

between experiment and theory; it may well be a prototype of ceramic research programmes of the future.

There is no room here to give an account of the many adventures in processing which are associated with modern 'high-tech' ceramics. The most interesting aspect, perhaps, is the use of polymeric precursors which are converted to ceramic fibres by pyrolysis (Section 11.2.5); another material made by this approach is glassy carbon, an inert material used for medical implants. The standard methods of making high-strength graphite fibres, from poly(acrylonitrile), and of silicon carbide from a poly(carbosilane) precursor, both developed more than 25 years ago, are examples of this approach. These important methods are treated in Chapters 6 and 8 of Chawla's (1998) book, and are discussed again here in Chapter 11.

Another striking innovation is the creation, in Japan, of ceramic composite materials made by unidirectional solidification in ultra-high-temperature furnaces (Waku *et al.* 1997). This builds on the metallurgical practice, developed in the 1960s, of freezing a microstructure of aligned tantalum carbide needles in a nickel-chromium matrix. An eutectic microstructure in  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  mixtures involves two continuous, interpenetrating phases; this microstructure proves to be far tougher (more fracture-resistant) than the same mixture processed by sintering. The unidirectionally frozen structure is still strong at temperatures as high as 1600°C.

## 9.6. GLASS-CERAMICS

In Chapter 7, I gave a summary account of optical glasses in general and also of the specific kind that is used to make optical waveguides, or fibres, for long-distance communication. Oxide glasses, of course, are used for many other applications as well (Boyd and Thompson 1980), and the world glass industry has kept itself on its toes by many innovations, with respect to processing and to applications, such as coated glasses for keeping rooms cool by reflecting part of the solar spectrum. Another familiar example is Pilkington's float-glass process, a British method of making glass sheet for windows and mirrors without grinding and polishing: molten glass is floated on a still bed of molten tin, and slowly cooled – a process that sounds simple (it was in fact conceived by Alastair Pilkington while he was helping his wife with the washing-up) – but in fact required years of painstaking development to ensure high uniformity and smoothness of the sheet.

The key innovations in turning optical waveguides (fibres) into a successful commercial product were made by R.D. Maurer in the research laboratories of the Corning Glass Company in New York State. This company was also responsible for introducing another family of products, crystalline ceramics made from glass precursors – glass-ceramics. The story of this development carries many lessons for

the student of MSE: It shows the importance of a resolute product champion who will spend years, not only in developing an innovation but also in forcing it through against inertia and scepticism. It also shows the vital necessity of painstaking perfecting of the process, as with float-glass. Finally, and perhaps most important, it shows the value of a carefully nurtured research community that fosters revealed talent and protects it against impatience and short-termism from other parts of the commercial enterprise. The laboratory of Corning Glass, like those of GE, Du Pont or Kodak, is an example of a long-established commercial research and development laboratory that has amply won its spurs and cannot thus be abruptly closed to improve the current year's profits.

The factors that favour successful industrial innovation have been memorably analysed by a team at the Science Policy Research Unit at Sussex University, in England (Rothwell *et al.* 1974). In this project (named SAPPHO) 43 pairs of attempted similar innovations – one successful in each pair, one a commercial failure – were critically compared, in order to derive valid generalisations. One conclusion was: “The responsible individuals (i.e., technical innovator, business innovator, chief executive, and – especially – product champion) in the successful attempts are usually more senior and have greater authority than their counterparts who fail”.

The prime technical innovator and product champion for glass-ceramics was a physical chemist, S. Donald Stookey (b. 1915; Figure 9.14), who joined the Corning Laboratory in 1940 after a chemical doctorate at MIT. He has given an account of

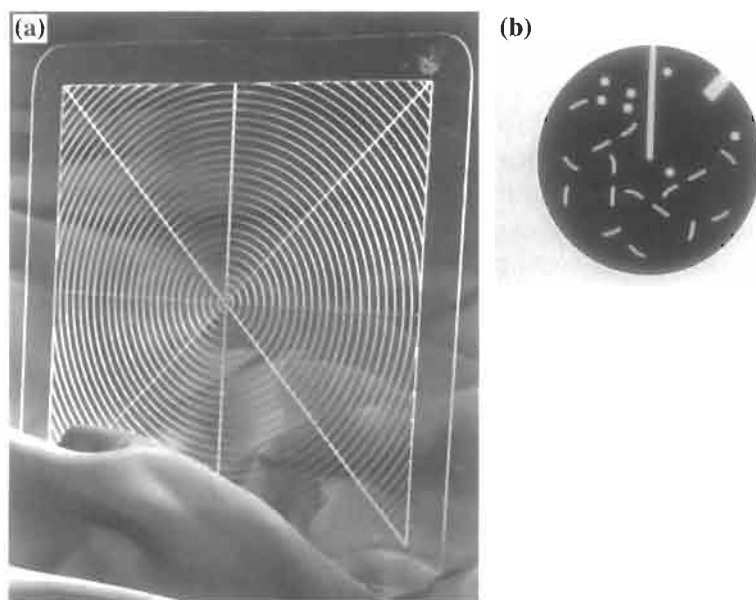


**Figure 9.14.** S. Donald Stookey, holding a photosensitive gold-glass plate (after Stookey 1985, courtesy of the Corning Incorporated Department of Archives and Records Management, Corning, NY).

his scientific career in an autobiography (Stookey 1985). His first assigned task was to study photosensitive glasses of several kinds, including gold-bearing 'ruby glass', a material known since the early 17th century. Certain forms of this glass contain gold in solution, in a colourless ionised form, but can be made deeply colored by exposure to ultraviolet light. For this to be possible, it is necessary to include in the glass composition a 'sensitizer' that will absorb ultraviolet light efficiently and use the energy to reduce gold ions to neutral metal atoms. Stookey found cerium oxide to do that job, and created a photosensitive glass that could be colored blue, purple or ruby, according to the size of the colloidal gold crystals precipitated in the glass. Next, he had the idea of using the process he had discovered to create gold particles that would, in turn, act as heterogeneous nuclei to crystallise other species in a suitable glass composition, and found that either a lithium silicate glass or a sodium silicate glass would serve, subject to rather complex heat-treatment schedules (once to create nuclei, a second treatment to make them grow). In the second glass type, sodium fluoride crystallites were nucleated and the material became, what had long been sought at Corning, a light-nucleated opal glass, opaque where it had been illuminated, transparent elsewhere. This was trade-named FOTALITE and after a considerable period of internal debate in the company, in which Stookey took a full part, it began to be used for lighting fittings. (In the glass industry, scaling-up to make industrial products, even on an experimental basis, is extremely expensive, and much persuasion of decision-makers is needed to undertake this.) Patents began to flow in 1950.

A byproduct of these studies in heterogeneous nucleation was Stookey's discovery in 1959 of photochromic glass, material which will reversibly darken and lighten according as light is falling on it or not; the secret was a reversible formation of copper crystallites, the first reversible reaction known in a glass. This product is extensively used for sunglasses.

Stookey recounts how in 1948, the research director asked his staff to try and find a way of 'machining' immensely complex patterns of holes in thin glass sheets. . . a million holes in single plate were mentioned, with color television screens in mind. Stookey had an idea: he experimented with three different photosensitive glasses he had found, exposed plates to light through a patterned mask, crystallised them, and then exposed them to various familiar glass solvents. His lithium silicate glass came up trumps: all the crystallized regions dissolved completely, the unaltered glass was resistant. "Photochemically machinable" glass, trademarked FOTO-FORM, had been invented (Stookey 1953). Figure 9.15 shows examples of objects made with this material; no other way of shaping glass in this way exists. Stookey says of this product: "(It) has taken almost 30 years to become a big business in its own right; it is now used in complexly shaped structures for electronics, communications, and other industries (computers, electronic displays, electronic



**Figure 9.15.** Photochemically machined objects made from FOTOFORM™ (after Stookey 1985, and a trade pamphlet, courtesy of the Corning Incorporated Department of Archives and Records Management, Corning, NY).

printers, even as decorative collectibles). Its invention also became a key event in the continuing discovery of new glass technology, proving that photochemical reactions, which precipitate mere traces (less than 100 parts per million) of gold or silver, can nucleate crystallization, which results in major changes in the chemical behavior of the glass.”

