

Solidification and Crystallization Processing in Metals and Alloys

Hasse Fredriksson and Ulla Åkerlind

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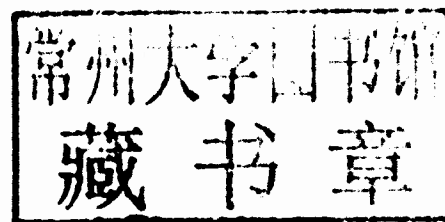
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Preface

The present book is the third and last book in a series of three:

1. Materials Processing during Casting, Wiley 2006
2. Physics of Functional Materials, Wiley 2008
3. Solidification and Crystallization Processing in Metals and Alloys, Wiley 2012

Solidification and Crystallization Processing in Metals and Alloys represents a deeper interpretation of the solidification and crystallization processes than that treated in the book *Materials Processing during Casting*, written for the undergraduate level. The aim of the present book is to analyze the solidification and crystallization processes from a general point of view and in accordance with generally accepted results and experimental evidence of modern research in the field. Hence, the book does not treat applications on casting other than as occasional examples.

The book may be useful and suitable as a text book on courses at the Master and PhD level. The mathematical level is not discouragingly high. Ordinary basic courses in Mathematics at university level are enough. On the other hand, genuine knowledge of Physics is often required. The second book, *Physics of Functional Materials*, or any other Physics book with any other equivalent content, will cover this want for those who need it. Numerous citations to the second book are given in the present book.

Solidification and Crystallization Processing in Metals and Alloys starts with a chapter of basic thermodynamics. Chapter 1 is a review of the thermodynamics that later will be applied on metals and alloys. It may be a tough and abstract introduction. Alternatively, it can be studied in connection with later applications. Energy conditions play an important role for understanding the driving forces of solidification processes in metals and alloys. These topics are treated in Chapter 2. The structure and properties of interfaces between two phases and the nucleation of embryos and forming of stable nuclei are closely related to crystallization processes. The basic outlines of these fields are given in Chapters 3 and 4, respectively.

After these four basic and general chapters, Chapters 5 and 6 follow, where the mechanisms of the solidification and crystallization processes in vapours and liquids are extensively discussed. Heat transport during solidification processes is treated in Chapter 7, which also includes an orientation about modern methods of thermal analysis. Chapter 8 deals with crystal growth controlled by heat and mass transport.

The rest of the book is devoted to the structures of the solid phases that form during different types of solidification processes, i.e. faceted and dendritic structures (Chapter 9), eutectic structures (Chapter 10), peritectic structures (Chapter 11) and structure of Metallic Glasses (Chapter 12).

Solidification and Crystallization Processing in Metals and Alloys contains many solved examples in the text and exercises for students at the end of each chapter. Answers to all the exercises are given at the end of the book. In a 'Guide to Exercises' full solutions to all the exercises are given on the Internet at <http://www.wiley.com/go/fredriksson3>

Acknowledgements

This book is based on lectures and exercises presented to PhD and Master students over the years. We want to express our sincere thanks to them for their engagement and for the fruitful discussions we

have had with them about different scientific topics in the field. The communication with them helped us to identify the items that were difficult for them to understand. In this way, we could try to explain better and improve the book.

We are most grateful to MSc Per Olov Nilsson for many fruitful mathematical discussions and general support through the years. We also wish to express our sincere thanks to Dr Jonas Åberg, Thomas Bergström (Casting of Metals, KTH, Stockholm), Dr Gunnar Edvinsson (University of Stockholm), Dr Bengt Örjan Jonsson (KTH), Dr Hani Nasser and Dr Sathees Ranganathan (Casting of Metals, KTH) for their valuable support concerning practical matters such as annoying computer problems and application of some special computer programs. We also thank Dr Lars Åkerlind warmly for patient assistance with checking parts of the manuscript.

We are very grateful for financial support from the Iron Masters Association in Sweden and the Foundation of Sven and Astrid Toresson, which made it possible for us to fulfill the last part of this project.

