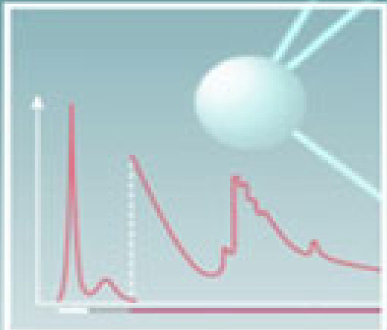
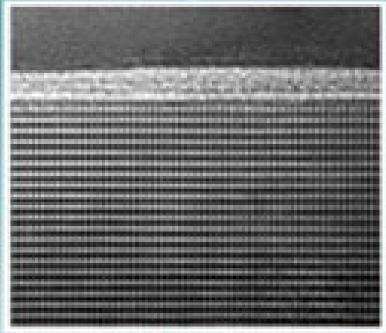
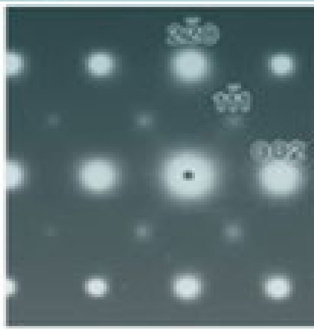
David Brandon and Wayne D. Kaplan

Microstructural Characterization of Materials







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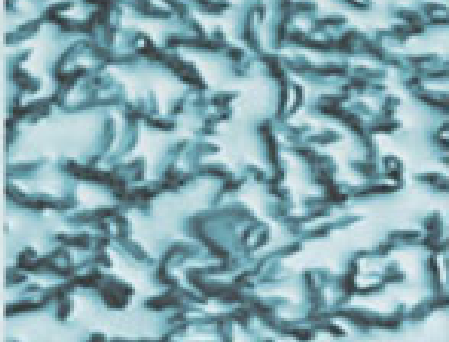

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Preface to the Second Edition

The last decade has seen several major changes in the armoury of tools that are routinely available to the materials scientist and engineer for microstructural characterization. Some of these changes reflect continuous technological improvements in the collection, processing and recording of image data. Several other innovations have been both dramatic and unexpected, not least in the rapid acceptance these tools have gained in both the research and industrial development communities.

The present text follows the guidelines laid down for the first edition, exploring the methodology of materials characterization under the three headings of *crystal structure, microstructural morphology* and *microanalysis*. One additional chapter has been added, on *Scanning Probe Microscopy*, a topic that, at the time that the first edition was written, was very much a subject for active research, but a long way from being commonly accessible in university and industrial laboratories. Today, *atomic force* and *scanning tunnelling microscopy* have found applications in fields as diverse as optronics and catalysis, friction and cosmetics.

It has proved necessary to split the chapter on *Electron Microscopy* into two chapters, one on *Transmission* techniques, and the other on *Scanning* methods. These two expanded chapters reflect the dramatic improvements in the resolution available for *lattice imaging* in transmission, and the revolution in sampling and micro-machining associated with the introduction of the *focused ion beam* in scanning technology.

The final chapter, on *Quantitative Analysis*, has also been expanded, to accommodate the rapid advances in three-dimensional reconstruction that now enable massive data sets to be assembled which include both chemical and crystallographic data embedded in a frame of reference given by microstructural morphology. Not least among the new innovations are *orientation imaging microscopy*, which allows the relative crystallographic orientations of the grains of a polycrystalline sample to be individually mapped, and *atom probe tomography*, in which the ions extracted from the surface of a sharp metallic needle are chemically identified and recorded in three dimensions. This last instrument is a long way from being widely available, but a number of laboratories do offer their services commercially, bringing three-dimensional analysis and characterization well below the nanometre range, surely the ultimate in microstructural characterization.

It only remains to note the greatest difference between the present text and its predecessor: digital recording methods have all but replaced photography in every application that we have considered, and we have therefore included sections on digital recording, processing and analysis. This 'digital revolution' has crept up on us slowly, following the on-going improvements in the storage capacity and processing speed for computer hardware and software. Today, massive amounts of digital image data can be handled rapidly and reliably.

