

The electronic theory of metallic superconduction was established by Bardeen, Cooper and Schrieffer in 1957, but the basis of superconduction in the oxides remains a battleground for rival interpretations. The technology of the oxide ("high-temperature") superconductors is currently receiving a great deal of attention; the central problem is to make windable wires or tapes from an intensely brittle material. It is in no way a negative judgment on the importance and interest of these materials that they do not receive a detailed discussion here: it is simply that they do not lend themselves to a superficial account, and there is no space here for a discussion in the detail that they intrinsically deserve.

The intimate mix of basic and technological approaches to the study of high-temperature superconductors, indeed their inseparable nature, was analysed recently by a group of historians of science, led by the renowned scholar Gerald Holton (Holton *et al.* 1996). Holton *et al.* conclude that "historical study of cases of successful modern research has repeatedly shown that the interplay between initially unrelated basic knowledge, technology and products is so intense that, far from being separate and distinct, they are all portions of a single, tightly woven fabric." This paper belongs to a growing literature of analysis of the backgrounds to major technical advances (e.g., Suits and Bueche 1967, TRACES 1968). Holton's analysis is timely in view of the extreme difficulties of applying high-temperature superconductivity to practical tasks (see a group of papers introduced by Goyal 1995).

Just one specific technological aspect of high-temperature superconductors will be explained here. The superconduction in the copper oxide-based ceramics essentially takes place in one crystal plane, and if adjacent crystal grains in a polycrystal (and these materials are always used as polycrystals) are mutually misoriented by more than about  $10^\circ$  then superconduction is impeded to the extent that quite modest magnetic fields can quench superconductivity. It is thus necessary to find a way of constructing thin films in epitaxial orientation so that neighbouring grains are only very slightly misoriented. So, once again, grain boundaries are a key to behaviour. One approach which generates a fairly strong alignment of the crystal grains is 'paramagnetic annealing', solidification of the compound in the presence of a magnetic field (de Rango *et al.* 1991); but the misorientations do not seem to be sufficiently small for practical purposes.

Recent research by a large group of materials scientists at Oak Ridge National Laboratory in America (Goyal *et al.* 1999) has established a means of depositing a superconducting ceramic film with a strong preferred orientation, on a highly oriented alloy sheet made by heavy rolling followed by annealing, using an intermediate epitaxial oxide layer. This is typical of the sophisticated methods in materials processing that are coming to the fore today.

Superconductivity research has reached out to other branches of physics and materials science; perhaps the strangest example of this is a study by Keusin-Elbaum

*et al.* (1993) in which the current-carrying capacity of a mercury-bearing ceramic,  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  is greatly enhanced by using a beam of high-energy protons to provoke nuclear fission in some mercury atoms; the consequent radiation damage is responsible for the changes in superconducting behaviour. The authors imply that this might become a production process!

Ceramic superconduction is no longer limited to materials containing copper oxide. Some striking research in India (Nagarajan *et al.* 1994, Gupta 1999) has demonstrated superconduction in a family of alloys of the type RE-Ni-B-C, the quaternary borocarbides, where 'RE' denotes a rare-earth metal. They exhibit interplay of superconductivity and long-range magnetic order. The transition temperatures are not yet exciting but it is reassuring to know that a range of quite distinct ceramics can display superconduction.

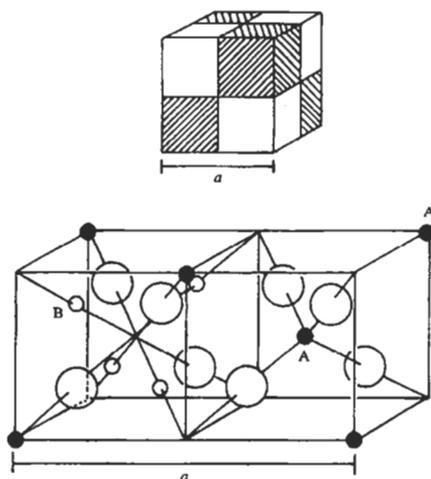
### 7.3. MAGNETIC CERAMICS

The research laboratory of Philips Gloeilampenfabrieken (incandescent lamp factories) in Eindhoven, Netherlands, is one of the glories of industrial science and engineering. A notable Dutch physicist, Hendrik Casimir (1909–2000), joined the company in 1942 after working with Bohr and Pauli, and has a chapter about the history of the company and laboratory in his book of memoirs (Casimir 1983). The company was founded by two Philips brothers, Gerard and Anton, and their father Frederick, in 1891. Shortly before World War I, Gerard, who had been deeply impressed by the research on lamps and tungsten filaments that he had witnessed at the new GE Research Laboratory in Schenectady, NY, resolved to open such a laboratory in Eindhoven. In early 1914, a young Dutch physicist, Gilles Holst, started work as the first research director, and remained until 1946, when Casimir and two others succeeded him as a triumvirate. Casimir's account of Holst's methods and principles is fascinating and is bound to intrigue anyone with a concern for industrial research. Holst "rarely gave his staff accurately defined tasks. He tried to make people enthusiastic about the things he was enthusiastic about – and usually succeeded". Neither did he "believe in strict hierarchic structure". Casimir goes further: he claims that Holst "steered a middle course between individualism and strict regimentation, based authority on real competence, but in case of doubt, preferred anarchy". Also, he did not subdivide the laboratory on disciplinary lines, but created multi-disciplinary teams. All this seems very similar to the principles applied to the GE Laboratory in its heyday.

This is by way of preliminary to an outline account of the genesis of the magnetic ferrites in the Philips Laboratory, before, during and just after World War II. The presiding spirit was Jacobus Louis Snoek (1902–1950), a Dutch physicist whom we

have already met in Section 5.1.1, in connection with the torsion pendulum for measuring internal friction which he invented in the late 1930s at Philips. Snoek was just the kind of scientist who would appeal to Holst – a highly original, self-motivated researcher. By 1934, Philips had already begun to diversify away from incandescent lamps, and Holst came to recognise that electromagnets and transformers with iron cores suffered from substantial losses from eddy currents. He reckoned that if it were possible to find an *electrically insulating* magnetic material to replace iron, it might become an extremely valuable industrial property. So Snoek was persuaded to have a look at magnetite (lodestone), the long-familiar oxide magnet, of composition  $\text{Fe}_3\text{O}_4$ . This mineral is better described as  $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$ ; 1/3 of the iron atoms are doubly ionised, 2/3 trebly. The initial plan was to look for other magnetic oxides of the form  $\text{Fe}_2\text{O}_3 \cdot \text{MeO}$ , where Me is another divalent metal. Cu, Zn, Co, Ni are a few of the Me's that were tried out. This was pursued energetically by Snoek from a physicist's standpoint and by his equally distinguished colleague E.J.W. Verwey from a chemist's perspective. The first of several papers by Snoek appeared soon after he began work (Snoek 1936). Snoek's life ended in a sad way. In 1950, he left Philips and the Netherlands, in search perhaps of a more prosperous lifestyle, or perhaps because he failed to secure the promotion he wished for at Philips (Verwey had become joint director of research). He joined an American consulting firm, but before the year was out, he died at the age of 48 in a car crash.

All these materials, which soon came to be named *ferrites* (no connection with the same word applied as a name for the body-centred allotrope of pure iron) share the spinel structure. Spinel is the type-name for  $\text{MgAl}_2\text{O}_4$ , and the crystal structure of that compound was first determined by Lawrence Bragg in 1915, a very early example of crystal structure determination. Figure 7.7 shows the structure. In the type structure, the divalent cations,  $\text{Mg}^{2+}$ , occupy the tetrahedral (A) sites, while the trivalent cations,  $\text{Al}^{3+}$ , occupy the octahedral (B) sites: this is the normal spinel structure. The oxygen atoms are slightly displaced from the body diagonals, to an extent depending upon the cation radii. Eventually, studying the crystal structures of the compounds made by Snoek, Verwey and Heilmann (1947) found that some of them had an 'inverse spinel structures; here, instead,  $\text{Fe}^{3+}$  occupies all the A sites while the B sites are occupied half by  $\text{Me}^{2+}$  and half by  $\text{Fe}^{3+}$ . There are also intermediate structures, and polymorphic changes are observed too: magnetite itself is distorted from a cubic form below 120 K. By years of painstaking study, Verwey established the subtle energetic rules that determined the way a particular ferrite crystallises; a clear, concise account of this can be found in Chapter 2 of a recent text (Valenzuela 1994). Snoek and Verwey also found a family of hexagonal ferrites, such as barium ferrite,  $\text{BaFe}_{12}\text{O}_{19}$  ( $\text{MeO} \cdot 6\text{Fe}_2\text{O}_3$ , generically).



**Figure 7.7.** The spinel structure. The unit cell can be divided into octants – tetrahedrally coordinated cations A, octahedrally coordinated cations B, and oxygen atoms (large circles) are shown in two octants only (adapted from Smit and Wijn 1959).

The inverse ferrites were found in general to have the most valuable soft magnetic properties (i.e., high permeability); as a family, Snoek called these *ferroxcube*. The hexagonal ferrites, barium ferrite in particular, (*hexaferrites*) were permanent magnets. The gradual development of these two families of ferrites owed everything to the intimate interplay of physical understanding and crystal chemistry. Snoek and Verwey were the joint progenitors of this extremely valuable family of materials.

Many of the ferrites (those which contain two distinct cations with magnetic moments) are *ferrimagnetic* – i.e., there are two populations of cations with oppositely directed but unequal magnetic moments, so that there is a macroscopically resultant magnetic moment. The understanding of this form of magnetism came after Snoek and Verwey had embarked on their study of ferrites, and was a byproduct of Louis Néel's extraordinary prediction, in 1936, of the existence of *antiferromagnetism*, where the two populations of opposed spins both involve the same numbers of the same species of ion so that there is *no* macroscopic resultant magnetisation (Néel 1936). (See also the background outlined in Section 3.3.3.) Néel (1904–2000), a major figure in the history of magnetism (Figure 7.8), recognised that under certain geometrical circumstances, neighboring ions could be so disposed that their magnetic spins line up antiparallel; his paper specifically mentioned manganese, which has no macroscopic magnetism but would have been expected to have shown this. Two years later, another French physicist duly discovered that MnO indeed has all the predicted characteristics of an antiferromagnet, and later the same thing was established for manganese itself.



Figure 7.8. L.E.F. Néel (photograph courtesy of Prof. Néel).

Soon after Verwey had shown that the magnetic spinels studied at Philips were in fact inverse spinels, Néel (1948) applied the ideas he had developed before the War for antiferromagnetism to these structures and demonstrated that the two kinds of cations should have antiparallel spins; he invented the term 'ferrimagnetism', and also recognised that at a certain temperature, analogous to a Curie temperature, both antiferromagnetism and ferrimagnetism would disappear. That temperature is now known as the Néel temperature. A little later, Shull *et al.* (1951) at Oak Ridge used the new technique of neutron diffraction, which is sensitive to magnetic spins, to confirm the presence of antiparallel spins in manganese. The recognition of ferrimagnetism had been achieved, and after that there was no holding back the extensive further development of this family of magnetic materials, both 'soft' and 'hard'. Holst's initial objective had been triumphantly achieved.

The intellectual stages baldly summarised here, and especially Néel's seminal role, are set out fully in an excellent historical treatment (Keith and Quédec 1992).

The many scientific and technological aspects of preparing, treating and understanding ferrites that are essential to their applications are treated in an early work by Smit and Wijn (1959) and the more recent one by Valenzuela (1994). An unusual book (Newnham 1975) treats a very wide range of functional materials (including magnetic materials) from the perspective of crystal chemistry, an approach which paid great dividends for the ferrites; it comes as close as any compilation to a complete overview of functional materials.

An early, striking use of a ferrite began in 1948, when a giant synchrotron was being designed at Brookhaven National Laboratory in America. The designers decided that the use of a metallic core for the electromagnets was impracticable because of the expected energy drain through hysteresis and eddy currents. One of the design team had heard of the brand new ferrites and invited Philips to tender; the shocking response was that Philips did not know how to make any pieces bigger than a matchbox. However, they determined to find out how to satisfy the Brookhaven team and began to supply large pieces in 1949. A recently published history of Brookhaven (Crease 1999) asserts with respect to ferrites that "the effort to make them in sufficiently large sizes at low cost opened the door for their use in many other kinds of devices", and that, when the synchrotron was finally completed in 1952, "it was the first important application of ferrite in the US".

Casimir, in his memoirs, mentions that the first Philips representative to visit Brookhaven gave the design team a set of guaranteed magnetic specifications which were too conservative, and Brookhaven was pleased to find that the material was better than they had been led to expect. Casimir reckons that Brookhaven must have concluded that Philips "was dumb but honest".

#### 7.4. COMPUTER MEMORIES

In his memoirs, Casimir gives an impressionistic account of the way random-access (RAM) memories were manufactured in the 1960s and early 1970s: "A factory of memory stores, for instance one run by North American Philips, always struck me as a remarkable outfit. On one side of the factory a better kind of rust and some equally mundane substances were ground, mixed, pressed into shape, and fired in large ovens... On the other side, ladies with manicured hands were threading coloured wires through little rings and weaving them into mats to the accompaniment of soft music - a kind of glorified kindergarten activity." He is referring here to magnetic core memories (Figure 7.9), an important early application of 'soft' ferrites. The composition chosen was one with a square hysteresis curve, so that the direction of

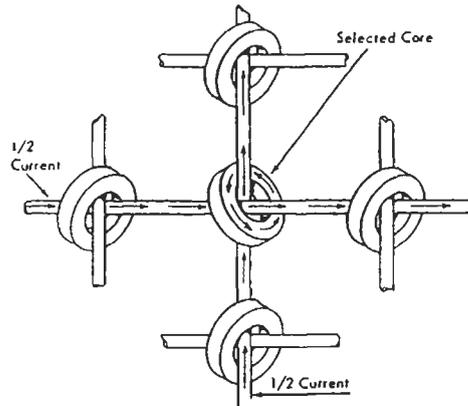


Figure 7.9. A small portion of a magnetic core memory (after *IBM News*, 1967).

magnetization could be reversed by applying a sharply defined critical magnetic field. A current flowing along a wire gives rise to a circular field around it; things were so arranged that a standard current flowing along one wire was insufficient to reverse magnetization in a ring, but if a similar current flows in the orthogonal wire as well, the joint effect of the two currents is enough to reverse the magnetization. Readout of the stored memory is destructive, requiring a rewrite operation for continued storage – which also applies to the semiconducting DRAM memories mentioned below.

According to a recent critical overview of memory design (Yeack-Scranton 1994), such core memories were cost-competitive in the 1960s, with access times of about  $1\ \mu\text{s}$  and a cost of about \$10,000 per megabyte. (Nowadays, a 48-megabyte semiconducting memory can be bought for less than \$100, more than 5000 times cheaper.) The complexity of the manual weaving operation was such that core memories were only made up to a few hundred bytes. It was at this time that “19” was left off the year in recording dates, to save a few bytes of expensive memory, and thus presaged the scare stories 30 years later about the expected ‘millennium bug’ resulting from the 1900–2000 transition.

Today, dynamic random-access memories (DRAMs) are transistor/capacitor-based semiconductor devices, with access times measured in nanoseconds and very low costs. Core memories were made of magnetic rings not less than a millimetre in diameter, so that a megabyte of memory would have occupied square metres, while a corresponding DRAM would occupy a few square millimetres. Another version of a DRAM is the read-only memory (ROM), essential for the operation of any computer, and unalterable from the day it is manufactured. We see that developments in magnetic memories involved dramatic reductions in cost and

volume as well as in cost – very much like the replacement of vacuum tubes, first by discrete transistors and eventually by integrated circuits.

Every computer needs a long-term memory store as well as an evanescent (RAM) store. Things have come a long way since punched paper tapes were used, before World War II. The history of magnetic recording during the past century is surveyed by Livingston (1998). The workhorse of longterm memory storage is the hard disc, in which a minute horseshoe electromagnet is made (by exploiting aerodynamic lift) to float just micrometres (now, a fraction of a micrometre) above a polished ferromagnetic thin film vacuum-deposited on a polished hard non-magnetic substrate such as an Al–Mg alloy, with a thin carbon surface layer to provide wear resistance in case the read/write head accidentally touches the surface. According to the above-mentioned overview, densities of 30 megabytes per  $\text{cm}^2$  were current in 1994, but increasing rapidly year by year, with (at that time) a cost of \$1/megabyte and data-writing rates of 9 megabytes per second. The first hard-disc drive was introduced by IBM in 1956... the RAMAC, or Random Access Method of Accounting and Control. It incorporated 50 aluminium discs 60 cm in diameter, and the device, capable of storing 5 million ‘characters’ (which today would occupy less than a square centimetre), weighed nearly a ton and occupied the same floor space as two modern refrigerators. This information comes from a survey of future trends in hard-disc design, (Toigo 2000); this article also claims that the magnetic coating of RAMAC was derived from the primer used to paint the Golden Gate Bridge in San Francisco.

One that ‘got away’ was the magnetic bubble memory, also described by Yeack-Scranton in 1994. A magnetic bubble is a self-contained, cylindrical magnetic domain polarised in direction opposite to the magnetization of the surrounding thin magnetic film, typically a rare-earth iron garnet deposited on a nonmagnetic substrate. Information is stored by creating and moving strings of such bubbles, each about a micrometre across, accessed by means of a magnetic sensor. This very ingenious and unconventional approach received a great deal of research attention for several years in the 1970s; it was popular for a time for such devices as handheld calculators, but in the end the achievable information density and speed of operation were insufficiently attractive. In the field of magnetic memories, competition is red in tooth and claw.

The most recent development in purely magnetic memories exploits so-called giant magnetoresistance. This phenomenon is one of a range of properties of magnetic ultrathin films. Néel, with his usual uncanny perception, foretold in 1954 that in very thin films (1–2 nm thick) the magnetization may be normal to the film, attributed in a way still not wholly understood to the reduced symmetry of surface atoms. The next stage was the study of multilayer thin films, with magnetic and nonmagnetic materials alternating (e.g., Co/Cu or Dy/Y), each layer of the order of

a very few nanometers in thickness. It turned out that if the thicknesses were just right, such multilayers could be antiferromagnetic. This was first observed as recently as 1986 (Grunberg *et al.*) and the origin of this curious anomalous magnetic coupling is still under debate. These researches are linked to others in which ultrathin multilayers such as Co/Cu or Fe/Cr were shown to have very large changes of electrical resistance when subjected to a magnetic field normal to the film (e.g., Baibich *et al.* 1988). This phenomenon is being increasingly exploited as an alternative means of storing information in computers; the key is that a readily measurable resistance change happens in small fields of an oerstedt or so, and some multilayer systems are approaching 3% change of resistance for 1 oerstedt of applied field. In such systems, information storage density can be significantly enhanced. These various developments based on ultrathin films and multilayers are explained with great clarity and economy in a review by Howson (1994). Another form altogether of magnetoresistance (sometimes called 'colossal' to distinguish it from the merely 'giant') is found in bulk orthomanganite compounds; these are discussed in Chapter 11. A recent overview (Simonds 1995) analyses computer hard-disc memories, including notably those based on magnetoresistance, in terms of storage density and the linkage of that to the ever-reducing spacing between disc and reading head.

Yet further approaches to computer memories are optical and magneto-optical recording. There is space here only to summarise the great range of developments here. Pure optical recording is used in the production of the various kinds of compact discs; these are not used for computer memories but for recording text, music and videos, mostly on a read-only basis. Strings of grooves and dips are 'burned' into a plastic surface, using semiconductor lasers to achieve the ultrafine focusing of light required to cram information into closely adjacent channels (Burke 1995). The materials used and the elaborate error-correcting codes that have been developed are described by Burke.

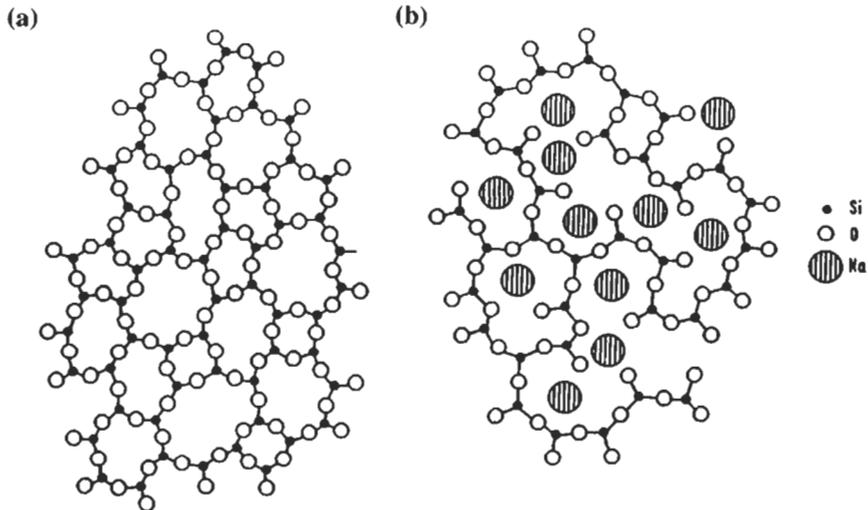
Magneto-optical recording depends on the Kerr effect, the rotation of the plane of polarisation of plane-polarised light when it is reflected from a magnetised surface, in a sense which depends on the type of magnetization. By use of highly selective analysers, the presence or absence of a bit of information can be detected. The kind of 'rewritable' system that is now in extensive use depends on phase changes: in outline, one laser beam heats the material (typically, a rare earth metal/transition metal alloy) above a critical temperature and remanent magnetization is achieved by an applied field as the spot cools; that magnetization is then read by a much weaker laser beam. If the memory is to be erased, a laser beam of suitable strength is used to restore the film to its pristine state. So, light is used both to 'print' the information and then to detect it and eventually to remove it, and magnetism is the form the memory takes (Buschow 1989, Burke 1995).

The foregoing paragraphs make it clear why the making and characterizing of films with thickness of the order of a nanometre (only 4–5 atoms thick) has become a major research field in its own right in recent decades. Molecular beam epitaxy, which we met earlier in this chapter, is one common technique.

## 7.5. OPTICAL GLASS

One of my most cherished possessions is a Leica camera, and what I like best about it is the superb quality of the lenses and of their combination into objectives. Such quality depends on several factors: the choice of glass compositions; rigorous uniformity of composition and freedom from internal stress; design of the objectives – the province of geometrical optics; precision of lens grinding, polishing and positioning.

Camera lenses, and a huge range of other optical components, are made of oxide glasses, which are also the basis of laboratory glassware, windows and containers of many kinds. Almost all practical glasses are mixes of different oxides, notably  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{BaO}$ , of which silica is crucial. When a suitable mixture of oxides is cooled in a crucible, even quite slowly, it fails to crystallise and on reheating, the solid gradually softens, without a well-defined melting temperature such as is characteristic of crystals. Curiosity about the internal structure of glasses as a category goes back a long way, but it was not until W.H. Zachariasen (an eminent Norwegian/American crystallographer whom we met in Section 3.2.4) addressed the problem that light was cast on it. In 1932 he published a renowned paper, still frequently cited today (Zachariasen 1932), about the structure of simple oxide glasses. Figure 7.10(a) shows (in two dimensions) his proposed model for a hypothetical pure  $\text{A}_2\text{O}_3$  glass, a glass-former, while Figure 7.10(b), based on Zachariasen's further work (much of it joint with B.E. Warren), shows a model for a sodium silicate glass.  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ , for example, are glass-formers, while  $\text{Na}_2\text{O}$  is not; but when  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  are mixed, a glass with better properties results. In an excellent overview of the formation and properties of oxide glasses, Rawson (1991) points out that Zachariasen's first paper "is remarkable in that it is entirely speculative and qualitative – no new observations were reported". The experiments followed in the subsequent papers. The central hypothesis of Zachariasen's paper is that the vitreous (glassy) form of an oxide should not have a significantly higher internal energy than the crystalline form, and this required that both forms must contain the same kind of oxygen polyhedra that Lawrence Bragg had already determined in crystalline silicates. His central hypothesis led him to corollaries for a pure glass-former, such as that no oxygen must be linked to more than two A atoms, the oxygen polyhedra share corners with each other but not edges or faces, and each



**Figure 7.10.** (a) Zachariassen's two-dimensional model of an  $A_2O_3$  glass, after Zachariassen (1932).  
 (b) Two-dimensional representation of a sodium silicate glass.

polyhedron must share at least three corners. In Figure 7.10(b), where a *glass-modifier* has been added to a *glass-former*, more oxygen become 'non-bridging', the viscosity goes down accordingly and other properties change too. Later experimental work by X-ray scattering, much of it involving Warren and his pupils at MIT, confirmed in detail the correctness of Zachariassen's model and generated statistical information about, for instance, the distribution of O–A–O angles. The gradual softening process of a glass when heated is characterised by a *glass transition temperature*, a temperature at which the glass viscosity falls to a critical level. The precise nature of the glass transition has led to much research and a huge journal literature; one of the key features of this transition is that a long anneal just below it slowly densifies the glass and also rids it of internal stresses. Annealing of optical glass is therefore a key part of the production of high-quality optical components.

Optical glasses, mostly oxide glasses, constitute a crucial class of materials. Their most important physical properties, apart from high transparency at all or most visible wavelengths, are the refractive index and the dispersion, the latter being the degree of variation of the refractive index with change of light wavelength. Another important property of all glasses, rarely spelled out explicitly, is their isotropy; the refractive index does not vary with direction of propagation, unlike many kinds of transparent crystals or polycrystals. These aspects are reviewed very clearly in an overview of optical glasses (Weber 1991). An important feature of glasses is that the refractive index and dispersion of glasses can be expressed by simple additive

relationships involving just the percentages of different constituents (Huggins and Sun 1943); this makes glass design for optical purposes relatively straightforward. These properties are *not structure-sensitive*, although they do of course depend on density and are thus slightly affected by annealing.

At this point, a brief aside about the concept of 'structure-sensitivity' is in order. A German physicist, Adolf Smekal, in 1933, first divided properties into those that depend on the 'structure' – meaning crystal structure, grain structure and crystal defects of all kinds – and those that depend merely on composition. Plastic mechanical properties are prime instances of structure-sensitivity; physical properties such as thermal expansion, specific heat, elastic moduli, electron energy band gap, refractive index, dispersion are among those which are not structure-sensitive. Photoelastic properties (the induced birefringence of glass when stressed, used to measure stress distributions by optical means) are again not structure-sensitive. This concept of Smekal's has found resonance in the materials science community ever since; its thorough recognition has accompanied the conversion of physicists from their original aloofness towards all aspects of solids to their present intense involvement with solids.

Most glasses have dispersions which follow a standard relation with change of wavelength. Some glasses have anomalous dispersion, and these are useful for the design of highly colour-corrected lens sets, so-called apochromatic objectives.

There are also a range of other optical properties which cannot be discussed in detail here, for instance, non-linear optical properties... polarisation not proportional to applied electric field. These properties include 'photoinduced nonlinearities': if a standing wave is induced in an optical fibre by a laser beam, it can lead to a permanent modulation of the refractive index, so that a photo-induced diffraction grating is thereby created. (The first report of photorefractive behaviour was in a crystal,  $\text{LiNbO}_3$ , by Ashkin *et al.* 1966.) This kind of advanced optical engineering of materials has become a large field of expertise in recent decades; it involves both glasses and crystals, and is driven by the objective of manipulating optical signals in telecommunications without the need to keep changing from optical to electronic media.

A concise survey of where the broad domain of optical information processing had got to a few years ago is in a book issued by the European Commission (Kotte *et al.* 1989), while a good overview of non-linear optical materials is by Bloor (1994).

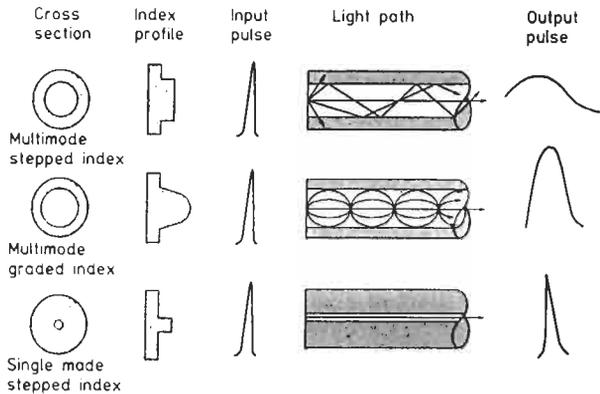
### 7.5.1 Optical fibres

One of the most spectacular modern developments in materials has been the design, improvement and exploitation of fine glass fibres for purposes of large-scale communication. Messages, above all telephone conversations, but also TV signals

and e-mail transmissions, are now converted into trains of optical pulses and sent along specially designed fibres, to be reconverted into electrical signals at the far end; hundreds of thousands of distinct messages can be sent along the same fibre, because the frequency of light is so high and the 'bandwidth' which decides the frequency range needed by one message becomes tiny compared to the available frequency when light is used, as distinct from microwaves which were standard vectors previously.

The fact that a glass fibre can 'capture' light and transport it over distances of a few meters – by repeated total internal reflection at the surface of the fibre – was known to French physicists in the 19th century, as is described in a fine popular book by Hecht (1999). In the 20th century, the various primary problems, such as leakage of light where adjacent fibres touch each other, had been solved, and bundles of fibres were applied to surgical instruments such as gastroscopes to examine defects in the stomach wall, and to face-plates to transport complex images over very short distances. The idea of using fibres for long-distance telecommunication was conceived and fostered in 1964–1966 by an imaginative and resolute Chinese immigrant to Britain, Charles K. Kao (b. 1933). He worked for Standard Telephone Laboratories in the east of England, a company which in the early 1960s concluded that none of the communications media used hitherto, up to and including millimetric microwaves, were capable of giving sufficient message capacity, and Kao's manager reluctantly concluded that "the only thing left is optical fibres", as reported in the careful historical account in Hecht's book. The reluctance stemmed from the daunting manufacturing tolerances required. When his manager was tempted away to a chair in Australia in 1964, pursuing this pipedream was left in the hands of Kao. There were two central problems: one was the need to arrange for a core and coating layer in the fibre, since uncoated fibres lost too much light at the imperfect surface; the other problem was absorption of light in the fibre, which in 1964 meant that in the best fibres, after 20 m, only 1% of the original light intensity remained.

