INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

Vysoká škola báňská – Technická univerzita Ostrava

Physical Metallurgy

Didactic Text

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Preface

Study support to the subject ***Physical Metallurgy*** is primarily intended for students of combined studies. In the combined form of study, there is a much smaller proportion of direct contact teaching, which makes this study much more difficult for students. Our study support to the subject *Physical metallurgy* can help you to eliminate this handicap to a certain extent. These is not a new textbook, there are enough of those. The study support is a replacement, if possible, for the lack of direct instruction and interlink to a subsequent study of professional literature itself, whether it be textbooks or other publications.

When writing this support I have tried to maximize the clarity of the text. This cannot be achieved, at least in my opinion, without some simplification, reduction and sometimes even inaccuracy. If someone feels that simplification is too much, I apologize in advance. But my experiences in teaching this subject led me to a result which is just this text.

Despite careful checking of the text, it is almost certain that I did not avoid errors, typing errors, etc., maybe even factual mistakes. I will be most grateful, if you notify me about them so I can gradually correct them. You can notify me either directly during classwork or by email to jaroslav.sojka@vsb.cz .

I wish all of you who will use this study support, a lot of strength in your study!

The Author

Study Guide

This study support is divided into four major units - chapters. Most of them are divided into smaller units - subchapters. For each subchapter, an indicative study time required is given. This is only a rough guide of how long it would take you to manage the whole unit. So do not take it as something that is clearly given and do not hesitate to get to study even if you have less.

How would you work with the study support?

Basic learning units (**subchapters**) are numbered as 2.1, 2.2, 3.1, etc.

- Try to read the entire subchapter.
- Try to draw most of the figures free hand, especially charts and diagrams.
- If the subchapter contains **solved examples**, solve them so that you rewrite them and perform calculations themselves.
- Then have a look at the **summary of terms** and try to answer whether these concepts say something to you.
- You can also look at the **questions** and try to formulate answers to at least some of them.

If you succeed right at first, it would be excellent, but rather we do not suppose it.

So read it once more, make notes about what you consider to be essential. Again, draw pictures, diagrams, etc. Read again the summary of the terms and try to describe them in your own words. Then you can start to answer the questions. The questions are worded simply so that you find the answer in the text. Answer briefly **in writing!!!** Answers to questions are in the **Key**, which is always at the end of major chapters. Compare the answers in the Key with your answers. Answers in the Key and your answers may not match exactly, but they should have the same meaning.

Then you can proceed to the tasks to be solved (if any).

If you have any problems with which you need help, please contact teachers whose names you will learn during the introductory lecture, either directly or via email. You can always approach the guarantor of the study subject, Prof Jaroslav Sojka, on the e-mail address jaroslav.sojka@vsb.cz or Tel. No. 596994245.

A semester thesis will be written within this study subject. You will get detailed guidance on its writing, scope, etc. in the course of the contact teaching, most likely during the second lecture, along with a recommendation on what literature sources are useful, etc.

Table of Contents

1. INTRODUCTION

Study time: I do not mention - this is a familiarization chapter only

Objective After reading this chapter, you should:

- Get a taste of embarking on a detailed study of all the other chapters.

The study subject ***Physical Metallurgy*** typically includes a variety of fields of metallurgy, which are relatively closely bound to physics, in particular to solid state physics. Since ***Physics of the Solid State*** is a separate study subject of the follow-up master's degree in *Advanced Technical Materials*, we agreed that the subject ***Physical Metallurgy*** will include only those sections that are not contained in other subjects, i.e. they are included neither in the subject ***Physics of the Solid State***, nor ***Phase Transitions***.

The subject ***Physical Metallurgy*** therefore focuses on four areas, namely:

- solid state diffusion,
- strengthening mechanisms in metallic materials,
- segregation phenomena in metallic materials, and
- recrystallization of metallic materials and related processes.

Each of these areas you have come across with in the bachelor's degree, especially in the following courses: Introduction to the Study of Materials, Materials Science, Structure and Properties of Solids, and partly in the course Fundamentals of Heat Treatment. ***Physical Metallurgy*** will therefore build on these courses and often you will have to refresh relevant passages that you have studied in the bachelor's degree, not to linger unnecessarily at something you have already completed and be able to pursue something new.

So let’s begin!

2. SOLID STATE DIFFUSION

2.1. Basic characteristics and classification

Study time: 0.5 hours

Objective After reading this part, you should be able to:

- Define the concept of solid state diffusion and explain how diffusion takes place.
- Describe some types of classification of diffusion processes.
- Explain how solid state diffusion is related to the vibrational motion of atoms.

Presentation

❑ From the history of diffusion as a scientific discipline

Our ancestors, of course, were aware of the existence of diffusion processes a very, very long time ago. But the scientific basis was given to diffusion by Thomas Graham (British, 1805-1860), Adolf Eugen Fick (German, 1829-1901) and William Chandler Roberts-Austen (British, 1843-1902). Partly also the work of Albert Einstein and Svante August Arrhenius (Sweden, 1859-1927) dealt with diffusion.

Thomas Graham was a chemist and the first to formulate the theory of diffusion in gaseous substances. Adolf Eugen Fick was born into a family of German civil engineer. He was interested in mathematics from his childhood and wished to study it. On the advice of older brothers, however, he became a doctor like them. But love of mathematics stayed with him his whole life and it was he who formulated the laws that you know as Fick's laws of diffusion. As far as the solid state diffusion is concerned, W. C. Roberts-Austen was probably the first man who described some of its laws and he is the same man, after whom the solid solution of carbon in gamma iron has been named, i.e. austenite. Roberts-Austen devoted himself, inter alia, to the study of diffusion of precious metals in metals having a relatively low melting point, such as lead, tin and bismuth and formulated one of the first findings that concern diffusion in solids. Also Albert Einstein, who formulated the theory of random jumps and the associated mean square displacement (we will pay a brief attention to it below), dealt with solid state diffusion. S. A. Arrhenius formulated his famous equation, which was named after him and which characterizes the dependence of thermally activated processes on the temperature. You will certainly recall that you have come across the term of Arrhenius equation.

❑ Definition of solid state diffusion

Diffusion ranks among the so-called transport phenomena. Diffusion can be defined as the transport of particles of matter, mostly of atoms or ions, where the driving force for diffusion is to reduce Gibbs free energy, or reduce the chemical potential of components of the system. Diffusion is therefore governed by the laws of thermodynamics. Most often, diffusion takes place so that particles of matter move (diffuse) from the locations of higher concentration to areas of lower concentration of a certain element. Thus, diffusion reduces the concentration gradient, but also, and more importantly Gibbs free energy, or chemical potential of the components of the system decreases. This conventional type of diffusion, in which the concentration gradient is reduced, is known in English as "down-hill diffusion". In certain cases, which will be discussed later, diffusion may take place so that the differences in concentration increase. It is essential, however, that despite higher concentration differences decrease in Gibbs free energy occurs in this type diffusion, or atoms in this case also move from the areas with a high value of chemical potential to regions with a low value of the chemical potential. This less conventional type of diffusion, which leads to the increase of the concentration gradient, has become known in English as "up-hill diffusion".

Diffusion generally stops when the value of chemical potential of the individual components at any point in the system is the same, i.e. the system is in equilibrium state.

❑ Some division in the area of diffusion

Solid state diffusion takes place through the so-called elementary jumps of atoms. You should already know how these elementary jumps can take place (or if you forgot, refresh your knowledge by reading the study support for the course *Structure and Properties of Solids*).

Just to repeat, we note that the mechanisms of jumps of atoms during diffusion can be divided into:

- **individual mechanisms,** which include an elementary jump in interstitial diffusion and vacancy diffusion of substitutional atoms;
- **group mechanisms,** which include e.g. direct exchange of atoms or cyclic exchange of atoms during diffusion of substitutional atoms.

In terms of atoms and components undergoing diffusion, the diffusion can be divided into:

- **Auto-diffusion** (sometimes also called self-diffusion), during which only atoms of the basic component of the system diffuse (strictly speaking auto-diffusion can occur only in single-component systems)**;**
- **heterodiffusion,** during which atoms of various components diffuse, mostly atoms of dissolved elements.

In case of heterodiffusion, we further distinguish whether diffusion of atoms of such solutes takes place that are present only in very low concentrations, i.e. their diffusion does not significantly affect the diffusion of atoms of the basic component. The second case is the one, where the concentration of atoms of dissolved components is higher and their diffusion causes also the diffusion of atoms of the basic component.

❑ With what the solid state diffusion is associated?

Solid state diffusion is associated with the vibrational motion of atoms. You may remember that we said that even in the solid state the atoms are not at rest, but they perform vibrational motion around the nodal points in a crystal lattice. The vibrational motion is characterized by two variables, namely the frequency and amplitude of the vibrational motion. In the case of the vibrational motion of atoms it applies that the frequency of vibrational motion is essentially independent of temperature, and is about 10^{13} s^{-1} (atoms vibrate extremely quickly; they accomplish 10 billion of vibrations per second!). With increasing temperature, however, the amplitude of the vibrational motion of atoms increases, and the mean vibrational energy of the atom is proportional to

$$3.k.T \, , \qquad \text{Eq. 2.1}$$

where k is Boltzmann constant;

T is absolute temperature.

Vibrational motion of the atoms leads to collisions between neighbouring atoms and thus the transfer of kinetic energy. As a result of the collision, some atoms may achieve energy sufficient to perform an elemental jump (e.g. in the case of interstitial atom, this will be the jump from one interstitial position to another interstitial position - neighbouring). Yet it is necessary that the adjacent atoms are in a position (outside their equilibrium position) to allow such a jump. And this is actually the elementary “step” in the solid state diffusion. The situation is schematically illustrated in Figure 2.1, which shows the jump of interstitial atom from one interstitial position to an adjacent interstitial position. In this elementary jump atom must overcome an energy barrier marked ΔG_m in the picture. Energy needed to jump is the vibrational energy plus energy derived from collisions with neighbouring atoms.

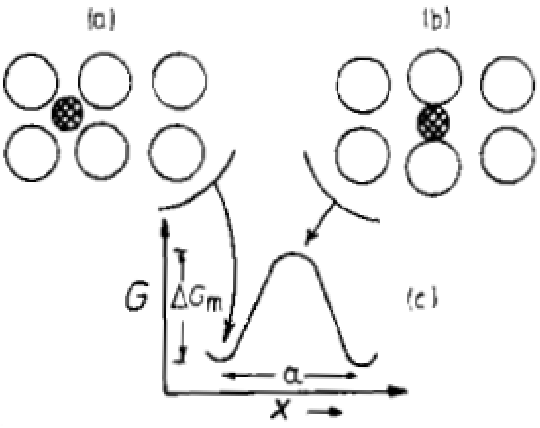


Fig. 2.1 Schematic representation of the elementary jump during the diffusion of interstitial atom and the corresponding energy barrier

Σ Summary of terms from 2.1

After studying this part, following terms should be clear to you:

- **Solid state diffusion, the driving force for diffusion**
- **Down-hill diffusion, up-hill diffusion**
- **Individual mechanisms of jumps, group mechanisms of jumps**
- **Auto-diffusion, heterodiffusion**
- **Vibrational motion of the atoms, the frequency and amplitude of vibrations of atoms**

? Questions to 2.1

1. Define diffusion.
2. What is the driving force for diffusion?
3. What does the term down-hill diffusion mean?
4. What does the term up-hill diffusion mean?
5. When does the solid state diffusion stop?
6. Which mechanisms are among the so-called individual mechanisms of diffusion?
7. Which mechanisms are among the so-called collective mechanisms of diffusion?
8. What does the term auto diffusion mean?

9. What does the term heterodiffusion mean?
10. Which process is necessary in order to allow the solid state diffusion?
11. What characterizes the vibrational motion?
12. What is the frequency of vibrational motion of atoms in solid state?
13. Does the frequency of vibrational motion of atoms depend on temperature?
14. Does the amplitude of vibrational motion of atoms depend on temperature?

2.2. Interstitial diffusion

Study time: 6 hours

Objective After reading this subchapter, you should be able to:

- Derive the first and second Fick's law for the case of interstitial diffusion.
- Characterize the effect of temperature on the coefficient of diffusion of interstitial elements.
- Solve selected tasks of unsteady state diffusion important in metallurgical practice.

Presentation

First, we will deal with interstitial diffusion or diffusion of interstitially dissolved atoms. The reason is very simple; interstitial diffusion is slightly easier than substitution diffusion, and so let’s start with it.

❑ Derivation of Fick’s First Law

You have probably already come across Fick's first law and so you know that it is the law that describes the steady state diffusion, i.e. diffusion, in which the concentration does not change over time and remains constant. (*In practice, this is a highly unusual example, but it is easier to solve and so we mention it as the first one*.) You also know that the Fick's first law connects the diffusion flux with diffusion coefficient and concentration gradient. So far you have not derived this law, but in the master's degree now we have to make reparation for it. If you derive something, you should remember it better and longer, and you should be able to look at the problem in a broader context.

We will therefore derive Fick's first law for the case of diffusion of interstitial atoms. For further simplification, we assume that diffusion takes place in a simple cubic lattice. In this type of lattice, the only interstitial positions are the centres of elementary cells. The situation is schematically illustrated in Figure 2.2.

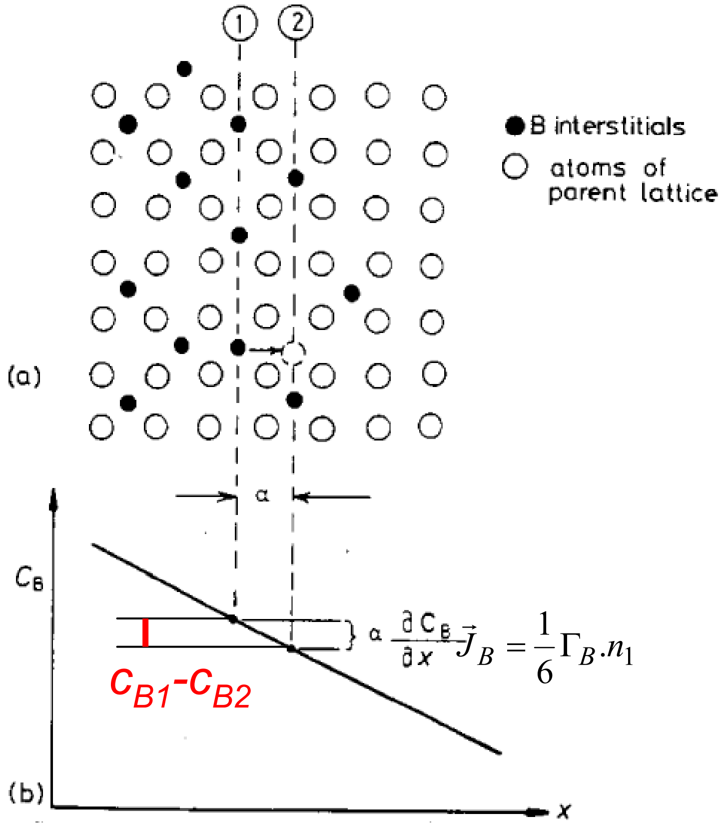


Fig. 2.2 Schematic picture to derive Fick's first law for interstitial diffusion

In the picture, we consider two planes 1 and 2, in which interstitial atoms are located marked by black dots like B atoms. The number of interstitial atoms in plane 1 per unit area is greater than the number of interstitial atoms per unit area in the plane 2.

Let the number of interstitial atoms per unit area of plane 1 be $\boldsymbol{n_1}$ at./m^2 and let the number of interstitial atoms per unit area of plane 2 be $\boldsymbol{n_2}$ at./m^2.

We therefore assume that:

$$n_1 > n_2 \qquad \text{Eq. 2.2}$$

Now we express the diffusion flux of B atoms from plane 1 to plane 2 and vice versa. *(To repeat - the diffusion flux is the amount of substance - such as the number of atoms that passes through unit area per unit time. It can be expressed e.g. as the number of at./m^2.s, but also otherwise.)*

Diffusion flux of interstitial atoms from plane 1 to plane 2 can be expressed as:

$$\vec{J}_B = \frac{1}{6}\Gamma_B.n_1, \qquad \text{Eq. 2.3}$$

where $\boldsymbol{\Gamma_B}$ is the jump frequency of B atoms from one interstitial position to another interstitial position (s^{-1}).

But still we have to explain where did that the sixth in Equation 2.3 emerge. If an atom in interstitial position is in plane 1, it has a total of six adjacent interstitial positions into which it can jump. But only one of these six positions is in plane 2, in which we are interested. Other 4 interstitial positions rest in plane 1, and one position is in the plane to the left of plane 1. If we are interested in diffuse flux from plane 1 to plane 2, the equation must contain one sixth.

Quite analogously, we can express the diffusion flux of B atoms from plane 2 to plane 1:

$$\overleftarrow{J}_B = \frac{1}{6}\Gamma_B . n_2 \qquad \text{Eq. 2.4}$$

Real diffusive flux of B atoms from plane 1 to plane 2 is given by the difference of the above diffusion fluxes, and can be expressed by the following equation:

$$J_B = \frac{1}{6}\Gamma_B .(n_1 - n_2) \qquad \text{Eq. 2.5}$$

Given that in the area of diffusion it is preferable to express the quantity of diffusing atoms using concentrations, we convert values $\boldsymbol{n_1}$ and $\boldsymbol{n_2}$ to the concentration of B component atoms (at/m^3).

It is true that the concentration of B component atoms in plane 1 is:

$$c_{B1} = \frac{n_1}{\alpha} \qquad \text{Eq. 2.6}$$

Completely analogous equation applies to the concentration of B component atoms in plane 2:

$$c_{B2} = \frac{n_2}{\alpha} \qquad \text{Eq. 2.7}$$

If we modify Equation 2.5 so that it features the concentration of B component, we get the following equation:

$$J_B = \frac{1}{6}\Gamma_B . \alpha .(c_{B1} - c_{B2}) \qquad \text{Eq. 2.8}$$

The difference in concentrations of B atoms in plane 1 and plane 2 can be expressed according to Figure 2.2 as follows:

$$(c_{B1} - c_{B2}) = -\alpha \frac{\partial c_B}{\partial x} \qquad \text{Eq. 2.9}$$

(Note: This follows from the fact that the partial derivative of the concentration of B component with respect to distance x is actually the slope of the line, which illustrates the dependence of the concentration of B component on the distance x in Figure 2.2. There must be a minus sign in front of the expression, because the concentration difference is positive, while the partial derivative of the concentration of B component with respect to distance is negative.)

If we introduce Equation 2.9 into Equation 2.8, we get the following relationship:

$$J_B = -\frac{1}{6}\Gamma_B.\alpha^2 \frac{\partial c_B}{\partial x} \qquad \text{Eq. 2.10}$$

Expression $\frac{1}{6}\Gamma_B.\alpha^2$ implies the diffusion coefficient of B component, we can therefore write:

$$D_B = \frac{1}{6}\Gamma_B.\alpha^2 \qquad \text{Eq. 2.11}$$

and after modification we get the resulting form from Equation 2.10 as follows:

$$J_B = -D_B \frac{\partial c_B}{\partial x}, \qquad \text{Eq. 2.12}$$

This is already the form of Fick's first law, which you have come across and which applies to the steady state diffusion running in one direction (in the direction of X axis).

Fick's first law therefore says that during the steady state diffusion, the diffusion flux of a diffusing component is directly proportional to the diffusion coefficient of the diffusing component and its concentration gradient. The minus sign before the expression is not a mistake. The diffusion flux of atoms from plane 1 to plane 2 is positive, the diffusion coefficient is also a positive value, but the partial derivative of concentration with respect to distance is a negative number, because the concentration versus distance is a downward sloping straight line in Figure 2.2. To get a positive number as the diffuse flow, the expression must be preceded by a minus sign.

From Equation 2.12, the **diffusion coefficient is** sometimes **defined as the amount of substance (e.g. atoms) which passes through unit area per unit time at unit concentration gradient of the diffusing component. The unit of diffusion coefficient is perhaps somewhat surprising – it is m^2/s. This can be easily determined from Equation 2.12.**

In practice, even in the steady state diffusion the situation is more complicated because the diffusion coefficient may depend e.g. on the concentration of the diffusing component. For example, the coefficient of diffusion of carbon in gamma iron increases with increasing carbon concentration, because there is some increase in the lattice parameter of gamma iron and carbon atoms then "travel more easily".

Solved example 2.1:

Problem:

Consider Feγ - C system at temperature of 1000°C. The diffusion coefficient of carbon in gamma iron at this temperature is $D_C = 2.5 \cdot 10^{-11}$ m^2/s; gamma iron lattice parameter a =

0.37 nm. Determine the frequency of carbon atom jumps from one interstitial position to another at a given temperature.

Solution:

We start from Equation 2.11, but it has to be modified for the gamma iron lattice, which has a face centred cubic (fcc) arrangement. Atom in the interstitial position here has a total of 12 neighbouring positions to which it can jump, yet only 4 out of 12 will lie in the direction of diffusion. The modified Equation 2.11 for fcc lattice will therefore be as follows:

$$D_C = \frac{1}{3}\Gamma_C.\alpha^2$$

Given that the lattice parameter is mentioned, we must ascertain its relationship with the distance between neighbouring planes for interstitial position in the fcc lattice. If you look at relevant pictures in the study support Introduction to the Study of Materials, you will find that the distance between the planes in which interstitial positions exist is equal to a/2, where a is the lattice parameter.

Therefore, it applies that:

$$\alpha = \frac{a}{2}.$$

After substituting it into the equation above we get:

$$D_C = \frac{1}{3}\Gamma_C.\frac{a^2}{4} = \frac{1}{12}\Gamma_C.a^2$$

If we substitute the numerical values into the equation after modification, the frequency of jumps of carbon atoms is as follows:

$$\Gamma_C = \frac{12.D_C}{a^2} = \frac{12 \cdot 2.5 \cdot 10^{-11}}{(0.37 \cdot 10^{-9})^2} \cong 2.2 \cdot 10^9 \text{ s}^{-1}.$$

Conclusion:

At a temperature of 1000°C, the frequency of jumps of carbon atoms during interstitial diffusion in gamma iron is about $2.2 \cdot 10^9$ s^{-1}, which means that roughly every ten thousandth thermal oscillation leads to the jump of atom from one interstitial position to another.

❑ Random jumps and the mean square displacement

Diffusing atoms are poor devils in a way, because they work awfully hard during diffusion. They in fact can't move solely in the direction of the concentration gradient. They gain the energy to jump by collisions with neighbouring atoms and sufficient energy may come from an atom which does not induce the jump in the direction of the diffusion gradient, but in a random direction. Jumps in the direction of a concentration gradient will be slightly predominant, but besides that atoms perform a huge amount of jumps in diffusion in other

directions, as well. This aspect of diffusion was dealt with, among others, by Albert Einstein, who formulated the thesis that most jumps in diffusion is essentially random.
Figure 2.3 shows how the random motion of atoms in diffusion may look like.

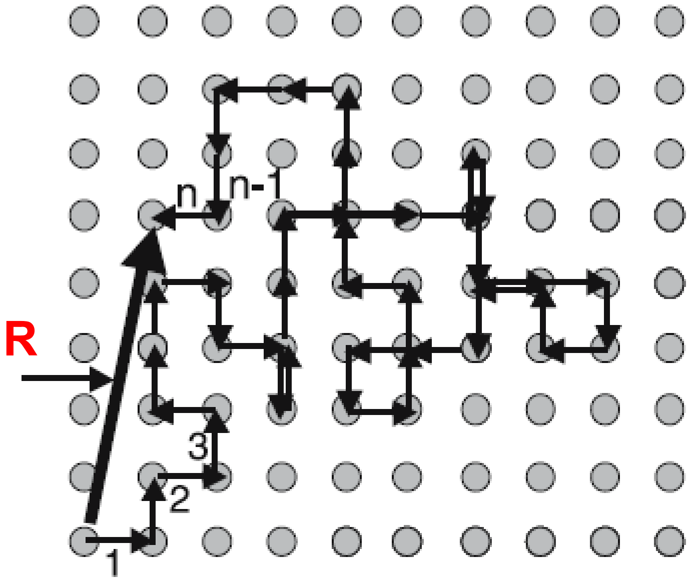


Fig. 2.3 Schematic representation of random jumps in diffusive motion of atoms

Figure 2.3 shows the overall movement of the atom in diffusion as a sequence of random jumps and the diffusion path R, which is defined as the distance between the initial and final position of the atom.
According to the theory of random jumps, the diffusion path R is:

$$R = \alpha\sqrt{n}\,, \qquad \text{Eq. 2.13}$$

where α is the length of the elementary jump, and
n is the number of elementary jumps.
If jump frequency is Γ and time is t, then it applies for n that:

$$n = \Gamma.t \qquad \text{Eq. 2.14}$$

Thus we can write for R:

$$R = \alpha\sqrt{\Gamma.t} \qquad \text{Eq. 2.15}$$

If we substitute the expression for Γ from Equation 2.12 into Equation 2.15, we get:

$$R = \alpha\sqrt{\frac{6.D_B}{\alpha^2}.t} = \sqrt{6.D_B.t} \Rightarrow$$
$$R = 2{,}4\sqrt{D_B.t} \cong \sqrt{D_B.t} \qquad \text{Eq. 2.16}$$

Equation 2.16 is sometimes written in the form as follows:

$$R^2 = D_B.t \qquad \text{Eq. 2.17}$$

The variable $\boldsymbol{R^2}$ is referred to as the **mean square displacement** that is proportional to the diffusion coefficient and the time over which diffusion takes place.

Equations 2.16 or 2.17 are very useful because they provide us with a simple method to determine the approximate distance at which a particular element can diffuse over time t.

Solved example 2.2

Problem:

Consider the task of example 2.1 and determine the diffusion path R and the total distance travelled by the carbon atom in 1 second.

