
Modern Physical Metallurgy

Fourth Edition

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Preface to the First Edition

After a period of intense activity and development in nearly all branches of the subject during the past decade, physical metallurgy appears to have again attained a state of comparative quiescence, with the difference that there is now fairly general agreement about the essential principles of the subject. This does not mean that we have a complete understanding of the science of metals, as the accounts on the electronic structure of metals and alloys, and on the work hardening of metals, given in Chapter 4 and Chapter 6 respectively, show. Nevertheless, we have a sufficient understanding to be able, in broad outline, to present a fairly consistent picture of metallic behaviour, and it would appear to be an appropriate moment to attempt to present in a single book the essential features of this picture.

In this book I have tried to give, in the simplest terms possible, the fundamental principles of physical metallurgy, and to show how the application of the principles leads to a clearer understanding of many technologically important metallurgical phenomena. Throughout the text I have adopted a uniform plan of first describing the experimental background of a particular phenomenon, and then attempting to explain the experimental facts in terms of atomic processes occurring in the metal. These processes usually involve the interaction between certain well-established features of the atomic structure of metals and alloys such as solute atoms, vacant lattice sites, dislocations and stacking-faults. In this way it has been possible to treat such problems as work hardening, annealing, creep, fatigue, fracture, yielding and strain-ageing, quenching, precipitation hardening, and radiation damage, and, it is hoped, to give the student some insight into their nature without including a mass of data in the text. The explanations are based substantially upon the accepted general climate of opinion which prevailed at the time of writing, but a personal viewpoint may well have coloured some of the topics discussed. If a theory is still speculative, this fact has been mentioned at the appropriate place in the text.

The book is intended primarily for students who wish to obtain a sound working knowledge of the subject, and I hope it will prove useful to those who are studying for Higher National Certificate and Associateship examinations in the various colleges of technology, and also those reading for a degree in metallurgy at a university.

A collection of questions has been added at the end of the book which should prove useful to the serious student. Questions requiring answers of a purely descriptive nature have not been included in the collection, since this type of question needs to be examined for quality of presentation and content, and, in consequence, is best set and examined by the student's tutor. Good examples of such questions can, of course, be obtained from past papers of the examination for which the student is studying. The questions given in the appendix are, therefore, entirely numerical and it is important that, wherever possible, students should work out the examples completely and obtain definite answers. In the past this aspect of the study of physical metallurgy has often been neglected.

Acknowledgements

I would like to express my thanks to the many friends and colleagues, too numerous to mention individually, who have helped me during the preparation of this book. Particular thanks are, however, due to Professor A.D. McQuillan of the University of Birmingham for his kindness in reading through the manuscript and giving suggestions on many points of presentation.

I am indebted to many associates in other universities and research institutions who have supplied original micrographs for reproduction. Reference to these workers and their work is given in the appropriate place in the text. Acknowledgement is also made to societies and publishers for permission to use certain diagrams whether in their original form or in a modified form.

R.E. Smallman

Preface to the Fourth Edition

It is now almost fifteen years since the last revision of the text and although the basic information contained in the book has stood the test of time remarkably well, there have been some developments in the subject which should be included in any treatise on Modern Physical Metallurgy. These developments have not been particularly dramatic compared with those that took place in the 1950s and 1960s, such as the application of dislocation ideas to alloy design or the advent of transmission electron microscopy. Instead there has been steady progress in the subject across a broad front.

The new edition therefore reflects this general development in our understanding of the subject and contains some fifty new diagrams and approximately thirty per cent new text, in some cases to give a better explanation, in others to include new features and in yet others to produce a more economical presentation. Apart from these additions and alterations the general development of the subject has necessitated a complete re-structuring of the previous material so that there are now fifteen chapters instead of the previous ten and some of the material from one former chapter has been combined with some of the material from a different chapter to produce, in the author's view, a better overall presentation.