In particular, we want to express our sincere gratitude to Karin Fredriksson and Lars Åkerlind. Without their constant support and great patience through the years this book would never have been written.

Finally, we want to thank each other for a more than 10 years long and pleasant cooperation. It has been the perfect symbiosis. Neither of us could have written this trilogy without the other. We complemented each other well. One of us (guess who) contributed many years of research in the field and an ever-lasting enthusiasm to his devoted subject. The other one contributed with some Mathematics and Physics together with many years experience of book production and teaching Physics at university level and also plenty of *time* for the extensive project.

Hasse Fredriksson
Ulla Åkerlind
Stockholm, May 2010

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1.1 Introduction

Solidification or crystallization is a process where the atoms are transferred from the disordered liquid state to the more ordered solid state. The rate of the crystallization process is described and controlled by kinetic laws. These laws give information of the movements of the atoms during the rearrangement. In most cases a driving force is involved that makes it possible to derive the rate of the solidification process.

The aim of this book is to study the solidification processes in metals and alloys. The laws of thermodynamics and other fundamental physical laws, which control the solidification, rule these processes.

In this preparatory chapter the basic concepts and laws of thermodynamics are introduced. They will be the tools in following chapters. In particular, this is true for the second chapter, where the driving forces of solidification for pure metals and binary alloys are derived and the relationship between energy curves of solid metals and metal melts and their phase diagrams is emphasized.

1.2 Thermodynamic Concepts and Relationships

1.2.1 First Law of Thermodynamics. Principle of Conservation of Energy

One of the most fundamental laws of physics is the law of conservation of energy. So far, it is known to be valid without any exceptions. When applied in thermodynamics it is called the first law of thermodynamics and is written

$$Q = U + W \quad (1.1)$$

where

Q = heat energy added to a closed system

U = the internal energy of the system or the sum of the kinetic and potential energies of the atoms

W = work done by the system.

Differentiating Equation (1.1) gives the relationship

$$dQ = dU + dW = dU + pdV \quad (1.2)$$

The added heat dQ is used for the increase dU of the internal energy of the system and for the external work pdV against the surrounding pressure p when the volume of the system increases by the amount dV .

1.2.2 Enthalpy

The enthalpy of a closed system is defined as

$$H = U + pV \quad (1.3)$$

The enthalpy H can be described as the 'heat content' of the system. In the absence of phase transformations we have

$$H = \int_0^T nC_p dT \quad (1.4)$$

where

H = enthalpy of the system

n = number of kmol

C_p = molar heat capacity of the system (J/kmol).

When the heat content of a system is changed the enthalpy changes by the amount ΔH . When the system *absorbs* heat from the surroundings the heat content of the system is *increased* and ΔH is *positive*.

When the system *emits* heat to the surroundings and *reduces* its heat content, ΔH is *negative*. The amount of heat absorbed by the surroundings is $(-\Delta H)$, which is a positive quantity.

Differentiating Equation (1.3) gives

$$dH = dU + pdV + Vdp \quad (1.5)$$

By use of Equation (1.2) we obtain

$$dH = dQ + Vdp$$

At constant pressure, the heat absorbed by a system equals its enthalpy increase:

$$(dH)_p = (dQ)_p \quad (1.6)$$

1.2.3 Second Law of Thermodynamics. Entropy

Second Law of Thermodynamics

By experience it is known that heat always is transferred spontaneously from a warmer to a colder body, never the contrary.

It is possible to transfer heat into mechanical work but never to 100%. Consider a closed system (no energy exchange with the surroundings) which consists of an engine in contact with two heat reservoirs. If an amount Q_1 of heat is emitted from reservoir 1 at a temperature T_1 to the engine and an amount Q_2 of heat is absorbed by reservoir 2 at temperature T_2 , the energy difference $Q_1 - Q_2$ is transferred into mechanical work in the ideal case.

The reversed process is shown in Figure 1.1. It can be described as follows.

- Heat can be transferred from a colder body to a warmer body only if work or energy is supplied.

This is one of many ways to express the second law of thermodynamics.