Solution:

For the diffusion path R, it applies that:

$$R = 2{,}4\sqrt{D_C.t}$$

After substitution:

$$R = 2{,}4\sqrt{2{,}5\cdot 10^{-11}.1} = 12\cdot 10^{-6}\ \text{m}$$

The total distance travelled by a carbon atom, is the product of the length of elementary jump α and the number of jumps n. We can therefore write:

$$n.\alpha = \Gamma.t.\alpha = 2\cdot 10^{9}.1\cdot 0\cdot 37\cdot 10^{-9}\ \frac{\sqrt{2}}{2} = 0.5\ \text{m}$$

(Note: The length of the elementary jump of carbon atom in the gamma iron lattice is half the length of the wall diagonal of elementary cube.)

Conclusion:

The mean diffusion path of carbon atom at a temperature of 1000°C and time of 1 second is equal to approximately 12 μm. But the total distance travelled by a carbon atom is much longer and is about half a metre.

That is the difference. So perhaps you agree that atoms work hard during diffusion.

❑ Effect of temperature on diffusion

From a probability viewpoint, the fraction of atoms having the energy required to overcome the energy barrier for diffusion, can be expressed as:

$$\exp\left(-\frac{\Delta G_m}{RT}\right) \qquad \text{Eq. 2.18}$$

where ΔG_m is the free activation enthalpy needed to diffusion,

R is the universal gas constant, and

T is absolute temperature.

The frequency of successful jumps will then be the product of the frequency of thermal vibrations of atoms ν and the above mentioned expression. Thus we can write:

$$\Gamma_B = \nu.\exp\left(-\frac{\Delta G_m}{RT}\right) \qquad \text{Eq. 2.19}$$

The free activation enthalpy can be expressed using the enthalpy and entropy as:

$$\Delta G_m = \Delta H_m - T.\Delta S_m \qquad \text{Eq. 2.20}$$

If we substitute equations 2.19 and 2.20 into the Equation 2.11 for calculation of the diffusion coefficient, we get:

$$D_B = \frac{1}{6}\Gamma_B.\alpha^2 = \left[\frac{1}{6}\alpha^2.\nu.\exp\left(-\frac{\Delta S_m}{R}\right)\right].\exp\left(-\frac{\Delta H_m}{RT}\right) \qquad \text{Eq. 2.21}$$

The member in square brackets is often referred to as the frequency or pre-exponential factor ***D***$\boldsymbol{D_{B0}}$ and when introduced, the relationship 2.21 can be converted to a much simpler form featuring only the activation enthalpy of diffusion ΔH or activation energy of diffusion ΔQ:

$$D_B = D_{B0}.\exp\left(-\frac{\Delta H_m}{RT}\right) \cong D_{B0}.\exp\left(-\frac{\Delta Q_m}{RT}\right) \qquad \text{Eq. 2.22}$$

Equation 2.22 means that the diffusion coefficient increases exponentially with the increasing temperature, i.e. at higher temperatures the diffusion takes place more easily and atoms can diffuse over a longer distance during the same time.

Now let us consider how we could find the activation energy of diffusion for a particular element or possibly the value of the frequency factor. To do this, we need to know the values of diffusion coefficients at different temperatures.

Equation 2.22 can be converted to a linear, i.e. straight line dependency, by logarithmic calculation:

$$\ln D_B = \ln D_{B0} - \frac{\Delta Q_m}{R}.\frac{1}{T} \qquad \text{Eq. 2.23}$$

This equation is actually the equation of a line

$$y = q + k.x, \qquad \text{Eq. 2.24}$$

where $y = \ln D_B$ and $x = \frac{1}{T}$.

Thus we represent the dependency of lnD_B on $1/T$. If we obtain values k and q using regression analysis, we can calculate both the activation energy of diffusion and pre-exponential factor from them as follows:

$$q = \ln D_{B0} \Rightarrow D_{B0} = e^q \qquad \text{Eq. 2.25}$$

$$k = -\frac{\Delta Q_m}{R} \Rightarrow \Delta Q_m = -k.R \qquad \text{Eq. 2.26}$$

Solved example 2.3

Problem:

For temperature dependence of the diffusion of carbon in alpha iron, following values of the carbon diffusion coefficient D_C depending on temperature were obtained:

Temperature (°C)	C diffusion coefficient ($cm^2.s^{-1}$)
300	4.3986E-09
400	6.0418E-08
500	4.2132E-07
600	1.8829E-06
700	6.1859E-06
800	1.6281E-05

Determine the pre-exponential factor D_0 and activation energy ΔQ_C for diffusion of carbon in alpha iron.

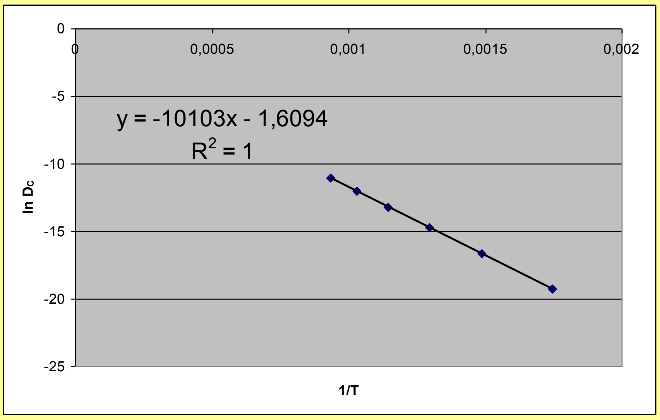
Solution:

We know from the above that for finding the values of the activation energy of diffusion and pre-exponential factor we must convert the temperature dependence of the diffusion coefficient to the linear dependence in the coordinates of 1/T versus $\ln D_C$. This is best done in EXCEL.

Temperature (°C)	Temperature (K)	D ($cm^2.s^{-1}$)	1/T (K^{-1})	lnD
300	573	4.3986E-09	0.001745	-19.242
400	673	6.0418E-08	0.001486	-16.622
500	773	4.2132E-07	0.001294	-14.6799
600	873	1.8829E-06	0.001145	-13.1827
700	973	6.1859E-06	0.001028	-11.9932
800	1073	1.6281E-05	0.000932	-11.0255

We construct the graph 1/T versus lnD and run regression analysis.

The graph is shown below:



Slope of the line k = -10103; quotient (segment on Y axis) =-1.6094

We determine the pre-exponential factor D_0 from Equation 2.25:

$$D_{C0} = e^{q} = e^{-1.6094} = 0.2 \text{ cm}^2.\text{s}^{-1}.$$

We determine the activation energy for diffusion of carbon in alpha iron from Equation 2.26:

$$\Delta Q_m = -k.R = -(-10103)\cdot 8.314 = 83996 \text{ J.mol}^{-1}.$$

Conclusion:

For the specified values, the pre-exponential factor for diffusion of carbon in alpha iron is 0.2 $\text{cm}^2.\text{s}^{-1}$ and the activation energy for diffusion of carbon in alpha iron is 83996 J.mol^{-1}.

❑ Derivation of Fick’s Second Law

You have probably come across Fick's second law, too and know that it relates to such diffusion processes where the concentration in each location varies with time. These processes are, in practical terms, much more common, so we can say that Fick's second law is more important than the first one.

Again, we will derive this law for interstitial diffusion that takes place in one direction and it will be the usual downhill diffusion.

Schematic picture that will help us in derivation of Fick's second law is shown in Figure 2.4.

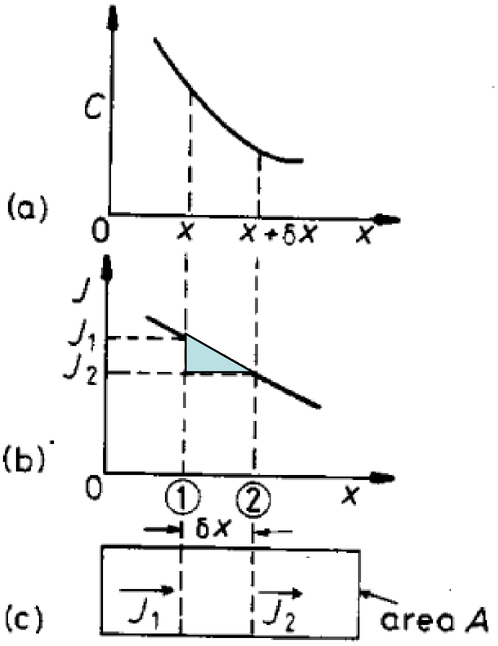


Fig. 2.4 Schematic picture to derive Fick's second law

Consider a material in which there is a diffusion of interstitial B element along the X axis. The dependence of the concentration of B element on the distance is shown in Figure 2.4a, while Figure 2.4b shows the dependence of diffusion flux of B element on the distance. Consider two planes (1 and 2) in the material, a short time distance away (δx) and define an area with size A in both planes.

The number of B atoms that pass to plane 1 from the left in a short period of time δt can be expressed by the following equation:

$$at_{B1} = J_1.A.\delta t \qquad \text{Eq. 2.27}$$

where J_1 is the diffusion flux in plane 1,

A is an area defined in plane 1,

δt is the examined short period of time.

By analogy, the number of B atoms that pass from plane 2 to the right in a short period of time δt can be expressed as:

$$at_{B2} = J_2.A.\delta t \qquad \text{Eq. 2.28}$$

At time δt, the number of atoms between planes 1 and 2 changes by:

$$(J_1 - J_2).A.\delta t \qquad \text{Eq. 2.29}$$

This change can be expressed using the change in the concentration of B element as follows:

$$\delta c_B.A.\delta x = (J_1 - J_2).A.\delta t \qquad \text{Eq. 2.30}$$

where δc_B is the change in the concentration of B element between planes 1 and 2.

It can be derived from Figure 2.4 that the difference of diffusion fluxes J_1 and J_2 is equal to:

$$(J_1 - J_2) = -\delta x.\frac{\partial J}{\partial x} \qquad \text{Eq. 2.31}$$

because $\frac{\partial J}{\partial x}$ is the slope of the line that expresses the dependence of diffusion flux on the distance x.

After substituting Equation 2.31 into Equation 2.30 we obtain equation:

$$\frac{\delta c_B}{\delta t} = -\frac{\partial J}{\partial x} \qquad \text{Eq. 2.32}$$

and for time t converging to zero we obtain the equation:

$$\frac{\partial c_B}{\partial t} = -\frac{\partial J}{\partial x} \qquad \text{Eq. 2.33}$$

If we substitute the expression corresponding to the Fick's first law (Eq. 2.12) into Equation 2.33 for the diffusion flux, we obtain the equation:

$$\frac{\partial c_B}{\partial t} = \frac{\partial}{\partial x}\left(D_B \frac{\partial c_B}{\partial x}\right) \qquad \text{Eq. 2.34}$$

This equation already expresses the Fick's second law provided that the diffusion coefficient depends on the concentration.

If the diffusion coefficient is independent of concentration, Fick's second law is mentioned in the form as follows:

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} \qquad \text{Eq. 2.35}$$

Equation 2.35 is the most common expression of Fick's second law for diffusion taking place in one direction. This relationship can be very simply interpreted so that the change in concentration of a diffusing element with time is directly proportional to the diffusion coefficient and the second derivative of concentration with respect to distance.

Equation 2.35 is a differential equation whose solution can be very difficult. Consequently, we will tackle some specific diffusion problems, which are based on Fick's second law and which are very important in metallurgy.

❑ Constant source diffusion – e.g. carburization of steel

One of the most important problems of unsteady state diffusion is the diffusion from a constant diffusion source. Typical example might be the saturation of steel surface with e.g. carbon, but in general it might be the saturation of surface of any metal material with any element. This process is shown schematically in Figure 2.5.

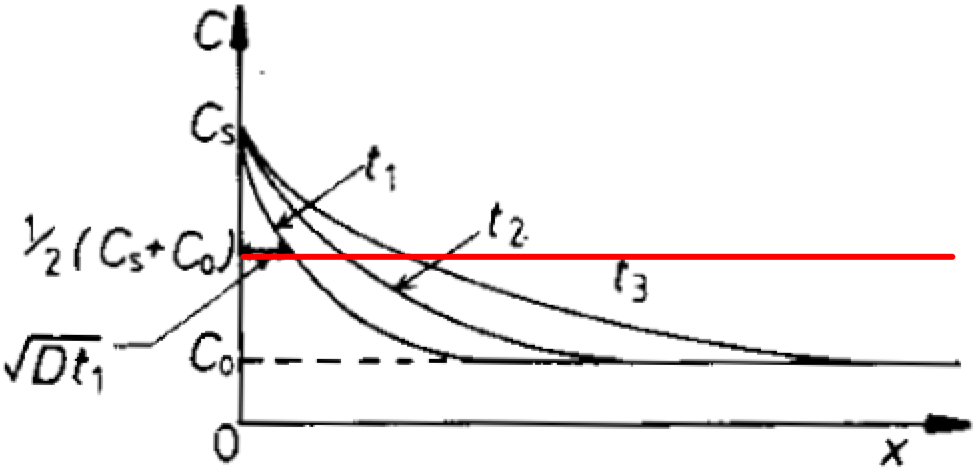


Fig. 2.5 Schematic representation of diffusion from a constant source – carburization of steel

The problem can be seen as follows: At time t = 0, the carbon content at any point below the steel surface, i.e., for x> 0, is equal to c_0. There is a constant carbon concentration c_s on the steel surface at all times, i.e. over arbitrary time interval *(this concentration is given by e.g. composition of the gaseous atmosphere during steel cementation*).

The concentration of carbon in subsurface layers will change just as shown by curves in Figure 2.5 for three different diffusion times, with $t_1 < t_2 < t_3$.

This concentration c (x, t), which is a function of depth below the surface x and diffusion time t can be calculated from the equation:

$$\frac{c(x,t)-c_0}{c_S-c_0}=1-erf\left[\frac{x}{2\sqrt{D.t}}\right] \qquad \text{Eq. 2.36}$$

where c_0 is the initial concentration of the corresponding element in the material,

c_S is the surface concentration of the element (given by intensity of the diffusion source) and is a constant,

x is the depth under surface,

D is the diffusion coefficient for the element in question,

t is the time of diffusion.

Equation 2.36 is the solution to Fick's second law for this particular case. In the equation, there is a special function that is marked *erf*. *Erf* is the so called error function, which also appears in the Gaussian (normal) distribution.

If we want to calculate the distribution function for a standard normal distribution, we arrive at the relation:

$$\Phi(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{x}e^{-t^2/2}\,dt=\frac{1}{2}\left[1+\operatorname{erf}\left(\frac{x}{\sqrt{2}}\right)\right],\quad x\in\mathbb{R}. \qquad \text{Eq. 2.37}$$

In the case of a general normal distribution, following relation applies to the calculation of the distribution function:

$$F(x;\,\mu,\sigma^2)=\Phi\left(\frac{x-\mu}{\sigma}\right)=\frac{1}{2}\left[1+\operatorname{erf}\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)\right],\quad x\in\mathbb{R}. \qquad \text{Eq. 2.38}$$

Error functions occur in both equations.

The course of error function is shown in Figure 2.6.

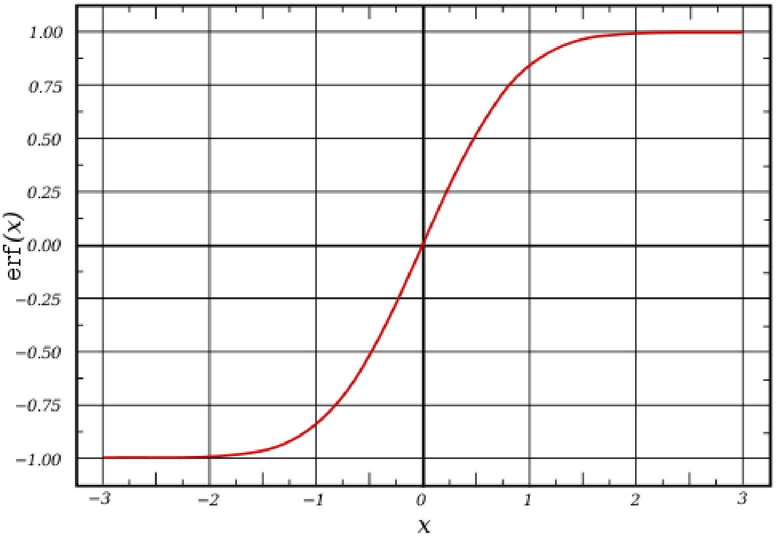


Fig. 2.6 The course of error function

The error function is tabulated, a simple table is given below (Table 2.1).

Tab. 2.1 Values for error function *erf* (x) for selected values of the variable x.

x	*erf*(x)
0.01	0.011283
0.02	0.022565
0.03	0.033841
0.04	0.045111
0.05	0.056372
0.06	0.067622
0.07	0.078858
0.08	0.090078
0.09	0.101281
0.1	0.112463
0.15	0.167996
0.2	0.222703
0.25	0.276326
0.3	0.328627
0.35	0.379382
0.4	0.428392
0.45	0.475482
0.5	0.5205
0.55	0.563323
0.6	0.603856
0.65	0.642029
0.7	0.677801

0.75	0.711155
0.8	0.742101
0.85	0.770668
0.9	0.796908
0.95	0.820891
1	0.842701
1.1	0.880205
1.5	0.966105
2	0.995322
3	0.999978
4	1
5	1

Error function values can be also determined by a series expansion:

$$\operatorname{erf}(z)=\frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n z^{2n+1}}{n!(2n+1)}=\frac{2}{\sqrt{\pi}}\left(z-\frac{z^3}{3}+\frac{z^5}{10}-\frac{z^7}{42}+\frac{z^9}{216}-\cdots\right) \qquad \text{Eq. 2.39}$$

So that is about the error function.

A special situation occurs for concentration, which is the arithmetic mean of concentrations c_0 and c_S.

For this case, the left side of Equation 2.36 is as follows:

$$\frac{c(x,t)-c_0}{c_S-c_0}=\frac{\frac{c_S+c_0}{2}-c_0}{c_S-c_0}=\frac{\frac{c_S+c_0-2.c_0}{2}}{c_S-c_0}=\frac{1}{2} \qquad \text{Eq. 2.40}$$

By substituting into Equation 2.36 we obtain:

$$\frac{1}{2}=1-erf\left[\frac{x}{2\sqrt{D.t}}\right]\Rightarrow erf\left[\frac{x}{2\sqrt{D.t}}\right]=\frac{1}{2} \qquad \text{Eq. 2.41}$$

If the error function of variable x is equal to 0.5, then (see Tab. 2.1) variable x is also equal to approximately 0.5. Thus it is true that:

$$erf(\frac{1}{2})\cong\frac{1}{2} \qquad \text{Eq. 2.42}$$

The it also applies that:

$$\frac{x}{2\sqrt{D.t}}=\frac{1}{2}\Rightarrow x=\sqrt{D.t} \qquad \text{Eq. 2.43}$$

For concentration, which is the arithmetic mean of concentrations c_0 and c_S, a very simple relationship applies between the depth to which an element diffuses, diffusion coefficient and diffusion time.

Solved example 2.4

Problem:

Steel containing 0.2% carbon is carburized in a gas atmosphere having a carbon potential of 0.9%. Carburizing is performed at 920°C, at which the diffusion coefficient of carbon in gamma iron equals to $1.13076 \cdot 10^{-7}$ $cm^2.s^{-1}$. Determine graphically the dependence of carbon concentration at a depth below the surface for periods of cementation lasting 2, 4, 8 and 20 hours. Determine how much time is needed for the carbon concentration below the surface at a depth of 0.5 mm to become equal to 0.55%.

Solution:

The solution is preferable to perform in EXCEL. For the calculation, it will be useful to consider the distance in cm and time in seconds.

The key is to solve the modified Equation 2.36

$$c(x,t) = c_0 + (c_S - c_0).\left\{1 - erf\left[\frac{x}{2\sqrt{D.t}}\right]\right\}$$

and subsequently obtain the relation between x and c(x, t).

We can do this gradually, as shown in the example of table from EXCEL.

Depth (mm)	Depth (cm)	Temperature (°C)	Temperature (K)	$D_{C(\gamma)}$	$\frac{x}{2\sqrt{D.t}}$ 2 hours	$\frac{x}{2\sqrt{D.t}}$ 4 hours	$\frac{x}{2\sqrt{D.t}}$ 8 hours	$\frac{x}{2\sqrt{D.t}}$ 20 hours
0	0	920	1193	1.13076E-07	0	0	0	0
0.01	0.001	920	1193	1.13076E-07	0.0175234	0.0123909	0.0087617	0.0055414
0.02	0.002	920	1193	1.13076E-07	0.0350469	0.0247819	0.0175234	0.0110828
0.03	0.003	920	1193	1.13076E-07	0.0525703	0.0371728	0.0262851	0.0166242
0.04	0.004	920	1193	1.13076E-07	0.0700937	0.0495637	0.0350469	0.0221656
0.05	0.005	920	1193	1.13076E-07	0.0876171	0.0619547	0.0438086	0.027707
0.06	0.006	920	1193	1.13076E-07	0.1051406	0.0743456	0.0525703	0.0332484
0.07	0.007	920	1193	1.13076E-07	0.122664	0.0867365	0.061332	0.0387898
0.08	0.008	920	1193	1.13076E-07	0.1401874	0.0991275	0.0700937	0.0443312
0.09	0.009	920	1193	1.13076E-07	0.1577108	0.1115184	0.0788554	0.0498725
0.1	0.01	920	1193	1.13076E-07	0.1752343	0.1239093	0.0876171	0.0554139
0.12	0.012	920	1193	1.13076E-07	0.2102811	0.1486912	0.1051406	0.0664967
0.14	0.014	920	1193	1.13076E-07	0.245328	0.1734731	0.122664	0.0775795
0.16	0.016	920	1193	1.13076E-07	0.2803748	0.1982549	0.1401874	0.0886623
0.18	0.018	920	1193	1.13076E-07	0.3154217	0.2230368	0.1577108	0.0997451
0.2	0.02	920	1193	1.13076E-07	0.3504685	0.2478187	0.1752343	0.1108279

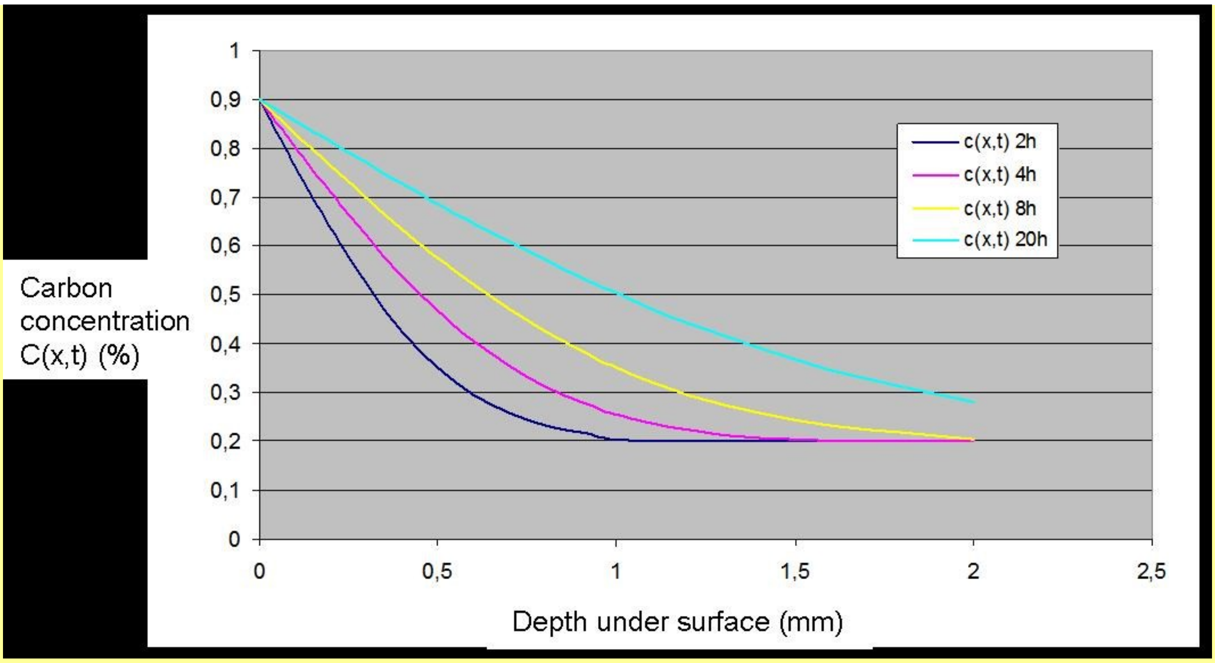
We enter the depth below the surface x in mm, then in cm, the temperature in °C and in K, and the coefficient of diffusion of carbon in gamma iron. Then we can calculate the value of the member $\frac{x}{2\sqrt{D.t}}$ for each period of cementation.