Figure 7.11 shows the ways in which the first problem could be tackled – multimode and single mode transmission of light. In multimode transmission, the light follows many paths, in single mode transmission, there is only a single path. The main problem with multimode transmission is the gradual spreading-out of a sharp pulse; this can be ameliorated but not entirely cured by replacing the outer coating of low-refractive glass with a stepped layer of gradually changing refractive index. The difficulty with single-mode fibre is that the highly refractive core must have a diameter of the order of the light wavelength, around one micrometre, and this is technologically extremely difficult to achieve. Kao also began to study the theory of light absorption, and concluded that the only way to improve transparency in a dramatic way was to aim for purity. He and his assistant Hockham also looked



**Figure 7.11.** Optical fibres, showing light trajectories for different refractive index profiles (after MacChesney and DiGiovanni 1991).

at the communications theory in depth, and then Kao and Hockham (1966) published a very detailed study of a future light-optic communication channel, assuming that the practicalities of fibre design and manufacture could be solved. The paper attracted worldwide attention and brought others into the hunt, which had been Kao's objective. Many companies now became active, but many quickly became discouraged by the technical difficulties and dropped the research. Kao remained focused, and in the end his determination and collaboration with others brought success. A consequence was that the practical demonstration of optical communication was achieved by Kao's company and their close collaborators, the British Post Office. The chronological steps in this fascinating history are carefully set out by Hecht.

Kao can best be described as a 'product champion': various studies of the innovation process in industry have demonstrated the central importance of the product champion in driving a difficult innovation to the point of success. Many years ago (Cahn 1970) I published an analysis of the kinds of case history of innovations from which this conclusion eventually emerged in the 1970s. Kao would have been the perfect exemplar in this analysis, but he was still striving to convince the doubters when I wrote that paper.

Attempts by Kao and others to enhance transparency by chemically removing impurities from glass met with little success: the level of purity required was indeed comparable with that needed in silicon for integrated circuits. In the event, the required purification was achieved in the same way in which semiconductor-grade silicon is now manufactured, by going through the gas phase (silicon tetrachloride), which can be separated from the halides of impurity species because of differences in vapour pressures. This breakthrough was achieved by R.D. Maurer and his

collaborators at the Corning Glass Company in New York State; that company's research laboratory was the world leader in glass research. The stages are set out in detail in Hecht's book, but the crucial invention was to start with a glass tube with a high refractive index and to deposit a soot of silica on the inner surface from the gas vector; thereupon the treated tube was drawn out into a fine fibre. To get the right refractive index, combined with mechanical toughness, the key was to codeposit some germania by mixing pure germanium tetrachloride with the silicon tetrachloride. This fibre bettered Kao's declared objective of 20 decibels attenuation per kilometre, i.e., 1% of the original intensity remained. The tube/soot approach also allowed excellent single-mode fibres with stepped coatings to be made. The detailed techniques involved are well set out by two Bell Labs scientists (MacChesney and DiGiovanni 1991). Today, after many changes of heart, single-mode fibres carry the bulk of optical messages, and transparency has been improved to better than 1 decibel per km at the preferred wavelength 'windows', 1.33 and 1.55  $\mu\text{m}$  wavelength.

Efforts to improve the transparency of glass fibres even further are still continuing. In a very recent study (Thomas *et al.* 2000), the role of water – or, more specifically, the light-absorbent  $\text{OH}^-$  ion – in reducing the transparency of silica glass from the theoretical limit of about 0.2 decibel per km at 1.55  $\mu\text{m}$  wavelength was examined. Water enters the glass through the use of a hydrogen/oxygen torch and this study measured the diffusion rate of water into the fibre; it turns out that the transparency is a function of radial position in the fibre, matching the decrease of  $\text{OH}^-$  ion concentration towards the centre line. This study indicates that further improvement in transparency should result from an abandonment of the hydrogen/oxygen torch.

Four other issues required to be addressed before optical communications could reach their destined perfection: a light source; a means of modulating light intensity in synchrony with an electrical signal, in the form of pulse modulation, was needed; a convenient form of amplification of the light intensity, repeaters in effect, was needed for long-distance signals through transatlantic cables and the like; and a reliable detector was needed to reconvert light into electronic signals. There is no space to go into details here: suffice it to say that heterostructured semiconductor lasers are the preferred light source, and after years of trouble with instabilities they are now reliable; there is a surfeit of possible modulators and detectors depending on magneto-optic, acousto-optic and other approaches (Nishizawa and Minikata 1996); light amplification has become possible by laser excitation of a length of fibre doped with erbium, as independently discovered in Southampton and Bell Labs in 1987. The engineering practicalities of the circuits have become extremely complex and expensive, because if millions of channels are to be passed along a single fibre with a micrometer-sized core, multiple wavelengths have to be used which requires rapidly

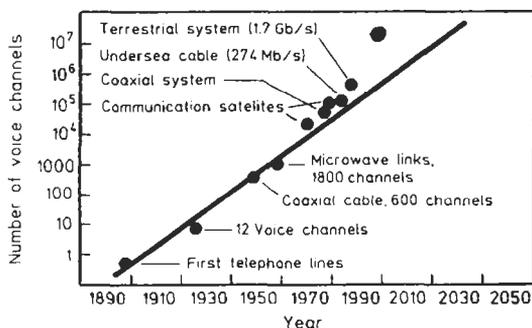
tunable lasers and elaborate detectors. As Figure 7.12 shows, this level of 'multiplexing' channels had become possible by 1995.

Not only the number of messages that can pass along one fibre, but also the speed of transmission, has increased steadily over the past two decades; according to Sato (2000), in Japan this speed has increased by about an order of magnitude per decade, as a consequence of improved fibres and lasers and also improved networking hardware.

## 7.6. LIQUID CRYSTALS

One is inclined to think of "materials" as being solids; when editing an encyclopedia of materials some years ago, I found it required an effort of imagination to include articles on various aspects of water, and on inks. Yet one of the most important families of materials in the general area of consumer electronics are liquid crystals, used in inexpensive displays, for instance in digital watches and calculators. They have a fascinating history as well as deep physics.

Liquid crystals come in several varieties: for the sake of simplified illustration, one can describe them as collections of long molecules tending statistically to lie along a specific direction; there are three types, nematic, cholesteric and smectic, with an increasing measure of order in that sequence, and the variation of degree of alignment as the temperature changes is akin to the behaviour of spins in ferromagnets or of atomic order in certain alloys. The definite history of these curious materials goes back to 1888, when a botanist-cum-chemist, Friedrich Reinitzer, sent some cholesteric esters to a 'molecular physicist', Otto Lehmann.



**Figure 7.12.** Chronology of message capacity showing exponential increase with time. The number of voice channels transmitted per fibre increases rapidly with frequency of the signalling medium.

The three right-hand side points refer to optical-fibre transmission (after MacChesney and DiGiovanni 1991, with added point).

They can be considered the joint progenitors of liquid crystals. Reinitzer's compounds showed two distinct melting-temperatures, about 30° apart. Much puzzlement ensued at a time when the nature of crystalline structure was quite unknown, but Lehmann (who was a single-minded microscopist) and others examined the appearance of the curious phase between the two melting-points, in electric fields and in polarised light. Lehmann concluded that the phase was a form of very soft crystal, or 'flowing crystal'. He was the first to map the curious defect structures (features called 'disclination' today). Thereupon the famous solid-state chemist, Gustav Tammann, came on the scene. He was an old-style authoritarian and, once established in a prime chair in Göttingen, he refused absolutely to accept the identification of "flowing crystals" as a novel kind of phase, in spite of the publication by Lehmann in 1904 of a comprehensive book on what was known about them. Ferocious arguments continued for years, as recounted in two instructive historical articles by Kelker (1973, 1988). Lehmann, always eccentric and solitary, became more so and devoted his last 20 years to a series of papers on Liquid Crystals and the Theories of Life.

During the first half of this century, progress was mostly made by chemists, who discovered ever new types of liquid crystals. Then the physicists, and particularly theoreticians, became involved and understanding of the structure and properties of liquid crystals advanced rapidly. The principal early input from a physicist came from a French crystallographer, Georges Friedel, grandfather of the Jacques Friedel who is a current luminary of French solid-state physics. It was Georges Friedel who invented the nomenclature, nematic, cholesteric and smectic, mentioned above; as Jacques Friedel recounts in his autobiography (Friedel 1994), family tradition has it that this nomenclature "was concocted during an afternoon of relaxation with his daughters, especially Marie who was a fine Hellenist." Friedel grandpère recognised that the low viscosity of liquid crystals allowed them readily to change their equilibrium state when external conditions were altered, for instance an electric field, and he may thus be regarded as the direct ancestor of the current technological uses of these materials. According to his grandson, Georges Friedel's 1922 survey of liquid crystals (Friedel 1922) is still frequently cited nowadays. The very detailed present understanding of the defect structure and statistical mechanics of liquid crystals is encapsulated in two very recently published second editions of classic books, by de Gennes and Prost (1993) in Paris and by Chandrasekhar (1992) in Bangalore, India. (Chandrasekhar and his colleagues also discovered a new family of liquid crystals with disc-shaped molecules.)

Liquid crystal displays depend upon the reorientation of the 'director', the defining alignment vector of a population of liquid crystalline molecules, by a localised applied electric field between two glass plates, which changes the way in which incident light is reflected; directional rubbing of the glass surface imparts a

directional memory to the glass and thence to the encapsulated liquid crystal. To apply the field, one uses transparent ceramic conductors, typically tin oxide, of the type mentioned above. Such applications, which are numerous and varied, have been treated in a book series (Bahadur 1991). The complex fundamentals of liquid crystals, including the different chemical types, are treated in the first volume of a handbook series (Demus *et al.* 1998). The linkage between the physics and the technology of liquid crystals is explained in very accessible way by Sluckin (2000). A particularly useful collection of articles covering both chemistry and physics of liquid crystals as well as their uses is to be found in the proceedings of a Royal Society Discussion (Hilsum and Raynes 1983). A more popular treatment of liquid crystals is by Collins (1990).

It is perhaps not too fanciful to compare the stormy history of liquid crystals to that of colour centres in ionic crystals: resolute empiricism followed by fierce strife between rival theoretical schools, until at last a systematic theoretical approach led to understanding and then to widespread practical application. In neither of these domains would it be true to say that the empirical approach sufficed to generate practical uses; such uses in fact had to await the advent of good theory.

## 7.7. XEROGRAPHY

In industrial terms, perhaps the most successful of the many innovations that belong in this Section is xerography or photocopying of documents, together with its offspring, laser-printing the output of computers. This has been reviewed in historical terms by Mort (1994). He explains that “in the early 1930s, image production using electrostatically charged insulators to attract frictionally charged powders had already been demonstrated.” According to a book on physics in Budapest (Radnai and Kunfalvi 1988), this earliest precursor of modern xerography was in fact due to a Hungarian physicist named Pal Selenyi (1884–1954), who between the Wars was working in the Tungsram laboratories in Budapest, but apparently the same Zworykin who has already featured in Section 7.2.2, presumably during a visit to Budapest, dissuaded the management from pursuing this invention; apparently he also pooh-poohed a (subsequently successful) electron multiplier invented by another Hungarian physicist, Zoltan Bay (who died recently). If the book is to be believed, Zworykin must have been an early exponent of the “not invented here” syndrome of industrial scepticism.

Returning to Mort’s survey, we learn that the first widely recognised version of xerography was demonstrated by an American physicist, Chester Carlson, in 1938; it was based on amorphous sulphur as the photosensitive receptor and lycopodium powder. It took Carlson 6 years to raise \$3000 of industrial support, and at last,

in 1948, a photocopier based on amorphous selenium was announced and took consumers by storm; the market proved to be enormously greater than predicted! Later, selenium was replaced by more reliable synthetic amorphous polymeric films; here we have another major industrial application of amorphous (glassy) materials. Mort recounts the substantial part played by John Bardeen, as consultant and as company director, in fostering the early development of practical xerography. A detailed account of the engineering practicalities underlying xerographic photocopying is by Hays (1998). It seems that Carlson was severely arthritic and found manual copying of texts almost impossible; one is reminded of the fact that Alexander Graham Bell, the originator of the telephone, was professionally involved with hard-of-hearing people. Every successful innovator needs some personal driving force to keep his nose to the grindstone.

There was an even earlier prefiguration of xerography than Selenyi's. The man responsible was Georg Christoph Lichtenberg, a polymath (1742–1799), the first German professor of experimental physics (in Göttingen) and a name to conjure with in his native Germany. (Memoirs have been written by Bilaniuk 1970–1980 and by Brix 1985.) Among his many achievements, Lichtenberg studied electrostatic breakdown configurations, still today called 'Lichtenberg figures', and he showed in 1777 that an optically induced pattern of clinging dust particles on an insulator surface could be repeatedly reconfigured after wiping the dust off. Carlson is reported as asserting: "Georg Christoph Lichtenberg, professor of physics at Göttingen University and an avid electrical experimenter, discovered the first electrostatic recording process, by which he produced the so-called 'Lichtenberg figures' which still bear his name." Lichtenberg was also a renowned aphorist; one of his sayings was that anyone who understands nothing but chemistry cannot even understand chemistry properly (it is noteworthy that he chose not to use his own science as an example). His aphorism is reminiscent of a *New Yorker* cartoon of the 1970s in which a sad metallurgist tells his cocktail party partner: "I've learned a lot in my sixty years, but unfortunately almost all of it is about aluminum".

Just as the growth of xerographic copying and laser-printing, which derives from xerography, was a physicists' triumph, the development of fax machines was driven by chemistry, in the development of modern heat-sensitive papers most of which have been perfected in Japan.

## 7.8. ENVOI

The many and varied developments treated in this chapter, which themselves only scratch the surface of their theme, bear witness to the central role of functional materials in modern MSE. There are those who regard structural (load-bearing)

materials as outdated and their scientific study as of little account. As they sit in their load-bearing seats on a lightweight load-bearing floor, in an aeroplane supported on load-bearing wings and propelled by load-bearing turbine blades, they can type their critiques on the mechanical keyboard of a functional computer. All-or-nothing perceptions do not help to gain a valid perspective on modern MSE. What is undoubtedly true, however, is that functional materials and their applications are a development of the postwar decades: most of the numerous references for this chapter date from the last 40 years. It is very probable that the balance of investment and attention in MSE will continue to shift progressively from structural to functional materials, but it is certain that this change will never become total.

## REFERENCES

- Adams, W.G. and Day, R.E. (1877) *Proc. Roy. Soc. Lond. A* **25**, 113.
- Agullo-López, F. (1994) *MRS Bulletin* **19**(3), 29.
- Amato, I. (1997) *Stuff: The Materials the World is Made of* (Basic Books, New York) p. 205.
- Ames, I., d'Heurle, F.M. and Horstmann, R. (1970) *IBM J. Res. Develop.* **14**, 461.
- Anon. (1998) Article on copper-based chip-making technology, *The Economist (London)* (June 6), 117.
- Ashkin, A., Boyd, G.D., Dziedzic, J.M., Smith, R.G. and Ballman, A.A. (1966) *Appl. Phys. Lett.* **9**, 72.
- Attardi, M.J. and Rosenberg, R. (1970) *J. Appl. Phys.* **41**, 2381.
- Bachmann, K.J. (1995) *The Materials Science of Microelectronics* (VCH, Weinheim).
- Bahadur, B. (ed.) (1991) *Liquid Crystals: Applications and Uses*, 3 volumes (World Scientific, Singapore).
- Baibich, M.N. *et al.* (1988) *Phys. Rev. Lett.* **61**, 2472.
- Baker, W.O. (1967) *J. Mater.* **2**, 915.
- Bartha, L., Lassner, E., Schubert, W.-D. and Lux, B. (eds.) (1995) *The Chemistry of Non-Sag Tungsten* (Pergamon Press, Oxford).
- Bednorz, J.G. and Müller, K.A. (1986) *Z. Phys. B* **64**, 189.
- Bilaniuk, O.M. (1970–1980) in *Dictionary of Scientific Biography*, ed. Gillispie, C.C., vol. 7 (Charles Scribner's Sons, New York) p. 320.
- Bloor, D. (1994) in *The Encyclopedia of Advanced Materials*, ed. Bloor, D. *et al.*, vol. 3 (Pergamon Press, Oxford) p. 1773.
- Boyd, I.W. (1985) *Nature* **313**, 100.
- Briant, C.L. (ed.) (1999) *Impurities in Engineering Materials: Impact, Reliability and Control* (Marcel Dekker, New York).
- Brix, P. (1985) *Physikalische Blätter* **41**, 141.
- Brown, R.G.W. and Pike, E.R. (1995) in *Twentieth Century Physics*, ed. Brown, L.M., Pais, A. and Pippard, B. vol. 3 (American Institute of Physics, Britol, Institute of Physics Publication and New York) p. 1385.

- Burke, J.J. (1995) *Encyclopedia of Applied Physics*, vol. 12 (VCH Publishers, New York) p. 369.
- Busch, G. (1991) *Condensed Matter News* **1**(2), 20.
- Busch, G. (1993) *Condensed Matter News* **2**(1), 15.
- Buschow, K.H.J. (1989) *J. Less-Common Metals* **155**, 307.
- Cahn, R.W. (1970) *Nature* **225**, 693.
- Cahn, R.W. (1983) *Nature* **302**, 294.
- Casimir, H.B.G. (1983) *Haphazard Reality: Half a Century of Science*, Chapter 8 (Harper and Row, New York) p. 224.
- Chandrasekhar, S. (1992) *Liquid Crystals*, 2nd edition (Cambridge University Press, Cambridge).
- Chaplin, D.M., Fuller, C.S. and Pearson, G.L. (1954) *J. Appl. Phys.* **25**, 676.
- Cho, A.Y. (1995) *MRS Bull.* **20**(4), 21.
- Clogston, A.M., Hannay, N.B. and Patel, C.K.N. (1978) *J. Less-Common Metals* **62**, vii (also Raub, C., p. xi).
- Colborn, R. *et al.* (eds.) (1966) Interview with Bernd Matthias, in *The Way of the Scientist* (Simon and Schuster, New York) p. 35.
- Collins, P.J. (1990) *Liquid Crystals: Nature's Delicate Phase of Matter* (Princeton University Press, Princeton, NJ).
- Crease, R.P. (1999) *Making Physics: A Biography of Brookhaven National Laboratory, 1946–1972* (University of Chicago Press, Chicago) p. 133.
- Cross, L.E. and Newnham, R.E. (1986) History of Ferroelectrics, in *High-Technology Ceramics, Past, Present and Future*, ed. Kingery, W.D. (American Ceramic Society, Westerville, Ohio) p. 289.
- Dash, W.C. (1958, 1959) *J. Appl. Phys.* **29**, 736; *ibid* **30**, 459.
- De Gennes, P.G. and Prost, J. (1993) *The Physics of Liquid Crystals*, 2nd edition (Clarendon Press, Oxford).
- Demus, D. *et al.* (eds.) (1998) *Handbook of Liquid Crystals, Vol. 1, Fundamentals* (Wiley-VCH, Weinheim).
- De Rango, P. *et al.* (1991) *Nature* **349**, 770.
- Devonshire, A.F. (1949) *Phil. Mag.* **40**, 1040.
- Esaki, L. and Tsu, R. (1970) *IBM J. Res. Develop.* **4**, 61.
- Fair, R.B. (editor) (1993) *Rapid Thermal Processing* (Academic Press, San Diego).
- Faupel, F., Willecke, R. and Thran, A. (1998) *Mater. Sci. Eng.* **R22**, 1.
- Fasor, G. (1997) *Science* **275**, 941.
- Friedel, G. (1922) *Ann. Phys.* **18**, 273.
- Friedel, J. (1994) *Graine de Mandarin* (Odile Jacob, Paris) p. 111.
- Geballe, T.H. and Hulm, J.K. (1992) Superconducting Materials: An Overview, in *Concise Encyclopedia of Magnetic and Superconducting Materials*, ed. Evetts, J.E. (Pergamon Press, Oxford) p. 533.
- Glanz, J. (1996) *Science* **271**, 1230.
- Gleason, R.E. (2000) *How far will circuits shrink? Science Spectra*, issue 20, p. 32.
- Goldsmid, H.J. (1964) *Thermoelectric Refrigeration* (Plenum Press, New York).
- Goyal, A. (1995) *JOM* **47**(8), 55
- Goyal, A. *et al.* (1999) *JOM* **51**(7), 19.

- Grunberg, P. *et al.* (1986) *Phys. Rev. Lett.* **57**, 2442.
- Gupta, L.C. (1999) *Proc. Indian Nat. Sci. Acad., Part A* **65A**, 767.
- Haller, E.E. (1995) *J. Appl. Phys.* **77**, 2857.
- Harvey, E.N. (1957) *History of Luminescence* (American Philosophical Society, Philadelphia).
- Hays, D.A. (1998) in *Encyclopedia of Applied Physics*, vol. 23 (VCH Publishers, New York) p. 541.
- Hecht, J. (1999) *City of Light: The Story of Fiber Optics* (Oxford University Press, Oxford).
- Hensch, H.K. (1964) Electroluminescence, in *Reports on Progress in Physics*, vol. 27, p. 369.
- Herman, F. (1984) *Physics Today*, June 1984, p. 56.
- Herring, C. (1991) Solid State Physics, in *Encyclopedia of Physics*, ed. Lerner, R.G. and Trigg, R.L. (VCH Publishers, New York).
- Hicks, L.D., Harman, T.C. and Dresselhaus, M.S. (1993) *Appl. Phys. Lett.* **63**, 3230.
- Hilsum, C. and Raynes, E.P. (editors) (1983) *Liquid Crystals: Their Physics, Chemistry and Applications* (The Royal Society, London).
- Hoddeson, L., Schubert, H., Heims, S.J. and Baym, G. (1992) in *Out of the Crystal Maze*, ed. Hoddeson, L. *et al.* (Oxford University Press, Oxford) p. 489.
- Hodgson, S. and Wilkie, J. (2000) *Mater. World* **8**(8), 11.
- Holton, G., Chang, H. and Jurkowitz, E. (1996) *Am. Sci.* **84**, 364.
- Howson, M.A. (1994) *Contemp. Phys.* **35**, 347.
- Huggins, M.L. and Sun, K.H. (1943) *J. Am. Ceram. Soc.* **26**, 4.
- Ioffe, A.F. (1957) *Semiconductor Thermoelements and Thermoelectric Cooling* (English version) (Infosearch, London).
- Jackson, K.A. (editor) (1996) in *Processing of Semiconductors, Materials Science and Technology: A Comprehensive Treatment*, vol. 16, ed. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim).
- Joffe, A.F. and Stil'bans, L.S. (1959) *Rep. Progr. Phys.* **22**, 167.
- Junod, P. (1959) *Helv. Phys. Acta* **32**, 567.
- Känzig, W. (1991) *Condens. Mat. News* **1**(3), 21.
- Kao, K.C. and Hockham, G.A. (1966) *Proc. IEE.* **113**, 1151.
- Kasper, E., Herzog, H.J. and Kibbel, H. (1975) *Appl. Phys.* **8**, 199.
- Kay, H.F. (1948) *Acta Crystallog.* **1**, 229.
- Keith, S.T. and Quédec, P. (1992) Magnetism and magnetic materials, in *Out of the Crystal Maze*, Chapter 6, ed. Hoddeson, L. *et al.* (Oxford University Press, Oxford) p. 359.
- Kelker, H. (1973) *Mol. Cryst. Liq. Cryst.* **21**, 1; (1988) *ibid* **165**, 1.
- Keusin-Elbaum, L. *et al.* (1997) *Nature* **389**, 243.
- Kotte, E.-U. *et al.* (1989) *Technologies of Light: Lasers, Fibres, Optical Information Processing, Early Monitoring of Technological Change* (Springer, Berlin).
- Kraner, H.M. (1924) *J. Amer. Ceram. Soc.* **7**, 868.
- Kraner, H.M. (1971) *Amer. Ceram. Soc. Bull.* **50**, 598.
- Kulwicki, B.M. (1981) *PTC Materials Technology, 1955–1980*, in *Grain Boundary Phenomena in Electronic Ceramics – Advances in Ceramics*, vol. 1, ed. Levinson, L.M. (American Ceramic Society, Columbus, Ohio) p. 138.

- Lenard, P., Schmidt, F. and Tomaschek, R. (1928) *Handbuch der Experimentalphysik*, vol. 23.
- Levinson, L.M. (editor) (1981) *Grain Boundary Phenomena in Electronic Ceramics – Advances in Ceramics*, vol. 1 (American Ceramic Society, Columbus, Ohio).
- Levinson, L.M. (1985), private communication.
- Li, J., Duewer, F., Chang, H., Xiang, X.-D. and Lu, Y. (2000) *Appl. Phys. Lett.* (in press).
- Lifshitz, E.M. and Kosevich, A.K. (1953) *Dokl. Akad. Nauk SSSR* **91**, 795.
- Livingston, J.D. (1998) 100 Years of Magnetic Memories, *Sci. Amer.* (November) 80.
- Loferski, J.J. (1995) Photovoltaic devices, in *Encyclopedia of Applied Physics*, vol. 13, ed. G.L. Trigg, p. 533.
- MacChesney, J.H. and DiGiovanni, D.J. (1991) in *Glasses and Amorphous Materials*, ed. Zarzycki, J.; *Materials Science and Technology*, vol. 9, Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 751.
- Mahajan, S. and Sree Harsha, K.S. (1999) *Principles of Growth and Processing of Semiconductors* (McGraw-Hill, New York).
- Megaw, H. (1945) *Nature* **155**, 484; **157**, 20.
- Megaw, H. (1957) *Ferroelectricity in Crystals*, Methuen 1957 (London).
- Miyayama, M. and Yanagida, H. (1988) Ceramic semiconductors: non-linear, in *Fine Ceramics*, ed. Saito, S. Elsevier (New York and Ohmsha, Tokyo) p. 275.
- Moharil, S.V. (1994) *Bull. Mater. Sci. Bangalore* **17**, 25.
- Mort, J. (1994) *Phys. Today* **47**(1), 32.
- Mott, N.F. and Jones, H. (1936) *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford) p. 310.
- Moulson, A.J. and Herbert, J.M. (1990) *Electroceramics: Materials, Properties, Applications* (Chapman and Hall, London).
- Nagarajan, R. et al. (1994) *Phys. Rev. Lett.* **72**, 274.
- Nakamura, S. (1996) *Japanese J. Appl. Phys.* **35**, L74–L76.
- Néel, L. (1936) *Compt. Rend. Acad. Sci. Paris* **203**, 304.
- Néel, L. (1948) *Annal. Phys.* **3**, 137.
- Newnham, R.E. (1975) *Structure-Property Relations* (in a monograph series on *Crystal Chemistry of Non-Metallic Materials*) (Springer, Berlin).
- Newnham, R.E. (1997) *MRS Bull.* **22**(5), 20.
- Nishizawa, J. and Minakata, M. (1996) *Encyclopedia of Applied Physics*, vol. 15 (VCH Publishers, New York) p. 339.
- Notis, M.R. (1986) in *High-Technology Ceramics, Past, Present and Future*, vol. 3, ed. Kingery, W.D. (American Ceramic Society, Westerville, Ohio) p. 231.
- Paul, D. (2000) *Phys. World* **13**(2), 27.
- Pfann, W.G. (1954) *Trans. AIME* **194**, 747.
- Pfann, W.G. (1958, 1966) *Zone Melting*, 1st and 2nd editions (Wiley, New York).
- Pippard, B. (1994) Obituary of John Bardeen, *Biograp. Mem. Fellows R. Soc.* **39**, 21.
- Pippard, B. (1995) Electrons in solids, in *Twentieth Century Physics*, vol. 3, ed. Brown, L.M., Pais, A. and Pippard, B. (Institute of Physics Publications, Bristol and Amer. Inst. of Physics, New York) p. 1279.
- Ponce, F.A. and Bour, D.P. (1997) *Nature* **386**, 351.

