text{Eq. 2-6} \quad t = \ell^2 / 2D_k$$

2.2.1 Example: Diffusion Through a Tube Wall

Consider a tube in a power station where carbon-rich gas flows at a temperature of 500 °C. The wall thickness of the tube is 10 mm. The diffusion coefficient for carbon at this temperature is $2 \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1}$.



Task: Assess if there is any leakage from the tube during the life time of the power station (80 years). Will there be any changes in the composition of the tube at earlier times, for example, one year?



Using Eq. 2-6 you find the following (remember to use SI units, i.e. to express the distance in m):

$$t = (10^{-2})^2 / 2 * 2 \cdot 10^{-15} = 2.5 \cdot 10^{10} \text{ s} \cong 800 \text{ years}$$

We can then conclude that for shorter times in the range of a few years we would hardly expect any “leakage” but on the time scale of the life time of the power station the effect may become important. It may be tempting to conclude that the calculation tells us that nothing is happening in the material at shorter times, say a year. However, this conclusion is wrong and may be illustrated by calculating the average diffusion distance for one year using Eq. 2-5:

$$\ell = \sqrt{2 * 2.2 * 10^{-15} * 3600 * 24 * 365} \cong 0.4 * 10^{-3} m$$

That is, the material is affected to a depth of 0.4 mm from the inner and outer sides.

To judge to what degree the composition is affected requires a more detailed calculation described later.



See the continuation of this example in the advanced section below and then continued in "Stationary Diffusion Through a Tube Wall " on page 31.

2.2.2 Advanced Example: Diffusion Through a Tube Wall

Eq. 2-1 is readily extended to general 3D geometry and is then written

$$\text{ADV Eq. 2-1} \quad \mathbf{J}_k = -D_k \mathbf{grad} c_k$$

where the flux \mathbf{J}_k and the concentration gradient $\mathbf{grad} c_k$ now are vectors. The "nabla" symbol is often used and one writes $\nabla c_k = \mathbf{grad} c_k$.

In a Cartesian frame of reference with the axes x_1, x_2, x_3 we write the gradient operator:

$$\text{ADV Eq. 2-2} \quad \nabla = \mathbf{grad} = \left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3} \right)$$

The Einstein formula as expressed by Eq. 2-4 gives the average diffusion distance in a certain direction.

- If we are interested in how long the average distance in a plane is the formula reads $\ell = \sqrt{4D_k t}$.
- If we are interested in how far from the origin the atom has moved in all three directions the formula reads $\ell = \sqrt{6D_k t}$.

In most practical situations one is only interested about the diffusion distance in a certain direction and Eq. 2-4 should be used.

2.3 Frame of Reference

Diffusion represents a transport of material and that must be expressed relative to some reference. The choice of reference has no effect on the physics and is completely arbitrary. One may thus choose the reference that is most convenient for a certain problem. However, the flux will be different in different frames of reference. The value of the diffusion coefficient thus depends on the chosen frame of reference.

In diffusion it is common to use the following frames of reference:

- Lattice-fixed frame
- Number-fixed frame
- Volume-fixed frame



More frames of reference as well as variants of the above frames are included in the literature.

In the *lattice-fixed frame* of reference diffusion is measured relative the crystal lattice. In this frame of reference there may be a net-flow of atoms and crystal planes may be created or annihilated by migration of dislocations as a consequence of diffusion. The diffusion coefficients given in the lattice-fixed frame of reference are often referred to as the *intrinsic diffusion coefficients*.

In the *number-fixed frame* of reference diffusion is defined in such a way that there is no net flow of atoms. This is sometimes referred to as *interdiffusion* or simply as *atomic mixing*. In a binary system A-B this mean that the flux of A is the same as the flux of B but in the opposite direction when the number-fixed frame is used. The diffusion coefficients given in the number-fixed frame of reference are often referred to as the *interdiffusion coefficients* or the *chemical diffusion coefficients*.

The *volume-fixed frame* of reference is similar to the number-fixed frame but defined in such a way that there is no net flow of volume.

2.4 Fick's Second Law: The Calculation of Concentration Profiles

"[Frame of Reference](#)" on the [previous page](#) discussed how to calculate the diffusional flux when the concentration gradient is given. This section discusses how to calculate the gradient of the concentration profile for a given situation and how the concentration profile develops in time. The starting point is the so-called *Fick's second law*. Despite its name Fick's second law is not really a 'law of nature' in itself but it can be derived from Fick's law. Without giving any mathematical details we conclude that the resulting equation is a so-called partial differential equation, the solution of which gives the composition as a function of time and distance as described in the advanced example below.

The equation can be solved by numerical methods or in simple cases analytical methods using standard mathematical functions. When using the latter case of analytical methods it is required, almost without exception, that the diffusion coefficient can be approximated as being independent of the composition which in practice is never the case. Moreover, the temperature is required to be constant, i.e. only isothermal conditions can be considered. Consequently the analytical methods are very limited and can seldom be used for practical calculations. Despite this they are valuable to give some understanding and to illustrate general trends.

The solution of Fick's second law gives the concentration as a function of time and location, i.e. the concentration profile as a function of time. In physics such a function of space and time is usually called a *field*, which can also be called the *concentration field*.

To find a solution one must give boundary conditions. First of all the concentration field must be given at some time, usually set as $t = 0$. Other boundary conditions are also required, which can be done in many ways. The simplest case is the *closed system* in which all diffusional fluxes on the boundary of the system vanish. In this case no material can enter into or leave the system. For more detail go to "[Boundary Conditions](#)" on the next page.

2.4.1 Advanced Example: Fick's Second Law

For the general 3D case Fick's second law may be written:

$$\text{ADV Eq. 2-3} \quad \frac{\partial c_k}{\partial t} = \mathbf{div}(D_k \mathbf{grad} c_k)$$

where div is the divergence operator. Using the Nabla notation the above equation is written

$$\text{ADV Eq. 2-4} \quad \frac{\partial c_k}{\partial t} = \nabla(D_k \nabla c_k)$$

In a Cartesian frame of reference the divergence operator is

$$\text{ADV Eq. 2-5} \quad \text{div} = \left(\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2} + \frac{\partial}{\partial x_3} \right)$$

A solution of [ADV Eq. 2-3](#) or [ADV Eq. 2-4](#) is of the type $c_k(t, x_1, x_2, x_3)$ describing the concentration as a function of time and location, i.e. the concentration field as a function of time. To find a solution one must give boundary conditions. For more information about these mathematical details, refer to the suitable text books.

2.5 Boundary Conditions

In practice one may distinguish between two major types of boundary conditions. If surface reactions are very rapid the surface concentration will quickly adjust to a composition in equilibrium with the surrounding media. In a thermodynamic language this means that the element under consideration will have the same activity or chemical potential at the surface as in the surrounding media.

If the surface reactions occur with a finite rate it will instead be the flux of a component that is given. A special case, which is very common, is that the surface reaction is so slow that it can be completely neglected and then the flux at the surface vanishes. In a material with several components it is common to have different types of boundary conditions for different elements. For example, the fluxes of substitutional elements such as Fe, Mn and so forth vanish but for interstitial elements like C and N there may be a finite flux or even a fixed activity at the surface.

It should be emphasized that in practice the boundary conditions are thus more complex than the idealized Dirichlet and Neumann conditions discussed in mathematics.

2.6 Analytical Solutions

The analytical solutions are based on approximations that are seldom valid in reality. Nevertheless they are handy and easy to use and give some valuable insight. The most important ones are the *error-function* and the *sinusoidal solution*.

2.6.1 The Error-Function Solution

This solution expresses the concentration profile along the x -axis as

$$\text{Eq. 2-7} \quad c_k = A + B \operatorname{erf} \frac{x}{\sqrt{4D_k t}}$$

The error function is denoted erf and is depicted in the figure below. It is available in most computers. A and B are constants determined by the boundary conditions. The error function solution predicts a step in composition at $x = 0$ at the time $t = 0$.

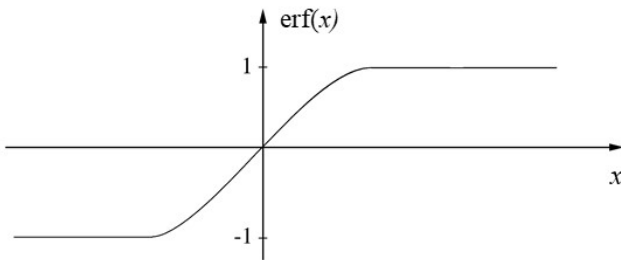


Figure 2-3: The error function.

2.6.2 Example: Carburization of Steel

Carburization is a part of the case-hardening process in which the steel surface is hardened by adding carbon to it and then letting carbon diffuse into the material. Suppose that a steel with an initial carbon content c_0 is exposed to an environment that yields the carbon content c_1 at the steel surface.



Task: Give an expression for how the carbon concentration profile will develop in time.

Use the error function and $x \geq 0$ as the distance from the surface. Determine A and B to fulfill the boundary conditions. At $t = 0$ and at $x > 0$ we have $x/\sqrt{4D_C t} \rightarrow \infty$ and Eq. 2-7 yields:

$$c_0 = A + B$$

For $t > 0$ and $x = 0 \rightarrow \text{erf}(0) = 0$ and Eq. 2-7 yields $c_1 = A$.

We thus find that $B = c_0 - A = c_0 - c_1$.

The solution then is:

$$c = c_1 + (c_0 - c_1) \text{erf} \frac{x}{\sqrt{4D_C t}}$$

2.6.3 The Sinusoidal Solution

This solution is based on a periodic concentration profile with the wave length ℓ and is given by

$$\text{Eq. 2-8} \quad c = A \exp\left(\frac{-4\pi^2 Dt}{\ell^2}\right) \sin\left(\frac{2\pi x}{\ell}\right)$$

A is given by the boundary condition and the factor $A \exp(-4\pi^2 Dt/\ell^2)$ describes how the amplitude decays exponentially with time, the shorter the wave length the quicker the decay.

2.6.4 Example: Homogenization of an Alloy

After casting, an alloy usually has more or less periodic concentration variations caused by micro segregation during the solidification process. In order to level out these variations one performs homogenization annealing.



Task: Estimate the homogenization time required to reduce concentration variation to 10% of its original amplitude.

Eq. 2-8 yields $\exp(-4\pi^2 Dt/\ell^2) = 0.1$ i.e. $t = \frac{2,3}{4\pi^2} \cdot \frac{\ell^2}{D}$. It is worth noting that the required time is proportional to the square of the wave length. If the wave length can be decreased, say by a factor 10, due to plastic deformation during hot rolling, the homogenization will be 100 times faster.



Remark on internal oxidation: Simulations based on the homogenization method are time consuming in such cases where the contents of the diffusing elements are low in the matrix phase. Unfortunately, this is the case particularly for internal oxidation which is of large practical importance. Nevertheless, the calculations are stable and the results will eventually be found even for complex cases.

2.7 Materials with Many Components

Most real materials such as steels, superalloys or light metals contain many different alloy elements. In principle the equation

$$\text{Eq. 2-9} \quad J_k = -D_k \frac{d c_k}{d x}$$

may be formulated for each element. However, there is a severe complication that has very important practical consequences. It has been found that diffusion of an element k does not only depend on the concentration gradient of k but on the concentration gradient of other elements as well. This was demonstrated in a very famous experiment by Darken where he welded together two steels with the same carbon content but different silicon content and then heated the joint.



See "Example: Darken's Experiment " on page 51.

Darken found that carbon diffused from the Si-rich side to the silicon poor side.

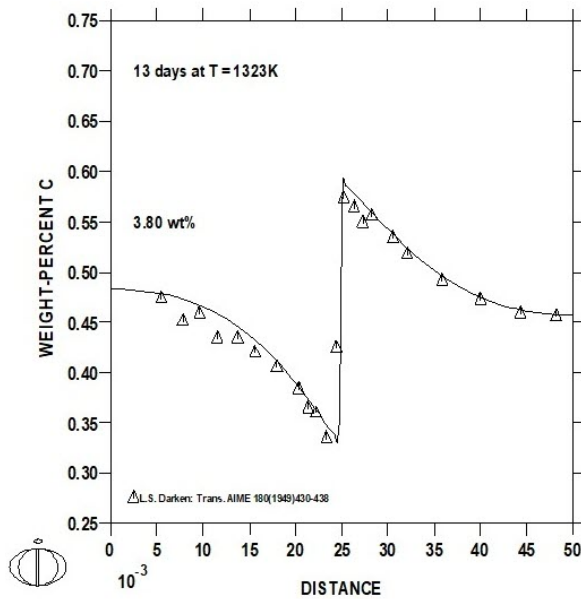


Figure 2-4: Solid line: DICTRA simulation of Darken's experiment, symbols: Darken's experimental points. The left side contains 3.80 mass% Si.

Suppose we have N elements in the alloy. For example, in a low-alloy steel (Fe the major element) with C, Mn and Si $N = 4$. Mathematically the coupling effect between the different elements is taken into account by replacing Eq. 2-9 with the equation below:

$$\text{Eq. 2-10} \quad J_k = - \sum_{j=1}^{N-1} D_{kj}^N \frac{d c_j}{d x} = -D_{k1}^N \frac{d c_1}{d x} - D_{k2}^N \frac{d c_2}{d x} \dots$$

Instead of one diffusion coefficient for element k we now have $N - 1$ diffusion coefficients for each k with respect to the concentration of each element except one arbitrarily chosen element which will be dependent. We then have $(N - 1)N$ different diffusion coefficients in an alloy with N elements. The diffusion coefficient D_{kj}^N denotes the diffusion coefficient for element k caused by a concentration gradient of element j when element N has been chosen as the dependent element. The number of different diffusion coefficients thus becomes large in real alloys which can have five or more alloying elements and computer- based methods

need to be applied. It should be emphasized that if one would like to change dependent component it is straight forward but certain rules must be obeyed.

2.7.1 Example: Diffusion in a High-Entropy Alloy

Consider a so-called high-entropy alloy consisting of equal atomic amounts of Co-Cr-Fe-Mn-Ni. During casting there will be micro segregation yielding concentration variations.



Task: Write down the diffusion coefficients needed to describe the homogenization process in the alloy. How many are there? Write Eq. 2-10 for this alloy.

This system consists of five components and one of them must be chosen as a reference. We thus have $4 \cdot 5 = 20$ diffusion coefficients. This choice of reference is arbitrary so let us choose Co as reference. We then obtain:

$$\begin{aligned}
 J_{Cr} &= -D_{CrCr}^{Co} \frac{d c_{Cr}}{d x} - D_{CrFe}^{Co} \frac{d c_{Fe}}{d x} - D_{CrMn}^{Co} \frac{d c_{Mn}}{d x} - D_{CrNi}^{Co} \frac{d c_{Ni}}{d x} \\
 J_{Fe} &= -D_{FeCr}^{Co} \frac{d c_{Cr}}{d x} - D_{FeFe}^{Co} \frac{d c_{Fe}}{d x} - D_{FeMn}^{Co} \frac{d c_{Mn}}{d x} - D_{FeNi}^{Co} \frac{d c_{Ni}}{d x} \\
 J_{Mn} &= -D_{MnCr}^{Co} \frac{d c_{Cr}}{d x} - D_{MnFe}^{Co} \frac{d c_{Fe}}{d x} - D_{MnMn}^{Co} \frac{d c_{Mn}}{d x} - D_{MnNi}^{Co} \frac{d c_{Ni}}{d x} \\
 J_{Ni} &= -D_{NiCr}^{Co} \frac{d c_{Cr}}{d x} - D_{NiFe}^{Co} \frac{d c_{Fe}}{d x} - D_{NiMn}^{Co} \frac{d c_{Mn}}{d x} - D_{NiNi}^{Co} \frac{d c_{Ni}}{d x} \\
 J_{Co} &= -D_{CoCr}^{Co} \frac{d c_{Cr}}{d x} - D_{CoFe}^{Co} \frac{d c_{Fe}}{d x} - D_{CoMn}^{Co} \frac{d c_{Mn}}{d x} - D_{CoNi}^{Co} \frac{d c_{Ni}}{d x}
 \end{aligned}$$

2.7.2 Advanced Example: Diffusion in a High-Entropy Alloy

Choice of Independent Concentration Gradients

Here we will discuss how to change from one dependent concentration gradient to another. Introducing the mole fraction and approximating the molar volume is independent of concentration we write instead of Eq. 2-10:

ADV Eq. 2-6

$$J_k = -\frac{1}{V_m} \sum_{j=1}^N D_{kj} \nabla x_k$$

Observe that the summation is now performed over all N elements. However, the mole fractions must sum up to unity, i.e. the sum of their gradients must vanish,

ADV Eq. 2-7

$$\sum_{k=1}^N \nabla x_k = 0$$

and we may thus use relation [ADV Eq. 2-6](#) to eliminate any of the gradients, e.g. that of element N .

We then rewrite Fick's equation $J_k = -D_k \frac{d c_k}{d x}$ in terms of only independent gradients:

ADV Eq. 2-8

$$J_k = -\frac{1}{V_m} \left(\sum_{j=1}^{N-1} D_{kj} \nabla x_j - D_{kN} \sum_{j=1}^{N-1} \nabla x_j \right) = -\frac{1}{V_m} \sum_{j=1}^{N-1} D_{kj}^N \nabla x_j$$

ADV Eq. 2-9

$$D_{kj}^N = D_{kj} - D_{kN}$$

It should be observed that only the coefficients D_{kj}^N affect the result and not the individual coefficients D_{kj} . However, the dependent component N can of course be chosen arbitrarily but the diffusion coefficients D_{kj}^N will then be different. In fact from [ADV Eq. 2-9](#) one may derive relations like

ADV Eq. 2-10

$$\begin{aligned} D_{kN}^N &= 0 \\ D_{kN}^j &= -D_{kj}^N \\ D_{kj}^l &= D_{kj}^N - D_{kl}^N \end{aligned}$$

It is easy to convince oneself that the resulting fluxes are independent of the choice of dependent component N provided that the diffusion coefficients are transformed in accordance with [ADV Eq. 2-10](#).

It is convenient to write the equations in vector-matrix notation provided that. Instead of

$$J_k = -\frac{1}{V_m} \sum_{j=1}^{N-1} D_{kj}^N \nabla x_j$$

we thus write

$$\text{ADV Eq. 2-11} \quad \mathbf{J} = -\frac{1}{V_m} \mathbf{D}^N \nabla \mathbf{x}$$

where

$$\mathbf{J} = \begin{pmatrix} J_1 \\ J_2 \\ \cdot \\ \cdot \\ J_N \end{pmatrix}$$

$$\mathbf{D}^N = \begin{pmatrix} D_{11}^N & D_{12}^N & \cdot & \cdot & 0 \\ D_{21}^N & D_{22}^N & & & 0 \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & 0 \\ D_{N1}^N & \cdot & \cdot & D_{NN-1}^N & 0 \end{pmatrix}$$

$$\nabla \mathbf{x} = \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \\ \cdot \\ \cdot \\ \nabla x_N \end{pmatrix}$$

The diffusion coefficient matrix thus has zeros in the N:th column.

Transformation Between Different Frames of Reference

We may transform the flux from one frame of reference to another by multiplying with a transformation matrix \mathbf{A} :

$$\text{ADV Eq. 2-12} \quad \mathbf{J}' = \mathbf{A}\mathbf{J}$$

It is easy to convince oneself that the gradients are not affected by this transformation but the diffusion coefficients will transform accordingly

$$\begin{aligned} \text{ADV Eq. 2-13} \quad \mathbf{J}' &= \mathbf{A}\mathbf{J} = -\frac{1}{V_m} \mathbf{A}\mathbf{D}^N \nabla \mathbf{x} \\ \mathbf{D}^{N'} &= \mathbf{A}\mathbf{D}^N \end{aligned}$$

and consequently

$$\text{ADV Eq. 2-14} \quad \mathbf{J}' = -\frac{1}{V_m} \mathbf{D}^{N'} \nabla \mathbf{x}$$

As an example, it is instructive to consider a binary system. Suppose the fluxes are given in a lattice-fixed frame of reference and that the individual (intrinsic) diffusion coefficients are known. We would like to transform to a number-fixed frame of reference, i.e. we want to consider interdiffusion. This is achieved by the transformation

$$J_1' = J_1(1 - x_1) - x_1 J_2 = -J_2'$$

Here information is lost because we now have only one independent flux. In order not to lose any information we may introduce the net flux of atoms in the lattice-fixed frame of reference as a second independent flux

$$J_2' = J_1 + J_2$$

The flux is related to the Kirkendall effect because the velocity of Kirkendall markers in the number-fixed frame of reference v_K is

$$v_K/V_m = -(J_1 + J_2) = -J_2'$$

The transformation matrix \mathbf{A} thus is

$$\text{ADV Eq. 2-15} \quad \mathbf{A} = \begin{pmatrix} (1 - x_1) & -x_1 \\ 1 & 1 \end{pmatrix}$$

and the new diffusion coefficients become

ADV Eq. 2-16

$$\mathbf{D}^{N'} = \begin{pmatrix} (1-x_1) & -x_1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} D_{11}^N & 0 \\ D_{21}^N & 0 \end{pmatrix} = \begin{pmatrix} (1-x_1)D_{11}^N - x_1 D_{21}^N & 0 \\ D_{11}^N + D_{21}^N & 0 \end{pmatrix}$$

These expressions are identical to Darken's classical expressions remembering that he denoted the individual diffusion coefficients as $D_1 = D_{11}^2$ and $D_2 = D_{22}^1 = -D_{21}^2$ using our notation. In the left column of $\mathbf{D}^{N'}$ matrix the upper element is the interdiffusion coefficient, called the chemical diffusion coefficient by Darken, and the lower is the difference in individual coefficients giving the Kirkendall effect.

Thermodynamic Driving Forces and Onsager Relations

If one assumes that the fluxes are independent in the lattice-fixed frame of reference one may postulate:

$$\begin{aligned} \text{ADV Eq. 2-17} \quad \mathbf{J}_k &= -\frac{1}{V_m} x_k M_k \nabla \mu_k \\ \mathbf{J} &= -\mathbf{L} \nabla \mu \end{aligned}$$

Here M_k denotes the mobility of element k and

$$\mathbf{L} = \frac{1}{V_m} \begin{pmatrix} x_1 M_1 & 0 & \cdot & \cdot & 0 \\ 0 & x_2 M_2 & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & 0 \\ 0 & \cdot & \cdot & 0 & x_N M_N \end{pmatrix}$$

and

$$\nabla \mu = \begin{pmatrix} \nabla \mu_1 \\ \nabla \mu_2 \\ \cdot \\ \cdot \\ \nabla \mu_N \end{pmatrix}$$

Observe that $\mathbf{L} = \mathbf{L}^T$ i.e. the L-matrix is symmetric in accordance with Onsager reciprocity law. In the case of a diagonal matrix this observation is trivial. This property must remain even when off-diagonal elements are included. It should be noted that the Manning theory for the correlation effect gives a symmetric L-matrix where all matrix elements only depend on the diagonal mobilities.