In the late 1950s, a classic instance happened of accident favouring the prepared mind. Stookey was engaged in systematic etch rate studies and planned to heat-treat a specimen of FOTOFORM™ at 600°C. The temperature controller malfunctioned and when he returned to the furnace, he found it had reached 900°C. He knew the glass would melt below 700°C, but instead of finding a pool of liquid glass, he found an opaque, undeformed solid plate. He lifted it out, dropped it unintentionally on a tiled floor, and the piece bounced with a clang, unbroken. He realised that the chemically machined material could be given a further heat-treatment to turn it into a strong ceramic. This became FOTOCERAM™ (Stookey 1961). The sequence of treatments is as follows: heating to 600°C produces lithium metasilicate nucleated by silver particles, and this is differentially soluble in a liquid reagent; then, in a second treatment at 800–900°C, lithium disilicate and quartz are formed in the residual glass to produce a strong ceramic.

This was the starting-point for the creation of a great variety of bulk glass-ceramics, many of them by Corning, including materials for radomes (transparent to radio waves and resistant to rain erosion) and later, cookware that exploits the properties of certain crystal phases which have very small thermal expansion coefficients. Of course many other scientists, such as George Beall, were also involved in the development. Another variant is a surface coating for car windscreens that contains minute crystallites of such phases; it is applied above the softening temperature so that, on cooling, the surface is left under compression, thereby preventing Griffith cracks from initiating fracture; because the crystallites are much smaller than light wavelengths, the coating is highly transparent. As Stookey remarks in his book, glass-ceramics are made from perfectly homogeneous glass, yielding perfect reliability and uniformity of all properties after crystallisation; this is their advantage, photomachining apart, over any other ceramic or composite structure.

Stookey's reflection on a lifetime's industrial research is: "An industrial researcher must bring together the many strings of a complex problem to bring it to a conclusion, to my mind a more difficult and rewarding task than that of the academic researcher who studies one variable of an artificial system".

In today's ferocious competitive environment, even highly successful materials may have to give way to new, high-technology products. Recently the chief executive of Corning Glass, "which rivals Los Alamos for the most PhDs per head in the world" (Anon. 2000), found it necessary to sell the consumer goods division which includes some glass-ceramics in order to focus single-mindedly on the manufacture of the world's best glass fibres for optical communications. Corning's share price has not suffered.

From the 1960s onwards, many other researchers, academic as well as industrial, built on Corning's glass-ceramic innovations. The best overview of the whole topic of glass-ceramics is by a British academic, McMillan (1964, 1970). He points out that the great French chemist Réaumur discovered glass-ceramics in the middle of the 18th century: "He showed that, if glass bottles were packed into a mixture of sand and gypsum and subjected to red heat for several days, they were converted into opaque, porcelain-like objects". However, Réaumur could not achieve the close control needed to exploit his discovery, and there was then a gap of 200 years till Stookey and his collaborators took over. McMillan and his colleagues found that  $P_2O_5$  serves as an excellent nucleating agent and patented this in 1963. Many other studies since then have cast light on heterogeneously catalysed high-temperature chemical reactions and research in this field continues actively. One interesting British attempt some 30 years ago was to turn waste slag from steel-making plant into building blocks ("Slagceram"), but it was not a commercial success. But at the high-value end of the market, glass-ceramics have been one of the most notable success stories of materials science and engineering.

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## Chapter 10

# Materials in Extreme States

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## Chapter 10

# Materials in Extreme States

### 10.1. FORMS OF EXTREMITY

In this chapter I propose to exemplify the many categories of useful materials which depend on extreme forms of preparation and treatment, shape, microstructure or function. My subject-matter here should also include ultrahigh pressure, but this has already been discussed in Section 4.2.3. As techniques of preparation have steadily become more sophisticated over the last few decades of the twentieth century, materials in extreme states have become steadily more prevalent.

My chosen examples include rapid solidification, where the extremity is in cooling rate; nanostructured materials, where the extremity is in respect of extremely small grains; surface science, where the extremity needed for the field to develop was ultrahigh vacuum, and the development of vacuum quality is traced; thin films of various kinds, where the extremity is in one minute dimension; and quasicrystals, where the extremity is in the form of symmetry. Various further examples could readily have been chosen, but this chapter is to remain relatively short.

### 10.2. EXTREME TREATMENTS

#### 10.2.1 *Rapid solidification*

The industrial technique now known as Rapid Solidification Processing (RSP) is unusual in that it owes its existence largely to a research programme executed in one laboratory for purely scientific reasons. The manifold industrial developments that followed were an unforeseen and welcome by-product.

The originator of RSP was Pol Duwez (1907–1984). This inspirational metallurgist was born and educated in Belgium, then found his way to Pasadena, California and spent the rest of his productive life there, at first at the Jet Propulsion Laboratory and then, 1952–1984, as a professor at the California Institute of Technology. Before he turned to the pursuits with which we are concerned here, he had a number of major discoveries to his credit, such as, in 1950, the identification and characterisation of the sigma phase, a deleterious, embrittling phase in a number of mostly ferrous alloys. This did much to kindle an enthusiasm for the study of intermetallic compounds. For what happened next, I propose to reproduce some sentences from a biographical memoir of Duwez (Johnson 1986a), from which the portrait (Figure 10.1) is also taken: “(From 1952) with several graduate students

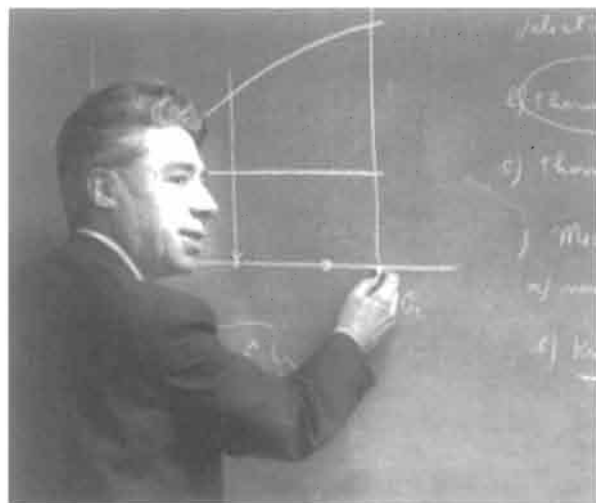


Figure 10.1. Portrait of Pol Duwez in 1962 (after Johnson 1986a).

Duwez continued his systematic investigations of the occurrence of intermetallic phases. The work of Hume-Rothery, Mott and Jones, and others had begun to provide a fundamental basis for understanding the occurrence of extended (solid) solubility and intermetallic phases in binary alloys. These theoretical efforts were based on the electronic structure of metals. As these ideas developed, questions were raised regarding the apparent absence of complete solubility in the simple binary silver–copper system (though there was such complete solubility in the Cu–Au and Ag–Au systems). Duwez raised this issue in particular during discussions with students as early as 1955 and 1956. He suggested that perhaps the separation of silver–copper into two (solid) solutions could be avoided by sufficiently rapid cooling of a thin layer of melt. Two students, Ron Willems and William Klement, ultimately devised a method to perform the necessary experiments using a primitive apparatus consisting of a quartz tube containing a metal droplet and connected to a pressurised gas vessel. The droplet was melted using a flame, the pressure applied, and the liquid alloy propelled against a strip of copper. A homogeneous solid solution was obtained (Duwez *et al.* 1960a). The modern science of rapid quenching was born. What is most remarkable was Duwez's grasp of the significance of this event. Within a matter of weeks, a more sophisticated apparatus was built and a systematic study of noble metals was begun. Within months, the simple eutectic alloy system, silver–germanium, had been rapidly quenched to reveal a new metastable crystalline intermetallic phase (Duwez *et al.* 1960b). Duwez recognised this as a missing 'Hume-Rothery' phase. Shortly thereafter in an effort to look for other such phases, a gold–

silicon alloy was rapidly quenched from the melt to yield the first metallic glass (Klement *et al.* 1960)." Most metallic glasses since then follow that same formula... major constituent, a metal, minor constituent, a metalloid. A few years later, Duwez (1967) gave his own account of those first few productive years devoted to RSP; Johnson (1986a) lists 41 of Duwez's most important papers.