At the same time, it is still up to the microscopist and the engineer to make the critical decisions associated with the selection of samples for characterization, the preparation of suitable sections and the choice of characterization methods. This task is just as difficult today as it always was in the past. Hopefully, this new text will help rather than confuse!

Most of the data in this book are taken from work conducted in collaboration with our colleagues and students at the Technion. We wish to thank the following for their contributions: David Seidman, Rik Brydson, Igor Levin, Moshe Eizenberg, Arnon Siegmann, Menachem Bamberger, Michael Silverstein, Yaron Kauffmann, Christina Scheu, Gerhard Dehm, Ming Wei, Ludmilla Shepelev, Michal Avinun, George Levi, Amir Avishai, Tzipi Cohen, Mike Lieberthal, Oren Aharon, Hila Sadan, Mor Baram, Lior Miller, Adi Karpel, Miri Drozdov, Gali Gluzer, Mike Lieberthal, and Thangadurai Paramasivam.

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W.D.K.

Preface to the First Edition

Most logical decisions rely on providing acceptable answers to precise questions, e.g. *what, why and how?* In the realm of scientific and technical investigation, the first question is typically *what is the problem* or *what is the objective?* This is then followed by a *why* question which attempts to pinpoint priorities, i.e. the urgency and importance of finding an acceptable answer. The third type of question, *how* is usually concerned with identifying means and methods, and the answers constitute an assessment of the available resources for resolving a problem or achieving an objective. The spectrum of problems arising in materials science and technology very often depends critically on providing adequate answers to these last two questions. The answers may take many forms, but when materials expertise is involved, they frequently include a need to characterize the *internal microstructure* of an engineering material.

This book is an introduction to the expertise involved in assessing the microstructure of engineering materials and to the experimental methods which are available for this purpose. For this text to be meaningful, the reader should understand why the investigation of the internal structure of an engineering material is of interest and appreciate why the microstructural features of the material are so often of critical engineering importance, This text is intended to provide a basic grasp of both the methodology and the means available for deriving qualitative and quantitative microstructural information from a suitable sample.

There are two ways of approaching *materials characterization*. The first of these is in terms of the engineering properties of materials, and reflects the need to know the physical, chemical and mechanical properties of the material before we can design an engineering system or manufacture its components. The second form of characterization is that which concerns us in this book, namely the *microstructural characterization* of the material. In specifying the internal microstructure of an engineering material we include the chemistry, the crystallography and the structural morphology, with the term materials characterization being commonly taken to mean just this specification.

Characterization in terms of the chemistry involves an identification of the chemical constituents of the material and an analysis of their relative abundance, that is a determination of the chemical composition and the distribution of the chemical elements within the material. In this present text, we consider methods which are available for investigating the chemistry on the microscopic scale, both within the bulk of the material and at the surface.

Crystallography is the study of atomic order in the crystal structure. A crystallographic analysis serves to identify the phases which are present in the structure, and to describe the atomic packing of the various chemical elements within these phases. Most phases are highly ordered, so that they are *crystalline* phases in which the atoms are packed together in a well-ordered, regularly repeated array. Many solid phases possess no such long-range order, and their structure is said to be *amorphous* or *glassy*. Several *quasicrystalline* phases have also been discovered in which classical long-range order is absent, but the material nevertheless possesses well-defined rotational symmetry.

The *microstructure* of the material also includes those *morphological* features which are revealed by a microscopic examination of a suitably prepared specimen sample. A study of the microstructure may take place on many levels, and will be affected by various parameters associated with specimen preparation and the operation of the microscope, as well as by the methods of data reduction used to interpret results. Nevertheless, *all* microstructural studies have some features in common. They provide an image of the internal structure of the material in which the image contrast depends upon the interaction between the specimen and some incident radiation used to probe the sample morphology. The image is usually magnified, so that the region of the specimen being studied is small compared with the size of the specimen. Care must be exercised in interpreting results as being ‘typical’ of the bulk material. While the specimen is a threedimensional object, the image is (with few exceptions) a two-dimensional projection. Even a qualitative interpretation of the image requires an understanding of the spatial relationship between the two-dimensional imaged features and the three-dimensional morphology of the bulk specimen.

