# The Science of Engineering Materials

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*by* C. R. TOTTLE
M.MET., M.Sc., F.I.M., F.Inst.P., M.Inst.W.
*Professor of Metallurgy, University of Manchester*

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# Preface

This book is intended for engineers taking university and similar courses which include materials and as an introduction to materials science for metallurgists and those who require a general review. It is not intended to be a complete course in materials science nor to give details of commercial materials available.

In ancient times, the materials used for construction, and for weapons, tools, and ornaments, were limited to seven metals, stone, clay (dried and sometimes fired), earth, wood, animal hide and bone, and vegetable fibres woven into mats, twisted into ropes, or mixed with clay or earth. Little change in numbers or variety of materials occurred for thousands of years, but the technology of their use improved enormously. Bricks were made much stronger by better selection of clays, appropriate weathering and homogenizing, and higher temperature of firing. Alloys were developed from the traditional metals, although bronze had been known for some thousands of years. Nevertheless, wood continued to be the most flexible material for construction, possessing high strength-to-weight ratio, and capable of being joined by wood dowels, metal nails, or thongs of vegetable fibre or animal hide. The roof of the Tabernacle in Temple Square, Salt Lake City, Utah, is an excellent example of an unsupported large span formed from timber, joined only by dowels and thongs, and built just over one hundred years ago.

During the beginnings of scientific discovery, from the seventeenth century onwards, many materials, both elemental and compound, were explored, but very few indeed were of value in engineering. Charcoal continued to set the limit of very high temperatures attained on a large scale, until the Darby family carried out experiments to utilize a shaft furnace with coal previously purified by coking. Henry Cort's puddling process purified iron by utilizing coal fuel in a reverberatory furnace but could not melt the pure iron to separate the slag. An early appreciation of the value of ductility nevertheless stemmed from this association of low-carbon iron with slag in laminations, which allowed rolling into longer bars than had previously been possible and joining by hammer welding. The carrying capacity of structures increased as a result, and some composite structures were developed, to combine the best properties of more than one material. Many early locomotives employed sandwich frames of wood and iron.

One of the most significant steps in the development of steel occurred in 1740, when Benjamin Huntsman learned how to melt it in a coke-fired crucible furnace. The real advance, however, required an increase in the scale of operations. This became possible first by the Bessemer converter, and then by the Siemens–Martin open-hearth furnace. Steel remained a crude material until development of the deoxidation process for Bessemer steel by Mushet led to the addition of other alloying elements to modify properties. Men like Whitworth were then able to develop machine tools and, in turn, precision engineering, employing more stable materials exhibiting a wide variety of properties as a result of heat treatment. Non-ferrous metals did not advance so rapidly until the commercial exploitation of aluminium, which subsequently contributed so much to the aeroplane. In recent times, almost every metallic element in the periodic table has been prepared on a commercial scale and has been investigated as a possible engineering material.

Chemical compounds in profusion followed the industrial revolution and its new demands. Portland cement made possible bricks of larger size and different shapes and monolithic structures in complex forms. In more recent times, new fibres have replaced many traditional ones, not only for clothing but also for reinforcement of plastics, replacement of metal wires, etc. The plastics industry alone offers an immense variety of materials, most of which can be 'tailor-made' for the conditions of service. The electrical industry replaced porcelain and similar ceramic insulators for indoor use with the phenol formaldehyde resins at an early stage. Before the second world war, not only these resins, but also the urea formaldehyde types, the transparent acrylics and the cellulose esters, were commercially available and applied in engineering. In the twenty-five years following, an enormous quantity of synthetic polymer materials has replaced much of the metal in the domestic kitchen, leather, wool, and cotton in furnishings, and natural rubber, wood, and metal in vehicles, prime movers. Plastics are still limited for high-temperature applications, but the so-called ceramic materials, normally metal oxides, carbides, silicides, nitrides, and borides, are likely to supersede metals to a considerable extent in this field.