- Radnai, R. and Kunfalvi, R. (1988) *Physics in Budapest* (North-Holland, Amsterdam) pp. 64, 74.
- Rawson, H. (1991) in *Glasses and Amorphous Materials*, ed. Zarzycki, J.; *Materials Science and Technology*, vol. 9, ed. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 279.
- Regain, B.O. and Grätzel (1991) *Nature* **353**, 637.
- Reid, T.R. (1984) *The Chip* (Simon and Schuster, New York).
- Roth, W.L. (1972) *J. Solid-State Chem.* **4**, 60.
- Riordan, M. and Hoddeson, L. (1997) *Crystal Fire: The Birth of the Information Age* (W.W. Norton and Co., New York and London).
- Sales, B.C. (1997) *Current Opinion in Solid State and Materials Science*, vol. 2, p. 284.
- Sato, K.-I. (2000) *Phil. Trans. Roy. Soc. Lond. A* **358**, 2265.
- Scaff, J.H. (1970) *Metall. Trans.* **1**, 561.
- Schropp, R.E.I. and Zeeman, M. (1998) *Amorphous and Microcrystalline Silicon Solar Cells* (Kluwer Academic Publishers, Dordrecht).
- Seitz, F. (1996) *Proc. Amer. Philo. Soc.* **140**, 289.
- Seitz, F. and Einspruch, N.G. (1998) *Electronic Genie: The Tangled History of Silicon* (University of Illinois Press, Urbana and Chicago).
- Shick, A.B., Ketterson, J.B., Novikov, D.L. and Freeman, A.J. (1999) *Phys. Rev. B* **60**, 15480.
- Shull, C.G., Wollan, E.O. and Strauser, W.A. (1951) *Phys. Rev.* **81**, 483.
- Simonds, J.L. (1995) *Phys. Today* (April), 26.
- Slack, G.A. (1995) in *CRC Handbook of Thermoelectrics*, ed. Rowe, D.M. (Chemical Rubber Co. Boca Raton, FL) p. 470.
- Sluckin, T.J. (2000) *Contemp. Phys.* **41**, 37.
- Smekal, A. (1933) Aufbau der zusammenhängende Materie, in *Handbuch der Physik*, vol. 24 (part 2), p. 795.
- Smit, J. and Wijn, H.P.J. (1959) *Ferrites* (Philips Technical Library, Eindhoven).
- Snoek, J.L. (1936) *Physica* **3**, 463.
- Sondheimer, E.H. (1999) Biographical memoir of Sir Alan Herries Wilson, *Biog. Mem. Fell. R. Soc. Lond.* **45**, 547.
- Spear, W.E. (1974) in *Proc. Int. Conf. on Amorphous and Liquid Semiconductor*, ed. Stuke, J. and Brenig, W. (Taylor and Francis, London) p. 1.
- Street, R.A. (1991) *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge).
- Suits, C.G. and Bueche, A.M. (1967) Cases of research and development in a diversified company, in *Applied Science and Technological Progress* (no editor cited) (National Academy of Sciences, Washington, DC) p. 297.
- Sze, S.M. (editor) (1991) *Semiconductor Devices: Pioneering Papers* (World Scientific, Singapore).
- Thomas, G.A., Shraiman, B.I., Glodis, P.F. and Stephen, M.J. (2000) *Nature* **404**, 262.
- Toigo, J.W. (2000) Avoiding a data crunch, *Sci. Amer.* **282**(5), 40.
- TRACES (1968) *Technology in Retrospect and Critical Events in Science (TRACES)*. Illinois Institute of Technology, Research Institute; published for the National Science Foundation (no editor or author named).

- Valenzuela, R. (1994) *Magnetic Ceramics* (Cambridge University Press, Cambridge).
- Verwey, E.J.W. and Heilmann, E.I. (1947) *J. Chem. Phys.* **15**, 174.
- Weber, M.J. (1991) in *Glasses and Amorphous Materials*, ed. J. Zarzycki; *Materials Science and Technology*, vol. 9, ed. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 619.
- Whall, T.E. and Parker, E.C.H. (1995) *J. Mater. Elect.* **6**, 249.
- Wilson, A.H. (1931) *Proc. Roy. Soc. Lond. A* **133**, 458; **134**, 277.
- Wilson, A.H. (1939) *Semi-conductors and Metals* (Cambridge University Press, Cambridge).
- Wilson, A.H. (1980) *Proc. Roy. Soc. Lond. A* **371**, 39.
- Yeack-Scranton, C.E. (1994) *Encyclopedia of Applied Physics*, vol. 10 (VCH Publishers, New York) p. 61.
- Zachariasen, W.H. (1932) *J. Amer. Ceram. Soc.* **54**, 3841.
- Ziman, J.M. (1960) *Electrons and Phonons* (Clarendon Press, Oxford) p. 396.
- Zweibel, K. (1990) *Harnessing Solar Power: The Photovoltaics Challenge* (Plenum Press, New York).

# Chapter 8

## The Polymer Revolution

8.1. Beginnings	307
8.2. Polymer Synthesis	308
8.3. Concepts in Polymer Science	310
8.4. Crystalline and Semicrystalline Polymers	312
8.4.1 Spherulites	312
8.4.2 Lamellar Polymer Crystals	313
8.4.3 Semicrystallinity	317
8.4.4 Plastic Deformation of Semicrystalline Polymers	319
8.4.5 Polymer Fibers	321
8.5. Statistical Mechanics of Polymers	321
8.5.1 Rubberlike Elasticity: Elastomers	323
8.5.2 Diffusion and Reptation in Polymers	326
8.5.3 Polymer Blends	326
8.5.4 Phase Transition in Polymers	328
8.6. Polymer Processing	329
8.7. Determining Molecular Weights	330
8.8. Polymer Surfaces and Adhesion	331
8.9. Electrical Properties of Polymers	332
8.9.1 Semiconducting Polymers and Devices	333
References	336



## Chapter 8

# The Polymer Revolution

### 8.1. BEGINNINGS

The early years, when the nature of polymers was in vigorous dispute and the reality of long-chain molecules finally came to be accepted, are treated in Chapter 2, Section 2.1.3. For the convenience of the reader I set out the sequence of early events here in summary form.

The understanding of the nature of polymeric molecules was linked from an early stage with the stereochemical insights due to van 't Hoff, and the recognition of the existence of isomers. The main argument was between the followers of the notion that polymers are “colloidal aggregates” of small molecules of fixed molecular weight, and those, notably Staudinger, who insisted that polymers were long-chain molecules, covalently bound, of high but variable molecular weight. That argument was not finally settled until 1930. After that, numerous scientists became active in finding ever more ingenious ways of determining MWs and their distributions.

The discovery of stereoactive catalysts to foster the polymerisation of monomers transformed the study of polymers from an activity primarily to satisfy the curiosity of a few eccentric chemists into a large-scale industrial concern. These discoveries started in the 1930s with the finding, by ICI in England, that a combination of high pressure and oxygen served to create an improved form of polyethylene, and peaked in the early 1950s with the discoveries by Ziegler and Natta of low-pressure catalysts, initially applicable to polyethylene but soon to other products as well. In a separate series of events, Carothers in America set out to find novel synthetic fibres, and discovered nylon in the early 1930s. In the same period, chemists struggled with the difficult task of creating synthetic rubber.

After 1930, when the true nature of polymers was at last generally, recognised, the study of polymers expanded from being the province of organic specialists; physical chemists like Paul Flory and physicists like Charles Frank became involved. In this short chapter, I shall be especially concerned to map this broadening range of research on polymers.

A number of historically inclined books are recommended in Chapter 2. Here I will only repeat the titles of some of the most important of these. The best broad but concise overview is a book entitled *Polymers: The Origins and Growth of a Science* (Morawetz 1985); it covers events up to 1960. A very recent, outstanding book is *Inventing Polymer Science: Staudinger, Carothers and the Emergence of Macromolecular Chemistry* (Furukawa 1998). His last chapter is a profound consideration of

“the legacy of Staudinger and Carothers”. These two books focus on the underlying science, though both also describe industrial developments. A British multiauthor book, *The Development of Plastics* (Mossman and Morris 1994), edited by specialists at the Science Museum in London, covers industrial developments, not least the Victorian introduction of parkesine, celluloid and bakelite. Published earlier is a big book classified by specific polymer families and types (e.g., polyesters, styrenes, polyphenylene sulfide, PTFE, epoxys, fibres and elastomers) and focusing on their synthesis and uses: *High Performance Polymers: Their Origin and Development* (Seymour and Kirshenbaum 1986). Still earlier was a fine book about the discovery of catalytic methods of making synthetic stereoregular polymers, which in a sense was the precipitating event of modern polymer technology (McMillan 1979).

## 8.2. POLYMER SYNTHESIS

For any of the many distinct categories of materials, extraction or synthesis is the necessary starting-point. For metals, the beginning is the ore, which has to be separated from the accompanying waste rock, then smelted to extract the metal which subsequently needs to be purified. Extractive metallurgy, in the 19th century, was the central discipline. It remains just as crucial as ever it was, especially since ever leaner ores have to be treated and that becomes ever more difficult; but by degrees extractive metallurgy has become a branch of chemical engineering, and university courses of materials science keep increasingly clear of the topic. There are differences: people who specialise in structural and decorative ceramics, or in glass, are more concerned with primary production methods. . . but here the starting-point is apt to be the refined oxide, as distinct from the raw material extracted from the earth.

The point of this digression is to place the large field of polymer chemistry, alternatively polymer synthesis, in some kind of perspective. The first polymers, in the 19th century, were made from natural precursors such as cotton and camphor, or were natural polymers in the first place (rubber). Also the objective in those early days was to find substitutes for materials such as ivory or tortoiseshell which were becoming scarce: ‘artificial’ was the common adjective, applied alike to polymers for billiard balls, combs, and stiff collars (e.g., celluloid), and to the earliest fibres (‘artificial silk’). Bakelite was probably the first truly synthetic polymer, made from laboratory chemicals (phenol and formaldehyde), early in the twentieth century, invented independently by Leo Baekeland (1863–1944) and James Swinburne (1858–1958); bakelite was not artificial anything. Thereafter, and especially after ICI’s perfection, in 1939, of the first catalyst for polymerising ethylene under high pressure, the classical methods of organic chemistry were used, and steadily

improved. At first the task was simply to bring about polymerisation at all; soon, chemists began to focus on the equally important tasks of controlling the *extent* of polymerisation, and its stereochemical character. If one is to credit an introductory chapter (*Organic chemistry and the synthesis of well-defined polymers*) to a very recent text on polymer chemistry (Müllen 1999), even today “organic chemists tend to avoid polymers and are happy when ‘polymers’ remain at the top of their chromatography column. They consider polymers somewhat mysterious and the people who make them somewhat suspect. Polydisperse compounds (i.e., those with variable MWs) are not accepted as ‘true’ compounds and it is believed that a method of bond formation, once established for the synthesis of a small compound, can be extended without further complication toward polymer synthesis.” Polymer specialists have become a chemical breed apart. As Müllen goes on to remark “While a synthesis must be ‘practical’ and provide sufficient quantities, the limitations of the synthetic method, with respect to the occurrence of side products and structural defects, must be carefully investigated, e.g., for establishing a reliable structure-property relationship”. The situation was reminiscent of the difficulties encountered by the early semiconductor researchers who found their experimental materials too impure, too imperfect and too variable.

The 665 pages of the up-to-date text for which Müllen wrote cover an enormous range of chemical and catalytic techniques developed to optimise synthetic methods. One feature which sets polymer chemistry apart from traditional synthetic organic chemistry is the need to control mean MWs and the range of MWs in a polymeric product (the degree of ‘polydispersity’). Such control is feasible by means of so-called ‘living radical polymerisation’ (Sawamoto and Kamigaito 1999); initiators are used to start the polymerisation reaction and ‘capping reagents’ to terminate it. The techniques of making polymers with almost uniform MWs are now so well developed that such materials have their own category name, ‘model polymers’, and they have extensive uses in developing novel materials, structures and properties and in testing concepts in polymer physics (Fettes and Thomas 1993). Quite generally, recent developments in polymerisation catalysis have made possible the precise control not only of molecular weight but also of co-monomer sequence and stereo-sequence (Kobayashi 1997).

A special form of polymerisation is in the solid state; in this way, single crystals of diacetylenes have been made, and this was the starting-point of the major developments now in progress with electrically conducting polymers. Yet another unexpected approach is the use of radiation to enhance polymerisation or cross-linking of polymers, for instance of rubbers during tire manufacture (Charlesby 1988).

Occasionally, a completely new family of polymers is discovered, and then the synthesizers have to start from scratch to find the right methods: an example is the

family of dendrimers (Janssen and Meijer 1999), discovered in the 1980s, polymers which spread radially from a nucleus, with branching chains like the branches of a tree (hence the name, from the Greek word for a tree). Such polymers can be made with virtually uniform MWs, but at the cost of slow and extremely laborious synthetic methods.

The standard textbook of polymer science in the 1960s was that by Billmeyer (1962); of its 600 pages, 125 were devoted to polymerisation, i.e., to polymer chemistry. But this has changed: the important domain of polymer chemistry has become, by degrees, a branch of science almost wholly divorced from the rest of polymer science, with its own array of journals and conferences, and certainly not an integral part of materials science, and not treated in most general texts on polymer science. Accordingly, I will not treat it further in this chapter. The aspects of polymer science that form part of MSE nowadays are polymer processing and polymer physics.

### **8.3. CONCEPTS IN POLYMER SCIENCE**

The whole of polymer science is constructed around a battery of concepts which are largely distinct from those familiar in other families of materials, metals in particular. This is the reason why I invited an eminent polymer scientist who was originally a physical metallurgist to write, for a textbook of physical metallurgy edited by me, a chapter under the title "A metallurgist's guide to polymers" (Windle 1996). The objective was to remove some of the mystery surrounding polymer science in the eyes of other kinds of materials scientists.

In outline form, here are some of the key concepts treated in that chapter. Polymers can be homopolymers (constituted of only one kind of monomer) or copolymers, constituted of (usually) two chemically different kinds of monomers. Copolymers, in turn, can be statistically mixed (random copolymers) or else made up of blocks of the two kinds of monomers... block copolymers or, if there are sidechains, graft copolymers; the lengths of the blocks can vary widely. Both kinds of polymer have variable MWs; the 'polydispersity' can be slight or substantial. The chains can be linear or branched, and linear chains can be stereotactic (with sidegroups arranged in a regular conformation), or disordered (atactic). According to the chemistry, a polymer can be resoftened by reheating (thermoplastic) or it can harden irreversibly when fully polymerised (thermoset).

Many polymers are amorphous, i.e., a kind of glass, complete with a glass transition temperature which is dependent on heating or cooling rate. Even crystalline polymers have a melting range depending on molecular weight. (It was these two features – variable MWs, and absence of a well-defined melting

temperature – which stuck in the craw of early organic chemists when they contemplated polymers).

A polymer can consist of a three-dimensional, entangled array of chains of various lengths, which can be cross-linked to a greater or lesser degree. The chain lengths and cross-linking, together with the temperature, decide whether the material is rigid, fluid or – as an in-between condition – elastomeric, that is, rubber-like. Fluid polymers have a visco-elastic character that distinguishes their mechanical behaviour from fluids like water or molten metals. Elastomeric polymers are ultra-resilient and their elasticity is of almost wholly entropic origin; such materials become stiffer when heated, unlike non-polymeric materials.

Amorphous stereotactic polymers can crystallise, in which condition neighbouring chains are parallel. Because of the unavoidable chain entanglement in the amorphous state, only modest alignment of amorphous polymer chains is usually feasible, and moreover complete crystallisation is impossible under most circumstances, and thus many polymers are semi-crystalline. It is this feature, semicrystallinity, which distinguished polymers most sharply from other kinds of materials. Crystallisation can be from solution or from the melt, to form spherulites, or alternatively (as in a rubber or in high-strength fibres) it can be induced by mechanical means. This last is another crucial difference between polymers and other materials. Unit cells in crystals are much smaller than polymer chain lengths, which leads to a unique structural feature which is further discussed below.

Most pairs of homopolymers are mutually immiscible, so that phase diagrams are little used in polymer science. . . another major difference between polymers on the one hand, and metals and ceramics on the other. Two-phase fields can be at lower or higher temperatures than single-phase fields. . . another unique feature.

Plastic deformation in polymers is not usually analysed in terms of dislocations, because crystallinity is not usually sufficiently perfect for this concept to make sense. Nevertheless, polymers do work-harden, like metals. . . indeed, strongly drawn fibres become immensely strong, because the intrinsic strength of the carbon-carbon backbone of a polymer chain then makes itself felt. Deformed polymers, especially amorphous ones, develop ‘crazes’, thin regions filled with nanosized voids; the fracture mechanics of polymers is intimately bound up with crazes, which are not known in other materials. Crazes propagate like cracks, but unlike cracks, they can support some load. As Windle puts it, “development of a craze is a potent, albeit localised, energy absorption mechanism which makes an effective contribution to resisting the propagation of a crack which follows it; a craze is thus both an incipient fracture *and* a toughening mechanism”.

The methods used to characterise polymers are partly familiar ones like X-ray diffraction, Raman spectroscopy and electron microscopy, partly less familiar but widespread ones like neutron scattering and nuclear magnetic resonance, and partly

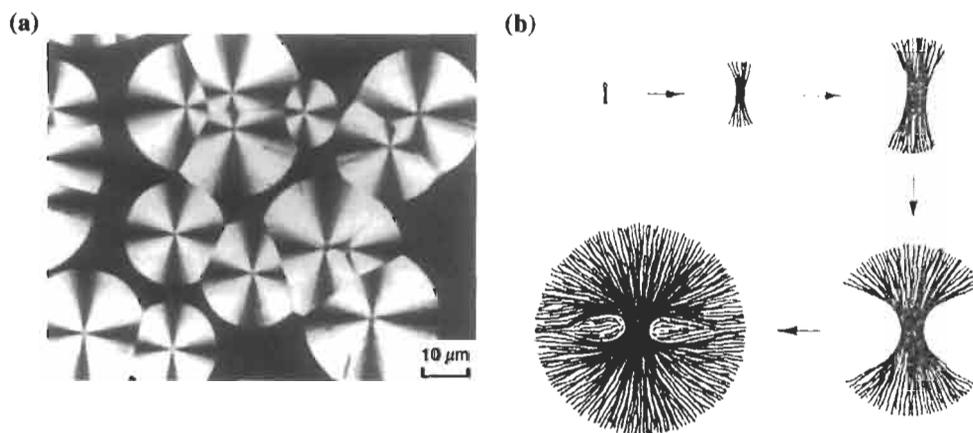
unique to polymers, in particular, the many methods used to measure MWs and their distribution.

It is clear enough why polymers strike many materials scientists as very odd. However, since the 1930s, some physical chemists have made crucial contributions to the understanding of polymers; in more recent decades, many physicists have turned their attention wholly to polymer structures, and a number of metallurgists, such as the writer of the chapter referred to in this Section, have done likewise. As we will see in the next Section, some cross-fertilisation between polymer science and other branches of MSE has begun.

#### 8.4. CRYSTALLINE AND SEMICRYSTALLINE POLYMERS

##### 8.4.1 Spherulites

The most common form of crystallization in polymers is the *spherulite* (Figure 8.1(a) and (b)), which can grow from solution, melt or the solid amorphous form of a polymer. Spherulites do form in a number of inorganic systems, but only in polymers are they the favoured crystalline form. The first proper description of spherulites was by two British crystallographers, working in the chemical industry (Bunn and Alcock 1945); they used optical microscopy and X-ray diffraction to characterise the nature of the spherulites. In general, the individual polymer chains run tangentially (normal to the radius vector). The isothermal growth rate is found to be constant,



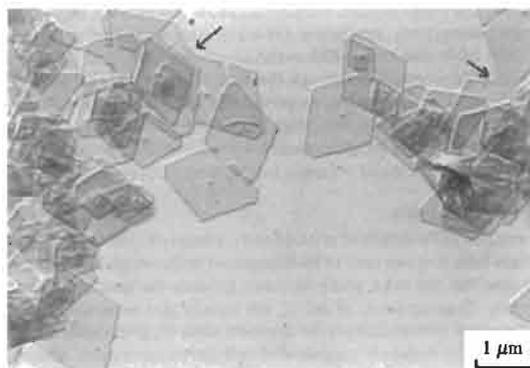
**Figure 8.1.** (a) Spherulites growing in a thin film of isotactic polystyrene, seen by optical microscopy with crossed polars (from Bassett 1981, after Keith 1963). (b) A common sequence of forms leading to spherulitic growth (after Bassett 1981). The fibres consist of zigzag polymer chains.

independently of the radius. The universality of this morphology has excited much theoretical analysis. A good treatment is that by Keith and Padden (1963), which draws inspiration from the then-new theory of freezing of alloys due to Chalmers and Rutter; the build-up of rejected impurities or solute leads to 'constitutional supercooling' (see ch. 9, sect. 9.1.1). Here, the 'impurities' are disordered (atactic) or branched chains. This leads to regular protuberances on growing metal crystal interfaces, while in polymers the consequence is the formation of fibrils, as seen schematically in Figure 8.1(b).

Spherulites are to be distinguished from dendrimers, which also have spherical form. A dendrimer is a single molecule of a special kind of polymer which spreads from a nucleus by repeated branching.

#### 8.4.2 Lamellar polymer crystals

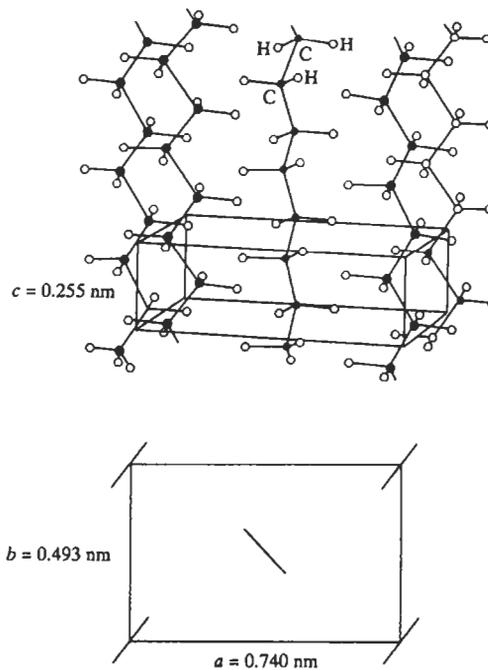
A very different morphology develops in a few polymers, grown from solution. Early experiments, in the 1930s and again the early 1950s, were with gutta-percha, a rather unstable natural polymer. The first report of such a crystal morphology from a well characterised, synthetic polymer was by Jaccodine (1955), who grew thin platelets from a solution of linear polyethylene, of molecular weight  $\approx 10,000$ , in benzene or xylene. Figure 8.2 shows a population of such crystals. Jaccodine's report at once excited great interest among polymer specialists, and two years later, three scientists independently confirmed and characterised such polyethylene crystals (Till 1957, Keller 1957, Fischer 1957) and all showed by electron diffraction in an electron microscope that the polymer chains were oriented normal to the lamellar plane. They thereby started a stampede of research, accompanied by extremely vigorous disputes as to interpretation, which continues to this day. These monocystal lamellae can



**Figure 8.2.** Lozenge-shaped monocrystals of polyethylene grown from solution by a technique which favors monolayer-type crystals. Electron micrograph (after Bassett 1981).

only be made with stereoregular polymers in which the successive monomers are arranged in an ordered pattern; Figure 8.3 shows the unit cell of a polyethylene crystal according to Keller (1968).

One of the active researchers on polymer crystals was P.H. Geil, who in 1960 reported nylon crystals grown from solution; in his very detailed early book on polymer single crystals (Geil 1963) he remarks that all such crystals grown from dilute solution consist of thin platelets, or lamellae, about 100 Å in thickness; today, a compilation of published data for polyethylene indicates that the thickness ranges between 250 and 500 Å (25–50 nm), increasing sharply with crystallization temperature. The exact thickness depends on the polymer, solvent, temperature, concentration and supersaturation. Such a crystal is much thinner than the length of a polymer chain of M.W. 10,000, which will be in excess of 1000 Å. The inescapable conclusion is that each chain must fold back on itself several times. As Keller put it some years later, “folding is a straightforward necessity as the chains have nowhere else to go”. It has been known since 1933 that certain paraffins can crystallize with two long, straight segments and one fold, the latter occupying approximately five carbon atoms’ worth of chain length. To make this surprising conclusion even harder

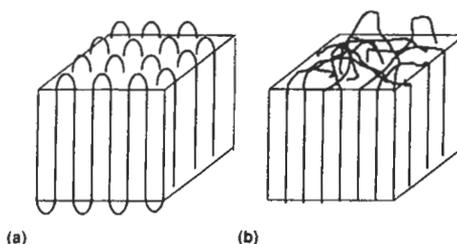


**Figure 8.3.** Unit cell of crystalline polyethylene, adapted from a figure by Keller 1968.

to accept than it intrinsically is, it soon became known that annealing of the thin crystals allowed them gradually to thicken; what this meant in terms of the comportment of the multiple folds was mysterious.

In the decade following the 1957 discovery, there was a plethora of theories that sought, first, to explain how a thin crystal with folds might have a lower free energy than a thick crystal without folds, and second, to determine whether an emerging chain folds over into an adjacent position or folds in a more disordered, random fashion. . . both difficult questions. Geil presents these issues very clearly in his book. For instance, one model (among several 'thermodynamic' models) was based on the consideration that the amplitude of thermal oscillation of a chain in a crystal becomes greater as the length of an unfolded segment increases and, when this as well as the energy of the chain ends is considered, thermodynamics predicts a crystal thickness for which the total free energy is a minimum, at the temperatures generally used for crystallization. The first theory along such lines was by Lauritzen and Hoffman (1960). Other models are called 'kinetic', because they focus on the kinetic restrictions on fold creation. The experimental input, microscopy apart, came from neutron scattering (from polymers with some of the hydrogen substituted by deuterium, which scatters neutrons more strongly), and other spectroscopies. Microscopy at that time was unable to resolve individual chains and folds, so arguments had to be indirect. The mysterious thickening of crystal lamellae during annealing is now generally attributed to partial melting followed by recrystallisation. The issue here is slightly reminiscent of the behaviour of precipitates during recrystallisation of a deformed alloy; one accepted process is that crystallites are dissolved when a grain boundary passes by and then re-precipitate.

The theoretical disputes gradually came to center on the question whether the folds are regular and 'adjacent' or alternatively are statistically distributed, as exemplified in Figure 8.4. The grand old man of polymer statistical mechanics, Paul Flory, entered the debate with rare ferocity, and the various opponents came together in a memorable Discussion of the Faraday Society (by then a division of the Royal Society of Chemistry in London). Keller (1979) attempted to set out the different points of view coolly (while his own preference was for the 'adjacent' model), but his attempted role as a peacemaker was slightly impeded by a forceful General Introduction in the same publication by his Bristol colleague Charles Frank, who by 1979 had converted his earlier concern with crystal growth of dislocated crystals into an intense concern with polymer crystals, and by even more extreme remarks by the aged Paul Flory, who was bitterly opposed to the 'adjacent' model. Frank included a "warning to show what bizarrely different models can be deemed consistent with the same diffraction evidence". He also delivered a timely reminder that applies equally to neutron scattering and X-ray diffraction: "All we can do is to make models and see whether they will fit the scattering data within experimental



**Figure 8.4.** Schematic representation of chain folds in polymer single crystal. (a) regular adjacent reentry model; (b) random switchboard model.

error. If they don't, they are wrong. If they do, they are not necessarily right. You must call in all aids you can to limit the models to be tested." After the Discussion, Flory sent in the following concluding observations: "As will be apparent from perusal of the papers. . . denunciation of those who have the temerity to challenge the sacrosanct doctrine of regular chain folding in semicrystalline polymers is the overriding theme and motivation. This purpose is enunciated in the General Introduction, with a stridency that pales the shallow arguments mustered in support of chain folding with adjacent re-entry. The cant is echoed with monotonous iterations in ensuing papers and comments. . ." (Then, with regard to papers by some of the opponents of the supposed orthodoxy:) "The current trend encourages the hope that rationality may eventually prevail in this important area".

It is not often that discussion in such terms is heard or read at scientific meetings, and the 1979 Faraday Discussion reveals that disputatious passion is by no means the exclusive province of politicians, sociologists and litterateurs. Nevertheless, however painful such occasions may be to the participants, this is one way in which scientific progress is achieved.

The arguments continued in subsequent years, but it is beginning to look as though the enhanced resolution attainable with the scanning tunneling microscope may finally have settled matters. A recent paper by Boyd and Badyal (1997) about lamellar crystals of poly(dimethylsilane), examined by atomic force microscopy (Section 6.2.3) yielded the conclusion: "It can be concluded that the folding of polymer chains at the surface of polydimethylsilane single crystals can be seen at molecular scale resolution by atomic force microscopy. Comparison with previous electron and X-ray diffraction data indicates that polymer chain folding at the surface is consistent with the regular adjacent reentry model." The most up-to-date general overview of research on polymer single crystals is a book chapter by Lotz and Wittmann (1993).

Andrew Keller (1925–1999, Figure 8.5), who was a resolute student of polymer morphology, especially in crystalline forms, for many decades at Bristol University



**Figure 8.5.** Andrew Keller (1925-1999) (courtesy Dr. P. Keller).

in company with his mentor Charles Frank, was a chemist who worked in a physics department. In a Festschrift for Frank's 80th birthday (Keller 1991), Keller offered a circumstantial account of his key discovery of 1957 and how the special atmosphere of the Bristol University physics department, created by Frank, made his own researches and key discoveries possible. It is well worth reading this chapter as an antidote to the unpleasant atmosphere of the 1979 Faraday Discussion.

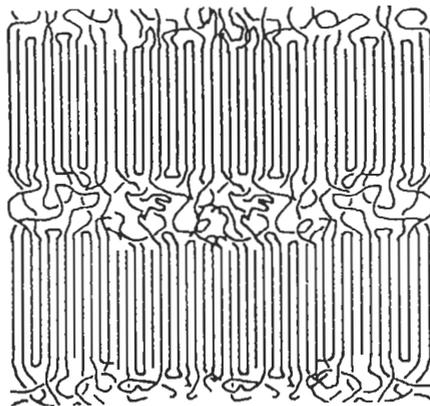
In concluding this discussion, it is important to point out that crystalline polymers can be polymorphic because of slight differences in the conformation of the helical disposition of stereoregular polymer chains; the polymorphism is attributable to differences in the weak intermolecular bonds. This abstruse phenomenon (which does not have the same centrality in polymer science as it does in inorganic materials science) is treated by Lotz and Wittmann (1993).

