CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

1
Introduction

Since metals constitute a class of solids it might well be asked what aspects of Physical Metallurgy do not already fall within the scope of solid state physics. If Kittel's book [1.1]† is taken as a guide there is at least one basic metallurgical concept which is unfamiliar to solid state physicists. Metallurgy relates the properties of metals and metallic 'mixtures' or *alloys* to their *microstructure*. Whereas solid state physics is based on the *crystal structure* of a single crystal in which all the atoms occupy sites in a three-dimensional lattice, metallurgy takes into account that the perfect regularity of the arrangement is often restricted to microscopic regions and differs from that in neighbouring regions. In other words, superimposed on a macroscopic piece of metal there is another pattern known as the *microstructure*, much coarser than the crystal structure which forms the foundation of solid state physics.

It happens that many of the properties of metals, especially those that are technologically important, are determined by the microstructure. The most important property from the point of view of mechanical engineering is the strength. This is strongly influenced by the microstructure and is thus one, but by no means the only, *microstructure sensitive property*. In order to define 'strength' and give it some physical meaning (chapters 12 and 14) we must first (chapters 3, 4, 11, 13, 15, etc.) examine the microstructure of metals and describe it quantitatively. The experimental techniques used to characterize the metallic microstructure are described in chapter 2.

A second difference between solid state physics and metallurgy is that the former is concerned with simple, pure materials and the latter with alloys. The physicist is inclined to consider the dependence of a property on the composition of the material as a chemical phenomenon. It is, however, by no means true that a given composition defines the properties of an alloy. For example, the 'hardness' HV (see section 2.6.3) of a steel

† Numbers in square parenthesis indicate specific references listed on pp. 403–14.

© Cambridge University Press

CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

consisting of iron with 0.3% carbon can have values of between 10^9 and 7×10^9 N/m^2 depending on how the material has been heat-treated. This treatment changes the distribution of the carbon in the iron, hence the microstructure and hence the mechanical properties. The distribution which arises is determined by the thermodynamics and kinetics of the alloy system and thus by a few parameters describing the energy, entropy and geometry. These will be discussed in chapters 5, 8 and 10 before examining typical atomic configurations in alloys (e.g. in chapters 7 and 9). The thermodynamics and kinetics of atomic distributions really fall within the domain of physical chemistry, and it was from physical chemistry that Gustav Tammann developed physical metallurgy in Göttingen in the period between 1903 and 1938. The physicist is inclined to enquire into the atomistic origin, in the case of metals the electron–theoretical explanation of the energy terms determining the thermodynamics and kinetics of metallic systems. Some theories along these lines are described in chapter 6; by considering the present state of the theory of multi-particle, multi-component systems, thermodynamics itself is much better able to yield information and be tested experimentally and is therefore discussed in relative detail in chapter 5.

Further information can be found in the literature. The book of Cottrell [1.2] contains introductory chapters about the pre-requisites for physical metallurgy, Shewmon's book [1.3] provides a good introduction to some branches of metallurgy, while a more detailed description of the field is given in the two volumes of *Physical Metallurgy*, edited by R. W. Cahn and P. Haasen, and in the new series *Materials Science and Technology*, edited by R. W. Cahn, P. Haasen and E. Kramer.

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

2
Experimental methods for the physical examination of metals

Metallurgists employ a number of experimental methods not normally encountered by the solid state physicist. Several of these will be described and critically assessed in the following chapter because the data they can provide will be drawn upon in subsequent chapters. Naturally many experimental techniques are standard for both solid state physicists and metallurgists, for example X-ray methods for the determination of crystal structure, lattice parameters and crystallographic orientation [2.1], [2.2], based on the Bragg relationship for constructive interference of X-rays scattered by the atoms in the lattice. Similarly, both physicists, and metallurgists make use of measurements of electrical conductivity, Hall voltage, macroscopic density and its variation with temperature (thermal expansion), although the metallurgist usually measures the latter uni-dimensionally in a dilatometer. Nor do measurements of elastic moduli, specific heat or magnetic susceptibility introduce the physicist to any new methods. Results of these and related investigations will be referred to without any detailed description of the procedure. Relevant techniques are summarized in [2.3], [2.4], [2.5].

2.1 Microscopy of surfaces

Apart from their crystal structure, metals possess a *microstructure*, in that they consist of differently oriented grains or differently constituted phases. The observation and if possible quantitative description of this microstructure is the aim of *metallography*, which employs optical, electron, ion and X-ray microscopical methods, some of which are described in sections 2.2 and 2.4.