Throughout this book we are concerned with the interpretation of the interaction between the probe and a sample prepared from a given material, and we limit the text to probes of X-rays, visible light or energetic electrons. In all cases, we include three stages of investigation, namely specimen preparation, image observation and recording, and the analysis and interpretation of recorded data. We will see that these three aspects of materials characterization interact: the microstructural morphology defines the phase boundaries, and the shape and dimensions of the grains or particles, the crystallography determines the phases present and the nature of the atomic packing within these phases, while the microchemistry correlates with both the crystallography of the phases and the microstructural morphology.

This text is intended to demonstrate the versatility and the limitations of the more important laboratory tools available for microstructural characterization. It is *not* a compendium of all of the possible methods, but rather a teaching outline of the most useful methods commonly found in student laboratories, university research departments and industrial development divisions.

Most of the data in this book are taken from work conducted in collaboration with our colleagues and students at the Technion. We wish to thank the following for their contributions: Moshe Eizenberg, Arnon Siegmann, Menachem Bamberger, Christina Scheu, Gerhard Dehm, Ming Wei, Ludmilla Shepelev, Michal Avinun, George Levi, Mike Lieberthal, and Oren Aharon.

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The Concept of Microstructure

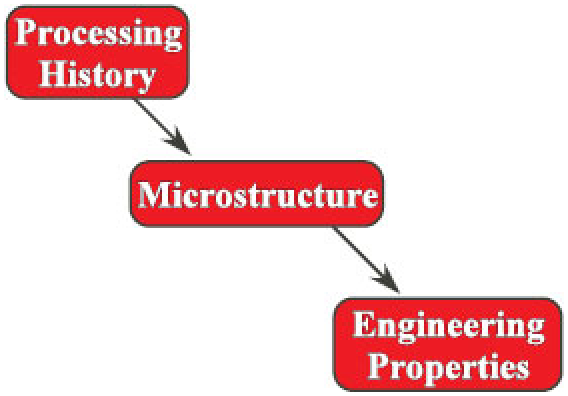
This text provides a basic introduction to the most commonly used methods of microstructural characterization. It is intended for students of science and engineering whose course requirements (or curiosity) lead them to explore beyond the accepted causal connection between the engineering properties of materials and their microstructural features, and prompt them to ask how the microstructures of diverse materials are characterized in the laboratory.

Most introductory textbooks for materials science and engineering emphasize that the processing route used to manufacture a component (shaping processes, thermal treatment, mechanical working, etc.) effectively determines the microstructural features (Figure 1.1). They note the interrelation between the microstructure and the chemical, physical, and/or mechanical properties of materials, developing expressions for the dependence of these properties on such microstructural concepts as *grain size* or *precipitate volume fraction*. What they do *not* usually do is to give details of either the methods used to identify microstructural features, or the analysis required to convert a microstructural observation into a parameter with some useful engineering significance.

This book covers three aspects of microstructural characterization (Table 1.1). First, the different crystallographic phases which are present in the sample are identified. Secondly, the morphology of these phases (their size, shape and spatial distribution) are characterized. Finally, the local chemical composition and variations in chemical composition are determined.

In all three cases we will explore the characterization of the microstructure at both the qualitative and the quantitative level. Thus, in terms of crystallography, we will be concerned not only with qualitative phase identification, but also with the elementary aspects of applied crystallography used to determine crystal structure, as well as with the quantitative determination of the volume fraction of each phase. As for the microstructure, we will introduce *stereological relationships* which are needed to convert a qualitative observation of morphological features, such as the individual grains seen in a cross-section, into a clearly defined microstructural parameter, the grain size. Similarly, we shall not be satisfied with the microanalytical identification of the chemical elements present in a specific microstructural feature, but rather we shall seek to determine the local chemical composition through microanalysis. Throughout the text we shall attempt to determine both the sensitivity of the methods described (the limits of detection) and their accuracy (the spatial or spectral resolution, or the concentration errors).