Many years later, an electronic-structure calculation for the three systems, Cu–Ag, Cu–Au and Ag–Au which had sparked Duwez's initial experiments, showed (Terakura *et al.* 1987) that the different behaviour in the three systems could be rigorously interpreted. It is a mark of the compartmentalisation of research nowadays that this paper makes no reference to Duwez, though two of the authors work in metallurgical laboratories. There was an ingenious attempt, even earlier, to interpret the anomaly of the Cu–Ag system: Gschneidner (1979) sought to associate a high Debye temperature with what he called "lattice rigidity"; silver has a higher Debye temperature than gold, and correspondingly Gschneidner found that a range of lanthanide (rare earth) metals dissolved more extensively in gold than in silver. These two papers are cited to show that the anomaly which prompted Duwez's initiative has indeed exercised the ingenuity of metallurgists and physicists.

It appears that there was an independent initiative in RSP by I.V. Salli in Russia in 1958 (Salli 1959), but it was not pursued.

Duwez and, in due course, a number of people working in industry (especially Allied-Signal in New Jersey) developed ever-improving devices for RSP; it is interesting that at first these became more complicated, and then again simpler, until the chill-block melt-spinner materialised in the late 1960s and was energetically exploited in the USA and Japan. In its final form, this is simply a jet of molten alloy impinging on a rapidly rotating, polished copper wheel, producing a thin ribbon typically 1–3 mm wide. Later, a variant was developed in which the bottom of the nozzle is held less than a millimetre from the wheel and the nozzle is in the form of a slit, so that a wide sheet (up to 20 cm wide) can be manufactured.

The evolution of RSP (melt-quenching) devices carries an intriguing lesson. As mapped out by Cahn (1993) in a historical overview, some devices were introduced well before Duwez started his researches, but purely as a cheap method of manufacturing shapes such as steel wires for tire cords; when the original technological objective was not achieved, interest in these devices soon waned. It was Duwez's team, sustained by its scientific curiosity, that carried this technical revolution through to completion. There have been two major consequences of his work on RSP: (1) The exploitation of metastable (supersaturated) metallic solid solutions, such as tool steels and light alloys which could be age-hardened particularly effectively because so much excess solute was available for pre-precipitation. (2) The study of metallic glasses in all their variety, which both created an extensive new field for experimental and theoretical research (Cahn 1980) and, in due course, offered



major technological breakthroughs. On a larger view still, Duwez's work created the whole concept of non-equilibrium processing of materials (including techniques such as surface treatment by laser), which has just been surveyed (Suryanarayana 1999). There is also substantial coverage in Cahn's historical review and in the whole book in which it appeared in 1993. One of the topics covered there is the gradual development of techniques, both theoretical and experimental, for estimating the cooling rates in an RSP device. A rate of as much as a million degrees per second is feasible, compared with a very few thousand degrees per second in the best solid-state quench.

**10.2.1.1 Metallic glasses.** With regard to metallic glasses, which were so unexpected that for years Duwez was still sceptical of his own group's discovery, an explosion of research followed in the 1960s and 1970s, on such topics as the factors governing the ability to form such glasses (primarily, what compositions?), their plastic behavior, diffusion mechanisms, electrical conduction and, especially, ferromagnetic behavior of certain glasses (Spaepen and Turnbull 1984). Johnson, in his biographical memoir, says that in or about 1962, Duwez met the great Peter Debye at a conference and discussed the possibility of ferromagnetism in a metallic glass, in spite of the absence of a crystal lattice which would provide a vector for the spins to align themselves along. Debye must have been encouraging, for Duwez began to modify an early glass composition,  $\text{Pd}_{80}\text{Si}_{20}$ , by substituting Fe for some of the Pd, and in 1966 weak ferromagnetism was observed. Further substitutions eventually led to  $\text{Fe}_{75}\text{P}_{15}\text{C}_{10}$  which was strongly ferromagnetic. A composition close to this is still used nowadays in transformer manufacture.

The use of ferrous glasses in making small 'distribution transformers' for stepping down voltages of several thousand volts to domestic voltages developed by degrees, and a technical history of this fascinating story has been published by DeCristofaro (1998). The point here is that core losses (magnetic and eddy-current losses) are much lower than in grain-oriented silicon-iron, which has held sway for a century; part of the reason is that the absence of magnetocrystalline anisotropy means that the coercive field for a magnetic glass can be particularly small. The upshot is that the power loss in a transformer is so much reduced that the slightly greater cost of the glass is acceptable.

The final development of metallic glasses is the discovery of 'bulk metallic glasses'. Since the 1960s, certain compositions, such as one in a Cu-Pd-Si ternary, had been found to require a cooling rate of only a few hundred degrees per second to bypass unwanted crystallisation during cooling. W.L. Johnson, one of Duwez's right-hand collaborators, and T. Masumoto and A. Inoue in Sendai, Japan, independently developed such compositions into complex mixtures, usually with

four or five constituents, that had critical cooling rates of only  $10^\circ$  per second or sometimes even  $1^\circ$  per second... almost like siliceous oxide melts! Objects several centimetres thick could be made glassy. A Zr-Ti-Ni-Cu-Be mixture was the first, and Johnson has pursued this theme with pertinacity: one recent review is by him (Johnson 1996). These compositions are usually close to a deep eutectic, which is an established feature favouring glass formation. A so-called "confusion principle" also operates; not all the multiple diffusions needed for such a glass to crystallise can take place freely, and some sluggish diffusers will in effect stabilise the glass against crystallisation. Up to now, applications are fewer than might have been expected; the manufacture of golf clubs that are more forgiving of duff strokes than earlier clubs (because of the low damping in these glasses) is the most lucrative. A range of bulk glasses based on aluminium has been energetically developed by Masumoto and Inoue in Sendai, Japan, from 1990 onwards, and several of the early papers are listed in Johnson's 1996 overview. Inoue has also written a range of interesting reviews of the field. Inoue's team also pioneered the creation of ultrastrong aluminium-base metallic glasses reinforced by nanocrystalline crystallites through appropriate heat-treatment (e.g., Kim *et al.* 1991). Johnson and his many coworkers (e.g., Löffler *et al.* 2000) have shown by detailed physical analysis why bulk glasses inherently favour copious crystallization in the form of nanocrystalline grains. They are likely to have an important future as useful materials in the partly or wholly crystallised form.

**10.2.1.2 Other routes to amorphisation.** RSP is not the only way to make metallic glasses. One unexpected approach, discovered by Johnson and coworkers in 1983 and later reviewed by Johnson (1986b) is the *solid-state amorphisation reaction*. Here adjacent thin layers of crystalline elements are heated to interdiffuse them and the mixed zone then becomes amorphous, because crystallisation of a thermodynamically stabler intermetallic compound is kinetically inhibited. An alternative approach to amorphization exploits ball-milling, i.e., intense mechanical deformation of a (usually) metallic or intermetallic compound powder by impacting with tumbling steel or ceramic balls in a mill; this has lately become a major research field in its own right. Such amorphization was first observed by A.E. Yermakov in Russia in 1981. A good review is by Koch (1991). A theoretical study by Desré in 1994 has shown that when the mean grain size of a ball-milled powder has been reduced to a critical size, it will in effect 'melt' to form a thermodynamically stable glass. In fact, amorphization and true melting have been found to be intimately related (Cahn and Johnson 1986).

