

Preface

Diffusion in solids plays an important role in many processes in Material Science and is the basis for numerous technological applications. In the nineteenth century, diffusion in a solid material was hard to imagine because of densely packed structure. In fact, the first systematic diffusion study in solid state was carried out only in the late nineteenth century.

Before the work of Ernst O. Kirkendall and Fredrick Seitz in the 1940s, it was a common belief that all the components diffuse at the same rate in solid materials. Based on this assumption, direct exchange and ring mechanisms were wrongly suggested to explain the diffusion of the components in crystalline solids. (Surprisingly, the ring mechanism was rediscovered in molecular dynamic simulation of grain boundary diffusion!) Kirkendall's work played an important role in formulating the basis of the theory of defect, i.e. vacancy-dependent diffusion mechanism. Following this thought-provoking concept many outstanding papers were published to further establish the relations to estimate the different diffusion parameters from experiments. In the mean time, based on Georg Karl von Hevesy's work, radiotracer technique to study diffusion was developed which sheds light on the fundamental aspect of the atomic nature of diffusion. In fact Seitz, based on the available tracer diffusion study on pure Cu and Kirkendall's experiment, proved beyond doubt that diffusion of substitutional atoms occurs by vacancy mechanism.

Looking back to the many books published on this subject by other researchers, it is evident that there exists no book with a special emphasis on interdiffusion and on the Kirkendall effect. Further, as thermodynamics plays an important role in interdiffusion, without a proper understanding of the subject, many fundamental aspects of interdiffusion may remain unclear. Therefore, we introduce the important aspects of thermodynamics from the solid-state diffusion perspective and then discuss the phenomenological process of interdiffusion extensively. Moreover, the understanding of the interdiffusion process is not complete without understanding the atomic mechanism of diffusion and different types of diffusion, such as lattice and grain boundary diffusion. Therefore, these topics are discussed in detail. Still, we are limiting the present consideration by metallic systems with uncharged defects.

Chapter 1 starts with very basic concepts of thermodynamics. The laws of thermodynamics are introduced and different extensive and intensive properties

and variables are briefly discussed. The chapter is focused on a short and concise description of the approaches to represent and utilize the thermodynamic data in a manner suitable for interdiffusion studies. Therefore, many different ways to represent the thermodynamic data of a given system graphically are introduced. Special emphasis is given to Gibbs energy diagrams, phase diagrams and different types of potential diagrams. Many of the relations developed and diagrams introduced in this chapter will be frequently used in subsequent chapters.

Chapter 2 introduces different aspects of the hierarchical structure of solids: atomic structure, unit cells, grain structure, defects, microstructure, etc., which are very essential for understanding of the material systems. Some aspects related to the defect structures in intermediate compounds, including the effect of atomic order, are also discussed.

Chapter 3 starts with the Fick's laws of diffusion. The second law is derived from the first law. Subsequently, several solutions for diffusion problems with different kinds of initial and boundary conditions are given. Limitations of the solutions obtained are discussed, too. This chapter is written in such a way that new students in the field or undergraduate students can understand the very basics of Fick's laws and their solutions, so that the formalism could directly be applied for processing of the experimental data.

Chapter 4 relates thermodynamics with interdiffusion of components. Different kinds of microstructures, which are expected to grow in the interdiffusion zone, depending on the given phase diagram and composition of the end members of the diffusion couples are explained in detail.

Chapter 5 discusses the atomic mechanisms of diffusion in detail. The main difference between the interstitial and substitutional diffusion mechanisms is discussed. Anisotropy of diffusion, effect of temperature, and the fundamental concept of a correlation factor are introduced in detail. The analytical and numerical approaches for calculation of the correlation factors are introduced. Diffusion in ordered phases is also discussed with a highlight on specific atomistic mechanisms and correlation effects.

Chapter 6 concentrates on interdiffusion in systems with a wide composition range. First, the limitations of the error function analysis are discussed based on the topics introduced in Chap. 3. After that, different approaches that are used to estimate the diffusion data are explained. The Kirkendall effect and the concept of intrinsic diffusion coefficients are introduced. The estimation of the tracer diffusion coefficients indirectly from a diffusion couple is also explained.

Chapter 7 discusses the estimation of the diffusion parameters in line compounds and phases with a narrow homogeneity range. Few practical examples are introduced to explain the steps needed for quantitative analysis.

Chapter 8 concentrates in the very recent developments in understanding the Kirkendall effect and the physicochemical approach. By using this approach, one can not only estimate the diffusion parameters, but also achieve more profound understanding of the microstructural evolution of an interdiffusion zone.

Chapter 9 concentrates on diffusion in multicomponent systems. The mathematical and experimental difficulties in estimating the diffusion parameters in

ternary or higher order systems are discussed. A pseudo-binary approach, which simplifies the conditions for the estimation of the diffusion parameter with much better efficiency, is introduced. The usefulness of the diffusion couple technique for the determination of phase diagrams is also discussed.

Chapter 10 concentrates mainly on short-circuit diffusion. Microstructures with a hierarchy of short-circuit paths are explained and the kinetic regimes of diffusion in such structures are introduced and discussed. Many practical examples are given in order to explain the practical estimation of the diffusion parameters. Finally, the effect of grain boundary diffusion on interdiffusion and Kirkendall effects are briefly discussed.

Chapter 11 introduces the complications arising from the growth of the phases as thin films. The roles of nucleation barriers, interfacial energies and elastic strains in reactive diffusion are discussed. Further, nucleation issues in solid-state amorphization are also discussed. Finally, it is shown that there is no fundamental difference between thin film and bulk diffusion couples and the complications in the former arise mainly from the structural features of thin films.

It should be noted that this book is biased towards experimental techniques. Important developments are going on simulation, which are not covered here. Three different groups have joined together to write on few important aspects such as thermodynamics, interdiffusion, atomic mechanism and short-circuit diffusion. In this also, few aspects are not covered extensively, which are beyond the requirements for the students or available in other books.

As usual, we don't expect it to be complete error-free. We would appreciate if you write us with your comments and feedback so that we can take care in the next edition.

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Solids

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