#### **8.4.3 Semicrystallinity**

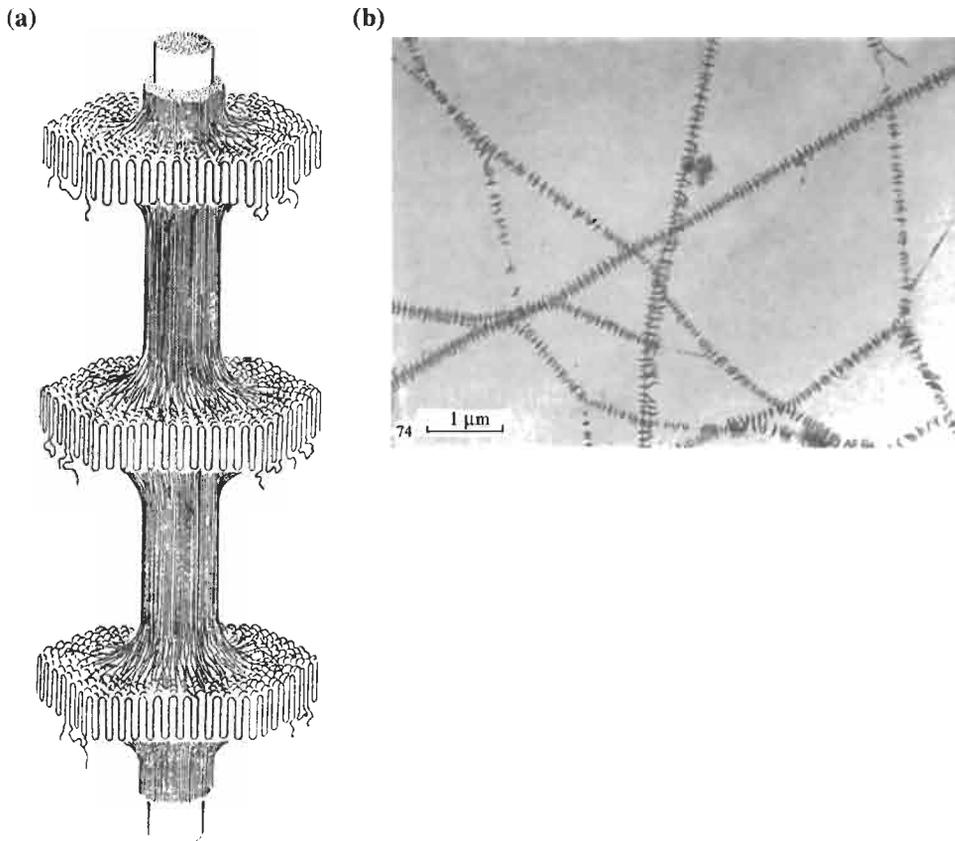
The kind of single crystals discussed above are all made starting from solution. In industrial practice, bulk polymeric products are generally made from the melt, and

such polymers (according to their chemistry) are either wholly amorphous or have 30–70% crystallinity. Indeed, even ‘perfect’ lamellar monocrystals made from solution have a little non-crystalline component, namely, the parts of each chain where they curl over for reentry at the lamellar surface. The difference is that in bulk polymers the space between adjacent lamellae gives more scope for random configuration of chains, and according to treatment, that space can be thicker or thinner (Figure 8.6). Attempts to distinguish clearly between the ‘truly’ crystalline regions and the disturbed space have been inconclusive; indeed, the terms under which a percentage of crystallinity is cited for a polymer are not clearly defined.

Perhaps the most remarkable polymeric configuration of all is the so-called shish-kebab structure (Figure 8.7). This has been familiar to polymer microscopists for decades. Pennings in the Netherlands (Pennings *et al.* 1970) first studied it systematically; he formed the structure by drawing the viscous polymer solution (a gel) from a rotating spindle immersed in the solution. Later, Mackley and Keller (1975) showed that the same structure could be induced in flowing solution with a longitudinal velocity gradient, and thereby initiated a sequence of research on controlled flow of solutions or melts as a means of achieving desired polymer morphologies. A shish-kebab structure consists of substantially aligned but non-crystalline chains, so arranged that at intervals along the fibre, a proportion of the chains splay outwards and generate crystalline lamellae attached to the fibre. Quite recently, Keller and Kolnaar (1997) discuss the formation of shish-kebab morphology in depth, but my impression is that even today no one really understands how and why this form of structure comes into existence, or what factors determine the periodicity of the kebabs along the shish.



**Figure 8.6.** A diagrammatic view of a semicrystalline polymer showing both chain folding and interlamellar entanglements. The lamellae are 5–50 nm thick (after Windle 1996).



**Figure 8.7.** (a) Idealised view of a shish-kebab structure (after Pennings *et al.* 1970, Mackley and Keller 1975). (b) Shish kebabs generated in a flowing solution of polyethylene in xylene (after Mackley and Keller 1975).

#### **8.4.4 Plastic deformation of semicrystalline polymers**

Typically, a semicrystalline polymer has an amorphous component which is in the elastomeric (rubbery) temperature range – see Section 8.5.1 – and thus behaves elastically, and a crystalline component which deforms plastically when stressed. Typically, again, the crystalline component strain-hardens intensely; this is how some polymer fibres (Section 8.4.5) acquire their extreme strength on drawing.

The plastic deformation of such polymers is a major research area and has a triennial series of conferences entirely devoted to it. The process seems to be drastically different from that familiar from metals. A review some years ago (Young 1988) surveyed the available information about polyethylene: the yield stress is linearly related to the fraction of crystallinity, and it increases sharply as the thickness

of the crystalline regions increases; surprisingly, the molecular weight does not seem to have any systematic effect. All this shows clearly enough that only the crystalline regions deform irreversibly. As early as 1972 (Petermann and Gleiter 1972), screw dislocations, with Burgers vectors parallel to the chains, were observed by electron microscopy in semicrystalline polyethylene; these investigators also obtained good evidence that these dislocations were activated by stress to generate slip steps. Young (1974) interpreted the measured yield stress in terms of thermal activation of dislocations at the edges of crystal platelets with assistance by the applied shear stress. . . an approach just like that current in examining yield in metals or ceramics.

Isotactic (sterically ordered) polypropylene, made with Ziegler–Natta catalysts, has become a major commodity polymer, typically 60% crystalline, and an important reason for this success is the discovery of the *polypropylene hinge* (Hanna 1990). It was found many years ago (there seems to be no documentation of the original discovery) that a sheet of this polymer with a local thin area, when intensely but locally deformed by repeated bending forward and backwards, undergoes “orientation by folding”; the site becomes very strong and completely immune to fatigue failure. Figure 8.8 shows a typical design of such an “integral, living polypropylene hinge”. Hanna (1990) opines that this kind of hinge has accounted for

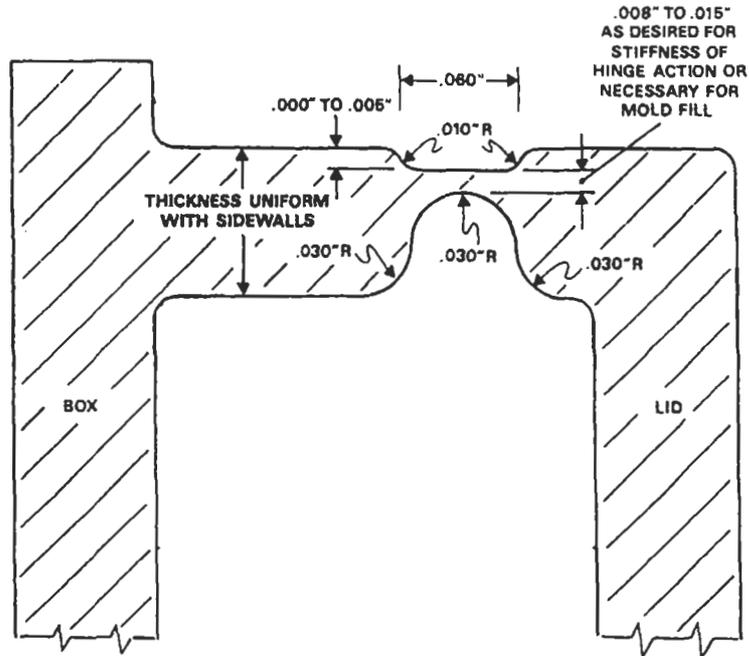


Figure 8.8. Design for a polypropylene hinge (modified from Hanna 1990).

much of the rapid growth of the industrial usage of polypropylene. It should be added that no interpretation has been offered for this unique immunity to fatigue failure.

The mechanical behavior of polymers, as well as many other topics in polymer engineering, are presented in an up-to-date way in a book by McCrum *et al.* (1998).

#### 8.4.5 Polymer fibres

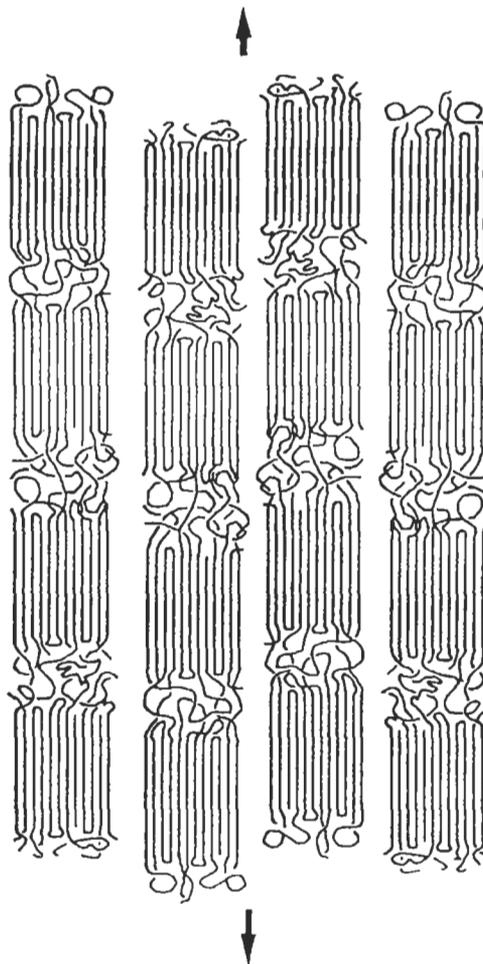
Leaving aside rayon and 'artificial silks' generally, the first really effective polymeric textile fibre was nylon, discovered by the chemist Wallace Hume Carothers (1896–1937) in the Du Pont research laboratories in America in 1935, and first put into production in 1940, just in time to make parachutes for the wartime forces. This was the first of several major commodity polymer fibres and, together with high-density polyethylene introduced about the same time and 'Terylene', polyethylene terephthalate, introduced in 1941 (the American version is Dacron), transformed the place of polymers in the materials pantheon.

The manufacture of nylon fibre involves a drawing step, rather like the drawing of an optical glass fibre (Section 7.5.1), which serves to align the chains. This form of drawing has been developed to the point, today, where immensely strong fibres with very intense chain alignment are routinely manufactured. It seems to have been Frank (1970) who originally analysed, from first principles, the strength and stiffness that might be expected of such products when strongly aligned. A schematic view of such a fibre is shown in Figure 8.9. The secret of obtaining a high elastic modulus is not only to achieve high alignment of the chains but also to minimise the volume of the intercrystalline tangles. Different treatments and different polymers generate different properties: thus nylon ropes, with large elastic extensibility, are used by mountaineers because they can absorb the high kinetic energy of a falling body without breaking, while terylene (dacron) cords with their very high modulus are used by archers for bowstrings.

The problems involved in orienting polymers for improved properties were first surveyed in a special issue of *Journal of Materials Science* (Ward 1971b). Another early survey of this important modern technology was a book edited by Ciferri and Ward (1979), while a recent authoritative account of the modern technology is by Bastiaansen (1997).

### 8.5. STATISTICAL MECHANICS OF POLYMERS

From about 1910 onwards, physical chemists began studying the characteristics of polymer solutions, measuring such properties as osmotic pressure, and found them



**Figure 8.9.** Diagram of the structure of a drawn polymer fibre. The Young's modulus of the crystallised portions is between 50 and 300 GPa, while that of the interspersed amorphous 'tangles' will be only 0.1–5 GPa. Since the strains are additive, the overall modulus is a weighted average of the two figures (after Windle 1996).

to be non-ideal; an outline of the stages is to be found in Chapter 16 of Morawetz (1985). The key event was the formulation, independently by the Americans Huggins (1942) and Flory (1942), of a statistical theory of the (Gibbs) free energy of mixed homopolymers in solution. (One of these papers was published in the *Journal of Physical Chemistry*, the other in the *Journal of Chemical Physics*). The theory was worked out on the understanding, which itself took a long time to gel, that polymer

chains are highly flexible and can assume a great many alternative shapes in solution. This theory formed part of one of the most enduring of polymer texts, Flory's *Principles of Polymer Chemistry* (1953), which is still regularly cited today; it was followed by the same author's *Statistical Mechanics of Chain Molecules* (1969). Paul Flory (1910–1985) was stimulated to his crucial researches by William Carothers whom he joined at Du Pont in 1934 as a young physical chemist; he constituted part of that “restoration of the physicalist approach” to polymer science which is treated in the illuminating Chapter 5 of Furukawa's book on Staudinger and Carothers. Flory was awarded the Nobel Prize for Chemistry in 1974.

The Flory–Huggins equation has assumed a central place in the understanding of the mixing of different polymers, both in solution and in the melt. Any expression for a free energy must include enthalpy (internal energy) and entropy terms. The key conclusion is that the *configurational entropy* of mixing of polymer chains is very much smaller than that for individual atoms in a metallic solid solution. A crude way of explaining this is to point out that the constituent atoms in a polymer chain are linked inseparably together and thus have less freedom to rearrange themselves than the ‘free’ atoms in a metallic alloy; the difference is the greater, the higher the mean molecular weight of the polymer chains. The enthalpy term differs much less as between polymeric and metallic systems. The result is, in the words of Windle (1996), “For polymeric systems where the MWs of the chains are high, the enthalpic term (in the expression for free energy) will be very dominant. Given that, in bonding terms, like tends to prefer like, and thus the enthalpic term will usually be positive, solubility, or ‘miscibility’ as it is known in polymer parlance, will be unlikely. This is in accord with observation. *In general, dissimilar polymers are insoluble in each other.* There are, however, important and interesting exceptions.” According as the constituent atoms of distinct chain types attract or repel each other, one can find polymer pairs in solution which mix at high temperatures but phase-separate below a critical temperature, or else be intersoluble at low temperatures and phase-separate as they are heated. It is fair to say, however, that solid-solution formation is rare enough that phase diagrams play only a modest role in polymer science, compared with their very central role in metallurgy and ceramics.

#### **8.5.1 Rubberlike elasticity: elastomers**

Rubber was a very major component of the polymer industry from its very beginning. From the beginning of the 20th century, attempts were made to make synthetic rubber, because the natural rubber industry was beset by severe economic fluctuations which made supplies unpredictable. A wide range of synthetic rubberlike materials were made from the late 1930s onwards, initially by the German chemical industry under ruthless pressure from Hitler. The German methods were

known by some American companies and were taken over and quickly improved by those companies from 1942 onwards, once America had entered the War. The pressure for reliable rubber supplies in America can be attributed to the fact that in the late 1930s, the USA, with twice the population of Germany, manufactured 15 times as many automobiles. All these variegated rubbers – ‘elastomers’ in polymer language – were chemically distinct from natural rubber, polyisoprene; an elastomer chemically identical to natural rubber was successfully synthesised only in 1953, in the US; until then, heavy-duty truck tires, a particularly demanding product, could only be made from natural rubber, but thereafter all products could, if necessary, be manufactured from synthetics. The complicated story is told from a chemical viewpoint by Morawetz (1985) in his Chapter 8, and by Morris (1994) from a more political and economic viewpoint.

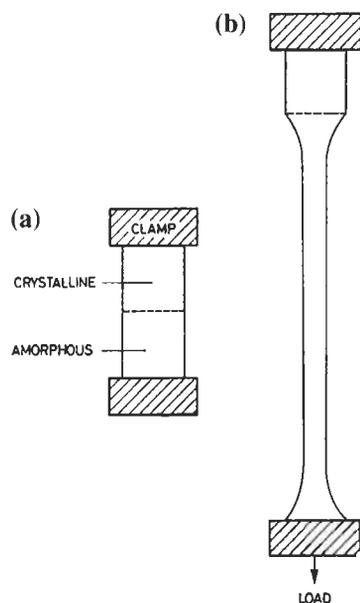
By the 1960s, a great range of synthetic rubbers were available to tire designers. David Tabor at the Cavendish Laboratory in Cambridge, whose research expertise was in friction between solids, formulated a hypothesis relating tire adhesion to the road surface to the resilience of the rubber (the degree to which it rebounds in shape after deformation); he took out a patent in 1960. This view soon became more elaborate, and adhesion was linked to hysteresis, the delay in resilience. Since highly hysteretic rubber generates much heat on cyclic deformation, it became necessary to use different elastomers for the tread and the tire sidewall where much of the heat is generated by flexure during each rotation of the wheel. For a time, this kind of tire construction became the orthodoxy. The subtle linkage between the viscoelastic properties of elastomers and tire properties is very clearly set out by Bond (1990), who put Tabor’s ideas into effect.

Throughout the early stages of the synthetic rubber industry, there was essentially no understanding why rubbers have the extraordinary elastic extensibility which is the *raison d’être* of their many applications. The sequence of events which finally dispelled this ignorance is set out in Chapter 15 of Morawetz’s admirable book. They began in Germany. The suggestion that the origin of rubberlike elasticity lay in configurational entropy, based on careful measurements of heat absorption and emission during stretching and retraction of rubber, was made in a key paper by Meyer *et al.* (1932). In 1934, W. Kuhn presented evidence that, contrary to Staudinger’s conviction at that time, polymer chains in the rubbery or molten state are not rigid but are free to rotate at each bond, and in the same year, Guth and Mark (1934) put forward the essential feature of modern theory, relating rubberlike elasticity to the probability distribution of different degrees of curling of a long, flexible chain. (This is the same Herman Mark who featured in early research on metal single crystals, 12 years before, Section 4.2.1.) A completely straight chain has only one possible configuration, but the more curled up a chain is, i.e., the shorter the distance between its ends, the more distinct configurations are compatible with

that distance. This means that a force will resist attempts to change a chain from a more probable to a less probable configuration, and that is the restoring force that causes a stretched rubber band to retract. Rubberlike elasticity is entropy made tangible.

For the behavior of the individual chain to be reflected in the behavior of the aggregate, neighbouring chains must be crosslinked at intervals, which is done by partial vulcanisation of rubber. It became clear that rubber progressively crystallises, reversibly, as it is stretched. Rubber can also be crystallised thermally, by cooling to the right temperature, and then the chains have no preferred orientation. If rubber is cooled below its glass transition, the chains cease to be flexible and rubberlike behavior ceases. An early exposition of the modern theory can be found in Chapter 3 of an influential little book by Treloar (1958). One of Treloar's figures (Figure 8.10), taken from a later book (Treloar 1970), refers to a rubber sample which has been thermally crystallized and then half of it has been heated enough to convert it back to the amorphous form; if the specimen is then kept at the right temperature, both parts stay metastably as they are, and on stretching only the amorphous part extends.

An idea of the present complexity of the statistical theory of rubberlike elasticity can be garnered from Chapter 7 of a recent book on *The Physics of Polymers*, by Strobl (1996).



**Figure 8.10.** A sample of rubber treated to make it half crystalline, half amorphous. On stretching, measurable extension is restricted to the amorphous part (after Treloar 1970).

### 8.5.2 Diffusion and reptation in polymers

In Section 4.2.2 the central role of atomic diffusion in many aspects of materials science was underlined. This is equally true for polymers, but the nature of diffusion is quite different in these materials, because polymer chains get mutually entangled and one chain cannot cross another. An important aspect of viscoelastic behavior of polymer melts is ‘memory’: such a material can be deformed by hundreds of per cent and still recover its original shape almost completely if the stress is removed after a short time (Ferry 1980). This underlies the use of shrink-fit cling-film in supermarkets. On the other hand, because of diffusion, if the original stress is maintained for a long time, the memory of the original shape fades.

The principal way in which a polymer molecule can diffuse through a population of chains is by *reptation*, which can also be described as the Brownian diffusion of a polymer chain among fixed obstacles. This idea and its ramifications are due to de Gennes (1971) and Edwards (1976), and the process is schematically shown in Figure 8.11. The notion is that a chain is constrained by its neighbours, shown as dots (cross-sections of chains); the wriggling molecule is constrained to stay within a ‘virtual tube’ but it can move by a snake-like progression within that tube. The mobility, of course, diminishes as the chain becomes longer. The kinetics of the process and its relation to a traditionally defined diffusion constant are concisely set out by Léger and Viovi (1994). Reptation has proved a highly influential concept.

### 8.5.3 Polymer blends

Polymer ‘alloys’ are generally named *polymer blends* within the polymer community. In a recent overview of such blends, Robeson (1994) points out that “the primary reason for the surge of academic and industrial interest in polymer blends is directly related to their potential for meeting end-use requirements”. He points out that, in general, miscible polymer pairs confer better properties, mechanical ones in particular, than do phase-separated pairs. For instance, the first commercial



**Figure 8.11.** Reptation of a polymer chain. The chain moves snake-like through its confining virtual tube.

miscible blend of synthetic polymers emerged in the early 1940s: poly(vinyl chloride) and butadiene-acrylonitrile copolymer (a form of rubber) were mixed in order to improve oxidative and ultraviolet stability of the rubber. Robeson cites an early survey of polymer blends in 1968 which listed only 12 miscible pairs, of which several were actually copolymers.

A copolymer, random or block, should not really be counted as an example of a miscible blend, because there is only a single population of polymer chains, albeit with variable composition along their lengths. Very important examples of such a block copolymer are the various forms of rubber-toughened polystyrene (PS). Polystyrene is in itself a cheap and strong mass polymer, but very brittle. It was found in the 1930s that the brittleness could be obviated by copolymerising PS with a synthetic elastomer (rubber) such as polybutadiene; the key product is ABS, acrylonitrile-butadiene-styrene copolymer, which was finally commercialised in 1953 after more than 10,000 laboratory experiments to get the chemistry right (Pavelich 1986). The interesting feature of such copolymers is that the rubber blocks on different chains dispose themselves adjacent to each other, so that chunks (often, microspheres) of rubber are dispersed regularly in the PS matrix. Unmodified PS fractures in tension at very small strains by crazing (see Section 8.3, above), while rubber-modified polystyrene can be elongated by  $\approx 50\%$ . Argon and Cohen (1989) showed that this large strain comes from a large number of minute crazes originating at interfaces between the glassy matrix and the more compliant inclusions; the crazing strain acts as a stress-relief mechanism, retarding fracture. The early development of rubber-toughened polymers was described in a book by Bucknall (1977).

The separation of the polybutadiene and polystyrene blocks into separate 'phases' poses an intriguing conceptual question. Can they really be considered as distinct phases in view of the fact that the blocks are linked together by covalent bonds in the same polymer chains? This poses a problem for established ideas, such as Findlay's phase rule that governs the form of phase diagrams. I do not know the answer. A very general treatment of the processing and properties of block copolymers with 'interphase' interfaces by Inoue and Maréchal (1997) includes a comparison of the structures of such products made from preexisting copolymeric chains with the same product made by dispersing homopolymers and then copolymerising them in situ in the solid state. This again underlines the fact that polymer science is replete with procedures and issues that have no parallel elsewhere in materials science.

Some very peculiar features have been discovered in the microstructures of copolymers. Thus, Hanna *et al.* (1993) showed that a *random* copolymer of two aromatic monomers has chains in which random but similar sequences of the two monomers on distinct chains 'find' each other and "come into register to form a

layered structure with crystalline periodicity perpendicular to the chains but with no periodicity parallel to the chains". This is an early example of *self-assembly* in controlling polymer chain shape, a topic which has become very much to the fore in materials chemistry. Another recent paper (Percec *et al.* 1998) is entitled "Controlling polymer shape through the self-assembly of dendritic side-groups".

#### **8.5.4 Phase transitions in polymers**

In the preceding section, I asked how the phase rule should apply to the structure of block copolymers and confessed to puzzlement. Altogether, phase transitions in polymers are even more complex than in metals and ceramics, and a number of new principles are beginning to emerge. One thing is clear: in the polymer literature, one does not often see phase (equilibrium) diagrams, and I know of no collection of polymer phase diagrams (unlike the situation with metals and ceramics, where many thousands of diagrams have been collected and are in very frequent use by researchers).

One of the few investigators to have homed in on phase transitions in polymers, especially in two-component systems, and to introduce phase diagrams from time to time, is Hugo Berghmans in Belgium. An example of his work is in a paper by Aerts *et al.* (1993): here the polythene/diphenyl ether system is examined and the linkage between phase behavior and morphology is examined and a phase diagram established. One crucial point he emphasises is that the classical phase rule does not apply to such systems: a state with two liquid phases and one crystalline phase should be temperature-invariant according to the phase rule, but it is not so (the authors claim) because of the 'polydispersity' of the polymers, i.e., the fact that the molecular weight of each polymer shows a broad distribution. This is a variable which obviously has no analogue in metal alloys and ceramics.

The most striking treatment I know of phase transitions in polymers, and of metastability in particular, is by Keller and his coworkers. When Keller (1995) first addressed this issue, he pointed out that in polymers the state of ultimate equilibrium is hardly ever attained, and metastability is the rule. He even claimed the existence of stability inversion as crystallite size changes. His ideas were further developed in two papers written shortly before his death (Cheng and Keller 1998, Keller and Cheng 1998). One extraordinary observation presented and discussed here is that a single polymer crystal can have regions of different thicknesses and thus different degrees of metastability and also different melting temperatures. In another system, crystal thicknesses were shown to be 'quantised' as a function of changing crystallisation temperature. There is no space here to go further into these subtleties, but clearly there is enormous scope for research into the linked thermodynamic, kinetic and morphological aspects of phase transformations in polymers.

## 8.6. POLYMER PROCESSING

In no other branch of MSE, perhaps, is the role of processing in determining properties quite so intense as with polymers. Methods such as injection-molding, extrusion, drawing for 'ultimate properties', blow-molding, film-casting, each have to be controlled in fine detail to ensure the desired morphology and consequent properties, and the whole matter is further complicated by the fact that the viscoelastic properties of polymer melts depend not only on the chemical nature of the polymer in question, but also on the mean molecular weight and its distribution. Most (but by no means all) processing starts from the melt, but drawing of ultrastrong fibres takes place in the solid state. Casting, in the sense familiar from metals, plays little part, likewise, the sintering of powders. Computer modelling plays a particularly important part in improving processing technology; this is briefly discussed in Chapter 12.

Quite generally, the details of processing methods play an exceptionally central role in determining the resultant polymer properties; this is underlined by the title of the opening chapter in a major text on processing of polymers (Meijer 1997) – "Processing for properties". Properties are determined alike by the processing route and by the intrinsic chemical structure. This linkage is underlined by a famous polymer reference book, *Properties of Polymers* (van Krevelen 1990) which is devoted to the "correlation of properties with chemical structure, their numerical estimation and prediction from additive group contributions".

It is not feasible here to go in any detail into the history of processing methods; let it suffice to point out that that history goes back to the Victorian beginnings of polymer technology. Thus, as Mossman and Morris (1993) report, the introduction of camphor into the manufacture of parkesine in 1865 was asserted to make it possible to manufacture more uniform sheets than before. Processing has always been an intimate part of the gradual development of modern polymers.

Another important part of polymer science which I do not have space to consider in the detail it deserves is the theory of flow of viscoelastic polymeric melts – a topic closely linked to diffusion and, indeed, to processing. The science of fluid flow generally is the province of *rheology*. That discipline takes its name from the Greek... 'panta rhei', everything flows, a motto enunciated by the Greek philosopher Heraclitus. The term was introduced in 1929, when the first national society devoted to that field was founded in the USA. Since that time, much of the emphasis in rheology has been devoted to polymeric fluids and their peculiar behavior under stress (see, particularly, Ferry 1980). An outstanding treatment of the history of rheology, with vignettes of dozens of the founding fathers, and accounts of the schools of thoughts and disputes between them, has recently been published by Tanner and Walters (1998). These two books make excellent partners

for the leading early treatment of the mechanical properties of solid polymers (Ward 1971a).

### 8.7. DETERMINING MOLECULAR WEIGHTS

At the end of the 1930s, the only generally available method for determining mean MWs of polymers was by chemical analysis of the concentration of chain end-groups; this was not very accurate and not applicable to all polymers. The difficulty of applying well tried physical chemical methods to this problem has been well put in a reminiscence of early days in polymer science by Stockmayer and Zimm (1984). The determination of MWs of a solute in dilute solution depends on the ideal, Raoult's Law term (which diminishes as the reciprocal of the MW), but to eliminate the non-ideal terms which can be substantial for polymers and which are independent of MW, one has to go to ever lower concentrations, and eventually one "runs out of measurement accuracy". The methods which were introduced in the 1940s and 1950s are analysed in Chapter 11 of Morawetz's book.

In the 1930s, one novel method was introduced by a Swedish chemist, The Svedberg, who invented the ultracentrifuge, an instrument in which a solution (of colloidal particles, proteins or synthetic polymers) is subjected to forces many times greater than gravity, and the equilibrium distribution of concentration (which may take weeks to attain) is estimated by measuring light absorption as a function of position along the length of the specimen chamber as the centrifuge spins. It took a long time for this approach to be widely used for polymers because of the great cost of the instrument; Du Pont acquired the first production instrument in 1937. Eventually it became a major technique and Svedberg (who himself was mainly concerned with proteins) earned a Nobel Prize. The theory that related equilibrium concentration gradients to molecular weight is the same as that put forward in Einstein's 1905 paper that was applied to Brownian motion and thus served to cement the atomic hypothesis (Section 3.1.1).