In practice, heat is transferred into mechanical work in heat engines. The process in such a machine can theoretically be described by the Carnot cycle (Figure 1.2a). Fuel is burned and the combustion gas runs through the following cycle in the engine

1. The gas absorbs the amount Q_1 of heat and expands isothermally at temperature T_1 .
2. The gas expands adiabatically. The temperature decreases from T_1 to T_2 .
3. The gas is compressed isothermally at temperature T_2 and emits the amount Q_2 of heat.
4. The gas is compressed adiabatically. The temperature changes from T_2 back to T_1 .

Calculations of the expansion and compression works show that

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad (1.7)$$

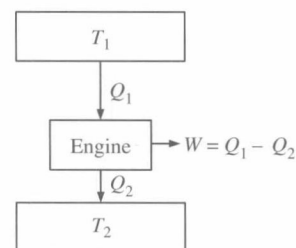


Figure 1.1 Engine in contact with two heat reservoirs. $T_1 > T_2$. The energy law gives $Q_1 = Q_2 + W$.

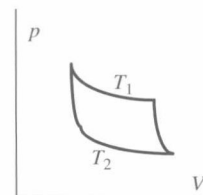


Figure 1.2a The Carnot cycle. The enclosed area represents the work done by the heat engine during a cycle.

In the ideal case, the efficiency η of the Carnot cycle is

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \quad (1.8)$$

Entropy

A very useful and important quantity in thermodynamics is the entropy S . Entropy is defined by the relationship

$$dS = \frac{dQ}{T} \quad (1.9)$$

As an example we represent the Carnot cycle in a TS diagram (Figure 1.2b). Horizontal lines represent the isothermal expansion and compression. The vertical lines illustrate the adiabatic steps of the cycle. The area of the rectangle equals the work done by the gas. A reversible adiabatic process is also called *isentropic*.

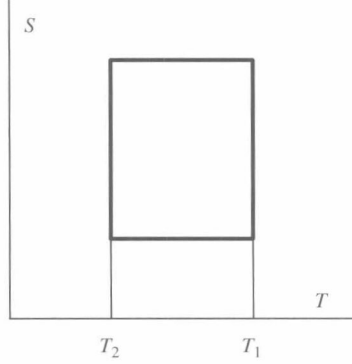


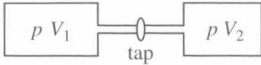
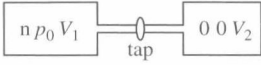
Figure 1.2b The Carnot cycle. The enclosed area represents the work done by the heat engine during a cycle.

Entropy Change at an Isothermal Irreversible Expansion of a Gas

In many solidification processes the entropy change is of great interest. As a first example we will consider the isothermal, irreversible expansion of an ideal gas and calculate the entropy change.

Example 1.1

Calculate the change in entropy when n kmol of an ideal gas with the pressure p_0 and the volume V_1 expands irreversibly to the volume $V_1 + V_2$ in the way shown in the figure.



Solution:

There are no forces between the molecules in the gas and therefore there is no change of internal energy when the gas expands. No change of internal energy means no temperature change.

When the tap is opened, the gas expands isothermally from volume V_1 to $V_1 + V_2$. The first law of thermodynamics and the definition of entropy give

$$\Delta S = \int \frac{dq}{T} = \int_{V_1}^{V_1 + V_2} \frac{pdV}{T} \quad (1')$$

Using the general gas law $pV = nRT$ to eliminate T we obtain

$$\Delta S = \int_{V_1}^{V_1 + V_2} \frac{nRdV}{V} = nR \ln \frac{V_1 + V_2}{V_1} \quad (2')$$

Answer: The entropy increases by the amount $nR \ln \frac{V_1 + V_2}{V_1}$.

The final state in Example 1.1 is far more likely than the initial state. When the tap is opened the molecules move into the empty container until the pressures in the two containers are equal rather than that no change at all occurs. Hence, the system changes spontaneously from one state to another, more likely state and the entropy increases.