Diffusion is an irreversible process and this is expressed by the second law stating that the entropy production must be positive or vanish when there is equilibrium. Under isothermal conditions and if the fluxes are expressed in the lattice-fixed frame of reference the local entropy production σ is given by

$$\text{ADV Eq. 2-18} \quad T\sigma = -\mathbf{J}^T \nabla \mu$$

The entropy production is a measure of how irreversible the process is and must be independent of the frame of reference which is chosen by the scientist. If the fluxes are transformed to \mathbf{J}' by a transformation matrix \mathbf{A} the product $-(\mathbf{J}')^T \nabla \mu' \neq -\mathbf{J}^T \nabla \mu$ unless also the driving forces are transformed $\nabla \mu' = \mathbf{B} \nabla \mu$. We thus find \mathbf{B} in the following way

$$\begin{aligned} -(\mathbf{J}')^T \nabla \mu' &= -\mathbf{J}^T \nabla \mu \\ -(\mathbf{A}\mathbf{J})^T \mathbf{B} \nabla \mu &= -\mathbf{J}^T \nabla \mu \\ -\mathbf{J}^T \mathbf{A}^T \mathbf{B} \nabla \mu &= -\mathbf{J}^T \nabla \mu \end{aligned}$$

Obviously we must have $\mathbf{A}^T \mathbf{B} = \mathbf{U}$ where \mathbf{U} is the unity matrix and consequently $\mathbf{B} = (\mathbf{A}^T)^{-1}$ i.e.

$$\nabla \mu' = (\mathbf{A}^T)^{-1} \nabla \mu$$

and consequently

$$\nabla \mu = \mathbf{A}^T \nabla \mu'$$

The \mathbf{L} matrix thus is transformed

$$\begin{aligned} \text{ADV Eq. 2-19} \quad \mathbf{J}' &= \mathbf{A}\mathbf{J} = -\mathbf{A}\mathbf{L}\nabla \mu = -\mathbf{A}\mathbf{L}\mathbf{A}^T \nabla \mu' \\ \mathbf{L}' &= \mathbf{A}\mathbf{L}\mathbf{A}^T \end{aligned}$$

It is seen that if \mathbf{L} is symmetric also \mathbf{L}' is.

3 One-Phase Diffusion Problems

3.1 Setting Up a Simulation

In order to make diffusion calculations one needs data on diffusion coefficients and the appropriate boundary conditions that represent a certain problem. In the following sections we will discuss how to solve a number of practical problems. Our main tool for the numerical calculation is using the Diffusion Module (DICTRA) in Graphical Mode. A calculation using the Diffusion Calculator is based on the original DICTRA Console Mode code.



There are many examples and tasks included in this tutorial. For the [One-Phase Diffusion Problems](#) step-by-step instructions are included to help you begin to learn how to reproduce the simulations that are described in the theory and in the relevant sections. For the rest of the tasks throughout this guide, the parameters needed to reproduce the plots using Graphical Mode are included within the text but the specific instructions are not always provided. See "[List of Examples](#)" on page 8 to see what is available in each section.

3.1.1 Simulations in Graphical Mode versus Console Mode

Console Mode

When using Console Mode commands, building a macro file to create the simulation typically involves the following steps:

1. Define thermodynamic and kinetic data for the system.
2. Define the initial system.
 - a. Define size and grid.
 - b. Define initial concentration profile.
3. Define temperature as a function of time.
4. Define boundary conditions that may be functions of time.

5. Perform the simulation for the chosen time.
6. Plot the results – many choices possible.

Graphical Mode

The overall sequence of what you define in Graphical Mode for the Diffusion Module is similar to the process in Console Mode. However, instead of using commands you are adding nodes and then entering settings for each of the nodes. Some advanced functionality is only available in Console Mode, and some of the commands available in Console Mode are not needed in Graphical Mode because it is automatically integrated into the Activity nodes, e.g. the Diffusion Calculator.

The following is a general overview of the steps to set up the simulation.

1. Use the **Diffusion Simulation** template to add the System Definer, Diffusion Calculator and Plot Renderer activity nodes.
2. On the **System Definer**, you select the thermodynamic and kinetic databases and add elements, which automatically include all phases.
3. On the **Diffusion Calculator**, you set the geometry (by default the geometry is planar), add region(s) and enter grid(s) and phase(s) in the region(s). You then enter composition(s) of phase(s).
4. On the **Plot Renderer**, you choose what to plot and then run the simulation, i.e. you **Perform** the sequence of nodes you have defined in the tree to produce the output simulation. You can also add a **Table Renderer** to tabulate the results of a single equilibrium calculation or a stepping operation.

3.2 Stationary Diffusion Through a Tube Wall

Here we will revisit the example *Diffusion Through a Tube Wall* first described in the theory section, "[Fick's Law and the Diffusion Coefficient](#)" on page 13. The next two sections show you how to recreate these plots using both Graphical Mode and Console Mode.



Task: Consider a tube in a power station where carbon-rich gas flows at a temperature of 500 °C. The wall thickness of the tube is 10 mm. The diffusion coefficient for carbon at this temperature is $2 \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1}$. Assess if there will be any leakage from the tube during the life time of the power station, 80 years. Will there be any changes in the composition of the tube at earlier times, say one year?

We shall make the calculation a bit more realistic by considering the evolution of the carbon concentration profile and take into account the concentration dependence of the diffusion coefficient, i.e. it no longer has the constant value given above. That value is actually only valid for very low C content. In order to solve this problem we must define boundary conditions. For simplicity we consider only a binary Fe-C alloy with an initial carbon content of 0.1 mass% C. On the outer side of the wall we take a very low carbon content (e.g. 0%) and on the inside we assume sooting which corresponds to a carbon activity relative graphite of unity or higher.

Results of the Simulation

Figure 3-1 shows the calculated carbon concentration profiles in the tube wall at different times. It is notable that already after one year there is a substantial carburization of the inner side of the wall and a corresponding decarburization of the outer side. We may also notice that the depth agrees well with 0.4 mm obtained in the original example using Einstein's formula, i.e. $\ell = \sqrt{2D_k t}$.

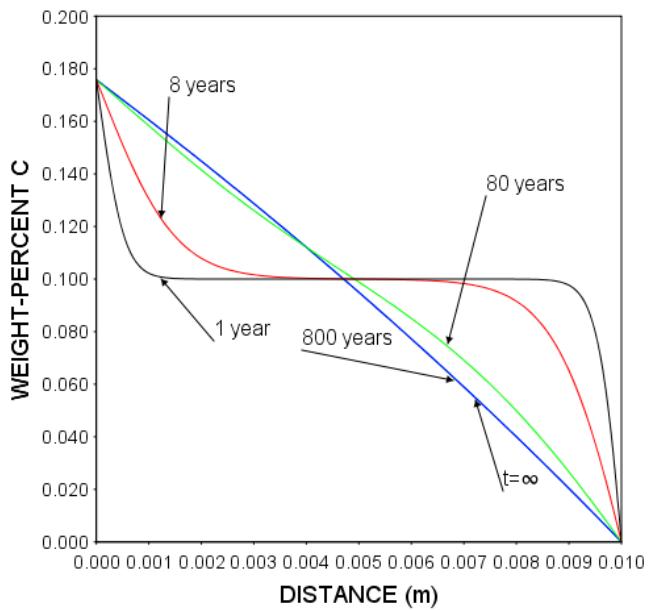


Figure 3-1: Calculated carbon concentration as function of distance (m) from inner tube wall at different times as indicated.

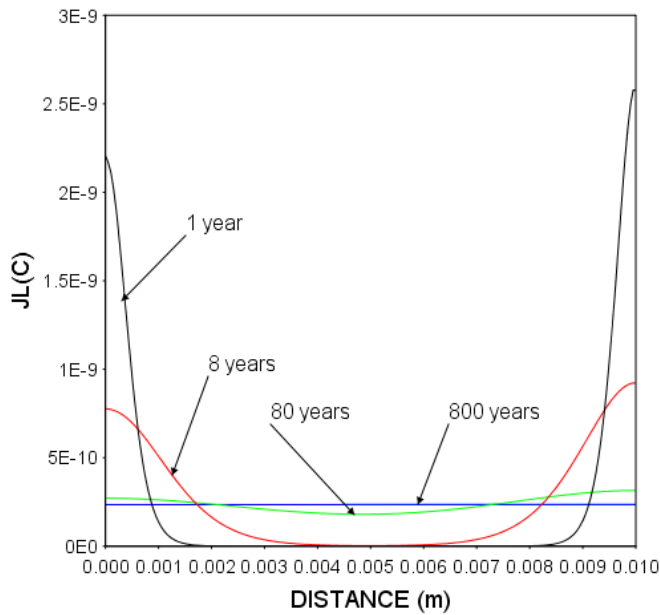


Figure 3-2: Calculated carbon flux in moles per second and square meter as a function of distance (m) from inner tube wall at different times as indicated.

It is also notable that close to the end of the life time the concentration profile is very close to the one after 800 years. The carbon flux calculated from the concentration profiles using $J_k = -D_k \frac{d c_k}{d x}$ is shown in Figure 3-2. As can be seen it is always positive although it is first

quite low except at the inner and outer sides of the wall. Carbon is thus flowing from the inside towards the outside. At very long times a steady state is approached if the boundary conditions are constant. In the steady state the flux has the same value everywhere in the system and it may be obtained by the approximate form of Fick's law:

$$J_k \cong -D_k \frac{\Delta w_k M_{\text{solvent}}}{V_m \ell M_k}$$

where ℓ is the thickness of the wall and Δw_k the difference in weight fraction carbon between the two sides. Inserting the appropriate values for the present example we obtain

$$J_k \cong 2 \cdot 10^{-15} \frac{0.0018 \cdot 55.85}{7 \cdot 10^{-6} \cdot 0.01 \cdot 12} = 2.4 \cdot 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$$

which agrees quite well with the blue line ($t \rightarrow \infty$) in [Figure 3-2](#).

3.2.1 Graphical Mode - Diffusion Through a Tube Wall

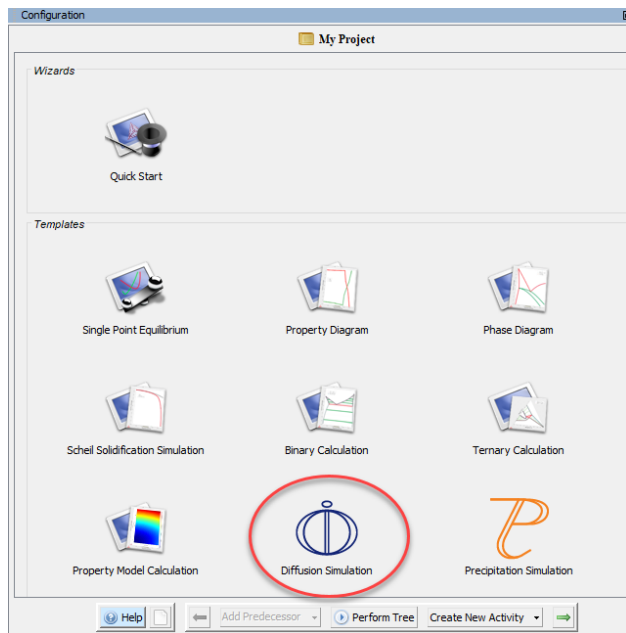
Below are the step-by-step instructions to recreate the example described in "[Stationary Diffusion Through a Tube Wall](#)" on page 31.



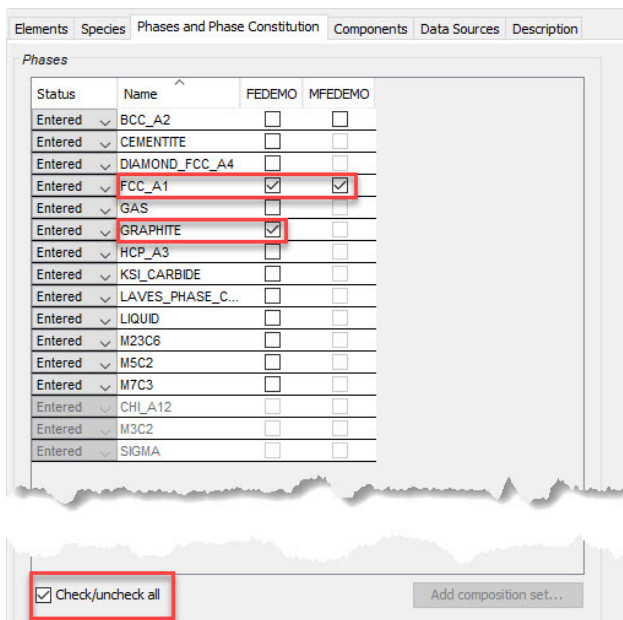
For comparative purposes only, you can also look at the Console Mode example that uses commands in "[Console Mode Commands - Diffusion Through a Tube Wall](#)" on page 40.

Configure the System Definer

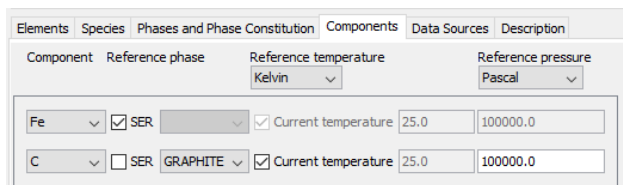
1. Open Thermo-Calc and go to Graphical Mode. The mode defaults to the one last used. If necessary click the **Switch to Graphical Mode** button in the toolbar.
2. On the **Configuration** window under Templates, click **Diffusion Simulation**. Three nodes are added to the **Project** tree (System Definer, Diffusion Calculator and Plot Renderer).



3. On the **System Definer** → **Configuration** window under **Package**, select **Demo: Steels and Fe-alloys (FEDEMO, MFEDEMO)**.
4. In the **Periodic Table** click to select the elements **Fe** and **C**.
5. Click the **Phases and Phase Constitution** tab. At the bottom of the window click to clear the **Check/uncheck all** box then select the **FCC_A1** check boxes for FEDEMO and MFEDEMO and the **GRAPHITE** check box for FEDEMO.



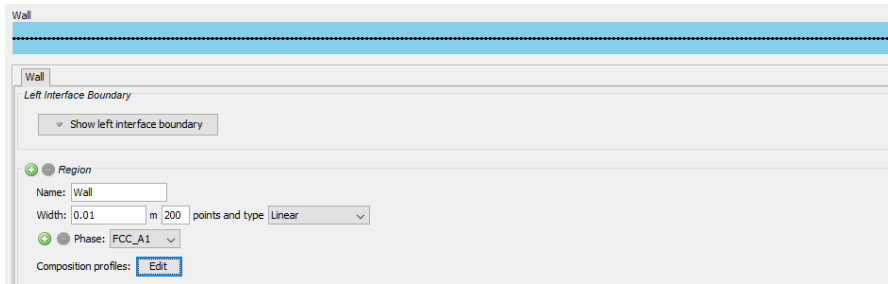
- Click the **Components** tab. Next to carbon (C) click to clear the **SER** check box and then select **GRAPHITE** from the list.



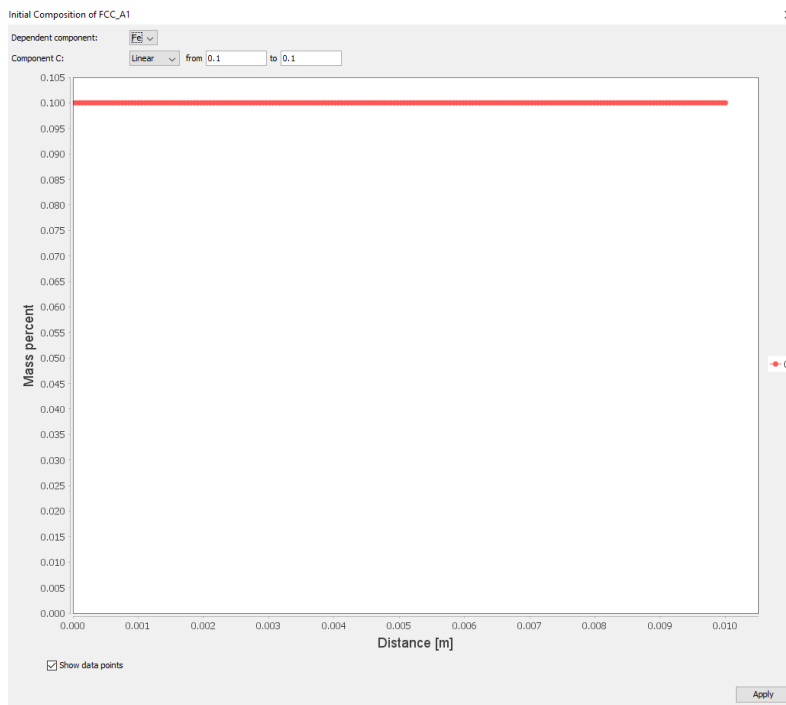
Configure the Diffusion Calculator

- In the **Project** window, click the **Diffusion Calculator**. In the **Configuration** window select a **Cylindrical** geometry and enter 0.02 in the *First interface position* field.
- Under *Region* enter the following in the fields:
 - Name*: Wall
 - Width*: 0.01 m
 - Points* : 200. Keep the default, **Linear** grid type.
 - Choose **FCC_A1** as the *Phase*.

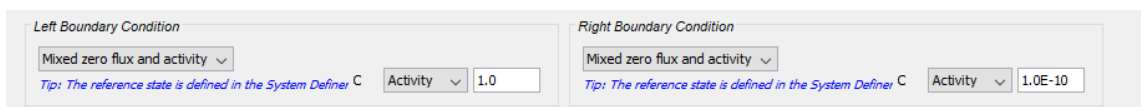
e. Next to *Composition Profiles* click **Edit**.



f. In the **Initial composition of FCC_A1** window, for *Component C*, enter 0.1 in both fields then click **Apply**.



3. For both the *Left Boundary Condition* and *Right Boundary Condition*, select **Mixed zero flux and activity**. Then for both choose **Activity** from the lists and enter 1.0 for the *Left Boundary Condition* and 1.0E-10 for the *Right Boundary Condition*.



4. Under *Thermal Profile*, set the following:
 - a. *Temperature*: 500 **Celsius**
 - b. *Simulation time*: 2.5E11 **Seconds**

Thermal Profile

Isothermal Non-isothermal

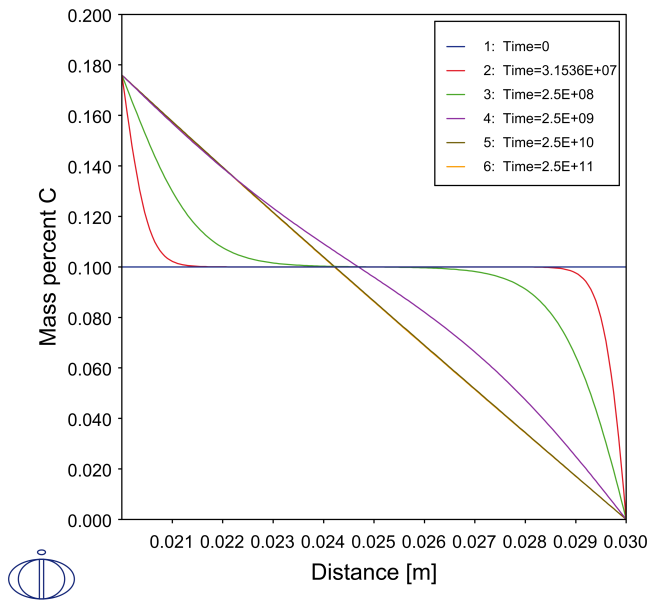
Temperature: 500.0 Celsius

Simulation time: 2.5E11 Seconds

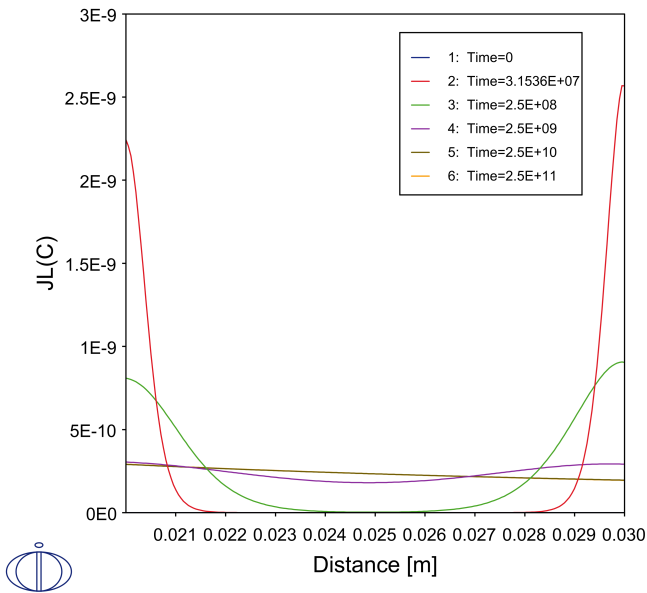
5. Click the **Options** tab.
 - a. For the *Time integration method*, choose **Euler backwards**.
 - b. Keep all the other defaults.

Configure the Plots

1. In the **Project** window, click the **Plot Renderer 1** node. In the **Configuration** window, under *Y-axis* click to clear the **Automatic scaling** check box. Then in the fields enter the *Limits* 0.0 to 0.2 with a *step* of 0.02.
2. In the *Time* field, enter the following numbers as a series with a space between each number (in Seconds): 0.0 3.1536E7 2.5E8 2.5E9 2.5E10 2.5E11.
3. Click **Perform** to plot the first diagram showing the concentration profiles.



4. Add a second plot by right-clicking the Diffusion Calculator and choosing **Create New Successor → Plot Renderer**.
5. Click **Switch to advanced mode**. Under *Y-axis* choose **User-defined** and enter $J_L(C)$ in the field.
6. In the *Plot condition* field, enter (or copy and paste) the same series of times as for the first plot: 0.0 3.1536E7 2.5E8 2.5E9 2.5E10 2.5E11.
7. Click **Perform** to plot the carbon flux as function of distance for the chosen times.



3.2.2 Console Mode Commands - Diffusion Through a Tube Wall

The following commands (indicated by a code font) are used with the DICTRA module in Console Mode to perform the simulation described in "[Stationary Diffusion Through a Tube Wall](#)" on page 31. In the example below, some descriptive text is included to help guide you through the logic of setting up the simulation. This example is also created using Graphical Mode in "[Graphical Mode - Diffusion Through a Tube Wall](#)" on page 34.



The details of the commands (which are abbreviated in this example) and the use of macro files is described in the online help (press F1 in Thermo-Calc). This section is intended only for comparative purposes as Graphical Mode is used throughout the rest of this tutorial guide and is recommended for new users.

Define thermodynamic data and kinetic data for the system

```
goto da
```

```
sw
```

```
fedemo
```



```
def-sys fe c
rej ph * all
res ph fcc,grap
get
app
mfedemo
def-sys fe c
get
goto d-m
```

Define the initial system: Size and grid

```
en-reg
wall
en-grid
WALL
10e-3
LINEAR
200
```

Define initial concentration profile

```
en-phase
ACTIVE
WALL
MATRIX
fcc_a1#1
en-com
```

```
WALL
FCC_A1
w-p
C
LINEAR
0.1
0.1
```

Define temperature as a function of time

```
set-cond
GLOBAL
t
0
773
N
```

Define boundary conditions

In order to define the boundary conditions we want to use graphite as reference state for carbon. First we set the reference state:

```
set-ref
c
graphite
*
100000
```

Then we set the boundary conditions and use mixed conditions and set the activity for C on each side of the system. First the lower side which we take as the inner side of the wall having a high C activity

```
set-cond  
boundary  
lower  
mixed  
activity  
0  
1.0; (C activity is set as unity)  
*  
N
```

Then the upper side which we take as the outer side of the wall having a very low C activity

```
set-cond  
boundary  
upper  
mixed  
activity  
0  
1e-10; (a low value but for numerical reasons we do not chose 0)  
*  
N
```

Perform the simulation for the time chosen

Set the end time of simulation to $2.5 \cdot 10^{11}$ s (8 000 years) and set some other conditions.

```
s-s-time
```

```
2.5e11
```

```
YES
```

```
2.5E+10
```

```
1E-07
```

```
1E-07
```

```
s-sim-cond
```

```
1
```

And start the simulation

```
Simulate
```

Plot the results

Start by going to the postprocessor module.

```
Post
```

Define axes variables and scaling of y axis

```
s-d-a x distance
```

```
s-d-a y w-p c
```

```
s-sca y no 0.0 0.2
```

Next define at what times (in seconds) to show the concentration profiles.

```
s-p-c
```

```
time
```

```
31536000 2.5e8 2.5e9 2.5e10 2.5e10 2.5e11
```

```
plot
```

```
@?
```

This command halts the program after the plot. The user needs to press the return to continue to the next plot. The next plot is the carbon flux as function of distance for the chosen times.

```
s-d-a y j1(c)
```

```
plot
```

3.3 Example: Diffusion in a Joint Between Dissimilar Materials

Consider two materials in the same phase but with different compositions. These two materials are joined together in a weldment and then kept at an elevated temperature for a period of time. This results in diffusion because the composition differences tend to level out. In the scientific literature such a joint is often referred to as a *diffusion couple*.