Then we can calculate the error function of argument $\frac{x}{2\sqrt{D.t}}$, preferably by a series expansion, according to Equation 2.39 up to the member z^{17}. This is shown by another table from EXCEL.

erf(2h)	erf(4h)	erf(8h)	erf(20h)
0	0	0	0
0.01977606	0.0139845	0.0098888	0.0062543
0.039539978	0.0279647	0.0197761	0.0125082
0.059279637	0.0419363	0.0296603	0.0187614
0.078982963	0.0558951	0.03954	0.0250134
0.098637948	0.0698367	0.0494136	0.0312639
0.118232674	0.083757	0.0592796	0.0375125
0.137755333	0.0976516	0.0691366	0.0437587
0.157194249	0.1115164	0.078983	0.0500023
0.176537898	0.1253471	0.0888172	0.0562428
0.19577493	0.1391397	0.0986379	0.0624798
0.233884725	0.166594	0.1182327	0.0749421
0.271437039	0.1938467	0.1377553	0.087386
0.308349255	0.220866	0.1571942	0.0998085
0.34454328	0.2476213	0.1765379	0.1122066
0.379946031	0.2740824	0.1957749	0.1245773

Finally, we can calculate the appropriate concentrations of carbon depending on the depth below the surface and time of cementation and construct a graph. This is shown in the third table and the corresponding graphical representation.

aC	cC	**c(x,t) 2h**	**c(x,t) 4h**	**c(x,t) 8h**	**c(x,t) 20h**
0.9	0.2	**0.9**	**0.9**	**0.9**	**0.9**
0.9	0.2	**0.8861568**	**0.8902108**	**0.8930778**	**0.895622**
0.9	0.2	**0.872322**	**0.8804247**	**0.8861568**	**0.8912442**
0.9	0.2	**0.8585043**	**0.8706446**	**0.8792378**	**0.886867**
0.9	0.2	**0.8447119**	**0.8608734**	**0.872322**	**0.8824906**
0.9	0.2	**0.8309534**	**0.8511143**	**0.8654105**	**0.8781153**
0.9	0.2	**0.8172371**	**0.8413701**	**0.8585043**	**0.8737413**
0.9	0.2	**0.8035713**	**0.8316439**	**0.8516044**	**0.8693689**
0.9	0.2	**0.789964**	**0.8219386**	**0.8447119**	**0.8649984**
0.9	0.2	**0.7764235**	**0.812257**	**0.8378279**	**0.8606301**
0.9	0.2	**0.7629575**	**0.8026022**	**0.8309534**	**0.8562641**
0.9	0.2	**0.7362807**	**0.7833842**	**0.8172371**	**0.8475405**
0.9	0.2	**0.7099941**	**0.7643073**	**0.8035713**	**0.8388298**
0.9	0.2	**0.6841555**	**0.7453938**	**0.789964**	**0.8301341**
0.9	0.2	**0.6588197**	**0.7266651**	**0.7764235**	**0.8214554**
0.9	0.2	**0.6340378**	**0.7081423**	**0.7629575**	**0.8127959**



This graph represents essentially the solution of the first, the most difficult part of the task.

The second part of the task, i.e. to determine how much time is needed for the carbon concentration below the surface at a depth of 0.5 mm to become equal to 0.55%, is very easy. The concentration of 0.55% of carbon is the arithmetic mean of the initial and surface concentration. The calculation is then performed according to Equation 2.43:

$$x = \sqrt{D.t} \Rightarrow t = \frac{x^2}{D} = \frac{0.05^2}{1.13076 \cdot 10^{-7}} = 22109 s = 6.14 hours$$

Certain control of accuracy can be done in the graphical dependence of concentration on the depth below the surface.

Conclusion:

The dependence of concentration of carbon on the depth below the surface is graphically represented for specified periods of cementation; time needed for the carbon concentration to be 0.55% in the depth of 0.5 mm below the surface is approximately 6.14 hours.

❑ Constant source diffusion – e.g. decarburization of steel

Very similar diffusion problem is the case where the concentration of a certain element is higher inside the material and due to certain effects (e.g. composition of the surrounding atmosphere) the decrease in concentration of the element concerned takes place in the subsurface layers. The surface concentration may be zero, but not necessarily. This depends on the composition of the ambient atmosphere. A typical example of this problem is decarburization of steel. In this case, the solution of Fick's second law leads to equation:

$$\frac{c(x,t)-c_S}{c_0-c_S}=erf\left[\frac{x}{2\sqrt{D.t}}\right] \qquad \text{Eq. 2.44}$$

where c_0 is the initial concentration of the respective element within the material,

c_S is the surface concentration of an element (depends mostly on the composition of the ambient atmosphere) and is a constant; at that it must be true that $c_0 > c_S$.

x is the depth below surface,

D is the diffusion coefficient of the respective element,

t is the time of diffusion.

For concentration, which is the arithmetic mean of concentrations c_0 and c_S again there is a simple relation between the time of diffusion, depth below the surface and diffusion coefficient:

$$x=\sqrt{D.t} \qquad \text{Eq. 2.45}$$

Example of the dependence of carbon concentration in the subsurface layers in steel containing 0.95% of carbon and is annealed at 780°C in an atmosphere having a carbon potential of 0.4% is shown in Figure 2.7.

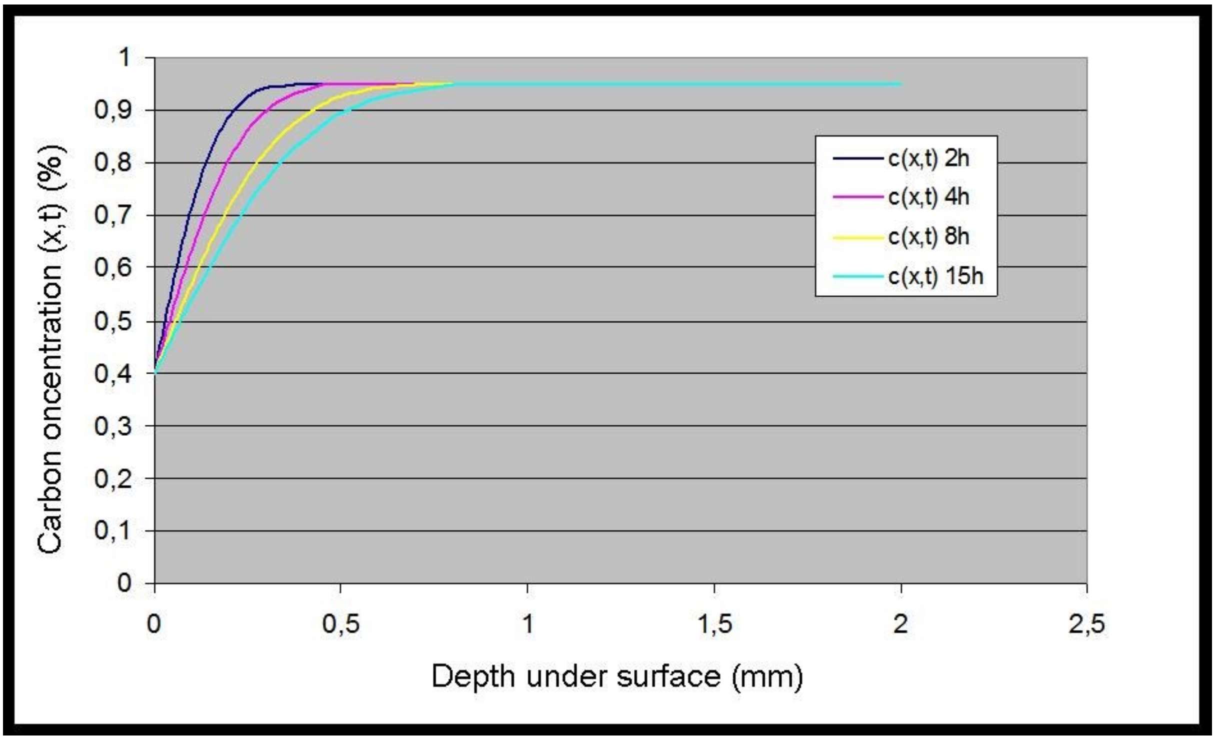


Fig. 2.7 Example of decarburization of steel during annealing at temperatures of 780°C

The figure shows that even after a relatively long time of annealing (15 hours), the depth of decarburized layer does not exceed 1 mm. The method for obtaining the graphical dependence in Figure 2.7 is in principle identical to the procedure as described for the solved example 2.4.

Solved example 2.5

Problem:

You perform austenitization of steel at 900°C. Steel contains 0.7% of carbon. What is the maximum time of austenitization for the carbon content not to drop below 0.6% at depth of 0.1 mm below the surface at 0.4% carbon potential of the atmosphere.

Temperature dependence of the diffusion coefficient of carbon in austenite is given by the equation:

$$D_C = 0{,}25.\exp\left(-\frac{144900}{R.T}\right)\ \mathrm{cm^2.s^{-1}}$$

Solution:

First, we can calculate the diffusion coefficient of carbon at a temperature of 900°C by simply substituting into the above equation. We obtain:

$$D_C = 0{,}25.\exp\left(-\frac{144900}{R.T}\right) = 0{,}25.\exp\left(-\frac{144900}{8{,}314.1173}\right) = 8{,}814.10^{-8}\ \mathrm{cm^2.s^{-1}}$$

The task itself can be solved using Equation 2.44, i.e.:

$$\frac{c(x,t)-c_S}{c_0-c_S} = erf\left[\frac{x}{2\sqrt{D.t}}\right]$$

Since we know all the members on the left side, we can quantify the left side as follows:

$$\frac{c(x,t)-c_S}{c_0-c_S} = \frac{0.6-0.4}{0.7-0.4} = \frac{2}{3}$$

Thus we can write that

$$erf\left[\frac{x}{2\sqrt{D.t}}\right] = \frac{2}{3}$$

Error function is thus equal to 2/3 and we find the value in table 2.1 corresponding to the value of the argument, which is a member $\frac{x}{2\sqrt{D.t}}$.

From Table 2.1, we can roughly estimate that the value of argument is about 0.68 (In Table 2.1 we look for a value in the left column corresponding to the value in the right).

Thus we can write that:

$$\frac{x}{2\sqrt{D.t}} = 0.68$$

And we solve this equation for the unknown t, because we have to determine time. After modification, we get:

$$t = \frac{x^2}{(2\cdot 0.68)^2.D} = \frac{0.01^2}{1.36^2\cdot 8.814\cdot 10^{-8}} = 613s \approx 10\,\mathrm{min}$$

Conclusion:

Maximum time of steel austenitization in the given atmosphere for the carbon content not to drop below 0.6% at a depth of 0.1 mm below the surface is about 10 minutes.

❑ Compensating the content of an element that periodically varies

This is a task which again has a wide application in metallurgy and is tied up with the dendritic segregation in metallic materials. As a result of dendritic segregation, the content of many elements in metallic materials varies and this variation can be simply regarded as a periodic. The difference between the maximum and minimum content of elements can be quite substantial, and it has a negative impact on both the structure of the material and its properties. Therefore, we sometimes try to reduce such concentration differences by e.g. homogenization annealing. It will be of interest to us, then, what will be the variation in the content of an element after a certain annealing time.

Figure 2.8 can help us to illustrate this task.

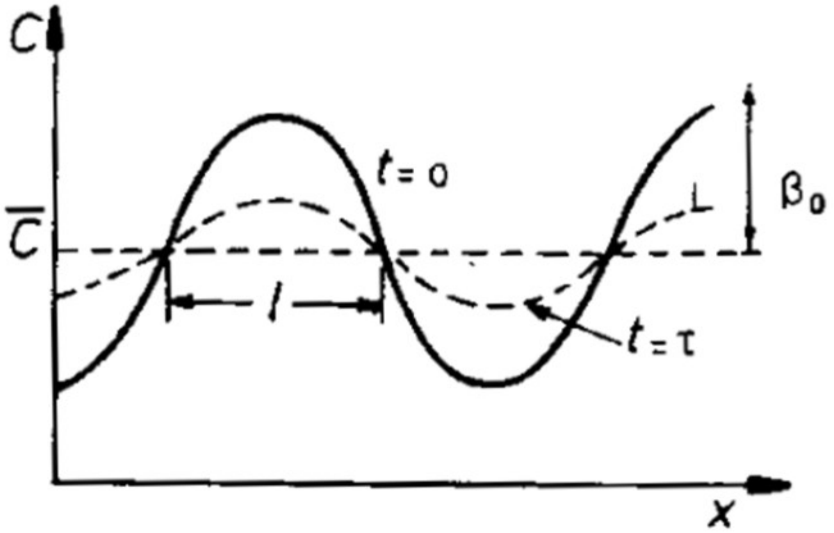


Fig. 2.8 Illustrative picture to the diffusion task that addresses the compensation of content of an element, which periodically varies

The picture shows the following quantities:

$\overline{C}$	the mean concentration of an element
β_0	the initial amplitude of content of an element
l	the distance between mean concentrations of an element (half-period)

The full line indicates the course of the concentration at time t = 0, while the dashed line indicates the course of the concentration after a certain annealing time.

Again, it is the problem of unsteady state diffusion, which is solved using Fick's second law.

At time t = 0, the course of concentration of a certain element can be expressed using the following equation:

$$\boldsymbol{C(x) = \overline{C} + \beta_0 . \sin\frac{\pi . x}{l}} \qquad \text{Eq. 2.46}$$

The course of concentration at time t can be expressed by the equation:

$$\boldsymbol{c(x,t) = \overline{c} + \beta_0 . \sin\frac{\pi . x}{l} . \exp(-\frac{t}{\tau})} \qquad \text{Eq. 2.47}$$

where τ is a time constant for which:

$$\boldsymbol{\tau = \frac{l^2}{\pi^2 . D_B}} \qquad \text{Eq. 2.48}$$

where D_B is the diffusion coefficient of an element.

In some cases, we do not need to know the exact course of concentration, but it is enough for us to know the amplitude of concentration that will exist after a certain annealing time.
This amplitude *β(t)* may be determined from the equation:

$$\boldsymbol{\beta(t) = \beta_0 . \exp(-\frac{t}{\tau})} \qquad \text{Eq. 2.49}$$

Equation 2.49 is sometimes presented in a slightly different form - as:

$$\boldsymbol{\frac{\beta(t)}{\beta_0} = \exp(-\frac{t}{\tau})} \qquad \text{Eq. 2.50}$$

Solved example 2.6

Problem:

In steel containing 1.0% of Cr, variations occur due to the dendritic segregation in the range between 0.6 and 1.4% of Cr. Calculate how long steel must be treated by homogenizing annealing at 1200°C so that the chromium content varies only in the range between 0.8 to 1.2%. The diffusion coefficient of chromium at a temperature of 1200°C is $7.2 \cdot 10^{-11}$ $cm^2.s^{-1}$. Distance l (half the length of the period of Cr content variation) is 20 μm.

Solution:

This example can be solved by using Equation 2.50, which we will solve for the unknown t.

The initial Cr content amplitude is $\beta_0 = (1.4-0.6)/2=0.4$. The amplitude, which we are to arrive is $\beta(t) = (1.2-0.8)/2=0.2$.

Next, we must calculate a parameter τ according to the Equation 2.48:

$$\tau = \frac{l^2}{\pi^2 . D_B} = \frac{0.002^2}{\pi^2 \cdot 7.2 \cdot 10^{-11}} = 5653 s$$

Note that due to the diffusion coefficient unit, also other lengths must be given in cm.

Take a log of the Equation 2.50 to get at the following equation:

$$\ln\left(\frac{\beta(t)}{\beta_0}\right) = -\frac{t}{\tau}$$

From it, time t is:

$$t = -\tau.\ln\left(\frac{\beta(t)}{\beta_0}\right) = -5653.\ln\left(\frac{0.2}{0.4}\right) = -5653.\ln(0.5) = 3918\,s \cong 1.1\,hour$$

Conclusion:

To reduce variations in the content of chromium in the steel to 0.8-1.2%, i.e. with the variation amplitude of 0.2%, we must anneal the steel at 1200°C for about 1.1 hours.

Summary of terms from 2.2

After studying this part, following terms should be clear to you:

- **Steady state diffusion and unsteady state diffusion**
- **Fick’s first and second laws**
- **Random jumps; mean squared displacement**
- **Constant source diffusion**
- **Error function**

Questions to 2.2

15. How can a diffusion flux be characterized?
16. Explain concisely Fick's first law (without using the equation – in words).
17. Which members are hidden in the pre-exponential (frequency) member in the expression of dependence of the diffusion coefficient on temperature?
18. How to verbally express Fick's second law?
19. What do we mean by unsteady state diffusion?
20. In which characteristics of the Gaussian distribution we encounter the error function?

Task to solve 2.1

Problem:

You perform cementation of steel containing 0.2% of carbon in the carburizing atmosphere with a carbon potential of 1.0% at 900°C. Calculate the concentration of carbon at a depth of 1 mm below the surface for cementation times of 10, 20, and 40 hours. Temperature dependence of the diffusion coefficient of carbon in gamma iron is given by the equation:

$$D_C = 0{,}25.\exp\left(-\frac{144900}{R.T}\right)$$

Results:

The concentration of carbon at a depth of 1 mm below the surface is as follows:

Cementation time of 10 hours	0.37%
Cementation time of 20 hours	0.50%
Cementation time of 40 hours	0.62%.

2.3. Substitutional diffusion – auto diffusion, diffusion of admixtures - impurities

Time to study: 2 hours

Objective After reading this part, you should be able to:

- Explain the principle of auto diffusion.
- Explain the effect of vacancies on the course of substitutional diffusion.
- Characterize the diffusion from an inconstant source.
- Solve typical tasks of unsteady state diffusion of substitutional atoms.

Presentation

❑ Auto diffusion

In the previous chapter 2.2 we focused on the diffusion of interstitial atoms, because its description is easier. But it must be said that almost everything that we derived for interstitial diffusion is also true for the diffusion of substitutional atoms. Basically, the only difference we discover when we deal with the effects of temperature for the case of substitutional diffusion (for the case of interstitial diffusion, we derived the equations 2.19 to 2.22).

The difference is explained on the case of auto diffusion, which is the diffusion of own atoms (strictly speaking in a single-component system). It can be detected by radioisotopes of the respective element.

Let A* be a radioactive isotope of element A.

For the diffusion coefficient of a radioisotope it is true, that:

$$D_A^* = D_A = \frac{1}{6}\Gamma.\alpha^2 \tag{Eq. 2.51}$$

Also in the case of substitutional diffusion, an equation analogous to Equation 2.19 will apply to the frequency of successful jumps, i.e. that frequency is proportional to the frequency of thermal vibrations of atoms ν and probability that atoms obtain activation energy necessary to overcome the energy barrier, i.e.:

$$\Gamma \approx \nu . \exp(-\frac{\Delta G_m}{RT}) \qquad \text{Eq. 2.52}$$

In the case of diffusion of substitutional atoms we must, however, take into account the effect of the presence of vacancies, because we already know that the vacancy mechanism is the least energy-consuming mechanism of diffusion of substitutional atoms. In other words, we must take into account the probability that a nodal point adjacent to the atom, which should diffuse, is unoccupied – a vacancy. The situation is schematically illustrated in Figure 2.9.

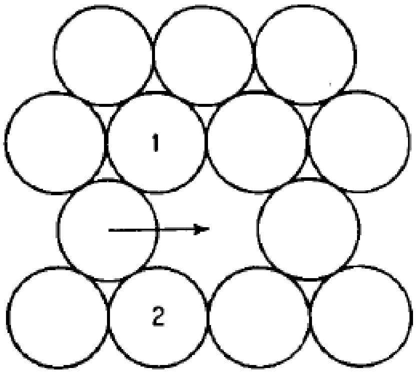


Fig. 2.9 Schematic picture illustrating the influence of vacancies on the diffusion of substitutional atoms

The probability that neighbouring location is vacant is given by the product of $b.X_V$,

where b is the number of nearest neighbouring nodal points,

X_V is the mole fraction of vacancies.

The equilibrium mole fraction of vacancies is given by the relation:

$$\boldsymbol{X_V^{equil} \approx \exp(-\frac{\Delta G_V}{RT})} \qquad \text{Eq. 2.53}$$

where ΔG_V is free activation enthalpy associated with the formation of vacancies (J.mol^{-1}).

For the frequency of successful jumps in the diffusion of substitutional atoms (auto diffusion) then applies that:

$$\Gamma_B = b.\nu.X_V \exp\left(-\frac{\Delta G_m}{RT}\right) = b.\nu.\exp\left(-\frac{\Delta G_m + \Delta G_V}{RT}\right) \qquad \text{Eq. 2.54}$$

The essential difference between this Equation 2.54 and Equation 2.19 is that besides the own energy barrier for jump, Equation 2.54 moreover features free activation enthalpy associated with the formation of vacancies. Considering that both quantities, ΔG_m, and ΔG_V, can be expressed using the enthalpy H and entropy S, we can express the relationship for determining the coefficient for auto diffusion as follows:

$$D_A^* = D_A = \left[\frac{1}{6}\alpha^2.b.\nu.\exp\left(-\frac{\Delta S_m + \Delta S_V}{R}\right)\right].\exp\left(-\frac{\Delta H_m + \Delta H_V}{RT}\right) =$$

$$D_{0A}.\exp\left(-\frac{\Delta H_m + \Delta H_V}{RT}\right) = D_{0A}.\exp\left(-\frac{\Delta Q_{AD}}{RT}\right)$$

Eq. 2.55

The meaning of individual members in the equation should be obvious.

The main difference between Equation 2.55 and the analogous equation for diffusion of interstitial atoms is again that in Equation 2.55 the activation energy of auto diffusion ΔQ_{AD} contains the own energy barrier for jump, as well as the energy required to form a vacancy.

The following example shows how big the effect of temperature on the course of the substitutional diffusion is.

Solved example 2.7

Problem:

Consider auto diffusion of copper at temperatures of 800°C and 20°C. At 800°C, the coefficient of copper auto diffusion is $D^*_{Cu} = 5\cdot10^{-9}$ mm^2/s, while at 20°C it is $D^*_{Cu} = 5\cdot10^{-34}$ mm^2/s. The distance of planes between which jumps take place is $\alpha = 0.25$ nm. Determine the frequency of successful jumps Γ for both temperatures and the diffusion path for the diffusion time of 1 hour.

Solution:

For solution, we will use Equation 2.51.

For a temperature of 800°C, it applies that:

$$D = \frac{1}{6}\alpha^2.\Gamma \Rightarrow \Gamma = \frac{6.D}{\alpha^2} = \frac{6.5\cdot10^{-9}}{0.0625\cdot10^{-12}} \cong 5\cdot10^5\ \text{s}^{-1}.$$

So at this temperature it is approximately true that every ten millionth thermal vibration leads to the jump of atom from one node to another position, adjacent. From the other side - half a million of successful jumps takes place in one second.

For the diffusion path at 800°C, it applies that:

$$x \cong \sqrt{D.t} = \sqrt{5\cdot10^{-9}\cdot3600} = 4\cdot10^{-3}\ \text{mm, i.e. } 4\ \mu\text{m}.$$

At 20°C, it applies to the frequency of successful jumps that:

$$\Gamma = \frac{6.D}{\alpha^2} = \frac{6 \cdot 10^{-34}}{0.0625 \cdot 10^{-12}} \cong 10^{-20} s^{-1} = 10^{-12} \text{ year}^{-1}$$

The result can be interpreted in such a way that one jump occurs in just about every trillion years. The diffusion path is not worth counting....

Conclusion:

We will not give any numbers, we only state that the substitutional diffusion (auto diffusion) is strongly affected by temperature.

❑ Determination of coefficient of auto diffusion

How can we determine the coefficient of auto diffusion? Also in this case we need a radioactive isotope of the respective element, but we also need a device capable of measuring the concentration of radioactive isotopes, and otherwise we will utilize the diffusion task for transient diffusion, i.e. task, which is based on Fick's second law. Both Fick's laws apply equally to the interstitial diffusion and substitutional diffusion. Imagine that a thin layer of radioactive isotope is put between two cylinders made from common isotope of the respective element. Couple diffusively all three parts (so that diffusion can proceed between the individual parts) and anneal at elevated temperature. At different distances from the thin layer of a radioactive isotope we then measure the concentration of the radioactive isotope in the cylinders manufactured from conventional isotope. Schematic layout and graphical dependence of concentration of the radioactive isotope after a certain time of annealing for gold is shown in Figure 2.10.

The solution to Fick's second law for this diffusion problem leads to the following equation:

$$\boldsymbol{c(x,t) = \frac{M_A}{2\sqrt{\pi.D^*.t}}.\exp(-\frac{x^2}{4D^*.t}) = \frac{\rho.th}{2\sqrt{\pi.D^*.t}}.\exp(-\frac{x^2}{4D^*.t})} \text{ ;} \qquad \text{Eq. 2.56}$$

where c(x,t) is the concentration of a radioactive isotope at a distance x from the boundary line between the thin layer of a radioactive isotope and cylinder made from a conventional isotope for the annealing time t; concentration in this case is mostly expressed as density, e.g., in kg/m^3,

M_A is a radioactive isotope mass per unit area,

ρ is a radioactive isotope density,

th. is the thickness of the radioactive isotope layer.

This problem is sometimes called the **diffusion from an inconstant source**, because during annealing, i.e. during the diffusion, the maximum concentration decreases (the layer is "consumed"). This is schematically illustrated in Figure 2.11 for different annealing times.

