C. Ernest Birchenall

Physical Metallurgy

PHYSICAL METALLURGY

C. Ernest Birchenall

ASSOCIATE PROFESSOR OF CHEMISTRY
PRINCETON UNIVERSITY

McGRAW-HILL BOOK COMPANY, INC.

New York Toronto London

1959

PHYSICAL METALLURGY

 Library of Congress Catalog Card Number 58-13855

THE MAPLE PRESS COMPANY, YORK, PA.

Preface

The science of metals has taken enormous strides in the last few decades. Each new issue of the principal journals records penetrating experiments and theories reaching to the present foundations of the subject. New concepts are being introduced; some of the most important are only slightly assimilated. New attention is being directed at old phenomena; controversies rage about the nature of long-known processes. At the risk of including some ideas which will fall by the wayside and misinterpreting proposals which have not quite crystallized, I have tried here to produce a record at elementary level that reflects in some measure the progress of recent years, the ferment and vitality of the field at present.

The engineering aspects of physical metallurgy are slighted in favor of the scientific content, lest the underlying framework be obscured. There is no apology for the strongly scientific approach, since the so-called facts on which the empiricists insist are never presented without some degree of interpretation. Abstraction is less likely to lead to error for the inexperienced student than are recipes. Qualitative reasoning from complex instances is for the seasoned old hand, whose job it is to take over the educational process where the universities leave it. It is hoped that the exposition of fundamentals without too much padding with examples will help to emphasize the unity underlying all aspects of the subject.

Another departure from the norm is that no effort has been made to avoid mathematical equations, occasional mathematical development, and numerical problems. I feel that it is an injustice to the student to smooth the path so that his college training in mathematics lies dormant until it can no longer be called upon for use.

On the other hand, a serious effort is made to avoid the introduction of concepts which cannot be developed adequately and used in the book. Unfortunately the elaboration cannot always be made to follow the introduction immediately. To give what is perhaps the major instance: the formal discussion of crystal imperfections occurs before enough material about individual processes has been developed to show why these imperfections are convenient abstractions. I have chosen this method of presentation to emphasize the interrelations of the defects, which become obscured when they are introduced piecemeal to explain dissimilar observations.

It is assumed that the student has had a college course in physics, chemistry, and calculus. If necessary, he should review the elements of atomic structure and chemical binding. If he has not taken or is not concurrently taking a course on thermodynamics, additional lectures on this subject of a descriptive type will be required, even though the quantities employed are described briefly in the text. Although this book is intended mainly as a text for college courses in physical metallurgy, it may prove useful to those scientists and engineers who have escaped college without formal training in metals science only to find themselves employed in the metals-producing or -consuming branches of industry.

This book has grown from a one-term lecture course given to junior and senior students, principally of engineering, at Princeton University. I owe a debt to their patience with my experiments. To the late Professor Donald P. Smith, who introduced me to physical metallurgy, and to Professor Robert F. Mehl, who showed me many of its interesting byways, I owe much of the stimulus for writing these pages, and some of their content.

The painstaking reviews of the complete original manuscript by Professor Mehl and Professor Michael B. Bever have added greatly to its clarity, precision, and balance. Reviews of individual chapters by Dr. Walter R. Hibbard, Jr., and Dr. R. J. Borg have also been helpful.

I am greatly indebted to the many authors and publishers who consented to the reproduction of illustrations. Unfortunately the list of names is too long to record here. The references identifying the sources of the illustrations are commended to the reader's attention, for, in addition to giving credit to the original source, many represent ideal starting points for further reading on the subject under discussion.

In many parts of the text credit could not be distributed adequately without making the subject matter impenetrable to those approaching it for the first time. I hope the interested reader will learn more about the fascinating story of the ways in which information is gathered and ideas are developed, and of the dedicated persons responsible for this work, by following several subjects back through the review literature cited at the ends of the chapters into the original publications in the technical journals. An attempt has been made to associate names with very recent work not likely to be covered adequately by review articles, treatises, and monographs.