Task: Consider a steel plate 0.5 mm thick with a 0.1 mm (100 μm) Ni-foil added. For simplicity we approximate the steel as pure Fe. The whole assembly is then kept at 1200 $^{\circ}\text{C}$ for 10 h. Assess what happens with the Ni concentration.

Results of the Simulation

First the result is shown and then how to do the calculation. As can be seen the Ni foil has started to dissolve in the steel already after 1 h. The calculation is quite simple and is shown next.

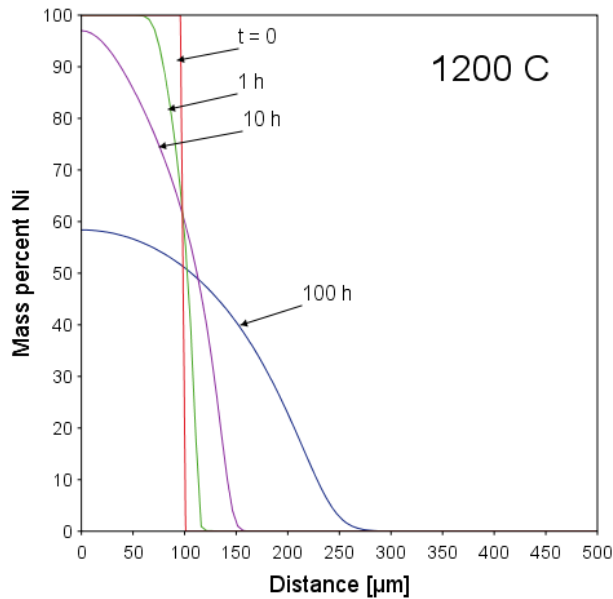


Figure 3-3: Calculated Ni concentration profiles after different times at 1200 °C. Initially there is a 100 μm thick foil of pure Ni on the left hand side.

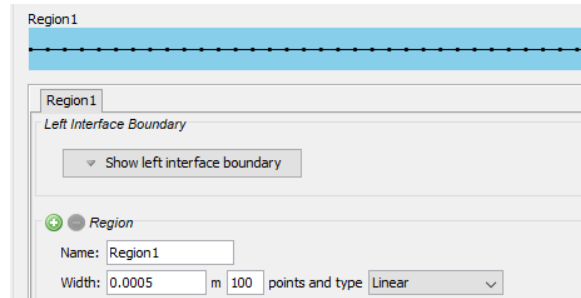


Below is information about how to recreate this example. The instructions build on the previous example described in "[Graphical Mode - Diffusion Through a Tube Wall](#)" on page 34.

3.3.1 Simulating Diffusion in a Joint Between Dissimilar Materials

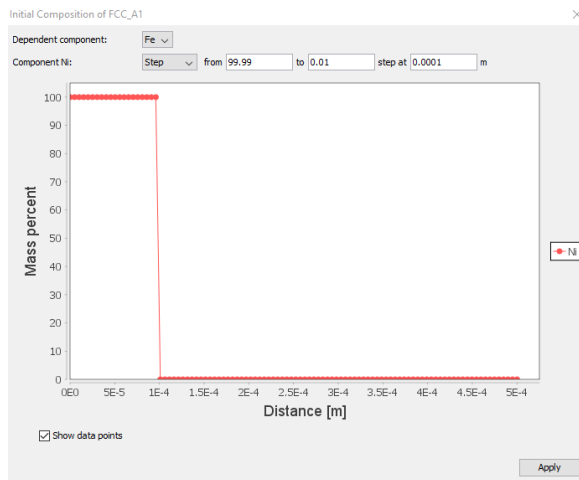
1. Add a **Diffusion Simulation** template.
2. For the System Definer add the **Demo: Steels and Fe-alloys (FEDEMO, MFEDEMO)** databases and select the elements **Fe** and **Ni**.
3. Define `Region 1` for the **Diffusion Calculator**. You can rename the region if you want:
 - a. *Width*: 0.0005 m
 - b. 100 *points*

c. **Linear grid type**

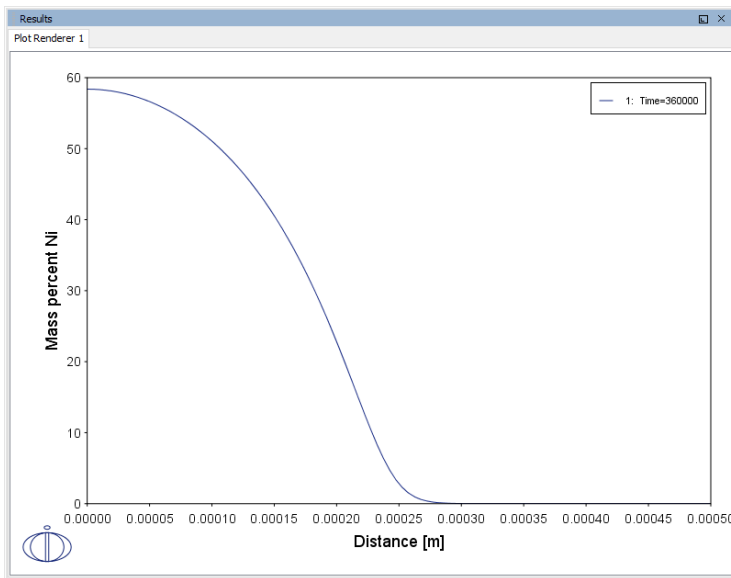


d. **Phase: FCC_A1**

- e. **Composition profiles:** Click **Edit** then keep the default, **Fe**, as the **Dependent component** and choose **Step** for the composition of **Component Ni**. In the fields, enter from 99.99 to 0.01 mass% with a step at 0.0001 m (0.1 mm). Click **Apply**.

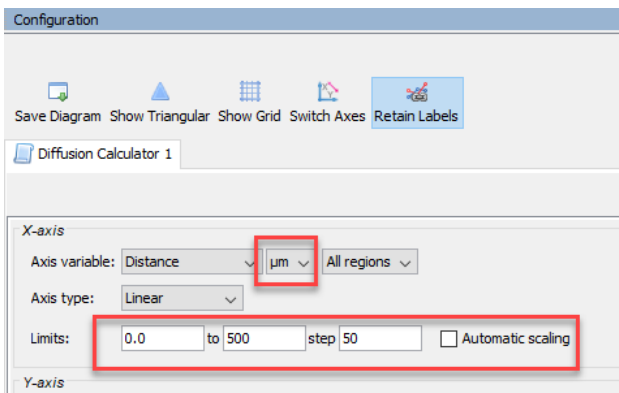


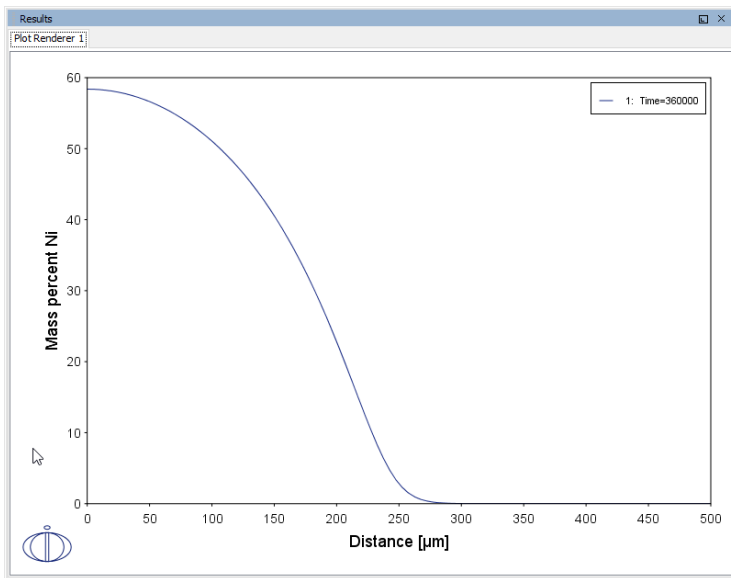
- f. Under **Thermal Profile**, choose **Celsius** as the **Temperature** scale and enter 1200 in the field. Choose **Hours** for the **Simulation time** and enter 100.
4. Click **Perform Tree** and the calculation starts. Click to open the **Event Log** window to watch the calculation perform. A concentration profile displays in the **Results** window.



Now you will adjust and experiment with the plot parameters on the **Configuration** window for the **Plot Renderer**.

- The default axes have the **Distance** in **m** and the Ni content. Change the Distance to **μm** and click to clear the **Automatic scaling** check box. Enter the *Limits* 0.0 to 500 with step 50. Click **Perform** and observe the change to the plot.





You can also change the size of the plot window. Right-click in the plot and choose **Properties**. In the **Plot Properties** window that opens, click **Define the plot area size** and use the suggested values.

Plot Area Size

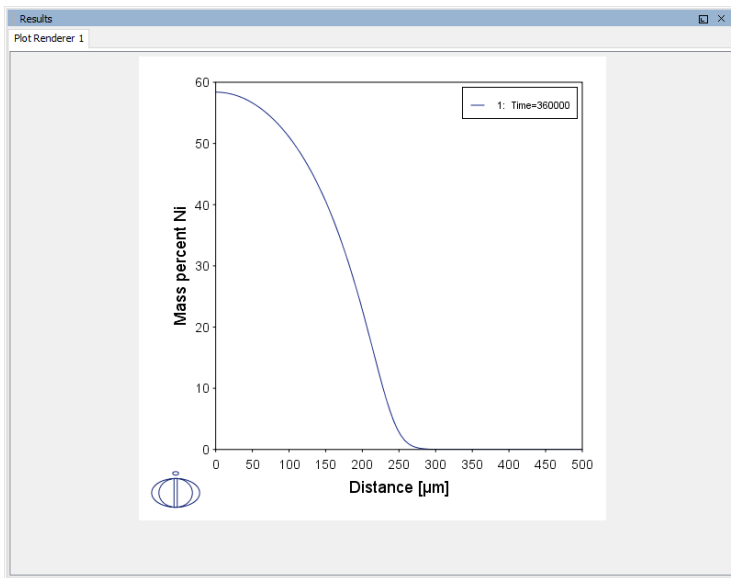
Fit the plot area size to the enclosing window

Define the plot area size

Plot area height:

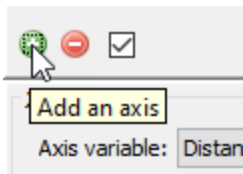
Plot area width (not applicable to triangular plots):

Click **OK** and the plot window has a different format as shown below.

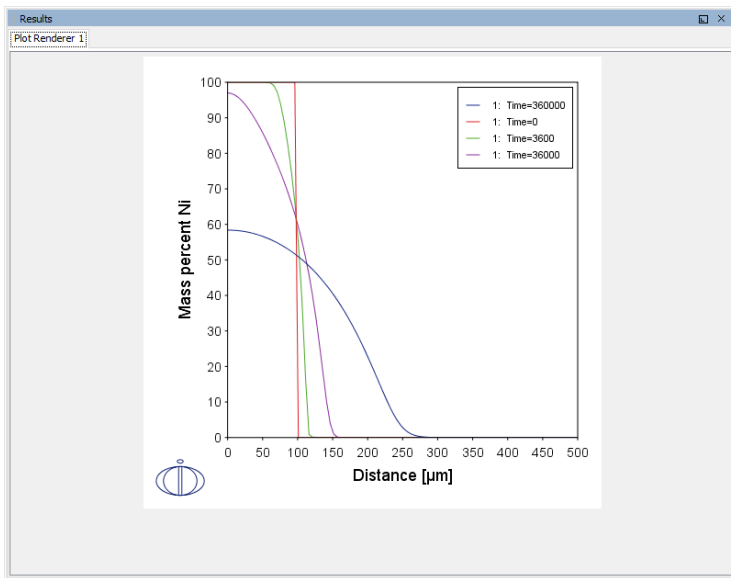


Next we will recreate the plot in [Figure 3-3](#).

6. Go to the Plot Renderer **Configuration** window. Click the green plus button to **Add an axis**.



7. You can now add another time to be plotted in the same diagram. Click the button twice more and add 0, 1 and 10 hours and click **Perform**. You can also add labels to mark the time. To do this, right-click in the plot and choose **Add Label**.



3.4 Example: Darken's Experiment



This example requires a license for the TCFE and MOBFE databases. If you do not have these databases, you can still follow along but you will not be able to perform the simulation.

In a famous experiment Darken welded together two steels of similar carbon contents but different Si content, see the table below. The joint was then heat treated for some time at 1050 °C (1323 K).



Task: Predict how the composition of the weld develops in time.

Table 3-1: Composition of steels in Darkens experiment

Steel	Mass% C	Mass% Si
Si-rich	0.49	3.80
Si-poor	0.45	0.05



The following example builds on some basic concepts used in the "Example: Diffusion in a Joint Between Dissimilar Materials" on page 45. See that example for more information as required.

Define the System

1. Open Thermo-Calc in Graphical Mode.
2. On the **Configuration** window under Templates, click **Diffusion Simulation**.
3. On the System Definer **Configuration** window click to select the elements **Fe, Si** and **C**.
4. Under **Package** in the upper right of the Configuration window, select **Steels and Fe-alloys (TCFE9, MOBFE4)**. The version of the databases available depends on your license.

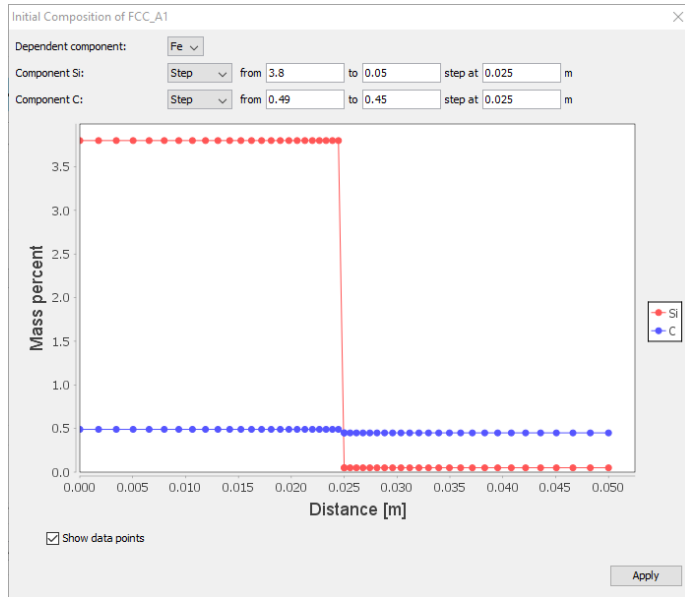
Define the Diffusion Parameters and Plot

1. In the **Project** window, click the **Diffusion Calculator**.
2. Under **Region** in the **Width** field, enter 0.05 m. Then enter 100 points and choose a **Double geometric** grid type. Enter a **Lower ratio** of **0.95** and an **Upper ratio** of **1.05**. This means that the grid will be denser in the middle where there is the step in composition. You will immediately see the distribution of grid points as partially shown below.



3. Choose **FCC_A1** as the **Phase** and then click **Edit**.
4. Keep the default, **Fe**, as the **Dependent component** and choose **Step** for both of the composition profiles of **Component Si** and **Component C**.
 - a. For Si, enter from **3.8** to **0.05** with a step of **0.025**.
 - b. For C, enter from **0.49** to **0.45** with a step of **0.025**.

The **Initial Composition** profile should now look like this:



5. Click **Apply**.
6. Enter a **Temperature** of **1323** Kelvin and choose **Days** for the **Simulation time** and enter **13** in the field.
7. Click **Perform Tree**. Click to open the **Event Log** window to watch the calculation perform. A concentration profile displays in the **Results** window.

Adjust the Plot Parameters

1. In the **Project** window, click the **Plot Renderer** to open its **Configuration** window.
2. For the X-axis, keep the default **Distance** as **m**.
3. For the Y-axis, choose **All** for the **Composition** .
4. Click to clear the **Automatic scaling** check box and enter **Limits 0** to **4** with step **0.25**.

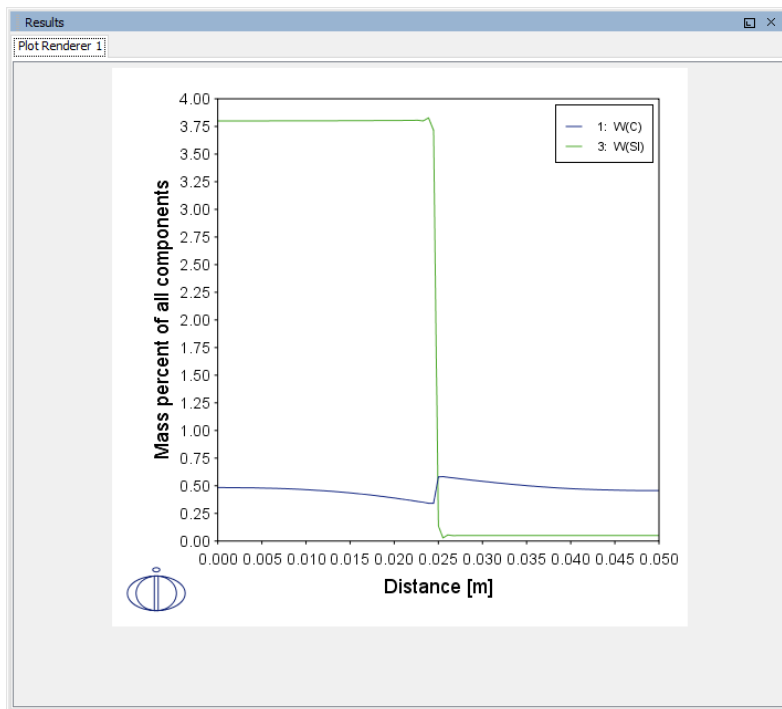
Click **Perform**.

X-axis
Axis variable: Distance m All regions
Axis type: Linear
Limits: 0.0 to 1.0 step 0.1 Automatic scaling

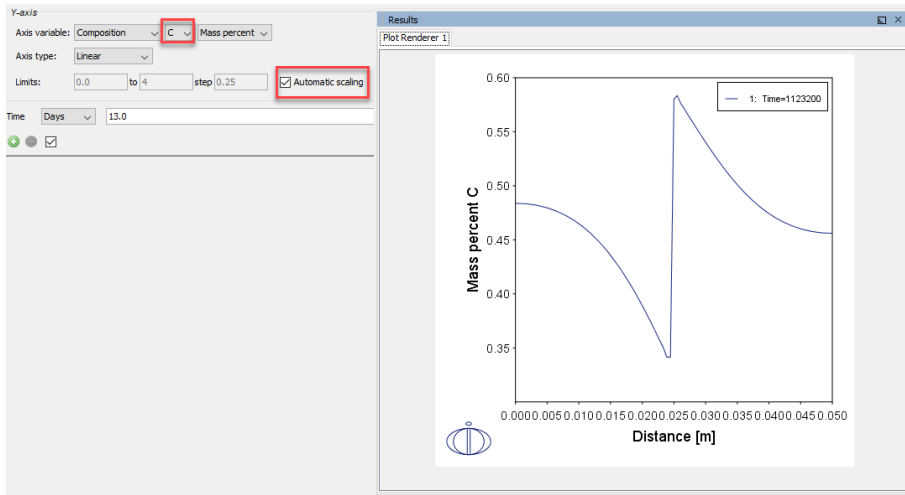
Y-axis
Axis variable: Composition All Mass percent
Axis type: Linear
Limits: 0.0 to 4 step 0.25 Automatic scaling

Time Days 13.0

You can also change the size of the plot window. Right-click in the plot and choose **Properties**. In the Plot Properties window that opens, click **Define plot area size** and use the suggested values. Click **OK** and the plot window has a different format as shown below.



If we choose to plot the Carbon content only and rescale the Y-axis on the Plot Renderer then click **Perform**, you will get a plot like the one below.



3.5 Example: Carbon Diffusion in a Ni-Plated Steel

We now revisit the example described in "Stationary Diffusion Through a Tube Wall " on page 31. This example is solved using the so-called homogenization method to improve numerical stability.



Remark on internal oxidation: Simulations based on the homogenization method are time consuming in such cases where the contents of the diffusing elements are low in the matrix phase. Unfortunately, this is the case particularly for internal oxidation which is of large practical importance. Nevertheless, the calculations are stable and the results will eventually be found even for complex cases.



Task: In order to avoid the problems caused by the carbon-rich gas flowing in a tube at 500 °C, we would like to protect the steel with a thin layer of pure Ni. We hope that the Ni-layer acts as a diffusion barrier for C. This is expected from the fact that the carbon solubility is at least one order of magnitude lower in Ni than in Fe, see Figure 3-4 calculated with Thermo-Calc. Predict how the Ni-plating affects the carbon diffusion through the tube wall.

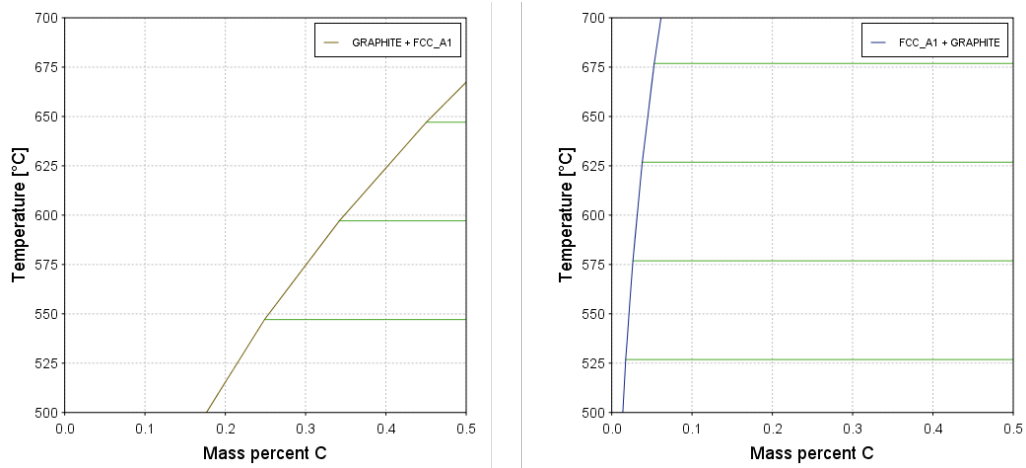


Figure 3-4: Calculated C content in a) Fe and b) in Ni at a carbon activity of unity relative graphite.



Have a look at the example "Example: Darken's Experiment " on page 51. This classic example demonstrates that an inhomogeneous distribution of alloy elements has a strong effect on the quite rapid carbon diffusion.