Two classical approaches for MWs of polymers, osmometry and viscometry, both go back to the early years of the 20th century: the former was plagued by technical difficulties with membranes, the latter, by long drawn-out arguments about the theory. Staudinger worked out his own theory of the relation between viscosity and MW, but on the assumption of rigid chains. Morawetz claims that "although the validity of Staudinger's 'law' proved later to have been an illusion, there can be little doubt that its acceptance at the time advanced the progress of polymer science". This is reminiscent of Rosenhain's erroneous views about amorphous layers at grain boundaries in metals, which nevertheless stimulated research on grain boundaries, mainly by those determined to prove him wrong. Motives in scientific research are

not always impeccable. Viscometry has considerable drawbacks, including the fact that viscosities depend on chain shape, unbranched or branched.

An approach which began during the War was light scattering from polymer solutions. This again depended on an Einstein paper, this time dated 1910, in which he calculated scattering from density and compositional fluctuations. The technique was applied early to determine particle size in colloidal solutions, especially by Raman in India (e.g. Raman 1927), but its application to the more difficult problem of polymers awaited the input of the famous Dutch physical chemist Peter Debye (1884–1966), who in the 1940s had become a refugee in the USA. Stockmayer and Zimm describe in detail how Debye's theory (Debye 1944) opened the doors, by stages, to MW determination by light scattering.

The crowning development in MW determination was the invention of gel permeation chromatography, the antecedents of which began in 1952 and which was finally perfected by Moore (1964). A column is filled with pieces of cross-linked 'macroporous' resin and a polymer solution (gel) is made to flow through the column. The polymer solute permeates the column more slowly when the molecules are small, and the distribution of molecules after a time is linked not only to the average MW but also, for the first time with these techniques, to the vital parameter of MW distribution.

This brief outline of the gradual solution of a crucial characterisation dilemma in polymer science could be repeated for other aspects of characterisation; in polymer science, as in other parts of MSE, characterisation techniques and theories are crucial.

## 8.8. POLYMER SURFACES AND ADHESION

Most adhesives either are wholly polymeric or contain major polymeric constituents, and therefore the study of polymer surfaces is an important branch of polymer science, and it turns out that polymer diffusion is of the essence here. A great battery of characterisation techniques has been developed to study the structure of surfaces and near-surface regions in polymers, and the high activity in this field is attested by the fact that in 1995, a Faraday Discussion (volume 98) was held on *Polymers at Surfaces and Interfaces*. Not only adhesion depends on the nature of polymer surfaces. In Section 7.6 we saw that the functioning of liquid-crystal displays depends on glass plates coated with polyimide in contact with a liquid crystal layer, which induce alignment of the liquid-crystal 'director'. It has recently been proved that light brushing of the polyimide coating generates substantial chain alignment; such brushing had been found empirically to be necessary to prepare the glass plates for their function.

Adhesion generally requires the polymer(s) involved to be above their glass transition temperature, so that polymer diffusion (reptation) can proceed. Polymers can diffuse not only into other polymers but also, for instance, into slightly porous metal surfaces. The details have been effectively studied by Brown (1991, 1995): one approach is to use a diblock copolymer and deuterate one of the blocks, so that after interdiffusion the location of residual deuterium (heavy hydrogen) can be assessed. It turns out that according to the length of the chains, the adhesive layer fractures either by pullout or by 'scission' at the join between the blocks. Another aspect of the behaviour of adhesive layers depends on the energy required to develop and propagate crazes at the interface, which has been intensively studied by E.J. Kramer and others. When an adhesive has the right elastomeric character, it may be possible to generate very weak bonds by simple finger pressure, readily reversible without damage to the surface; this is the basis of the well-known Post-it<sup>TM</sup> notes.

The broader issues of adhesion are beyond my scope here; a good source is a book by Kinloch (1987).

### 8.9. ELECTRICAL PROPERTIES OF POLYMERS

Until about twenty years ago, the concept of "electrical properties of polymers", or indeed of any organic chemicals, was equivalent to "dielectric properties"; organic conductors and semiconductors were unknown. Polymers were (and still are) used as dielectrics in condensers and to insulate cables, especially in demanding uses such as radar circuits, and latterly (in the form of polyimides) for dielectric layers in integrated circuits. The permittivity and loss factor (analogous to permeability and hysteresis in ferromagnets) are linked to structural relaxations in individual polymer molecules, and through this they are linked to mechanical hysteresis when a polymer is reversibly stressed. The variables need to be accurately measured at frequencies from main frequency (50 cycles/s) to microwave frequencies (up to  $10^{11}$  cycles/s). The needed techniques were developed in America by Arthur von Hippel and in Britain by Willis Jackson, both of whom were early supporters of the concept of materials science. This early work, which included researches on polymers, was assembled in a renowned monograph (von Hippel 1954). This was supplemented by a different kind of book which has also achieved classic status, (McCrum *et al.* 1967), devoted to a discussion, side by side, of dielectric and mechanical forms of relaxation and hysteresis in polymers. The origins of the different kinds of relaxation were discussed in terms of the underlying molecular motional processes. An updated treatment of these matters is by Williams (1993).

In 1972, the first stable organic conductor was reported, one of the forms of TCNQ, TetraCyaNo-Quinodimethane. Its room-temperature conductivity was

found to be close to that of metals like lead or aluminium; it is a one-dimensional property linked to the long shape of the molecules. Study of such organic conductors (dubbed 'synthetic metals') grew apace and the field soon had its own journal. Even before this, there was a short burst of research on organic superconductors (with very low critical temperatures), and the first (it was also the last) international conference on organic superconductors was held in 1969. The story of organic (non-polymeric) conductors and superconductors is outlined by Jérôme (1986). A later concise view of this intriguing field, with a estimate of successes and failures, is by Campbell Scott (1997); he points out that around 1980, "the 'holy grail' became an air-stable polymer with the conductivity of copper. In retrospect, it is hard to believe that serious consideration was given to the use of plastics to replace wiring, circuit board connections, major windings, or solenoid coils." So it is probably fair to say that 'synthetic metals' have come and gone.

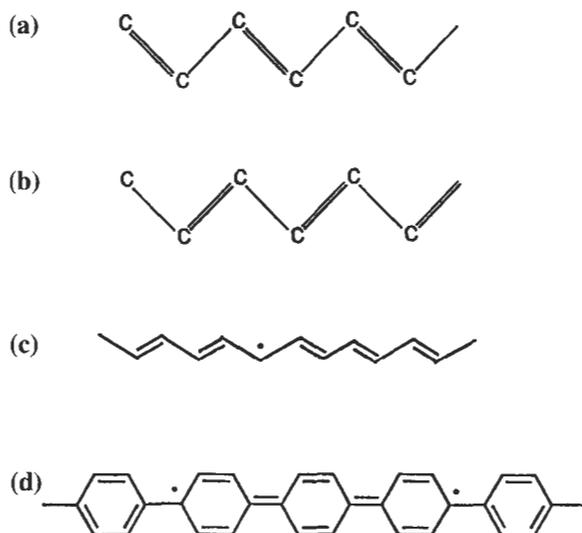
By the time the next overview of 'electrical properties of polymers' was published (Blythe 1979), besides a detailed treatment of dielectric properties it included a chapter on conduction, both ionic and electronic. To take ionic conduction first, ion-exchange membranes as separation tools for electrolytes go back a long way historically, to the beginning of the twentieth century: a polymeric membrane semipermeable to ions was first used in 1950 for the desalination of water (Jusa and McRae 1950). This kind of membrane is surveyed in detail by Strathmann (1994). Much more recently, highly developed polymeric membranes began to be used as electrolytes for experimental rechargeable batteries and, with particular success, for fuel cells. This important use is further discussed in Chapter 11.

About the time that 'synthetic metals' reached their apogee, twenty years ago, research began on semiconducting polymers. Today, at the turn of the century, such polymers have taken the center of the stage, and indeed promise some of the most important applications of polymers.

A completely separate family of conducting polymers is based on ionic conduction; polymers of this kind (Section 11.3.1.2) are used to make solid electrolyte membranes for advanced batteries and some kinds of fuel cell.

### 8.9.1 Semiconducting polymers and devices

The key concept in connection with semiconducting polymers is that of the *conjugated chain*. This is readily appreciated by examining a simplified diagram of the structure of poly(acetylene),  $C_nH_n$  (Figure 8.12), with the hydrogen atoms omitted. It can be seen that there is an alternation of single and double bonds. There are different ways of looking at the consequences of this conjugated configuration; one involves an examination of the electronic charge distribution in the bond orbitals (well explained, for instance, by Friend *et al.* 1999), but this falls outside my limits



**Figure 8.12.** A conjugated chain in poly(acetylene). (a) changes to (b) when a charge passes along the backbone of the molecule. (c) and (d) show chains of poly(acetylene) and poly(para phenylene) respectively, each containing solitons (after Windle 1996).

here. Another way (after Windle 1996) is that one can visualise charge moving along the chain by the stepwise movement of double bonds from (say) right to left (going from (a) to (b) in the figure). The key factor, now, is that in equilibrium the double bond is shorter than the single one by about 0.003–0.004 nm (only 1–2%), but this is still very significant. The bond length cannot catch up with the movement of electrons, because the latter is much faster than the phonon-mediated process which allows the bond length to change. This mismatch between actuality and equilibrium in the bond lengths brings about strain and hence an energy band gap, allowing semiconducting behaviour. The band gap is modified if there are ‘errors’ along the chain, in the form of solitons (Figure 8.12(c) and (d)); such defects are brought about by doping; in polymers, dopants have to be used at per cent levels instead of parts per million, as in inorganic semiconductors. An electron or hole will bind itself to a soliton, forming a charged defect called a polaron. For such conjugated chains to operate well in semiconducting mode, the polymer needs to be, and remain, highly stereoregular.

One of the earliest observations of high conductivity in such a material was in a form of poly(acetylene) by a Japanese team (Shirakawa and Ikeda 1971). Perhaps one should date the pursuit of semiconducting polymer devices from that experiment. It soon became clear that conjugated polymers had a severe drawback; most of them are extremely stable against potential solvents; they cannot be forced

into solution and furthermore are infusible (they decompose before they melt), hence the standard forms of polymer processing are unavailable. One way in which this was overcome was by starting with a single crystal of a monomer, diacetylene, and polymerising this in the solid state. However, cheapness is crucial to the success of polymer devices, in competition with other devices which have a headstart of decades, and further development awaited the invention of a synthetic trick (the 'Durham route', Edwards and Feast 1980), by which a precursor polymer which *is* soluble in common solvents was prepared cheaply and then heat-treated to produce poly(acetylene). More recently, the most useful semiconducting polymer, poly(phenylene vinylene), or PPV, has been made soluble by attaching appropriate sidechains to the phenylene rings. It can then be processed by spin-coating (in which a drop of solution is placed on a rapidly spinning substrate), which is a cheap way of preparing a thin uniform film. These processing tricks are surveyed by Friend (1994), who had set up two highly active research groups in Cambridge (one academic and one industrial), and also from a chemical perspective by Wilson (1998), who at that time was working with Friend.

By 1988, a number of devices such as a MOSFET transistor had been developed by the use of poly(acetylene) (Burroughes *et al.* 1988), but further advances in the following decade led to field-effect transistors and, most notably, to the exploitation of electroluminescence in polymer devices, mentioned in Friend's 1994 survey but much more fully described in a later, particularly clear paper (Friend *et al.* 1999). The polymeric light-emitting diodes (LEDs) described here consist in essence of a polymer film between two electrodes, one of them transparent, with careful control of the interfaces between polymer and electrodes (which are coated with appropriate films). PPV is the polymer of choice.

Friend *et al.* (1999) explain that polymeric LEDs have advanced so rapidly that they are now as efficient as the traditional tungsten-filament light bulb, and as efficient as the InGaN semiconductor lasers with their green light, announced at about the same time (Section 7.2.1.4). They also point out that, when a way is found to deposit polymeric LEDs on a polymer substrate instead of glass, they will become so cheap (especially if printing techniques can be used for deposition) that they will presumably make substantial inroads into the huge market for backlights in devices such as mobile telephones. If polymeric LEDs can be developed that will emit well-defined colours (at present they emit a broad wavelength range) then they will become candidates for full-color flat-screen displays, which is a market worth tens of billions of dollars a year.

The latest review of the status and prospects of 'polymer electronics' (Samuel 2000), by a young physicist working in Durham University, England, goes at length into the possibilities on the horizon, including the use of copolymer chains with a series of blocks with distinct functions, and the possible use of dendrimer molecules

designed to “have the designed electronic properties at the core and linked by conjugated links to surface groups, which are selected to control the processing properties”. Samuel also goes out of his way to underline the value of having “flexible electronics”, based on flexible substrates which will not break.

Polymers have come a long way from parkesine, celluloid and bakelite: they have become functional as well as structural materials. Indeed, they have become both at the same time: one novel use for polymers depends upon precision micro-embossing of polymers, with precise pressure and temperature control, for replicating electronic chips containing microchannels for capillary electrophoresis and for microfluidics devices or micro-optical components.

#### REFERENCES

- Aerts, L., Kunz, M., Berghmans, H. and Koningsveld, R. (1993) *Makromol. Chemie* **194**, 2697.
- Argon, A. and Cohen, R.E. (1989) *Adv. Polymer Sci.* **90/91**, 301.
- Bassett, D.C. (1981) *Principles of Polymer Morphology* (Cambridge University Press, Cambridge).
- Bastiaansen, C.W.M. (1997) High-modulus and high-strength fibres based on flexible macromolecules, in *Processing of Polymers*, ed. Meijer, H.E.H.; *Materials Science and Technology, A Comprehensive Treatment*, vol. 18, eds. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 551.
- Billmeyer, F.W. (1962) *Textbook of Polymer Science* (Wiley, Interscience, New York).
- Blythe, A.R. (1979) *Electrical Properties of Polymers* (Cambridge University Press, Cambridge).
- Bond, R. (1990) Tire adhesion: role of elastomer characteristics, in *Supplementary Volume 2 of the Encyclopedia of Materials Science and Engineering*, ed. Cahn, R.W. (Pergamon Press, Oxford) p. 1338.
- Boyd, R.D. and Badyal, J.P.S. (1997) *Adv. Mater.* **9**, 895.
- Brown, H.R. (1991) Adhesion between polymers, *Annu. Rev. Mater. Sci.* **21**, 463.
- Brown, H.R. (1995) *Phys. World* (January) p. 38.
- Bucknall, C.B. (1977) *Toughened Plastics* (Applied Science, London).
- Bunn, C.W. and Alcock, T.C. (1945) *Trans. Faraday Soc.* **41**, 317.
- Burroughes, J.H., Jones, C.A. and Friend, R.H. (1988) *Nature* **335**, 137.
- Campbell Scott, J. (1997) *Sci.* **278**, 2071.
- Charlesby, A. (1988) Radiation processing of polymers, in *Supplementary Volume 1 of Encyclopedia of Materials Science and Engineering*, ed. Cahn, R.W. (Pergamon Press, Oxford) p. 454.
- Cheng, S.Z.D. and Keller, A. (1998) *Annu. Rev. Mater. Sci.* **28**, 533.
- Ciferri, A. and Ward, I.M. (eds.) (1979) *Ultra-High Modulus Polymers* (Applied Science Publishers, London).
- Debye, P.J.W. (1944) *J. Appl. Phys.* **25**, 338.

- De Gennes, P.G. (1971) *J. Chem. Phys.* **55**, 572.
- Edwards, J.H. and Feast, W.J. (1980) *Polymer Commun.* **21**, 595.
- Edwards, S.F. (1976) The configuration and dynamics of polymer chains, in *Molecular Fluids*, eds. Balian, R. and Weill, G. (Gordon & Breach) London.
- Ferry, J.D. (1980) *Viscoelasticity of Polymers*, 3rd edition (Wiley, New York).
- Fettes, L.J. and Thomas, E.L. (1993) Model polymers for materials science, in *Structure and Properties of Polymers*, ed. Thomas, E.L. *Materials Science and Technology, A Comprehensive Treatment*, vol. 12, eds. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 1.
- Fischer, E.W. (1957) *Z. Naturforsch.* **12a**, 753.
- Flory, P.J. (1942) *J. Chem. Phys.* **10**, 51.
- Frank, F.C. (1970) *Proc. Roy. Soc., (London)* **319A**, 127.
- Friend, R.H. (1994) Conductive polymers, in *Encyclopedia of Advanced Materials*, vol. 1, eds. Bloor, D. *et al.* (Pergamon Press, Oxford) p. 467.
- Friend, R., Burroughes, J. and Shimoda, T. (1999) *Phys. World* **12**(6), 35.
- Furukawa, Yasu (1998) *Inventing Polymer Science: Staudinger, Carothers and the Emergence of Macromolecular Chemistry* (University of Pennsylvania Press, Philadelphia).
- Geil, P.H. (1963) *Polymer Single Crystals* (Wiley, Interscience, New York).
- Guth, E. and Mark, H. (1934) *Monatshefte Chem.* **65**, 93.
- Hanna, R.D. (1990) Polypropylene, in *Handbook of Plastic Materials and Technology*, ed. Rubin, I.I. (Wiley, New York).
- Hanna, S., Romo-Urbe, A. and Windle, A.H. (1993) *Nature* **366**, 546.
- Huggins, M.L. (1942) *J. Phys. Chem.* **46**, 151.
- Inoue, T. and Maréchal, P. (1997) Reactive processing of polymer blends: polymer-polymer interface aspects, in *Processing of Polymers*, ed. Meijer, H.F.H.; *Materials Science and Technology, A Comprehensive Treatment*, eds. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 429.
- Jaccodine, R. (1955) *Nature* **176**, 305.
- Janssen, H.M. and Meijer, E.W. (1999) Dendritic molecules, in *Synthesis of Polymers*, ed. Schlüter, A.-D. (Wiley-VCH, Weinheim) p. 403.
- Jérome, D. (1986) *Phys. Bull. (London)* **37**, 171.
- Jusa, W. and McRae, W.A. (1950) *J. Am. Chem. Soc.* **72**, 1044.
- Keith, H.D. (1963) in *Physics and Chemistry of the Organic Solid State*, eds. Fox, D. *et al.* (Wiley, Interscience, Chichester).
- Keith, H.D. and Padden, F.J. (1963) *J. Appl. Phys.* **34**, 2409.
- Keller, A. (1957) *Phil. Mag.* **2**, 1171.
- Keller, A. (1968) Polymer crystals. *Rep. Progr. Phys.* **31**, 623.
- Keller, A. (1979) Organization of macromolecules in the condensed phase, *Faraday Discussions of the Chem. Soc. (London)* (68), 145.
- Keller, A. (1991) in *Sir Charles Frank, OBE, FRS: An 80th Birthday Tribute*, eds. Chambers, R.G. *et al.* (Adam Hilger, Bristol) p. 265.
- Keller, A. (1995) *Macromol. Symp.* **98**, 1.
- Keller, A. and Cheng, S.Z.D. (1998) *Polymer* **39**, 4461.

- Keller, A. and Kolnaar, H.W.H. (1997) Flow-induced orientation and structure formation, in *Processing of Polymers*, ed. Meijer, H.E.H.; *Materials Science and Technology, A Comprehensive Treatment*, eds. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 189.
- Kinloch, A.J. (1987) *Adhesion and Adhesives* (Chapman & Hall, London).
- Kobayashi, S. (ed.) (1997) *Catalysis in Precision Polymerisation* (Wiley, New York).
- Lauritzen, J.I. and Hoffman, J.D. (1960) *J. Res. Natl. Bur. Standards* **A64**, 73.
- Léger, L. and Viovy, J.L. (1994) Polymers: diffusion and reptation, in *Encyclopedia of Advanced Materials*, vol. 3, eds. Bloor, D. et al. (Pergamon, Oxford) p. 2063.
- Lotz, B. and Wittmann, J.-C. (1993) Structure of Polymer Single Crystals, in *Structure and Properties of Polymers*, ed. Thomas, E.L.; *Materials Science and Technology, A Comprehensive Treatment*, eds. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 79.
- Mackley, M.R. and Keller, A. (1975) *Phil. Trans. Roy. Soc., (London)* **278A**, 29.
- McCrum, N.G., Read, B.E. and Williams, G. (1967) *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, London and New York) (Reprinted in 1991 by Dover).
- McCrum, N.G., Buckley, C.P. and Bucknall, C.B. (1998) *Principles of Polymer Engineering*, 2nd edition, (Oxford University Press, Oxford).
- McMillan, F.M. (1979) *The Chain Straighteners – Fruitful Innovation: The Discovery of Linear and Stereoregular Synthetic Polymers* (Macmillan, London).
- Meijer, H.E.H. (1997) Processing for properties, in *Processing of Polymers*, ed. Meijer, H.E.H.; *Materials Science and Technology, A Comprehensive Treatment*, vol. 18, eds. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 3.
- Meyer, K.H. Susich, G. von and Valkó, E. (1932) *Kolloid Z.* **59**, 208.
- Moore, J.C. (1964) *J. Polymer Sci.* **2**, 835.
- Morawetz, H. (1985) *Polymers: The Origins and Growth of a Science* (Wiley, New York, Constable, London) (Reprinted as a Dover edition in 1995).
- Morris, P.J.T. (1994) Synthetic rubber: autarky and war, in *The Development of Plastics*, eds. Mossman, S.T.I. and Morris, P.J.T. (Royal Society of Chemistry, London).
- Mossman, S.T.I. and Morris, P.J.T. (eds) (1994) *The Development of Plastics* (Royal Society of Chemistry, London).
- Müllen, K. (1999). Organic chemistry and the synthesis of well-defined molecules, in *Synthesis of Polymers*, ed. Schlüter, A.-D. (Wiley-VCH, Weinheim) p. 1.
- Pavelich, W.A. (1986) A path to ABS thermoplastics, in *High Performance Polymers: Their Origin and Development*, eds. Seymour, R.B. and Kirshenbaum, G.S. (Elsevier, New York) p. 125.
- Pennings, A.J., van der Mark, J.M.A.A. and Kiel, A.M. (1970) *Kolloid Z. und Z. Polymere* **236**, 99.
- Percec, V. et al. (1998) *Nature* **391**, 161.
- Petermann, J. and Gleiter, H. (1972) *Phil. Mag.* **25**, 813; *J. Mater. Sci.* **8**, 673.
- Raman, C.V. (1927) *Indian J. Phys.* **2**, 1.
- Robeson, I.M. (1994) Polymer blends, in *Encyclopedia of Advanced Materials*, vol. 3, eds. Bloor, D. et al. (Pergamon, Oxford) p. 2043.
- Samuel, I.D.W. (2000) *Phil. Trans. Roy. Soc., (London)* **A 358**, 193.

- Sawamoto, M. and Kamigaito, M. (1999) Living radical polymerisation, in *Synthesis of Polymers*, ed. Schlüter, A.-D. (Wiley-VCH, Weinheim) p. 163.
- Seymour, R.B. and Kirshenbaum, G.S. (eds.) (1986) *High Performance Polymers: Their Origin and Development* (Elsevier, New York).
- Shirakawa, H. and Ikeda, S. (1971) *Polymer J.* **2**, 231.
- Stockmayer, W.H. and Zimm, B.H. (1984) When polymer science looked easy, *Annu. Rev. Phys. Chem.* **35**, 1.
- Strathmann, H. (1994) Ion-exchange membranes, in *Encyclopedia of Advanced Materials*, vol. 2, eds. Bloor, D. *et al.* (Pergamon Press, Oxford) p. 1166.
- Strobl, G. (1996) *The Physics of Polymers* (Springer, Berlin).
- Tanner, R.I. and Walters, K. (1998) *Rheology: An Historical Perspective* (Elsevier, Amsterdam).
- Till, P.H. (1957) *J. Polymer Sci.* **24**, 301.
- Treloar, L.R.G. (1958) *The Physics of Rubberlike Elasticity* (Oxford University Press, Oxford).
- Treloar, L.R.G. (1970) *Introduction to Polymer Science* (Wykeham Publications, London).
- Van Krevelen, D.W. (1990) *Properties of Polymers*, 3rd edition (Elsevier, Amsterdam).
- Von Hippel, A.R. (1954) *Dielectric Materials and Applications* (Wiley, New York).
- Ward, I.M. (1971a) *Mechanical Properties of Solid Polymers* (Wiley, Interscience, New York).
- Ward, I.M. (ed.) (1971b) Orientation phenomena in polymers, *J. Mat. Sci.* (special issue) **6**, 451.
- Williams, G. (1993) Dielectric properties of polymers, in *Structure and Properties of Polymers*, ed. Thomas, E.L.; *Materials Science and Technology, A Comprehensive Treatment*, vol. 12, eds. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 471.
- Wilson, L.M. (1998) Conducting polymers and applications, in *Processing of Polymers*, ed. Meijer, H.E.H.; *Materials Science and Technology, A Comprehensive Treatment*, vol. 18, eds. Cahn, R.W., Haasen, P. and Kramer, E.J. (VCH, Weinheim) p. 659.
- Windle, A.H. (1996) A metallurgist's guide to polymers, in *Physical Metallurgy*, 4th edition, vol. 3, eds. Cahn, R.W. and Haasen, P. (North-Holland, Amsterdam) p. 2663.
- Young, R.J. (1974) *Phil. Mag.* **30**, 85.
- Young, R.J. (1988) *Materials Forum* (Australia) **11**, 210.



# Chapter 9

## Craft Turned into Science

9.1. Metals and Alloys for Engineering, Old and New	343
9.1.1 Solidification and Casting	343
9.1.1.1 Fusion Welding	348
9.1.2 Steels	348
9.1.3 Superalloys	352
9.1.4 Intermetallic Compounds	355
9.1.5 High-purity Metals	357
9.2. Plastic Forming and Fracture of Metals and Alloys and of Composites	358
9.3. The Evolution of Advanced Ceramics	362
9.3.1 Porcelain	362
9.3.2 The Birth of High-Tech Ceramics: Lamps	364
9.4. Sintering and Powder Compaction	367
9.4.1 Pore-free Sintering	372
9.5. Strong Structural Ceramics	375
9.5.1 Silicon Nitride	377
9.5.2 Other Ceramic Developments	379
9.6. Glass–Ceramics	380
References	385



## Chapter 9

# Craft Turned into Science

### 9.1. METALS AND ALLOYS FOR ENGINEERING, OLD AND NEW

In Section 3.2.1, something was said of the birthpangs of a new metallurgy early in the 20th century, and of the fierce resistance of the ‘practical men’ to the claims of ‘metallography’, which then meant ‘science applied to metals’. In this chapter, I shall rehearse some examples, necessarily in a cursory fashion, of how the old metallurgy became new, and then go on to say something of the conversion of the old ceramic science into the new. The latest edition of my book on physical metallurgy (Cahn and Haasen 1996) has nearly 3000 pages and even here, some parepistemes receive only superficial treatment. It will be clear that this chapter cannot do more than scratch the surface if it is not to unbalance the book as a whole.

#### *9.1.1 Solidification and casting*

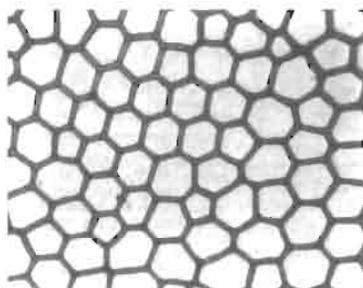
Metal objects can be shaped in one of three common ways: casting, plastic deformation, or the sintering of powder. For many centuries, shading back into prehistory, casting was a craft, with more than its due share of superstition. All kinds of magical additives, to the melt and to the mold, were sought to improve the soundness of cast objects; the memoirs of the great renaissance sculptor Benvenuto Cellini, for instance, are full of highly dramatic accounts of the problems in casting his statues and the magical tricks for overcoming them. Casting defects were a serious problem until well into this century. As recently as 1930, according to a memoir by Mullins (2000), the huge stern-post castings of heavy cruisers of the US Navy were apt to be full of defects and give poor service. Robert Mehl (see Section 3.2.1) then conceived the technique of gamma-ray radiography to detect defects in these large castings and, in the words of the memoir, “created a great sensation in engineering and practical metallurgical circles”; this was before the days of artificial radioisotopes.

Developments in casting since then fall into two categories, engineering innovations and scientific understanding of the freezing of alloys. It will come as no surprise to readers of this book that the two branches came to be linked. Among the engineering innovations I might mention are developments in molds – high-speed die-casting of low-melting alloys into metallic molds, casting into permanent ceramic molds – and then continuous casting of metallic sections, and ‘thixocasting’ (the use

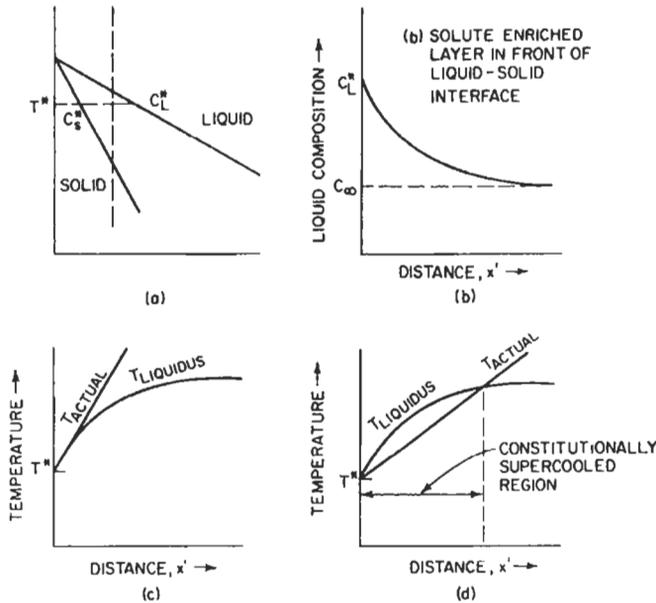
of a prolonged semi-solid stage to obviate casting defects). This is all set out in a classic text by Flemings (1974).