Often the geometrical dimensions of the microstructure can be resolved in the light microscope. Because of their opacity, metals must be observed in reflection in the vertical microscope. For this purpose the surface is made optically plane by grinding, followed by mechanical, chemical or electrolytic *polishing*. As a rule the polished metal surface appears smooth

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

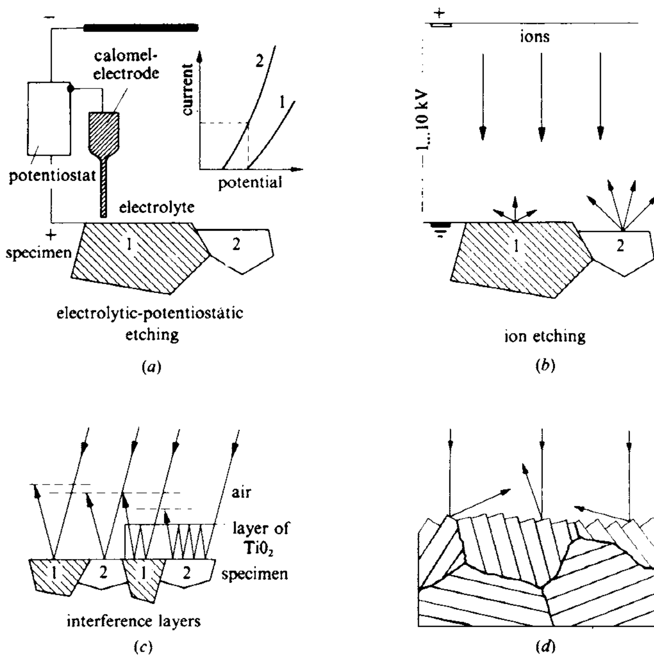


Fig. 2.1. Methods of revealing microstructural constituents ((*a*) to (*c*) after E. Hornbogen and G. Petzow, *Z. Metallkunde*, **61** (1970), 81). (*d*) Preferential chemical etching.

and uniformly coloured under the microscope. In order to distinguish the individual microstructural components, different techniques are used to produce or accentuate contrast. One way of producing specific changes in the specimen surface is by *etching*. In addition to empirical chemical techniques, reproducible physical methods (several of which are illustrated in fig. 2.1) are becoming increasingly important. Whereas in figs. 2.1(*a*) and (*b*) the structural components are revealed by the removal of different amounts of material, fig. 2.1(*c*) illustrates the exploitation of the different reflectivities of light at the interface to a vapour deposited layer. Chemical etching reagents often expose particular crystallographic planes as a series of steps, as shown in fig. 2.1(*d*). Differently oriented grains reflect the light in different directions and thus appear of different brightness in the vertical microscope. If the reflecting lattice plane is known, the orientation of the grains (or crystallites) in the specimen can be determined. 'Orientation' signifies the position of the crystal lattice in relation to the external features of the specimen (surface, longitudinal axis).

On the other hand, the contrast of a microstructure can be enhanced

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

by the use of a suitable optical arrangement, e.g. by observation in polarized light, using phase contrast, interference contrast or in 'dark field'. In the latter, the contours of a surface relief are revealed in glancing incidence (more strongly than in vertical incidence in 'bright field'). The surface relief can be measured quantitatively using an *interference microscope* which has a vertical resolution of a fraction (about $\frac{1}{20}$) of the wavelength of light used. (In the case of multiple beam interference, structures with depth variations of 3 nm can be resolved.) The resolution in the plane of observation is, however, that of the optical microscope, about 300 nm.

A better resolution of the microstructure observed directly in reflection can be obtained using electron waves. (Observations in transmission will be discussed in section 2.2.) In *reflection electron microscopy* a glancing beam of electrons impinges on the surface. The electrons are scattered mainly in the direction symmetrical to the normal to the surface and can then be used to form a magnified image. The resolving power is several tens of nanometres but the surface appears very distorted because of the oblique angle of observation. The *emission electron microscope* avoids this disadvantage by forming the image with secondary electrons released directly from the surface at right angles. UV light is one possible primary exciting radiation unless thermal emission is used, in which case this electron microscope is particularly suitable for the high-resolution observation of high-temperature processes.