All experience shows that the result in Example 1.1 can be generally applied. The following statements are generally valid:

- If a process is reversible the entropy change is zero.

$$\Delta S = 0.$$

- The entropy increases in all irreversible processes.

$$\Delta S > 0.$$

Entropy of Mixtures

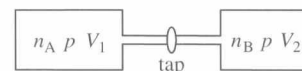
Entropy Change at Mixing Two Gases

As a second example of deriving entropy changes we will calculate the entropy change when two gases mix.

Example 1.2

A short tube and a closed tap connect two gases A and B of equal pressures, each in a separate closed container. When the tap is opened the two gases mix irreversibly. No changes in pressure and temperature are observed.

Calculate the total change of entropy as a function of the initial pressure p and the final partial pressures when the two gases mix. The data of the gases are given in the figure.



n = number of kmol
 p = pressure
 V = volume
 The temperature T is constant.

Solution:

When the tap is opened the two gases mix by diffusion. The diffusion goes on until the composition of the gas is homogeneous. It is far more likely that the gases mix by diffusion than that the gases remain separate. Hence, the total entropy change is expected to be positive.

In a gas, the distances between the molecules are large and the interaction between them can be neglected. The diffusion of each gas is independent of the other. The total entropy change can be regarded as the sum of the entropy change of each gas after its separate diffusion from one container into the other.

$$\Delta S^{\text{mix}} = \Delta S_A^{\text{mix}} + \Delta S_B^{\text{mix}} \quad (1')$$

n_A kmol of gas A change their pressure from p to p_A where p_A is its final partial pressure. In the same way n_B kmol of gas B change their pressure from p to p_B .

The initial pressure and the final total pressure are equal as no pressure change is observed.

$$p = p_A + p_B \quad (2')$$

Using the result of Example 1.1 we obtain

$$\Delta S_A^{\text{mix}} = n_A R \ln \frac{V_1 + V_2}{V_1} \quad (3')$$

and

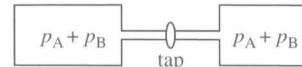
$$\Delta S_B^{\text{mix}} = n_B R \ln \frac{V_1 + V_2}{V_2} \quad (4')$$

The partial pressures can be calculated with the aid of Boyle's law applied on each gas:

$$pV_1 = p_A(V_1 + V_2) \quad (5')$$

and

$$pV_2 = p_B(V_1 + V_2) \quad (6')$$



After the diffusion the gases are mixed and the pressure is equal in the two containers. The temperature T is constant.

The ratio of the volumes from Equations (5') and (6') are inserted into Equations (3') and (4') and we obtain

$$\Delta S_A^{\text{mix}} = n_A R \ln \frac{p}{p_A} \quad (7')$$

and

$$\Delta S_B^{\text{mix}} = n_B R \ln \frac{p}{p_B} \quad (8')$$

The total entropy change is

$$S^{\text{mix}} = \Delta S_A^{\text{mix}} + \Delta S_B^{\text{mix}} = n_A R \ln \frac{p}{p_A} + n_B R \ln \frac{p}{p_B} \quad (9')$$

The ratio of the pressures is > 1 and the entropy change is therefore positive, as predicted above.

Answer: The total entropy change when the gases mix is

$$n_A R \ln \frac{p}{p_A} + n_B R \ln \frac{p}{p_B}, \quad \text{where } p = p_A + p_B.$$

Entropy Change at Mixing Two Liquids or Solids

Diffusion occurs not only in gases but also in liquids and solids. The entropy change ΔS^{mix} or simply S^{mix} , owing to mixing of two compounds in a melt or a solid can be calculated if we make a minor modification of Equation (9') in Example 1.2.

Instead of the partial pressures of the two gases we introduce the mole fractions x_A and x_B :

$$x_A = \frac{p_A}{p_A + p_B} \quad \text{and} \quad x_B = \frac{p_B}{p_A + p_B}$$

Equation (9') can then be written as

$$S^{\text{mix}} = -n_A R \ln x_A - n_B R \ln x_B \quad (1.10)$$

By use of the relationship $n = n_A + n_B$ where n is the total number of kmole we obtain

$$S^{\text{mix}} = -nR(x_A \ln x_A + x_B \ln x_B) \quad (1.11)$$

The molar entropy of mixing will then be

$$S_m^{\text{mix}} = -R(x_A \ln x_A + x_B \ln x_B) \quad (1.12)$$

Equations (1.11) and (1.12) are directly applicable on mixtures of gases but also on liquids and solids. These applications will be discussed later.