We may thus repeat the calculation performed earlier with only Fe and C and now add the 0.1 mm Ni layer with a very low carbon content at the side of the high carbon activity.

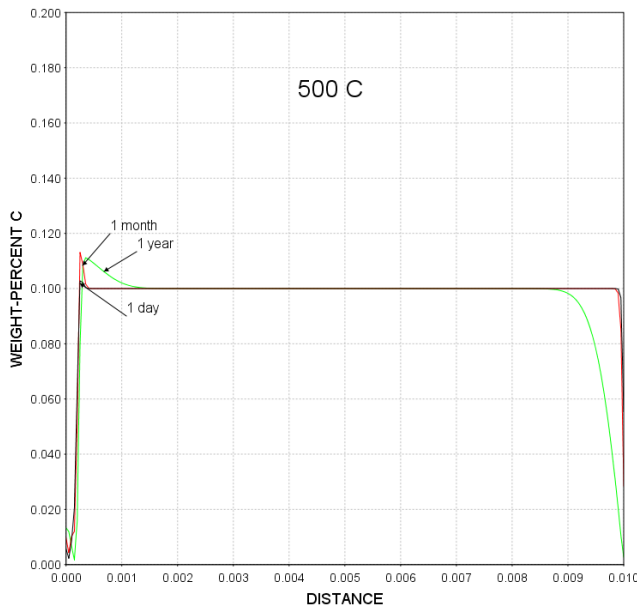


Figure 3-5: Calculated carbon concentration as function of distance (m) from inner tube wall at different times as indicated. Inner tube wall coated by 0.2 mm Ni layer.

The diagram is plotted with the same scaling as shown in the first part of this example (see [Figure 3-1](#)) and we see that the Ni-coating has a strong effect on the C diffusion as expected. However, we also note that even though the C content is very low in the Ni-layer it starts to increase in the steel layer after some time. In fact, it looks almost as if the C content in the steel close to the Ni plate is almost the same as without the coating. It thus seems as the coating is the most effective in the early stage but loses its efficiency later. This seems to be a rather general conclusion. The diffusion coefficient for carbon is very similar in Fe and Ni and we can use Einstein's formula ($t = \ell^2 / 2D_k$) to estimate after how long time the effect of the Ni coating becomes less important. We insert 0.2 mm as the distance and obtain

$$t = (10^{-4})^2 / 2 * 2 \cdot 10^{-15} = 2.5 \cdot 10^6 \text{ s} \cong 29 \text{ days}$$

The conclusion is that the Ni barrier loses its efficiency within four months. This is in good agreement with the simulation. A simulation for 10 years is added in [Figure 3-6](#).

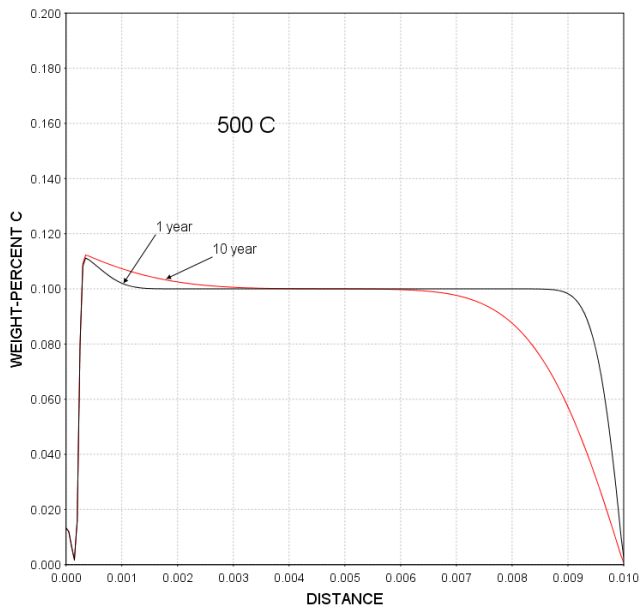


Figure 3-6: Calculated carbon concentration as function of distance (m) from inner tube wall at different times as indicated. Inner tube wall coated by 0.2 mm Ni layer.

3.5.1 Simulating Carbon Diffusion in a Ni-Plated Steel

These instructions build on the previous examples, in particular the first in this series described in "Graphical Mode - Diffusion Through a Tube Wall " on page 34.

1. Add a **Diffusion Simulation** template. Add the **Demo: Steels and Fe-alloys (FEDEMO, MFEDEMO)** databases for an Fe-0.01Ni-0.01C alloy.
2. Click the **Components** tab. For the C component, click to clear the **SER** check box and choose **GRAPHITE** as the reference phase.
3. Add the settings to the Diffusion Calculator as follows. Add a **Linear** grid region named **Couple** with 0.01 m width and 200 points for the **FCC_A1** phase.
4. Define the initial composition of the FCC_A1 phase. For the Ni component, add a step from 99.99 to 1.0E-5 step at 2.0E-4 m. For the C component, add a step from 0.001 to 0.1 with a step at 2.0E-4 m. Click **Apply**.

Initial Composition of FCC_A1

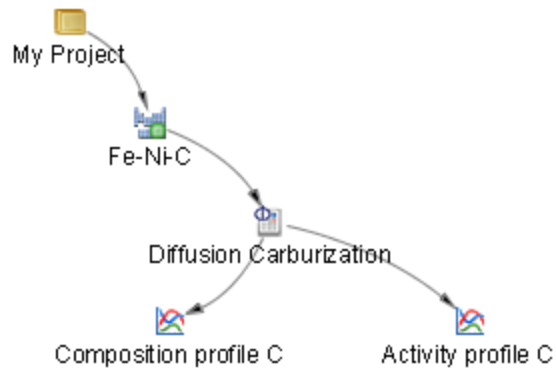
Dependent component:	Fe							
Component Ni:	Step	from	99.99	to	1.0E-5	step at	2.0E-4	m
Component C:	Step	from	0.001	to	0.1	step at	2.0E-4	m

5. Define the left and right boundary conditions and the thermal profile.
 - a. *Left Boundary Condition*: **Mixed zero flux and activity**, **Zero flux** for Ni , and for C an **Activity** of 1.0.
 - b. *Right Boundary Condition*: **Mixed zero flux and activity**, **Zero flux** for Ni , and for C an **Activity** of 1.0E-5.
 - c. *Thermal Profile*: 500 **Celsius** and a time of 36500 **days** (10 years).

Left Boundary Condition		Right Boundary Condition	
Mixed zero flux and activity	Ni Zero flux	Mixed zero flux and activity	Ni Zero flux
<small>Tip: The reference state is defined in the System Definer</small>	C Activity 1.0	<small>Tip: The reference state is defined in the System Definer</small>	C Activity 1.0E-5
Thermal Profile			
<input checked="" type="radio"/> Isothermal <input type="radio"/> Non-isothermal			
Temperature:	500.0	Celsius	
Simulation time:	36500.0	Days	

Now you will define the homogenization method to improve numerical stability. For details about these options, press F1 and search the help.

6. Click the **Options** tab and choose **Homogenization** as the *Default solver*. Then choose **Euler backwards** as the *Time integration method*.
7. Next you will plot the carbon activity and composition profiles. First, add a second **Plot Renderer** to the Project tree (*hint*: right-click the Diffusion Calculator). If you want you can also right-click the nodes in the tree and rename the System Definer, Diffusion Calculator and Plot Renderer nodes.



- For the **Activity profile C** plot, click **Switch to advanced mode**. Then for the *Y-axis*, choose *Axis variable* **Activity of component** for **C**.

Y-axis

Axis variable: Activity of component SER C

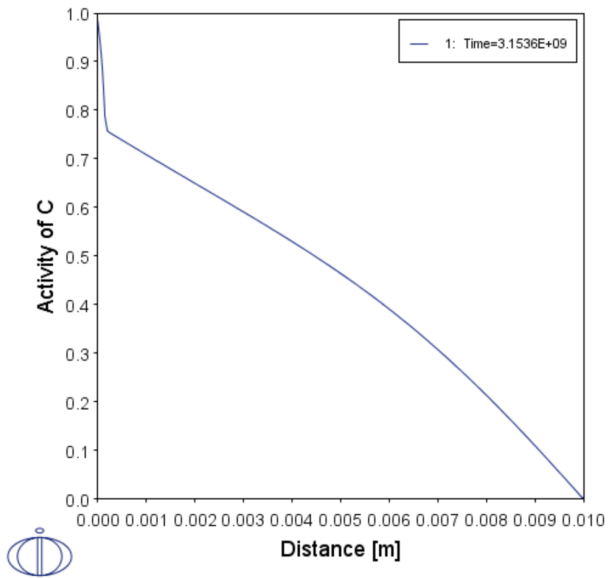
Axis type: Linear

Limits: 0.0 to 1.0 step 0.1 Automatic scaling

Plot condition: Time Days 36500.0

Independent variable: Distance Global

- Click **Perform** and compare to the plot below.



10. For the **Composition profile C** plot, add two axes. Then keep the defaults except as follows.

- For all *X-axis* **Distance** variables, change **m** to **μm**.
- For the first *Y-axis*, set the limits between 0.0 and 0.2 with a step of 0.05.
- For the second *Y-axis*, click to clear the **Automatic scaling** check box and then keep the defaults. Edit the *Time* to be 365 **Days**.
- For the third *Y-axis*, click to clear the **Automatic scaling** check box and then keep the defaults. Edit the *Time* to be 30 **Days**.

Diffusion Carburization

X-axis

Axis variable: Distance μm All regions

Axis type: Linear

Limits: 0.0 to 1.0 step 0.1 Automatic scaling

Y-axis

Axis variable: Composition C Mass percent

Axis type: Linear

Limits: 0.0 to 0.2 step 0.05 Automatic scaling

Time Days 36500.0

X-axis

Axis variable: Distance μm All regions

Axis type: Linear

Limits: 0.0 to 1.0 step 0.1 Automatic scaling

Y-axis

Axis variable: Composition C Mass percent

Axis type: Linear

Limits: 0.0 to 100.0 step 10.0 Automatic scaling

Time Days 365.0

X-axis

Axis variable: Distance μm All regions

Axis type: Linear

Limits: 0.0 to 1.0 step 0.1 Automatic scaling

Y-axis

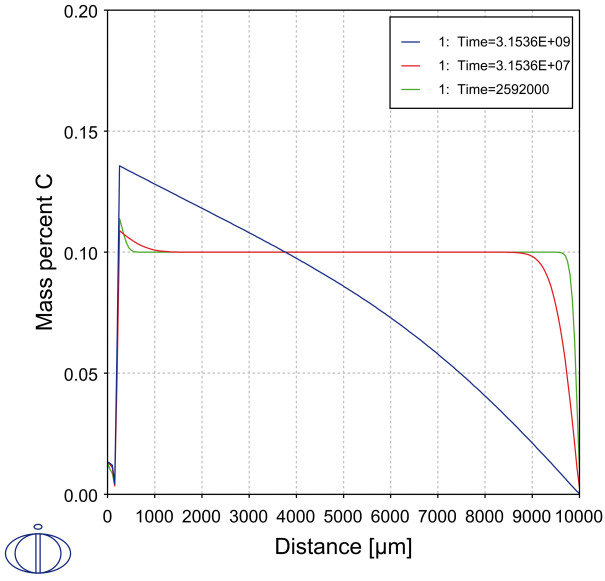
Axis variable: Composition C Mass percent

Axis type: Linear

Limits: 0.0 to 100.0 step 10.0 Automatic scaling

Time Days 30.0

11. Click **Show Grid** to include the grid on the plot. Click **Perform** and compare to the plot below.



4 Two-Phase Diffusion Problems in Binary Alloys

4.1 Diffusion Controlled Growth or Shrinkage of Phases

Consider an assembly made by joining two materials having different composition as well as different phases, say bcc and fcc. If the assembly is in equilibrium nothing will happen despite the difference in composition. If the composition on each side is not in equilibrium there will be a reaction. One phase will grow on behalf of the other phase.

4.1.1 Local Equilibrium Approximation

A common and very useful approximation is to consider the two phases on each side of a phase interface as being locally in thermodynamic equilibrium. In a binary system this means that the composition on each side of the phase interface can be read from the binary phase diagram for the temperature under consideration. This is illustrated in the figure below where a schematic concentration profile is plotted on the left side and a part of the binary phase diagram with concentration axis vertically on the right side. As can be seen this construction results in concentration differences in each phase close to the interface. Such concentration differences cause diffusion in each phase.

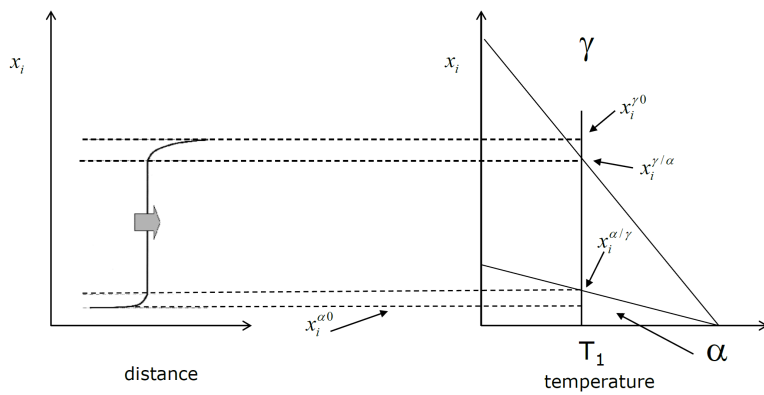


Figure 4-1: Local equilibrium approximation to establish the compositions on each side of the α (bcc) / γ (fcc) in a diffusion couple between two parts having initial composition $x_i^{\alpha 0}$ and $x_i^{\gamma 0}$.

4.1.2 The Flux Balance Equations

If the fluxes balance, i.e. if the amount of i that leaves one phase is exactly the same as the amount that enters the other phase the interface does not move. However, in general they will differ and the interface moves. The rate of migration v is calculated from the flux balance for element i

$$\text{Eq. 4-1} \quad \frac{v}{V_m} (x_i^\gamma - x_i^\alpha) = J_i^\gamma - J_i^\alpha$$

For simplicity the molar volume is approximated as constant and the same in both phases. All quantities in the equation are evaluated close to the migrating phase interface. The assumption of local equilibrium allows us to read the content in γ and α on the left side directly from the binary phase diagram for the temperature under consideration. By solving the diffusion problem in each phase and calculate the fluxes on each side of the interface its migration rate may be calculated.

From the general form of the equation a number of conclusions about the migration direction may be drawn by looking at the shape of the concentration profiles without making any calculations. Some of these are shown in the figure below. As can be seen a conclusion can be drawn directly when there is no diffusion in one the phases. We also find from [Eq. 4-1](#)

that if diffusion is in opposite directions in the two phases a conclusion may be drawn without the need of calculation. Only when diffusion occurs in the same direction in both phases we need to do a detailed calculation to see how the fluxes balance and in what direction the interface will move.

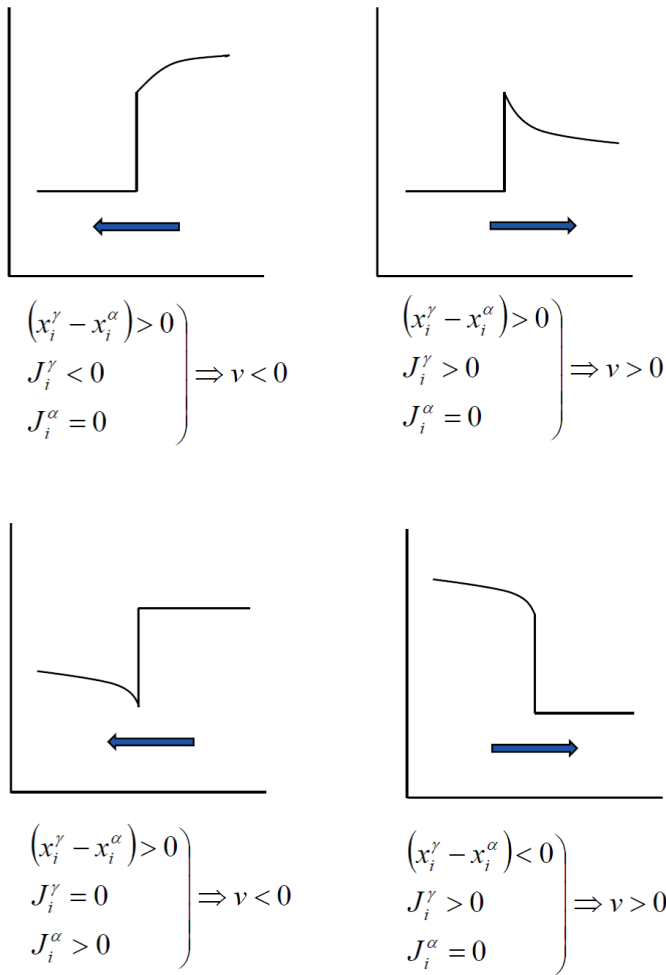


Figure 4-2: Direct prediction of migration direction from shape of concentration profiles without need of calculation.

4.1.3 Advanced: Diffusion Controlled Growth or Shrinkage

Number of Atoms Crossing a Moving Phase Interface and the Volume Change

In this section we shall discuss in more detail the conditions at a moving phase interface between α and β , see Figure 4-3. When the two phases have different compositions, the phase transformation must be accompanied by some diffusion in either one or both of the two phases. Suppose that the β phase grows a distance dz^β and the α phase shrinks a distance dz^α , as indicated in the figure. The increments are defined consistently positive in the positive direction of the z-axis and thus dz^α is positive when it is on the right-hand side of the

interface despite the fact that it shrinks when β grows. Also the fluxes are defined consistently as positive in the positive direction of the z-axis.

We may set up local mass balance of a small element containing the migrating interface as follows: A is the area of the interface and dt the time increment. It is instructive to consider the two phases separately and keep in mind that what leaves one phase must enter the other.

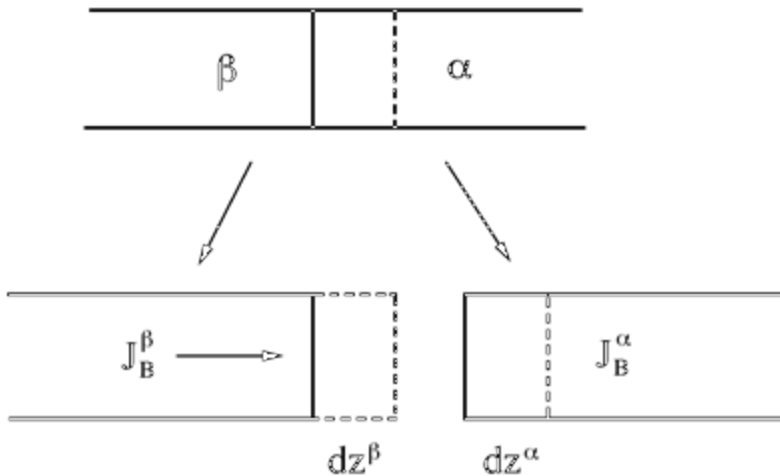


Figure 4-3: Upper part: schematic representation of the growth of β phase and shrinkage of α . Solid line indicates the initial position of the interface and the dashed line position after interface migration. Lower part: The two phases are treated separately.

Number of moles of B leaving the β side of the element and crossing the interface:

$$\text{ADV Eq. 4-1} \quad J_B^\beta A dt - dz^\beta A \frac{x_B^\beta}{V_m^\beta}$$

Number of moles of B added to the α side of the element:

$$\text{ADV Eq. 4-2} \quad J_B^\alpha A dt - dz^\alpha A \frac{x_B^\alpha}{V_m^\alpha}$$

It is thus possible to write the number of B atoms crossing the interface \hat{J}_B in two different ways. Nevertheless the two numbers must be identical in order for the total amount of B to be conserved. Introducing $v^\alpha = dz^\alpha/dt$ and $v^\beta = dz^\beta/dt$ we write

$$\text{ADV Eq. 4-3} \quad \hat{J}_B = J_B^\beta - \frac{v^\beta}{V_m^\beta} x_B^\beta = J_B^\alpha - \frac{v^\alpha}{V_m^\alpha} x_B^\alpha$$

Similar equations may be set up for all component i regardless of the number of components. We thus find in general

$$\text{ADV Eq. 4-4} \quad \frac{v^\alpha}{V_m^\alpha} x_i^\alpha - \frac{v^\beta}{V_m^\beta} x_i^\beta = J_i^\alpha - J_i^\beta$$

It must be emphasized that for full consistency the fluxes and the displacement of the interface must be expressed in the same local frame of reference in each phase. However, in principle different types of frame of reference may be used in the different phases although it may often be less convenient.

In a system with N components summation of [ADV Eq. 4-4](#) for all elements yields

$$\text{ADV Eq. 4-5} \quad \frac{v^\alpha}{V_m^\alpha} - \frac{v^\beta}{V_m^\beta} = \sum_{i=1}^N J_i^\alpha - \sum_{i=1}^N J_i^\beta$$

Suppose we want to express the fluxes in each phase using the number fixed frame of reference, then the right-hand side vanishes and we obtain

$$\text{ADV Eq. 4-6} \quad \frac{v^\alpha}{V_m^\alpha} = \frac{v^\beta}{V_m^\beta}$$

We may now eliminate v^α and may rewrite the balance equation for component i as

$$\text{ADV Eq. 4-7} \quad \frac{v^\beta}{V_m^\beta} (x_i^\alpha - x_i^\beta) = J_i^\alpha - J_i^\beta$$

Which is the same as $\frac{v}{V_m} (x_i^\gamma - x_i^\alpha) = J_i^\gamma - J_i^\alpha$ because it was assumed that the molar volume is the same in both phases. It should be noticed, as already mentioned, that the migration rates v^α and v^β also must be expressed in the number fixed frame of reference.

In a system with N components we have only $N - 1$ independent equations of type [ADV Eq. 4-7](#) because summation over all just gives $0 = 0$.

The volume change accompanied by the transformation is $dV/dt = A(v^\beta - v^\alpha)$ and using [ADV Eq. 4-6](#) one obtains

$$\text{ADV Eq. 4-8} \quad \frac{dV}{dt} = A v^\beta \left(1 - \frac{V_m^\alpha}{V_m^\beta} \right)$$

If both phases have the same molar volume there is no volume change but if the growing β has a larger volume than there will be a volume increase.

4.1.4 Precipitation and Dissolution of Particles

The method discussed in the previous sections also applies to the precipitation or dissolution of particles in a matrix phase. However, for precipitation we have not yet discussed nucleation of a new particle. In many cases nucleation is very important but there are also cases of practical importance where it can be treated in a very simple way. We shall thus first discuss the growth of a particle when it has been already nucleated. Consider a binary alloy Fe-C which has been kept at a high temperature T_0 for such a long time that it consists of homogeneous γ with composition $x_C^{\gamma_0}$, see part of the phase diagram in [Figure 4-4](#). When the alloy is cooled to the temperature T_1 in the $\alpha + \gamma$ two-phase field there will be a tendency to form α . Suppose α has been nucleated and now grows. We can use the local equilibrium assumption and sketch a concentration profile as we did for the diffusion couple, see [Figure 4-1](#), but the profile will be different, see [Figure 4-5](#).