In contrast to the microscopes described above the *scanning electron microscope* does not use electron optics for magnification but scans the specimen surface with a very finely focussed electron beam (diameter $\geqslant 20$ nm). The secondary electrons are amplified and control the brightness of a television tube, the scanning system of which is synchronized with that of the primary electron beam (fig. 2.2). Because of the asymmetrical ray path, the brightness, i.e. the intensity of the secondary electrons emitted from a particular point, depends on the local surface relief as well as on the material of the specimen. This together with the extraordinarily good depth of focus (e.g. 35 μm at a magnification of $\times 1000$) produces a three-dimensional image. The interference pattern of the secondary electrons allows the orientation of the specimen to be determined.

The primary electron beam can also excite the characteristic X-radiation of the target atoms. If the spectrum of this fluorescent radiation is analysed using a standard crystal, a localized chemical analysis of the specimen is obtained. In addition to the topographical image of the surface due to the secondary electrons (fig. 2.3), the scanning technique can be

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

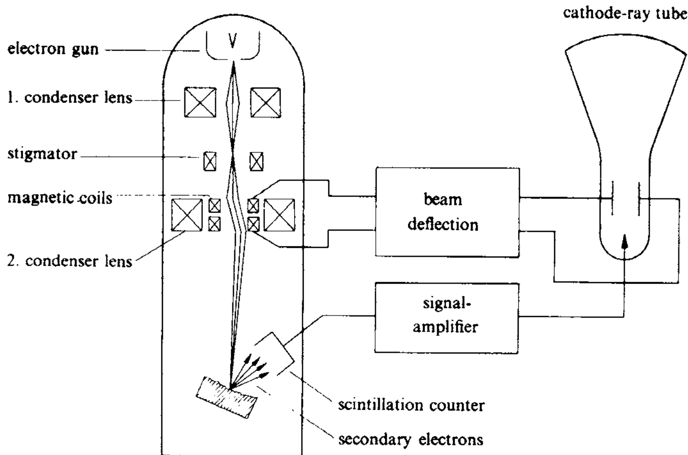


Fig. 2.2. Schematic representation of the scanning electron microscope, after [2.8].

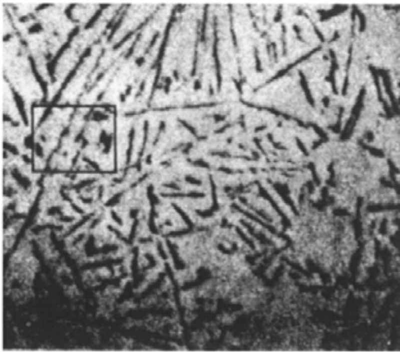


Fig. 2.3. Solidified Al–11.7 wt.% Si alloy (185 ×).

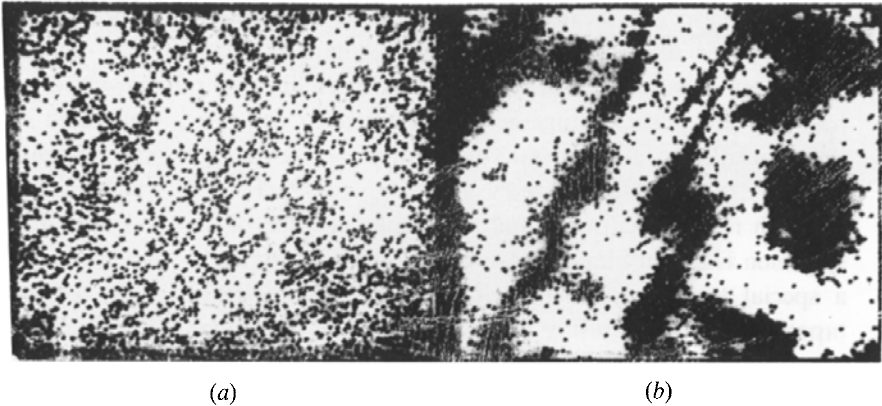
used to obtain other pictures using the various characteristic X-radiations which then show the distribution of particular chemical elements (fig. 2.4). This analysis can be undertaken quantitatively by X-ray emission in the electron beam microprobe. Concentrations $\geqslant 10^{-4}$ in surface regions of about 1 μm diameter (equivalent to 10^{-11} g of the element) can be detected.