There is also a large body of research on crystal-to-glass transformation induced by nuclear irradiation, beginning with the observation by Bloch in 1962 that  $U_6Fe$

was amorphised by fission fragments. The physics of this process is surveyed in great depth in relation to other modes of amorphization, and to theoretical criteria for melting, by Okamoto *et al.* (1999).

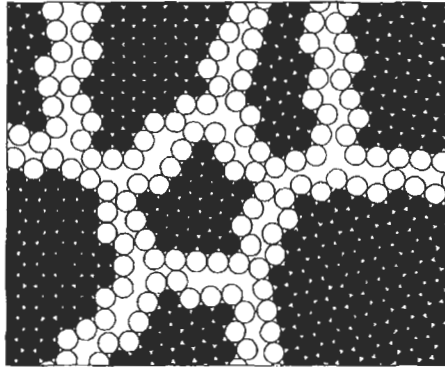
### 10.3. EXTREME MICROSTRUCTURES

#### *10.3.1 Nanostructured materials*

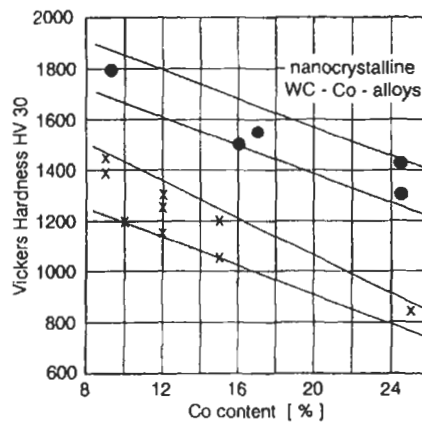
At a meeting of the American Physical Society in 1959, the Nobel prize-winning physicist, Richard Feynman, speculated in public about the likely effects of manipulating tiny pieces of condensed matter: “I can hardly doubt that when we have some control of the arrangements of things on a small scale, we will get an enormously greater range of possible properties that substances can have”. A few years previously, in 1953, as we saw in Section 7.2.1.4, Lifshitz and Kosevich in Russia predicted quantum size effects in what have since come to be known as quantum wells and quantum dots, leading on to Esaki and Tsu’s discovery of semiconducting ‘superlattices’ in 1970–1973. A little later, the pursuit of atomic clusters, predominantly of metals or semiconductors, took wing, because of an interest in the way properties, such as melting behavior, varies with cluster size for minute clusters. In 1988, a lengthy survey was published (Brus, Siegel *et al.* 1988) of both clusters and “cluster-assembled materials”. The term in quotes was one of many synonyms in use at that time for polycrystalline solids made up of extremely small grains; recently, the international community interested in such materials has settled on “nanostructured materials” as the preferred term, with “nanophase materials” and “nanocrystalline materials” as backups. (“Nanostructures” is also sometimes used, but risks confusion with another burgeoning field, the production of minute mechanisms such as nano-electric motors, often from silicon monocrystals, which I do not discuss here; the term ‘micromechanoelectrical’ devices, or MEMs, is now often used for these. In 1959 Feynman offered a cash prize for the first electric motor less than 1/64 inch across, and it was not very long before he was called upon to make good his promise.)

Attention had been focused on nanostructured materials by a lecture delivered in Denmark by Herbert Gleiter (1981); in a recent outline survey of the field, Siegel (1996) describes this lecture as a ‘watershed event’. A little later, Gleiter and Marquardt (1984) set forth some further ideas. Gleiter proposed that the kind of solid materials he envisaged could be made by evaporating substances into a space occupied by an inert gas at high pressure; nanoclusters would condense, be harvested without breaking the enclosure and be compressed by a piston to form a ‘green’ solid, which would then need further compaction by heat treatment. This for a while became the orthodox way of producing small samples for the study, primarily, of

mechanical properties. Gleiter's view of the essential structure of these materials, when single phase, is shown in Figure 10.2: a substantial fraction of the atoms lies in the disordered grain boundaries. It was predicted that resistance to plastic deformation by dislocation motion would steadily increase as grain size is reduced, and this proved to be true, except that at the very smallest grain sizes there is often an inversion and strength again diminishes; this aspect is still a matter of frequent investigation. Such studies have also been made for 'nanocomposites': Figure 10.3 shows that nanostructured WC-Co 'cermet', now a commercial product used for cutting tools, is substantially harder than the same material with conventional grain size; the fine-grained cermet is also considerably tougher (more resistant to cracking).



**Figure 10.2.** Schematic of the microstructure of a nanostructured single-phase material (after Gleiter 1996).



**Figure 10.3.** Hardness of WC-Co cermets with nanostructured and conventional grain sizes (after Gleiter 1996, reproduced from a report by Schlump and Willbrandt).

The most intriguing aspect of nanostructured metals and, especially, ceramics such as titania is that the very small grain size encourages Herring-Nabarro creep which, in turn is the precondition of superplastic forming under stress. The essential facts concerning this process are laid out in Section 4.2.5. Nanostructured ceramics can be plastically formed, in spite of extreme resistance to dislocation motion, and this has been plentifully documented in many studies. Examples are set out in Gleiter's own (1996) overview of nanostructured materials. The ability to form nano-ceramics to 'near net shapes' looks to have very promising industrial potential.

The exploitation of easy superplastic forming of nanostructured ceramics is hindered by one major flaw: the heat treatment needed to sinter a 'green' solid to 100% density also leads to grain growth, so that by the time the material is fully dense, it is no longer nanocrystalline. Very recently, a way has been found round this difficulty. Chen and Wang (2000), studying  $Y_2O_3$ , have found that a two-stage sintering process allows full density to be attained while grain growth is arrested during the second stage. Typically, the compact is briefly heated to 1310°C and the temperature is then lowered to 1150°C; if that lower temperature were applied from the start, complete densification would not be possible. The paper analyses various conceivable explanations, but it is not at present clear why a brief high-temperature anneal inhibits grain growth at a subsequent lower temperature; this valuable finding is likely to engender much consequential research.

A number of 'functional' properties can also be affected by nanocrystallinity. The most interesting of these is soft ferromagnetism. Yoshizawa *et al.* (1988) discovered that a bulk metallic glass (trade-named "Finemet") of composition  $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ , on partial crystallization, assumes a structure with nanometre-sized (5–20 nm) crystallites embedded in a residual glassy matrix. The small amount of copper in the glass provides copious nucleation sites (rather as copper does in glass-ceramics, Section 9.6); the very high magnetic permeability of such glass/crystal composites can be attributed to the fact that the equilibrium magnetic domain thickness exceeds the average crystallite size.

Another functional nanostructured material is porous silicon, monocrystalline silicon chemically etched to produce a fine hairlike morphology: this material, unlike unetched silicon, shows photoluminescence (the emission of light of a wavelength – variable – longer than the incident light). The phenomenon was discovered by Canham (1990) and is surveyed by Prokes (1996). Its mechanism is still under lively debate; it appears to be a variant of quantum confinement. Frohnhoff and Berger (1994) have succeeded, by varying the formation current density, in making superlattices with porous and non-porous silicon alternating; such superlattices can be tuned to reflect the photoluminescence and therefore enhance light emission. There is hope of exploiting porous silicon in light-emitting devices based on silicon

chips, as part of 'optoelectronic' circuitry. The prospects of success in this have been discussed by Miller (1996).