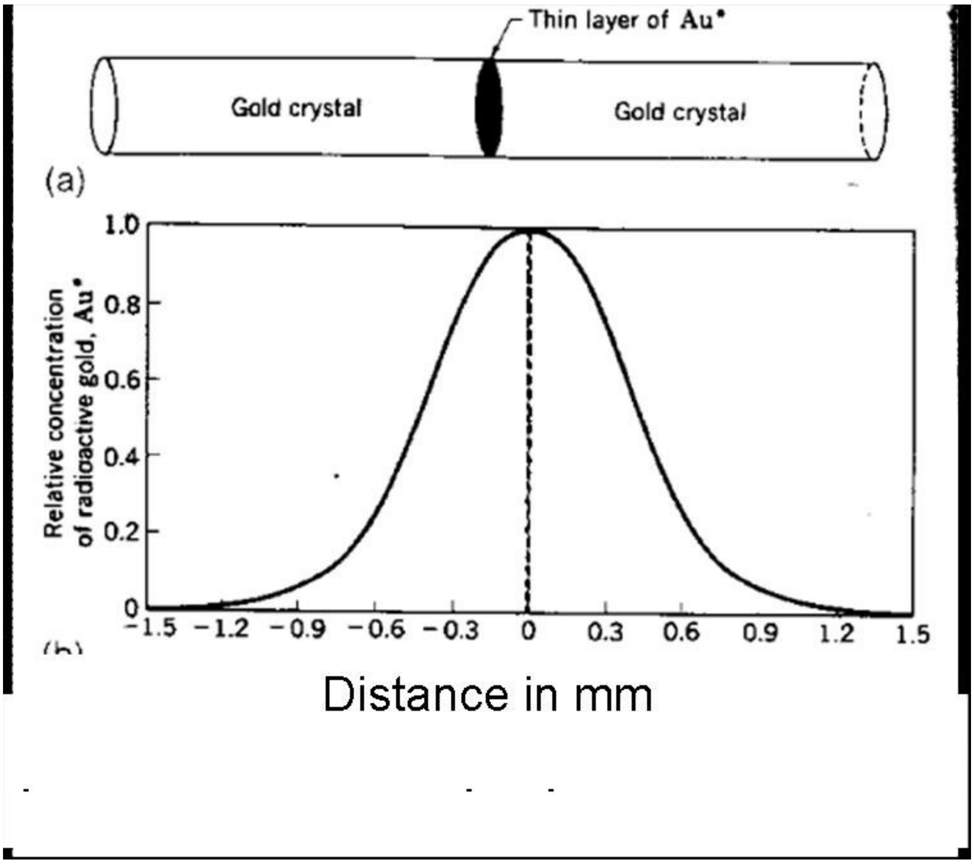


Fig. 2.10 Schematic picture to determine the auto diffusion coefficient of gold

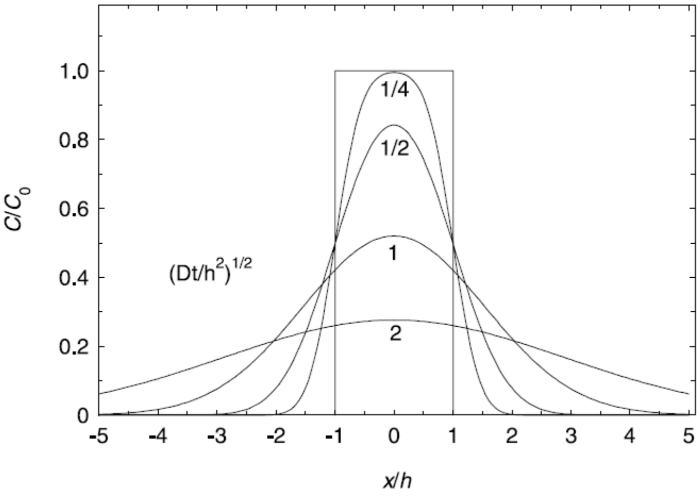


Fig 2.11 Schematic representation of the concentration of radioactive isotope for different annealing times

If a thin layer of a radioactive isotope is applied to the surface of only one cylinder, the equation is modified as follows:

$$c(x,t)=\frac{M_A}{\sqrt{\pi.D^*.t}}.\exp(-\frac{x^2}{4D^*.t})=\frac{\rho.th}{\sqrt{\pi.D^*.t}}.\exp(-\frac{x^2}{4D^*.t}) \qquad \text{Eq. 2.57}$$

(in denominator, 2 is not at the first member).

The course of concentration for a layer applied on one side only and different annealing times is shown in Figure 2.12.

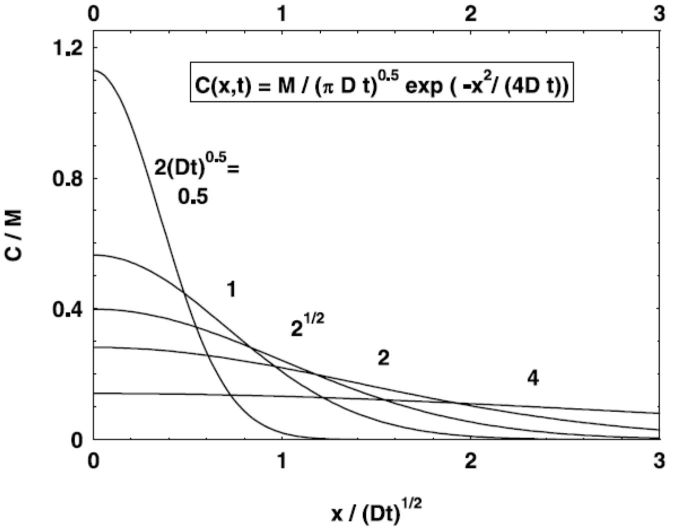


Fig. 2.12 Schematic representation of the concentration of radioactive isotope for different annealing times at unilaterally applied layer

Equation 2.57 (or 2.56) can be logarithmed, which leads to a simplified equation:

$$\ln c(x,t)\approx -\frac{x^2}{4.D^*.t} \qquad \text{Eq. 2.58}$$

So there is a linear relationship between ln c(x,t) and x^2. If we obtain experimental values of concentration for different distances x at the same time t, we can use regression analysis to obtain the equation of the line in the following form:

$y = k.x + q.$

We can deduce from Equation 2.58 that the slope of the line will be equal to:

$$k=-\frac{1}{4.D.t}\Rightarrow D^*=-\frac{1}{4.k.t} \qquad \text{Eq. 2.59}$$

Equation 2.59 is the resulting equation by which we can determine the coefficient of auto diffusion of a particular element.

Important information:

All that we have said so far for the case of auto diffusion is true also for substitutional diffusion of admixtures or impurities, i.e. such admixtures which are present in the material only in small amounts, generally not exceeding 1%. In these cases, it is believed that diffusion of admixtures does not cause diffusion of the basic element of the system.

Solved example 2.8

Problem:

Cover the cylinder made of pure nickel by a foil made of pure gold with thickness of 5 μm and anneal at 1000°C for 10 hours. The density of gold is $\rho_{Au} = 19.02$ g/cm^{-3}. After annealing, measure the concentration of gold in the nickel cylinder at different distances from the boundary line to obtain the following results:

Distance from boundary line (μm)	Gold concentration g/cm^3
1	8.88
10	4.47
20	0.556
30	0.0173

On the basis of these results, determine the coefficient of diffusion of gold in nickel.

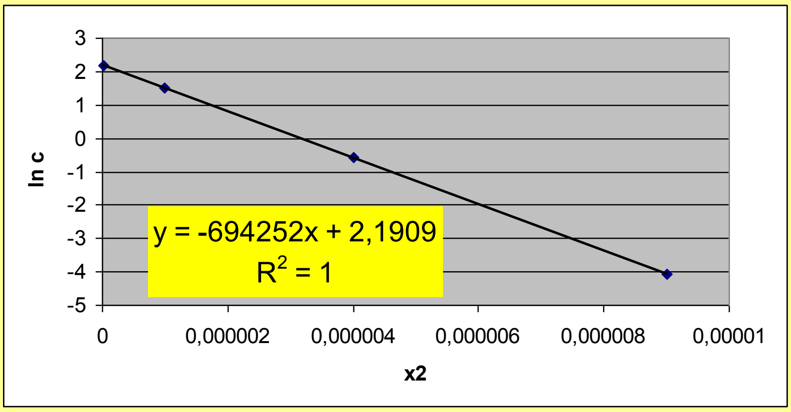
Solution:

We start from Equation 2.58, i.e. we get the relationship between the natural logarithm of concentration and square of the distance x^2. Task will be best solved in EXCEL.

We can get the following table of values:

Distance x (cm)	x^2	Concentration c (g/cm3)	ln c
0.0001	0.00000001	8.88	2.183802
0..001	0.000001	4.47	1.497388
0.002	0.000004	0.556	-0.58699
0.003	0.000009	0.0173	-4.05705

We will construct graph $\ln(c)= f(x^2)$ as shown and determine the equation of the regression line.



Slope of the line is -694252.

This value is substituted into Equation 2.59

$$(D_{Au})_{Ni} = -\frac{1}{4.k.t} = -\frac{1}{-4\cdot 694252\cdot 10\cdot 3600} = 1.0\cdot 10^{-11}\ \mathrm{cm^2/s}$$

Conclusion:

It works out for entered values that coefficient of diffusion of gold in nickel at a temperature of 1000°C is equal to 1.0·10^{-11} cm^2/s.

∑ Summary of terms from 2.3

After studying this part, following terms should be clear to you:

- **Auto diffusion; substitutional diffusion of impurities.**
- **Diffusion from an inconstant source.**

? Questions to 2.3

21. Why auto diffusion takes place?
22. How auto diffusion of a certain element can be studied?
23. What should be taken into account when determining the frequency of successful jumps in the case of substitutional diffusion?
24. What does the activation energy of diffusion express in the case of substitutional diffusion?
25. What does the term diffusion from an inconstant source mean?
26. Among which characteristics we obtain the linear dependence for determining the coefficient of auto diffusion or diffusion of impurities?

Task to solve 2.2

Problem:

Cover the cylinder made of pure iron by foil made of pure manganese with thickness of 5 μm and anneal at 1300°C for 20 hours. After annealing, measure the concentration of manganese in the iron cylinder at different distances from the boundary line to obtain the following results:

Distance from boundary line (μm)	Manganese concentration g/cm^3
1	0.48
10	0.47
50	0.29
100	0.06

On the basis of these results, determine the coefficient of diffusion of manganese in gamma iron at 1300°C.

Result:

$(D_{Mn})_{Fe\gamma} = 1.67 \cdot 10^{-10}$ **cm^2/s.**

2.4. Mutual diffusion of substitutionally dissolved elements - interdiffusion

Time to study: 3 hours

Objective After reading this part, you should be able to:

- Explain the principle of interdiffusion.
- Describe the Kirkendall effect.
- Explain the basic principles of interdiffusion.
- Derive the speed of motion of the boundary layer during interdiffusion.
- Describe Darken's equation.

Presentation

❑ Kirkendall effect

In the previous part we dealt with auto diffusion and we said that mentioned laws were valid also for diffusion of substitutionally dissolved impurities, if their concentration was low, i.e. not resulting in any significant diffusion of atoms of the basic element of the system.

Now let's focus on the case, when the concentration of an impurity is higher and the diffusion of its atoms must necessarily cause diffusion of another element, mostly the basic element of the system. This type of diffusion is called interdiffusion.

The first information about one of the phenomena related to the interdiffusion was made public by Ernest Kirkendall in 1947, when he performed his famous experiment. Principle of the experiment is shown schematically in Figure 2.13.

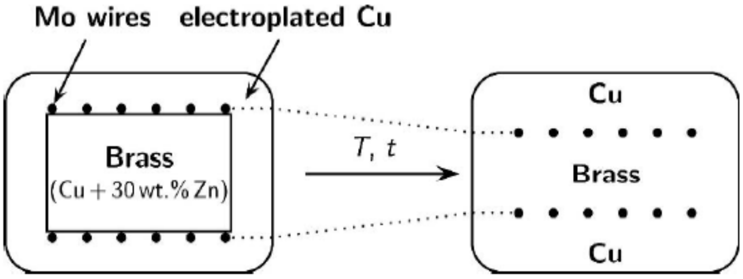


Fig 2.13 Scheme of experiment to Kirkendall effect

What Mr. Kirkendall, American physicist did? He take a specimen of α-brass, which contained 30% of zinc and 70% of copper, and wrapped it with thin molybdenum wires serving as "measuring points" to determine the size of the brass specimen. Pure copper was then electrolytically applied on this specimen. Then he annealed the resulting specimen at elevated temperatures. After prolonged annealing, he cut the specimen and measured the distance of molybdenum wires, i.e. "measuring points". And he found that the wires were closer together after annealing. This should mean that the brass specimen diminished during annealing, while the part originally formed by copper increased. So Kirkendall arrived at an important and true conclusion that during the mutual diffusion of two substitutionally dissolved elements (in this case copper and zinc) the original boundary line is displaced. And why this happens? This stems from the fact that diffusion rates of the elements mentioned are not the same, usually one element diffuses faster and the other slower. In the case of Kirkendall's experiment, zinc diffuses faster. This means that zinc leaves the brass specimen faster. Copper, which in turn diffuses into the brass, diffuses slowly and is not able to replace all of dwindling zinc, which results, among others, in a displacement of the original boundary line. It is true that the part of material, which contains faster diffusing element at the beginning, diminishes.

But we will now try to derive it.

❑ Derivation of the basic characteristics of interdiffusion, Darken's equation

The scheme to derive interdiffusion patterns is shown in Figure 2.14. Let us assume that we have two specimen. The first specimen is a single-component system consisting of element A. The second specimen is a single-component system consisting of element B. There is unlimited solubility in the solid state among the elements A and B. We combine both specimens together, anneal at elevated temperature and will explore how the concentration of elements A and B changes near the boundary line after annealing. The concentration of element A at the boundary line at the beginning (before annealing) is shown in blue, while the concentration of element A after some time of annealing is shown by the black curve. The concentration of element B after the same time of annealing is shown by the red curve. Assuming that diffusion coefficients of both elements are not identical and that it is true that the coefficient of diffusion of element A is greater than the coefficient of diffusion of element B.

Thus we can write: $\mathbf{D_A \neq D_B;\ D_A > D_B}$

Consider now that during annealing, there is a diffusion flux of atoms of component A to specimen B and vice versa diffusive flux of atoms of component B to specimen A.

This can be written by following equations:

$$\vec{J}_A = -D_A \frac{\partial c_A}{\partial x} \quad \text{and} \quad \overleftarrow{J}_B = -D_B \frac{\partial c_B}{\partial x} \qquad \text{Eq. 2.60a,b}$$

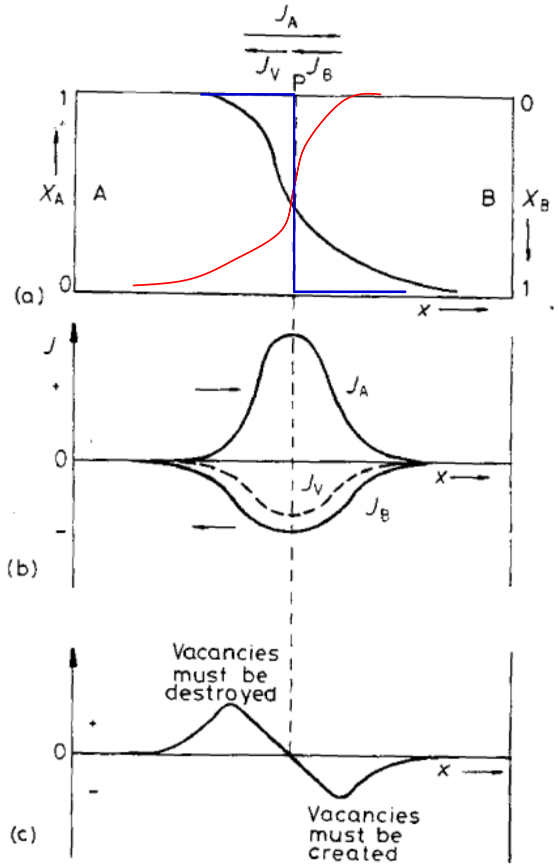


Fig. 2.14 Scheme to derive interdiffusion patterns

Furthermore, assume that total number of atoms per unit volume c_0 is constant and is equal to the sum of $c_A + c_B$.

Under this assumption, we can express the gradient of concentration of component B with respect to distance as follows:

$$\frac{\partial c_B}{\partial x} = \frac{\partial (c_0 - c_A)}{\partial x} = -\frac{\partial c_A}{\partial x}$$

Eq. 2.61

So it is true that concentration gradients of the two components are identical, but with an opposite orientation.

Then we can modify Equation 2.60a,b to the form:

$$\vec{J}_A = -D_A \frac{\partial c_A}{\partial x} \text{ and } \overleftarrow{J}_B = +D_B \frac{\partial c_A}{\partial x}$$

Eq. 2.62a,b

When assuming the vacancy mechanism of diffusion, it can be considered that the difference between diffusion fluxes J_A and J_B is compensated by the flow of vacancies from specimen B to specimen A.

The flow of vacancies can be written as:

$$J_V = D_A \frac{\partial c_A}{\partial x} - D_B \frac{\partial c_A}{\partial x} = (D_A - D_B) \frac{\partial c_A}{\partial x}$$

Eq. 2.63

Rate of change in vacancy concentration over time can be expressed by the equation:

$$\frac{\partial c_V}{\partial t} = -\frac{\partial J_V}{\partial x}$$

Eq. 2.64

This equation is analogous to equation 2.33, with which we met in the derivation of Fick's second law.

As a result of the flow of atoms and vacancies across the boundary, the boundary line is displaced downstream of vacancies, i.e. from B to A. This means that specimen A decreases, while specimen B increases. But how can we imagine this? This is schematically shown in Figure 2.15.

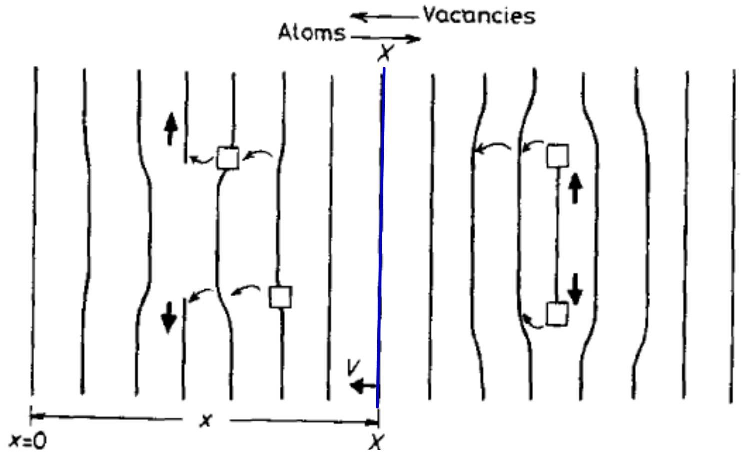


Fig. 2.15 Schematic representation of the boundary line motion during interdiffusion

Let us imagine that linear defects – dislocations are present in both specimens A and B (let us consider edge dislocations). The diffusion flux of atoms prevails in the direction of A→B. The atoms of element A, which diffuse into specimen B, can join here the existing dislocations until a dislocation ceases to exist by emergence of a "standard" atomic plane. On the other hand, the diffusion flux of vacancies prevails in the direction of B→A. Vacancies that move from specimen B to specimen A can also join dislocations in specimen A near the boundary line, which will lead to disappearance of crystallographic planes. The boundary between specimens A and B is therefore gradually displaced in the direction from B to A, i.e. specimen A decreases and specimen B increases.

The rate $\boldsymbol{v}$, at which the boundary moves, can be applied to the flow of vacancies across the boundary line. Let us consider area A and a short time interval δt.

Plane A is passed through by $\boldsymbol{A.v.\delta t.c_0}$ atoms in time δt.

The number of vacancies which passes through area A over the same period of time is $\boldsymbol{J_V.A.\delta t}$.

Given that the number of atoms and number of vacancies must be equal, we can write:

$$\boldsymbol{A.v.\delta t.c_0 = J_V.A.\delta t} \qquad \text{Eq. 2.65}$$

Hence it follows that the flow of vacancies is equal to:

$$\boldsymbol{J_V = v.c_0} \qquad \text{Eq. 2.66}$$

When considering the validity of Equation 2.63, we get:

$$J_V = v.c_0 = (D_A - D_B)\frac{\partial c_A}{\partial x}$$ Eq. 2.67

Instead of concentration, we may reflect the mole fractions of components A and B, i.e. X_A and X_B. It will apply:

$$c_A = X_A.c_0 \Rightarrow X_A = \frac{c_A}{c_0}$$ Eq. 2.68

By considering the mole fractions of the components A and B, we can modify Equation 2.67 to the form:

$$v.c_0 = (D_A - D_B)\frac{\partial c_A}{\partial x} = (D_A - D_B)\frac{\partial (X_A.c_0)}{\partial x}$$ Eq. 2.69

Applying a rule for the derivation of the product of $\frac{\partial (X_A.c_0)}{\partial x}$, we get:

$$v.c_0 = (D_A - D_B)\frac{\partial (X_A)}{\partial x}.c_0$$ Eq. 2.70

Then you can already express the rate of motion of the boundary line in interdiffusion by means of the following equation:

$$v = (D_A - D_B)\frac{\partial (X_A)}{\partial x}$$ Eq. 2.71

This equation is therefore the mathematical notation for the motion of boundary line in interdiffusion, i.e. notation for what Kirkendall observed.

What does Equation 2.71 say?

1. The greater is the difference between the values of diffusion coefficients of the two components, the greater is the rate of motion of the boundary line in interdiffusion.
2. Rate of motion of the boundary line is proportional to the gradient of the mole fraction of the component with respect to distance. Gradient of the mole fraction changes during the annealing process (decreases). This means that the rate of motion of the boundary line is highest at the beginning and then gradually decreases.

In some cases, we can come across another phenomenon in the interdiffusion, the so-called ***diffusion porosity***. This occurs near the boundary on the side of the element with higher diffusion coefficient (in our model case, element A). Atoms of this element diffuse faster to specimen B, and if they are not replaced by atoms of element B and if the boundary line does not move sufficiently quickly, small pores emerge in specimen A having the size of up to tenths of micrometres.

In 1948, Lawrence S. Darken derived the coefficient of mutual diffusion of two substitutional elements, the interdiffusion coefficient $\tilde{D}$. This coefficient is expressed by ***Darken's equation***:

$$\tilde{D} = X_A . D_B + X_B . D_A \qquad \text{Eq. 2.72}$$

Note that if the concentration (or the mole fraction in this equation) of component B is very low, the interdiffusion coefficient is equal to the diffusion coefficient of component B, and i.e. the following applies:

$$\tilde{D} \cong D_B \qquad \text{Eq. 2.73}$$

In the case of interdiffusion, both Fick's laws apply, but the interdiffusion coefficient is considered in them, i.e. the corresponding equations of Fick's laws have following forms for the case of interdiffusion:

Fick's first law:

$$J_A^i = -\tilde{D} \frac{\partial c_A}{\partial x} \qquad \text{Eq. 2.74}$$

Fick's second law:

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D} \frac{\partial c_A}{\partial x}\right) \qquad \text{Eq. 2.75}$$

∑ Summary of terms from 2.4

After studying this part, following terms should be clear to you:

- **Interdiffusion**
- **Kirkendall effect**
- **Motion of boundary line in interdiffusion**
- **Diffusion porosity**
- **Interdiffusion coefficient**
- **Darken's equation**

? Questions to 2.4

27. With what materials did Kirkendall work in his experiment?
28. What role do molybdenum wires play in the Kirkendall's experiment?

29. Why does the motion of boundary line between two different materials occur in interdiffusion?
30. What determines the rate of motion of the boundary line in interdiffusion?
31. On the side of which material we can expect the emergence of the so called diffusion porosity during interdiffusion?

2.5. Up-hill diffusion

Time to study: 0.5 hours

Objective After reading this part, you should be able to:

- Explain the principle of up-hill diffusion.
- Explain the relationship of the chemical potential and course of up-hill diffusion.

Presentation

Special case of diffusion

In section 2.1 we have seen that the driving force for diffusion is the reduction in Gibbs energy, i.e. for equilibration of the chemical potential of the system components. In most cases, the differences between the concentrations of elements in different parts of the material are reduced in diffusion. (It was a classical diffusion, *the downhill diffusion*). However, we said that there is also another kind of diffusion, where in the course of diffusion the concentration differences in some elements may increase. This is the so called *up-hill diffusion*. Now we will explain it with an example.

Let us consider two steels that differ only little in the carbon content. In steel A the carbon content is somewhat higher than in steel B. But they significantly differ in the silicon content. Steel A contains a high content of silicon, while the silicon content in settle B is very low. We realize that silicon increases very significantly the activity of carbon in the steel.

We combine both steels and will anneal them at temperature below A_{c1}, i.e. so that the two steels are in the ferrite stability region, and examine how the carbon concentration will change near the boundary line. Situation is schematically illustrated in Figure 2.16.

In part (a) of the picture, the solid line shows the carbon concentration at the beginning of annealing. Situation after annealing time t is shown in part (b). In “normal” diffusion, we would expect that the concentration difference in the carbon content will become equilibrated close to the boundary line. This is indicated by a blue dashed line. In fact, the course of the carbon content will be such as characterized by a solid black line. This means that in the vicinity of the boundary line, a significant decrease of carbon content in steel A will occur and vice versa, there will be an increase in carbon content in steel B. *Why will this happen?*

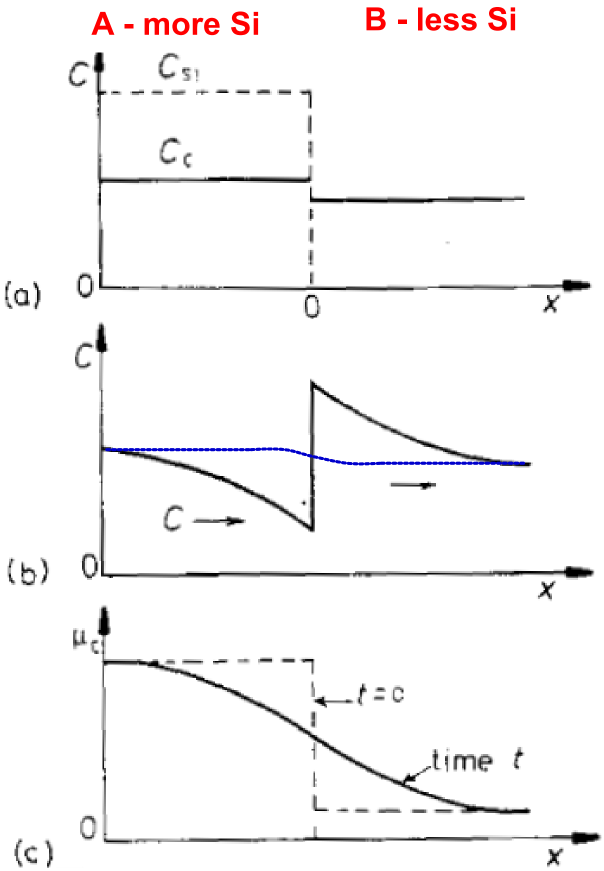


Fig. 2.16 Scheme to explain the up-hill diffusion

It is related to the presence of other element, in this case silicon, which has a significant influence on the activity of the carbon. It is true that with increased silicon content, a significant growth in the activity of carbon takes place. And you know that the activity of an element is associated with its chemical potential μ by equation:

$$\mu_i \approx R.T.\ln a_i \qquad \text{Eq. 2.76}$$

where μ_i is the chemical potential of element i,

a_i is the activity of element i.

