Helmut Mehrer

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Diffusion in Solids

Fundamentals, Methods, Materials, Diffusion-Controlled Processes

固体中的扩散

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Preface

Diffusion is the transport of matter from one point to another by thermal motion of atoms or molecules. It is relatively fast in gases, slow in liquids, and very slow in solids. Diffusion plays a key rôle in many processes as diverse as intermixing of gases and liquids, permeation of atoms or molecules through membranes, evaporation of liquids, drying of timber, doping silicon wafers to make semiconductor devices, and transport of thermal neutrons in nuclear power reactors. Rates of important chemical reactions are limited by how fast diffusion can bring reactants together or deliver them to reaction sites on enzymes or other catalysts.

Diffusion in solid materials is the subject of this book. Already in ancient times reactions in the solid state such as surface hardening of steels were in use, which according to our present knowledge involves the diffusion of carbon atoms in the crystal lattice of iron. Nevertheless, until the end of the nineteenth century the paradigm *'Corpora non agunt nisi fluida'* was widely accepted by the scientific community. It was mainly due to the pioneering work of William Roberts-Austen and Georg von Hevesy that this paradigm had to be abandoned.

Diffusion in solids is fundamental in the art and science of materials and thus an important topic of solid-state physics, physical chemistry, physical metallurgy, and materials science. Diffusion processes are relevant for the kinetics of many microstructural changes that occur during preparation, processing, and heat treatment of materials. Typical examples are nucleation of new phases, diffusive phase transformations, precipitation and dissolution of a second phase, homogenisation of alloys, recrystallisation, high-temperature creep, and thermal oxidation. Diffusion and electrical conduction in ionic conductors are closely related phenomena. Direct technological applications of diffusion concern, e.g., doping during fabrication of microelectronic devices, solid electrolytes for batteries and fuel cells, surface hardening of steel through carburisation or nitridation, diffusion bonding, and sintering.

Appreciable diffusion in solids mostly takes place at temperatures well above room temperature. Knowledge of diffusion is therefore particularly important for scientists who design materials for elevated temperatures and for engineers who build equipment for operation at such temperatures. However, processes connected with diffusion at room temperature pose problems, too.

Creep, atmospheric corrosion, and embrittlement of solders are among the more prominent of those. With the downscaling of microelectronic circuits to nanometer dimensions, diffusion and electromigration in these circuits must be taken into account.

A deeper knowledge about diffusion requires information on the position of atoms and how they move in solids. The atomic mechanisms of diffusion in crystalline solids are closely connected with defects. Point defects such as vacancies or interstitials are the simplest defects and often mediate diffusion in crystals. Dislocations, grain-boundaries, phase boundaries, and free surfaces are other types of defects. They can act as high-diffusivity paths (diffusion short circuits), because the mobility of atoms along such defects is usually much higher than in the lattice. In solids with structural disorder such as glasses or crystals with highly disordered sublattices the concept of defects is no longer useful. Nevertheless, diffusion is fundamental for transport of matter and for ionic conduction in disordered materials.

The content of this book is divided into seven parts. After a historical introduction and a diffusion bibliography, *Part I* introduces basic concepts of diffusion in solid matter such as continuum description, random walk theory, point defects, atomic mechanisms, correlation effects, dependence of diffusion on temperature, pressure and isotope mass, diffusion with driving forces , and some remarks about the relation between diffusion and thermodynamics of irreversible processes. The necessary background is a course in solid-state physics. In *Part II* we describe experimental methods for the determination of diffusion coefficients in solid matter. Direct methods based on Fick's laws and indirect methods such as anelastic relaxation, internal friction, nuclear magnetic relaxation, Mössbauer spectroscopy, quasielastic neutron scattering, impedance spectroscopy, and spreading resistance measurements are treated. In further parts we provide access to information on diffusion in various types of materials such as metals, intermetallics and quasicrystalline alloys (*Part III*), semiconductors (*Part IV*), ionic materials including fast ion conductors (*Part V*), metallic and oxide glasses (*Part VI*). Finally, rapid diffusion paths such as grain-boundary diffusion and diffusion in nanomaterials are considered (*Part VII*). Although these parts cannot replace a comprehensive data collection, typical up-to-date resources available on diffusion for various types of materials are noted.

A thorough understanding of diffusion in materials is crucial for materials development and engineering. Graduate students in solid state physics, physical metallurgy, physical and inorganic chemistry, and geophysical materials will benefit from this book as will physicists, chemists and metallurgists, working in academia and industry.

Münster, May 2007 Helmut Mehrer

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1 History and Bibliography of Diffusion

If a droplet of ink is placed without stirring at the bottom of a bottle filled with water, the colour will slowly spread through the bottle. At first, it will be concentrated near the bottom. After a few days, it will penetrate upwards a few centimeters. After several days, the solution will be coloured homogeneously. The process responsible for the movement of the coloured material is diffusion. Diffusion is caused by the BROWNian motion of atoms or molecules that leads to complete mixing. In gases, diffusion progresses at a rate of centimeters per second; in liquids, its rate is typically fractions of millimeters per second; in solids, diffusion is a fairly slow process and the rate of diffusion decreases strongly with decreasing temperature: near the melting temperature of a metal a typical rate is about one micrometer per second; near half of the melting temperature it is only of the order of nanometers per second.

The science of diffusion in solids had its beginnings in the 19th century, although the blacksmiths and metal artisans of antiquity already used the phenomenon to make such objects as swords of steel, gilded copper or bronce wares. Diffusion science is based on several corner stones. The most important ones are: (i) The continuum theory of diffusion originated from work of the German scientist *Adolf Fick*, who was inspired by elegant experiments on diffusion in gases and of salt in water performed by *Thomas Graham* in Scotland. (ii) The BROWNian motion was detected by the Scotish botanist *Robert Brown*. He observed small particles suspended in water migrating in an erratic fashion. This phenomenon was interpreted many decades later by *Albert Einstein*. He realised that the 'dance' described by *Brown* was a random walk driven by the collisions between particles and the water molecules. His theory provided the statistical cornerstone of diffusion and bridged the gap between mechanics and thermodynamics. It was verified in beautiful experiments by the French Nobel laureate *Jean Baptiste Perrin*. (iii) The atomistics of solid-state diffusion had to wait for the birth date of solid-state physics heralded by the experiments of *Max von Laue*. Equally important was the perception of the Russian and German scientists *Jakov Frenkel* and *Walter Schottky* that point defects play an important rôle for properties of crystalline substances, most notably for those controlling diffusion and the many properties that stem from it.

This chapter is not meant to be a systematic history of diffusion science. It is devoted in its first section to some major landmarks and eminent people