The comparatively new field of nanostructured materials has its own journals (though the first one has now been merged with another, broader journal) and frequent conferences; it is a good example of a *parepisteme* which appears to be successful. The best single source of information about the many aspects of the field is a substantial multiauthor book edited by Edelstein and Cammarata (1996).

The original 'Gleiter method' of making nanostructured solids is fine for research but not a feasible commercial method of making substantial quantities, for instance of a nanostructured cermet such as Co-WC. A whole range of chemical methods has now been developed, as described in the Edelstein/Cammarata book. These methods are mostly dependent on colloidal precursors, often using the so-called sol-gel approach. A sol is a colloidal liquid solution, often in water; on evaporation or other treatment, a sol turns into a gelatinous 'gel' which in turn can be converted into a nanostructured solid. A range of organometallic colloidal precursors can be converted into oxide ceramics by such an approach. Spray pyrolysis or conversion via an 'aerosol' (a suspension of colloidal particles in air or other gas) offer other potentially large-scale routes to make nanostructured materials, and yet another route, chemically sophisticated, is by stabilising metal clusters with 'ligands', chemical radicals which bind to and coat the clusters to stabilise them against agglomeration. This approach allows a population of uniformly sized clusters to be made, but it is not appropriate for conversion into continuous solid materials.

Gleiter, who effectively created this field of research, has very recently surveyed its present condition in a magisterial overview (Gleiter 2000).

It must be added that in the opinion of some observers, the claims of what is coming to be called 'nanotechnology' are often exaggerated, and long-term hopes are sometimes presented as though they were present-day reality. A carefully nuanced critical view can be found, for example, in a review by an engineer, Dobson (2000), of a large book entitled *Nanotechnology*. To balance this, again, there are some sober overviews of what may be in prospect; an example is a survey of work currently in progress at Oak Ridge National Laboratory, in America (ORNL 2000). In this survey, an intriguing remark is attributed to Eugene Wong of the National Science Foundation in America: "The nanometre is truly a magical unit of length. It is the point where the smallest manmade thing meets nature".

### 10.3.2 *Microsieves via particle tracks*

Small holes are the negative correlative of small objects, and there is in fact an industrial product, considerably antedating Gleiter's initiative, which is based on such holes.

Two physicists, R.M. Walker and P.B. Price, working at the GE central laboratory in Schenectady, NY (see Section 1.1.2) discovered in 1961 that heavy fission fragments from uranium leave damage trails in insulators such as mica which, on subsequent chemical attack, act as preferential loci for rapid etching. A population of fission tracks in a thin cleaved sliver of mica can be converted into a population of holes of fairly uniform size; the mean size is determined by the duration of etching. Holes typically 3–4  $\mu\text{m}$  across were formed. (This specific research was stimulated by a colleague at GE who needed a controllable, ultraslow vacuum leak.) Together with a third physicist, R.L. Fleischer, the discoverers developed this finding into a means of studying many features and processes, such as the age of geological specimens, the scale of radon seepage from radioactive rocks, and even features of petroleum deposits. The really unexpected development, however, came in 1962, when a cancer researcher in New York got wind of this research; he was just then needing an ultrafilter for blood which would hold back the larger, more rigid cancer cells while allowing other cells to pass through. GE's etched mica slivers proved to be ideal. This led to the setting-up of a dedicated small manufactory to make such filters; Fleischer found that sieves made with GE's own polycarbonate resin (used in automotive lighting) were stronger and more durable than those made with mica. A major medical product resulted which soon made GE a sales of some ten million dollars a year. When, 17 years later, the patents expired, other companies began to compete, and the total sales of microfilters, used to analyse aerosols, etc., as well as cancerous blood, now exceeds 50 million dollars per annum.

The antecedents and circumstances of this research program are spelled out in some detail by Suits and Bueche (1967), two former research directors of GE, and much more recently in a popular book by Fleischer (1998). Both publications analyse why a hard-headed industrial laboratory saw fit to finance such apparently 'blue-sky' research. Suits and Bueche say: "...the research did not arise from any direct or specific need of GE's businesses and was related to them only in a general way. Why, then, was the research condoned, supported and encouraged in an industrial laboratory? The answer is that a large company and a large laboratory can invest a small fraction of its funds in speculative ventures in research; these ventures promise, however tentatively, departures into entirely new businesses." This research met "no recognised pre-existent need"; indeed, to adopt my preferred word, it was a pure *parepisteme*. A recent historical study of a number of recent practical inventions, with a focus on high-temperature superconduction (Holton *et al.* 1996) concludes: "...above all, 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".

Fleischer, from his perspective 31 years later, points out that (as it turned out) track etching had been independently discovered in the late 1950s at Harwell Laboratory in England a little before GE did, but because the laboratory was then not commercially oriented, nothing was done to follow up the possibilities. In a hard-hitting analysis (pp. 171–176 of his book) Fleischer examines the gradual decay of this kind of industrial research in industry across the world (“even in Japan”), to be replaced by demands from American industrial executives that government should finance universities to undertake more of this kind of *parepistemic* research that had formerly been done in industrial laboratories, specifically in order to help industrial firms. Fleischer remarks that such pleadings are “if not actually hypocritical, at least futile. Is it reasonable to expect decision-makers in government to be eager to invest in science from which industry has withdrawn?” In my own country, Britain, in the face of the closure of ICI’s New Materials Group and of the entire New Ventures laboratory of BP, one can only echo this bitter rhetorical question.

#### 10.4. ULTRAHIGH VACUUM AND SURFACE SCIENCE

##### *10.4.1 The origins of modern surface science*

The earliest transistors (Section 7.2.1), starting at the end of the 1940s, were made of germanium; silicon only followed some years later. However, germanium transistors proved disconcertingly unreliable. The experience of manufacturers in those early days was forcefully put in a book by Hanson (1980): “It was wondrous that transistors worked at all, and quite often they did not. Those that did varied widely in performance, and it was sometimes easier to test them after production and, on that basis, find out what kind of electronic component they had turned out to be. . . It was as if the Ford Motor Company was running a production line so uncontrollable that it had to test the finished product to find out if it was a truck, a convertible or a sedan.”

In an illuminating overview of the linkage between semiconductor problems and the genesis of surface science, Gatos (1994) describes the research on germanium surfaces performed at MIT and elsewhere in the early 1950s. The erratic performance of germanium transistors was gradually linked to the unstable properties of germanium surfaces, especially the solubility of germanium oxide in water; the electronic ‘surface states’ on Ge were thus unstable. In spite of prolonged studies of etching procedures intended to stabilise Ge surfaces, “their reliable and permanent stabilisation, indispensable in solid-state electronics, remained a moving target”, to quote Gatos verbatim. “Naturally, the emphasis shifted from Ge to Si. The very thin surface oxide on Si was found to be chemically refractory and, thus, assured surface chemical stability”. The manufacturer was now able to predetermine whether he was making a truck or a convertible!



According to Gatos, the needs of solid-state electronics, not least in connection with various compound semiconductors, were a prime catalyst for the evolution of the techniques needed for a detailed study of surface structure, an evolution which gathered pace in the late 1950s and early 1960s. This analysis is confirmed by the fact that Gatos, who had become a semiconductor specialist in the materials science and engineering department at M.I.T., was invited in 1962 to edit a new journal to be devoted specifically to semiconductor surfaces. As Gatos remarks in his historical overview, "it was clear to me that the experimental and theoretical developments achieved for the study of semiconductor surfaces were being rapidly transplanted to the study of the surfaces of other classes of materials". He thus insisted on a broader remit for the new journal, and *Surface Science*, under Gatos' editorship, first saw the light of day in 1964. Gatos' essay is the first in a long series of review articles on different aspects of surface science to mark the 30th anniversary of the journal, making up volumes 299/300 of *Surface Science*.

