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PRINCIPLES
OF PHYSICAL
METALLURGY

MORTON C. SMITH

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Bombay

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P R E F A C E

The impressive body of metallurgical knowledge accumulated in the thousands of years since man has been possessed of both metals and curiosity has filled many handbooks. These are an essential part of the literature of metallurgy, and familiarity with them is an essential part of the metallurgist's background. However, informative as they are concerning *how* metals behave under specific conditions, handbooks are remarkably unenlightening with regard both to *why* metals behave as they do, and to the principles in accordance with which their behavior can be controlled. Unfortunately, the essentially descriptive treatment of most current textbooks of physical metallurgy is little more enlightening in these respects.

For selection, preparation, and treatment of the common engineering metals in applications and environments that have become routine, the handbook will serve. Here, therefore, the literate designer, metal worker, heat treater, and mechanic actually make the metallurgist superfluous. It is when the unexpected occurs in a supposedly routine application of the metals, or when longer life or better properties or lighter sections or lower costs or a totally new material are needed that the handbook becomes inadequate, and the metallurgist's professional work begins.

In attacking the complex, varied, and always new problems imposed upon him by modern science and industry, the metallurgist must rely first upon his own organized understanding of the behavior of metals, and second upon whatever relevant data he can discover for himself in the handbooks and other reference sources. His professional education—which ends only with his professional career—must, then, develop in him both a basic understanding of metal behavior, and a real facility in using the reference literature of metallurgy. It is to assist the thoughtful metallurgist in the first of these efforts, achieving a fundamental understanding of metal behavior, that this book has been written. The further efforts of learning what data have already been accumulated in his special fields of interest, and of locating these data, are ones that he must make for himself.

This book is an attempt to develop and to present a science of metal behavior as an integrated, consistent, and satisfying chain of reasoning,

extending from the familiar principles of physics and chemistry to the observed behavior of the industrial metals and their alloys. In preparing it, a real effort has been made to select and to condense the subject matter that was essential to such an attempt, and to exclude all else. Even so, in discussing a field so broad as that of metal behavior, an uncomfortably thick book has been produced. It has therefore been necessary to divide it between two less-bulky volumes, of which this is the first. The second, *Alloy Series in Physical Metallurgy*, begins where the present volume ends, and considers in a systematic manner the effects of composition and of heat treatment upon the structures and properties of metals and their alloys.

Undoubtedly, the author's efforts in both volumes are open to criticism by the real scientist on the grounds of naïvete, superficiality, and oversimplification; by the down-to-earth engineer because of complexity and overelaboration; and by the teacher with regard to selection and organization of material. Criticism on these or any other grounds will be welcomed by the author, especially where errors in fact, reasoning, or conclusion are noted, or an improvement in material, presentation, or emphasis can be suggested.

The author is, of course, responsible for the facts, reasoning, and conclusions here offered. He must, however, at least acknowledge his tremendous debt and real gratitude to the many able scientists, engineers, and authors, who have advanced the field of physical metallurgy to the position in which it is here viewed, and especially to:

Gilbert E. Doan, who encouraged the interest and guided the early thinking of the author in this field, and whose viewpoints are, of course, often reflected here.

Daniel S. Eppelsheimer, for his interest in an early manuscript, and his encouragement to complete this one.

The many authors of the *Metals Handbook*, whose data—particularly with regard to constitutional diagrams—have been used freely by the author, and often in such ways that proper acknowledgement of it has been impossible.

Sir H. C. Carpenter and J. M. Robertson, Charles S. Barrett, Frederick Seitz, Sir William Hume-Rothery, Walter Boas, A. H. Cottrell, G. Sachs and K. R. Van Horn.

The published works of all of these authors are earnestly recommended to every serious student of the science of metals.

MORTON C. SMITH

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CHAPTER 1

The Atom

All substances, whether solids, liquids, or gases, are composed entirely of atoms whose individual properties and arrangements relative to each other determine completely the properties of the substance as a whole.