The understanding of the fundamentals of solidification is primarily the creation of Bruce Chalmers and his research school, first at Toronto University and from 1953 at Harvard. As it happens, I have an inside view of how this research came about. In 1947–1948, Chalmers (1907–1990; an English physicist turned metallurgist who had taken his doctorate with an eminent grower and exploiter of metal crystals, Neville Andrade in London) was head of metallurgy at the recently established Atomic Energy Research Establishment in Harwell, England, where I was a ‘new boy’. In his tiny office he built a simple meccano contraption with which he studied the freezing of tin crystals, a conveniently low-melting metal, whenever he had a spare moment from his administrative duties. (I recall exploiting this obsession of his by getting him to sign, without even glancing at it, a purchase order for some hardware I needed.) He would suddenly decant the residual melt from a partly frozen crystal and examine what had been the solid/liquid interface. Its appearance was typically as shown in Figure 9.1 – a ‘cellular’ pattern – and when at his request I prepared an etched section from just behind the interface, its appearance was similar; this suggested that impurities might be concentrated at the cell boundaries. He was determined to get a proper understanding of what was going on, for which he needed more help, and so in 1948 he accepted an invitation to join the University of Toronto in Canada. Two famous papers in 1953 (Rutter and Chalmers 1953, Tiller *et al.* 1953) established what was happening. The second of these papers appeared in the first volume of *Acta Metallurgica*, a new journal of fundamental metallurgy which Chalmers himself had helped to create and was to edit for many years (see Section 14.3.2).

Figure 9.2 shows the essentials. The metal being solidified is assumed to contain a small amount of dissolved impurity. (a) shows a typical portion of a phase diagram,



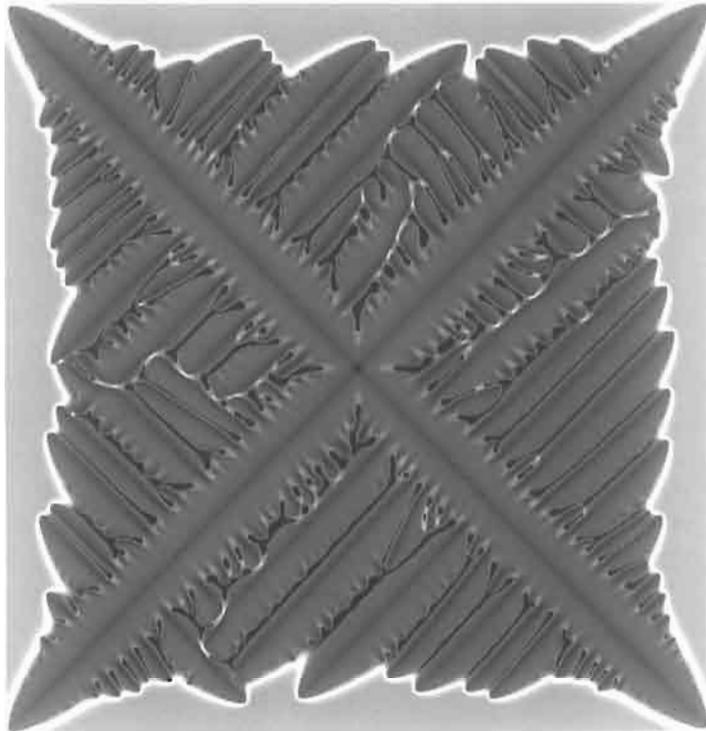
**Figure 9.1.** Decanted interface of cellularly solidified Pb–Sn alloy. Magnification  $\times 150$  (after Chadwick 1967).



**Figure 9.2.** Constitutional supercooling in alloy solidification: (a) phase diagram; (b) solute-enriched layer ahead of the solid/liquid interface; (c) condition for a stable interface; (d) condition for an unstable interface.

while (b) shows a steady-state (but non-equilibrium) enhanced distribution of the corresponding solute, caused by the limited diffusion rate of the solute during continuous advance by the solid. (c) and (d) show the corresponding distribution of the *equilibrium* liquidus temperature ahead of the solid/liquid interface, related to the local solute content. What happens then depends on the imposed temperature gradient: when this is high, (c), solidification takes place by means of a stable plane front; if a protuberance transiently forms in the interface, it will advance into a superheated environment and will promptly melt back. If the temperature gradient is lower, (d), the situation represents what Chalmers called *constitutional supercooling*. Instabilities in the form of protuberances now develop because the impure metal in these 'bumps' is below its equilibrium freezing temperature; each protuberance rejects some solute to its periphery, leading to the configuration of Figure 9.1. It is straightforward to formulate a theoretical criterion for constitutional supercooling: the ratio of temperature gradient to growth rate has to exceed a critical value. Numerous studies in the years following all confirmed the correctness of this analysis, which constitutes one of the most notable postwar achievements of scientific metallurgy. An account in recollection of this research can be found in Chalmers's classic text (1974).

Some years later, the analysis of the stability of inchoate protuberances was taken to a more sophisticated level in further classical papers by Mullins and Sekerka (1963, 1964) and Sekerka (1965), which took into account further variables such as thermal conductivities. The next stage, in the 1970s, was a detailed theoretical and experimental study of the formation of dendrites; these are needle-shaped crystals growing along favoured crystallographic directions, branching (like trees) into secondary and sometimes tertiary side-arms, and their nucleation is apt to be linked to interfacial instability of the type discussed here. Figure 9.3 shows a computer simulation of a dendrite array growing from a single nucleus into a supercooled liquid. The analysis of dendrite formation in terms of the geometry of the rounded tips and of supersaturation has been a hardy perennial for over two decades, and many experiments have been done throughout this time with transparent organic chemicals as means of checking the various elaborate theories. A treatment of this field can be found in a very detailed book chapter by Biloni and Boettinger (1996).



**Figure 9.3.** Computer simulation of dendrites growing into a Ni-Cu alloy with 41 at.% of Cu. The tints show local composition (courtesy W.J. Boettinger and J.A. Warren).

Earlier, a special issue of *Materials Science and Engineering* (Jones and Kurz 1984) to mark the 30th anniversary of the identification of constitutional supercooling includes 21 concise survey papers which constitute an excellent source for assessing the state of knowledge on solidification at that stage. Another source is a textbook (Kurz and Fisher 1984) published the same year.

The thixocasting mentioned above exploits dendritic solidification of alloys: a semi-solidified alloy is forged under pressure into a die; the dendrites are broken up into small fragments and a sound (pore-free) product is generated at a relatively low temperature, prolonging die-life. The array of related techniques of which this is one was introduced by Flemings and Mehrabian in 1971 and Flemings (1991) has recently reviewed them in depth.

Another major technical innovation in the casting field is the creation of non-brittle cast irons by doping with magnesium, causing the elemental graphite which is unavoidably present to convert from the embrittling flake form to harmless spherulites (rather like those described in Chapter 8 with respect to polymers). This work, perfected in the 1970s (Morrogh 1986), was an early example of nucleation control which has become very important in foundry work. A further example is the long-established 'modification' of Al-Si cast alloys by the addition of traces of sodium metal; the interpretation of this empirical method has given rise to decades of fundamental research. It is an example, not uncommon, of explanation after the event.

Such episodes of empirical discovery, followed only years later by explanation, were a major argument of the 'practical men' against the supposed uselessness of 'metallographists' (Section 3.2.1) but in fact the research leading to an explanation often smooths the way to subsequent, non-empirical improvements. A good recent instance of this was a study of the way in which grain-refining agents work in the casting of aluminium alloys. Fine particles of intermetallic compounds,  $\text{TiB}_2$  and  $\text{Al}_3\text{Ti}$ , have long been used to promote heterogeneously catalysed nucleation from the melt of solid grains, on an empirical basis. Schumacher *et al.* (1998) have shown how a metallic glass based on aluminum can be used to permit analysis of the heterogeneous nucleation process: grain-refining particles are added to an Al-Y-Ni-Co composition which is cooled at about a million degrees per second to turn it into a metallic glass (in effect a congealed liquid). This is equivalent to stopping solidification of a melt at a very early stage, so that the interface between the nucleation catalyst and the crystalline Al-alloy nucleus, and the epitaxial fit between them, can be examined at leisure by electron microscopy: it was shown that nucleation is catalysed on particular crystal faces of an  $\text{Al}_3\text{Ti}$  crystallite which is itself attached to a  $\text{TiB}_2$  particle. From this observation, certain methods of improving grain refinement were proposed. This is an impressive example of modern physical metallurgy applied to a practical task.

**9.1.1.1 Fusion welding.** One of the most important production processes in metallurgy is fusion welding, the joining of two metallic objects in mutual contact by melting the surface regions and letting the weld metal resolidify. Many different methods of creating the molten zone have been developed, but they all have in common a particular set of microstructural zones: primarily there is the fusion zone itself, then the heat-affected zone, a region which has not actually melted but has been unavoidably modified by the heat flowing from the fusion zone. In addition, internal stresses result from the thermal expansion and contraction acting on the rigidly held pieces that are being welded. The microstructure of the fusion zone in particular is sensitive to composition; in the case of steels, the carbon content has a particular influence.

Concise but very clear summaries of the microstructure of weld zones in steels are in book chapters by Honeycombe and Bhadeshia (1981, 1995), and by Porter and Easterling (1981), both of which also give references to more substantial treatments.

### **9.1.2 Steels**

Steel, used for armour, swords and lesser civilian purposes, had been the aristocrat among alloys for the best part of a millennium. European, Indian and Japanese armorers vied with each other for the best product. The singular form of the word is appropriate, since for much of that time 'steel' meant a simple carbon-steel, admittedly with variable amounts of carbon remaining after crude pig iron has been refined to make steel. That refining process, steelmaking, has been slowly improved over the centuries, with major episodes in the nineteenth century, involving brilliant innovators like Bessemer, Siemens and Thomas in Britain, and leading to quite new processes in the 20th century, developed in many parts of the world (notably the USA, Austria and Japan). A good summary of the key technological events in the evolution of steel, together with a consideration of economic and social constraints, is a lecture by Tenenbaum (1976). A concise summary of the key events can also be found in a very recent book (West and Harris 1999); even a British prime minister, Stanley Baldwin, a member of an ironmaster's family, played a small part. By the end of the 19th century, 'steels' properly had to be discussed in the plural, because of the plethora of alloy steels which had begun to be introduced.

Lessons can be learned from the aristocrat among early steel products, the Japanese samurai sword, which reached its peak of perfection in the 13th century. This remarkable object consists of a tough, relatively soft blade joined by solid-state welding to a high-carbon, ultrahard edge, complete with a decorative pattern rather like the later Damascus steel. The most recent discussion of the samurai sword is to be found in an essay by Martin (2000), significantly titled *Stasis in complex artefacts*.

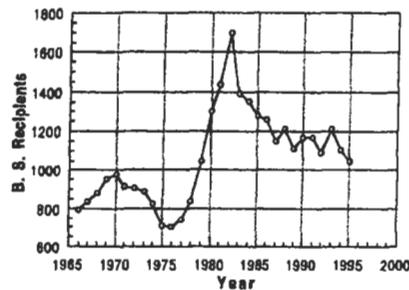
Martin points out the extremely complicated (and wholly empirical) steps which had evolved by long trial and error, involving multiple foldings and hammerings (which incidentally led to progressive carbon pickup from burning charcoal), followed by controlled water-quenching moderated by clay coatings of graded thickness. As Martin remarks: "The Japanese knew nothing of carbon. Neither did anyone else in the heyday of the sword: it was not identified as a separate material, an element, until the end of the 18th century. Nor did they know that they were adding this all-important material accidentally during the process of extraction of the iron from its ore, iron oxide (and more later, during hammering)." The clay-coating process had to be just right; the smallest error or peeling away of the coating would ruin the sword. So, as Martin emphasises, once everything at last worked perfectly, nothing must be changed in the process. "Having found a clay that works, in spite of (its) violent treatment, you treasure it. You lay hands on enough to last you through your career. . . . You will develop extreme caution in the surface finish of the steel to which you apply the slurry – not a hint of grease, not too smooth, a nice even oxide coating, but not a scale which could become detached. . . . The only way to achieve a success rate that can be lived with is to repeat each stage as exactly as possible." That represents craft at its highest level, but there is no science here. Once a craftsman has perfected a process, it must stay put. A scientific analysis, however, because it eventually allows an understanding of what goes on at each stage, allows individual features of a process to be progressively but rather rapidly improved. This change is essentially what began to happen in the late 19th century. It has to be admitted, though, that the classical Japanese sword, perfected empirically over centuries by superbly skilled and patient craftsmen, has never been bettered.

The scientific study of phase transformations in steel in the solid state during heat treatment, as a function of specimen dimensions and composition, then became a major branch of metallurgy; the way was shown by such classic studies as one by Davenport and Bain (1930) in America. This early study of the isothermal phase transformation of austenite (the face-centred cubic allotrope of iron), and the associated hardening of steel, was reprinted in 1970 by the American Society for Metals as one of a selection of metallurgical classics, together with a commentary placing this research in its historical context (Paxton 1970). This kind of research, including the study of the 'hardenability' of different steels in different sizes, is very well put in the perspective of the study of phase transformations generally in one of the best treatments published since the War (Porter and Easterling 1981).

After the Second World War, the technical innovations, both in steelmaking and in the physical metallurgy of steels, continued apace. A number of industrial research laboratories were set up around the world, of which perhaps the most influential was the laboratory of the US Steel Corporation in Pennsylvania, where some world-

famous research was done, both technological and scientific. In the 1970s, a wave of optimism supported industrial metallurgy, especially in America, and university enrolments in metallurgy and MSE courses burgeoned (Figure 9.4). Then, by 1982, to quote a recent paper (Flemings and Cahn 2000), “newspapers, magazines and the television were full of stories about the non-competitiveness of the steel industry, the automotive industry, and a host of other related industries. Hiring of engineers by these industries came to a halt and a long period of ‘downsizing’ began. Students associated the materials departments with these distressed industries and enrollments dropped abruptly. By 1984, the reduced enrollments had worked their way through to the graduating class.” This is very clear in Figure 9.4. Not only university courses felt the pinch; numerous industrial metallurgical laboratories, both ferrous and non-ferrous, were unceremoniously closed in America and in Europe, but not in Japan, where steelmaking and steel exploitation continued to make rapid progress. Since that time, steelmaking has acquired the unjust cachet of a ‘smokestack’ or ‘rustbelt’ industry.

Like all reactions, this one overshot badly. Steels are still by far the major class of structural metallic materials and the performance of steels, both high-grade alloy steels and routine carbon steels, has been steadily improved by the application of modern physical metallurgy and of modern process control. The most important development has been in microalloying – the evolution, via research, of steel types with small alloying additions, in fractions of 1%, and often also very low carbon contents. As a class, these are called high-strength low-alloy (HSLA) steels. One variant, used in large amounts for building work and bridges, is weathering steel, which is resistant to corrosion in the open, hence the name. A good account of this large and variegated new family of steels is by Gladman (1997). Other novel steel families, such as the dual-phase family (martensite in a matrix of ferrite), maraging steels (precipitation-hardened martensites, used where extreme strength is needed),



**Figure 9.4.** US bachelor's degrees in metallurgy and materials, numbers graduating 1966–1995 (after Flemings and Cahn 2000).

and a variety of tool steels for shaping and cutting tools, have been developed for special needs; much of this development has been done in the past two decades in the supposedly decaying smokestack plants, in spite of the gradual disappearance of research laboratories dedicated to steels.

Perhaps the most important innovation of all is in the thermomechanical control processes, involving closely controlled simultaneous application of heat and deformation, to improve the mechanical properties, especially of ultra-microalloyed compositions. Processes such as 'controlled rolling' are now standard procedures in steel mills.

The Nippon Steel Corporation in 1972 pioneered the use of 'continuous annealing lines', in which rolled steel sheet is heat-treated and quenched under close computerised control while moving. For this advanced process to give its best results, especially when the objective is to make readily shapable sheet for automobile bodies, steel compositions have to be tailored specifically for the process; composition and processing are seamlessly tied to each other. Today, dozens of these huge processing lines are in use worldwide (Ohashi 1988).

Part of the 'specific tailoring' of steel compositions to both the processing procedure and to the end-use is the steady move towards *clean steels*, alloys with, typically, less than 20 parts per million in all of undesired impurities, and especially of insoluble inclusions. Such steels are now standard for automobile bodies, drawn steel beverage cans, shadow masks for colour TV tubes, ball-bearings and gas piping. The elements that need specific control include P, C, S, N, H, Cu, Ni, Bi, Pb, Zn and Sn (many of these threaten to increase when scrap steel is used in steelmaking). It is noteworthy that carbon, once the defining constituent of steel, is now an element that needs to be kept down to a very low concentration for some applications. An account of 'high-purity, low-residual clean steels' and the methods of removing unwanted impurities is by Cramb (1999). Advanced modern methods of high-temperature chemistry, such as electroslag refining, are needed for such purification.

Two good general overviews of the design and processing of modern steels are by Pickering (1978, 1992).

To conclude this section, I want to return to the 'anti-smokestack' convulsion of the early 1980s. Figure 9.4 shows clearly that even after the shakeout in student numbers, numbers graduating remain above the levels of the 1960s and 1970s, which were a time of greater optimism. As the few comments here have shown, steel metallurgy, as a kind of indicator for metallurgy as a whole, is in rude good health; much has been achieved in recent decades, and there is more to do. I will conclude with a comment at the end of a recent survey article entitled *From the Schrödinger Equation to the Rolling Mill* (Jordan 1996): "The present time is one of unprecedented opportunities for alloy research, particularly for exciting basic science and its possible exploitation".

### **9.1.3 Superalloys**

Superalloys as a class constitute the currently reigning aristocrats of the metallurgical world. They are the alloys which have made jet flight possible, and they show what can be achieved by drawing together and exploiting all the resources of modern physical and process metallurgy in the pursuit of a very challenging objective.

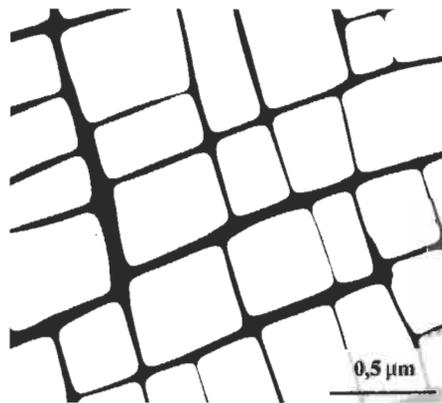
Steam turbines were patented by Charles Parsons in England in 1884 and in 1924, Ni–Cr–Mo steels were introduced to improve the performance of turbine rotors. These can be regarded as early precursors of superalloys. The modern gas turbine, a major enhancement of the steam turbine because combustion was no longer external to the turbine, was invented independently in Germany and Britain in 1939. The adjective ‘modern’ is needed here because simpler forms were developed much earlier. Old country houses open to visitors in Britain dating from the 17th century sometimes contain simple turbine wheels that turn in the warm updraft from a domestic fireplace and are linked to a rotating spit for roasting meat. In the early 1930s, turbochargers, essentially small gas turbines used to compress and heat incoming air, were developed to allow internal combustion (reciprocating) aero engines to work at high altitudes where the partial oxygen pressure is low, and they are used now to upgrade the acceleration of advanced automobile engines even at sea level. Propelling a plane entirely by means of a pure jet powered by a gas turbine was another challenge altogether, first met by Hans von Ohain in Germany and Frank Whittle in Britain about the time the Second World War began in 1939. Alloys had to be found to make the turbine blades, the disc on which they are mounted and the remaining hot constituents such as the combustion chamber, as well as the compressor blades at the front of the engine which do not become so hot. Since the first engines, the ‘hot alloys’ have been nickel-based and remain so today, 60 years later, though at intervals cobalt gets a look-in as a base metal when the African producers are not so embroiled in chaos that supplies are endangered. The operating temperature limit of superalloys increased from 700°C in 1950 to about 1050°C in 1996.

The evolution of superalloys has been splendidly mapped by an American metallurgist, Sims (1966, 1984), while the more restricted tale of the British side of this development has been told by Pfeil (1963). I have analysed (Cahn 1973) some of the lessons to be drawn from the early stages of this story in the context of the methods of alloy design; it really is an evolutionary tale. . . the survival of the fittest, over and over again. The present status of superalloy metallurgy is concisely presented by McLean (1996).

Around 1930, in America, presumably with the early superchargers in mind, several metallurgists sought to improve the venerable alloy used for electric heating elements, 80/20 nickel–chromium alloy (nichrome), by adding small amounts of titanium and aluminum, and found significant increase in creep resistance.

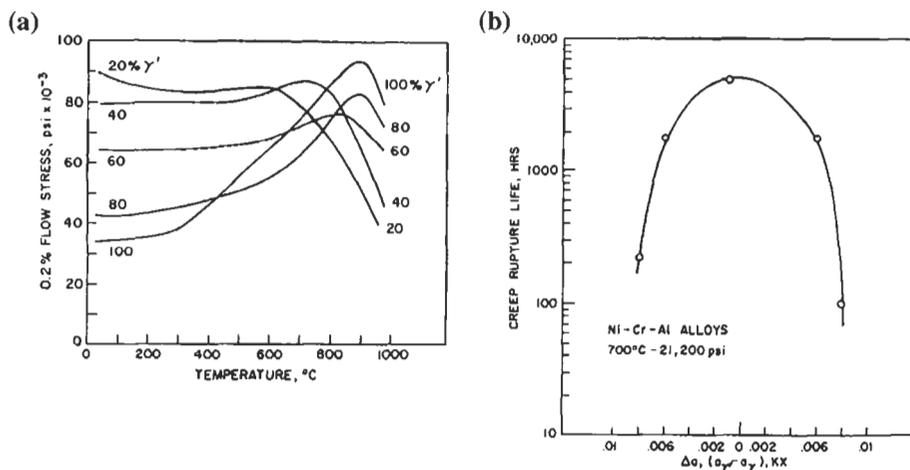
According to Pfeil's version of events, in Britain in the early 1940s, creep tests were at first made on ordinary commercial nichrome, but the results were not self-consistent; this was traced to differences in titanium and carbon content resulting from the use of titanium as a deoxidiser. A little later, a nickel–titanium additive with some aluminum was tried. The first superalloy, Nimonic 75, was made by 'doping' nichrome with controlled small amounts of carbon and titanium. From there, development continued on the hypothesis (which metallurgists had formulated in the 1930s but had been unable to prove) that creep resistance was conditional on precipitation-hardening. At this stage, in a British industrial laboratory in Birmingham, phase diagram work was thought essential, and the key to all superalloys was established by Taylor and Floyd (1951–1952), at the time of what I have called the 'quantitative revolution': they found that age-hardening in the early superalloys was entirely due to the ordered intermetallic phases  $\text{Ni}_3\text{Al}$  and  $\text{Ni}_3\text{Ti}$ , or rather a mixed intermetallic,  $\text{Ni}_3(\text{Al}, \text{Ti})$ , a phase they dubbed  $\gamma'$ , gamma prime, as it is still called, dispersed in a more nickel-rich, disordered matrix, called gamma. A little later it became clear that the microstructure (Figure 9.5) was an epitaxial arrangement; both phases were of cubic crystallography and their cube axes were parallel (this was the epitaxial feature); also the structure was extremely fine in scale. The microstructure was reminiscent of the Widmanstätten structures studied by Barrett and Mehl in Pittsburgh in the 1930s (see Section 3.2.2 and Figure 3.16) but finer, and with one important difference: the lattice parameters (length of the sides of the cubic unit cells) of gamma and gamma prime were almost identical. This turned out to be the key to superalloy performance.

The gamma prime phase has the highly unusual characteristic, first discovered by Westbrook (1957), of becoming stronger with increasing temperature, up to



**Figure 9.5.** Electron micrograph of a superalloy, showing ordered (gamma prime) cuboids dispersed epitaxially in a disordered (gamma) matrix (courtesy of Dr. T. Khan, Paris).

about 800°C. The reasons for this, closely linked to the geometry of dislocations in this ordered phase, have been argued over for decades and have at last been resolved at the end of the century – but the details do not matter here. As Figure 9.6(a) – taken from an important study, by Beardmore *et al.* (1969) – demonstrates, the  $\gamma/\gamma'$  alloys, if they contain only about 50% of the disordered matrix, no longer show this anomaly, but they are as strong at room temperature as the ordered phase is at high temperature; this is the synergistic effect of the two phases together. Even more important is the quality of the fit between the two phases. Figure 9.6(b) shows that the creep-rupture life (the time to fracture under standardised creep conditions) rises to a very intense maximum when the lattice parameter mismatch is only a small fraction of 1%. In fact, it turned out that the creep resistance is best when (a) the parameter mismatch is minimal, and (b) the volume fraction of gamma prime is as high as feasible. (Decreasing the lattice mismatch from 0.2% to zero led to a 50-fold increase in the creep rupture life!) These insights come under the heading of ‘phenomenological’. The conditions for optimum creep resistance are quite clear in terms of measurable variables, but *why* just this microstructure is so effective is still today the subject of vigorous discussion: the consensus seems to be that dislocations are constrained to stay in the narrow ‘corridors’ of the matrix and are prevented from crossing into the ordered cuboids, in part because the equilibrium dislocation configuration is quite different in the corridors and in the cuboids. We have here an example of a clear phenomenology and a disputed



**Figure 9.6.** (a) The temperature dependence of the flow stress for a Ni-Cr-Al superalloy containing different volume fractions of  $\gamma'$  (after Beardmore *et al.* 1969). (b) Influence of lattice parameter mismatch, in kX (effectively equivalent to Å) on creep rupture life (after Mirkin and Kanchev 1967).

aetiology to go with it (see footnote on page 206) – a common enough situation in materials science.

There is one other feature that distinguishes the microstructure of Figure 9.5, and that is its stability. Normally, a metallurgist would expect a population of tiny precipitates to coarsen progressively at high temperature. This crucial process, known as *Ostwald Ripening*, after the German physical chemist Wilhelm Ostwald whom we met in Chapter 2 and who first recognised it, arises because the solubility of a small sphere in the matrix is greater than that of a large sphere, so that the large precipitates will grow larger, the small will disappear. The kinetics of increase of average particle size, which turn out to be linear in time  $1/3$ , depend on the interfacial energy, the diffusion rate of the solute in the matrix, and its solubility. The theory was developed more or less simultaneously by scientists in England, Germany and Russia, but the father of the theory is usually held to be Greenwood (1956) in England. The theory indicates that one way of reducing the rate of coarsening is to reduce the interfacial energy between the particles and the matrix, and in the case of superalloys, this energy is reduced to a negligible value by ensuring a very close match of lattice parameters. This helps to explain the form of the plot in Figure 9.6(b).

As we learn from Sims's reviews, many other improvements have been made to superalloys and to their exploitation in recent decades. Solid-solution strengthening, grain-boundary strengthening with carbides and other precipitates, and especially the institution, some twenty years ago, of clean processing which allows the many unwanted impurities to be avoided (Benz 1999) have all improved the alloys to the point where (McLean 1996) the best superalloys now operate successfully at a Kelvin temperature which is as much as 85% of the melting temperature; this shows that the prospect of significant further improvement is slight.

On top of this alloy development, turbine blades for the past two decades have been routinely made from single crystals of predetermined orientation; the absence of grain boundaries greatly enhances creep resistance. Metallic monocrystals have come a long way since the early research-centred uses described in Section 4.2.1.

All the different aspects of the processing and properties of superalloys, including monocrystals, are systematically set out in chapters of an impressive book (Tien and Caulfield 1989). The latest subtleties in the microstructural design of monocrystal superalloys are set out by Mughrabi and Tetzlaff (2000); among other new insights, it now appears that the optimum misfit between the two major phases is not exactly zero.

#### **9.1.4 Intermetallic compounds**

In Section 3.2.2, I briefly introduced the family of ordered intermetallic compounds, of which  $\text{Cu}_3\text{Au}$  was the first to be identified, early in the 20th century. We saw in the discussion of superalloys that such phases,  $\text{Ni}_3\text{Al}$  in particular, have a crucial role

to play in modern metallurgy as constituents of multiphase heat-resistant alloys. Following the Second World War, moreover, resolute attempts have been pursued to develop single-phase intermetallics (as they are called for short) as engineering materials in their own right. A substantial fraction of published papers in physical metallurgy at present is devoted to intermetallics, in pursuit of what some regard as a hopeless dream and others perceive as a sober venture.

In the 1950s and 1960s, research focused on 'reversibly ordered' intermetallics, such as  $\text{Cu}_3\text{Au}$ ,  $\text{CuAu}$ ,  $\text{FeCo}$ ,  $\text{Fe}_3\text{Al}$ ,  $\text{Ni}_4\text{Mo}$ . The idea was to compare the properties, especially mechanical and electrical properties, of the same specimen in fully ordered, imperfectly ordered and disordered states, and these states could be produced by suitable heat-treatment and quenching (e.g., Stoloff and Davies 1966). Of those listed above, only  $\text{Ni}_4\text{Mo}$  has found appreciable use in high-temperature alloys. From the 1970s onwards, attention was drastically transferred to 'permanently ordered' alloys, alloys which are so strongly ordered that they remain so on heating until they melt, such as  $\text{Ni}_3\text{Al}$ ,  $\text{NiAl}$ ,  $\text{FeAl}$ ,  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ ,  $\text{Nb}_3\text{Al}$ , and investigation focused on creep resistance (closely linked to the magnitude of the ordering energy) and also on the Achilles's heel of the entire family, brittleness at room temperature (Yamaguchi and Imakoshi 1990). The brittleness results partly from the difficulty of driving dislocations through the strongly bonded unlike atom pairs making up the crystal structure, and partly, as we now know, from 'environmental embrittlement' the passage of hydrogen, from water vapour, along grain boundaries. Once again, grain boundaries have proved to be a key concern in determining the behaviour of a new family of metallic materials. In these researches, all the sophisticated techniques of modern characterisation, processing and mechanical analysis are in constant use, and alloying has been systematically used both to reduce the brittleness and to enhance high-temperature strength. This field is unmistakably in the province of the 'new metallurgy'.