Electrical developments have given rise to the utilization of hitherto uninteresting elements such as silicon and germanium, and superconducting alloys are likely to provide an outlet for some intermetallic compounds of little mechanical significance. Faced with such sweeping developments and with changes in demand, the design engineer can no longer limit himself to traditional materials, nor to the traditional reliance on catalogues of properties or manufacturers' specifications. Interactions between widely diverse properties may be involved in new developments, and more stringent service conditions are continually to be expected. The lifetime of a material is not always necessarily long. A manned space craft may have a lifetime of a few hours, the rocket that carries it aloft even less. Power-station generators may be expected to last for twenty to twenty-five years, motor-cars for only ten. Economic considerations obviously enter into this argument, but knowledge of the properties and the effect of time are far more restricting than they were, and generous safety factors are becoming less welcome.

To cope with this situation, an understanding of the basic science that explains the variation in properties between elements, compounds, alloys, and mixtures becomes essential. The modification of the fundamental properties by manufacturing operations and subsequent service conditions has to be superimposed on this background, but the detailed consideration is really the realm of the metallurgist, chemist, or physicist. The engineer can, in these days, normally draw on the services of these materials scientists for this detail, and so requires a less detailed approach to individual materials and more of the broad overall picture of those which are feasible.

This book attempts to provide the broad background, to illustrate the basic reasons for the properties of elements, and to explain the consequences of chemical combination, alloying, and mixing. Most previous books have touched only lightly on the atom itself, but my experience in teaching engineers in the University of Manchester suggests that a greater depth of approach is welcome, perhaps because it can account for so much of the subsequent behaviour of metals. I acknowledge the advice and comment of my engineering colleagues in this matter, particularly Professors J. Diamond, M. R. Horne, and W. B. Hall, and their academic staff. Inevitably, such an approach has its own limitations. This book does not deal in any *detail* with metallic alloy systems and their equilibrium, nor with the specialized metal compounds used as engineering materials. It does, however, compare and contrast them in terms of structure and the dependence of properties on the atomic configuration. Books produced especially to deal with the details of specific classes of materials are best consulted in the light of this scientific background.

It is also my hope that many engineers of long standing may find in this book some explanation of the apparent perversity of certain materials, some confirmation of the reluctance of materials scientists to commit themselves in certain respects, and a more tolerant attitude to producers and research departments alike. I have in mind particularly the chief design engineer who refused to believe that temperatures in the cylinders of a compression-ignition oil engine reached the level indicated by microscopic examination of a fissured piston crown. Twenty years ago he wrote 'rubbish' across my report to this effect, but I did have the satisfaction some months later of noting that my recommendation for replacement of the material by a low-alloy steel had been implemented in the machine shops. Today there are alternative solutions to this and other problems, and no doubt design engineers are more willing to examine each possibility. May this book help them to clarify the whole picture.

*Manchester, April* 1964 C. R. Tottle

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*Western Springs, Illinois* C. R. T.

*May* 1965

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# 1

# The Free Atom

## 1.1. *The contribution of spectroscopy*

The original work on the nature of substances was carried out by chemists, who were anxious to explain the variation in behaviour of the various elements and their compounds. John Dalton, for example, established the existence of atoms, and defined them as the smallest part of an element that could exist alone and still be representative of that substance. Later work by physicists delved into the atom itself, and demonstrated the existence of elementary particles (chiefly electrons and protons), which varied in number with the element concerned. At this stage, however, the internal arrangement of these particles was inadequately understood, and it was not possible to correlate the properties of atoms with their structure. The investigation of the radiation emitted by excited atoms and the diffraction of X-radiation by atoms gradually changed this situation. Kirchhoff first suggested in 1859 that each species of atom has a uniquely characteristic spectrum. He and Bunsen analysed the sun's atmosphere in 1861 and discovered two alkali metals (rubidium and caesium) by investigating atomic spectra.