Because of their unique significance in establishing the behavior and therefore the usefulness of all material things, atoms have been the subject of continuing investigation since the physical tools for such research were first developed. As a result their structures, properties, and behavior are now quite thoroughly understood. Unfortunately for the layman (and here most scientists and engineers are laymen), much of the present detailed knowledge of the atom can be expressed only in the form of complex mathematical equations understandable only to the theoretical physicist. In considerably simplified form, however, a mental picture of atomic structures and interactions is possible for everyone. If not too drastically simplified with introduction of significant inaccuracies, such a mental picture has real usefulness in any rationalization of the behavior of metals. Accordingly, the present study of metals and their alloys begins with a nonmathematical discussion of the atom itself and with a review of some of its important physical and chemical characteristics. With this as background, the arrangement of atoms into metal crystals and of crystals into useful metallic bodies can then be explained systematically in later chapters. This, in turn, will lead finally to real understanding of the observed structures, properties, and behavior of the metals and alloys of modern metallurgy.

1-1. General Structure of the Atom

An atom consists of a small mass called the *nucleus*, which carries a positive electrostatic charge and is surrounded by a variable number of almost equally small, negatively charged particles called *electrons*.

In the simplest representation of atomic structure it is assumed that

electrons revolve around the nucleus of the atom in definite orbits to which they are confined by a precise balance between the kinetic energy of their rotation and the electrostatic attraction for them exerted by the nucleus. Such an atom obviously resembles a tiny solar system, with electrons playing the part of planets and the nucleus that of the sun. As in a solar system, most of the atom is empty space. The average diameter of an atomic nucleus is of the order of 10^{-12} or 10^{-13} centimeter, and that of an electron is generally assumed to be only slightly larger. The average diameter of the atom as a whole is something like 10^{-8} centimeter, which is about ten thousand to a hundred thousand times as great as either.

Most of the mass of an atom is concentrated in its nucleus, whose dense structure and remarkable stability are still not completely understood. An atomic nucleus consists principally of one or more particles called *protons*, each of which has the same mass and carries an identical positive electrostatic charge of $1e$, where e is a unit of electrical quantity equal to 4.8×10^{-10} electrostatic unit or 1.6×10^{-19} coulomb. All atoms of the same chemical element contain the same number of protons in their nuclei. Associated with these protons, however, is a variable number of *neutrons*, each having almost exactly¹ the same mass as a proton, but no electrostatic charge. Atomic nuclei having the same number of protons may still contain different numbers of neutrons, and so may differ considerably in mass. However, since the chemical properties of an atom are determined entirely by its electrical nature and since this is unaffected by the number of uncharged neutrons present in its nucleus, atoms which vary in mass for this reason only are found to have identical chemical properties. They are therefore described as *isotopes* of the same chemical element.

In its "fundamental" or lowest-energy condition, every atom is electrically neutral. There must, then, be present in its structure, a number of electrons (each having an electrostatic charge of $-1e$) exactly equal to the number of positively charged protons present in its nucleus. This number, which is distinctive for each chemical element, is called the *atomic number* of the element, and is traditionally indicated by the letter Z . Atomic numbers vary in steps of one unit from hydrogen, the lightest atom ($Z = 1$, representing 1 proton and 1 electron per neutral atom), to uranium ($Z = 92$, with 92 protons and 92 electrons)

¹ The neutron is actually about 0.1% heavier than the proton. F. O. Rice and E. Teller, *The Structure of Matter*, New York, John Wiley & Sons, Inc., 1949.

and the unstable transuranium elements of still higher atomic number recently produced by bombardment of uranium in nuclear reactors.

The experimentally determined *atomic weight* of an element, usually represented by the letter A , is roughly proportional to the atomic number but is not ordinarily an integer—as the atomic number, by definition, must be. Most of the chemical elements as they occur in nature are actually mixtures of two or more stable isotopes which are identical in atomic number and chemical properties but differ in atomic mass. If the proper units of mass were used to account for variations in the number of neutrons present in the atomic nucleus, it should be possible to represent by integers the atomic weights of all the isotopes present in the mixture. However, as it is ordinarily determined, the atomic weight of an element occurring in nature is the weighted average of the atomic weights of all the isotopes which compose it. Except by coincidence this average value is never an integer, no matter what units of mass are adopted to express it. Therefore, as a matter of chemical convenience, atomic weights are now always expressed in terms of an arbitrary unit equivalent to one-sixteenth of the mass of an oxygen atom.