In steel A, there is a much higher activity of carbon due to higher silicon content and the carbon here has much higher chemical potential. In contrast, the carbon activity in steel B is much lower due to the low content of silicon and therefore the chemical potential of carbon is lower as well. Thus, diffusion takes place so as to equilibrate the chemical potential of carbon in the vicinity of the boundary line, though it will mean that the carbon content will significantly increase in steel B in the vicinity of the boundary line. The course of the chemical potential of carbon near the boundary line is shown in Figure 2.16c.

Summary of terms from 2.5

After studying this part, following terms should be clear to you:

- **Up-hill diffusion**

Questions to 2.5

32. What is the course of up-hill diffusion related to in most cases?
33. What practical impact the up-hill diffusion may have in the case of joining various steels?

	Key to the solution – answers to questions to Chapter 2
A1	Diffusion is the transfer of particles of matter, mostly of atoms or ions, which leads to higher thermodynamic stability of the system.
A2	The driving force for diffusion is the reduction of the free enthalpy of the system.
A3	Downhill diffusion proceeds so that equilibration of concentration differences in various locations of the system takes place during it.
A4	Up-hill diffusion proceeds so that concentration differences increase during it.
A5	Diffusion stops when the value of chemical potential of the components at any point in the system is the same.
A6	The individual diffusion mechanisms include e.g. elementary jump in interstitial diffusion, or vacancy mechanism of substitutional diffusion.
A7	Among the collective diffusion mechanisms, there is e.g. the direct exchange or cyclic exchange in substitutional diffusion.
A8	Auto diffusion means the motion of atoms of the basic element of the system.
A9	Heterodiffusion means the diffusion of impurity elements.
A10	The processes necessary for solid state diffusion are thermal vibrations of atoms.
A11	The vibrational motion is characterized by frequency and amplitude of vibrations.
A12	The frequency of vibrational motion of atoms in solid state is approximately $10^{13}\ s^{-1}$.
A13	In principle, the frequency of vibrational motion of atoms does not depend on temperature.
A14	The amplitude of vibrational motion of atoms depends on the temperature and increases with the increasing temperature.
A15	The diffusion flux is such amount of a substance (e.g. atoms), which passes through unit area per unit time.
A16	The diffusion flux is directly proportional to the diffusion coefficient and concentration gradient of a diffusing element.
A17	In pre-exponential member, inter alia, the frequency of vibrational motion of atoms and entropy associated with the energy barrier that must be overcome in the elementary jump are hidden.
A18	Fick's second law says that the change in concentration of the diffusing element in time is proportional to its diffusion coefficient and the second derivative of concentration with respect to distance.
A19	Unsteady state diffusion means such case when concentration of diffusing elements changes over time.
A20	We have encountered the error function in the distribution function of the Gaussian distribution.
A21	Auto diffusion takes place because it equilibrates the energy fluctuations of thermal vibrations of atoms.
A22	Auto diffusion of an element can be studied using its radioactive isotope.
A23	Account should be taken of the presence of vacancies.
A24	The activation energy in substitutional diffusion involves the own energy barrier of the elementary jump and activation energy for the formation of vacancies.
A25	Diffusion from inconstant source represents a diffusion, in which the diffusion source – diffusing element – is consumed, i.e. its concentration gradually decreases.
A26	The linear relationship is obtained between the square of the distance from the diffuse source and concentration of the diffusing element.
A27	Kirkendall worked with alpha brass and electrolytically applied copper.
A28	Molybdenum wires served as “gauges”, measuring points by means of which the thickness of alpha brass specimen was measured.

A29	The displacement of the boundary line occurs due to the different values of diffusion coefficients of diffusing elements.
A30	Rate of motion of the boundary line depends on the difference in diffusion coefficients of diffusing elements and on the gradient of mole fraction of the component with respect to distance.
A31	Diffusion porosity can be expected on the side of the element that diffuses faster.
A32	Up-hill diffusion mostly relates to the different active concentration of a diffusing element in different locations.
A33	Up-hill diffusion in the case of steel joints may mean e.g. local carburization or local decarburization, which may be reflected in different mechanical properties.

Other sources

Porter, D. A., Easterling, K. E., Sherif, M. Y.: *Phase Transformations in Metals and Alloys*. CRC Press, 2009, 500 s.

Mehrer, H.: *Diffusion in Solids*. Springer Verlag, Berlin, 2007, 651 s.

Callister, W. D.: *Fundamentals of Materials Science and Engineering*. John Wiley&Sons, USA, 2005, 712 s.

3. STRENGTHENING MECHANISMS IN METALLIC MATERIALS

In the case of construction materials, there are efforts to improve their mechanical properties, especially to increase the strength and toughness of materials. The increase in toughness of materials is very problematic. In contrast, there are several ways leading to increased strength, i.e. the reinforcement of materials. With regard to the focus of our study program, we will give our attention to strengthening of metallic materials. At the outset, we must mention one correction. When we write about strengthening, we would say, probably, that the quantity we want to increase is the ultimate strength. But it is not the case. Given the fact that metallic materials may only be stressed in operation in the elastic deformation region, the key quantity we want to increase in strengthening is the yield point or yield strength. We already know that the yield point is the maximum stress prior to which the material will deform elastically. Above the yield point, plastic deformation occurs, which means that dislocations move in the metallic materials and new dislocations are formed. To increase the yield point of the material, we have to make the movement of dislocations more difficult so that they will begin to move only when exposed to higher stresses. So we try to have obstacles in the material that will hinder the movement of dislocations.

There are several ways to increase the yield point of metallic materials, i.e. to strengthen them The most commonly used mechanisms include:

- strengthening by plastic deformation
- grain boundary strengthening
- solid solution strengthening
- precipitation strengthening

Subsequently, we will give at least basic information to individual mechanisms.

3.1. Strengthening by plastic deformation

Time to study: 1 hour

Objective After reading this part, you should be able to:

- Explain how metallic materials can be strengthened by plastic deformation.
- Specify what determines the degree of strengthening by plastic deformation.
- Describe the main advantages and disadvantages of strengthening by plastic deformation.

Presentation

It is as though the strengthening of metallic materials by plastic deformation contains a certain contradiction in terms. We wrote that the strengthening meant to restrict the movement of dislocations and now we are writing about plastic deformation. More specifically, we can write that it is a plastic deformation that precedes the normal use of the material. We will try to show you how this strengthening occurs through the example of a tensile test. Imagine that we perform a tensile testing of metallic material and record the working diagram. Example is shown in Figure 3.1.

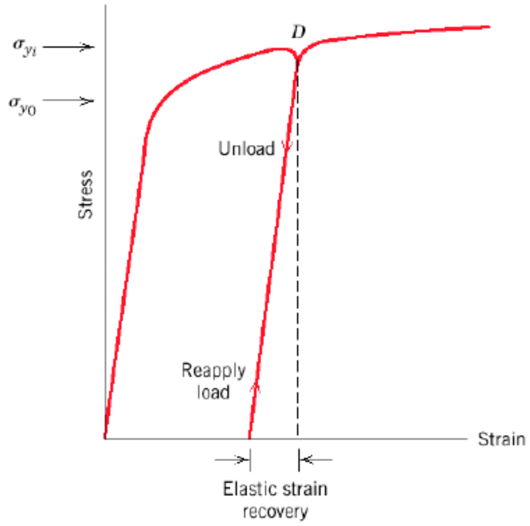


Fig. 3.1 Diagram of tensile test to explain the strengthening by plastic deformation

But the tensile test will not be performed until the test bar breaks, but we will disburden it in the region of uniform plastic deformation (approximately at point D in Figure 3.1). It can be seen from Figure 3.1 that in its initial state the material had a yield strength marked $\sigma_{y0.}$ If we subject the bar to a repeated loading after disburdening, the material will not have the same yield strength σ_{y0}, but its yield strength will correspond to approximately the stress at point D, i.e. the yield strength will be higher (in Figure 3.1, the yield strength under repeated loads is marked σ_{yi}). Previous loading into the plastic deformation region thus led to an increase in yield strength during subsequent loading of the material. How this happened?

We know that when plastic deformation occurs, dislocations start to move in the material, and also new dislocations are formed, i.e. their number increases (to speak professionally, the density of dislocations increases). Every dislocation creates a stress-strain field around itself and thereby the more dislocations are in the material, the more important these fields become; they may interact, which leads to the fact that the movement of dislocations is more and more difficult. We can simply say that the barriers to the movement of dislocations are the dislocations themselves when they are too many in the material. They prevent one another from moving. Plastic deformation thus leads to an increase in the density of dislocations, and it has the effect of increasing the yield strength during subsequent loading.

In practice, of course, the strengthening by plastic deformation does not take place by means of tensile tests, but by cold forming, e.g. cold sheet rolling, cold wire or pipe drawing, etc. Therefore, this strengthening is sometimes also called **deformation strengthening**. Cold forming leads both to the modification of shapes of grains, which is shown in Figure 3.2, and to the increase in the density of dislocations. Dislocations can be almost exclusively observed through transmission electron microscopy (Fig. 3.3).

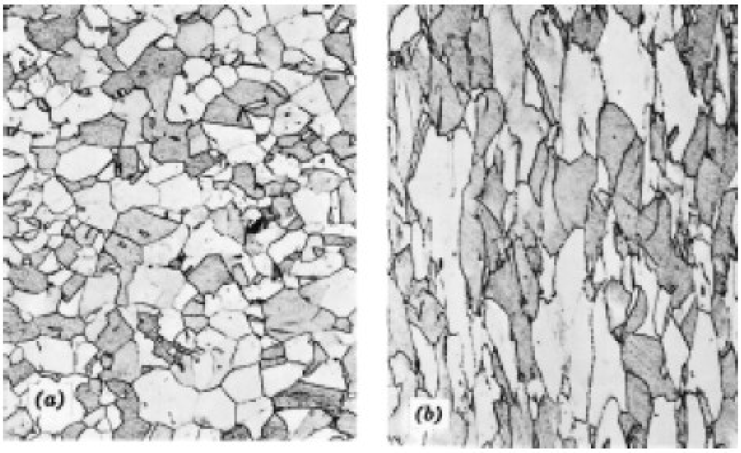


Fig. 3.2 Shapes of grains prior to cold forming (a) and after cold forming (b)

For determining the increase in yield strength by plastic deformation, the density of dislocations after plastic deformation of the material is important. This is denoted by the letter ρ and is defined as the ratio of lengths of dislocation lines to volume. Most frequently it is expressed in cm^{-2}. The equation for the density of dislocations can be written as follows:

$$\rho = \frac{L_{disl}}{V} \qquad \text{Eq. 3.1}$$

where L_{disl} is the length of dislocation lines,

V is the material volume.

For the materials in an annealed state, the usual density of dislocations is about 10^5 cm^{-2}, while for the materials in the state after cold forming it is between10^9 and 10^{11} cm^{-2}.

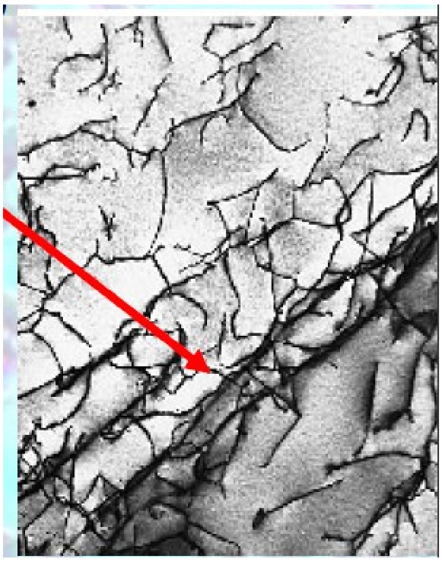


Fig. 3.3 Dislocations in aluminium viewed by transmission electron microscopy method

The increase in yield strength after strengthening by plastic deformation can be expressed by the equation:

$$\Delta R_e \cong 2.\alpha.G.b.\sqrt{\rho} \approx \sqrt{\rho} \qquad \text{Eq. 3.2}$$

where α is a constant equal to about 0.5,

G is the shear modulus,

b is the Burgers vector of dislocations,

ρ is the dislocation density.

Equation 3.2 shows that the rate of strengthening by plastic deformation is directly proportional to the square root of the dislocation density ρ.

Solved example:

Calculate the increase in yield strength for low carbon steel, for which the density of dislocations after cold forming was found to be $\rho=10^{10}$ cm^{-2}. Consider the shear modulus G = 70000 MPa and the Burgers vector of dislocations b= $2.8\cdot 10^{-10}$ m.

Solution:

We substitute the above specified values into Equation 3.2 and enumerate.

$$\Delta\tau \cong 2.\alpha.G.b.\sqrt{\rho} = 2\cdot 0.5\cdot 70000\cdot 2.8\cdot 10^{-10}\cdot\sqrt{10^{14}} \cong 196MPa$$

Conclusion: After the said cold forming, the yield strength of steel increases by 196 MPa. (And that's pretty much.)

Strengthening by plastic deformation is used for low carbon steels, but very often also in metals and alloys with fcc lattice, which have only low mechanical properties in the annealed state.

Unfortunately, strengthening by plastic deformation has also some very distinct disadvantages. The greatest disadvantage is a decrease of toughness, the embrittlement of material. In this respect, the strengthening by plastic deformation is probably the most dangerous type of strengthening. The possible decrease of toughness is illustrated in Figure 3.4 a, b, where the increase in yield strength and ultimate strength after cold deformation is indicated for copper, brass and low carbon steel (a), as well as the decrease of ductility depending on the degree of cold deformation (b).

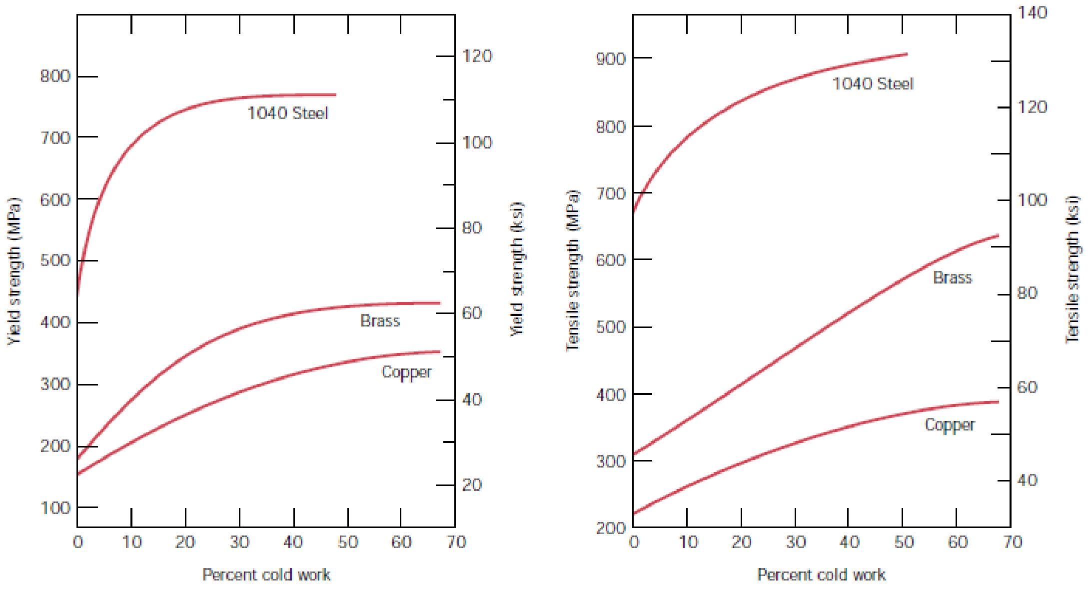


Fig 3.4a The increase in yield strength and ultimate strength for copper, brass and steel depending on the degree of cold deformation

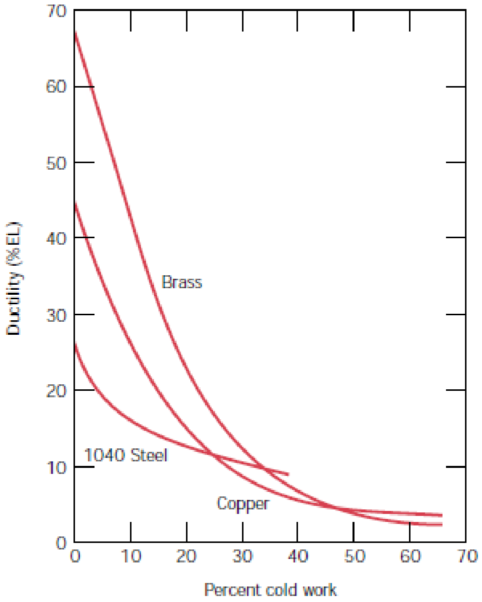


Fig. 3.4b The decrease of ductility for copper, brass and steel depending on the degree of cold deformation

Figure 3.4b shows that the decrease of ductility is rather drastic already after 20% of cold deformation. The decrease of ductility after cold forming to some extent reduces the possibility of using this mechanism of strengthening for those applications where a higher value of material toughness is requested.

Σ Summary of terms from 3.1.

After studying this part, following terms should be clear to you:

- **Strengthening by plastic deformation or cold forming**
- **Density of dislocations**

? Questions to 3.1.

1. What is a barrier to dislocation movement in dislocation strengthening?
2. What other term is used for dislocation strengthening?
3. How is the dislocation density defined?
4. On which parameter namely the rate of strengthening by plastic deformation depends?
5. For what metallic materials the strengthening by plastic deformation is used?
6. What is the main disadvantage of strengthening by plastic deformation?

3.2. Grain boundary strengthening

Time to study: 1 hour

Objective After reading this part, you should be able to:

- Explain how metallic materials can be strengthened by grain boundary strengthening.
- Specify what determines the degree of grain boundary strengthening.
- Describe the main advantages and disadvantages of grain boundary strengthening.

Presentation

Very important mechanism that allows to increase the yield strength, i.e. strengthening of metallic materials, is the grain boundary strengthening. Generally, the higher yield strength can be expected in materials with a small grain size, i.e. in fine grained materials. In contrast, lower yield strength can be expected in coarse-grained materials. Why is it that fine-grained materials have a higher yield strength, i.e. grain refinement leads to strengthening? We will try to answer in reverse, i.e. to answer why the coarse-grained materials have lower yield strength.

First, we must realize that the grain boundaries represent an obstacle in polycrystalline materials that dislocations cannot overcome. Dislocations are always in their movement restricted to grain, in which they were formed. Imagine a situation which is illustrated in Figure 3.5. Consider a coarse-grained polycrystalline material in which tensile stress σ operates. Then imagine that there is just one grain in this material oriented so that the plane of maximum shear stress (i.e. the stress that sets a dislocation in motion) is identical to the slip plane in this grain (i.e. the plane on which dislocations move). And also imagine that the maximum shear stress τ is just so large that in this single grain a plastic deformation can occur. If plastic deformation takes place, it means that dislocations will move around this grain and new dislocations will be formed. Dislocations will move on slip planes to the boundary of the grain, where they stop. As more dislocations propagate to this grain boundary, dislocation "pile up" $\Delta\tau_{pup}$ occurs. And this dislocation pile up is associated with the existence of a certain stress, which acts even into neighbouring grains. The bigger the grain is, the more dislocations pile up at the grain boundaries and the higher is the stress from this accumulation. This stress will be summed up with the shear stress on the slip planes in neighbouring grains τ_b, which are less favourably oriented, and the level of stress needed to cause plastic deformation may be exceeded. This means that plastic deformation may occur in a larger number of grains and macroscopic yield point is reached.

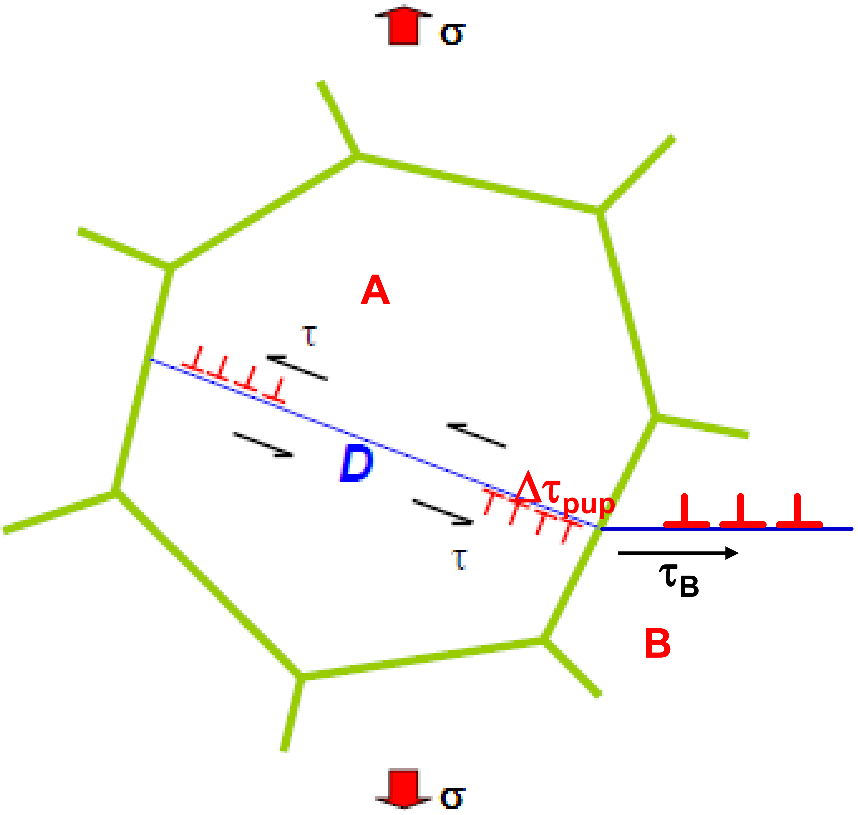


Fig. 3.5 Schematic illustration to explain the low yield strength in coarse-grained material

If the material is fine-grained and if plastic deformation is possible in just only one grain under the action of a certain stress σ, the dislocation pile up here at the grain boundaries will be lower. So also the stress from this pile up $\Delta\tau_{pup}$ will be lower, and it is very likely that no plastic deformation occurs in neighbouring grains. This will occur only if a higher stress σ will act in the material. Finer grain thus means an increase in the yield strength of the material.

The dependence of the yield strength upon the grain size is described by Hall-Petch relationship, which can be simply written as follows:

$$\Delta R \cong \tau_0 + \frac{K}{\sqrt{d}} \qquad \text{Eq. 3.3}$$

where τ_0 is the friction stress,

K is a constant,

d is the grain diameter.

In the case of steels with bcc lattice, the following empirical equations are given:

$$R_e = 60 + 0.727.\frac{1}{\sqrt{d}} \tag{Eq. 3.4}$$

$$R_e = 80 + 0.523.\frac{1}{\sqrt{d}} \tag{Eq. 3.5}$$

(d is entered in m, R_e in MPa).

The question is, how far it makes sense to refine the grain size in order that there is still the increase in the yield strength. The limit is indicated by values between 10 and 100 nm. The size of grains in conventional materials is mostly in units of micrometres. Further refinement of grains below the level of micrometres makes sense as another possibility for increasing the yield strength of the material.

Grain boundaries strengthening depends quite significantly on the type of crystal lattice of the metallic material. This type of strengthening is more effective in metals with bcc lattice. For metals having fcc lattice, the strengthening by grain refinement is less efficient, which is evident from Figure 3.6.

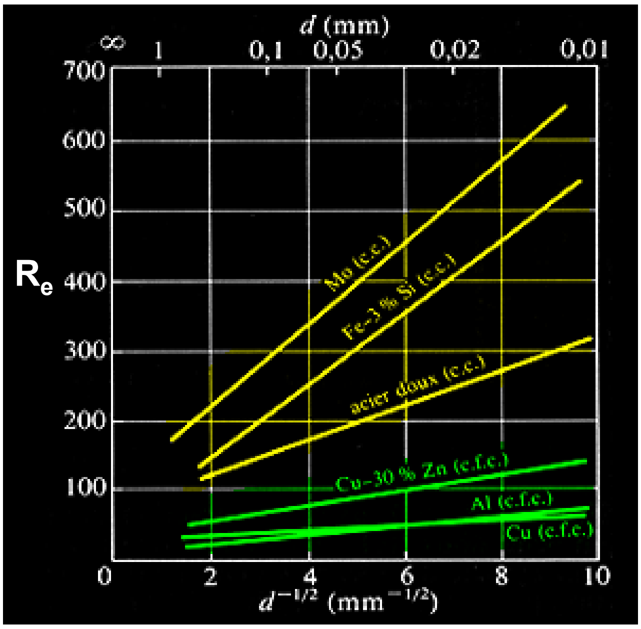


Fig. 3.6 The influence of grain size on yield strength for selected materials with bcc and fcc lattice

Solved example:

Use Equation 3.4 to determine how much the yield strength of the steel increases, if there is a decrease in the mean grain size from 10 μm to 1 μm.

