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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Professor Dr. Helmut Mehrer
Universität Münster
Institut für Materialphysik
Wilhelm-Klemm-Str. 10
48149 Münster
Germany

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For Karin and my family, who wonder what I did all the time.

In particular I express my enduring thanks to my wife Karin. Without her patience, understanding, and love I could not have completed this book.

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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