C. Ernest Birchenall

Contents

List of Symbols

The numbers in parentheses give one page where the symbol is used as designated.

a	constant (62), lattice parameter (14), thermodynamic activity (229), mass (58)
b	constant (62), lattice parameter (14), distance (40), mass (58)
c	elastic constant (117), lattice parameter (14), concentration (193)
d	distance (17), density (170)
e	value of a property (168), base of natural logarithms (196), elongation (112)
f	weight fraction (73), atom fraction (164), volume fraction (168), distance (16)
h	distance (113), crystallographic index (16), Planck's constant (35)
i	enumerative subscript (230), current density (232), crystallographic index (20)
k	crystallographic index (16), wave number (53), solubility constant (194), rate constant (217), Boltzmann's constant (36), distribution coefficient (189)
l	crystallographic index (16), length (109), rate constant (217)
m	electron mass (53), mass (193), integer (17)
n	integer (14), exponent (254), defect concentration (210), electron change in electrode process (229)
o	subscript (51)
p	distance (16), pressure (161)
q	quantity of material (196), integer (17)
r	radius (66)
s	elastic coefficient (118), marker displacement (212)
t	time (185)

v velocity (53)
x distance or length (16), thickness (29)
y distance (16)
z distance (16)

$\parallel$ parallel to (163)
$\perp$ perpendicular to (163), edge dislocation (38)
$>$ greater than (178)
$<$ less than (190)
∞ infinity (14)

A Helmholtz free energy (60), integer (14), area (109), frequency factor (251)
B activation energy (251)
C integer (14), constant (164), concentration (189)
D diameter (254), diffusion constant (198), distance (40), integer (14)
E energy (various kinds) (51), Young's modulus (112)
F Gibbs' free energy (60), force (109)
G torsional modulus (114), rate of growth (249)
H enthalpy (59)
I intensity of radiation (29)
J flow rate (193)
K equilibrium constant (229)
M mass (58)
N periodic group (47), rate of nucleation (249), atom fraction (213), density of states (51), number of cycles to failure (155)
P pressure (58)
Q activation energy (178), heat absorbed (60)
R rate (178), gas constant (58), radius (218), resistance (162)
S entropy (60), stress (155)
T absolute temperature (36)
V volume (58)
W depth of potential energy well (51), weight (73)
X force (116)
Y force (116)
Z force (116), frequency factor (178), valency (164)

$\mathcal{F}$ Faraday's constant (229)
$\mathcal{E}$ electromotive force (229)

α angle (17), thermal coefficient of expansion (162), phase designation (77)
β angle (17), compressibility (161), phase designation (77)

γ angle (17), interfacial energy (67), shear strain (114), phase designation (83)
δ phase designation (83), distance (147)
ϵ energy (35), normal strain (112)
η angle (15)
θ angle (15), phase designation (259)
κ conductivity (162), phase designation (83)
λ wavelength (27), angle (115)
μ absorption coefficient (29), chemical potential (60), direction cosine (15)
ν direction cosine (15), frequency of vibration (35), Poisson's ratio (113), coefficient (229)
ξ integration variable (198), deformation energy (151)
π mathematical constant (53)
ρ resistivity (162)
σ direction cosine (15), normal stress (110)
τ shear stress (110)
ϕ angle (15), threshold energy for photoemission (51)
Δ distance (27)
Φ error integral (198)
Θ characteristic temperature (36)

I and II phase labels (66)

( ) [ ] ⟨ ⟩ { } for identification of crystallographic indices (used extensively)

⬭ △ □ ⬡ symbols used to denote degree of symmetry axis (33)

CHAPTER 1

Introduction; Physical and Process Metallurgy

HISTORICAL PERSPECTIVE

For many millennia metallurgy has been one of the important occupations among men. The art of metallurgy has provided a wide variety of tools, utensils, and weapons to serve the diverse needs of human societies. The earliest of these devices depended on the availability of native metals or, some believe, metallic meteorites. The initial source may have been one or the other in different locations. As men achieved control over fire and learned to design more effective furnaces, the easily reducible metals were won. With further improvement in techniques, more stable ores yielded their treasure. Concurrent developments in shaping the refined metals such as casting, forging, and welding widened the field of application. The procedures were often very ingenious; the products frequently were of good quality, both metallurgically and artistically. Metallurgy has always been so involved with human affairs—the construction of physical objects, the service of practical ends—tha it is difficult to separate the artistic, the scientific, and the engineering aspects of the subject. It is not fruitful to attempt very sharp distinctions. In fact, the subject matter is often the same; only the outlook varies. In this introductory book emphasis is given to those aspects which yield most readily to systematic treatment—the science of metals. The nomenclature of metallurgy contains many nonsystematic terms, often derived from the names of early workers, which reflect its development as an art rather than as a science; some of the names, however, honor the founders of scientific metallurgy.