The spectrometer used in such techniques allowed the light from the source (high-temperature flame, gas-discharge tube, electric arc, or high-frequency spark) to pass through a narrow slit into a collimator, and thence through a prism, where refraction and dispersion took place, and finally via a telescope to an eyepiece for visual examination, or to a photographic plate. A series of lines resulted, one for each wavelength of radiation emitted, each line being an image of the slit produced by that particular wavelength. The more complex the atom, the more wavelengths were emitted, and thus the greater the number of lines produced.

Utilizing an electric discharge through a glass tube filled with a pure gas, the spectra of gaseous elements can also be investigated. In 1885 BALMER discovered a relationship between the lines produced as part of the hydrogen spectrum. He expressed the wavelength of the lines as

$$\lambda = \frac{3{,}646{\cdot}13m^2}{m^2 - 4}\ \text{Å} \tag{1.1}$$

where $m$ has values 3, 4, 5, 6 . . . ∞.

These measurements were made in air, and thus they are not perfectly reproducible, but by changing to vacuum measurement and using $\lambda_{vac} = 3{,}647{\cdot}16m^2/(m^2 - 4)$ they can be reproduced anywhere in the world. Thus, when $m = 3$, $\lambda = 6{,}563$ Å; when $m = \infty$, $\lambda = 3{,}647{\cdot}16$, giving the longest and shortest wavelength lines in the series, known as the *Balmer series*. In spectroscopy, it is more customary to use the wave number

$$\nu = \frac{n}{c} = \frac{\text{Frequency}}{\text{Velocity}} = \frac{1}{\text{Wavelength}}$$

i.e. the number of waves per centimetre. Rewriting the Balmer series in this way, and rearranging the equation,

$$\nu = \frac{109{,}675}{2^2} - \frac{109{,}675}{m^2} \tag{1.2}$$

where $m = 3, 4, \ldots \infty$. RYDBERG, working on the spectra of alkali metals, followed Balmer's work in predicting further series of lines covered by a simple formula. Rydberg and RITZ also predicted that the hydrogen spectrum should contain other series, given by a formula similar to that of the Balmer series. Subsequent experiment established these series, namely:

$$\nu = \frac{109{,}675}{1^2} - \frac{109{,}675}{m^2}$$

where $m = 2, 3, \ldots \infty$ (discovered by LYMAN in the ultraviolet).

$$\nu = \frac{109{,}675}{3^2} - \frac{109{,}675}{m^2}$$

where $m = 4, 5, 6, \ldots \infty$ (discovered by PASCHEN in the infrared).

At a later stage, improvements in instruments led to yet one more series (due to BRACKETT) which occurs in the far infrared of the hydrogen spectrum:

$$\nu = \frac{109{,}675}{4^2} - \frac{109{,}675}{m^2}$$

where $m = 5, 6, 7 \ldots \infty$.

These four series embrace the normal line spectrum of hydrogen, from infrared (long wavelength) to ultraviolet (short wavelength). Rearranging these equations covering the hydrogen spectrum in order

$$\nu = \frac{R}{(1+0)^2} - \frac{R}{(m+1)^2} \quad \text{(Lyman)}$$

$$\nu = \frac{R}{(1+1)^2} - \frac{R}{(m+2)^2} \quad \text{(Balmer)}$$

$$\nu = \frac{R}{(1+2)^2} - \frac{R}{(m+3)^2} \quad \text{(Paschen)}$$

$$\nu = \frac{R}{(1+3)^2} - \frac{R}{(m+3)^2} \quad \text{(Brackett)}$$

where $R$ is 109,675 $cm^{-1}$, the Rydberg constant, and $m$ is now an integer varying from 1 to $\infty$.