Figure 1.1 *The microstructure of an engineering material is a result of its chemical composition and processing history. The microstructure determines the chemical, physical and mechanical properties of the material, and hence limits its engineering performance.*



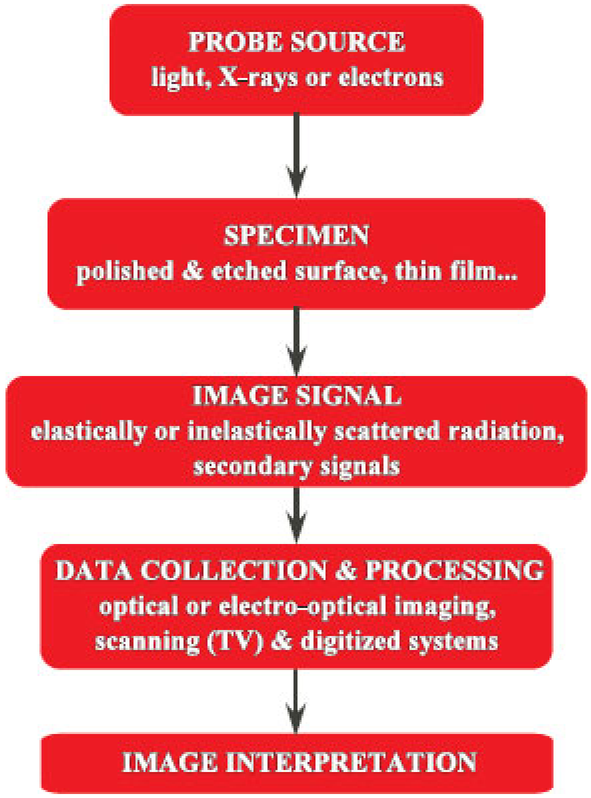
In general terms, microstructural characterization is achieved by allowing some form of probe to interact with a carefully prepared specimen sample. The most commonly used probes are visible light, X-ray radiation and a high energy electron beam. These three types of probe, taken in the same order, form the basis for optical microscopy, X-ray diffraction and electron microscopy. Once the probe has interacted with the sample, the scattered or excited signal is collected and processed into a form where it can be interpreted, either qualitatively or quantitatively. Thus, in microscopy, a two-dimensional image of the specimen is obtained, while in microanalysis a *spectrum* is collected in which the signal intensity is recorded as a function of either its energy or wavelength. In diffraction the signal may be displayed as either a diffraction pattern or a diffraction spectrum.

All the instrumentation that is used to characterize materials microstructure includes components that have five distinct functions (Figure 1.2). First, the probe is generated by a source that is filtered and collimated to provide a well-defined beam of known energy or wavelength. This probe beam then interacts with a prepared sample mounted on a suitable object stage. The signal generated by the interaction between the probe and the sample then passes through an optical system to reach the image plane, where the signal data are collected and stored. Finally, the stored data are read out, processed and recorded, either as a final image, or as diffraction data, or as a chemical record (for example, a composition map). The results then have to be interpreted!

Table 1.1 *On the qualitative level, microstructural characterization is concerned with the identification of the phases present, their morphology (size and shape), and the identification of the chemical constituents in each phase. At the quantitative level, it is possible to determine the atomic arrangements (applied crystallography), the spatial relationships between microstructural features (stereology), and the microchemical composition (microanalysis)*.

Qualitative analysis	Phase identification	Microstructural morphology	Microchemical identification
Quantitative analysis	Applied crystallography	Stereology	Microanalysis

Figure 1.2 *Microstructural characterization relies on the interaction of a material sample with a probe. The probe is usually visible light, X-rays or a beam of high energy electrons. The resultant signal must be collected and interpreted. If the signal is elastically scattered an image can be formed by an optical system. If the signal is inelastically scattered, or generated by secondary emission the image is formed by a scanning raster (as in a television monitor)*.