Nickel and iron aluminides have now been improved to the point where they are routinely used for a number of terrestrial applications, especially for components of furnaces (Deevi *et al.* 1997). These two families have also been critically evaluated in depth (Liu *et al.* 1997). The central hope of the large and international research community, however, is to improve lightweight intermetallics, especially  $\text{TiAl}$ , to the point where they can be used to make key components of jet engines, especially turbine discs and blades. Technologically, that stage seems to be within sight, in spite of the very limited ductility of  $\text{TiAl}$ , but in terms of expense, the very cost-conscious jet-engine industry is proving hard to convince. Another usage,  $\text{TiAl}$  blades for the rotors of automotive turbochargers (a kind of return to the first gas turbines of the 1930s but at a higher temperature) has required years of painstaking development, and is at last about to go into large-scale use, especially in Japan where those who finance such research have proved strikingly patient (see a group of 27 Japanese

papers devoted to intermetallics, Yamaguchi 1996). A fine recent overview of the whole intermetallics field is a book by Sauthoff (1995). A cynical comment made by one industrial researcher some 30 years ago, that intermetallics are the materials of the future and always will be, is not being echoed so frequently now. The jury remains out.

### **9.1.5 High-purity metals**

Repeatedly in this book, the important functions of 'dopants', intentional additives made in small amounts to materials, have been highlighted; the use of minor additives to the tungsten used to make lamp filaments is one major example. The role of impurities, both intentional and unintentional, in matters such as phase transformations, mechanical properties and diffusion, was critically reviewed in one of the early seminar volumes published by the American Society for Metals (Marzke 1955). But extreme purity was not considered; that came a little later.

In Chapter 7 the invention, by William Pfann at the Bell Telephone Laboratories, of zone-refining of silicon and germanium was outlined. This process, in which successive narrow molten zones are made to pass along a crystal so that dissolved impurities are swept along to one end where they can be cut off and discarded, made a huge impact at the time (1954) because it was rightly seen as one of the keys to the creation of the transistor. It was thus to be expected that metallurgists would wish to apply the technique to traditional metals with a view to improving their engineering properties, and this approach got under way in the late 1950s. By 1961, enough progress had been made, in North America and France, for a seminar to be organised in 1961 and its proceedings published the next year (Smith 1962). Pfann himself gave the inspirational opening talk, entitled "Why ultra-pure metals?" Both chemical and electrolytic methods of achieving extreme purity, and zone-refining methods, were treated, as well as the mechanical, electrical, thermoelectric properties of a range of metals (iron particularly) and their recovery and recrystallization after plastic deformation. It has to be admitted that nothing remotely comparable in importance with zone-refining of semiconductors was discovered.

Meanwhile, a group of researchers at the GE Corporate Research Laboratory, led by J.D. Cobine, had made a striking discovery. The company was interested in manufacturing an effective high-amperage sealed vacuum circuit breaker (power switch) for electrical utilities, to obviate fire hazard and to allow reduction of the gap between the electrodes and thus very rapid operation. Electrical engineers had been striving to perfect such a device ever since the 1920s, but it turned out that the operation of the switch released gases from the copper electrodes and this destroyed the vacuum in the sealed enclosure. In 1952, Cobine and his team zone-refined the copper from which the electrodes were to be made and found, to their astonishment, that the residual gas content in the resultant single crystals was less than one part in

10 million. A little later, GE's switchgear division used this copper for experimental sealed vacuum circuit breakers and the procedure was patented, from 1958 on, and led to a major industry. This was not sufficiently well known outside the world of electrical engineering to have found its way to the 1961 ASM Seminar. A detailed account of the sequence of events that led to this important breakthrough was published by two retired GE research directors in a little-known book which deserves to be widely read even today (Suits and Bueche 1967).

40 years later, ultra-pure copper is still being manufactured, in Japan, by a combination of electrolytic refining, vacuum-melting and floating-zone zone-refining (Kato 1995). The long-established 5N grade (i.e., 99.999% pure) is now replaced by 7N grade, that is, less than 0.1 part per million of (non-gaseous) impurities. Residual resistivity (at liquid helium temperature) is the best approximate way of estimating purity of such metals, since chemical analysis is approaching its limits. Industrially, this ultrapure copper is used in Japan for wires in hi-fi audio systems (it is actually claimed that its use improves the quality of sound reproduction!), and also as starting-material for lightly alloyed wires for various robotic and microcircuit uses. A more fundamental approach was taken by Abiko (1994) who continued the long-established tradition of purifying iron (by electrolytic refining) so as to establish a database of the properties and, again, to have a pure base for subsequent trace alloying. A few highly unconventional uses have been described, for instance, a German procedure for making highly reflective X-ray monochromator devices for synchrotron sources, using ultrapure beryllium monocrystals.

Independently of all this, for many years an isolated institute in East Germany (Dresden) carried out careful research on ultrapure refractory metals such as Mo, W, Nb (Köthe 1994); this was at a time when these heat-resistant metals were exciting more interest than they are now.

The upshot of all this research since 1954 is rather modest, with the exception of the GE research, which indicates that techniques and individual materials have to be married up; an approach which is crucial for one material may not be very productive for another. This is of course not to say that this 40-year programme of research was wasted. The initial presumption of the potential value of ultra-pure metals was reasonable; it is the obverse of the well-established principle that minor impurities and dopants can have major effects on the properties of metals.

## **9.2. PLASTIC FORMING AND FRACTURE OF METALS AND ALLOYS AND OF COMPOSITES**

In this book, the process of plastic deformation and the related crystal defects have been discussed repeatedly. In Section 2.1.6, the distinction between continuum

mechanics and atomic mechanics was set out; in Section 3.2.3.2, the early history of research on dislocations was outlined, Section 4.2.1 was devoted to the crucial role of metal crystals in studying plasticity, and in Section 5.1, the impact of quantitative approaches on the understanding of dislocations and their interactions was reported. If there were space, it would be desirable now to give a detailed account of one of the most active fields of research in the whole of MSE – the interpretation of yield stresses, strain-hardening, fatigue damage and creep resistance in terms of dislocation geometry and dynamics, and also of the related field of fracture mechanics. The study of plasticity is largely an exercise in what I have called atomic mechanics; the study of fracture, one in continuum mechanics. However, to avoid unbalancing the book, I can only find space for a bare outline of these fields, together with a brief discussion of the engineering use of plastic forming methods in what is sometimes unkindly called ‘metal bashing’.

The resistance to plastic flow at ambient temperature is linked to the ‘strength’ of dislocation sources such as that illustrated in Figure 3.14, together with the operation of various obstacles to dislocation motion (dispersed particles, solutes and, indeed, other dislocations intersecting the moving ones). In some metals the Peierls force ‘tying’ a dislocation to the lattice is high enough to affect flow stresses as well. Other structural features, such as stacking-faults in close-packed metals and partial long-range order, also influence the motion of dislocations. All these interactions have been modelled and the ‘constitutive equations’ which emerged are used, *inter alia*, to draw deformation-mechanism maps (Section 5.1.2.2). The theme that has proved most obdurate to accurate modelling is strain-hardening, the gradual hardening of any metal as it is progressively deformed, because here dislocation dynamics have to be combined with a statistical approach. An outline history of some of these themes, especially the transition from monocrystal to polycrystal mechanics, has recently been published (Cahn 2000). Detailed facts and models are to be found in a comprehensive and authoritative volume (Mughrabi 1993), while the distinctive topic of fatigue damage after cycles of stressing in opposed directions, a most crucial theme in engineering practice, has been excellently treated by Suresh, in a book (1991) and also in the Mughrabi volume.

The termination of plastic deformation by fracture, or brittle fracture in the absence of plastic deformation, might be thought to be something that does not warrant much attention since fracture signals the end of usefulness. This would be a big mistake: the quantitative study of fracture, *and its avoidance*, has been one of the most fruitful fields since the Second World War. That field is nowadays called *fracture mechanics*, and it emerged from the ideas of A.A. Griffith (Section 5.1.2.1 and Figure 5.4), first applied in the 1920s to the statistically very variable fracture stress of glass fibers. Griffith, as we have seen, postulated a population of sharp surface cracks of varying depth, together with a simple but potent elastic analysis of

how such a crack will magnify an applied tensile stress, to an extent depending simply on the crack depth. When the applied stress is large enough, but very much smaller than the theoretical intrinsic strength of the perfect crystal, Griffith's analysis shows that it is energetically favourable for the crack to advance explosively and lead to fracture, unless the material is capable of plastic deformation which will blunt the crack, impede its stress-magnifying function and thus arrest its spread. Although it took many years before the postulated 'Griffith cracks' were observed micrographically (Ernsberger 1963), his theory was widely accepted 'sight unseen', so to speak. Griffith's ideas, combined with statistical arguments, were particularly fruitful in interpreting the brittle fracture resistance of glass and ceramics. Because of the statistical distribution of crack sizes and the crucial role of the surface in initiating fracture, fracture resistance of strong, brittle fibres is a function of surface area and therefore of fibre diameter. The standard text is by Lawn and Wilshaw (1975, 1993).

There is in fact a continuous gradation from highly brittle materials to thoroughly ductile ones, those in which cracks cannot advance because they are at once blunted by local plastic deformation. In others, finely dispersed obstacles keep on diverting and finally arresting advancing cracks, all the time absorbing energy, that is, enhancing the work of fracture. The aim is always to secure as large a work of fracture as possible, together with a high yield stress. Section 9.5, below, cites examples of this strategy in action.

Fracture of plastically deformable metals and alloys, steels in particular, became a matter of great concern during the Second World War because large numbers of merchant ships were for the first time fabricated by welding (to save construction time) and some of them broke in two when buffeted by storms in cold winter waters. This was, to put the matter crudely, because a steel has a brittle/ductile transition in a critical temperature range, and welded ships (as distinct from rivetted ships) have no discontinuity to stop a running crack from propagating. The brittleness fostered by notches that locally enhance the applied stress was analysed by Orowan (1952), followed by a more sophisticated treatment of Griffith's model by Irwin (1957), called the stress-intensity approach, which then gave birth to the modern science of *fracture mechanics*. This allows the fracture risk of semi-brittle or plastic metals, complete with intrinsic defects, to be rationally assessed, and a stress limit for safe use to be calculated. The approach is crucial in engineering design today, for ships, bridges, pressure vessels in particular, and many other structures, and allows such structures to be designed with high confidence that fracture will be avoided under specified conditions of loading. The standard text is by Knott (1973).

Not all fracture is by crack propagation. Highly ductile materials stressed at high temperature will eventually break by the growth, through absorption of lattice vacancies, of plastic voids. This shades into the phenomenon of superplasticity, which was examined in Section 4.2.5.

There is a paradox at the heart of the design of very strong solids: in general, the higher the intrinsic strength (largely a matter of very strong covalent chemical bonds as found in ceramics), the more subject the solid is to premature fracture by crack propagation. The way round this paradox is to combine ultrastrong ceramic or graphite fibers with a relatively soft matrix, normally either of polymer or of metal, but latterly also of ceramic. (It is even possible to have a composite in which both phases are chemically identical, such as carbon/carbon composites, used for aircraft brakepads – graphite fibers dispersed in a vapour-generated amorphous carbon matrix.) The fibers both reinforce the matrix (like the steel rods in reinforced concrete) and act as efficient crack-arresters, so that the material can be fracture-resistant (tough) even if neither constituent is plastically deformable (as in rubber-toughened polymer blends, Section 8.5.3). This strategy has led to the large domain of *synthetic composite materials*, of which glass-reinforced epoxy resins were the first and best known, used from about 1950 on; wood, of course, is the archetype of a natural composite material. Again, there is no space here to do more than indicate the existence of this very important field, and to point to an early standard text (Kelly 1966, 1986), a detailed account of the microstructural design of fiber composites (Chou 1992), together with a recent text about the various kinds of reinforcing fibers (Chawla 1998) and another book focused on metal–matrix composites (Clyne and Withers 1993). The various types of fiber-reinforced composites have in common the theory that governs their mechanical behaviour: this quite elaborate body of micromechanics covers such features as pullout of fibers from the matrix, statistics of strength of fibers as a function of diameter, arresting and diversion of advancing cracks, anisotropy of properties in relation to orientation distribution of fibers. Kelly's book in its first (1966) edition was the first compilation of this body of general theory of composites. In a recent article (Kelly 2000) he illustrates modern applications of fibre-reinforced composites and also goes in some detail into the history of their development, with special emphasis on Britain.

The main reason why metals are the principal category of structural materials is that they are plastically deformable, which both prevents sudden, catastrophic fracture and allows the material to be plastically shaped to a desired form. Again, no room can be found here to discourse on the large field of metal-forming – rolling, forging, extrusion, wire-drawing, deep drawing of sheet. These techniques are mostly analysed by continuum mechanics, and in this way, for instance, the forces and power requirements in a planned rolling mill, say, or an extrusion press, can be estimated in advance of construction. I will point out only one aspect which cannot be encompassed by a continuum approach, and that is the generation of *deformation textures*. This is the statistical tendency of the millions of grains in a plastically deformed polycrystal to approximate to a single orientation, with statistical scatter. This is important for two reasons: the building up of texture can interfere with the

further plastic deformation of the material, and if the material is elastically or in some other way anisotropic, then the properties of the resultant sheet, rod or wire, mechanical properties in particular, will be different in different directions. This two-way interaction between textures and plastic deformation has been very clearly explained in a recent standard text (Kocks *et al.* 1998). The deep drawing (shaping) of steel sheet to make automobile bodies depends on close control of texture if the sheet is not to crack at sites of locally intense deformation, and the drawing of aluminum alloy sheet into beverage cans, now a huge industry worldwide, is only feasible if the texture is so controlled (inter alia, by annealing, which changes the texture) that deformation is accurately isotropic; this has required many years of development work on the optimum composition and precise processing of aluminum alloy sheet (e.g., Hutchinson and Ekström 1990). Textures are determined by a variant of polycrystal x-ray diffraction, and in the 80 years since research on this began, a huge mass of information and interpretation has been accumulated. Two recent overviews are by Cahn (1991), and by Randle and Engler (2000) who write especially on microtextures, which are concerned with the statistics of misorientations across a population of grain boundaries. We saw in Section 7.2.2.4 how microtextures in superconducting ceramics determine the magnitude of the current that can be carried before superconduction is destroyed.

### **9.3. THE EVOLUTION OF ADVANCED CERAMICS**

#### **9.3.1 *Porcelain***

The production of ceramic containers, and of statuettes, is the oldest of man's major crafts, certainly older than metalworking. Containers were needed to store liquids and grain, i.e., for use; statuettes were made for religious ritual and also to please the eye of aristocrats. Thus from early in man's development as a technologist, utility and beauty were twin criteria. Often these criteria were combined, in the manufacture of decorated pots and statuettes, and the high point of this pursuit was undoubtedly Chinese porcelain, which was first made during the Tang dynasty (618–907 AD) and reached perfection during the Sung dynasty, in the mid-13th century (about the same time as the Japanese sword reached its apogee). Marco Polo in that century brought back a specimen of Chinese porcelain, still exhibited in Venice today. For a long time, Chinese porcelain (and to a much lesser extent, Japanese and Indian forms of porcelain) was assiduously exported to Europe; western demand was insatiable for this magical material, white, thin, strong, translucent and beautifully decorated. Europeans tried over and over to reproduce it, increasingly from the late 16th century onwards, when Florentine potters came close; French potters succeeded in making a somewhat inferior version of porcelain (the

'soft-paste' variety) at St. Cloud and Vincennes from about 1720 onwards. This material, however, tended to sag in the kiln and shape control was thus very difficult. True Chinese-style porcelain, known as 'hard-paste', was not made until 1709, by Johann Böttger (1682–1719), who was kept as a captive for many years by Augustus, the ruler of Saxony. Böttger was a self-proclaimed alchemist, and Augustus kept him in his castle for many years under repeated threat of death if he did not manufacture gold, the key 'arcanum' of his time. Böttger did not make gold directly, but he did make it indirectly for his demanding master: he found out, instead, how to make true porcelain, and a few years later Augustus set up in Meissen the first large-scale factory for manufacturing an alternative to the expensive Chinese imports. The money rolled in.

The difficulty in making porcelain was 2-fold: first, the needed ingredients were unknown (the Chinese were good at preserving their arcane secret) and second, the high temperatures needed (at least 1350°C) to 'fuse' the ingredients together could not be reached in the comparatively primitive European kilns. The captive Böttger was diverted from the quest for gold by a courtier, Count von Tschirnhaus (1651–1708), who was an early 'natural philosopher' with a special interest in using large lenses to concentrate sunlight. The high temperatures thus attainable led naturally to the idea of seeking to make porcelain, and the two men worked together on this, and eventually they were able to make kilns which could reach the necessary high temperatures without the use of lenses.

Tschirnhaus recognised that specially pure clay had to be used to prevent coloration of the product, and that something had to be added to make the clay fusible (i.e., turn it partly into a melt) to create the partly glassy, translucent body of porcelain. After years of experimentation, in January 1708 Böttger tried different proportions of white kaolin (nowadays called China clay) and alabaster, a calcium sulphate. With a low alabaster content of around 12%, beautiful porcelain resulted, and Böttger had saved his neck from the axe again. It proved, in the words of the time, to be 'white gold', especially after ways of decorating the surface in colours under a subsequently applied glaze had been developed. Kaolin has ever since been an essential constituent of porcelain, though the additions needed to make it fusible have varied somewhat.

The difficulties of the search and the appalling conditions under which it had to be conducted are memorably depicted in a recent book by Gleeson (1998). (Böttger died at the age of only 37 from the effects of the terrible conditions under which he had worked.) A more technical account, showing phase diagrams and placing the achievement in the context of attempts elsewhere in Europe, is by Kingery (1986), as part of a multi-volume study of the emergence of modern ceramic science. He sets out the consequences of the Tschirnhaus/Böttger triumph during the remainder of the 18th century. When that century began, chemistry played no part in ceramic

craftsmanship. When Saxon porcelain was sent to France, the great chemist Réaumur (whom we have already met) analysed it and his analysis helped the French Sèvres pottery to make porcelain too, and somewhat later, Josiah Wedgwood (1730–1795) founded his famous pottery and introduced chemical methods to control raw materials better than before. In the 1780s he also introduced the first high-temperature pyrometer – actually pieces of ceramic of controlled composition which sagged at different temperatures (Dorn 1970–1980). Thus, a physical task (crude temperature measurement) was achieved by exploiting chemical expertise.

Kingery concludes: “By the end of the (18th) century chemical analysis and control of the constitution of bodies, glazes and raw materials was accepted. Ceramics had changed its role from that of an instigator of chemical studies to a net user of chemical studies.” This view of things is consistent with the remark by Wachtman (1999) that “the long process of moving ceramics from a tradition-based craft to a science-based technology conducted under the direction of engineers was underway in the 1800s and has continued to the present day”.

### ***9.3.2 The birth of high-tech ceramics: lamps***

Porcelain hardly comes under the rubric ‘structural material’, yet it is immensely strong. I recall an advertisement a few years ago showing a London doubledecker bus balanced on four inverted teacups under the tires. Once this feature of a high-grade ceramic came to be recognized, one path was open to more technological uses for this family of materials. But recognition of high compressive strength was certainly not the only factor in this development; the coming of the age of electricity at the end of the nineteenth century and the role of ceramics in helping that age along were even more important. This was much earlier than the developments in electronic and magnetic ceramics described in Chapter 7.

The title of this section is taken from the title of another essay by Kingery, one of the most eloquent and expert proponents of the central role of ceramics in MSE (for a sketch of his educational innovations, see Section 1.1.1). The essay is in a book series entitled *Ceramics and Civilization* (Kingery 1990).

The electrical age was built on the discovery in the early 1830s, independently by Joseph Henry (1797–1878) in America and Michael Faraday (1791–1867) in England, of electromagnetic induction, which led directly to the invention of the dynamo to generate electricity from steam-powered rotation. It came to fruition on New Year’s Eve, 1879, when Thomas Edison (1847–1931) in rural New Jersey, after systematic and exhaustive experiments, made the first successful incandescent lamp, employing a carbonised filament made from some thread taken from Mrs. Edison’s sewing cabinet. The lamp burned undimmed for 40 h, watched anxiously by Edison and some of his numerous collaborators. This lamp was ideal for

domestic use, unlike the arc lamp perfected a few years previously which was only thought suitable for open-air use. Edison not only made the first successful filament lamp, he also organised the building of the first central electric power station, after a brief interval when dispute reigned over the relative merits of central and individual domestic generation of electricity. The Edison Electric Light Company, both to generate electricity and to sell the lamps to use it, was incorporated in 1878. Thereupon, a no-holds-barred race took place between robber barons of various types for power generation and lamp design and manufacture. By 1890, Edison had six major competitors. All this is recounted in splendid detail in a book by Cox (1979), published to celebrate the centenary of Edison's momentous success.

Edison's lamps were primitive, and their life was limited because of the fragility of the carbon filaments, the expense of hand manufacture and the inadequacy of contemporary vacuum pumps. The extraordinary lengths to which Edison went to find the best organic precursor for filaments, including the competitive trying-out of beard-hairs from two men, is retailed in a racy essay by Jehl (1995). Many alternatives, notably platinum and osmium, were tried, especially after Edison's patents ran out in the mid-1890s, until in 1911 General Electric put on sale lamps made with the 'non-sag' tungsten filaments developed by William Coolidge and they swept all before them. These filaments are still, today, made essentially by the same elaborate methods as used in 1911, using sintering of doped metal powder (see Section 9.4). An entire book was recently devoted to the different stages and aspects of manufacture of tungsten filaments (Bartha *et al.* 1995). Many manufacturers tried to break GE's patents and the lawyers and their advisers had a splendid time: my wife's father, a metallurgist, to whose memory this book is dedicated, sent his three children to boarding school on the proceeds of his work as expert witness in one such trial over lamp patents.

The complicated history of General Electric's progressive development of the modern incandescent lamp is clearly told in a book about the GE Research Laboratory (Birr 1957). In particular, this includes a summary of the crucial researches, experimental and (particularly) theoretical by a brilliant metallurgist turned physical chemist, Irving Langmuir (1881–1957). He examined in a fundamental way the kinetics of metal evaporation, the possible role of inert gas filling in counteracting this, and the optimum configurations of coiled (and coiled coil) filaments to reduce heat loss and thus electricity wastage from the filaments. Langmuir joined the Laboratory in 1909 and had essentially solved the design problems of incandescent lamps by 1913. We shall meet Langmuir again in Section 11.2.3, in his guise as physical chemist.

The 32-year interval between 1879 and 1911 saw a classic instance of challenge and response, in the battle between electric and gas lighting, and between two rival

methods of electric lighting. Kingery, in his 1990 essay, describes the researches of Carl Auer, Baron von Welsbach, in Austria (1858–1929), who discovered how to improve ‘limelight’, produced when a flame plays on a block of lime, for domestic use. He discovered that certain rare-earth oxides generated a particularly bright incandescent light when heated with a Bunsen burner, and in 1866 he patented a mixture of yttria or lanthana with magnesia or zirconia, used to impregnate a loosely woven cotton fabric by means of a solution of salts of the elements concerned. He then spent years, Edison-fashion, in improving his ceramic mixture; in particular, he experimented with thoria, and found that the purer his sample was, the less efficiently did it illuminate. As so often in materials research, he tracked down these variations to contamination, in this instance with the oxide of cerium, and this oxide became the key to the commercial *Welsbach mantle*, marketed in 1890. Kingery remarks that “as far as I’m aware, the Auer incandescent gas mantle was the first sintered oxide alloy to be formed from chemically prepared raw materials”. Its great incandescent capacity “put renewed life into gas light as a competitor with the newer electric lighting systems”. Eventually, of course, electric lamps won the competition, but, as Kingery says, “for isolated and rural areas without electrification, the incandescent gas mantle remains the lighting system of choice” (using bottled gas).

In the 1890s, a third competitor arrived to challenge the electric filament lamp and the Welsbach gas mantle. This was the Nernst lamp. We have already briefly met the German chemist Walther Nernst (1864–1941) in Section 2.1.1. Nernst was acutely aware of the limitations of the filament lamp in its 1890 incarnation and especially of the poor vacuum pumps of the time, and decided to try to develop an electric lamp based, not on electronic conduction as in a metal, but on what we now know as ionic conduction. Of course at the time, so far as any chemist knew, ions were restricted to aqueous solutions of salts, so the mechanism of conduction must have been obscure. Nernst finally filed a patent in 1897 (just as Thomson announced the existence of the electron). His patent specified a conductor based on “such substances as lime, magnesia, zirconia, and other rare earths”. (Recently, a small fragment of one of Nernst’s surviving lamps was analysed for Kingery and found to be  $\approx 88$  wt% zirconia and 12 wt% yttria-group rare earths.) These ceramic ‘glowers’ did not conduct electricity sufficiently well at ambient temperature and had to be preheated by means of a platinum wire that encircled the glower; once the glower was operating, the preheater was automatically switched off and an overload surge protector was also built in. The need for preheating led to some delay in lighting up, and in later years Nernst, who had a mordant wit, remarked that the introduction of his lamp coincided with another major invention, the telephone, which “made it possible for the brokers at the Stock Exchange to ring up home when business was finished and ask their wives to switch on the light”. Nernst’s lamps were steadily improved

(Kingery 1990) and sold very widely, but they had to capitulate to the tungsten filament lamp after 1911. They had an effective commercial life of only 12 years.

The history of these three lamp types offers as good an example as I know of the mechanism of challenge and response in industrial design. Several more major electric lamp types have been introduced during the past century – one of them will be outlined in the next section – but competition did not eliminate any of them.

Kingery's 1990 essay also discusses another of Edison's inventions, the carbon granule microphone which he developed in 1877 for the new telephone, announced by Alexander Graham Bell the previous year (well before Nernst's lamp, in actual fact). Edison had in 1873 discovered the effect of pressure on electrical resistance in a carbon rheostat; building on that, he discovered that colloidal carbon particles made of 'lampblack' (soot from an oil lamp) had a similar characteristic and were ideal for operation behind an acoustic membrane. Telephones are still made today with carbon granules – a technology even longer-lived than tungsten filaments for lamps. This is one of many applications for different allotropic forms of carbon, which are often reckoned as ceramics (though carbon neither conducts electricity ionically nor is an insulator).

#### 9.4. SINTERING AND POWDER COMPACTION

When prehistoric man made and fired clay pots, he relied (although he did not know it) upon the phenomenon of *sintering* to convert a loosely cohering array of clay powder particles steeped in water into a firmly cohering body. 'Sintering' is the term applied to the cohesion of powder particles in contact without the necessary intervention of melting. The spaces between the powder particles are gradually reduced and are eventually converted into open, interconnected pores which in due course become separate, 'closed' pores. The production of porcelain involves sintering too, but at a certain stage of the process, a liquid phase is formed and infiltrates the open pores – this is liquid-phase sintering. The efficacy of the sintering process is measured by the extent to which pores can be made to disappear and leave an almost fully dense ceramic.

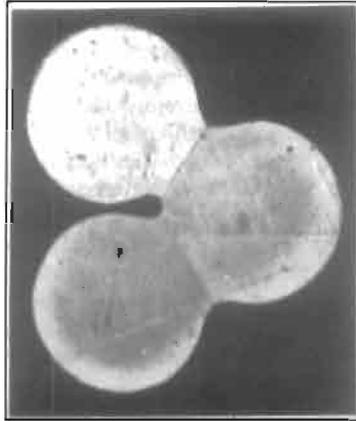
Sintering is not restricted to clay and other ceramic materials, though for them it is crucial; it has also long been used to fabricate massive metal objects from powder, as an alternative to casting. For many years, furnaces could not quite reach the melting-point of iron, 1538°C, and the reduction of iron oxide produced iron powder which was then consolidated by heat and hammering. The great iron pillar of Delhi, weighing several tons, is believed to have been made by this approach. The same problem attended the early use of platinum, which melts at  $\approx 1770^\circ\text{C}$ . It was William Hyde Wollaston (1766–1828) in London who first proved that platinum was an element

(generally accompanied by other elements of its group) and perfected a way of making 'malleable platinum' by precipitating the powder from solution and producing a cake, coherent enough to be heated and forged; this was reported just before Wollaston's death in 1828. The intriguing story of this metal and its 'colleagues' is concisely told in Chapter 8 of a recent book (West and Harris 1999). We have already seen that tungsten filaments for incandescent lamps were made from 1911 onwards by sintering of fine tungsten powder. Unlike the other historical processes mentioned here, these filaments were initially made by loose sintering, without the application of pressure, and it was this process which for many years posed a theoretical mystery. Sintered metal powders were not always made to be fully dense; between the Wars, sintered porous bronze, with communicating pores, was made in America to retain oil and thus create self-lubricating bearings. These early applications were reviewed by Jones (1937) and more recent uses and methods in accessible texts by German (1984) and by Arunachalam and Sundaresan (1991). These include discussions of sintering aided by pressure (pressure-sintering, especially the modern use of hot isostatic pressing (see Section 4.2.3)), methods which are much used in industrial practice.