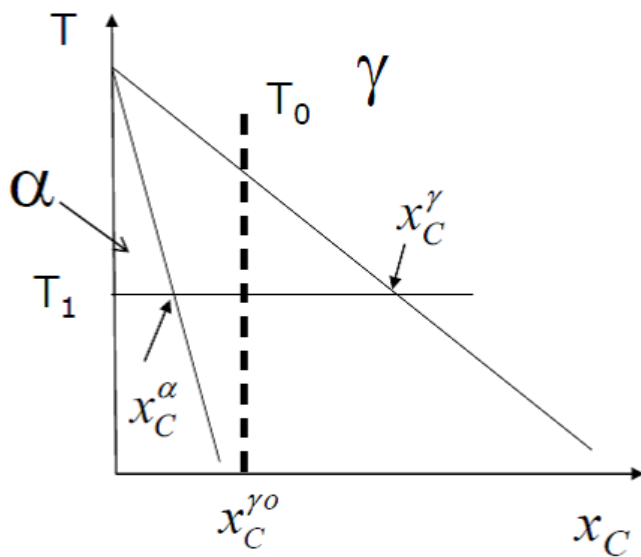


Figure 4-4: Part of the Fe-C phase diagram (schematic) showing the fcc (γ) and bcc (α) phases.

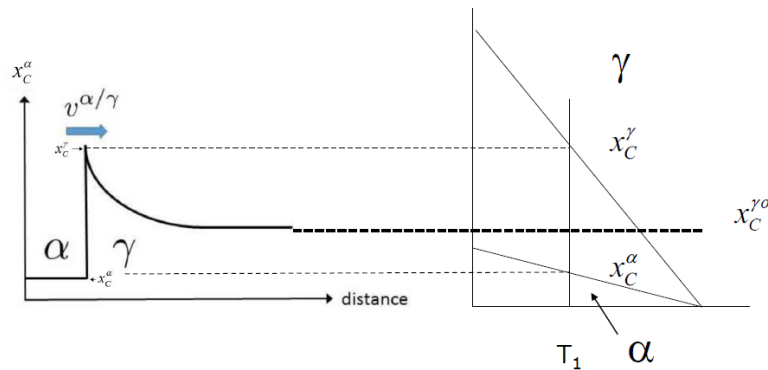


Figure 4-5: Local equilibrium approximation to establish the compositions on each side of α/γ interface during formation of α from supersaturated γ with composition $x_C^{\gamma 0}$.

We can see from the concentration profile that C will diffuse away from the C-poor α phase into γ . In this case the concentration in α is constant and thus there will be no diffusion in α . From the upper right in Figure 4-2 we conclude that α will grow. The growth rate is calculated from the flux-balance equation, i.e. $\frac{v}{V_m} (x_i^\gamma - x_i^\alpha) = J_i^\gamma - J_i^\alpha$.

The same reasoning holds also for dissolution of an α particle. Suppose that the alloy has been kept at T_1 for such a long time that we have reached equilibrium and the composition also in γ is constant. Remember that if we know the size of the system we can roughly

estimate the time needed to reach equilibrium from the Einstein formula $t = \ell^2 / 2D_k$. If temperature is now increased the composition on each side of the interface will change in accordance with the phase diagram and there will be gradients in both phases resulting in diffusion. It is left to the reader to sketch a reasonable concentration profile for this case. It is then seen that the fluxes go in opposite direction and result in shrinkage of α .

4.2 Example: Fe/Fe-10mass% Ni Diffusion Couple at 850 °C



Task: A 100 μm Fe foil is joined with a foil having the same thickness but consisting of an Fe-10mass%Ni. The joint is kept at 850 °C for a long time. The appropriate part of the Fe-Ni phase diagram is shown in the figure below and it is seen that Fe is bcc whereas the alloy with 10 mass% Ni is fcc at this temperature. Predict how the amount of fcc and bcc and the Ni-concentration profile evolves with time at 850 °C.

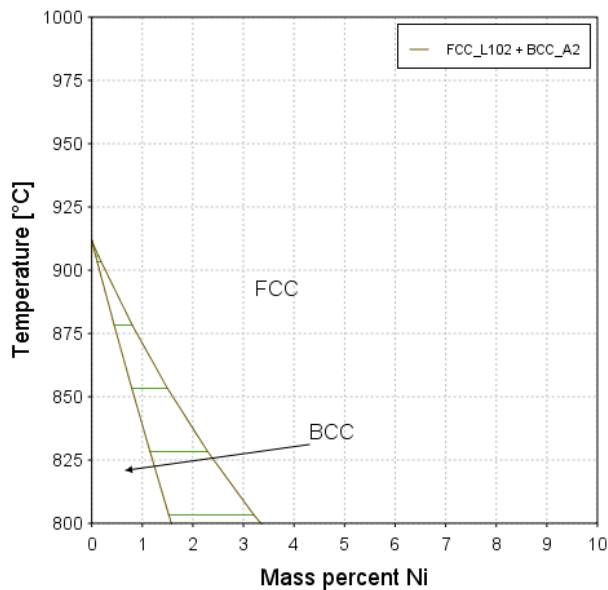


Figure 4-6: The appropriate part of the calculated Fe-Ni phase diagram.

From the phase diagram in the figure, it is seen that the equilibrium state should be one-phase fcc with 5 mass% Ni because the two foils have the same thickness. The bcc phase will thus be consumed during the equilibration. Nevertheless, we observe further that the concentration profile is of the type on the left part of [Figure 4-1](#) . It is thus clear that even if we know that the final state must be fcc we cannot say, without a calculation, how the reaction will proceed because Ni diffusion occurs in the same negative direction in both phases.

As diffusion is much faster in bcc than fcc we may conclude that the Ni-flux in bcc would dominate in the early stage when there is still a strong concentration gradient in bcc.

From [Eq. 4-1](#) ($\frac{v}{V_m}(x_i^\gamma - x_i^\alpha) = J_i^\gamma - J_i^\alpha$) we thus conclude that the interface will move to the right, i.e. the bcc phase will grow. This growth will continue until the concentration profile in bcc is leveled out and diffusion in fcc becomes important. When that has happened we conclude that the reaction will be reversed and the interface will move to the left, i.e. fcc will grow.

This behavior is now studied in a simulation using the Graphical Mode interface.



There are no step-by-step instructions included. Only the results are shown.

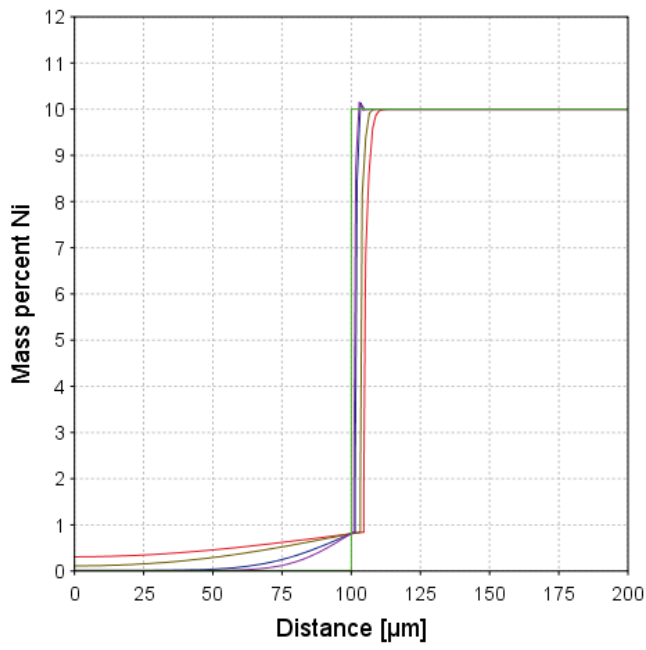


Figure 4-7: Calculated Ni concentration profiles at 850 °C after 0, 1, 2, 10 and 20 days. As can be seen the fcc phase shrinks.

The Ni-concentration profiles for the first 20 days are shown in [Figure 4-7](#) and confirm the expected growth of bcc. This is also shown in [Figure 4-8](#) showing the volume fraction of fcc as a function of time during the first 50 days.

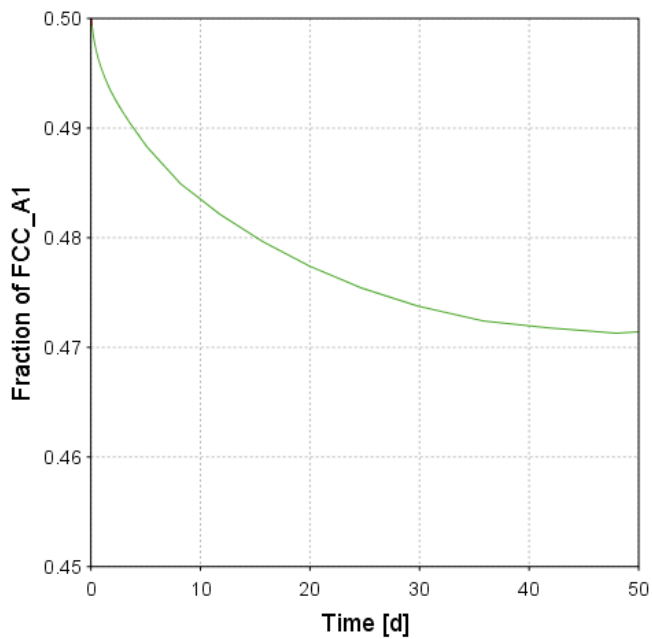


Figure 4-8: Calculated volume fraction of fcc during the first 50 days.

From Figure 4-8 it seems as there is a minimum in fcc fraction after around 50 days, i.e. when the concentration difference in the bcc phase has leveled out. Again we can use the Einstein formula in the form of $t = \ell^2 / 2D_k$ to estimate how long time it will take to achieve a homogeneous Ni content in bcc. At this temperature the diffusion coefficient of Ni in bcc is approximately $1.6 \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1}$ and the Einstein equation yields

$$t = (100 \cdot 10^{-6})^2 / 2 * 1.6 \cdot 10^{-15} = 3.125 \cdot 10^6 \text{ s} \cong 40 \text{ days}$$

in reasonable agreement with Figure 4-8.

The diffusion coefficient for Ni in fcc is approximately $1.6 \cdot 10^{-18} \text{ m}^2 \text{ s}^{-1}$ and the time estimated to achieve also equilibrium in fcc, i.e. full equilibrium, should be roughly 1000 times longer, i.e. $t \cong 40 \cdot 1000 \text{ days} \cong 110 \text{ years}$.

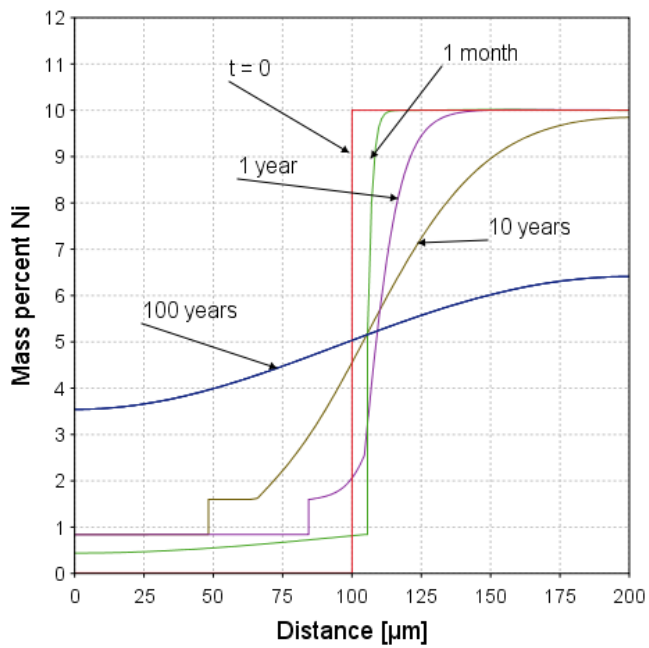


Figure 4-9: Calculated Ni concentration profile at various times as indicated.

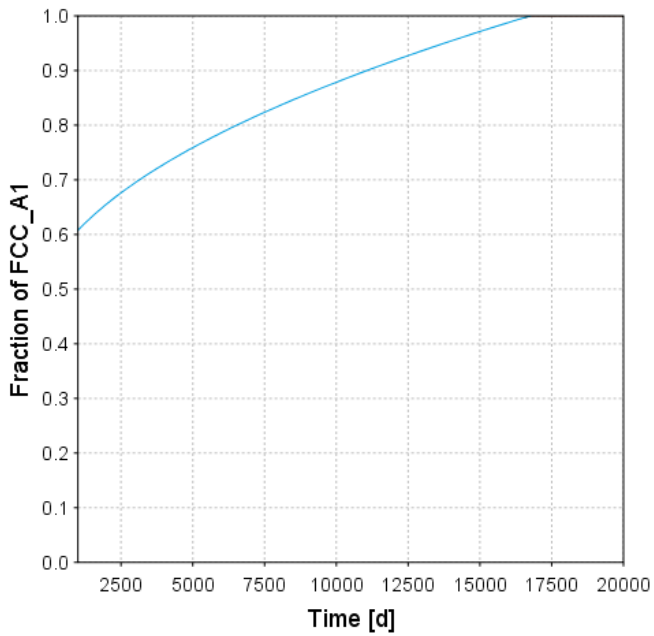


Figure 4-10: Calculated volume fraction of fcc during the later stages. The bcc is fully dissolved after 50 years.

The detailed calculations using the Diffusion Module (DICTRA) are in reasonable agreement with the simple estimates based on the Einstein formula but in addition they also give much more detailed information. The concentration profiles in [Figure 4-9](#) clearly reveals the jump in composition corresponding to the difference $x_{Ni}^{\gamma} - x_{Ni}^{\alpha}$. It should also be noted that even when the bcc has fully dissolved there is a concentration variation in fcc and full equilibrium is not established.

4.3 Example: Ferrite Formation and Dissolution in an Fe-0.2C Alloy

4.3.1 Isothermal Reaction

Consider a binary Fe-0.2 mass% C steel. First we will look at the formation of ferrite at 800 °C after austenitizing at 850 °C. As can be seen from the appropriate part of the phase diagram in [Figure 4-11](#), the alloy is in the one-phase fcc state at the higher temperature if equilibrium is established. In the next part of this exercise we will study the austenite formation from an initial normalized structure of ferrite and pearlite.

At the lower temperature equilibrium is a mixture of bcc and fcc, i.e. bcc should form when we cool to this temperature. According to the lever rule it should be a little bit less ferrite than austenite at equilibrium. Assume that ferrite forms along the austenite grain boundaries and that austenite grain size as 20 μm , which is a typical value. For simplicity you may approximate the system with a planar geometry and for symmetry reasons only consider only half the system, i.e. a size of 10 μm .



Task: Predict the ferrite formation during isothermal holding at 800 °C.

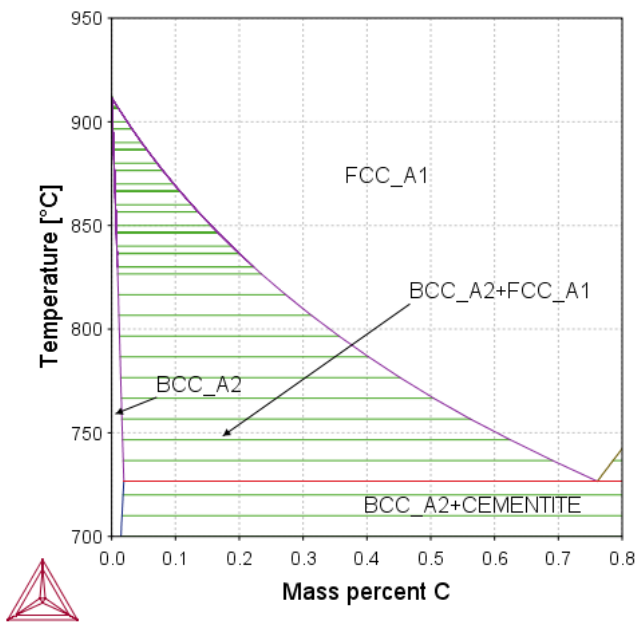


Figure 4-11: Calculated part of Fe-C phase diagram. The arrow marks the alloy under consideration.



The list of settings build on the examples starting in " [One-Phase Diffusion Problems](#)" on page 30.

System Definer Settings

- FEDEMO and MFEDEMO databases
- Fe-0.1 mass% C steel

Diffusion Calculator Settings

- Region named austenite of width 10 μm with fcc_A1 having a composition profile of constant C content of 0.2 mass%.
- Click on show left interface boundary and allow phase to form BCC_A2.
- Make an isothermal simulation at 800 °C for 120 seconds. This means that the temperature drops instantly from 850°C to 800 °C, which of course is unrealistic. In the next part of this example, the assumption will be refined.
- Set the integration method to Euler backwards.

Plot Renderer 1 Settings

- Add a node to plot the concentration at different times.
- For the x-axis choose distance in μm , linear axis type, automatic scaling
- For the y-axis choose composition C in mass percent, linear automatic scaling
- Enter a time to plot and then click the plus sign four times to add axes and times to plot the same plot at different times

The resulting concentration profiles at different times are plotted and shown below.

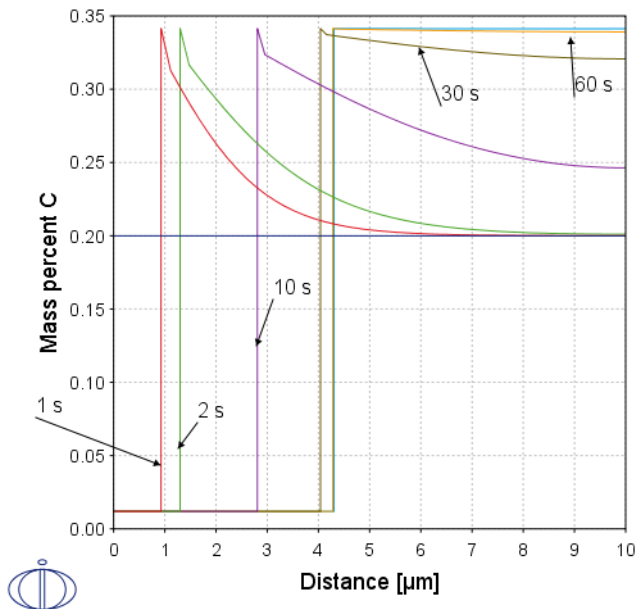


Figure 4-12: Calculated C concentration profiles at 800 °C for various times as indicated.

As can be seen already after 1 minute the concentration profiles in each phase level out and full equilibrium is established with a little bit less than 50 % bcc.

Plot Renderer 2 Settings

Next plot the bcc volume fraction as a function of time.

- Add a second Plot Renderer node.
- For the x-axis choose time in seconds, linear axis type, automatic scaling
- For the y-axis choose total phase fraction by volume for BCC_A2, linear automatic scaling

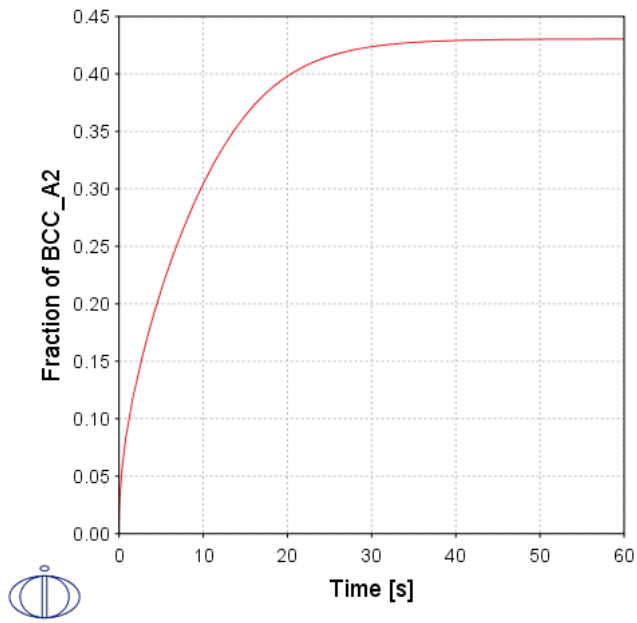


Figure 4-13: Calculated volume fraction bcc as function of time at 800 °C.

Plot Renderer 3 Settings

It is instructive to plot the diagram using logarithmic scales on both axes.

- Add a third Plot Renderer node. This time you can clone it as you will just change the axis type to logarithmic.



For your plot, you will not see the straight line included in [Figure 4-14](#).

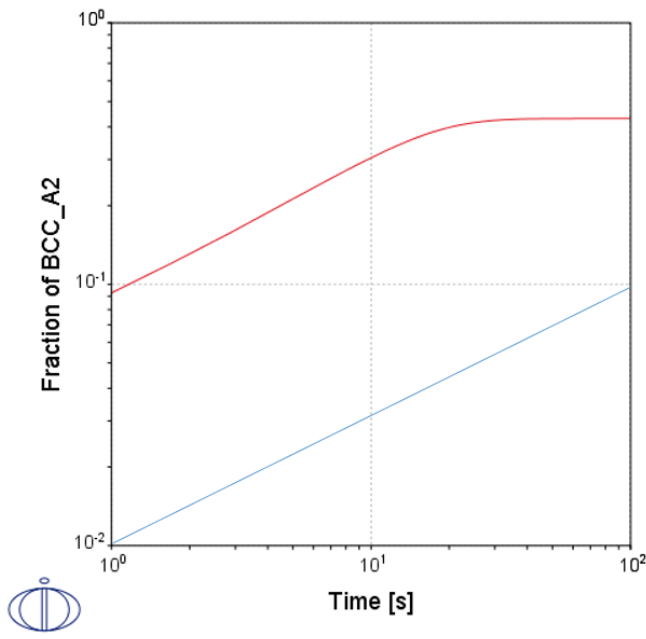


Figure 4-14: Calculated volume fraction bcc as function of time at 800 °C using logarithmic scales. The straight line indicates the slope $\frac{1}{2}$.

From Figure 4-14 it is clear that the slope is $\frac{1}{2}$ in the early stages. This is expected for a diffusion controlled reaction before impingement, i.e. before the diffusion field reaches the end of the system. Before impingement the thickness of ferrite is proportional to $\sqrt{\text{time}}$. From Figure 4-12 it can be seen that impingement becomes important already after 2 s which is also indicated in Figure 4-14.

4.3.2 Reaction During Cooling and Isothermal Holding

This part of the example refines the calculation by accounting for the finite cooling rate from at 850 °C to 800 °C followed by isothermal holding at the lower temperature.



Task: Predict the ferrite formation during cooling from 850 to 800 °C and subsequent isothermal holding. Consider the cooling rates 1 and 10 K/s, respectively.



The settings are the same as for the " Isothermal Reaction" on page 77 calculation except as follows. If you created a project file for the first part of the example, it is recommended you save a copy of the file and adjust the settings as needed.

Diffusion Calculator Settings

- Choose a non-isothermal profile and set the temperature to Celsius and the time unit in seconds.
- Edit the thermal profile. Enter times and temperatures into the table. Temperature is assumed to vary linearly between the different times.
- In the first calculation enter a high cooling rate i.e. at $t = 0$ set $T = 850$. At $t = 50$ s set $T = 800$. Then keep the temperature constant until the end of calculation at 120 s.

Edit Thermal Profile

Time [s]	Temperature [°C]
0.0	850.0
50.0	800.0
120.0	800.0

- Set the simulation time to 120 seconds.
- Set the integration method to Euler backwards.

Plot Renderer Settings

The settings for each plot is the same except for Plot Renderer 1 where you change the times for each axes to 0, 20, 30, 50 and 120 seconds (or any times you want).

The resulting concentration profiles as different times are shown in [Figure 4-15](#). Compare to [Figure 4-12](#).