1-2. Electrons

It is now generally agreed that electrons are particles of measurable mass, but that they also have many of the properties of electromagnetic wave motions. Thus, the mass of an electron can be determined experimentally, and is equal to about $1/1840$ of the mass of a single proton; yet a stream of electrons can be diffracted by a solid crystal in much the same way and according to exactly the same physical laws as can a beam of X-rays.

Much confusion results from this apparently dual nature of the electron, although it is actually only one manifestation of a general physical law that is applicable to all mechanical systems.

In general, any single arbitrarily selected property of a particle or system (such as its mass) can be measured to any desired degree of accuracy. When this is done, however, the system is so disturbed that any other of its properties (such as its velocity or position) cannot be determined at the same time with equal accuracy. When the mass considered is even as great as 1 gram,² the simultaneous determination of mass and of velocity or position, etc., involves uncertainties so small

² F. Seitz, *The Physics of Metals*, New York, McGraw-Hill Book Company, Inc., 1943.

that they can safely be neglected, and in dealing with ordinary mechanical systems they are neglected. But as mass diminishes, these uncertainties increase rapidly, and they are very large when a mass as small as that of an electron is considered.

One important implication of this *uncertainty principle* is that any attempt to describe an atom as a mechanical system in which mass, position, and motion of the electrons are simultaneously known must represent at best a drastic simplification of the facts. In view of the uncertainties involved in electron properties and behavior, a truly accurate description of the atom is possible only in terms of probability functions. This fact has led to the development of a mathematical treatment called *wave mechanics*, based upon the mathematics of probability—and so quite different in its principles and methods from the precise mathematics applicable to ordinary gross mechanical systems. Wave mechanics can and does reconcile the particle and the wave properties of the electron or of any other small particle, and further demonstrates that all finite particles in any mechanical system actually share this same dual nature. The wave motions associated with masses large enough to be familiar from direct observation are so restricted in amplitude as to be unobservable by any ordinary means. They become important only when the masses considered are very small, but they cannot be neglected when they are.

The major limitation upon wave mechanics results not from inaccuracy but from lack of understandability and credibility. Even to the atomic physicist a probability function offers a very incomplete view of the real, overall nature and behavior of an atom, the one mechanical system without which no others could exist. For clarity and usability, a simplified physical picture of the atom is irreplaceable. Accordingly, the wave properties of the electron will be neglected in most of the discussions which follow, and atomic behavior will be described in words rather than equations.

On this basis, an electron may be described as a small, but finite, negatively charged particle. Its mass is $1/1840$ that of a proton, and its diameter is generally believed to be slightly larger than that of an atomic nucleus.³ Its most important properties result, however, not so much from its mass as from its negative electrostatic charge ($-1e$) and

³ While there is some doubt concerning the physical significance of "diameter" in the case of an electron, a value frequently given for the electronic diameter is 2.8×10^{-13} cm. F. O. Rice and E. Teller, *op. cit.*

its position and movements relative to the nucleus of the atom or atoms with which it is associated.

1-3. Motion of the Electron

Within the atom an electron simultaneously describes two motions: it spins continuously around its own axis, and it revolves continuously around the nucleus of the atom in which it is contained. Each electron has a definite electrostatic charge, and any moving charge generates a magnetic field. Therefore, as it revolves around the nucleus, an electron carries with it a small magnetic field, and so in several respects its behavior resembles that of a tiny moving magnet. This is of fundamental importance in rationalizing the magnetic properties of metals, as will be described in Chapter 6. For the present, however, the spin of the electron and the magnetic effects which result from it will be considered as incidental to its major motion, i.e., its rotation around the atomic nucleus.

The neutral atom of any element contains a number of electrons exactly equal to its atomic number. Each electron revolves around the atomic nucleus in some specific orbit which, in the atomic scale of dimensions, is relatively remote from the nucleus. A natural order exists both in the arrangement of these orbits relative to the nucleus and in the sequence in which they are occupied as, with increasing atomic number, electrons appear successively within the atomic system. This order is best rationalized in terms of the *exclusion principle* and the *energy-level* concept, which are discussed individually in the two sections that follow.