In spite of the long and distinguished developments lending their names to great ages of history, metallurgy today displays more potential for growth than could easily be discerned in earlier times. The advances of the past century compare in many respects with the progress of all previous human history and have been especially rapid in the last 25 years. New factors have entered the picture which tie the activities of the metallurgist more and more intimately into the complex fabric of human endeavor. Cost and the availability of raw materials are important factors in any society. When the day-to-day activities and demands of the community change very slowly, reevaluation need be made only infrequently. The artisan learns his skill and is secure in his niche. But the joint demands of mass production and a rapidly evolving community intensify the problems of economics and availability, requiring careful and frequent reevaluation of alternatives and substitutes, finer control of processes, development of new procedures to meet new specifications, and economical utilization of by-products. The artisan is no longer secure in the possession of manual skill or even of a thorough empirical knowledge of past practice. Such skills and practices may become obsolete very quickly.

The present scene offers a challenge for those who, to this invaluable store of information based on known successful procedures, would add a flair and imagination stimulated by an awareness of the underlying relations governing the behavior of all physical processes, of materials and their properties. In what other way can one participate fully in a future in which the problems of the present must be worked out? The variety of these problems is evident from a brief list.

1. Progress in the field of nuclear energy is dependent upon the discovery, development, and production of materials able to maintain good structural properties at relatively high temperatures in corrosive media and in the presence of intense irradiation.

2. The utilization of semiconducting materials in devices like the transistor requires refining to extremely high purity and hairbreadth control of traces of intentional impurities.

3. The quest for superstrength materials has led to a study of filamentary crystals, frequently thinner than human hairs, often called "whiskers."

4. The rapid development of techniques and industrial capacity for refining titanium and preparation of its alloys has been stimulated by military demands. These metals must find their rightful place in the competitive scheme of peaceful applications as well.

5. New alloys must be developed to support the trend toward high-temperature processes in the transportation, chemical, and power industries. In this and other developments the use of scarce and expensive elements must be minimized.

These few scattered examples suggest something of the breadth of the field with which the metallurgist deals. They also suggest the impracticability of dealing with the whole field in even the most superficial way in a book of reasonable length. A few paragraphs are devoted here to specifying that part of the subject which will be covered, to locating its boundaries, and to a short description of related areas.

APPROACHES TO METALLURGY

It is customary to subdivide metallurgical operations into two broad categories. Those operations involved in the purification and concentration of ores, the reduction and refining of ores to produce intermediates or metals, melting, alloying, and casting, and the utilization of slags, mattes, and fluxes belong to *process metallurgy* (see pages 8–9). These complicated and important steps are characterized by their application to the ore or molten metal.

Once a solid metal or alloy has been prepared, it may be modified in size and shape and other properties by a wide variety of means, adjusted in every case to the particular material and its past history. The object is usually to convert a raw ingot into an article with useful shape and optimum properties for the task it is to perform. These operations belong to *physical metallurgy*. The variety of procedures is too great to examine instance by instance, but two other alternatives exist. One systematic approach studies the bulk changes in properties produced in materials by easily identifiable operations such as rolling, forging, drawing, annealing, casting, and sintering. The other examines the kinds of properties and changes produced in the materials by a variety of treatments from an atomistic point of view. Neither of these approaches can be followed consistently in the present state of knowledge, but the latter alternative will serve as the objective here, although the former will be used where necessary.

PHYSICAL METALLURGY

Definition. For the purposes of this book, physical metallurgy will be defined as the science of the properties of solid metals and the chemical or physical processes by means of which those properties are modified. The properties include those characteristic of the piece such as size and shape as well as those inherent in the metallic elements or their combinations. Processes in which only one stage is solid, like casting, will be included.

Like the boundaries of any active field, those of physical metallurgy are not sharply definable. Some of the matters with which it deals also belong properly to other conventional areas. Historical accident finds metallurgists interested in materials that are not properly metals at all. These limitations do not detract from the integrity of the subject but offer challenges to those with broad talents to work in the fruitful regions where the fields overlap.