Solution:

By simply substituting, we get the yield strength of 290 MPa for the grain size 10 μm, i.e. 0.00001 m.

$$R_e = 60 + 0.727 \cdot \frac{1}{\sqrt{0.00001}} = 290 MPa$$

For grain size 1 μm, i.e. 0,000001 m, Equation 3.4 gives the yield strength of 787 MPa.

$$R_e = 60 + 0.727 \cdot \frac{1}{\sqrt{0.000001}} = 787 MPa$$

The increase in yield strength is 787 – 290 = 497 MPa.

Conclusion: Decreasing the grain size from 10 μm to 1 μm gives the increase in yield strength of nearly 500 MPa (and this difference is extremely large).

Grain boundary strengthening has a privileged position in a sense among all the strengthening mechanisms, and this privileged position is a positive one. Grain boundary strengthening. i.e. strengthening by grain refinement is the only strengthening method that leads to higher toughness of the material. And this is particularly valuable.

Summary of terms from 3.2.

After studying this part, following terms should be clear to you:

- **Grain boundary strengthening, i.e. strengthening by grain refinement**
- **Dislocations pile up at the grain boundaries**
- **Hall-Petch relationship**

Questions to 3.2.

7. What is the barrier to the movement of dislocations in grain boundary strengthening?
8. What is the main reason for the lower yield strength in coarse-grained materials?
9. How to express the dependence of the yield stress on grain size?
10. In materials with what type of crystal lattice the grain boundary strengthening is more effective?

11. To what size does it have a sense to refine the grain with respect to any possible increase in the yield strength?
12. How does the grain boundary strengthening reflect in the material toughness?

3.3. Precipitation strengthening

Time to study: 1.5 hours

Objective After reading this part, you should be able to:

- Explain how to strengthen metallic materials using precipitates.
- Describe the mechanism of intersection of precipitates by dislocations.
- Characterize the mechanism of bowing of precipitates by dislocations.
- Compare both of these mechanisms and explain what structural characteristics of the precipitates they depend on.

Presentation

Another strengthening mechanism, which allows to increase significantly the yield strength of metallic materials is the so called precipitation strengthening. Precipitates are very small particles of minority phases, i.e. those phases which are present in the material in a relatively small amounts (usually about ones of per cents by volume). Minority phases in steels may be carbides or nitrides. In other metallic materials, minority phases are various intermetallic phases, for example in aluminium alloys that can be Al_2Cu phases, in nickel alloys Ni_3Al phases, etc.

The basic precondition for the precipitation strengthening to be effective is that the particles of precipitates are small and close to each other, i.e. there are relatively small distances between them.

More specifically, the precipitates are determined by the following stereological parameters that characterize them more accurately:

Volume fraction of precipitates	V_f (-)
Number of particles per unit volume	N_V (m^{-3})
Mean particle diameter (radius)	d (r) (m)
Mean interparticle spacing	λ (m)

Probably the most important parameter is the mean interparticle spacing and particle diameter or radius. For most materials, it is most advantageous when the values of these two parameters are in the tens of nanometres. It is therefore evident that particles of precipitates must be really very small and must be very close to each other so that the precipitation strengthening is effective. This configuration is schematically illustrated in Figure 3.7.

There is a wide range of relationships for the determination of the mean interparticle spacing, let us mention a few at random:

$$\lambda = \frac{4.(1-V_f).r}{3.V_f} \qquad \text{Eq. 3.6}$$

$$\lambda = \frac{1}{\sqrt{N_V.d}} - \frac{2}{3}.d \qquad \text{Eq. 3.7}$$

For a constant volume fraction of precipitates it is true that the smaller is the particle radius, the smaller is the interparticle spacing (since their number increases).

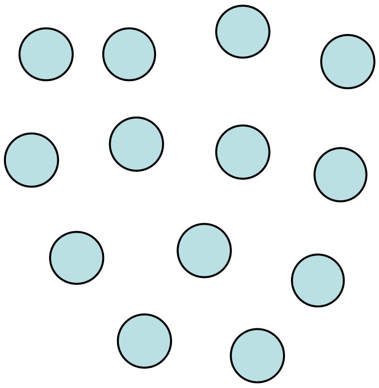


Fig. 3.7 The characteristic distribution of precipitates for optimal precipitation strengthening

In the case of precipitation strengthening, the barriers to the movement of dislocations are the particles of precipitates. If dislocations are to move in a metal matrix, where there are particles of other phases, often even with a different type of crystal lattice, they need a higher stress to start moving, which therefore means the strengthening, i.e. increase in the yield strength.

If a dislocation moves within the matrix, in which the particles of precipitates are present, there are basically two possible mechanisms of interaction between a dislocation and a precipitate. Which mechanism is applied, it depends primarily on the size of the precipitate and its nature.

Mechanism of intersection of precipitates by dislocations

If precipitates are small and so called coherent with a metal matrix, the **mechanism of intersection of a precipitate by dislocation** applies. But we have to explain what a coherent precipitate is. Coherence is a word derived from Latin and means among other things the continuity. Coherent precipitate is such a precipitate, which has a continuity of its crystallographic planes with crystallographic planes in the matrix. So we can say that certain crystallographic planes of the matrix are continuously passing to the crystallographic planes of the precipitate and then again to the crystallographic planes of the matrix. Any mismatch in the lattice parameters of the precipitate and metal matrix is compensated by elastic deformation. Coherent precipitates with most materials are particles up to about 10 nm, i.e. only very small particles. Example of a coherent precipitate is shown in Figure 3.8. Figure 3.9 then illustrates the mechanism of intersection of precipitates by dislocations.

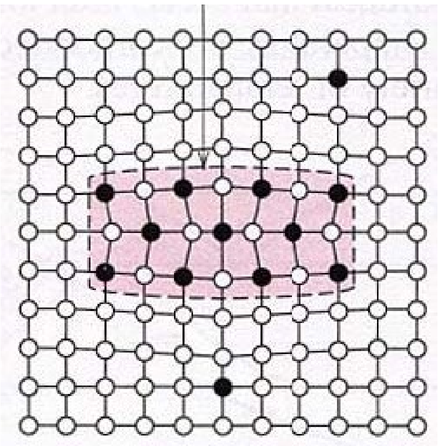


Fig. 3.8 Example of a coherent precipitate

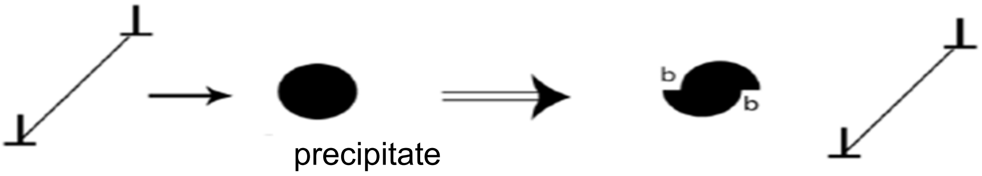


Fig. 3.9 Schematic illustration of intersection of a precipitate by a dislocation

As shown in Figure 3.9, when the precipitate is intersected by one dislocation, the two parts of the precipitate are displaced (above and below the slip plane in which the dislocation moves) by the value of the Burgers vector of dislocation b. Example of intersection of particles of Ni_3Si precipitates in Ni-6% Si system is shown in Figure 3.10. *(This is a quite exceptional example, because you can see that in this case the particles of precipitates are extremely large.)*

Numerous relationships were derived for the increment of strengthening induced by intersection of precipitates by dislocations. These are mostly semi-empirical relationships, and so they differ from each other. The simplest example is the relationship:

$$\Delta R_e \cong \frac{\gamma_{M-P} . \pi . r}{b . \lambda} \qquad \text{Eq. 3.8}$$

where γ_{M-P} is the specific surface energy of matrix – precipitate boundary (usually is between 0.01 and 0.03 $J.m^{-2}$),

r is the precipitate radius,

λ is the mean interparticle spacing,

b is the Burgers vector of dislocation.

When considering the deformation ε caused by the difference of lattice parameters of matrix and precipitate, we get the following relationship:

$$\Delta R_e \cong konst . \varepsilon^{4/3} . V_f^{\;2/3} . \left(\frac{r}{b} \right)^{1/3} \qquad \text{Eq. 3.9}$$

where ε is the elastic deformation caused by the difference of lattice parameters of matrix and precipitate;

V_f is the volume fraction of precipitate.

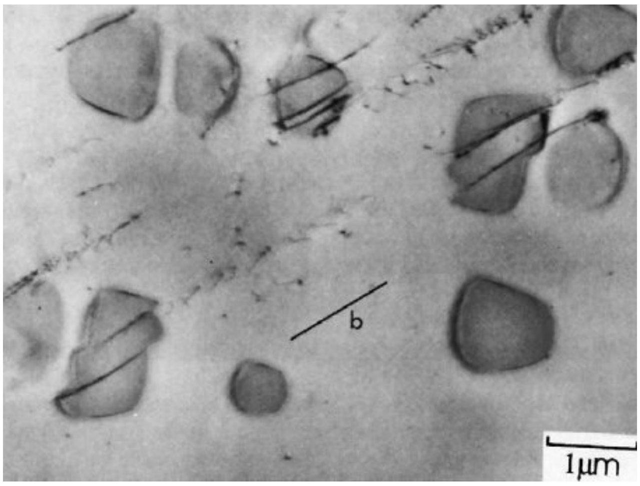


Fig. 3.10 Intersection of Ni_3Si particles in Ni-6%Si system *(viewed by transmission electron microscopy method)*

It will do the trick when we remember that in the case of the mechanism of intersection of precipitates by dislocations, it is true that the larger the precipitates are, the greater is the increase in strengthening. (This follows from the fact that in both Equations 3.8 and 3.9, the precipitate radius appears in the numerator).

Solved example:

Use Equation 3.8 to determine the strengthening increment (increase in the yield strength) by precipitation strengthening using carbide precipitates in the steel, when considering the surface energy of the boundary of 0.02 J.m^{-2}, mean radius of the precipitates of 20 nm and mean interparticle spacing of 50 nm.

Solution:

We substitute into Equation 3.8 (just be careful about the units, everything will be substituted in SI base units and only the end result will be converted to MPa).

Therefore it applies:

$$\Delta R_e \cong \frac{\gamma_{M-P}.\pi.r}{b.\lambda} = \frac{0.02 \cdot 3.14 \cdot 1 \cdot 10^{-9}}{2.8 \cdot 10^{-10} \cdot 50 \cdot 10^{-9}} = 224 \cdot 10^{6}\, N.m^{-2} = 224 MPa$$

Conclusion: For specified values, the intersection of precipitates by dislocations will cause an increase in yield strength of 224 MPa in the steel with carbide precipitates.

Mechanism of bowing dislocations around precipitates

If particles of precipitates are larger, and the precipitates are no longer coherent with the matrix (i.e. there is no longer a continuity of crystallographic planes in the matrix and in the precipitate), the mechanism of precipitate intersection cannot be applied, but a different mechanism of interaction precipitates and dislocation can apply. This mechanism is the so-called **bowing of dislocations around precipitates**. This mechanism was first described by Orowan and so it is often called Orowan mechanism. The principle of this mechanism is shown schematically in Figure 3.11.

The mechanism of bowing of dislocations around precipitates works as follows: if a dislocation moves in the material and approaches a precipitate, which is not coherent, and cannot therefore intersect it, the dislocation begins to curve gradually in the vicinity of the precipitate until it forms a closed dislocation loop around the precipitate. The straight parts of dislocation again join together after enlacing the precipitate and the dislocation can move on. Higher stress is needed to bend around a precipitate, which means strengthening, i.e. an increase in yield strength. The example of bowing dislocations around Ni_3Si precipitate in Ni-6% Si system is shown in Figure 3.12.

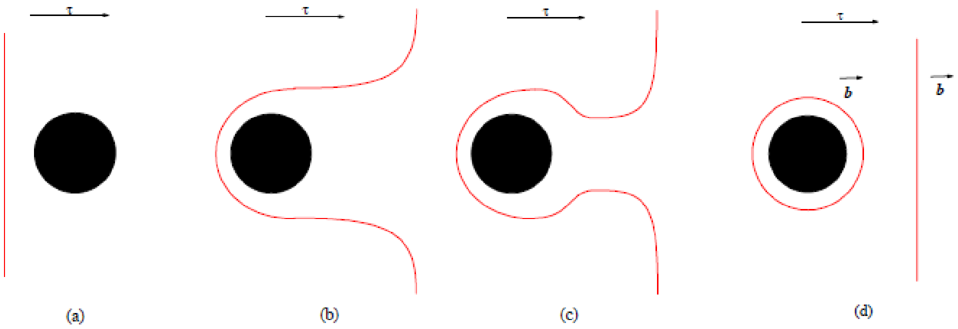


Fig. 3.11 Principle of Orowan mechanism

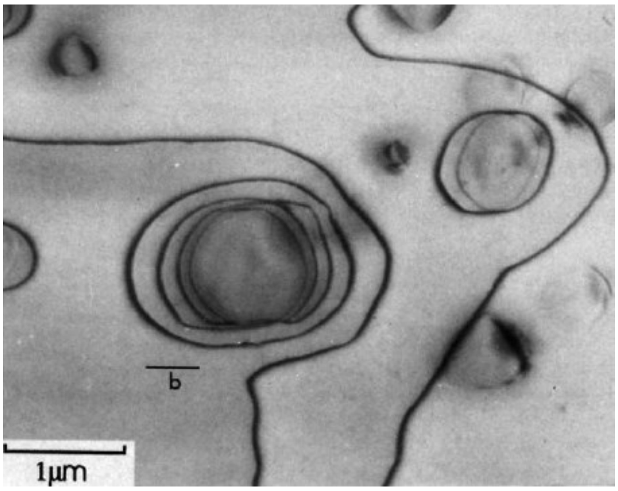


Fig. 3.12 Dislocation loops around Ni3Si particles in Ni-6%Si system *(viewed by transmission electron microscopy method)*

The strengthening increment in Orowan mechanism can be again expressed in a variety of different relationships, but we will mention only one. Increase in the strengthening can be described by the following equation:

$$\Delta R_e \cong konst.\frac{G.b.V_f^{1/2}}{r}, \qquad \text{Eq. 3.10}$$

Each member has been already described in the previous equations.

The point is that in Equation 3.10, the precipitate particle radius is in the denominator, which means that in bowing of precipitates the smaller the precipitates are, the higher is the strengthening. This stems from the fact that the smaller is the radius of dislocation curvature, the higher is the stress necessary for the dislocation to curve.

If we compare the two mechanisms of interaction of dislocations with precipitates, we may say that the maximum strengthening is achieved in the area where the mechanism of intersection of precipitates merges into the mechanism of bowing dislocations around precipitates.

The precipitation strengthening is used in a wide variety of steels, e.g. all steels for use at elevated temperatures (in different nodes of thermal power plants) are based on the precipitation strengthening. This strengthening is also used in many non-ferrous metals, such as aluminium, copper and nickel alloys, etc.

The negative feature of the precipitation strengthening (as in the case of strengthening by plastic deformation) is the decrease in plastic properties of the material, i.e. the decrease of toughness. But in the case of the precipitation strengthening, the decrease of toughness is not as dramatic as in the case of strengthening by plastic deformation.

Σ Summary of terms from 3.3.

After studying this part, following terms should be clear to you:

- **Precipitation strengthening**
- **Intersection of precipitates by dislocations**
- **Coherent precipitate**
- **Bowing of dislocations around precipitates – Orowan mechanism**

? Questions to 3.3.

13. What do we understand by the term of precipitates?
14. Which stereological parameters of the precipitates are the most important in terms of possible degree of precipitation strengthening?
15. What is the basic condition that the precipitates should meet for the precipitation strengthening to be effective?
16. How coherent precipitates can be characterized?
17. What is the mechanism of interaction that is applied between coherent precipitates and dislocations?
18. How does the strengthening increment depend on the radius of precipitates in the intersection of precipitates?
19. Up to what size of precipitates the mechanism of intersection of precipitates can be usually applied?
20. How the lattice mismatch between the matrix and precipitates is compensated in the case of coherent precipitates?

21. What formation a dislocation leaves around the precipitates in the case of bowing of precipitates by dislocations?
22. How does the strengthening increment depend on the radius of precipitates in the Orowan mechanism?

3.4. Solid solution strengthening

Time to study: 1 hour

Objective After reading this part, you should be able to:

- Explain the principle of solid solution strengthening.
- Characterize the difference between the so called elastic interaction and modular interaction.

Presentation

Increase in the yield strength of metallic materials can be even caused by atoms of impurities which are dissolved in the matrix, i.e. they constitute a solid solution with the basic component. Solid solution strengthening can be caused by both substitutionally and interstitially dissolved atoms.

Generally, dissolved atoms have a different size than the basic atoms in the matrix, which generates a stress field in the vicinity of a dissolved atom and associated elastic distortion of the lattice. Atoms of elements of smaller radiuses induce a local shrinkage of the crystal lattice, or they are preferably located into areas of tension field of dislocations (Fig. 3.13a,b). In contrast, the atoms of elements with a larger radius than is the radius of atoms of the basic element induce stretching (dilatation) of the crystal lattice or may be placed into areas of tension field of dislocations (Fig. 3.14a,b). A higher stress is required for the movement of dislocations in a given area, which means the strengthening of material or more precisely, the increase in its yield strength.

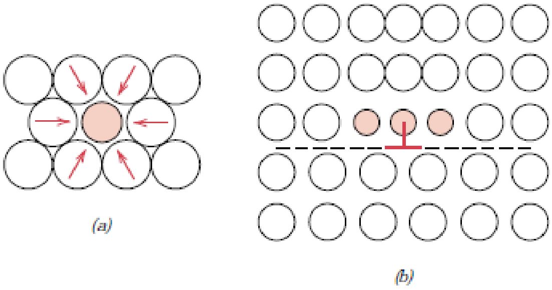


Fig. 3.13 Location of dissolved atoms with a smaller radius in the crystal lattice

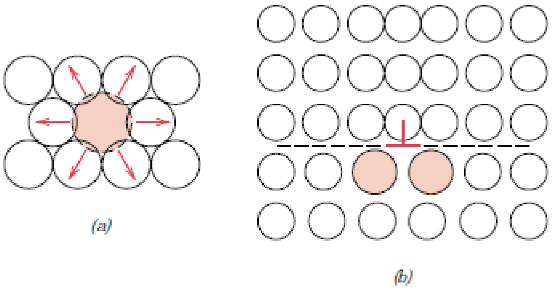


Fig. 3.14 Location of dissolved atoms with a larger radius in the crystal lattice

The strengthening increment depends both on the degree of lattice distortion induced by a dissolved element, and on its concentration.

This is just one of the existing relationships that describe the increment of strengthening caused by substitutionally dissolved atoms:

$$\Delta R_e \cong G.b.\varepsilon.\sqrt{c}$$ Eq. 3.11

where G is the shear modulus of the material,

b is the Burgers vector of dislocation,

ε is the elastic deformation caused by a dissolved atom,

c is the concentration of a dissolved element.

The above described strengthening by dissolved elements is sometimes called the **elastic interaction**.

Besides the elastic interaction, also the **modulus interaction** may take part in the strengthening by dissolved atoms, which reflects the fact that for some elements their bond energy with the basic element is higher than the bond energy between atoms of the basic element. This is shown, inter alia, by higher shear modulus of the material and the corresponding increment can be expressed as follows:

$$\Delta R_e \approx \Delta G.\sqrt{c}$$ Eq. 3.12

where ΔG is the increase in the shear modulus,

c is the concentration of a dissolved element.

In the case of steel, simple empirical relationships are often used, which include the effect of a higher number of dissolved elements, while an additive character is assumed for the increment of strengthening:

$$\Delta R_e = \sum_{i=1}^{n} k_i . c_i \qquad \text{Eq. 3.13}$$

where k is the constant that differs for each element dissolved (see Tab. 3.1),

c is the concentration of a dissolved element in % by mass.

Tab. 3.1. Constants k for the solid solution strengthening of steels by substitutionally dissolved atoms

Element	**P**	**Si**	**Ti**	**Mn**	**Cr**	**Mo**	**V**
Constant k	**350**	**80**	**100**	**50**	**-10**	**22**	**24**

From Table 3.1 it is seen that the highest solid solution strengthening of the steel would be ensured by phosphorus, but since it is a harmful element, it is not very useful in practice. In practical terms, in the case of steels the most significant is their strengthening by dissolved silicon atoms.

∑ Summary of terms from 3.4

After studying this part, following terms should be clear to you:

- **Solid solution strengthening**
- **Elastic interaction**
- **Modulus interaction**

? Questions to 3.4

23. What is the solid solution hardening based on?
24. What do we understand by the term of elastic interaction?
25. What do we understand by the term of modulus interaction?
26. Which element would ensure the highest level of solid solution strengthening in steel?
27. Which element is the most important for solid solution strengthening of steels from the practical standpoint?

	Key to the solution – answers to questions to Chapter 3
A1	The barrier to the movement of dislocations are dislocations occurred in the previous plastic deformation.
A2	Deformation strengthening or strengthening by cold forming.
A3	The dislocation density is the proportion of the lengths of dislocation lines and volume of the material.
A4	The rate of strengthening by plastic deformation depends primarily on the density of dislocations.
A5	Strengthening by plastic deformation is used for example in low-carbon steels, copper and aluminium alloys, etc.
A6	The main disadvantage of strengthening by plastic deformation is a decrease of toughness.
A7	The barrier to the movement of dislocations are grain boundaries themselves.
A8	The higher rate of dislocations pile up at the grain boundaries and the associated higher stress from this pile up.
A9	The yield strength is directly proportional to the inverse of square root of the grain diameter.
A10	Grain boundary strengthening is more effective for materials with bcc lattice.
A11	It has a sense to refine the grain to the size of about 10-100 nm.
A12	Grain boundary strengthening is manifested through increased toughness.
A13	The precipitates are fine particles of minority phases, carbides, nitrides, intermetallic phases, etc.
A14	The most important stereological parameters of the precipitates are their diameter and mean interparticle spacing.
A15	For the precipitation strengthening to be effective, precipitates must be small and close to each other.
A16	Coherent precipitates are such precipitates, for which there is a continuity of crystallographic planes of the precipitate and the matrix.
A17	Coherent precipitates are cut by dislocations.
A18	In the intersection of precipitates, the strengthening increases with the increasing radius of the precipitates.
A19	Mechanism of intersection of precipitates is applied up to the precipitate size of about 10 nm.
A20	In coherent precipitates, the lattice mismatch between the precipitates and matrix is compensated by elastic deformation.
A21	In the case of bowing of precipitates, the dislocation leaves a dislocation loop around the precipitate.
A22	In bowing of precipitates, the strengthening increment decreases with the increasing radius of the precipitates.
A23	Solid solution strengthening is primarily based on the different size of dissolved atoms and atoms of the basic element.
A24	Elastic interaction means the solid solution strengthening based on the different size of atoms of dissolved elements and basic element.
A25	Modular interaction means the solid solution strengthening based on a higher bond energy between atoms of the dissolved element and of the basic element.
A26	The highest level of solid solution strengthening in steel would be ensured by phosphorus.
A27	From the practical standpoint, the most important solid solution strengthening in steels is caused by dissolved silicon atoms.

Other sources

Callister W.D. jr., Rethwisch D. G.: *Fundamentals of Materials Science and Engineering. An Integrated approach.* Hoboken: Wiley, 2008. 3rd ed. 882 p. ISBN 978-0-470-12537-3.

4. SEGREGATION PROCESSES IN METALLIC MATERIALS

4.1. Division of segregation processes in metallic materials – macrosegregation, dendritic segregation

Time to study: 2 hours

Objective After reading this part, you should be able to:

- Divide segregation processes in metallic materials.
- Characterize the principle of macrosegregations and dendritic segregations.
- Describe further characteristics of dendritic segregation and possibilities of their reduction.

Presentation

❑ Division of segregation processes

Segregation processes in metallic materials can be simply divided into macrosegregations and dendritic segregations on the one hand, and microsegregations on the other. Occurrence of macrosegregations and dendritic segregations is associated with liquation of metallic material during their solidification.

In contrast, microsegregations mean enrichment of certain areas of the material by impurity elements, wherein this enrichment takes place in a very thin layer - typically monatomic or diatomic. Microsegregations most commonly occur at the boundaries of grains, then at the boundary of nonmetallic inclusion - matrix and at the boundary precipitates - matrix. The liquation during solidification of material is not the cause of microsegregations.

❑ Macrosegregations

Macrosegregations represent a phenomenon, in which the different parts of material have different chemical composition and this difference in chemical composition manifests itself across great distances comparable with the dimensions of ingots (in the classical method of casting). Given that you have dealt with this type of segregations in the bachelor's degree studies, it will not be addressed here in detail, we will just repeat what is its principle.

Macrosegregation is a consequence of liquation during solidification, i.e. redistribution of the elements between the solid and liquid phases. For each impurity element, a partition coefficient k can be defined, which indicates the ratio of its concentration in the solid phase (solidus) and liquid phase (liquidus).

Thus you can write that the partition coefficient ***k*** is

$$k = \frac{c_S}{c_L} \qquad \text{Eq. 4.1}$$

where c_S is the concentration of an element in the solid phase,

c_L is the concentration of an element in the liquid phase.

For most elements (e.g. in steel) it is true that their partition coefficient is less than one, i.e. that in those parts of the ingot, which solidify first, the concentration of these elements is the lowest, while the highest concentration of these elements is in those parts of the ingot, which solidify last.