Optical microscopy and general metallographic techniques are described in [2.3], [2.5], [2.6*a*], [2.6*b*], [2.6*c*], [2.6*d*] and electron microscopical techniques in [2.7], [2.8], [2.9]. Using stereometric methods and automatic instruments, it is now possible to give a quantitative description of the

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information



(*a*) (*b*)

Fig. 2.4. Distribution of the alloying elements within the framed area of fig. 2.3. (*a*) Al X-ray fluorescence, (*b*) Si X-ray fluorescence of the same area in the microscope. (G. Horn, Doduco, Pforzheim, Germany.) (945 ×).

microstructure [2.6*d*] (see section 3.3). Whereas the metallographic methods described up to now have made use of radiation reflected from a polished surface, the following technique requires thin films transparent to electrons.

2.2 Transmission electron microscopy (TEM)

At the present time, TEM represents one of the most important investigatory techniques in metallurgy. A thin film of metal (about 100 nm) is produced from a macroscopic specimen and then viewed in transmission in a normal electron microscope (using accelerating voltages $\leqslant$200 kV). Electron microscopes using even higher accelerating voltages (1 MV) are being used occasionally and these of course permit thicker foils to be observed. A well-established variation is the production of a *replica* of the metal surface for examination at high resolution in the electron microscope. In this technique the specimen is 'shadowed' by oblique deposition of a heavy metal to accentuate the contrast and then coated, usually with carbon, by deposition from the vapour phase. The film is peeled off the surface and placed on the specimen grid. The thickness variations in the shadowed film correspond to the surface relief of the specimen and the replica yields a three-dimensional image of the surface topography (extinction contrast, see section 2.2.1.1). Surface details greater than 2 nm can be rendered visible in this manner.

© Cambridge University Press www.cambridge.org

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

In the case of so-called *extraction replicas* the aim is to remove inclusions or small particles of a second hard phase with the replica, having previously loosened them by suitably etching the primary material (matrix). The particles, together with the replica, can then be observed in the transmission electron microscope with a view to determining their structure, size distribution, etc.

Much richer in contrast and more characteristic of the interior of the specimen is a thin film of the specimen itself. Thinning is carried out by a special technique, usually electrolytic polishing [2.7], [2.8]. At the tapered edges of a freshly formed perforation the metal film is thinner than 150 nm and thus transparent to electrons at normal accelerating voltages ($\leqslant$200 kV). Depending upon the microstructural features in their path, a proportion of these electrons reach the display screen by way of the magnifying ray path of the electron microscope. There they produce an intensity profile ('contrast'). The interpretation of this contrast in terms of the microstructure which gave rise to it is a science in its own right, which must be described in somewhat more detail in the following. In addition a normal *electron diffraction pattern* according to Bragg's law can be obtained from the specimen from which its crystal structure, orientation, etc., can be derived.

2.2.1 *Contrast theory*

2.2.1.1 Microscopically homogeneous specimen

The simplest case of contrast in the electron microscope arises on an amorphous layer which might consist of regions of different density (A, B, fig. 2.5). The electrons passing through B are more strongly scattered than those passing through A. Most of the scattered electrons are caught by the objective aperture. The intensity from A on the fluorescent screen of the electron microscope is thus greater than that from B. In the case of crystalline layers the scattering of the electrons is strongly anisotropic in accordance with Bragg's law ('diffraction'). The aperture angle of the electron microscope is so small ($\approx 10^{-2}$ radians at 100 kV) that in general none of the reflections (except those of the zeroth order) pass through the aperture (bright field case, fig. 2.6(*a*)). It is, however, possible to displace the aperture or tilt the primary beam I_0 so that only a particular reflection passes through the aperture (dark field case, fig. 2.6(*b*)). Only by using special imaging techniques can both the zero-order beam and the diffracted beam be made to pass together through the aperture and interfere to yield a true Abbé image (fig. 2.6(*c*)). Otherwise a 'contrast' is obtained with I or I_1 alone by virtue of the inhomogeneity of the specimen.

© Cambridge University Press

CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

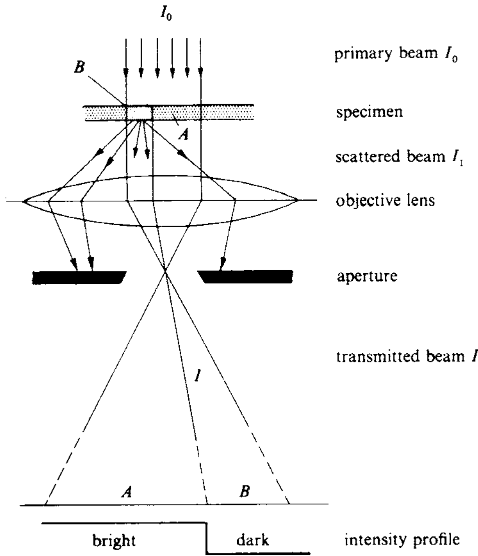


Fig. 2.5. Production of contrast in amorphous objects with regions *A*, *B* of differing density, after [2.8].