Other fields of surface study were of course developing: the study of catalysts for the chemical industry and the study of friction and lubrication of solid surfaces were two such fields. But in sheer terms of economic weight, solid-state electronics seems to have led the field.

Before 1950, it was impossible to examine the true structure of a solid surface, because, even if a surface is cleaned by flash-heating, the atmospheric molecules which constantly bombard a solid surface very quickly re-form an adsorbed monolayer, which is likely to alter the underlying structure. Assuming that all incident molecules of oxygen or nitrogen stick to the surface, a monolayer will be formed in  $3 \times 10^{-6}$  second at 1 Torr ( $=1$  mm of mercury), that is, at  $10^{-3}$  atmosphere; a monolayer forms in 3 s at  $10^{-6}$  Torr, or  $10^{-9}$  atmosphere; but a complete monolayer takes about an hour to form at  $10^{-9}$  Torr. The problem was that in 1950, a vacuum of  $10^{-9}$  Torr was not achievable;  $10^{-8}$  Torr was the limit, and that only provided a few minutes' grace before an experimental surface became wholly contaminated.

The scientific study of surfaces, and the full recognition of how much a surface differs from a bulk structure, awaited a drastic improvement in vacuum technique. The next Section is devoted to a brief account of the history of vacuum.

#### ***10.4.2 The creation of ultrahigh vacuum***

Early in the 17th century, there was still vigorous disagreement as to the feasibility of empty space; Descartes denied the possibility of a vacuum. The matter was put to the test for the first time by Otto von Guericke (1602–1686), a German politician who "devoted his brief leisure to scientific experimentation" (Krafft 1970–1980). He designed a crude suction pump using a cylinder and piston and two flap valves, and

with this, after many false starts, he succeeded in his famous 1657 public experiment, in Magdeburg, of evacuating a pair of tightly fitting copper hemispheres to the point that two teams of horses could not drag them apart. The reality of vacuum had been publicly demonstrated.

In fact, though probably von Guericke did not know about it, the Florentine Evangelista Torricelli (1608–1647) had also established the pressure of the atmosphere by showing in 1643 that there was a limiting height of mercury that could be supported by that pressure in a closed tube; a working barometer followed the next year. This famous experiment indirectly demonstrated the existence of the “Torricellian vacuum” above the mercury in the closed tube, hence the use of Torricelli’s name for the unit of gas pressure in a partial vacuum, the torr (equivalent to the pressure exerted by a mercury column of one millimetre height). In 1650, no less a scholar than Blaise Pascal showed that the height of the supported mercury column varied with altitude above sea-level.

In 1850, the Toepler pump was invented; this is a form of piston pump in which the reciprocating piston consists of mercury; it was followed in 1865 by the Sprengel pump, in which air is entrained away by small drops of mercury falling under gravity. In 1874, the first accurate vacuum gauge, the McLeod gauge, again centred around mercury columns, was devised. These and other dates are listed in a concise history of vacuum techniques (Roth 1976). The first rotary vacuum pump, the workhorse of rough vacuum, was not invented until 1905, by Wolfgang Gaede in Germany, and the first diffusion pump, invented by Irving Langmuir at GE, followed in 1916.

It is noteworthy that inventors well before Edison, notably the Englishman Joseph Swan who in some people’s estimation was the true inventor of the incandescent lamp, found it impossible to make a stable lamp because the vacuum pumps at their disposal simply were not effective enough, and also took an inordinate time to produce even a modest vacuum. By the time Edison developed his carbon filament lamp in 1879, the Toepler and Sprengel pumps had been sufficiently developed to enable him to protect his filaments from oxidation, by vacua of around 0.1 torr or even better. In due course, ‘getters’ were invented; these were small pieces of highly reactive metal inside light bulbs, which were briefly flashed by an electric current to absorb residual oxygen and nitrogen. It was only from 1879 onwards that vacuum quality began to be taken seriously.

With the rotary and diffusion pumps in tandem, aided by a liquid-nitrogen trap, a vacuum of  $10^{-6}$  Torr became readily attainable between the wars; by degrees, as oils and vacuum greases improved, this was inched up towards  $10^{-8}$  Torr (a hundred-billionth of atmospheric pressure), but there it stuck. These low pressures were beyond the range of the McLeod gauge and even beyond the Pirani gauge based on heat conduction from a hot filament (limit  $\approx 10^{-4}$  Torr), and it was necessary to

use the hot-cathode ionisation gauge, invented in 1937. This depends on a hot-wire cathode surrounded by a positively charged grid, which in turn is enclosed in an ion-collecting 'shell'. Electrons travelling outwards from the cathode occasionally collide with a gas molecule, ionising them; the positive ions are picked up by the negatively charged collection shell, and their number measures the quality of the vacuum.

As we have seen, by 1950 it had become clear that no proper surface science could begin until a vacuum considerably 'harder' than  $10^{-8}$  Torr could be attained. The  $10^{-8}$  Torr limit was therefore a great frustration. Then, in 1947, Wayne Nottingham of MIT came up with the suggestion that the limit was illusory: he thought that the limit was not in pumping, but in measurement: Nottingham suggested that the electrons bombarding the positively charged grid would generate X-rays, which would release more photoelectrons from the collector. So the gauge would register a signal even if there were no gas molecules whatever in the gauge! Two years later, Robert Bayard and Daniel Alpert, at the Westinghouse Research Laboratory in Pittsburgh, invented a way of circumventing the problem, if it had been correctly diagnosed (Bayard and Alpert 1950). They switched the positions of the cathode and the collector. Now the collector was no longer a large cylinder but just a wire, offering a very slender target to the X-rays from the grid, so that the "null signal" would be negligible. The strategy worked, indeed it worked better than predicted, because the ion gauge could operate as a pump at very low pressures as well as being an indicator. The new Alpert gauge was isolated by means of a novel all-metal valve that did not require an organic sealing compound with its unavoidable characteristic vapour pressure, and the quality of the vacuum sailed to  $5 \times 10^{-10}$  Torr. This was now a new limit; Alpert, who is the recognised father of ultrahigh vacuum, constructed a mass spectrometer to analyse the residual atmosphere, and found that the new  $5 \times 10^{-10}$  Torr limit was due to atmospheric helium percolating through the pyrex glass enclosure. Thereafter, glass was avoided and the bulk of vacuum apparatus for ultrahigh vacuum (UHV) was henceforth made of welded metal, usually stainless steel, with soft metallic gaskets that require no lubricant, and fully metallic valves.

Such vessels can also be 'baked' at a temperature of several hundred degrees, to drive off any gas adsorbed on metal surfaces. The pumping function of an ion gauge was developed into efficient ionic pumps and 'turbomolecular pumps', supplemented by low-temperature traps and cryopumps. Finally, sputter-ion pumps, which rely on sorption processes initiated by ionised gas, were introduced. A vacuum of  $10^{-11}$ – $10^{-12}$  Torr, true UHV, became routinely accessible in the late 1950s, and surface science could be launched.

An early account of UHV and its requirements is by Redhead *et al.* (1962); an even earlier summary of progress in vacuum technology, with perhaps the first tentative account of UHV, was by Pollard (1959). A lively popular account is by

Steinherz and Redhead (1962), while advances in vacuum techniques from a specifically chemical viewpoint were discussed by Roberts (1960).

The various new vacuum pumps certainly made possible much faster and more efficient pumping, but the essential breakthrough came from two events: the recognition that the older ionic vacuum gauges were drastically inaccurate, and the further recognition that UHV systems needed to be made from metal, with little or no glass and no organic greases, and that the systems had to be bakeable.