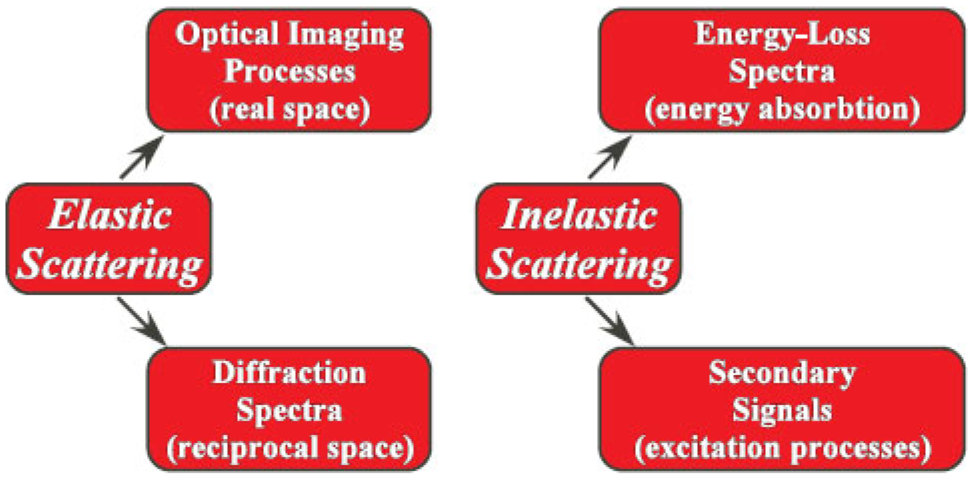
In all the methods of characterization which we shall discuss, two forms of interaction between the probe and the specimen occur (Figure 1.3):

1. *Elastic scattering*, which is responsible for the intensity peaks in X-ray diffraction spectra that are characteristic of the phases present and their orientation in the sample. Elastic scattering also leads to diffraction contrast in transmission electron microscopy (TEM), where it is directly related to the nature of the crystal lattice defects present in the sample (grain boundaries, dislocations and other microstructural features).

2. *Inelastic scattering*, in which the energy in the probe is degraded and partially converted into other forms of signal. In optical microscopy, microstructural features may be revealed because they partially absorb some wavelengths of the 'visible' light that illuminates the specimen. Gold and copper have a characteristic colour because they absorb some of the shorter wavelengths

(blue and green light) but reflect the longer wavelengths (red and yellow). The reflection is an *elastic* process while absorption is an *inelastic* process.

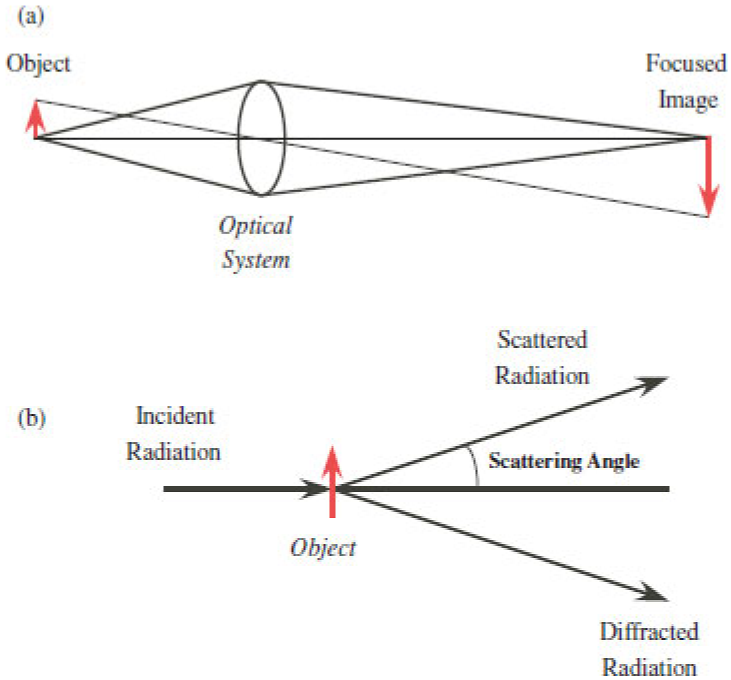
Figure 1.3 *An elastically scattered signal may be optically focused, to form an image in real space (the spatial distribution of microstructural features), or the scattering angles can be analysed from a diffraction pattern in reciprocal space (the angular distribution of the scattered signal). Inelastic scattering processes generate both an energy loss spectra, and secondary, excited signals, especially secondary electrons and characteristic X-rays*.