It is obvious that we can write a general equation covering these four series in which there is a limiting term and a variable term, the limiting term being constant for any one series but increasing in steps as we move from short wavelength (Lyman) to long wavelength (Brackett). This 'combination' principle was first proposed by Ritz. The limiting term in the Lyman series for hydrogen is $R/1^2 = R$, and the first variable term will be $R/(m+1)^2 = R/2^2$. The Balmer series has a limiting term $R/2^2$, which is the first variable term of the shorter wavelength Lyman series. The first variable term in the Balmer series is $R/3^2$, which in turn becomes the limiting term of the next, the Paschen, series. Likewise the first variable term of the Paschen series is $R/4^2$, and this is the limiting term of the Brackett series. There is obviously a continuous connection, through these series, of the factors affecting the emission of spectral lines. The denominator of the limiting terms is given by squaring the sum of a constant (1) plus an increasing integer (0, 1, 2, or 3). The denominator of the variable term is similarly made up by squaring the sum of a variable integer ($m = 1, 2, 3 \ldots \infty$) plus an increasing integer (1, 2, 3, or 4). Rewriting this as a general equation

$$\nu = \frac{R}{(m'+a')^2} - \frac{R}{(m+a)^2} \qquad (1.3)$$

For hydrogen

| | |
|---|---|
| $m' = 1$, | for each series |
| $a'$ has values 0, 1, 2, 3, | through the four series |
| $m = 1, 2, 3 \ldots \infty$, | for each series |
| $a$ has values 1, 2, 3, 4, | through the four series |

and substitution in the above equation would give all the series of spectral lines for hydrogen. The values of $a'$ and $a$ will not of course be the same when the general equation is applied to the spectra of all other elements, as they are in hydrogen, but the appropriate substitution will give the wave numbers for all spectral lines. Rydberg also observed that the lines in spectra were characterized by certain other properties, quite independent of the atom concerned. Certain of the lines were always very sharply defined: these he called 'sharp'; certain were 'diffuse'. Some lines appeared even when the element concerned was present in only small quantity, and these were given the name 'principal'. A fourth type was recognized later, and called 'fundamental'. These features, Rydberg suggested, were accounted for by the same close relationship between the series of spectral lines that had been observed for hydrogen, and therefore one could write this into the general equation by substitution for one of the variable integers. He suggested that $a$ in the general equation (1.3) took the values $s, p, d, f$, where these letters stood for sharp, principal, diffuse, and fundamental. The four variable terms would then be

$$\frac{R}{(m+s)^2};\quad \frac{R}{(m+p)^2};\quad \frac{R}{(m+d)^2};\quad \frac{R}{(m+f)^2}$$

In order to account for the relationship between the first variable term of the lowest series (Lyman for hydrogen) and the limiting term of the next (Balmer for hydrogen) Rydberg proposed a so-called 'selection rule'. Writing S–P–D–F to stand for the four series, he proposed that any one series, written in this order, was related to its immediate neighbours, but not with distant ones. Thus S can be related only to P; P to S or D; D to P or F; F only with D. In writing his general equation therefore, the selection rule implied that the limiting term of the sharp series was the first variable term of the principal. Hence,

$$\nu = \frac{R}{(2+p)^2} - \frac{R}{(m+s)^2} \tag{1.4}$$

where $m = 1 \ldots \infty$. This gives the SHARP series of lines.

Accordingly, the first variable term of this sharp series becomes the limiting term of the PRINCIPAL series

$$\nu = \frac{R}{(1+s)^2} - \frac{R}{(m+p)^2} \tag{1.5}$$

where $m = 2 \ldots \infty$.

The other two series follow suit:

DIFFUSE:

$$\nu = \frac{R}{(2+p)^2} - \frac{R}{(m+d)^2} \tag{1.6}$$

where $m = 3 \ldots \infty$.

FUNDAMENTAL:

$$\nu = \frac{R}{(3+d)^2} - \frac{R}{(m+f)^2} \tag{1.7}$$

where $m = 4 \ldots \infty$.