The curious behavior of ion gauges acting also as pumps has had a recent counterpart. Cohron *et al.* (1996) studied the effect of low-pressure hydrogen on the mechanical behavior of the intermetallic compound  $\text{Ni}_3\text{Al}$ . They found, to their astonishment, that the ductility of the compound with their ion gauge turned off was 3–4 times higher than with the gauge functioning. They discovered that Langmuir and Mackey (1914) had first identified hydrogen dissociation on a hot tungsten surface, and proved that the embrittlement was due to atomic hydrogen ‘manufactured’ inside the gauge that then diffused along grain boundaries of the compound and embrittled them. So it seems that one must always be alert to the possibility of a measuring device that influences the very variable that it is meant to measure... a very apposite precaution in the days of quantum ambivalence.

#### 10.4.3 An outline of surface science

My principal objective in Section 10.4 has been to underline the necessity for a drastic enhancement of a crucial experimental technology, the production of ultrahigh vacuum, as a precondition for the emergence of a new branch of science, and this enhancement was surveyed in the preceding Section. It would not be appropriate in this book to present a detailed account of surface science as it has developed, so I shall restrict myself to a few comments. The field has been neatly subdivided among chemists, physicists and materials scientists; it is an ideal specimen of the kind of study which has flourished under the conditions of the interdisciplinary materials laboratories described in Chapter 1.

UHV is necessary but not sufficient to ensure an uncontaminated surface. Certainly, the surface will not be contaminated by atoms arriving from the vacuum space, but such contamination as it had before the vacuum was formed has to be removed by bombardment with argon ions. This damages the surface structurally, and that has to be ‘healed’ by in situ heat treatment. That, however, allows dissolved impurities to diffuse to the surface and cause contamination from below. This problem has to be dealt with by many cycles of bombardment and annealing, until the internal contaminants are exhausted. This is a convincing example of Murphy’s Law in action: one of the many corollaries of the Law is that “new systems generate new problems”.

The first key technique (UHV apart) in surface science was low-energy electron diffraction (LEED). This was used for the first time by Davisson and Germer at Bell Labs in 1927; it did not then give much information about surfaces, but it did for the first time confirm the wave-particle duality in respect of electrons and thereby earned the investigators a Nobel Prize. The technique uses electrons typically at energies of 20–300 eV, which penetrate only one or two atom layers deep. The great difficulty is in interpreting the patterns obtained; the problems are well set out in a standard text by Woodruff and Delchar (1986); it is necessary to take account of multiple scattering. The early mystifications among LEED practitioners are explained in reminiscences by Marcus (1994). Not only the two-dimensional surface reconstruction as exemplified in Figure 6.9(b) in Chapter 6, but also the complications ensuing from domains, steps and defects at the surface need to be allowed for. One eminent practitioner, J.B. Pendry, in an opinion piece in *Nature* (Pendry 1984) under the title “Removing the black magic”, claimed that proper surface crystallography had only existed since about 1974. Now, pictures obtained by scanning tunnelling microscopy offer a direct check on conclusions reached by LEED. The other key technique which is now used in conjunction with LEED is Auger electron spectrometry: here an ionising primary beam unleashes a cascade of electron energy transitions until an ‘Auger electron’ with an energy that constitutes a finger print of the element emitting it is released into the vacuum. The ranges of Auger electrons are so small that effectively the technique examines and identifies the surface monolayer of atoms. An early survey of this key technique is by Rivière (1973).

One other technique has become central in surface research: this is X-ray photoelectron spectrometry, earlier known as ESCA, ‘electron spectroscopy for chemical analysis’. Photoelectrons are emitted from a surface irradiated by X-rays. The precautions which have to be taken to ensure accurate quantitative analysis by this much-used technique are set out by Seah (1980).

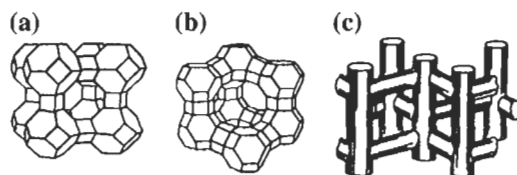
It is now clear that surface defects, steps in particular, and two-dimensional crystallographic restructuring of surfaces, are linked: there is a phenomenon of reconstruction-linked faceting. Surface steps, particularly on vicinal crystal faces (faces close to but not coinciding with low-index planes) are important for various electronic devices; in particular, the migration of steps and thus the instability of surface morphology needs to be understood. The elaborate complexity of current understanding of surface steps has just been surveyed by Jeong and Williams (1999).

As remarked above, surface science has come to be partitioned between chemists, physicists and materials scientists. Physicists have played a substantial role, and an excellent early overview of surface science from a physicist’s perspective is by Tabor (1981). An example of a surface *parepisteme* that has been entirely driven by physicists is the study of the *roughening transition*. Above a critical temperature but

still well below the melting temperature, many smooth surfaces begin to become rough. This was first theoretically predicted in the famous 1951 paper by Burton, Cabrera and Frank on the theory of crystal growth (see Section 3.2.3.3): roughening is in essence due to the prevalence of vacancies at surfaces and the consequential enhanced probability of creating additional defects near an existing defect; diffusing vacancies and adatoms will begin to cluster above the roughening temperature, forming growing mounds. In the mid-1970s, the roughening transition was shown to be also linked, improbable though it may seem, to a two-dimensional metal-insulator transition. The story of theory and experiment relating to this curious phenomenon can be found in a review article by Pontikis (1993).

Nevertheless, chemists have played the biggest role by far. A particular reason for this is that chemists need catalysts to accelerate many reactions used in chemical manufacturing, in particular the cracking of petroleum into fractions; this has been a major field of research, focused on surface behavior, ever since Johann Döbereiner (1780–1849) in 1823 discovered that platinum sponge (very fine particles) catalysed the combination of hydrogen and oxygen. Some of these catalysts are colloidal (nanostructured) particles, in some cases even metallic glass particles, but the most important catalysts nowadays are zeolites. These are typically crystalline aluminosilicates with the formal composition  $M_xO_y \cdot Al_2O_3 \cdot pSiO_2 \cdot qH_2O$ . They have structural tunnels – internal surfaces – as shown in Figure 10.4; these admit some reactants but not others and can thus function as highly selective catalysts.

Crucial though they are industrially, I do not propose to discuss catalysts further here. My reason is that I do not regard them as materials. Up to this point, I have not sought to define what I mean by a ‘material’, but this is a convenient point to attempt such a definition. In my conception, a material is a substance which is then further processed, shaped and combined with others to make a useful object. Something like a lubricant, fertiliser, food, drug, ink or catalyst by that definition is not a material, because it is used ‘as is’. Like all definitions, this is untidy at the edges: thus a drug may be combined with another substance to ensure slow release to the bodily tissues, and that auxiliary substance is then a material, and the status of cooked foods by my definition gives plentiful scope for casuistry.



**Figure 10.4.** Outline structures of (a) zeolite A, (b) its homologue faujasite, (c) the channel network of the ‘tubular’ zeolite ZSM-5.

An excellent, accessible overview of what surface scientists do, the problems they address and how they link to technological needs is in a published lecture by a chemist, Somorjai (1998). He concisely sets out the function of numerous advanced instruments and techniques used by the surface scientist, all combined with UHV (LEED was merely the first), and exemplifies the kinds of physical chemical issues addressed – to pick just one example, the interactions of co-adsorbed species on a surface. He also introduces the concept of ‘surface materials’, ones in which the external or internal surfaces are the key to function. In this sense, a surface material is rather like a nanostructured material; in the one case the material consists predominantly of surfaces, in the other case, of interfaces.