The situation is schematically illustrated in Figure 4.1 in the example of a diagram with unlimited solubility in both liquid and solid state. *(If you do not remember where you first came across it, it was in the Materials Science course in the first year of Bachelor's degree studies – please refresh your knowledge).*

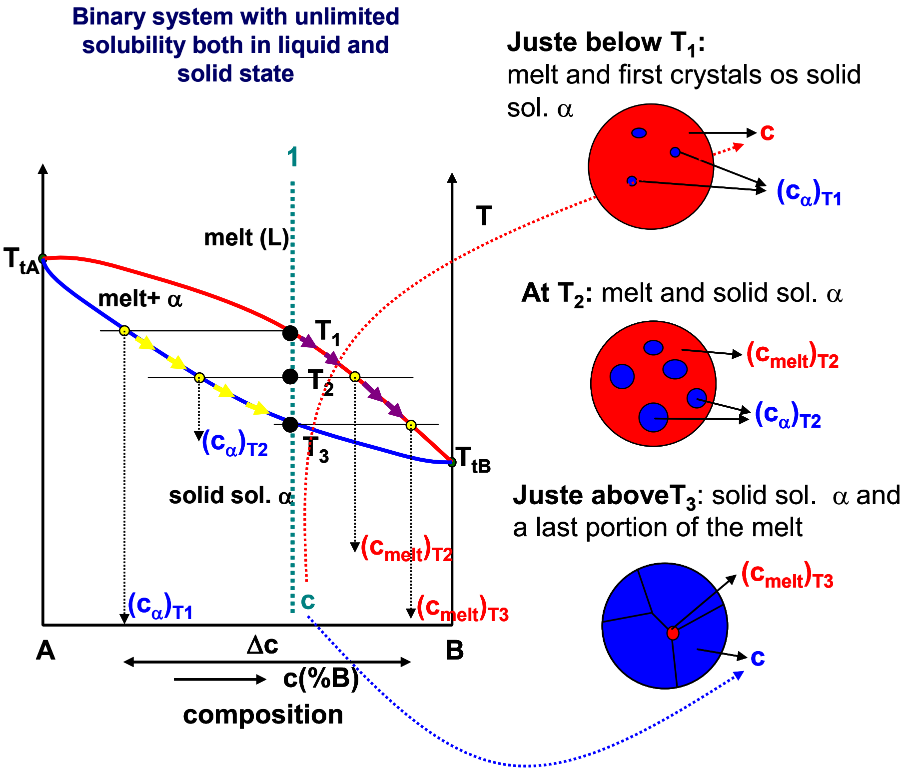


Fig. 4.1 Scheme to explain the liquation during solidification, which is the cause of the macrosegregation occurrence

Macrosegregations, as already mentioned, take place across large distances, and if they occur, they can neither be eliminated from the material nor their intensity reduced.

❑ Dendritic segregations

The dendritic segregations arise for the same reason as macrosegregations, i.e. due to liquation of material during solidification, but the distance, across which they occur, is much smaller and usually ranges up to hundreds of micrometres.

You will certainly recall that during solidification of the ingot, various kinds of crystals are produced, which is schematically shown in Figure 4.2, which represents the longitudinal and cross section through an ingot.

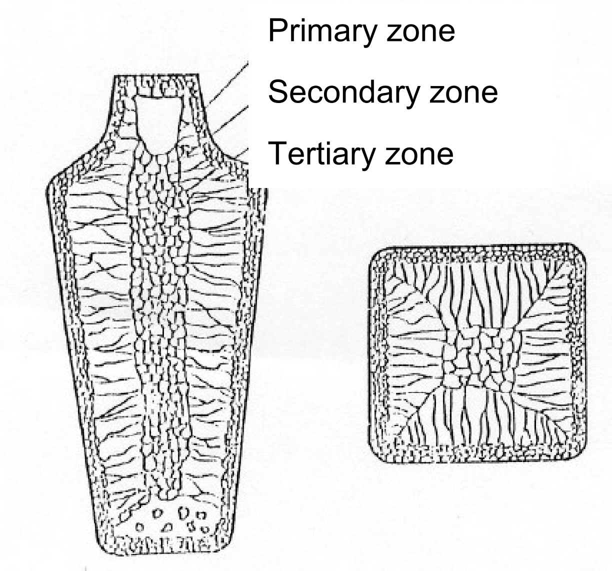


Fig. 4.2 Display of crystals on the longitudinal and cross sections through an ingot

Near the surface of the ingot, i.e. along the walls of the mould, there usually occur equiaxed grains. They are typically followed by the zone of columnar crystals. And in the middle of the ingot cross cut, there again appear equiaxed grains. In the area of columnar crystals, the so-called dendritic growth take place, when the heat is removed also through the liquid phase. In the case of dendritic growth, the crystals preferentially grow in the direction of the melt, in certain preferred crystallographic directions - for example, in the case of steel and solidification of the solid solution δ, the preferred direction is ⟨001⟩. Within one columnar crystal, even several dendrites can form. At first, they produce a primary axis and gradually even secondary and tertiary axes may occur. Dendrites thus receive their typical “tree” morphology. Example of a dendritic structure is shown in Figure 4.3.

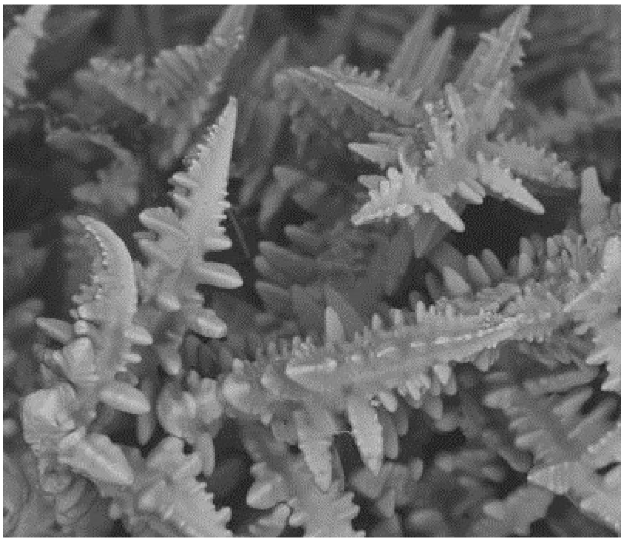


Fig. 4.3 Example of dendritic structure

Example of formation of dendrites within one columnar grain is shown in Figure 4.4.

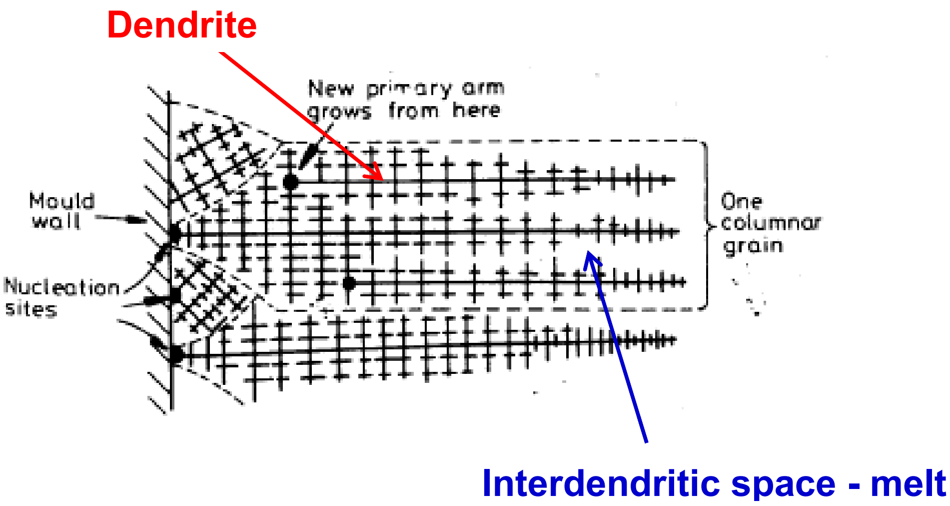


Fig. 4.4 Formation of dendrites within one columnar grain

First, primary axes of dendrites arise, then secondary and tertiary axes. The space between them, the interdendritic space, is filled with the melt and the concentration of all elements, the distribution coefficient k of which is smaller than 1, increases. This interdendritic space solidifies later and the increased concentration of the elements that liquate into the melt, is retained there.

Figure 4.5 shows an example of the etched metallographic specimen in nickel alloy casting for the aerospace industry, with visible dendritic liquation. Interdendritic spaces, which are enriched with elements liquating into melt, etch darker.

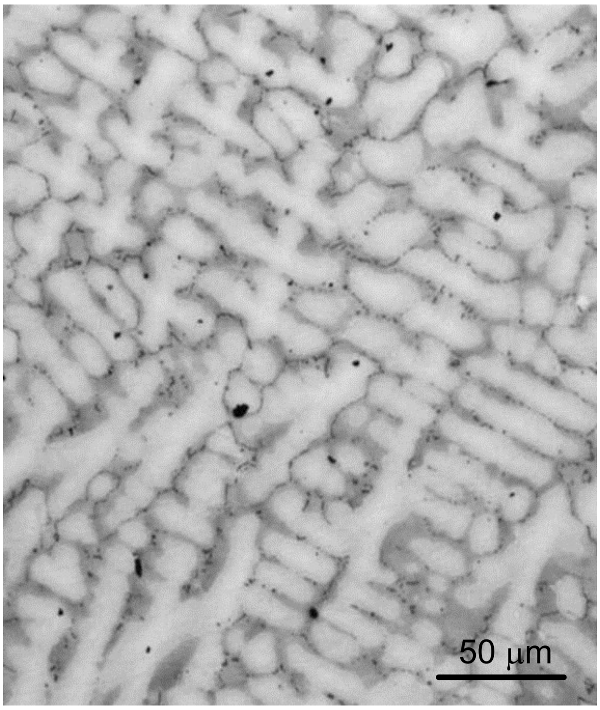


Fig. 4.5 The etched specimen in nickel alloy casting with visible dendritic segregations (areas of liquation etch darker)

Unlike macroscopic segregations, dendritic segregations can be at least partially reduced by a prolonged homogenizing annealing. Roughly it can be assumed that due to dendritic segregations, the content of certain elements periodically increases and decreases and the amplitude of this variation can be determined experimentally. In long-term annealing at high temperatures the amplitude of variations in the content of elements can decrease, which we dealt with in Chapter 2.2 on diffusion.

Σ Summary of terms from 4.1

After studying this part, following terms should be clear to you:

- **Macrosegregation and microsegregation**
- **Material liquation during solidification**
- **Columnar crystals**
- **Dendritic segregation**

? Questions to 4.1

1. As a result of what macrosegregations occur in metallic materials?
2. What is the value of the partition coefficient for most impurity elements in steels?

3. Can macrosegregations be eliminated by annealing?
4. What are dendrites in metallic materials?
5. Across what distance the dendritic segregation approximately occurs?
6. Is it possible to reduce the intensity of dendritic segregation in metallic materials in any way?

4.2. Microsegregation at the grain boundaries

Time to study: 3 hours

Objective After reading this part, you should be able to:

- Describe the basic characteristics of segregation at grain boundary.
- Solve problems related to the equilibrium grain boundary segregation.
- Explain under what conditions we can expect a non-equilibrium grain boundary segregation.

Presentation

❑ Basic characteristics of microsegregation at the grain boundares

Microsegregation at a grain boundary represents an enrichment of the grain boundary by certain impurity elements, in a very thin layer, either a monatomic or diatomic. The driving force for microsegregation at grain boundary is, of course, thermodynamic. If grain boundaries are enriched by certain impurity elements, the free enthalpy of the system decreases, i.e. the system of segregations to grain boundaries here passes into a more stable state. The impurity elements, which segregate to the grain boundaries, are called ***surface-active elements***.

Segregation at grain boundaries, however, takes place through diffusion of impurity elements, and thus whether there is equilibration or not depends also on the temperature level. From this perspective, segregation at the grain boundary is divided into equilibrium segregation (equilibrium state is achieved) and non-equilibrium segregation (equilibrium is not achieved, especially at low temperatures).

There is a whole range of factors determining why the free enthalpy of the system declines during segregation of certain elements at the grain boundaries. We mention here only one, and it is the factor of the size of atoms. For a number of elements, there is no simple relationship between the atomic number and size of the atom, some elements have larger atomic dimension than one might judge from their atomic number. Their presence in the nodal points of the lattice can cause a relatively large deformation, which reduces the stability of the system. When atoms of such elements diffuse to the grain boundaries and they are enriched at the grain boundaries, the stability of the system increases. Why? Large-angle boundaries of grains, about which we are talking, are disorders where there is more free space than in a normal crystal lattice and so the impurity elements more easily "fit in".

Is the segregation of impurity elements at the grain boundaries beneficial, detrimental or neutral from this point of view? There is no clear answer, but in many cases the segregation at the grain boundaries may be very harmful. For example, surface-active elements in steels include most of the harmful elements - phosphorus, sulphur, arsenic, antimony, and tin - and their segregation at the grain boundaries leads to embrittlement of steel and development of intercrystalline brittle fracture. As a result of segregation of detrimental elements at the grain boundaries, the cohesive strength of the grain boundary is reduced (the reduction of bond energy between atoms of the basic element - in the case of steel this means the reduction of bond energy between atoms of iron). Example of intercrystalline brittle fracture of structural steel induced by segregation of phosphorus at the grain boundaries is shown in Figure 4.6.

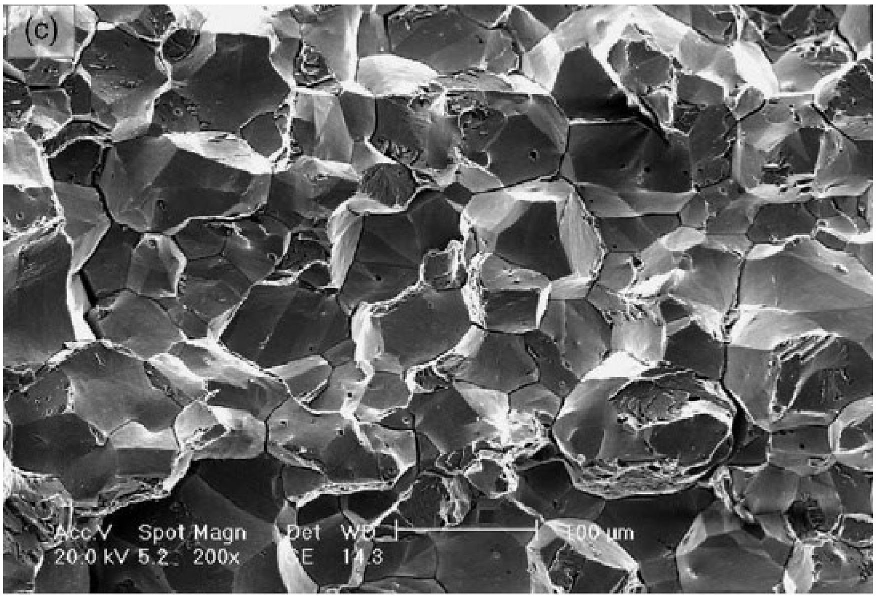


Fig. 4.6 Example of intercrystalline brittle fracture induced by segregation of phosphorus at the grain boundaries

In some cases, a quite clear correlation was found between the temperature of transition of brittle - ductile condition and the phosphorus concentration at the grain boundaries in the steel (Fig. 4.7).

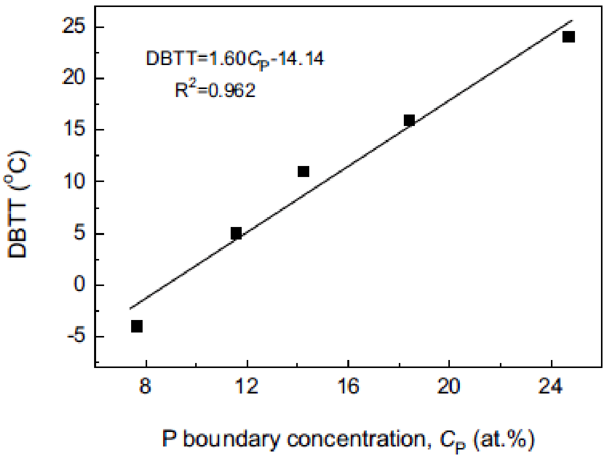


Fig. 4.7 Correlation between DBTT (ductile-brittle transition temperature) and concentration of phosphorus C_P at the grain boundaries in steel

It is therefore obvious that an increased content of phosphorus at the grain boundaries shifts the transition temperature towards higher values, which is undesirable.

Surface-active elements that segregate at the grain boundaries, include also some beneficial elements, such as molybdenum.

❑ Equilibrium segregation at grain boundaries in a binary system

Consider a binary system, in which the basic element is generally denoted M and surface active impurity is denoted I.

We would be interested to know what will be the equilibrium concentration of impurities at the grain boundaries. This equilibrium concentration is usually considered as the atomic fraction of impurities in monatomic layer at the grain boundary.

The solution is based on the Langmuir-McLean segregation theory and after a certain simplification it leads to the following equation:

$$\frac{n_i^{GB}}{1-n_i^{GB}} = \frac{n_i}{1-n_i}.\exp\left(-\frac{\Delta G_{M-i}^{segGB}}{RT}\right) \qquad \text{Eq. 4.2}$$

where

n_i^{GB} is the equilibrium rate of coverage of grain boundaries by atoms of impurity i (atomic fraction of impurity i at the grain boundary),

n_i is the atomic fraction of impurity i in the system,

ΔG_{M-i}^{segGB} is the free enthalpy of segregation of impurity i at the grain boundaries in the M-i system (J/mol),

R is the universal gas constant 8.314 J/mol.K

T is the absolute temperature (K)

Simplification of Equation 4.2 consists in the fact that it is assumed that the whole area of the grain boundaries is available for the segregation of impurity element.

For a very low content of impurity element i, it is true that:

$$\frac{n_i}{1-n_i} \cong n_i \qquad \text{Eq. 4.3}$$

Equation 4.2 can be then simplified using Equation 4.3 to the form:

$$\frac{n_i^{GB}}{1-n_i^{GB}} = n_i.\exp\left(-\frac{\Delta G_{M-i}^{segGB}}{RT}\right) \qquad \text{Eq. 4.4}$$

After adjustment, we obtain the relationship for the equilibrium rate of coverage of impurity i (its atomic fraction at the grain boundaries):

$$n_i^{GB} = \frac{n_i.\exp\left(-\frac{\Delta G_{M-i}^{segGB}}{RT}\right)}{1+n_i.\exp\left(-\frac{\Delta G_{M-i}^{segGB}}{RT}\right)} \qquad \text{Eq. 4.5}$$

Important: The free enthalpy of segregation of impurity *i* at the grain boundary ΔG_{M-i}^{segGB} is negative because it represents the energy which the system creates and not the energy that would have to be supplied to the system. Therefore, the argument of the exponent is a positive number and it will apply that with increasing temperature the equilibrium rate of coverage will decline.

From a thermodynamic point of view, the atoms of surface active elements want to be at the grain boundaries to the greatest possible extent at low temperatures. This has a certain logic, if we admit that one of the causes of segregation is the varied size of impurity atoms. At higher temperatures, due to a higher amplitude of the vibrational motion of atoms, it is not difficult for impurity atoms to “squeeze” into the crystal lattice of the basic element M. However, at low temperatures, when the amplitude of the vibrational motion of atoms is small, this problem is more pronounced and for the impurity atoms it will be more advantageous from a thermodynamic point of view to enrich the grain boundaries.

Temperature dependence of the equilibrium concentration of phosphorus at the grain boundaries of steel is shown in Figure 4.8.

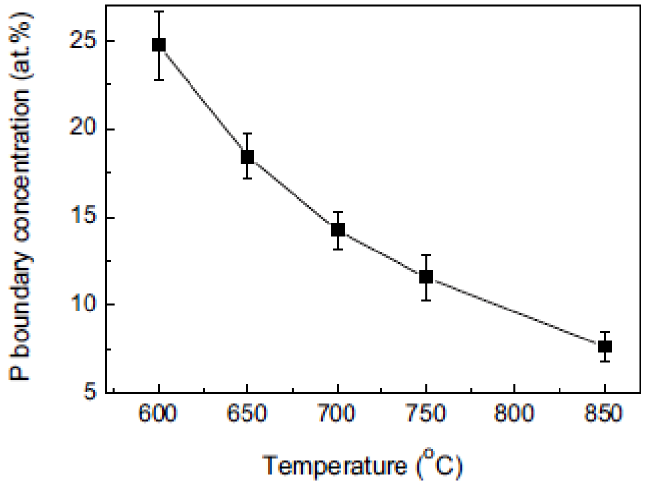


Fig. 4.8 Temperature dependence of the equilibrium concentration of segregation of phosphorus in the steel

Note:

Instead of free enthalpy of segregation, the segregation energy **ΔE (J/mol)** is often mentioned**.** Moreover, this energy is sometimes referred to as the **interaction energy of segregation and is considered as positive.** In the event that the **segregation energy ΔE is considered as positive**, it is necessary to modify the relationship for the calculation of n_i^{GB} as follows**:**

$$n_i^{GB} = \frac{n_i . \exp\left(\frac{\Delta E_{M-i}^{segGB}}{RT}\right)}{1 + n_i . \exp\left(\frac{\Delta E_{M-i}^{segGB}}{RT}\right)} \qquad \text{Eq. 4.6}$$

Solved example 4.1

Problem:

Consider Fe-P binary system with the phosphorus content of 0.03 % by weight. Calculate the equilibrium rate of coverage of boundaries by phosphorus atoms at a temperature of 500°C, if the atomic weight of iron is 55.85 and atomic weight of phosphorus 30.97 and if the interaction energy for phosphorus segregation at the iron grain boundaries ΔE_{Fe-P}^{segGB} = 50 kJ/mol.

Solution:

We can use Equation 3.6 for the solution.

But first we need to convert the weight percent of phosphorus to the atomic fraction of phosphorus.

This can be done as follows (see the textbook of chemistry):

$$at.fr.P = \frac{\dfrac{mass\%P}{at.massP}}{\dfrac{mass\%P}{at.massP} + \dfrac{mass\%Fe}{at.massFe}} = \frac{\dfrac{0.03}{30.97}}{\dfrac{0.03}{30.97} + \dfrac{99.97}{55.85}} = 0.0005408$$

Then we can calculate the member

$$n_P.\exp\left(\frac{\Delta E_{Fe-P}^{segGB}}{RT}\right) = 0.0005408\,.\exp\left(\frac{50000}{8.314.(500+273)}\right) = 1.292$$

And finally, we can calculate the degree of enrichment of the grain boundaries by phosphorus as follows:

$$n_P^{GB} = \frac{1.292}{1+1.292} = 0.5636$$

Conclusion:

At a temperature of 500°C, the degree of enrichment of the grain boundaries by phosphorus in Fe-P binary system is about 0.5636, i.e. about half of the possible places at the grain boundaries is occupied by phosphorus atoms.

☐ Non-equilibrium segregation at grain boundaries in a binary system

We encounter the non-equilibrium segregation preferably at lower temperatures, where the segregation is strongly favoured from a thermodynamic aspect, but the diffusion ability of atoms is so low that they are unable to diffuse sufficiently intensely to the grain boundaries. The relationship between equilibrium and non-equilibrium segregation is shown in Figure 4.9.

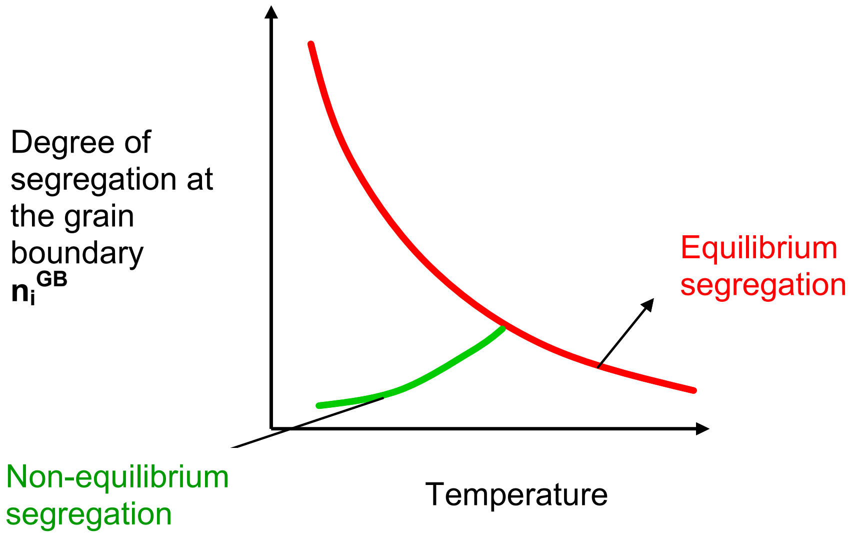


Fig. 4.9 Illustration of the relationship between equilibrium and non-equilibrium segregation

In non-equilibrium segregation, it is necessary to take into account the ability of atoms that are to segregate, at a given temperature and the time over which segregation takes place. Solution of the diffusion problem for non-equilibrium segregation leads to the following equation:

$$\frac{n_i^{GB}(t) - n_{i0}^{GB}}{n_i^{GB} - n_{i0}^{GB}} = 1 - \exp\left(\frac{4.D_i t}{\alpha^2 .d^2}\right).\left(1 - erf\left(\frac{2\sqrt{D_i .t}}{\alpha .d}\right)\right) \qquad \text{Eq. 4.7}$$

where

$n_i^{GB}(t)$	is the atomic fraction of element i at the grain boundary in time t,
n_{i0}^{GB}	is the atomic fraction of element i at the grain boundary in time t=0,
n_i^{GB}	is the equilibrium concentration (atomic fraction) of element I at the grain boundary,
$\alpha = \frac{n_i^{GB}}{n_i}$	is the degree of enrichment of the grain boundary by element i,
D_i	is the coefficient of diffusion of element i,
d	is the grain boundary thickness,
t	is the isothermal dwell time at temperature.

The non-equilibrium concentration need not occur only at low temperatures. The non-equilibrium segregation can take place even at higher temperatures, e.g. during rapid cooling from temperatures of 1200 (1300°C) to a temperature of about 700°C, where there is an excess of vacancies and complexes vacancy - segregating element are formed. Vacancies accelerate the diffusion of impurity elements to the grain boundaries and temporarily the concentration of the segregated element can increase above the equilibrium concentration.