In electron microscopy, the high energy electrons interacting with a specimen often lose energy in well-defined increments. These *inelastic* energy losses are then characteristic of the electron energy levels of the atoms in the sample, and the *energy loss spectra* can be analysed to identify the chemical composition of a region of the sample beneath the electron beam (the 'probe'). Certain electron energy losses are accompanied by the emission of characteristic X-rays. These X-rays can also be analysed, by either energy dispersive or wavelength dispersive spectroscopy, to yield accurate information on the distribution of the chemical elements in the sample.

Elastic scattering processes are characteristic of optical or electro-optical systems which form an image in *real space* (the three dimensions in which we live), but elastic scattering is also a characteristic of diffraction phenomena, which are commonly analysed in *reciprocal space*. Reciprocal space is used to represent the scattering angles that we record in real space (see below). In real space we are primarily concerned with the size, shape and spatial distribution of the features observed, but in reciprocal space it is the angle through which the signal is scattered by the sample and the intensity of this signal that are significant. These angles are inversely related to the size or separation of the features responsible for the characteristic intensity peaks observed in diffraction. The elastically scattered signals collected in optical imaging and diffraction are compared in Figure 1.4. In optical imaging we study the *spatial* distribution of features in the image plane, while in a diffraction pattern or diffraction spectrum we study the *angular* distribution of the signal scattered from the sample.

Figure 1.4 *Schematic representations of an optical image (a) and a diffraction pattern (b). In the former distances in the image are directly proportional to distances in the object, and the constant of proportionality is equal to the magnification. In the latter the scattering angle for the diffracted radiation is inversely proportional to the scale of the features in the object, so that distances in a diffraction pattern are inversely proportional to the separation of features in the object.*



Inelastic scattering processes dominate the contrast in scanning electron imaging systems (as in a *scanning electron microscope*; Figure 1.5). In principle it is possible to detect either the loss spectra (the energy distribution in the original probe after it has interacted with the sample) or a secondary signal (the excited particles or photons generated by the probe as a result of inelastic interaction).

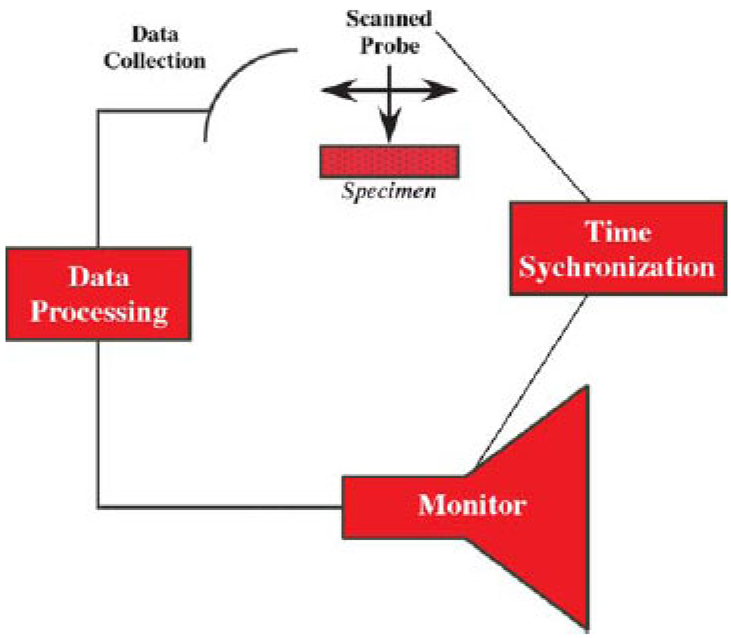
Large numbers of secondary electrons are emitted when an energetic electron beam strikes a solid sample. It is the detection of this secondary electron signal that makes possible the very striking high resolution images of surface features that are characteristic of scanning electron microscopy (SEM).