1-4. The Exclusion Principle

One of the most significant facts of atomic structure, demonstrated both by physical experiments and by the mathematics of wave mechanics, is that there are drastic limitations upon both the number and the motions of electrons that can occupy any given orbit within an atom. Pauli was the first to discover that a single electronic orbit can contain no more than two electrons, and that, to be accommodated simultaneously, these two electrons must necessarily be spinning in opposite directions. This is known as Pauli's principle, or the *exclusion principle*, and its application is perfectly general. Under no conditions can more than two electrons occupy the same orbit at the same time. Accordingly, in all elements whose atomic numbers are greater than 2,

there must exist more than one possible orbit in which electrons can be contained as they revolve around the nucleus.

1-5. Energy Levels Within the Atom

Since the nucleus of an atom is positively charged, it exerts a strong electrostatic attraction for all electrons that appear in its immediate vicinity. The fact that electrons do not actually "fall into" the nucleus and neutralize its positive charge demonstrates that, in their rotation about the nucleus, they have kinetic energy sufficient to balance exactly the attractive force exerted by the nucleus. Further, if it ever should fall into the nucleus through this attractive field, an electron would evidently give up an amount of energy which would be a direct function of the distance through which it fell. Within the atom, then, each electron has potential as well as kinetic energy, and its total energy is the sum of the two. Rotating in a specific orbit around a particular nucleus, the total energy of any given electron is a constant value determined by the geometry and position of its orbit relative to the nucleus. This value is identified as the energy of the orbit, and in general it is higher for orbits which are more remote from the nucleus.

Within a single atom, the number of orbits available for occupancy of electrons is definitely limited, and so of course is the energy represented by each of the possible electronic orbits. These limitations are typical rather of wave than of mechanical systems, and their rationalization requires that the wave properties of the electron again be considered briefly.

A wave motion of any kind represents energy, and, in general, the shorter its wave length (or the higher its frequency) the greater is its energy. Travelling alone in space, the wave motion is undisturbed by external factors, and so it can exist at any level of energy, i.e., with any wave length or frequency. When the wave motion is confined, however, either constructive or destructive interference may occur as it is "reflected" from the boundaries of the confining system. Constructive interference occurs only for those wave lengths which happen to have nodes at the boundaries of the system; all other wave motions promptly die out as a result of destructive interference. This is most simply exemplified by the fact that a stretched violin string of fixed length can vibrate only at those certain frequencies for which interference is constructive, and so can produce only certain specific tones. The same is true of a stretched drumhead. In three dimensions, only a few

characteristic tones can be produced by blowing across the mouth of a bottle or ringing a partially filled glass. Similar limitations apply to the reflection of light and other radiations, and they apply as well to electrons confined within any finite region, such as the interior of a single atom.

As a result, then, of interference effects, an electron can exist within an atom only if the wave motion associated with it has one of the limited number of possible wave lengths for which constructive interference will occur within the atomic system. Each different wave length represents a different level of electronic energy, and so the conclusion is reached that electrons can exist within an atom only if they possess certain specific amounts of energy. They cannot exist at energy levels which are intermediate between these possible values.

To return to the concept of an electron as a particle revolving in a fixed orbit around the atomic nucleus, it is evident that electrons can assume only those orbits which represent energy levels possible to them within the specific atom being considered. All other orbits, representing intermediate energy values, are impossible. It is in this important respect that atomic systems differ most drastically from their usual analogue, the solar system. Presumably new planets could enter the solar system to assume orbits at any arbitrary distance from the sun. Alternatively, by altering the kinetic energy of an existing planet by an appropriate amount, its orbit could be altered to any desired degree. Further, there is no reason why, in the solar system, a whole swarm of planets should not simultaneously occupy the same orbit—as witness the asteroids. In an atom, on the other hand, electrons can exist only with certain energies and in specific orbits, and no more than two electrons can ever occupy the same orbit at the same time.

1-6. Energy-Level Diagrams

The possible orbits which can be assumed by electrons within a given neutral atom are conveniently summarized in an energy-level diagram such as that in Fig. 1-1. Here the relative energies required to maintain a single electron in each successively higher orbit (i.e., each orbit successively more remote from the nucleus) are indicated by the vertical spacing of horizontal lines whose positions represent the energy levels of possible electronic orbits.

It must be remembered that, within the atom, electrons can exist only *at* these specific energy levels. Between them lie forbidden regions