Summary of terms from 4.2

After studying this part, following terms should be clear to you:

- **Microsegregation at the grain boundaries**
- **Equilibrium microsegregation at the grain boundaries**
- **Interaction energy of segregation**
- **Non-equilibrium microsegregation at the grain boundaries**

Questions to 4.2

7. How do we call elements having the ability to segregate at the grain boundaries?
8. What is the driving force for the segregation of elements at the grain boundaries?
9. How does the degree of coverage of grain boundaries by segregating element depend on the temperature in equilibrium segregation?
10. At what temperatures is the equilibrium rate of coverage of grain boundaries by segregating element highest?
11. At what temperatures is it most likely to encounter the non-equilibrium segregation?
12. How does the rate of coverage of grain boundaries by segregating element change with temperature in non-equilibrium segregation?

Task to solve 4.2

Problem:

Consider Fe-P binary system with the phosphorus content of 0.04 % by weight. Calculate the equilibrium rate of coverage of boundaries by phosphorus atoms at temperatures of 300°C and 700°C, if the atomic weight of iron is 55.85 and atomic weight of phosphorus 30.97 and if the interaction energy for phosphorus segregation at the iron grain boundaries ΔE_{Fe-P}^{segGB} = 50 kJ/mol.

Results:

For a temperature of 300°C, the rate of coverage of grain boundaries by phosphorus atoms is 0.963; For a temperature of 700°C, the rate of coverage of grain boundaries by phosphorus atoms is 0.258.

4.3. Microsegregation at the grain boundaries in the ternary and polycomponent systems

Time to study: 1.5 hours

Objective After reading this part, you should be able to:

- Explain the concept of competitive segregation.
- Describe the interactive segregation
- Explain how these phenomena can affect the properties of materials.

Presentation

In the ternary or polycomponent systems, there may exist more surface-active elements that will tend to segregate at the grain boundaries. In principle, two cases may occur in such systems:

1. There may be the so-called **competitive segregation** where the segregation of one element limits (decreases) the segregation of the other segregating element. This repulsive effect is encountered, for example, in the case of a simultaneous segregation of sulphur and phosphorus in steel, or phosphorus and carbon in steel, or molybdenum and phosphorus in steel.
2. **Interactive segregation or co-segregation** takes place where the segregation of two or more elements is mutually supported. Such a situation occurs, for example, in segregation of Mo and C, or Si and B in steels.

❑ Competitive segregation

As already mentioned, the competitive segregation means that the segregation of one surface-active element prevents the segregation of other surface-active element or elements. Preferentially segregates that element, which has the highest interaction energy of segregation. Example of a competitive segregation of carbon and phosphorus in steel is shown in Figure 4.10.

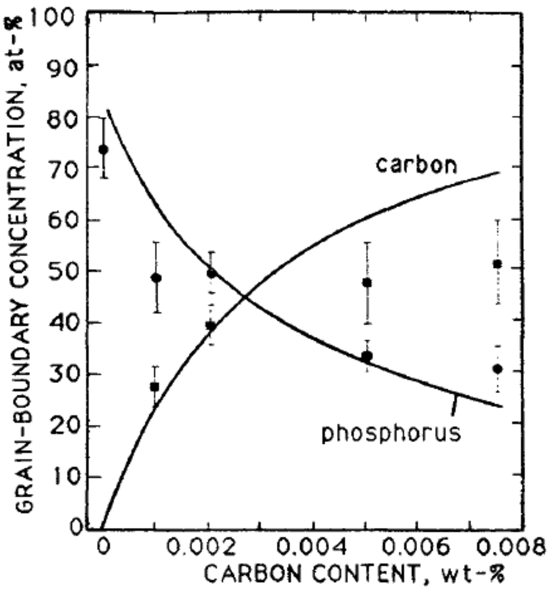


Fig. 4.10 Example of a competitive segregation of carbon and phosphorus in steel

Figure 4.10 shows that a relatively small increase in the content of carbon in steel leads to more intense carbon segregation at the grain boundaries, while segregation of phosphorus declines. The interaction energy of phosphorus segregation at the grain boundaries in steel is about 50 kJ/mol, while the interaction energy of carbon segregation is higher and reaches values of about 80 kJ/mol. The segregation of carbon is therefore thermodynamically more favourable, and therefore more likely than the phosphorus segregation. Even higher is the interaction energy of sulphur segregation at the grain boundaries in steel, which is about 130 kJ / mol.

The solution to the competitive segregation of two surface-active elements was presented by Guttmann in the seventies of the 20th century for the case of equilibrium segregation. Consider a system with two ternary surface-active elements i and j, which are able to segregate at the grain boundaries. You can then express the rate of coverage of grain boundaries by elements i and j under equilibrium conditions as follows:

$$n_i^{GB} = \frac{n_i \exp\left(\frac{\Delta E_i}{RT}\right)}{1 + n_i \exp\left(\frac{\Delta E_i}{RT}\right) + n_j \exp\left(\frac{\Delta E_j}{RT}\right)} \qquad \text{Eq. 4.8}$$

$$n_j^{GB} = \frac{n_j \exp\left(\frac{\Delta E_j}{RT}\right)}{1 + n_i \exp\left(\frac{\Delta E_i}{RT}\right) + n_j \exp\left(\frac{\Delta E_j}{RT}\right)} \qquad \text{Eq. 4.9}$$

where the symbols are analogous to those listed in section 4.2.

Solved example 4.2

Problem:

Consider Fe-C-P ternary system with the carbon content of 0.001% by weight and phosphorus content of 0.03% by weight. Calculate the equilibrium rate of coverage of grain boundaries by carbon and phosphorus atoms at a temperature of 300°C, if you know that the atomic weight of carbon is 12.01, atomic weight of phosphorus is 30.97 and atomic weight of iron is 55.85.

Solution:

In principle, the solution is directly given by Equations 4.8 and 4.9

To use these equations, we must express the content of carbon and phosphorus as atomic fractions.

We can write:

$$at.fr.P = \frac{\frac{mass\%P}{at.massP}}{\frac{mass\%P}{at.massP} + \frac{mass\%C}{at.massC} + \frac{mass\%Fe}{at.massFe}} = \frac{\frac{0.03}{30.97}}{\frac{0.03}{30.97} + \frac{0.001}{12.01} + \frac{99.97}{55.85}} = 0.0005408$$

$$at.fr.C = \frac{\frac{mass\%C}{at.massC}}{\frac{mass\%P}{at.massP} + \frac{mass\%C}{at.massC} + \frac{mass\%Fe}{at.massFe}} = \frac{\frac{0.001}{12.01}}{\frac{0.03}{30.97} + \frac{0.001}{12.01} + \frac{99.97}{55.85}} = 4.65.10^{-5}$$

Then we can calculate the members:

$$A = n_C \exp\left(\frac{\Delta E_C}{RT}\right) = 4.65 \cdot 10^{-5}.\exp\left(\frac{80000}{8.314 \cdot (300+273)}\right) = 908.88$$

$$B = n_P \exp\left(\frac{\Delta E_P}{RT}\right) = 0.0005408 \cdot \exp\left(\frac{50000}{8.314 \cdot (300+273)}\right) = 19.50$$

And now, we can calculate the rate of coverage of grain boundaries by carbon atoms on the one hand and phosphorus atoms on the other:

$$n_C^{GB} = \frac{A}{1+A+B} = \frac{908.88}{1+908.88+19.50} = 0.9779$$

$$n_P^{GB} = \frac{B}{1+A+B} = \frac{19.50}{1+908.88+19.50} = 0.0291$$

Conclusion:

In Fe-C-P system at a temperature of 300°C, the rate of equilibrium coverage of the grain boundaries by carbon atoms is 0.9779, while the rate of equilibrium coverage of the grain boundaries by phosphorus atoms is only 0.0291. The segregation of carbon atoms therefore significantly prevails, thanks to the higher interaction energy of carbon segregation.

The competitive segregation occurs, among others, in Fe-Mo-P or Fe-B-P systems, where both Mo and B reduce the intensity of phosphorus segregation at the grain boundaries. The mentioned behaviour is illustrated in Figures 4.11 and 4.12.

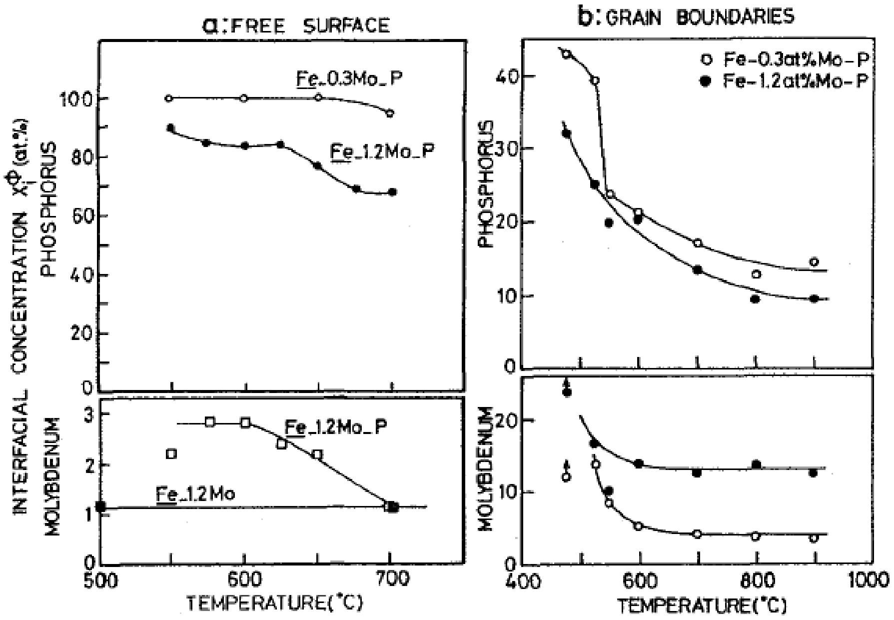


Fig. 4.11 Competitive segregation in Fe-Mo-P system

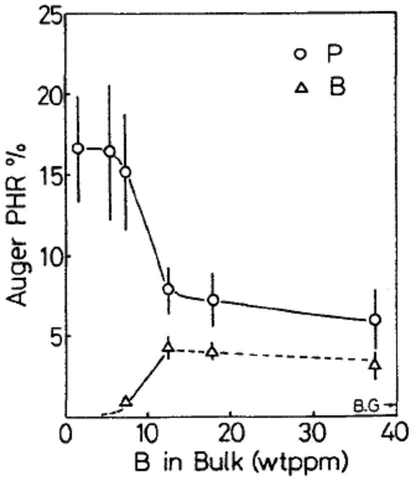


Fig. 4.12 Competitive segregation in Fe-B-P system

❑ Interactive segregation

The interactive segregation or co-segregation means that segregation of two or more elements segregating along grain boundaries can support each other. Or there may be situations where the presence of an element, which does not significantly segregate itself at the grain boundaries, increases the degree of segregation of other element. Figure 4.13 shows an example of co-segregation of titanium and antimony at the grain boundaries in pure iron. From the figure it is seen that the segregation of the two elements is mutually supported.

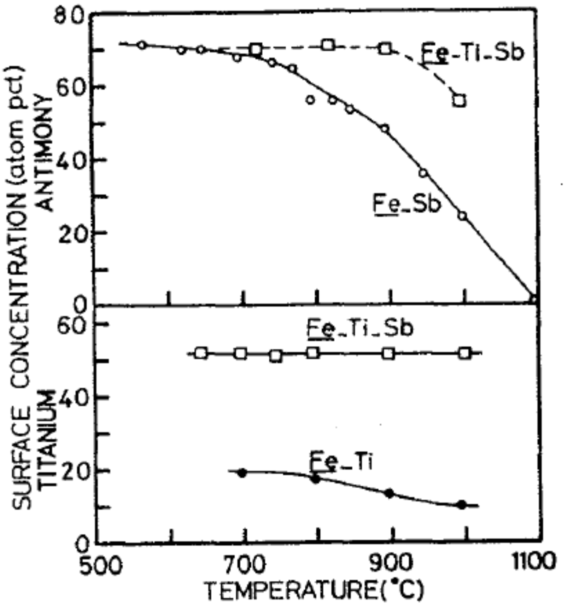


Fig. 4.13 Example of interactive segregation of Ti and Sb in pure Fe

Figure 4.14 shows how the varied content of nickel in iron affects the antimony segregation at the grain boundaries. In this case, the nickel itself does not segregate at the iron grain boundaries, but its higher content facilitates the grain boundary segregation of antimony in iron.

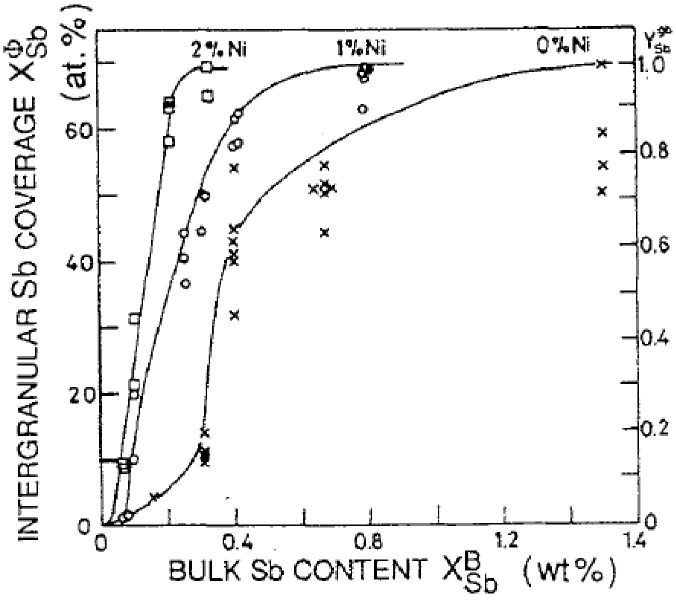


Fig. 4.14 Effect of Ni content on segregation of Sb at the iron (Fe) grain boundaries

Summary of terms from 4.3

After studying this part, following terms should be clear to you:

- **Competitive segregation**
- **Interactive segregation/co-segregation**

Questions to 4.3

13. What does the term competitive segregation in polycomponent systems mean?
14. In what pairs of elements that segregate at the grain boundaries in steels the effect of competitive segregation may apply?
15. Does the competitive segregation in steels seem to you to be rather beneficial or harmful?
16. What does the term interactive segregation mean?

Task to solve 4.3

Problem:

Consider Fe-C-P ternary system with the carbon content of 0.002% by weight and phosphorus content of 0.05% by weight. Calculate the equilibrium rate of coverage of grain boundaries by carbon and phosphorus atoms at a temperature of 500°C, if you know that the atomic weight of carbon is 12.01, atomic weight of phosphorus is 30.97 and atomic weight of iron is 55.85

Result:

In the given Fe-C-P system at a temperature of 500°C, the rate of equilibrium coverage of the grain boundaries by carbon atoms is 0.882, while the rate of equilibrium coverage of the grain boundaries by phosphorus atoms is 0.080.

4.4. Microsegregation at interphase boundaries

Time to study: 0.5 hours

Objective After reading this part, you should be able to:

- Explain the concept of microsegregation at interphase boundaries.
- Describe the segregation of hydrogen at interphase boundaries in steels and explain what consequences this segregation may have

Presentation

In addition to the grain boundaries, the surface active elements may segregate at many interphase boundaries, such as boundaries between nonmetallic inclusions and metal matrix, or boundaries between various precipitates and metal matrix. For the case of segregation at interphase boundaries, essentially all is true that was derived in Section 4.2 for the case of microsegregation at the grain boundaries.

Rate of coverage of the interphase boundary by segregating element i in the binary system M-i can be expressed by the equation:

$$\frac{n_i^{IF}}{1-n_i^{IF}} = \frac{n_i}{1-n_i}.\exp\left(-\frac{\Delta G_{M-i}^{segIF}}{RT}\right) \qquad \text{Eq. 4.10}$$

where IF is the interphase boundary; other quantities are analogous to quantities in Equation 4.2.

From a practical point of view, significant is the segregation of hydrogen at interphase boundaries between nonmetallic inclusions and matrix in steels, as this segregation may cause the so called hydrogen embrittlement, which is a very dangerous degradation mechanism of steel. In hydrogen atoms, which segregate at the interphase boundary between nonmetallic inclusions and matrix, recombination of atoms may in fact occur to form hydrogen molecules H_2. Hydrogen molecules induce such high stresses in the vicinity of the boundary that cracks may develop. Examples of hydrogen-induced cracking at the boundary between nonmetallic inclusions and matrix are shown in Figures 4.15 to 4.17.

Interaction energies for the segregation of hydrogen at interphase boundaries for different types of particles vary within a relatively wide range; the interval between 30 to 90 kJ/mol is specified. High levels of interaction energies for the hydrogen segregation were detected e.g. with particles of aluminium nitrides AlN, or titanium carbides TiC in steels.

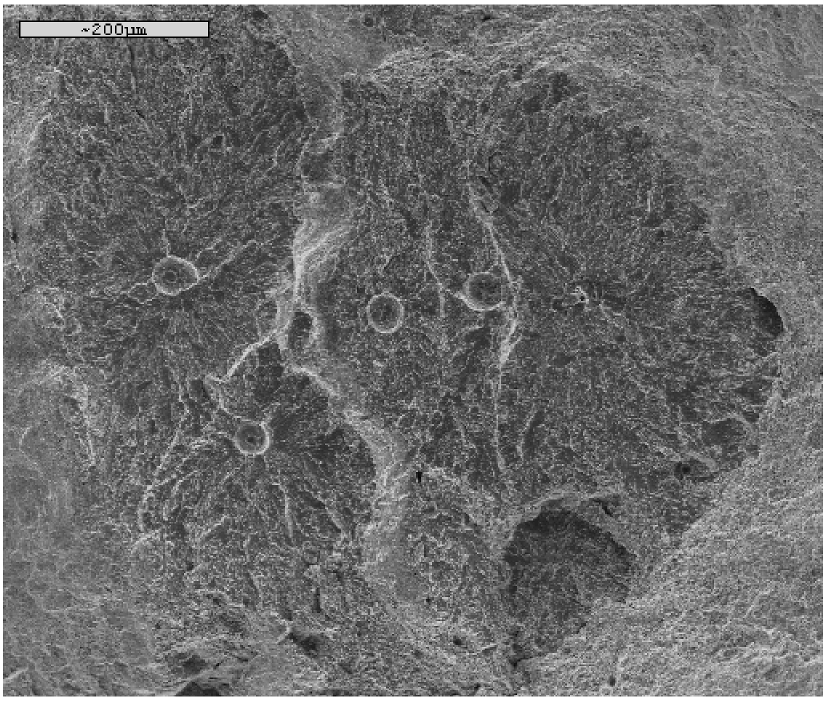


Fig. 4.15 Examples of cracks initiated at the boundary between globular oxide inclusions and matrix as a result of hydrogen segregation

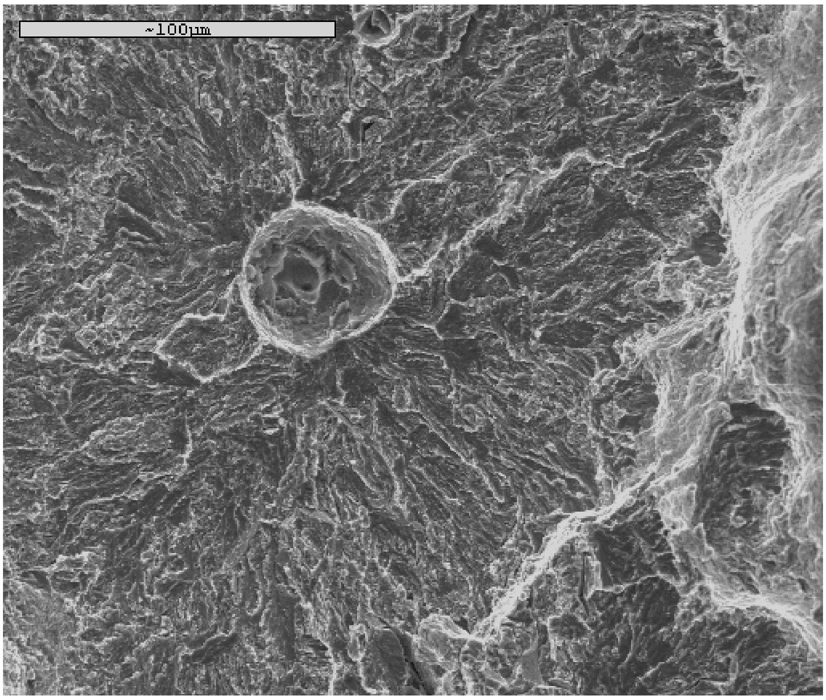


Fig. 4.16 Examples of cracks initiated at the boundary between globular oxide inclusions and matrix as a result of hydrogen segregation

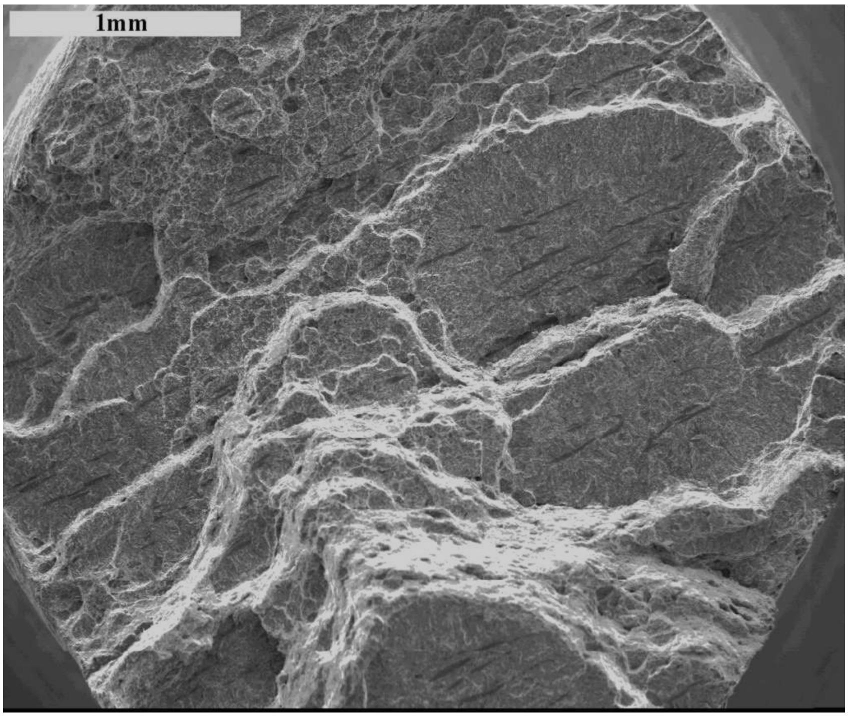


Fig. 4.17 Examples of cracks initiated at the boundary between globular oxide inclusions and matrix as a result of hydrogen segregation

Σ Summary of terms of 4.4

After studying this part, following terms should be clear to you:

- **Segregation at interphase boundaries**
- **Hydrogen segregation**

1.

? Questions to 4.4

17. On what types of interphase boundaries the segregation in metallic materials occurs most frequently
18. Why is the segregation of hydrogen at the boundary of nonmetallic inclusions and matrix in steels so important?
19. What can form hydrogen atoms, which segregate at the boundary of nonmetallic inclusions?

Other sources

Callister W.D. jr., Rethwisch D. G.: *Fundamentals of Materials Science and Engineering. An Integrated Approach*. Hoboken: Wiley, 2008. 3rd ed. 882 p. ISBN 978-0-470-12537-3.

Key to the solution

O 4.1	Macrosegregations occur as a result of liquation during solidification.
O 4.2	For the majority of elements in steels, the value of the partition coefficient is less than 1, i.e. they liquate into the liquid phase - melt.
O 4.3	No, macrosegregation cannot be eliminated by annealing, because diffusion across such a long distance is absolutely unreal.
O 4.4	Dendrites are crystals that grow into the melt at certain preferential crystallographic directions in the event that the temperature of the melt away from the boundary with the solid phase decreases.
O 4.5	The dendritic segregation occurs across the distances of tens to hundreds of micrometres.
O 4.6	The intensity of dendritic segregation can be reduced by homogenization annealing.
O 4.7	Elements that have the ability to segregate at the grain boundaries are called surface-active elements.
O 4.8	The driving force for segregation at the grain boundaries is the reduction of the free enthalpy of the system.
O 4.9	At equilibrium state, the lower is the temperature, the higher is the rate of coverage of the grain boundaries by a segregating element.
O 4.10	The rate of coverage of grain boundaries in the equilibrium segregation is highest at the lowest temperature.
O 4.11	We can encounter the non-equilibrium segregation primarily at low temperatures, up to about 300-400°C.
O 4.12	In the case of non-equilibrium segregation, the rate of coverage of grain boundaries usually increases with the increasing temperature.
O 4.13	Competitive segregation means that one segregating element segregates preferentially and reduces the segregation of another surface-active element.
O 4.14	Competitive segregation is applied for example in the case of C-P, S-P, Mo-P,B-P, etc.
O 4.15	Competitive segregation may be beneficial in many cases, because it can reduce the segregation of a harmful element (e.g., Mo-P, C-P, etc.).
O 4.16	The interactive segregation characterized a phenomenon where the segregations of two (or more) surface-active elements support each other.
O 4.17	The segregation occurs at the boundaries between nonmetallic inclusions – matrix, precipitates - matrix, etc.
O 4.18	Hydrogen segregation is important because it is dangerous; it may cause the hydrogen embrittlement, especially in steels.
O 4.19	The hydrogen atoms, which segregate at the boundary of non-metallic inclusions, may create molecules that induce stress which can lead to the development of cracks.