Perhaps the most remarkable development has been in the techniques for the assessment of microstructure and its microchemical analysis. These metallographic techniques are basic to the field of physical metallurgy and without them, none of the developments in plasticity, phase transformations, fracture, radiation damage, oxidation and corrosion, and alloy design added to the book, would have been achieved. Chapter 2 is thus largely new and contains text on all the techniques arising from the interaction of electrons with matter, namely x-ray topography, Auger spectroscopy, SEM, TEM, HVEM and STEM, with associated analytic facilities of back-scattering, x-ray analysis (EDX), energy-loss analysis (EELS) and convergent-beam diffraction (CBDPs). Developments such as weak-beam microscopy and direct lattice resolution microscopy are introduced later in a new Chapter 7. Material from the previous Chapter 2 has been included in a new Chapter 3 together with an introduction to ternary equilibrium diagrams, not previously included, and some further developments of solidification. Chapter 4 includes some modifications to the treatment of phase

changes and diffusion and in Chapter 6 dislocations in ordered structures has been added. Chapter 8 includes the yielding behaviour of ordered alloys and some new aspects of the structure of grain boundaries. The discussion on point defects in Chapter 9 now includes radiation growth and swelling, radiation-induced segregation and radiation effects in ordered alloys. Work hardening and annealing have been re-cast into a new Chapter 10 which now includes dispersion-hardening and ordered alloys as well as *in situ* observations on recovery and recrystallization.

Phase transformations are now considered in Chapters 11 and 12, with new material on mechanisms of precipitation hardening, vacancies and precipitation, spinodal decomposition, dispersion-strengthening alloys and superalloys in Chapter 11, and HSLA and dual-phase steels in Chapter 12. There are improved treatments of creep and fatigue in Chapter 13 including deformation mechanism maps, structure of persistent slip bands, and fatigue crack formation and propagation. Different aspects of brittle and ductile fracture, fracture toughness and crack propagation are now dealt with in Chapter 14 and are conveniently summarized in fracture mechanism maps. Oxidation and corrosion now treated in Chapter 15 include intergranular voiding, breakaway oxidation, and some further consideration of corrosion failures.

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The structure of atoms and crystals

1.1 Metallic characteristics

Before beginning the study of the physical principles of metallic behaviour, one must first have a clear idea of what qualities characterize the metallic state. Frequently, a metal is described as having a high lustre, good electrical and thermal conductivity, and as being malleable and ductile. Very many metals do have all these properties, but many non-metallic substances can also exhibit one or more of them. Furthermore, there are large variations in the magnitude of these properties among the metals themselves. One has only to look at the remarkable malleability and ductility of lead at room temperature, and compare it with the hardness and brittleness of tungsten at the same temperature to realize the great diversity of behaviour exhibited by metals.

The most characteristic property of a metal is its high electrical or thermal conductivity. For example, among the best and worst conductors of electricity are copper and lead respectively, yet the resistivity of lead is only twelve times greater than that of copper. A non-metallic material such as diamond has, however, a resistivity which is about one thousand million times greater than copper. The reason for the enormous difference in conductivity between a metal and a non-metal is that electrons, which are negatively charged fundamental particles, can move freely through a metal under the action of a potential difference, whereas in a non-metal this is not the case. Thus the fundamental characteristics of the metallic state must be sought in the electronic structure of a metal, and we must begin the study of physical metallurgy by examining the structure of the atoms out of which a metal is built.