Many of the reduction and refining aspects of metallurgy are also straightforward inorganic chemistry. Some aspects of physical metallurgy are indistinguishable from certain aspects of solid-state physics or physical chemistry. The mechanics of materials merges with mechanical metallurgy. Geological and ceramic materials have much in common with the slags used in process metallurgy and the oxides, sulfides, and other corrosion products which may form on solid metals. All these areas of overlap have a large enough content to form special and important subjects in themselves. A large central core remains that conventionally is not treated, or is not treated in the same way, by any of the peripheral fields.

History. Historically, in broad interpretation, it is likely that physical metallurgy antedates process metallurgy, for native metals were probably formed without melting before smelting processes were known. The production of metallurgical goods, first for home consumption and then for commerce, goes back beyond written history. The smith and armorer possessed for small-scale production many of the techniques of which modern manufacturers are now inordinately proud. Though the art is exceedingly old, understanding is a new and growing thing. Only a few of the memorable landmarks in the growth of understanding, and consequently the art, can be described here. Many historically important developments are discussed in connection with individual subjects.

Certainly the discovery that native metals and perhaps metallic meteorites could be made to yield implements superior to stone tools for some purposes was among the earliest and most basic discoveries. Through the ages, countless experiments followed in which techniques were developed for shaping metals, and various shapes were tested for different applications. The smith, the tinker, and the armorer were the social forerunners of the physical metallurgist who provides goods which perform roughly the same functions as the products of his predecessors. The science of metals is of much more recent vintage. The identification of various metals as chemical elements, and the recognition of alloys as solutions and mixtures of elements, could not have preceded the fundamental concepts painfully worked out in the latter eighteenth and early nineteenth centuries by Black, Priestley, Lavoisier, and others. During this period the great controversy raged over whether Dalton's atomic theory, interpreted by Proust to indicate that compounds must have definite, fixed compositions, or Berthollet's notion of compounds, that composition depends on the mass effect of the reactants, was correct. When Dulong and Petit derived their rule on atomic heats in 1819, Dalton's hypothesis was established and the extrapolated rule of definite composition gained ascendancy with it. It has taken a long time for Berthollet's general notion to regain its proper place in the guise of a theory of defects in solids.

Before 1820 Faraday was making discoveries of tremendous importance to metallurgy both theoretically and practically. He did not seem disturbed, as many moderns are, that theoretically and practically useful results may occur together, or even be the same thing. In addition to formulating his well-known laws of electrolysis, the basis of numerous metallurgical processes, he developed iron-nickel alloys, prepared alloys by sintering steel and platinum wires together without melting (indirectly showing that he recognized solid-state diffusion), learned about the undercooling of melts, suggested that elements other than carbon might confer on iron desirable and steellike properties and made many alloy steels to test his hypothesis, and dissolved annealed and quenched steels in hydrochloric acid, obtaining a carbide residue from the former. Thus the science of metals, though largely descriptive, was taking firm hold.

During the latter half of the nineteenth century Sorby carried on a series of brilliant researches based on his development of one of the most powerful tools of metallography, the microscopic examination of polished and etched cross sections of metal specimens. In his observations on steels he noted Widmanstätten figures and recorded their characteristics. He recognized the role of critical heat-treating temperatures in the reactions of steels. In 1887 he discovered recrystallization, the replacement of cold-worked grains by newly formed grains with the stresses annealed out.

By the last decade of the nineteenth century and continuing into the early twentieth century, Roberts-Austen, as an example, could work on a bewildering variety of subjects to which he made substantial contributions. He studied the reduction of some of the rarer metals, the relation of the physical properties of metals to their position in the periodic system of elements, the properties of gun tubes, factors affecting undercooling of melts, and the importance of the chemistry of alloys on their failure properties, particularly with regard to the inhomogeneities in commercial steels. The work of Gibbs on heterogeneous equilibria had become generally known, and Roberts-Austen worked on phase diagrams and the decreasing solid solubility of carbon in austenite with decreasing temperature. He made important contributions to the knowledge of diffusion, showing that steel could be made by carburizing iron in contact with diamond (though very slowly) in the absence of gases and without melting. He made the first good quantitative diffusion measurements