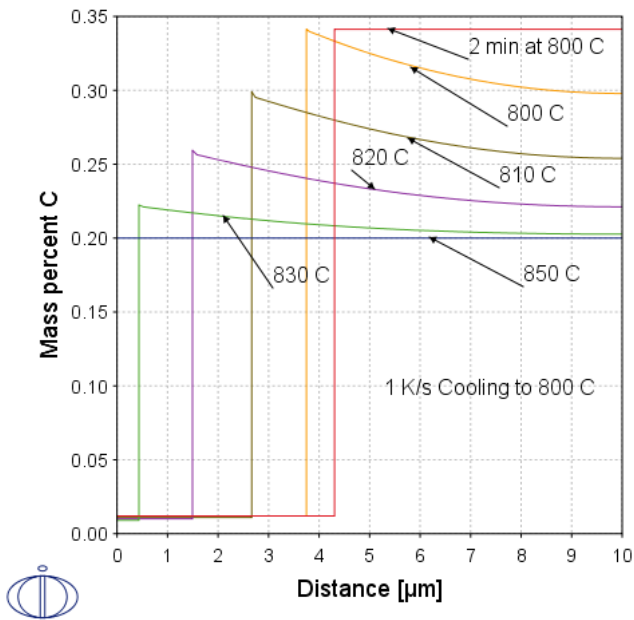


Figure 4-15: Calculated C concentration profiles at different temperatures. Cooling from 850 to 800 °C and with 1 K/s and thereafter isothermal holding. Temperatures indicated.

The lower temperature is reached after 50 s and there is still a substantial carbon gradient in austenite which should be compared with the almost equilibrium after 60 s in Figure 4-12. Nevertheless full equilibrium is established after 1 minute isothermal holding at 800 °C.

Figure 4-16 shows the corresponding concentration profiles assuming a cooling rate of 10 K/s, which is very high and can only be achieved in thin samples. In this case there is a stronger deviation from equilibrium during cooling but after 2 minutes equilibrium is established as in the previous cases.

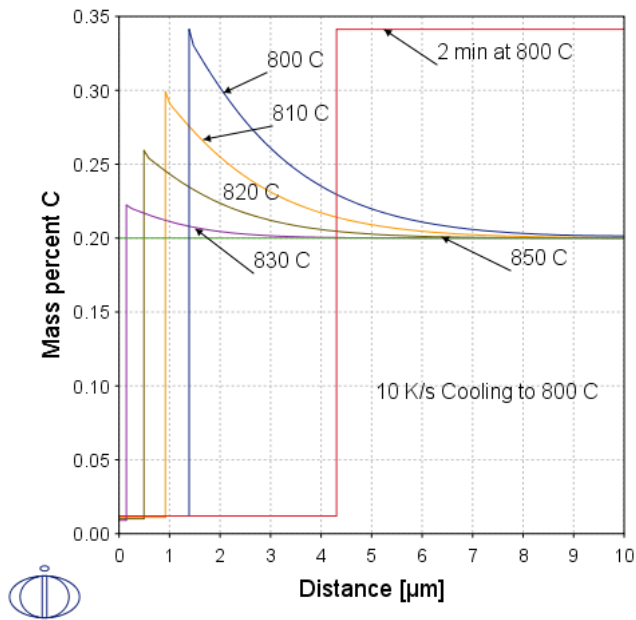


Figure 4-16: Calculated C concentration profiles at different temperatures. Cooling from 850 to 800 °C and with 10 K/s and thereafter isothermal holding. Temperatures indicated.

4.3.3 Austenite Formation During Heating



This example builds on the previous simulations "Isothermal Reaction" on page 77 and "Reaction During Cooling and Isothermal Holding" on page 81 although no specific instructions are included. See if you can reproduce the plots yourself.



Task: It may be interesting to find out how long time it would take to form a homogeneous austenite structure from the two-phase mixture that was the end result of the previous simulations. Start with the final structure of the previous example and consider the reverse transformation during heating to 850 °C.

The easiest way to solve the problem is to edit the thermal profile by simply adding a heating step from 800 to 850 °C and subsequent isothermal holding. The following figures show the

concentration profiles with heating rates of 0.1, 1 and 10 K/s, respectively. The heating thus takes 500, 50 and 5 s, respectively.

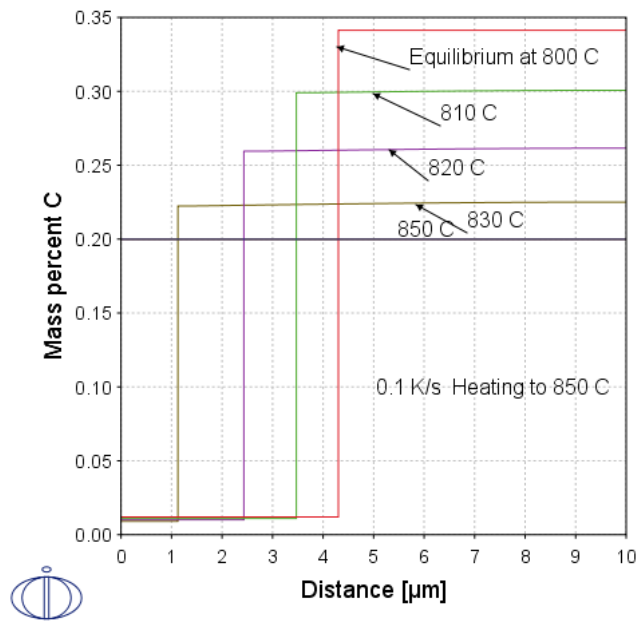


Figure 4-17: Calculated C concentration profiles at different temperatures. Heating from 800 to 850 °C and with 0.1 K/s and thereafter isothermal holding. Temperatures indicated.

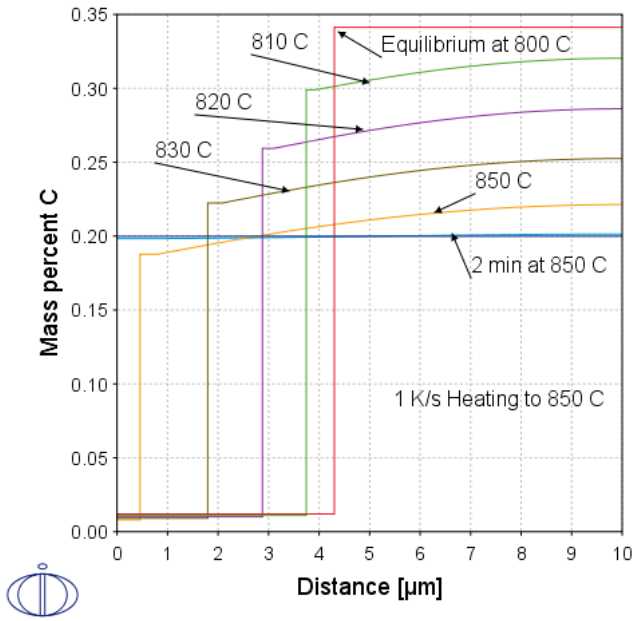


Figure 4-18: Calculated C concentration profiles at different temperatures. Heating from 800 to 850 °C and with 1 K/s and thereafter isothermal holding. Temperatures indicated.

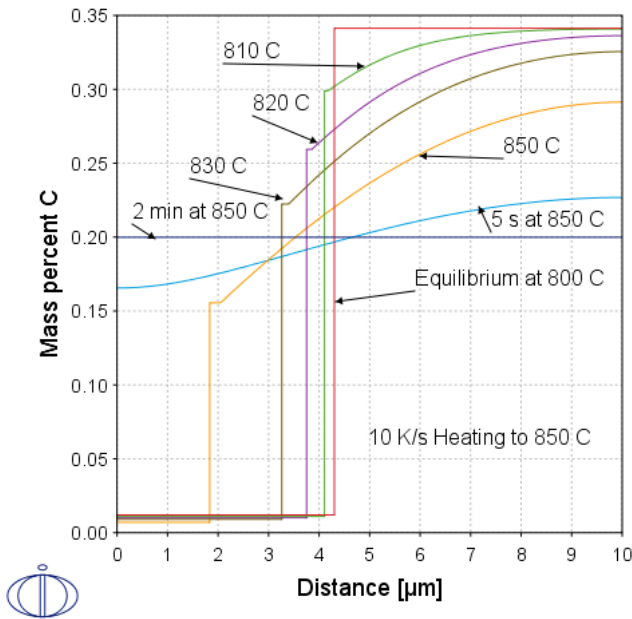


Figure 4-19: Calculated C concentration profiles at different temperatures. Heating from 800 to 850 °C and with 10 K/s and thereafter isothermal holding. Temperatures indicated.

As can be seen 0.1 K/s is slow enough to allow equilibration at each temperature whereas the higher heating rates yields more pronounced deviation from equilibrium during heating. Nevertheless, 2 minutes at 850 °C is enough for full equilibration.

4.4 Example: Austenite Formation in a Normalized Steel

In low alloy steels there is a common heat treatment operation called *normalizing*. The operation is performed in order to give the steel, which might have an unfavorable microstructure a “normal” structure consisting usually of a mixture of ferrite and pearlite. It is performed by fully austenitize the steel and then let it cool in air which corresponds to a cooling rate 0.1 K/s or less depending on the size of the steel component. It is common that a steel producer deliver the steel in the normalized condition. Consider now martensite hardening of a normalized steel. First it needs to be austenitized and then quenched to form martensite.



Task: Assess how rapidly the austenite forms in a normalized steel Fe-0.2C with the same grain size as in "Example: Ferrite Formation and Dissolution in an Fe-0.2C Alloy" on page 77 .

We will first make a simulation approximating the steel as a binary Fe-C alloy. We shall see later that this may not always be a good approximation, not even when the alloy content is low, but here we use the approximation for simplicity.

If we consider the same steel Fe-0.2 mass% C the simplest way to achieve the initial normalized structure is to start with the previous example involving cooling but change to a slow cooling rate, say 0.1 K/s and extend the cooling to the eutectoid temperature that is 727 °C in binary Fe-C. Below this temperature the remaining austenite will form pearlite. However, we shall neglect the pearlite formation and use the two-phase mixture of ferrite and austenite as our initial condition for simulation of austenite formation. This is a reasonable approximation because upon heating pearlite can transform to austenite without the need of any long-range diffusion in a rather quick process.

The result is shown in the following figure. As can be seen the heating is slow enough to allow almost full equilibrium at all temperatures.

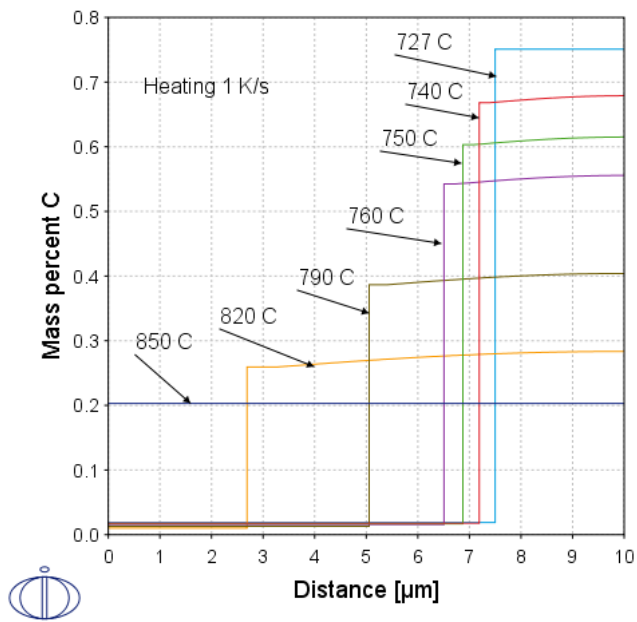


Figure 4-20: Calculated C concentration profiles at different temperatures during heating from 727 to 850 °C and with 1 K/s. Temperatures indicated.

5 Two-Phase Diffusion Problems in Multicomponent Alloys

5.1 Introduction to Diffusion Problems in Multicomponent Alloys

In principle the same approach is used as in binary alloys to treat growth and shrinkage in alloys with arbitrary number of components. However, there is a complication because the local equilibrium tie line at the phase interface cannot be directly read from the phase diagram. In a ternary system there is an infinite number of possible tie lines at a given temperature, see [Figure 5-1](#) showing an isothermal section in the Fe-Mn-C system. Consider for example an alloy with a composition marked by *. At equilibrium the tie line is the one passing through * and there will be a mixture of α and γ with fractions that can be evaluated from the lever rule, see [Figure 5-2](#).

But which tie line is the correct one during a phase transformation? It should be noticed from [Figure 5-1](#) and [Figure 5-2](#) that each tie line is represented by a given value of the carbon activity a_C . For this ternary case there is thus one more unknown than for the binary, where the only unknown was the migration rate v that could be calculated from the single flux-balance equation, i.e. $\frac{v}{\bar{V}_m}(x_i^\gamma - x_i^\alpha) = J_i^\gamma - J_i^\alpha$. However, in the ternary case we have two independent flux-balance equations. In the present case one for C and one for Mn. The correct tie line thus is the one that satisfies both flux balances. It turns out that for a general system with N components $N - 2$ activities must be fixed in order to define a unique tie line. We thus have $N - 2$ unknown activities and 1 unknown migration rate, i.e. totally $N - 1$ unknowns. We have the same number of independent flux balance equations, i.e. the flux balances are enough to calculate the interfacial tie line and the migration rate.

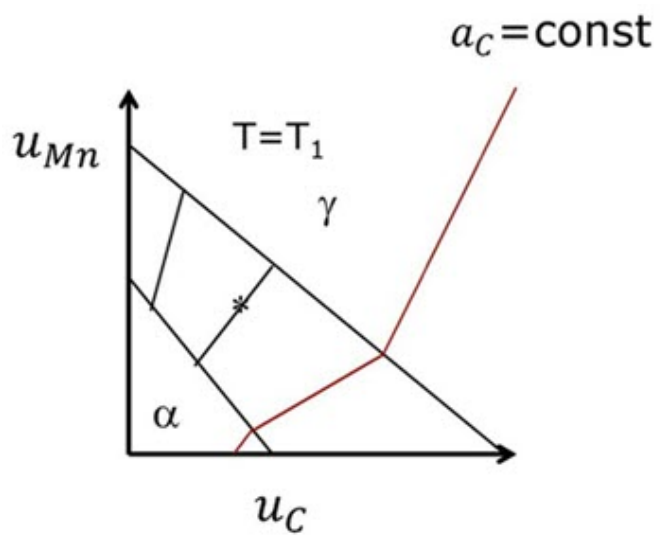


Figure 5-1: Schematic isothermal ($T = T_1$) section of the Fe-Mn-C phase diagram.

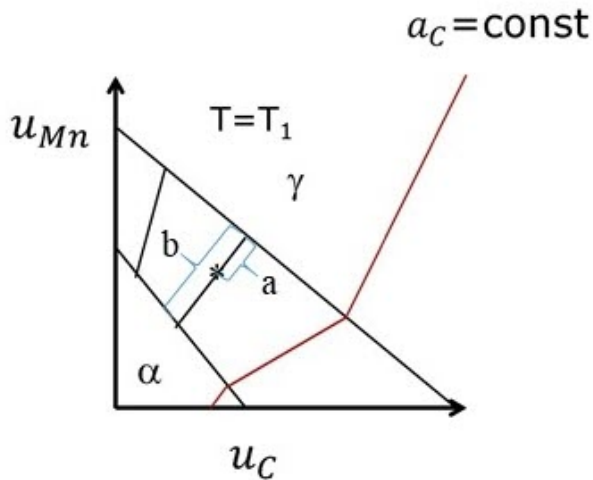


Figure 5-2: The lever rule in a ternary isothermal section. The fraction of α is $f^\alpha = a/b$.

5.1.1 Advanced: Two Phase Problems

Determination of Local-equilibrium Tie Line in a Multicomponent System

The Gibbs phase rule states the number of potential quantities f needed to specify equilibrium, f being referred to as the number of degrees of freedom. The phase rule reads

$$\text{ADV Eq. 5-1} \quad f = N + 2 - p$$

where N is the number of components and p the number of coexisting phases. Pressure and temperature are thermodynamic potentials and for the common case when they are fixed [ADV Eq. 5-1](#) becomes $f = N - p$, i.e. the same number of chemical potentials must be given. The chemical potential μ_i of a component i is related to its activity relative a reference state ref by means of

$$\text{ADV Eq. 5-2} \quad \mu_i = \mu_i^{ref} + RT \ln a_i^{ref}$$

where μ_i^{ref} is the chemical potential in the chosen reference state. In the phase transformations discussed so far we consider a phase interface between two phases, i.e. $p = 2$ and the number of potentials needed to specify an equilibrium tie line is

$$\text{ADV Eq. 5-3} \quad f = N - 2$$

Under full equilibrium in an alloy with over-all composition x_i^* the $N - 2$ potentials are chosen to obey $N - 1$ mass balances

$$\text{ADV Eq. 5-4} \quad x_i^* = f^\alpha x_i^\alpha + (1 - f^\alpha) x_i^\beta$$

where f^α is the fraction of α and $f^\beta = 1 - f^\alpha$ is the fraction of β . It may then seem as there is one equation more than unknowns but it should be kept in mind that also the fraction f^α is unknown and has to be determined from [ADV Eq. 5-4](#), i.e. there is a unique solution. The lever rule is obtained by rearranging the equation and then in a phase transformation the flux balance equations replace this equation.

5.2 Condition for Fast Reaction Controlled by a Fast Diffuser

In a system where there are large differences between the diffusion rates of the components there is a possibility to have a fast reaction without the need of any redistribution of the more sluggish elements. In metals elements such as H, C and N are smaller than the metal atoms and occupy the empty spaces between them, i.e. the interstices. They are thus often called interstitial elements in contrast to the metal atoms called substitutional elements. For example, in the previous example Mn can only replace Fe whereas C can go to any empty interstice. This means that diffusion of interstitials is usually much faster than that of substitutional atoms.

Obviously the conditions for a fast reaction can sometimes be fulfilled and sometimes not. In the example of the steel Fe-1Mn-0.2C they are fulfilled at 750 °C during the early stages but not at 800 °C, nor at the later stages at 750 °C.

As an illustration we now consider the transformation from austenite to ferrite in the system Fe-Mn-C. The migration rate and the interfacial tie line ([Figure 5-2](#) in "[Introduction to Diffusion Problems in Multicomponent Alloys](#)" on page 89) are obtained by solving the two independent flux balance equations of type $\frac{v}{V_m} (x_i^\gamma - x_i^\alpha) = J_i^\gamma - J_i^\alpha$, one equation for C and one for Mn. The question now is; is it possible to find an interfacial tie line without any long-range redistribution of Mn? Such a tie line is defined by the fact that the content of substitutional elements in the growing ferrite is the same as that of the initial austenite.

Consider the alloy marked with a star in [Figure 5-3](#). The tie line for no long-range redistribution of Mn is plotted to the left and the corresponding Mn profile to the right.

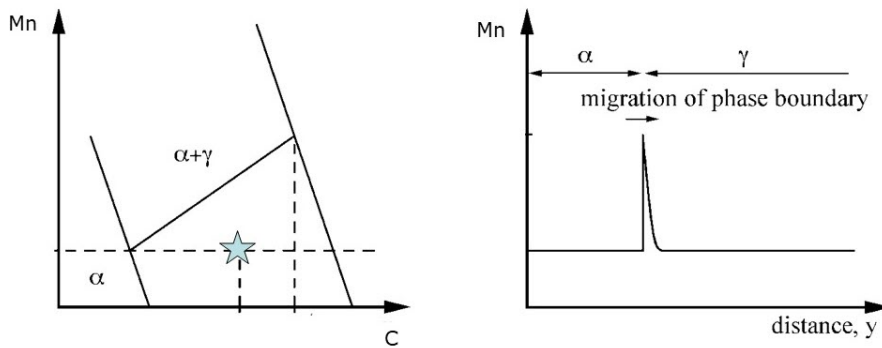


Figure 5-3: Left: schematic isothermal section of Fe-Mn-C. The alloy marked with a star denotes the over-all alloy composition, i.e. that of the initial austenite. Right: corresponding Mn profile when there is no long range redistribution of Mn.

In order to maintain the local equilibrium there must be a spike in Mn content in austenite close to equilibrium. As the growing ferrite has a much lower C content than the austenite there must be a driving force for C diffusion in austenite away from the moving interface. This means that the fast reaction can proceed as long as the carbon activity far away from the interface is lower than at the interface. In [Figure 5-3](#) the lines representing the carbon activity at the interface and far away from it have been indicated as dashed vertical lines. After some time the carbon activity far away will start to increase due to the finite size of the system and the migration rate will slow down and there is time for redistribution of Mn. The fast reaction has come to an end and the slow reaction can be seen. If the initial alloy is on the right-hand side of the line representing the carbon activity at the interface fast reaction is not possible. The critical alloy composition thus lies on the intersection of the Mn content and the C activity line representing the interface. If one plots this intersection for all possible Mn contents one gets approximately the line as indicated in [Figure 5-4](#).

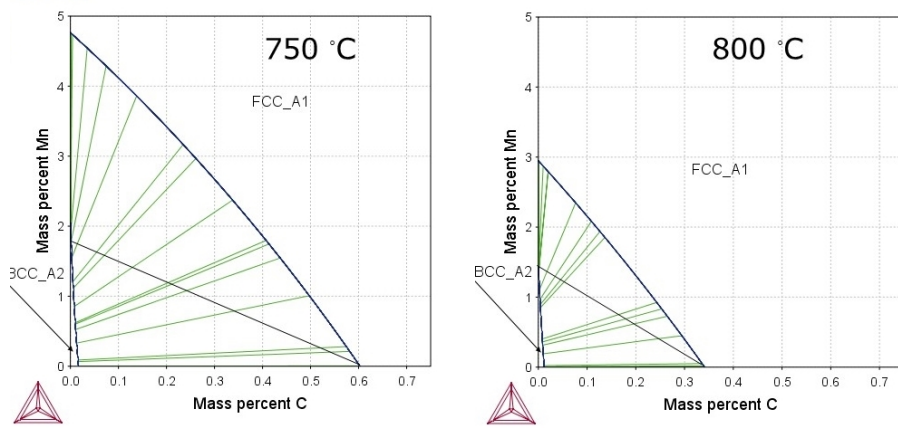


Figure 5-4: Left: isothermal section of Fe-Mn-C at 750 °C. Right: isothermal section of Fe-Mn-C at 800 °C. The line going from Fe-Mn side to Fe-C denotes the border line between fast and slow reaction.

Alloy compositions on the left side of the border line will grow initially by a fast reaction whereas those on the right side can only grow by slow reaction. From the lever rule or a thermodynamic calculation we find that at full equilibrium in the Fe-1Mn-0.2C steel at 750 °C there will be 55% ferrite. We can roughly estimate the fraction of ferrite that can form by a fast reaction from Figure 5-4 left. The tie line that represents no Mn partitioning, i.e. that end at 1 mass% Mn in ferrite, ends at around 0.27 mass% C in austenite. If we neglect the carbon content in ferrite we have from a mass balance for C that $0.2 \cong (1 - f^\alpha) * 0.27$ i.e. $f^\alpha \cong 0.26$ which is in reasonable agreement with the plateau shown in Figure 5-8 in "Example: Isothermal Formation of Ferrite from Austenite in Steel Fe-1Mn-0.2C" below.

5.3 Example: Isothermal Formation of Ferrite from Austenite in Steel Fe-1Mn-0.2C



This example is identical to the isothermal reaction described in "Example: Ferrite Formation and Dissolution in an Fe-0.2C Alloy" on page 77 with the difference that there is 1 mass% Mn.