1.2 The atom

The crude picture of the atom conceived by Rutherford, was a positively charged nucleus which carried the greater part of the mass of the atom, with electrons clustering around it. He suggested that the electrons were revolving round the nucleus in circular orbits so that the centrifugal force of the revolving electrons was just equal to the electrostatic attraction between the positively

charged nucleus and the negatively charged electrons. In order to avoid the difficulty that revolving electrons should, according to the laws of electrodynamics, continuously give off energy in the form of electromagnetic radiation, Bohr, in 1913, was forced to conclude that, of all the possible orbits, only certain orbits were in fact permissible. These discrete orbits were assumed to have the remarkable property that when an electron was in one of these orbits, no radiation could take place. The set of stable orbits were characterized by the criterion that the angular momenta of the electrons in the orbits were given by the expression $n\hbar/2\pi$, where \hbar is Planck's constant, and n could only have integral values (i.e., $n = 1, 2, 3, \dots$ etc.). In this way Bohr was able to give a satisfactory explanation of the line spectrum of the hydrogen atom, and lay the foundation of modern atomic theory.

In the later developments of the atomic theory, by de Broglie, Schrödinger and Heisenberg, it was realized that the classical laws of particle dynamics could not be applied to fundamental particles. In classical dynamics it is a prerequisite that the position and momentum of a particle is known exactly, but in atomic dynamics, if either the position or the momentum of a fundamental particle is known exactly, then the other quantity cannot be determined. In fact there must exist an uncertainty in our knowledge of the position and momentum of a small particle, and the product of the degree of uncertainty in each quantity is related to the value of Planck's constant [$\hbar = 6.6256 \times 10^{-34}$ J s]. In the macroscopic world this fundamental uncertainty is too small to be measurable, but when treating the motion of electrons revolving round an atomic nucleus, the application of the Uncertainty Principle (enunciated first by Heisenberg) is essential.

The consequences of the Uncertainty Principle is that we can no longer think of an electron as moving in a fixed orbit around the nucleus, but must consider the motion of the electron in terms of a wave function. This function specifies only the probability of finding one electron having a particular energy, in the space surrounding the nucleus. The situation is further complicated by the fact that the electron behaves, not only as if it were revolving round the nucleus, but also as if it were spinning about its own axis. Consequently, instead of specifying the motion of an electron in an atom by a single integer n , as in the case of the Bohr theory, it is now necessary to specify the electron state using four numbers. These numbers, known as quantum numbers, are n, l, m and s , where n is the principal quantum number, l the orbital quantum number, m the inner quantum number and s the spin quantum number. Another basic principle of the modern quantum theory of the atom is the Pauli Exclusion Principle which states that no two electrons in the same atom can have the same numerical values for their set of four quantum numbers.

If we are to understand the way in which the Periodic Table is built up in terms of the electronic structure of the atoms of the various elements, we must now consider the significance of the four quantum numbers and the limitation placed upon the numerical values they can assume. The most important quantum number is the principal quantum number since it is mainly responsible for determining the energy of the electron. The principal quantum number can have integral values beginning with $n = 1$, which is the state of lowest energy, and electrons having this value are the most stable, the stability decreasing as n

increases. Electrons having a principal quantum number n can take up integral values of the orbital quantum number between 0 and $(n-1)$. Thus if $n=1$, l can only have the value 0, while for $n=2$, $l=0$ or 1, and for $n=3$, $l=0$, 1 or 2. The orbital quantum number is associated with the angular momentum of the revolving electron, and determines what would be regarded in non-quantum mechanical terms as the shape of the orbit. For a given value of n , the electron having the lowest value of l will have the lowest energy, and the higher the value of l the greater will be the energy.

The two quantum numbers m and s are concerned respectively with the orientation of the electron's orbit round the nucleus, and with the orientation of the direction of spin of the electron. For a given value of l , an electron may have integral values of the inner quantum number m from $+l$ through 0 to $-l$. Thus for $l=2$, m can take on the values $+2$, $+1$, 0 , -1 and -2 . The energies of electrons having the same values of n and l but different values of m are the same, provided there is no magnetic field present. When a magnetic field is applied, the energies of electrons having different m values will be altered slightly, as is shown by the splitting of spectral lines in the Zeeman effect. The spin quantum number s may, for an electron having the same values of n , l and m , take one of two values $+\frac{1}{2}$ or $-\frac{1}{2}$. The fact that these are non-integral values need not concern us for the present purpose; we need only remember that two electrons in an atom can have the same values for the three quantum numbers n , l and m , and that the two electrons will have their spins oriented in opposite directions. Only in a magnetic field will the energies of the two electrons of opposite spin be different.