The lowest terms of the sequences are therefore

$$\frac{R}{(1+s)^2}; \quad \frac{R}{(2+p)^2}; \quad \frac{R}{(3+d)^2}; \quad \frac{R}{(4+f)^2}$$

To avoid writing this term in full, it is simpler to use a shorthand version, where $m$S stands for $R/(m+s)^2$. Hence 1S means $R/(1+s)^2$ the lowest term of the sharp series. The other lowest terms are then 2P; 3D; 4F.

Provided that values of $s$, $p$, $d$, $f$ are available for measurements of spectral lines, all other lines that exist should be predictable by substitution in these general equations for the various series. This proves to be so.

NIELS BOHR was the first to recognize a possible relationship between these series of spectral lines and the structure of the atom. He selected the hydrogen atom as his model, partly because of its simplicity (one proton in the nucleus and one extra-nuclear electron) and partly because the spectral series were best known for hydrogen.

## 1.2. *Bohr's early theory*

Bohr envisaged the electron in a hydrogen atom revolving round the nucleus in a planetary motion, in a fixed circular orbit. If external energy were applied to the atom, there would be an increase in the orbit radius. When, subsequently, the electron gave up this excess energy and returned to its normal orbital motion, the excess energy would appear as radiation. Thus, excitation of a hydrogen atom might increase the energy level of the electron temporarily, with a subsequent return to the 'ground state' of energy with the emission of radiation—detected by a spectrometer as a spectral line. If the energy level of the ground state of the electron is $W_0$, and that of the excited state $W_e$, then the difference must refer to the energy of the radiation given out, namely,

$$\Delta W = W_e - W_0 \tag{1.8}$$

where $\Delta W =$ work done in emitting radiation. PLANCK had meanwhile argued that vibrational energy was never absorbed or emitted in a continuous manner, but in discrete bundles, which he called 'quanta'. He postulated a *constant of action*, equal to the product of energy and time. Where spectral lines are involved, the emitted frequency is concerned also; hence

$$\text{Action} \times \text{Frequency} = \frac{\text{Action}}{\text{Time}} = \frac{\text{Energy} \times \text{Time}}{\text{Time}} = \text{Energy}$$

Thus the value of Planck's constant of action $h$ multiplied by frequency $n$ gives us a basic measure of energy $hn$. This is the basic unit of energy, the quantum.

This reasoning can be applied to the energy involved in emitting spectral lines. Substituting in the general Rydberg equation (1.3),

$$\nu = \frac{R}{m_1^2} - \frac{R}{m_2^2}$$

where $m_1$ and $m_2$ are integers as previously defined, $\nu = n/c$. Hence

$$n = \frac{cR}{m_1^2} - \frac{cR}{m_2^2} \quad \text{and} \quad hn = \frac{hcR}{m_1^2} - \frac{hcR}{m_2^2} \tag{1.9}$$

This gives an expression for one quantum of energy, in terms of the three constants $h$, $c$, $R$, and the inverse square of two integers, one quantum fixed, the other variable, for any given series of spectral lines.

There is a dimensional resemblance between the two equations (1.8) and (1.9)

$$hn = \frac{hcR}{m_1^2} - \frac{hcR}{m_2^2} \quad \text{and} \quad \Delta W = W_e - W_0$$

If $\Delta W$ is related to quanta, Bohr envisaged a situation in which one quantum of energy is involved, and $\Delta W = hn$. Then, in general terms,

$$W = \frac{hcR}{\bar{m}^2} \tag{1.10}$$

where $W$ is the energy level of an electron orbit and $\bar{m}$ is an integer. This would mean that energy levels of electron orbits were related inversely to the squares of natural numbers.

Bohr set out to calculate energy levels in the hydrogen atom, in terms of the forces involved, and showed that

$$W = -\frac{eZe}{2a}$$

where $e$ is the charge on the electron, $Ze$ the charge on the nucleus, and $a$ the 'radius' of orbit.

# Subject Index