Task: Consider the formation of ferrite at 800 °C.

The result of the calculation is now dramatically different. In the original example, see [Figure 4-13](#) and [Figure 4-14](#), we found that full equilibrium was established more or less within a minute whereas hardly anything has happened at this time when we have 1 mass % Mn. In fact we have to increase the simulation time to more than an hour to see any reaction. Compare [Figure 5-5](#) with [Figure 4-14](#).

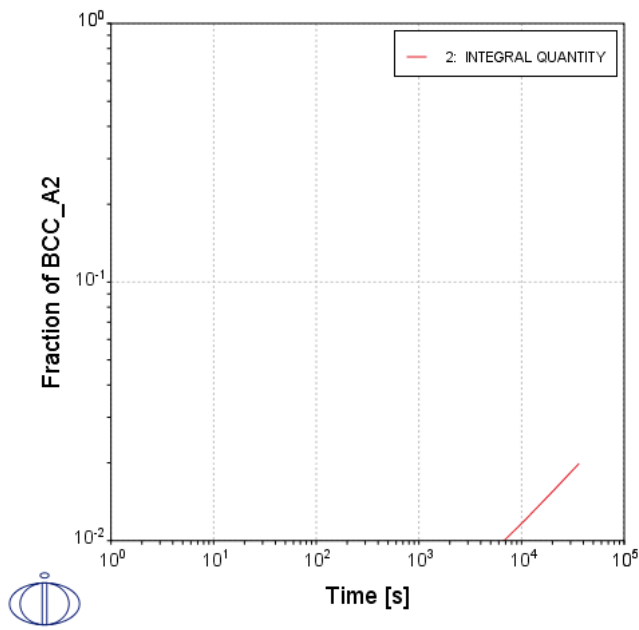


Figure 5-5: Calculated volume fraction bcc as function of time at 800 °C in Fe–1Mn–0.2C using logarithmic scales. Compare with [Figure 4-14](#) for Fe–0.2C.

If we repeat the calculation at a lower temperature, say 750 °C we find that ferrite forms, see [Figure 5-6](#) and [Figure 5-7](#).

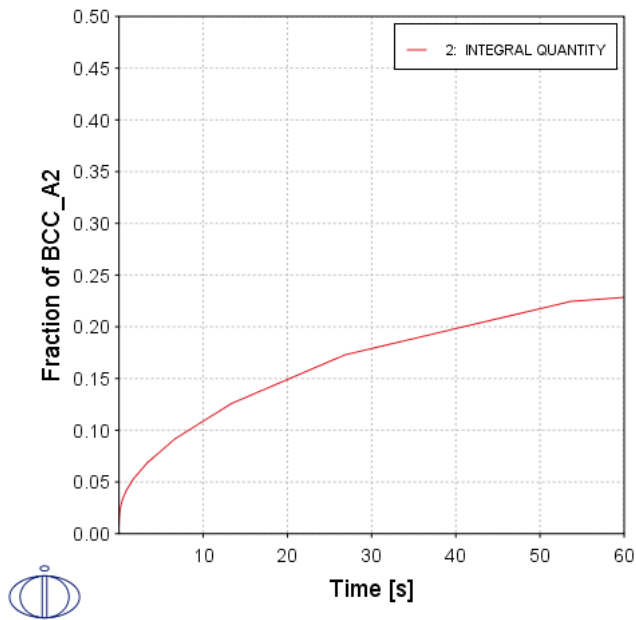


Figure 5-6: Calculated volume fraction bcc as function of time at 750 °C in Fe-1Mn-0.2C.

As can be seen a substantial fraction of ferrite has formed already within a minute although not as much as in the alloy without Mn at 800 °C. However, equilibrium is clearly not established within 1 minute and we prolong the calculation to 3 h (Figure 5-7), and plot the result using a logarithmic time scale.

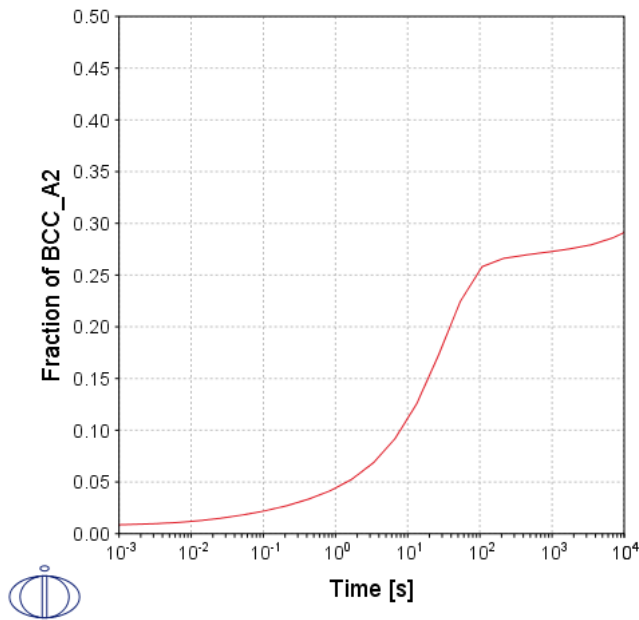


Figure 5-7: Calculated volume fraction bcc as function of time at 750 °C in Fe-1Mn-0.2C using logarithmic time scale.

Although the growth rate starts to level out for times longer than minutes, equilibrium is not established because the curve does not become completely horizontal. If we prolong the simulation to cover 1000 h and again plot the result, see Figure 5-8, we find a very interesting result. It seems as the reaction after slowing down and almost reaching a plateau, starts again at longer times. However, such a statement is incorrect; the plateau is just a consequence of the logarithmic time scale. A correct statement is rather that the reaction can be represented by two different reaction rates, one fast and one much slower. It seems reasonable to assume that the fast reaction is controlled by fast C diffusion in austenite and that the slow reaction is controlled by much slower Mn diffusion in austenite. We may check this idea by looking at the diffusivities of C and Mn in austenite; $D_C^{fcc} \cong 9 \cdot 10^{-13}$ and $D_{Mn}^{fcc} \cong 7 \cdot 10^{-19} \text{ m}^2 \text{ s}^{-1}$, respectively.

Mn thus diffuses 6 orders of magnitude slower than C! Again using the Einstein relation to estimate the time needed for equilibration of a system with size 10 μm we find around 1 minute for C and more than 10 000 h for Mn. This is in reasonable agreement with Figure 5-8. The following question then arises; how is it possible to have a reaction controlled by C diffusion?

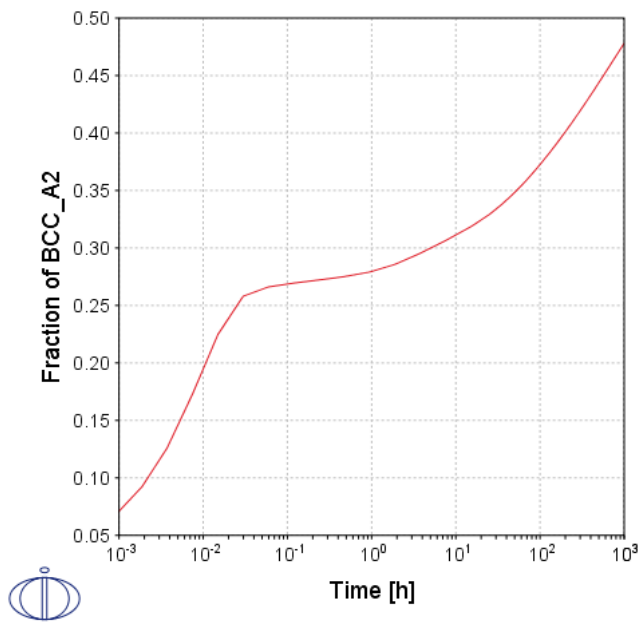


Figure 5-8: Calculated volume fraction bcc as function of time at 750 °C in Fe-1Mn-0.2C using logarithmic time scale.

The only possibility is that the reaction may occur without the need of Mn diffusion. If this is the case the ferrite that forms must inherit the Mn content of the parent austenite. We thus plot the C and Mn concentration profiles after 1 min (Figure 5-9) a time that is long enough to allow C diffusion but too short to allow any Mn diffusion.

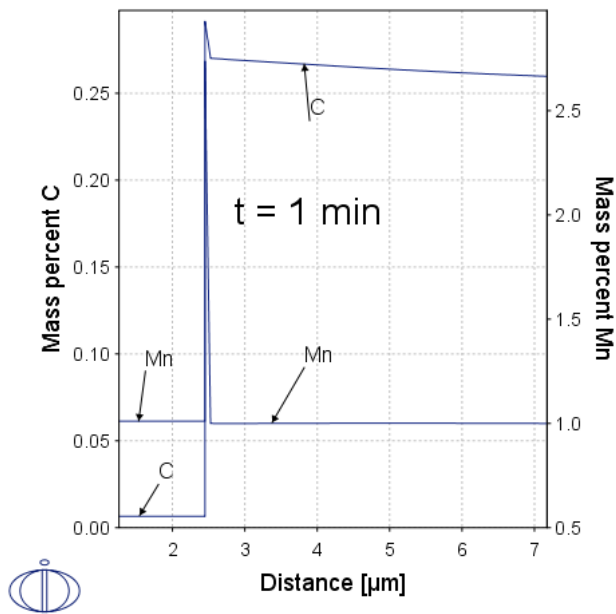


Figure 5-9: Calculated C and Mn concentration profiles close to phase interface after 1 min at 750 °C in Fe-1Mn-0.2C.

Figure 5-9 shows that although there is a substantial C redistribution the ferrite that forms has the same Mn content as the parent austenite except for a spike close to the interface. The Mn spike also yields a spike in C content but it is easy to check, by plotting, that the C activity is constant in the spike. This is clearly shown in Figure 5-10 that demonstrates the equilibration of C. A constant C activity is approached.

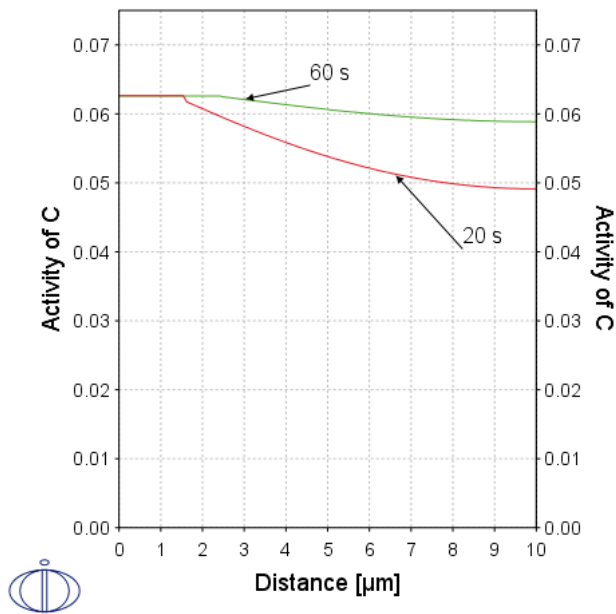


Figure 5-10: Calculated C activity profiles after 20 and 60 s at 750 °C in Fe-1Mn-0.2C.

5.4 Example: Ferrite Formation During Normalizing of Steel Fe-1Mn-0.2C



This is the same as "Example: Austenite Formation in a Normalized Steel" on [page 87](#) except that we now also have 1 mass % Mn. However, we shall start looking at the ferrite formation during normalizing.



Task: Investigate the ferrite formation during normalizing.

An isoplethal section (vertical section) calculated for 1 mass % Mn is shown in [Figure 5-11](#) and an isothermal section at 706 °C is shown in [Figure 5-12](#).

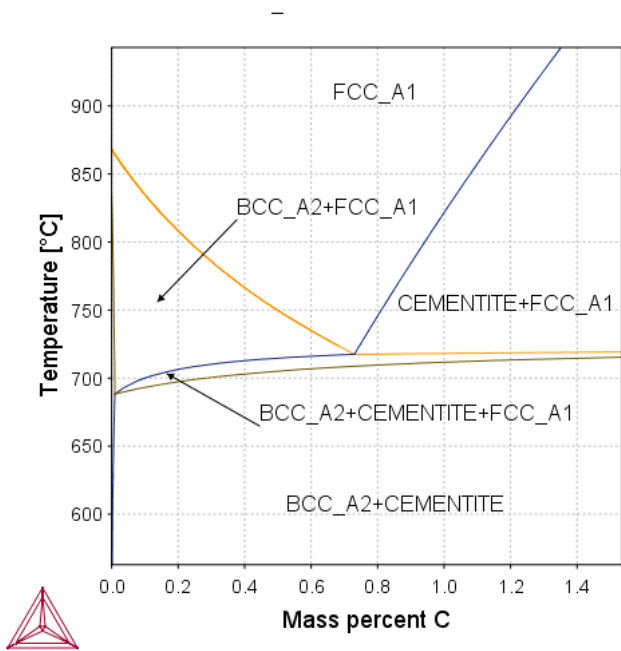


Figure 5-11: Calculated isoplethal section Fe-1 mass% Mn.

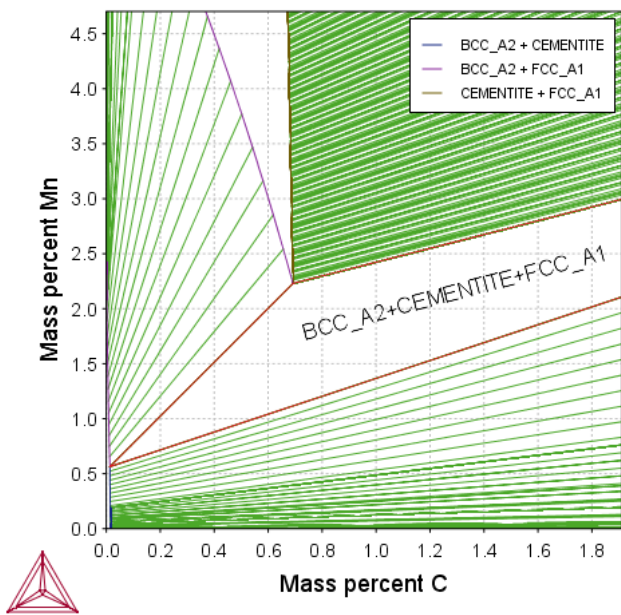


Figure 5-12: Calculated isothermal section Fe-Mn-C at 706 °C

The temperature 706 °C was chosen because it is the temperature below which cementite starts forming in Fe-1Mn-0.2C as in Figure 5-12. However, the calculation shows us that we

do not enter the ferrite + cementite two-phase field until a lower temperature; 698 °C (see [Figure 5-11](#)), where we expect normal pearlite to form.

Now we are going to use the Diffusion Module (DICTRA) to treat the cooling from 850 to 698 °C with a cooling rate of 0.1 K/s typical for normalizing. The conditions are similar to the previous simulations except that we now start with also 1 mass% Mn.

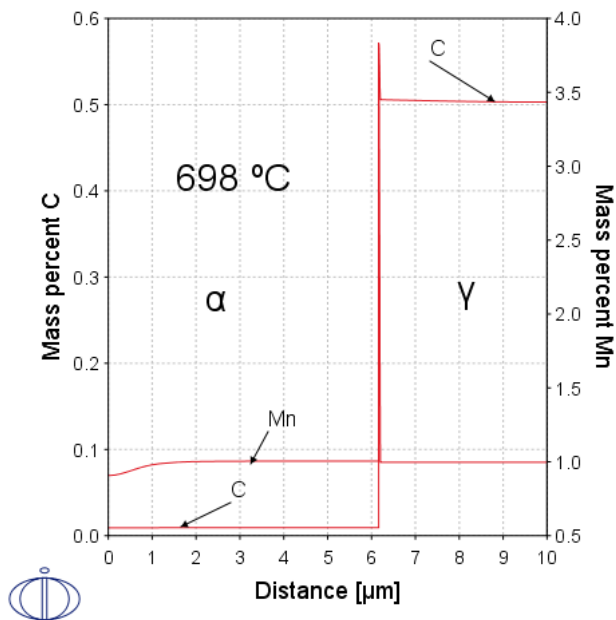


Figure 5-13: Calculated C and Mn concentration profiles after cooling from 850 to 698 °C with cooling rate 0.1 K/s. There is only long range redistribution of C.

[Figure 5-13](#) shows that there is only long-range redistribution of C during cooling and, except for a spike close to the α/γ phase interface the carbon content is constant. However, it is much lower than the eutectoid composition in the binary Fe-C system and what we would expect from an isothermal section at 698 °C.

In [Figure 5-14](#) we have plotted the Mn content only and we see that except for a very narrow spike in γ close to the interface there is no redistribution of Mn, i.e. the transformation is partitionless. The growing ferrite has the same Mn content as the initial austenite. Obviously the cooling is slow enough to allow equilibration of C but not of Mn. If this is the case the C activity should be the same all over the system. Such a plot is shown in [Figure 5-15](#) and indeed the carbon activity relative graphite is almost constant with a very small in the

austenite. Diffusion in austenite is much slower than in ferrite and there is not been time enough to completely level out the carbon activity.

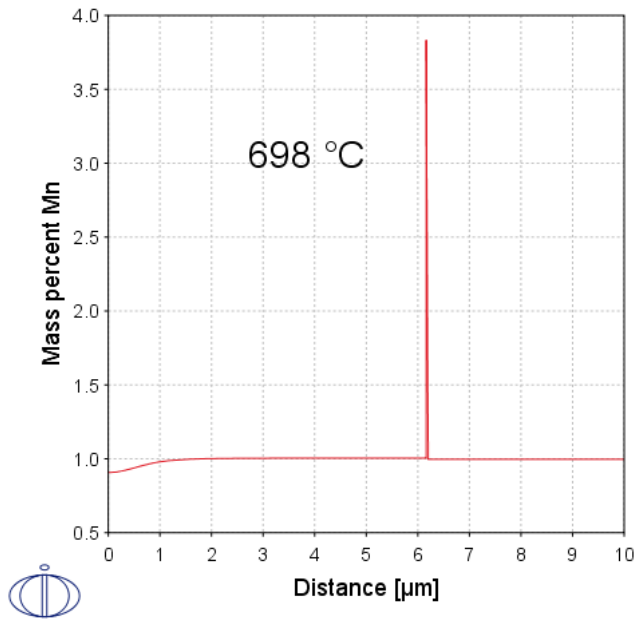


Figure 5-14: Calculated Mn concentration profile after cooling from 850 to 698 °C with cooling rate 0.1 K/s. Except for a very narrow spike in γ close to the interface there is no redistribution of Mn, i.e. the transformation is partitionless.

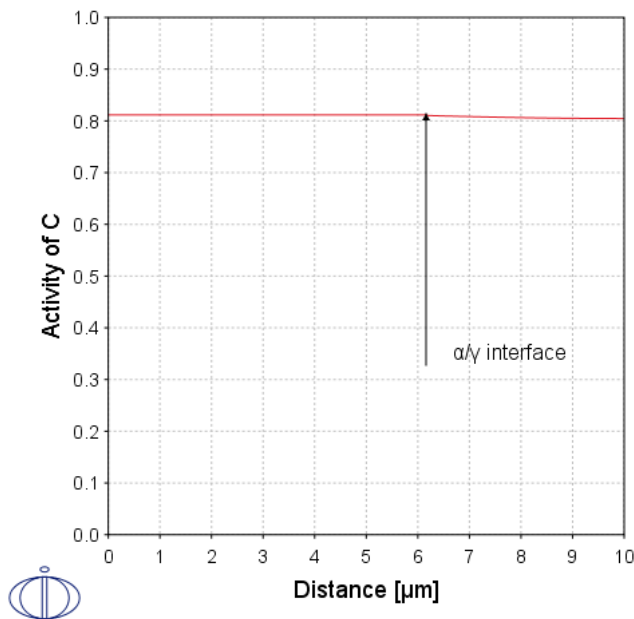


Figure 5-15: Calculated carbon activity relative graphite after cooling from 850 to 698 °C with cooling rate 0.1 K/s. The carbon activity is almost constant with a very small variation in austenite.

One may then wonder how long time it would take to also equilibrate Mn. As usual we may use the Einstein relation, i.e. $t = \ell^2 / 2D_k$. The diffusion coefficient for Mn in austenite at 698 °C is $1.5 \cdot 10^{-19} \text{ m}^2 \text{ s}^{-1}$ and if we insert a diffusion distance of 5 μm we find

$$t = (5 \cdot 10^{-6})^2 / (2 * 1.5 \cdot 10^{-19}) = 8.3 \cdot 10^7 \text{ s} \cong 2.6 \text{ years}$$

We may do an isothermal holding simulation at this temperature and extend to unrealistically long times. We then find that there is a slight Mn gradient in austenite after 3 years but after 6 years it is almost leveled out and full equilibrium is established. It thus clear that the simulations predict that after normalizing we could hardly have full equilibrium because there will be negligible Mn partitioning during cooling before pearlite starts forming.

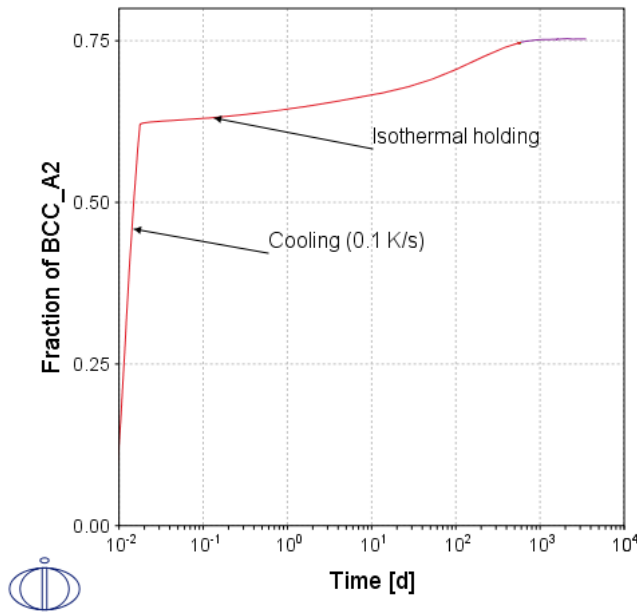


Figure 5-16: Calculated fraction of ferrite during cooling from 850 to 698 °C (0.1 K/s) and subsequent isothermal holding. Timescale logarithmic in days.

5.5 Example: Austenite Formation After Normalizing of Steel Fe-1Mn-0.2C



Task: Simulate the austenitizing after normalizing, i.e. the starting state in [Figure 5-13](#). This is easily done simply by adding a heating step in the thermal profile of the "Example: Ferrite Formation During Normalizing of Steel Fe-1Mn-0.2C" on [page 100](#) simulation. We add heating with a rate of 1 K/s up to 850 °C and then isothermal holding to totally 1 h.

The result is shown in [Figure 5-17](#) and [Figure 5-18](#).

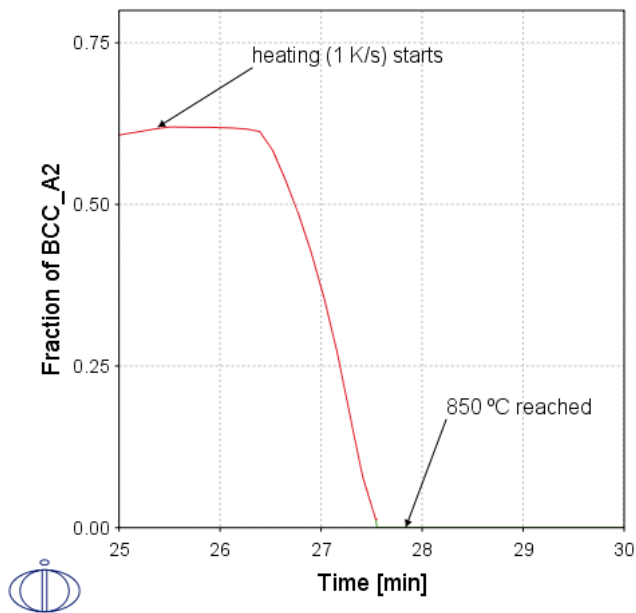


Figure 5-17: Calculated fraction of ferrite during heating from 698 to 850 °C (1 K/s) and subsequent isothermal holding.