Entropy and Probability

The two examples given above indicate that entropy in some way is related to probability. The probability function can be found by the following arguments.

Consider N molecules in a container with the volume V (Figure 1.3). The molecules do not interact at all. Each molecule is free to move within the volume V . The probability of finding it within a unit volume is the same everywhere. Hence the probability of finding a molecule within a volume V_1 is V_1/V . The probability of finding two molecules within the same volume V_1 equals the

product of their probabilities $(V_1/V)^2$. The probability of finding N molecules within a particular volume V_1 is $(V_1/V)^N$.

Equation (2') in Example 1.1 on page 4 and Equation (9') on page 6 give us the clue to relating entropy and probability. We have seen above that the overall probability is the *product* of the probabilities of independent events. We also know that the entropy of two systems is the *sum* of their entropies. It is striking that the logarithmic function converts the multiplicative property of probability to the additive property of entropy.

These arguments led the physicists Maxwell and Boltzmann in 1877 to suggest a relationship between entropy and probability. Boltzmann interpreted entropy as a measure of the order, or rather disorder, of a system. The more probable a state of a system is and the greater its disorder is, the higher will be its entropy.

Boltzmann derived an alternative expression of entropy by using statistical thermodynamics.

$$S = k_B \ln P \quad (1.13)$$

where

k_B = Boltzmann's constant

P = probability of the state.

Equation (1.13) is the fundamental relationship between entropy and probability. P is called the statistical weight of the state, i.e. its configuration.

Consider a binary system, a gas or a liquid, of two components B and C. N_B atoms of B and N_C atoms of C are arranged at random among $N = N_B + N_C$ sites. This can be done in many different ways and is equivalent to mixing the two components. The statistical weight P is the number of alternative ways to arrange the B and C atoms among the N sites. Statistical considerations give the result

$$P = \frac{N!}{N_B! N_C!} = \frac{N!}{N_B! (N - N_B)!} \quad (1.14)$$

We use Stirling's formula

$$\lim N! \rightarrow \sqrt{2\pi} N^{N+1/2} e^{-N} \quad \text{when } n \rightarrow \infty$$

for the very high numbers N , N_B and $N_C = N - N_B$ and obtain

$$P = \frac{N^{N+1/2}}{N_B^{N_B+1/2} (N - N_B)^{N - N_B + 1/2}} \frac{e^{-N}}{e^{-N_B} e^{-(N - N_B)}} \quad (1.15)$$

The last factor in Equation (1.15) is equal to 1. The term $1/2$ in the exponents can be neglected in comparison with N and N_B . Taking the logarithm of both sides of Equation (1.15) we obtain

$$\ln P = N \ln N - N_B \ln N_B - (N - N_B) \ln (N - N_B) \quad (1.16)$$

If we introduce the mole fractions

$$x_B = \frac{N_B}{N} \quad \text{and} \quad x_C = \frac{N - N_B}{N} \quad \text{and the relationship} \quad x_B + x_C = 1$$

Equation (1.16) can, after some calculations, be transformed into

$$\ln P = N(-x_B \ln x_B - x_C \ln x_C) \quad (1.17)$$

Instead of N we introduce n , the number of kmol with the aid of the relationship:

$$n = \frac{N}{N_A} \quad (1.18)$$

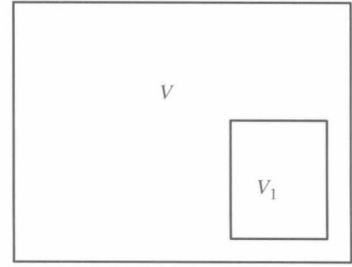


Figure 1.3 Volume element.