In what follows we will assume that the student is familiar with those aspects of microstructure and crystallography that are commonly included in introductory courses in materials science and engineering: some knowledge of the *Bravais lattices* and the concept of *crystal symmetry*; microstructural concepts associated with *polycrystals* and *polyphase materials* (including the significance of microstructural *inhomogeneity* and *anisotropy*); and, finally, the thermodynamic basis of *phase stability* and *phase equilibrium* in polyphase materials.

Throughout this book each chapter will conclude with results obtained from samples of three materials that are representative of a wide range of common engineering materials. We will explore the information that can be obtained for these materials from each of the methods of microstructural characterization that we discuss. The materials we have selected are:

- a low alloy steel containing approximately 0.4% C;
- a dense, glass-containing alumina;
- a thin-film microelectronic device based on the Al/TiN/Ti system.

Figure 1.5 *A scanning image is formed by scanning a focused probe over the specimen and collecting a data signal from the sample. The signal is processed and displayed on a fluorescent screen with the same time-base as that used to scan the probe. The magnification is the ratio of the monitor screen size to the amplitude of the probe scan on the specimen. The signal may be secondary electrons, characteristic X-rays, or a wide variety of other excitation phenomena*.



An engineering polymer or a structural composite could equally well have been selected for these examples. The principles of characterization would have been the same, even though the details of interpretation differed.

Our choice of the methods of microstructural characterization that we describe is as arbitrary as our selection of these 'typical' materials. Any number of methods of investigation are used to characterize the microstructure of engineering materials, but this text is not a compendium of all known techniques. Instead we have chosen to limit ourselves to those established methods that are commonly found in a well-equipped industrial development department or university teaching laboratory. The methods selected include *optical* and *electron microscopy* (both *scanning* and *transmission*), *X-ray* and *electron diffraction*, and the commoner techniques of *microanalysis* (energy dispersive and wavelength dispersive X-ray analysis, Auger electron spectroscopy, X-ray photospectroscopy and electron energy loss spectroscopy). We also discuss *surface probe microscopy* (SPM), including the *atomic force microscope* and the *scanning tunnelling microscope*, since one or more versions of this instrumentation are now commonly available. We also include a brief account of the remarkable chemical and spatial resolution that can be achieved by *atom probe tomography*, even though this equipment is certainly not commonly available at the time of writing.

In each case a serious attempt is made to describe the *physical principles* of the method, clarify the *experimental limitations*, and explore the extent to which each technique can be used to yield *quantitative* information

1.1 Microstructural Features

When sectioned, polished and suitably etched, nearly all engineering materials will be found to exhibit structural features that are characteristic of the material. These features may be visible to the unaided eye, or they may require a low-powered optical microscope to reveal the detail. The finest sub-structure will only be visible in the electron microscope. Many of the properties of engineering solids are directly and sensitively related to the microstructural features of the material. Such properties are said to be *structure sensitive*. In such cases, the study of microstructure can reveal a direct *causal relationship* between a particular microstructural feature and a specific physical, chemical or engineering property.

In what follows we shall explore some of these structure–property relationships and attempt to clarify further the meaning of the term *microstructure*.

1.1.1 Structure–Property Relationships

It is not enough to state that 'materials characterization is important', since it is usual to distinguish between those properties of a material that are *structure-sensitive* and those that are *structure-insensitive*. Examples of structure-insensitive properties are the *elastic constants*, which vary only slowly with composition or grain size. For example, there is little error involved in assuming that all steels have the same tensile (Young's) modulus, irrespective of their composition. In fact the variation in the elastic modulus of structural materials with temperature (typically less than 10 %) exceeds that associated with alloy chemistry, grain size or degree of cold work. The *thermal expansion coefficient* is another example of a property which is less affected by variations in microstructural morphology than it is by composition, temperature or pressure. The same is true of the *specific gravity* (or density) of a solid material.