In the above cases only electrons which are scattered coherently are considered. There is also incoherent scattering at the nucleus and at the core electrons according to Rutherford. Its intensity (in the range of 'large' scattering angles, of the order of 100 mrad) is proportional to the atomic number squared and therefore provides information on the chemical composition of the irradiated column ('*Z*-contrast method', according to [2.32]).

The contrast can be calculated making the following assumptions [2.31].

(*a*) Only elastic scattering according to Bragg's law is taken into account.

(*b*) Only one transmitted and one diffracted beam are taken into account: $I_0 = I + I_1$ (two-beam case).

(*c*) Interaction between I and I_1 is neglected. This is justifiable for $I \gg I_1$; in this way the Bragg reflection itself is excluded from the discussion (kinematical theory).

(*d*) The 'image' is composed of intensities from all regions of the specimen which is therefore considered to be divided into columns $\Delta x \times \Delta y \times t$ (t = layer thickness, see figs. 2.9 and 2.10, below). The intensities of all columns with longitudinal axes in the z-direction are calculated independently.

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521559251 - Physical Metallurgy, Third Edition
Peter Haasen
Excerpt
More information

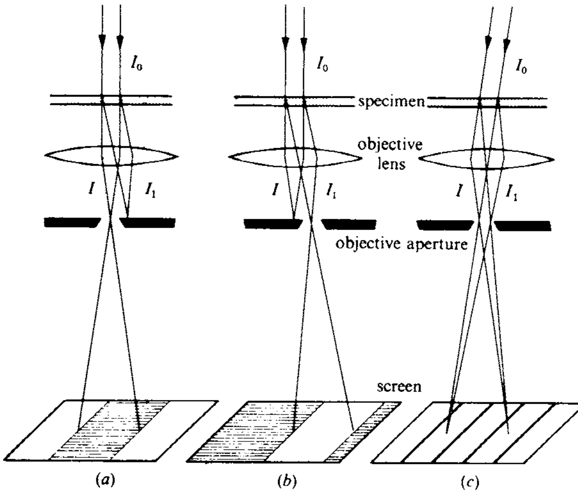


Fig. 2.6. Production of contrast in crystalline objects: (*a*) bright field contrast; (*b*) dark field contrast; (*c*) image produced by interference.

I_1 is calculated by summing the amplitudes in direction $\mathbf{k}$ of all secondary waves of the atoms (n) of one column (position vector $\mathbf{r}_n$)

$$A_1(\mathbf{k}) = \sum_n f_n \exp\{-2\pi i[(\mathbf{k} - \mathbf{k}_0)\mathbf{r}_n]\} \tag{2-1}$$

where f_n is the scattering amplitude of the individual atom proportional to its atomic form factor, $2\pi\mathbf{k}_0$ is the wave vector of the incident wave. In accordance with assumption (*c*) we must keep a finite distance $\mathbf{s}$ (corresponding to an angular difference $\Delta\theta > 0$) from the Bragg reflection itself, i.e. $\mathbf{k} - \mathbf{k}_0 = \mathbf{g} + \mathbf{s}$, where $\mathbf{g}$ is the reciprocal lattice vector of the lattice plane (hkl). If all the atoms are alike, i.e. $f_n = f$, and replacing the sum by an integral, then for lattice constant a we have

$$A_1(\mathbf{s}) = \left(\frac{f}{a}\right) \int_{-t/2}^{t/2} \exp[-2\pi i s_z \cdot z]\, dz = f\, \frac{\sin(\pi t s_z)}{\pi t s_z}\, \frac{t}{a}. \tag{2-2}$$

The scattered intensity $I_1 = A_1^2$ and the intensity of the zero-order beam complementary to it oscillate as a function of s_z and t. The s_z variation is realized in the case of a continuously bent layer; intensity bands are obtained as a function of position, so-called *bending contours*. If, however, the orientation, i.e. $\mathbf{s}$, is held constant and t is varied, e.g. in a tapered layer such as is present after electrolytic thinning, so-called *thickness contours* are obtained for I_1, fig. 2.7. The periodicity of the intensity due

© Cambridge University Press www.cambridge.org