1.3 The nomenclature of the electronic states in an atom

Before discussing the way in which the periodic classification of the elements can be built up by considering the electronic structure of the atoms, it is necessary to outline the system of nomenclature which will enable us to describe the states of the electrons in an atom. Since the energy of an electron is determined by the values of the principal and orbital quantum numbers alone, it is only necessary to consider these in our nomenclature. The principal quantum number is simply expressed by giving that number, but the orbital quantum number is denoted by a letter. These letters, which derive from the early days of spectroscopy, are s , p , d and f which signify that the orbital quantum numbers l are 0, 1, 2 and 3 respectively*.

When the principal quantum number $n=1$, l must be equal to zero, and an electron in this state would be designated by the symbol $1s$. Such a state can only have a single value of the inner quantum number $m=0$, but can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$ for the spin quantum number s . It follows, therefore, there are only two electrons in any one atom which can be in a $1s$ state, and these will have the electron spins in opposite directions. Thus when $n=1$, only s states can exist and

* The letters, s , p , d and f arose from a classification of spectral lines into four groups, termed sharp, principal, diffuse and fundamental in the days before the present quantum theory was developed.

TABLE 1.1 Allocation of states in the first three quantum shells

Shell	n	l	m	s	Number of states
1st	1	0	0	$\pm \frac{1}{2}$	2, 1s states
2nd		0	0	$\pm \frac{1}{2}$	2, 2s states
	2	1	+1 0 -1	$\pm \frac{1}{2}$ $\pm \frac{1}{2}$ $\pm \frac{1}{2}$	6, 2p states
3rd		0	0	$\pm \frac{1}{2}$	2, 3s states
		1	+1 0 -1	$\pm \frac{1}{2}$ $\pm \frac{1}{2}$ $\pm \frac{1}{2}$	6, 3p states
	3		+2 +1 0 -1 -2	$\pm \frac{1}{2}$ $\pm \frac{1}{2}$ $\pm \frac{1}{2}$ $\pm \frac{1}{2}$ $\pm \frac{1}{2}$	10, 3d states

these can be occupied by only two electrons. Once the two 1s states have been filled, the next lowest energy state must have $n = 2$. Here l may take up the value 0 or 1, and therefore electrons can be in either a 2s or 2p state. The energy of an electron in the 2s state is lower than in a 2p state, and hence the 2s states will be filled first. Once more there are only two electrons in the 2s state, and indeed this is always true of s states irrespective of the value of the principal quantum number. The electrons in the p state can have values of $m = +1, 0, -1$, and electrons having each of these values for m can have two values of the spin quantum number, leading, therefore, to the possibility of six electrons being in any one p state. This is shown more clearly in Table 1.1.

No further electrons can be added to the state for $n = 2$ after the two 2s and six 2p states are filled, and the next electron must go into the state for which $n = 3$ which is at a higher energy. Here the possibility arises for l to have the values 0, 1 and 2 and hence, besides s and p states, d states for which $l = 2$ can now occur. When $l = 2$, m may have the values $+2, +1, 0, -1, -2$ and each may be occupied by two electrons of opposite spin, leading to a total of ten d states.

Finally when $n = 4$, l will have the possible values from 0 to 4, and when $l = 4$ the reader may verify that there are fourteen 4f states.

1.4 The Periodic Table (see Table 1.2)

The simplest atom is the hydrogen atom which has a single proton as its nucleus, and may, therefore, have only one electron revolving round it in order that the atom shall be electrically neutral. In the free atom, in its lowest energy condition, the electron will be in a 1s state. For helium, which has a nucleus made up of two protons and two neutrons, the atomic mass will be four times greater than for hydrogen, but because the nuclear charge is governed solely by the