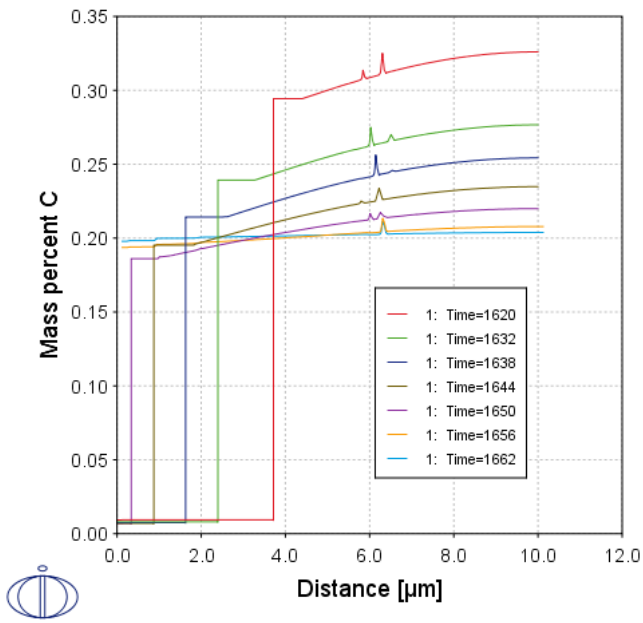


Figure 5-18: C concentration profile during heating and austenitization

The C concentration profiles in the above figure shows some interesting “spikes” at a distance around 6 μm . These stems from “spikes” in the Mn profile as shown in [Figure 5-19](#) plotted at 27 min, i.e. after 100 s of heating, when the temperature has reached 798 $^{\circ}\text{C}$.

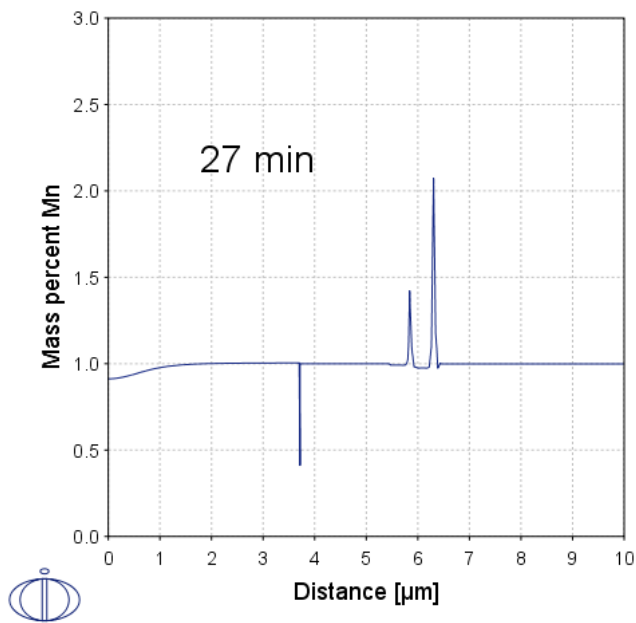


Figure 5-19: Mn concentration profile after 100 s of heating (1 K/s) at 798 °C.

Mn lower the C activity and where the Mn content is high the C will thus be high in order to have a constant C activity. The two spikes are related to reversion of the interface motion. In Figure 5-19, the phase boundary moves to the left and corresponds to a very sharp negative spike in Mn content. This spike is, however, in the ferrite.

From an industrial processing view it is very important that Mn partitioning is negligible because if it was substantial much longer austenitization times were needed because the process would then be controlled by slow Mn diffusion in austenite.

6 Diffusion in Dispersed Structures

6.1 Example: Internal Carburization of a Ni-Cr Alloy Using Homogenization

In many practical situations there is long-range diffusion in dispersed multiphase structures rather than in one phase. Important examples are oxidation of alloys containing very reactive elements which will lead to so-called internal oxidation. Oxygen then diffuses over long distances through a structure of dispersed oxides. Other examples are internal carburizing and nitriding of alloys. If we are not interested in the details of the microstructure but only the long-range diffusion one can use approximate methods based on a mathematical approximation called homogenization. The multiphase structure is then replaced by a hypothetical one-phase structure with effective properties.



Remark on internal oxidation: Simulations based on the homogenization method are time consuming in such cases where the contents of the diffusing elements are low in the matrix phase. Unfortunately, this is the case particularly for internal oxidation which is of large practical importance. Nevertheless, the calculations are stable and the results will eventually be found even for complex cases.

Different Ni-Cr alloys are exposed for a sooting environment at 850 °C and one finds that they have been unintentionally carburized. This can be seen because a population of carbide particles can be observed close to the surface of the alloy. This is expected because Cr forms a number of carbides whereas Ni is less prone to form carbides. We thus expect internal carburizing when the alloys are exposed for such high carbon activities.



Task: Set the C activity to unity relative graphite and simulate the carburization process in Ni-25mass % Cr and Ni-30 mass% Cr for 1000 h at 850 °C using the homogenization simulation.

This is done in the same way as the examples in the " [One-Phase Diffusion Problems](#)" on [page 30](#) except that we add in the region also the phases that we want to allow as dispersed phases. If there are several phases in a region the Diffusion Module (DICTRA) automatically launches a default homogenization simulation. Some results for two different alloys are shown in [Figure 6-1](#) and [Figure 6-2](#).

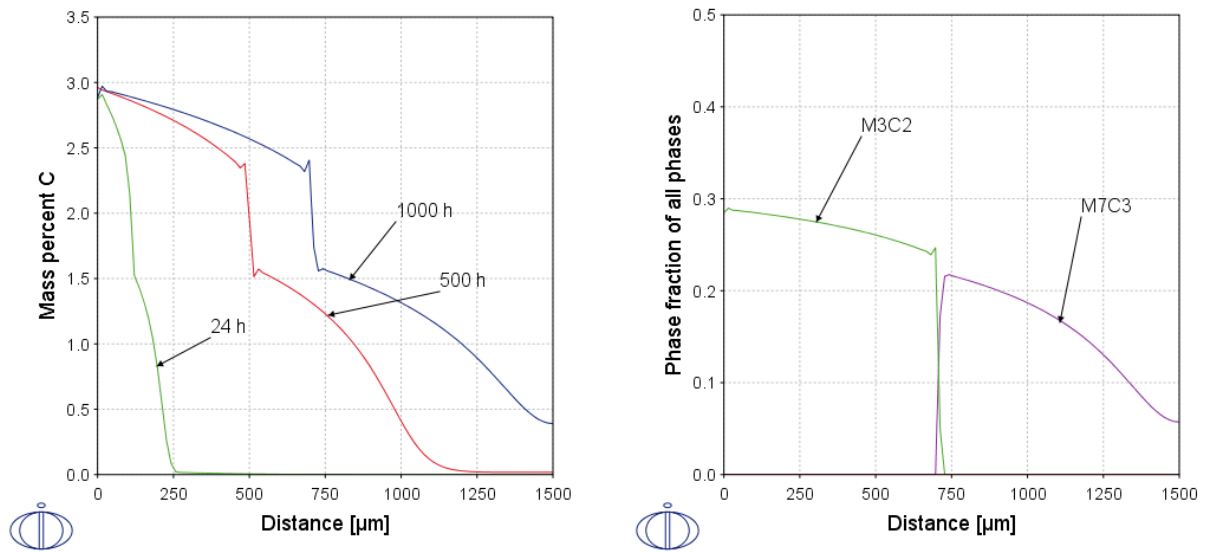


Figure 6-1: Internal carburizing of Ni-25Cr at 850 °C and carbon activity of unity relative graphite. Left: Carbon concentration profiles at different times indicated. Right: Fraction of carbides after 1000 h.

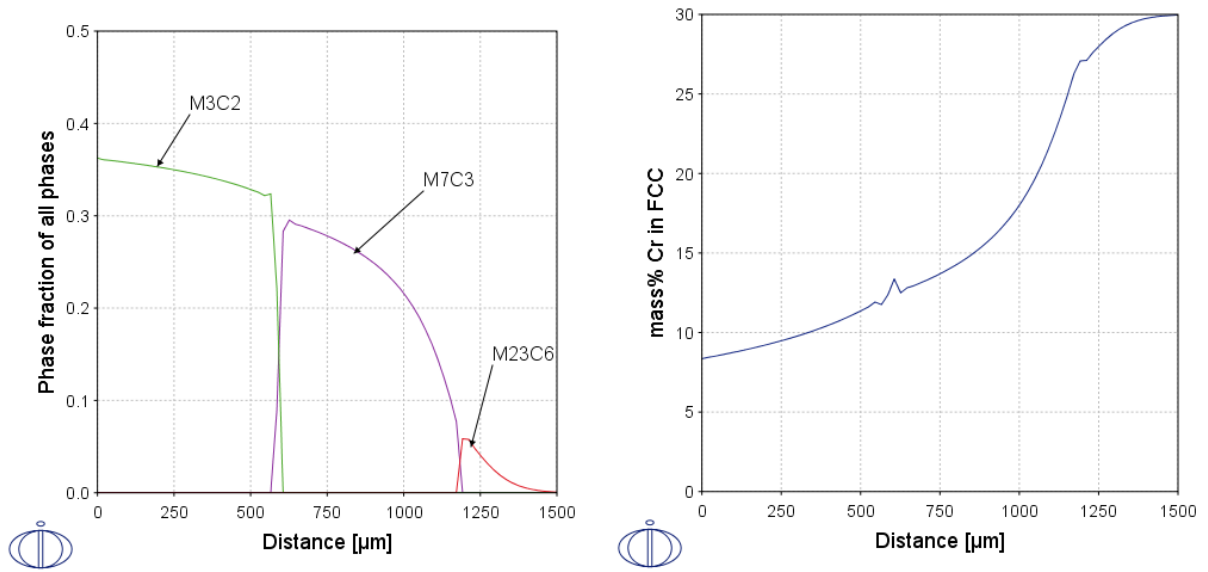


Figure 6-2: Internal carburizing of Ni-30Cr at 850 °C and carbon activity of unity relative graphite. Left: Fraction of carbides after 1000 h. Right: Cr content in fcc matrix after 1000 h.

As can be seen the more carbon-rich phases form closer to the surface where the carbon activity is highest. This is expected from thermodynamics because the higher the activity of an element the more stable are the phases which are rich in that component. Figure 6-2, bottom image clearly reveals the Cr depletion of the fcc matrix close to the surface as a consequence of the carburization.



There are two additional examples about diffusion in dispersed structures. However, these examples require the steel thermodynamic (TCFE) and kinetic (MOBFE) databases to actually run the simulations.

6.2 Example: Internal Nitriding an Fe-Ni-Cr Alloy Using Homogenization



This example requires a license for the TCFE and MOBFE databases. If you do not have these databases, you can still follow along but you will not be able to perform the simulation.

Consider internal nitriding in air of an austenitic stainless steel containing high contents of Cr. It should be pointed out that Fe itself cannot be nitrided by air but much higher nitrogen activities are needed. This means that an atmosphere of technically pure N_2 gas can be considered as inert when heat treating Fe. In fact, when deliberately nitriding Fe and low alloy-steels one must thus use very high nitrogen partial pressures, in the order of 0.5 – 1 Mbar. Such high partial pressure cannot be obtained by applying N_2 gas but one has to use very reactive N-containing substances, usually NH_3 . However, Cr has a very strong tendency to react with N and consequently Cr containing steels or superalloys will form nitrides by internal nitriding even in air.



Task: Consider an austenitic stainless steel Fe-20Ni-25Cr exposed for air ($P_{N_2} = 0.79$ atm) at 1000 °C. Predict the evolution of the nitriding process.

The partial pressure $P_{N_2} = 0.79$ atm is calculated to the N activity used in DICTRA

$a_N = \sqrt{P_{N_2}} \cong 0.89$ atm^{1/2}. The results are shown in the figure below.

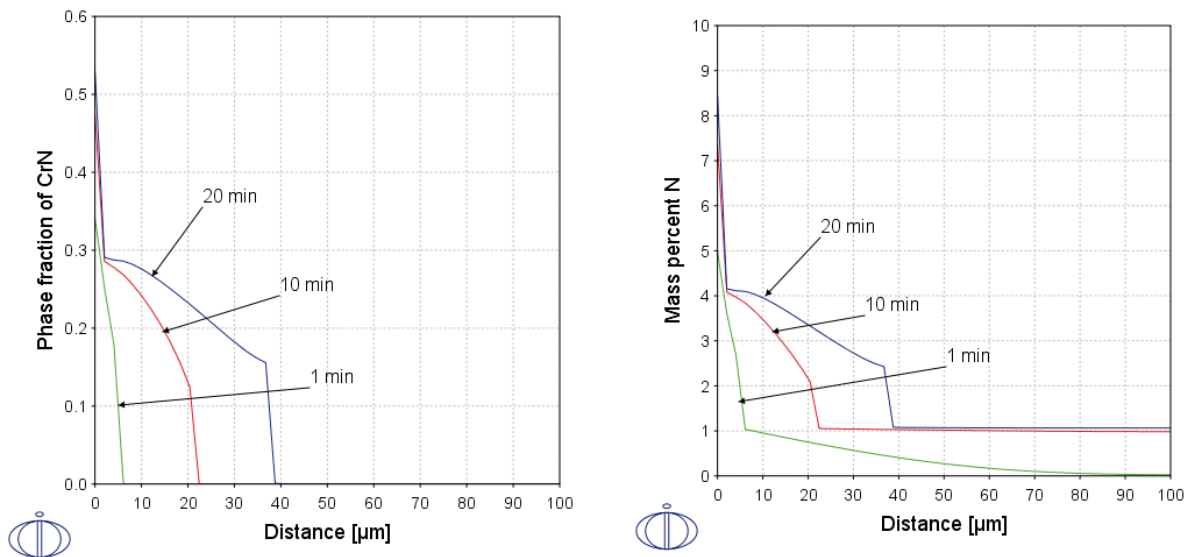


Figure 6-3: Internal nitriding of Fe-25Cr-20Ni in air at 1000 °C. Left: Fraction of CrN after times indicated. Right: Over-all N content at times indicated.

The simulations are in reasonable agreement with experimental results reported by Young and shows that N_2 can by no means be considered as inert when heat treating stainless steels. It should be emphasized that below the layer of internal nitriding there is a more or less complete nitriding of the austenitic matrix.

6.3 Example: Carbon Transfer in a Steel Composite: A Full Scale Industrial Problem



This example requires a license for the TCFE and MOBFE databases. If you do not have these databases, you can still follow along but you will not be able to perform the simulation.

In this example we will demonstrate the applicability of the homogenization method to a practical problem having the full scale industrial complexity. The composite is made by combining two different steels; one high-speed steel of type M2 and one low-alloy steel. The idea behind this composite is that the high-speed steel, a highly alloyed tool steel, should give hardness and wear resistance whereas the low-alloy steel should give the load bearing capacity. The composition of the two steels is given in [Table 6-1](#).

In the production of the steel composite the two steels are first welded together. The joint is subsequently annealed for several hours at 760 °C to get a softer structure to allow for machining of the high-speed steel. After this the whole composite is austenitized at 1215 °C and quenched to form martensite. However, the resulting properties are not as good as expected and a metallographic examination reveals a there is a reaction zone around the joint.



Task: Predict the change in composition during the two steps in the manufacturing of the steel composite.

Table 6-1: The two steel in the steel composite

	C	Cr	Mo	W	V
HSS	0.85	4	5	6	2
Low-alloy	0.45	1	1	-	0.15

To approach this problem we start by calculating the equilibrium state in each steel separately. This is easily done in Thermo-Calc. The equilibrium fraction of phases are given in Table 6-2. The temperature is high enough to dissolve all cementite in the low-alloy steel and the pearlite will thus transform to austenite. At this temperature there is ca 50/50 austenite/ferrite and minor fractions of alloy carbides in the low-alloy steel. The calculation also gives us the carbon activities in the two steels. Expressed relative graphite they are 0.058 in the high-speed steel and 0.59 in the low-alloy steel. It is remarkable that the low alloy steel has a 10 times higher carbon activity than the high-speed steel despite its much lower carbon content. The reason is that the latter has a much higher content of carbide forming elements and most of the carbon is tied up in carbides. Nevertheless, this difference has large consequences because it gives a strong driving force for carbon to diffuse from the low alloy to the high alloy steel despite the much higher carbon content of the latter, i.e. uphill diffusion. In fact, this example is similar to the Darken experiment discussed earlier except that we now have to consider several phases, mainly ferrite or austenite and different carbides, in the two parts of the composite.

We are now ready to set up the simulation. We add the six phases we found in the equilibrium calculation and the homogenization simulation will thus be activated automatically. Despite the fact that the calculation accounts for six different elements and six different phases it is surprisingly fast and is completed within a few minutes. It should be mentioned that we have neglected elements like Si and Mn that typically has a content below 0.5 mass%.

Table 6-2: Equilibrium fraction of phases in the two steels at 760 °C

Stable phase	Volume fraction	
	Low-alloy steel	High-speed steel
BCC_A2	0.496	0,833
FCC_A1	0,469	-
MC(FCC_A1#2)	0,003	0.034
M ₂ C (HCP_A3#2)	0,001	-
M ₂₃ C ₆	0,031	0.04
M ₆ C	0	0.093

From the simulation we notice that although the high-speed steel contains twice as much carbon as the low alloy steel C the latter is decarburized and the tool steel carburized. This is a direct consequence of its much lower carbon activity.

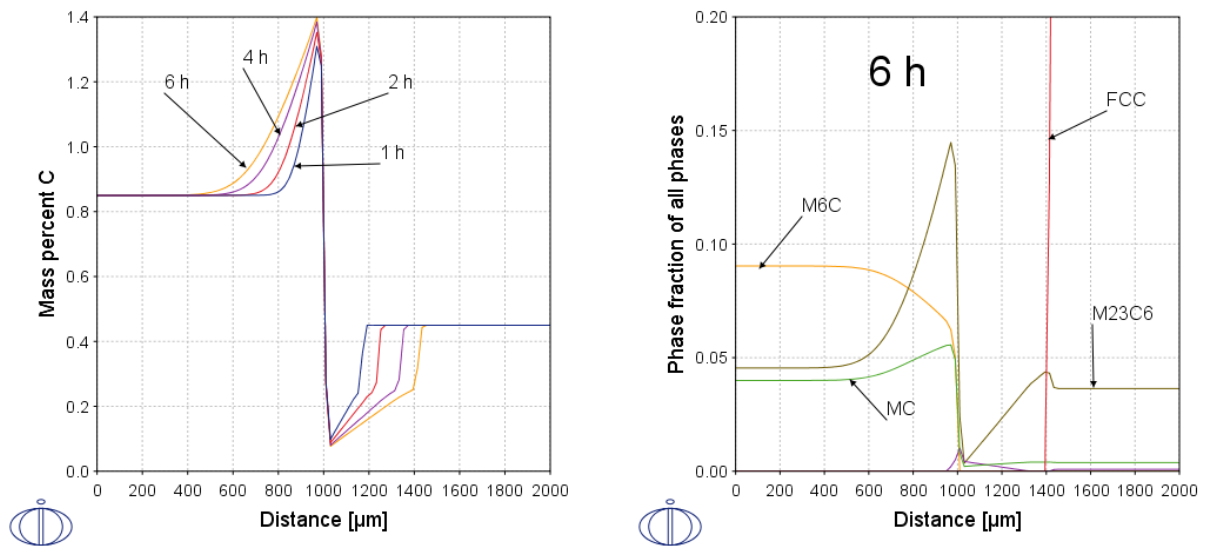


Figure 6-4: Left: Over-all C-concentration profiles in a steel composite heat treated at 760 °C for times indicated. Right: Fraction of phases after 6 h at 760 °C.

The decarburizing of the low alloy steel may lead to problems because its decarburized zone has a much lower strength than the original low-alloyed steel.

One may now wonder if the problem becomes worse as a consequence of the austenitizing or not. In a first step we calculate the equilibrium in each steel separately at the austenitizing temperature 1215 °C, i.e. assuming that there is no reaction between the steels. We then find that the low-alloy steel is fully austenitic with a carbon activity relative graphite of 0.10. The high-speed steel is austenitic with MC and M₆C carbides and a carbon activity relative graphite of 0.08. This simple calculations show that the difference in carbon activity is much smaller and almost negligible at the austenitizing temperature. This means that we would expect a considerable reversion of the carbon transfer during austenitizing, i.e. a healing.

This process can be simulated using DICTRA and the output after 6 h at 760 °C as input. The result is shown below.

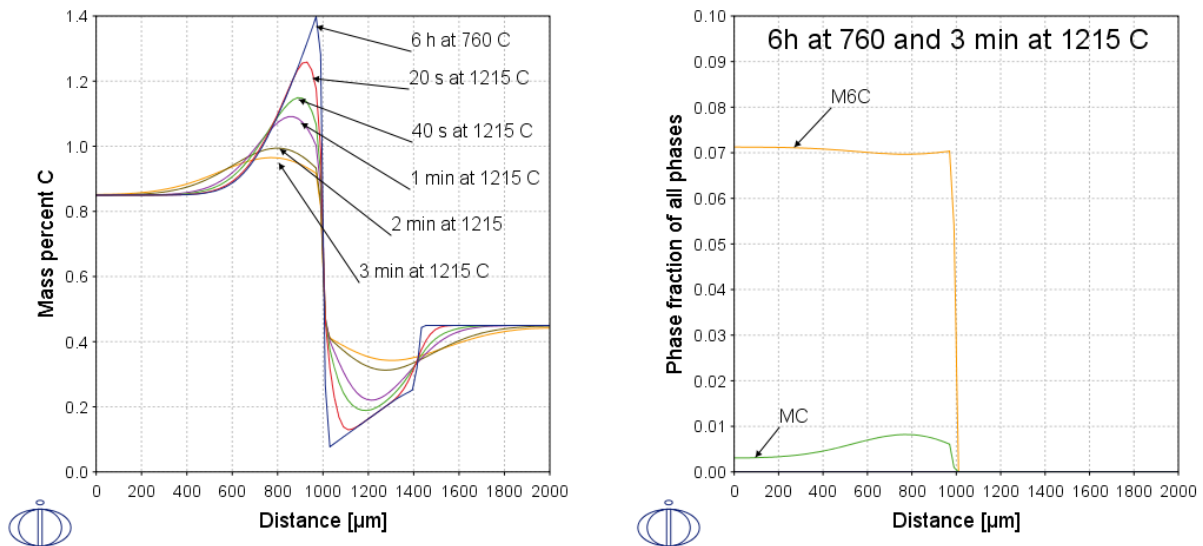


Figure 6-5: Left: Over-all C-concentration profiles in a steel composite heat treated at 760 and 1215 °C for times indicated. Right: Fraction of phases after 6h at 760 and 3 min at 1215 °C.

The simulation thus confirms the conclusion from the thermodynamic calculation, i.e. that there is a healing process during austenitizing.