In contrast, the *yield strength*, which is the stress that marks the onset of plastic flow in engineering alloys, is a sensitive function of several microstructural parameters: the *grain size* of the material, the *dislocation density*, and the distribution and *volume fraction* of second-phase particles. *Thermal conductivity* and *electrical resistivity* are also structure-sensitive properties, and *heat treating* an alloy may have a large affect on its thermal and electrical conductivity. This is often because both the thermal and the electrical conductivity are drastically reduced by the presence of alloying elements in solid solution in the matrix. Perhaps the most striking example of a structure-sensitive property is the *fracture toughness* of an engineering material, which measures the ability of a structural material to inhibit crack propagation and prevent catastrophic brittle failure. Very small changes in chemistry and highly localized grain boundary segregation (the migration of an impurity to the boundary, driven by a reduction in the boundary energy), may cause a catastrophic loss of ductility, reducing the fracture toughness by an order of magnitude. Although such segregation effects are indeed an example of extreme structure-sensitivity, they are also extremely difficult to detect, since the bulk impurity levels associated with segregation need only be of the order of 10^{-5} [10 parts per million (ppm)].

A classic example of a structure-sensitive property relation is the Petch equation, which relates an engineering property, the yield strength of a steel σ_y, to a microstructural feature, its grain size D, in terms of two material constants, σ_0 and k_y:

(1.1) $$\sigma_y = \sigma_0 + k_y D^{-1/2}$$

This relation presupposes that we are able to determine the grain size of the material quantitatively and unambiguously. The meaning of the term grain size, is explored in more detail in Section 1.1.3.1.

The fracture surfaces of engineering components that have failed in service, as well as those of standard specimens that have failed in a tensile, creep or mechanical fatigue test, are frequently subjected to microscopic examination in order to characterize the microstructural mechanisms responsible for the fracture (a procedure which is termed *fractography*). In *brittle*, polycrystalline samples much of the fracture path often lies along specific low-index crystallographic planes within the crystal lattices of the individual grains. Such fractures are said to be *transgranular* or *cleavage* failures. Since neighbouring grains have different orientations in space, the cleavage surfaces are forced to change direction at the grain boundaries. The line of intersection of the cleavage plane with the grain boundary in one grain is very unlikely to lie in an allowed cleavage plane within the second grain, so that cleavage failures in polycrystalline materials must either propagate on unfavourable crystal lattice planes, or else link up by *intergranular* grain boundary failure, which takes place at the grain boundaries between the cleavage cracks. A *fractographic* examination of the failure surface reveals the relative extent of intergranular and transgranular failure (Figure 1.6). By determining the three-dimensional nature of brittle crack propagation and its dependence on grain size or grain boundary chemistry we are able to explore critical aspects of the failure mechanism.

Ductile failures are also three-dimensional. A tensile crack in a ductile material typically propagates by the nucleation of small cavities in a region of hydrostatic tensile stress that is generated ahead of the crack tip. The nucleation sites are often small, hard inclusions, either within the grains or at the grain boundaries, and the distribution of the cavities depends on the spatial distribution of these nucleating sites. The cavities grow by plastic shear at the root of the crack, until they join up to form a cellular, ridged surface, termed a *dimpled* fracture (Figure 1.7). The complex topology of this dimpled, ductile failure may not be immediately obvious from a two-dimensional micrograph of the fracture surface, and in fractography it is common practice to image the failure twice, tilting the sample between the recording of the two images. This process is equivalent to viewing the surface from two different points of view, and allows a rough surface to be viewed and analysed stereoscopically, in threedimensions. The third dimension is deduced from the changes in horizontal displacement for any two points that lie at different heights with respect to the plane of the primary image, a phenomenon termed *parallax* (Figure 1.8, see Section 4.3.6.3). Our two eyes give us the same impression of depth when the brain superimposes the two views of the world which we receive from each eye separately.