Returning to history, a little later still, in 1925, the Krupp company in Germany introduced what was to become and remain a major product, a tough *cermet* (*ceramic-metal* composite) consisting of a mixture of sharp-edged, very hard tungsten carbide crystallites held together by a soft matrix of metallic cobalt. This material, known in Germany as 'Widia' (*Wie Diamant*) was originally used to make wire-drawing dies to replace costly diamond, and later also for metal-cutting tools. Widia (also called cemented carbide) was the first of many different cermets with impressive mechanical properties.

According to an early historical overview (Jones 1960), the numerous attempts to understand the sintering process in both ceramics and metals fall into three periods: (1) speculative, before 1937; (2) simple, 1937–1948; (3) complex, 1948 onwards. The 'complex' experiments and theories began just at the time when metallurgy underwent its broad-based 'quantitative revolution' (see Chapter 5).

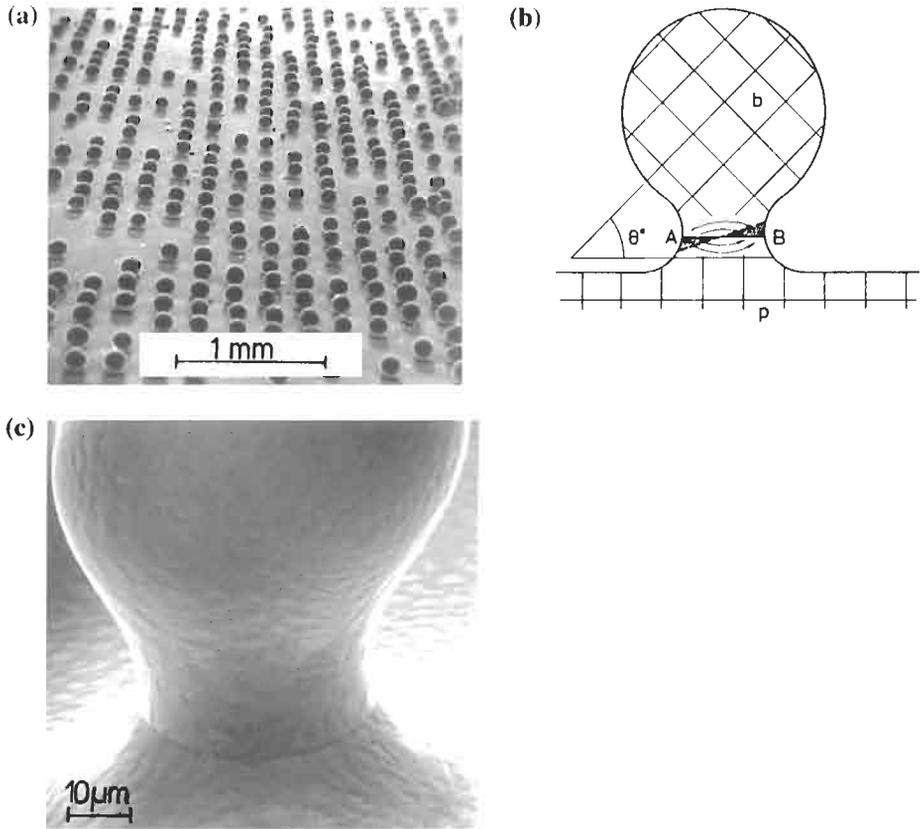
The elimination of surface energy provides the driving force for pressureless sintering. When a small group of powder particles is sintered (Figure 9.7), some of the metal/air surface is replaced by grain boundaries which have a lower specific energy; moreover, two surfaces are replaced by one grain boundary. The importance of the low grain-boundary energy in driving the sintering process is underlined by a beautiful experiment originally suggested by an American metallurgist, Paul Shewmon, in 1965 and put into effect by Herrmann *et al.* (1976). Shewmon was concerned to know whether the plot of grain-boundary energy vs angular misorientation, as shown in Figure 5.3 (dating from 1950), was accurate or whether there were in fact minor local minima in energy for specific misorientations, as later and more exact theories were predicting. He suggested that small metallic single-



**Figure 9.7.** Metallographic cross-section through a group of 3 copper particles sintered at 1300 K for 8 h. The necks are occupied by grain boundaries (after Exner and Arzt 1996).

crystal spheres could be scattered on a single-crystal plate of the same metal and allowed to sinter to the plate; he predicted that each sphere would 'roll' into an orientation that would give a particularly low specific energy for the grain boundary generated by sintering. Herrmann and his coworkers made copper crystal spheres about 0.1 mm in diameter, simply by melting and resolidifying small particles. These spheres were then disposed on a copper monocrystal plate (with a surface parallel to a simple crystal plane) and heated to sinter them to the plate, as shown in Figure 9.8(a). (The same was done with silver also.) X-ray diffraction was then used to find the statistical orientation distribution of the sintered spheres, and it was found that after sufficiently long annealing (hundreds of hours at 1060°C) all the spheres, up to 8000 of them in one experiment, acquired accurately the same orientation, or one of two alternative orientations. The authors argued that if a 'cusp' of low energy exists at specific misorientations between a sphere and the plate, a randomly oriented sphere which has already begun to sinter, so that a grain boundary has been formed, will then reorient itself by means of atom flow as shown in Figure 9.8(b) until the misorientation has become such that the boundary energy reaches a local minimum. An actual sintered sphere is shown in Figure 9.8(c). Subsequent work has shown very clearly (Palumbo and Aust 1992), by a variety of experimental and simulation techniques, that indeed the energy of a grain boundary varies with misorientation not as shown in Figure 5.3, but as shown in the example of Figure 9.9. The energy 'cusps' arise for orientation relationships marked by the 'sigma numbers' indicated at the top of the graph, for which the atomic fit at the boundaries is particularly good.

This experiment is discussed here in some detail both because it casts light on the driving force for sintering and because it is a beautiful example of the ingenious



**Figure 9.8.** Sintering of single-crystal copper spheres to a single-crystal copper substrate. (a) experimental arrangement; (b) mechanism for rotation of an already-sintered sphere; (c) scanning electron micrograph of a sintered sphere (courtesy H. Gleiter).

approaches used by the 'new metallurgy' after the quantitative revolution of  $\approx 1950$ , and further, because it serves to disprove David Kingery's assertion, quoted in Section 1.1.1, that "the properties and uses of metals are not very exciting". Finally, I urge the reader to note that the Herrmann experiment could equally well have been performed with a ceramic, and indeed a somewhat similar experiment was done a little later with polyethylene (Miles and Gleiter 1978), and the energy cusps which turned up were explained in terms of dislocation patterns. Attempts to reserve scientific fascination to a particular class of materials are doomed to disappointment. That is one reason why materials science flourishes.

Several of the early studies aimed at finding the governing mechanisms of sintering were done with metal powders. A famous study was by Kuczynski (1949) who also examined the sintering of copper or silver to single-crystal metal plates; but

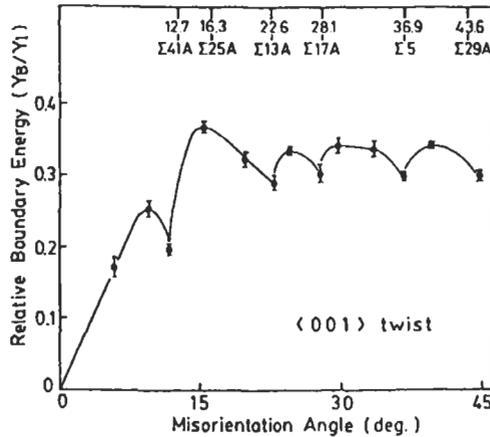


Figure 9.9. Relative boundary energy versus misorientation angle for boundaries in copper related by various twist angles about [1 0 0] (after Miura *et al.* 1990).

he was interested in sintering kinetics, not in orientations, and so he measured the time dependence of the radius of curvature,  $r$ , of the ‘weld’ interface between spheres and the plate. He then worked out the theoretical dependence of  $r$  on time,  $t$ , for a number of different rate-determining mechanisms, such as  $r^2$  proportional to  $t$  for diffusional creep (see Section 4.2.5),  $r^5$  proportional to  $t$  for volume diffusion of metal through the bulk, and  $r^7$  proportional to  $t$  for metal diffusion along surfaces. Kuczynski claimed to have shown that volume diffusion was the preponderant mechanism. In the past half-century, Kuczynski’s lead has been followed by numerous studies, of both metals and ceramics, (for instance an analysis by Herring (1950) of the effects of change of scale) and a number of research groups have been founded around the world to pursue both the theory and experimental testing of scaling and kinetic studies. Exner and Arzt (1996) survey these studies, which now suggest that surface diffusion and especially grain-boundary diffusion both play significant parts in the sintering process. This scaling approach to teasing out the truth is reminiscent of the use of the form of the observed grain-size dependence of creep rates to determine whether Nabarro–Herring (diffusional) creep is in operation.

In the same year as Kuczynski’s research was published, Shaler (1949), who had done excellent work on measuring surface energies and surface tensions on solid metals, argued that surface tension must play a major part in fostering shrinkage of powder compacts during sintering; his paper (Shaler 1949) led to a lively discussion, a feature of published papers in those more spacious days.

The chemistry of ceramics plays a role in their behaviour during sintering. Non-stoichiometry of oxides has been found to play a major role in the extent to which a

powder can be densified by sintering; this is linked to the emission of vacancies on the cationic and anionic sublattices from a pore. Sintering is better in anion-deficient ceramics. The role of departure from perfect stoichiometry is clearly set out by Reijnen (1970).

Sintering is now a component of a range of novel ceramic processing technologies: an important example is *tape casting*, a method of making very thin, smooth ceramic sheets that are widely used for functional applications. The technique was introduced in America in 1947: Hellebrand (1996) defines it as “a process in which a slurry of ceramic powder, binder and solvents is poured or ‘cast’ onto a flat substrate, then evenly spread, and the solvents subsequently evaporated”. Sintering then follows. An enormous range of consumer goods, such as kitchen appliances, computers, TV sets, photocopiers, make use of such tapes. A variant, since 1952, is the production of laminated ceramic multilayers, used for various forms of miniaturised circuits: the multilayers act as ‘skeletons’ to hold the components and metallic interconnects.

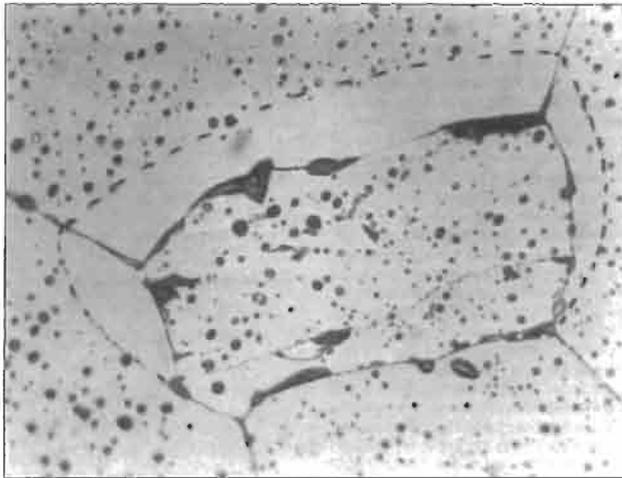
#### ***9.4.1 Pore-free sintering***

One aspect of sintering remains to be discussed, and that is the linkage between the efficiency of sintering and grain growth, that is, the migration of grain boundaries through a powder compact while sintering is in progress. The importance of this derives from the fact, first demonstrated at MIT by Alexander and Balluffi (1957) with respect to sintered copper, that pores lying on a grain boundary are eliminated while those situated in a grain interior remain. At about the same time, also at MIT, Kingery and Berg (1955), working with ceramics, pointed out that the ready diffusion of vacancies along grain boundaries, which according to Nabarro and Herring can be both sources and sinks for vacancies, provided a mechanism for shrinkage for powder compacts. These findings had a corollary: when grain boundaries sweep through a polycrystal, they can ‘gather up’ pores along their path provided they migrate slowly enough. This established the major link between grain growth and the late stage of sintering.

A brief word about grain growth, a major *parepisteme* in its own right, is in order here. This process is driven simply by the reduction of total grain-boundary energy (that is the ultimate driving force) and more immediately, by the usual unbalance of forces acting on three grain boundaries meeting along a line. Whether or not the microstructure responds to this ever-present pair of driving forces depends on the factors tending to hold the grain boundaries back; of these, the most important is the possible presence of an array of tiny dispersed particles which latch on to a moving boundary and slow it down or, if there are enough of them, stop it entirely. The reality of this effect has been plentifully demonstrated, and the

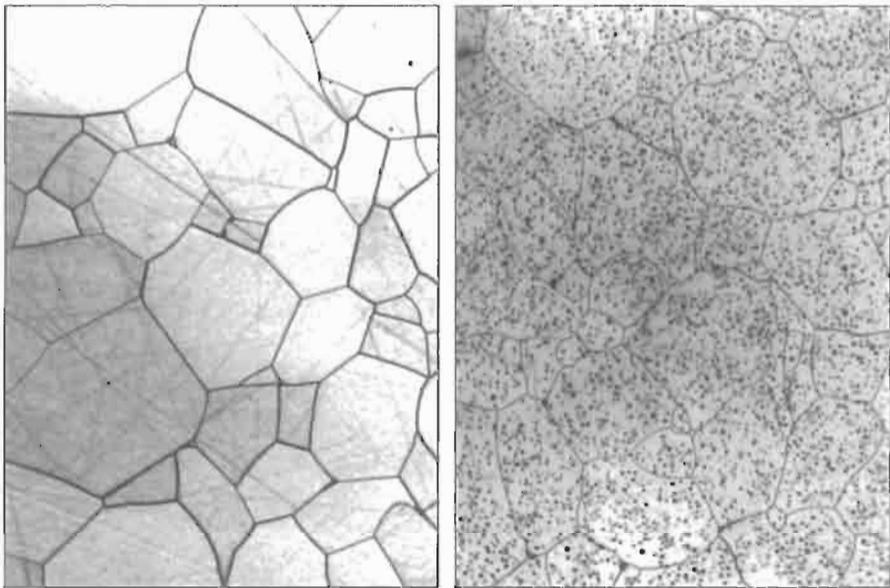
modelling of grain growth, especially in the presence of such particles, is a 'growth industry' which I discuss further in Section 12.2.3.3. In the presence of a critical concentration of dispersed particles, most grain boundaries are arrested but a few still move, and this leads to abnormal or 'exaggerated' grain growth, and the creation of a few huge grains. In this connection, pores act like dispersed particles. The complicated circumstances of this process are surveyed by Humphreys and Hatherly (1995). When exaggerated grain growth takes place, any one location in a densifying powder compact is passed just once, rapidly, by a moving grain boundary, whereas normal grain growth ensures repeated slow passages of the myriad of grain boundaries in the compact, giving time for vacancies to 'evaporate' from pores and diffuse away along intersecting grain boundaries. To ensure adequate pore removal and hence densification it is necessary to ensure that normal, but not abnormal, grain growth operates, and that furthermore the migration of boundaries is slowed down as much as possible. The famous micrograph reproduced in Figure 9.10, from Burke (1996), of a densifying powder compact of alumina, demonstrates the sweeping up of pores by a moving grain boundary.

Burke, and also Suits and Bueche (1967), tell the history of the evolution of pore-free, and hence translucent, polycrystalline alumina, dating from the decision by Herbert Hollomon at GE (see Section 1.1.2) in 1954 to enlarge GE's research effort on ceramics. In 1955, R.L. Coble joined the GE Research Center from MIT and



**Figure 9.10.** Optical micrograph of a powder compact of alumina at a late stage of sintering, showing pore removal along the path of a moving grain boundary. (The large irregular pores are an artefact of specimen preparation.) Grain boundaries revealed by etching. Micrograph prepared at GE in the late 1950s, and reproduced by Burke (1996) (reproduced by permission of GE).

began to study the mechanisms of the stages of sintering of alumina powder. The features outlined in the preceding paragraphs soon emerged and Coble then had the brilliant idea of braking migrating grain boundaries by ‘alloying’ the alumina with soluble impurities which might segregate to the boundaries and slow them down. Magnesia, at around 1% concentration, did the job beautifully. Figure 9.11 shows sintered alumina with and without magnesia doping. In 1956, a visiting member of GE’s lamp manufacturing division chanced to see Coble’s results with doped alumina and was struck by the near transparency of his sintered samples (there were no pores left to scatter light). From this chance meeting there followed the evolution of pore-free alumina, trademarked Lucalox, and its painstaking development as the envelope material for a new and very efficient type of high-pressure sodium-vapour discharge lamp. (Silica-containing envelopes were not chemically compatible with sodium vapour.) Burke, and Suits/Bueche, tell the tale in some detail and spell out the roles of the many GE scientists and engineers who took part. Nowadays, all sorts of other tricks can be used to speed up densification during sintering: for instance, the use of a population of rigorously equal-sized spherical powder particles ensures much better packing before sintering ever begins and thus there is less porosity to get rid of. But all this is gilt on the gingerbread; the crucial discovery was Coble’s



**Figure 9.11.** Microstructures of porous sintered alumina prepared undoped (right) and when doped with magnesia (left). Optical micrographs, originally 250 $\times$  (after Burke 1996).

identification of how sintering actually worked, and that insight was then effectively exploited.

The Lucalox story is a prime specimen of a valuable practical application of a parepistemic study begun for curiosity's sake.

## 9.5. STRONG STRUCTURAL CERAMICS

Intrinsically, ceramics are immensely strong, because they are made up of mostly small atoms such as silicon, aluminum, magnesium, oxygen, carbon and nitrogen, held together by short, strong covalent bonds. So, individual bonds are strong and moreover there are many of them per unit volume. It is only the tiny Griffith cracks at free surfaces, and corresponding internal defects, which detract from this great potential strength of materials such as silicon nitride, silicon carbide, alumina, magnesia, graphite, etc. The surface and internal defects limit strength in tension and shear but have little effect on strength in compression, so many early uses of these materials have focused on loading in compression. Overcoming the defect-enhanced brittleness of ceramics has been a central concern of modern ceramists for much of the 20th century, and progress, though steady, has been very slow. This has allowed functional ("fine") ceramics, treated in Chapter 7, to overtake structural ceramics in recent decades, and the bulk of the international market at present is for functional ceramics. Japanese materials engineers made a good deal of the running on the functional side, and recently they have similarly taken a leading role in improving and exploiting load-bearing ceramics.

In the preceding section, we saw that removing internal defects, in the form of pores, made sintered alumina, normally opaque, highly translucent. Correspondingly, advanced ceramists in recent years have developed methods to remove internal defects, which often limit tensile strength more than do surface cracks. This program began 'with a bang' in the early 1980s, when Birchall *et al.* (1982) at ICI's New Science Group in England showed that "macro-defect-free" (MDF) cement can be used (for demonstration purposes) to make a beam elastically deformable to a much higher stress and strain than conventional cement (Figure 9.12). The cement was made by moulding in the presence of a substantial fraction of an 'organic rheological aid' that allowed the liquid cement mix to be rolled or extruded into a highly dense mass without pores or cracks. Next year, the same authors (Kendall *et al.* 1983, Birchall 1983) presented their findings in detail: the elastic stiffness was enhanced by removal of pores, and not only the strength but also the fracture toughness was greatly enhanced. Later, (Alford *et al.* 1987), they showed the same features with regard to alumina; in this latest publication, the authors also revealed some highly original indirect methods of estimating the sizes of the largest flaws present. At its

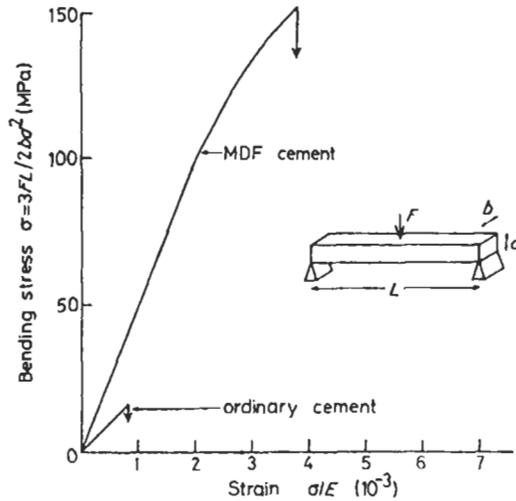


Figure 9.12. Bend strengths of ordinary and MDF cements (after Birchall *et al.* 1982).

high point, this approach to high-strength cements formed the subject-matter for an international conference (Young 1985).

The ICI group, with collaboration around the world, put a great deal of effort into developing this MDF approach to making ceramics strong in tension and bending, including the use of such materials to make bullet-resistant body armour. However, commercial success was not sufficiently rapid and, sadly, ICI closed down the New Science Group and the MDF effort. However, the recognition that the removal of internal defects is a key to better engineering ceramics had been well established. Thus, the experimental manufacture of silicon nitride for a new generation of valves for automotive engines deriving from research, led by G. Petzow, at the Powder Metallurgical Laboratory (which despite its name focuses on ceramics) of the Max-Planck-Institut für Metallforschung makes use of clean rooms, like those used in making microcircuits, to ensure the absence of dust inclusions which would act as stress-raising defects (Hintsches 1995). Petzow is quoted here as remarking that “old-fashioned ceramics using clay or porcelain have as much to do with the high-performance ceramics as counting on five fingers has to do with calculations on advanced computers”.

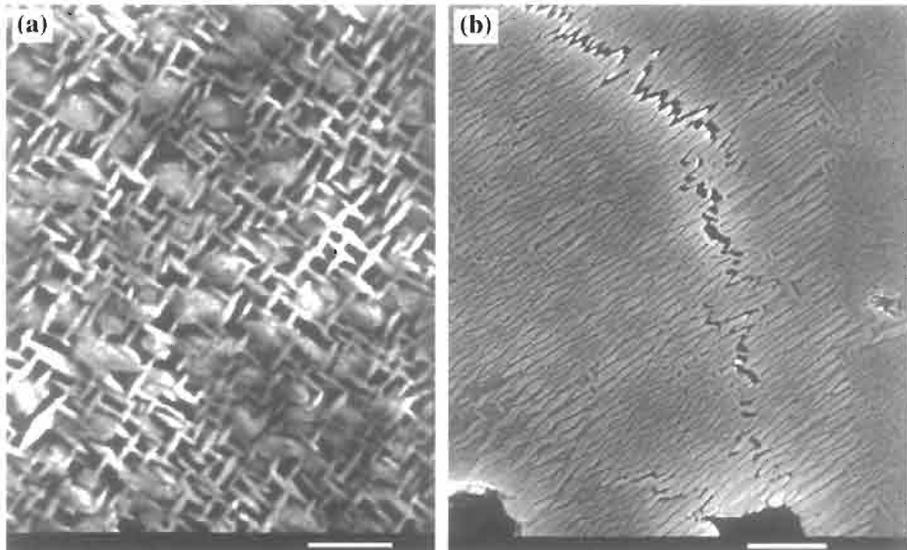
The removal of pores and internal cracks is also of value where functional ceramics are concerned. Dielectrics such as are used in capacitors in enormous quantities, alumina in particular, have long been made with special attention to removing any pores because these considerably lower the breakdown field and therefore the potential difference that the capacitors can withstand.

Another mode of toughening – transformation-toughening – was invented a little earlier than MDF cement. The original idea was published, under the arresting title “Ceramic Steel?”, by Garvie *et al.* (1975). These ceramists, working in Australia, focused on zirconia,  $ZrO_2$ , which can exist in three polymorphic forms, cubic, tetragonal or monoclinic in crystal structure, according to the temperature. Their idea exploits the fact that a martensitic (shear) phase transformation can be induced by an applied shear stress as well as by a change in temperature. Garvie and his colleagues proposed that by doping zirconia with a few percent of MgO, CaO,  $Y_2O_3$  or  $CeO_2$ , the tetragonal or even the cubic form can be ‘partially stabilised’ so that the martensitic transformation to a thermodynamically more stable form cannot take place spontaneously but can do so if a crack advancing under stress unleashes an embryo of the stable structure and enables it to form a crystallite. This process absorbs energy from the advancing crack and thus functions as a crack arrester. The end result is that a crack is diverted along a tortuous path, or completely stopped, and this toughens the ceramic. The material is pre-aged to the point where partial transformation has taken place; if the treatment is just right, a peak level of toughness is attained. This brilliant idea led to a burst of research around the world, and transformation-toughened zirconia, or alumina provided with a dispersed toughened zirconia phase, became a favourite engineering material, especially for applications such as wire-drawing dies which have to be hard and tough. Figure 9.13 shows two micrographs of this kind of material. It is good to record that the Australians who invented the approach also retained the market in the early days and indeed much of it still today. The extensive literature on this kind of material is discussed in a chapter on toughening mechanisms in ceramic systems (Becher and Rose 1994) and in a recent review by Hannink *et al.* (2000), while the fracture mechanics of transformation-toughened zirconia is analysed by Lawn (1993, p. 225). A limitation is that toughening by this approach is not possible at high temperatures.

The principle behind transformation-toughened zirconia was originally developed, a few years earlier (Gerberich *et al.* 1971), for a steel, called TRIP – TRansformation-Induced Plasticity. (Hence the name proposed in 1975 for the novel form of zirconia... “ceramic steel”.) The austenite phase is barely metastable and, where an advancing crack generates locally enhanced stress, martensite is formed locally and the fact that this requires energy causes the steel to be greatly toughened over a limited temperature range.

### 9.5.1 Silicon nitride

There is no space here to go into details of the many recent developments in ceramics developed to operate under high stresses at high temperatures; it is interesting that a



**Figure 9.13.** (a) Transmission electron micrograph of MgO-stabilised ZrO<sub>2</sub> aged to peak toughness. Tetragonal precipitates on cube planes are shown; the cubic matrix has been etched away with hydrofluoric acid. Bar = 0.5 μm. (b) Scanning electron micrograph of an overaged sample of MgO-stabilised ZrO<sub>2</sub> with coarsened precipitates, subjected to loading. Note the strong crack deflection and bridging. Bar = 2.5 μm (courtesy Dr. R.H.J. Hannink).

detailed memorandum on advanced structural ceramics and composites, issued by the US Office of Technology Assessment in 1986, remarks: “Ceramics encompass such a broad class of materials that they are more conveniently defined in terms of what they are not, rather than what they are. Accordingly, they may be defined as all solids which are neither metallic nor organic.” I shall restrict myself to just one family of ceramics, the silicon nitrides (Hampshire 1994, Leatherman and Katz 1989); the material was first reported in 1857. Si<sub>3</sub>N<sub>4</sub> has two polymorphs, of which one (β) is the stable form at high temperatures. The powder can be prefabricated and then hot-pressed (or hot isostatically pressed), or silicon powder can be sintered and then reacted with nitrogen, which has the advantage of preserving shape and dimensions and being a cheaper process. A range of additives is used to ensure good density and absence of porosity in the final product, and a huge body of research has been devoted to this ceramic since the War. In 1971/1972, two groups, one in Japan (Oyama, Kamigaito) and in England (Jack, Wilson) independently developed more complex variants of silicon nitrides, the ‘sialons’ (an acronym derived from Si–Al–O–N), complex materials some of which can be pressureless-sintered to full density. They are also fully presented in Hampshire’s book chapter.

Silicon nitride has been used for some years to make automotive turbine rotors, because its low density,  $3.2 \text{ g/cm}^3$ , ensures low centrifugal stresses. As we saw in Section 9.1.4, now titanium aluminide, also very light, is beginning to be used instead. Since about 1995, silicon nitride inlet and exhaust valves have been used on an experimental basis in German cars, and have recorded very long lives. The low density means that higher oscillation frequencies are feasible, and there is no cooling problem because the material can stand temperatures as high as  $1700^\circ\text{C}$  without any problems. As is typical for structural ceramic components, this usage still seems to remain experimental, although a German car manufacturer has ceramic valves running effectively in some 2000 cars. Over recent years, there has again and again been hopeful discussion of the 'all-ceramic engine', either a Diesel version or, in the most hopeful form, a complete gas turbine; the only all-ceramic engine currently in production is a two-stroke version. The action on ceramic Diesel engines has now shifted to Japan (e.g., Kawamura 1999). Silicon nitride has the benefit not only of high temperature tolerance and low thermal conductivity but also of remarkably low friction for rotating or sliding components. The main problem is high fabricating cost (as mentioned above, clean-room methods are desirable), but present results indicate a significant reduction of fuel consumption with experimental engines and the benefits of the engine needing little or no cooling. Determined efforts seem to be under way to reduce production costs. (As with titanium aluminide, the cost per kilogram comes almost entirely from processing costs; the elements involved are all intrinsically cheap.) When, recently, silicon nitride production costs in Germany dropped to DM 10 per valve, the makers of steel valves reduced their price drastically (Petzow 2000). This is classic materials competition in action!

### 9.5.2 Other ceramic developments

I should add here a mention of a peculiar episode, still in progress, which is based on an attempt to extrapolate from the known properties of silicon nitride to those of a postulated carbon nitride,  $\text{C}_3\text{N}_4$ , which should theoretically (because of the properties a C—N bond should possess) be harder than diamond. This idea was first promulgated by Liu and Cohen (1989) and led to an extraordinary stampede of research. Within a few years, several hundred papers had been published, but no one has as yet shown unambiguously that the postulated compound exists; however, very high hardnesses have been measured in imperfect approximants to the compound. Two reviews of work to date are by Cahn (1996) (brief) and Wang (1997) (detailed). The theoretically driven search for superhard materials generally has been surveyed by Teter (1998) under the title 'Computational Alchemy'. This whole body of research, squarely nucleated by theoretical prediction, has bounced back and forth