A further field of research is linked to the influence of the surface state on a range of bulk properties: a recent example is the demonstration of enhancement of ductility of relatively brittle materials such as pure chromium and the intermetallic NiAl by careful removal of mechanical damage from their surfaces. A further large field of research is the design and properties of surface coatings, with objectives such as oxidation resistance (notably for superalloys in jet engines), ultrahardness and reduction of friction. This is a domain cultivated by materials engineers, as is the study of *tribology*, which comes from the Greek word for ‘rubbing’ and includes the study of friction as well as the rate and mechanisms of wear when one surface rubs against another under load. Tribology, an increasingly elaborate and important field, links closely with the study of lubrication. Tribology has become a beautiful exemplar of the marriage of engineering and science. The notable classic of this field is a text by Bowden and Tabor (1954), while a more recent concise overview is by Furey (1986). The history of tribology is surveyed by Dowson (1979).

## 10.5. EXTREME THINNESS

### 10.5.1 Thin films

Thin metallic or semiconducting films, almost invariably deposited on a substrate, come essentially in three forms: monolayers or ultrathin films; continuous films with thicknesses of the order of micrometers; and multilayers of two interleaving species, each successive layer often being only a few nanometers in thickness. This form of material was originally investigated as a ‘pure’ *parepisteme*, beginning with metallic films and going on later to semiconducting ones; applications, which are nowadays extremely varied, arrived only by degrees (some of the important ones in microelectronics have already been outlined in Section 7.2.1.4). Today, thin films have their own major journals and conferences. The subject is clearly linked to surface science, particularly so the study of the initial, monolayer films.

Much interest attaches to the mechanisms of thin film deposition, and these in turn are linked to the mechanisms of epitaxial growth (see below). The very early stages, up to and including monolayer growth, used to be investigated largely by Auger electron spectrometry: the completion of the first layer is revealed by a bend in the plot of signal intensity versus time of deposition, and LEED helped to identify the nature of the initial deposit; progressively, electron microscopy, both by transmission and by scanning microscopy, has gradually taken over. This kind of research has been closely linked with the investigation of chemisorption. The early work on monolayers is very competently surveyed by Rhead (1983).

The workhorse methods used for depositing thin films are thermal evaporation and sputtering. The second (evocatively named) method allows much more exact control than does evaporation: it involves bombarding a target consisting of the material(s) to be deposited with high-energy noble-gas ions, causing atoms of the target to spring out and hit the substrate. One starts with UHV and then bleeds in small pressures of the bombarding gas, which does not contaminate the substrate surface. For the most complete control, especially when semiconductor films are in question, molecular-beam methods and atomic layer epitaxy, as outlined in Section 7.2.1.4, are now used. The subtleties of sputtering are surveyed by Kinbara (1997).

In recent years, it has been established that bombarding the substrate (as distinct from a target) directly with noble-gas ions while a film is being deposited can greatly enhance the quality of adhesion between substrate and deposit, and controlling the direction of the bombarding ions can influence the crystallographic orientation of the deposit as well as its microstructure. This whole family of effects, now widely exploited, is surveyed by Rossmagel and Cuomo (1988).

Of the many properties of films in their successive stages, those most commonly studied nowadays are the magnetic, electrical and mechanical ones. The magnetic properties and uses of thin films, especially multilayers, have been outlined in Section 7.4 and need not be repeated here; however, it is worth pointing out an excellent survey of magnetic multilayers (Grünberg 2000). Electrical properties have been covered by Coutts (1974).

The mechanical properties, especially the internal stresses set up by interaction of substrate and deposit, have a close bearing on the behavior of metallic interconnects (electrical conductors) in integrated circuits. Such interconnects suffer from more diseases than does a drink-sodden and tobacco-crazed invalid, and stress-states play roughly the role of nicotine poisoning. A very good review specifically of stresses in films is by Nix (1989).

On the broad subject of thin films generally, a well-regarded early text is by an Indian physicist, Chopra (1969), while a very broad, didactic treatment of thin films in all their aspects is by Ohring (1992). A recent survey of the effect of structure on properties of thin films relevant to microelectronics is by Machlin (1998).

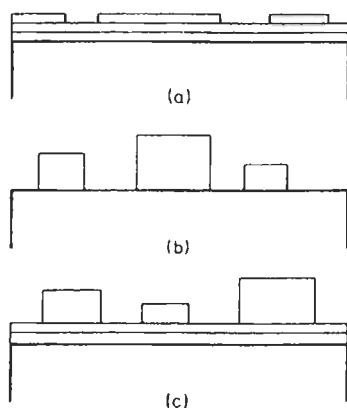


**10.5.1.1 Epitaxy.** There is often a sharp orientation relationship between a single-crystal substrate and a thin-film deposit, depending on the crystal structures and lattice parameters of the two substances. When such a relationship exists, the deposit is said to be *in epitaxy* with the substrate. The simplest relationship is parallel orientation, and this is common in semiconductor heterostructures, but more complex relationships are often encountered.

The word 'epitaxy' was introduced by a French mineralogist, L. Royer, who discovered the phenomenon (Royer 1928); the term, based on Greek, literally means 'arrangement on'. In the early years, the phenomenon was most commonly studied by evaporating metal films on to cleaved alkali halide monocrystals; before UHV was introduced, epitaxial studies were of course restricted to contaminated substrate surfaces. From the beginning, the crucial role of lattice misfit (the mismatch of lattice parameters of the two substances, whether or not they had the same crystal structure) in governing the appearance of epitaxy was fully recognised. A limiting misfit not more than 15% is often quoted as the empirical rule; this is reminiscent of Hume-Rothery's 15% rule governing extensive solid solubility between two isostructural metals (Section 3.3.1.1). A famous stage in the prolonged study of the factors governing the appearance of epitaxy was the publication of a group of papers by F.C. Frank (of crystal-growth fame) and his South African collaborator, J.H. van der Merwe (1949, 1950). They worked out the implications of the hypothesis that growth of an epitaxial deposit depends on the initial growth of a monolayer strained elastically to fit the substrate.

Figure 10.5 shows the three recognised forms of thin-film growth; epitaxy seems to depend on the initial operation of monolayer growth, as shown in Figure 10.5(a). Frank and van der Merwe analysed this in terms of the various surface and interfacial energies involved, including a term attributable to the elastically strained monolayer. These forms of initial growth, and coalescence of growth islands at a later stage, are crucial components of epitaxial growth, as are the defects (such as dislocation arrays) which are formed if the strain becomes too large. There is a detailed discussion of these stages and the factors governing them, and the many crystallographic forms of epitaxy, for metallic thin films, in a fine review by Pashley (1991), who played a major part in the early electron microscopic study of the phenomenon. The conditions governing epitaxy of semiconductors, with special reference to molecular-beam epitaxy, is treated for example by Bachmann (1995).

Oriented ultrathin overgrowth of a polymer on a non-polymeric substrate is the latest combination of materials to show epitaxy. The most recent, remarkable form of this phenomenon is the formation of an array of parallel polymer chains on a substrate by depositing monomers and then polymerising them *in situ*. The Japanese discoverer of this phenomenon (Sano 1996) has called it 'polymerisation-induced



**Figure 10.5.** The three modes of growth of films: (a) Frank and van der Merwe's monolayer (two-dimensional) mode; (b) the Volmer-Weber three-dimensional mode; (c) the Stranski-Krastanov mode involving two-dimensional growth followed by three-dimensional growth.

epitaxy'. This only works with properly crystallizable polymers; atactic polymer chains cannot be aligned in this way. Sano points out that this is a way of aligning (effectively, crystallising in a two-dimensional manner) polymers whose monomers are soluble in appropriate solvents, even though the polymer itself is not.

Another recently discovered form of epitaxy is 'graphoepitaxy' (Geis *et al.* 1979). Here a non-crystalline substrate (often the heat-resistant polymer polyimide, with or without a very thin metallic coating) is scored with grooves or pyramidal depressions; the crystalline film deposited on such a substrate can have a sharp texture induced by the geometrical patterns. More recently, this has been tried out as an inexpensive way (because there is no need for a monocrystalline substrate) of preparing oriented ZnS films for electroluminescent devices (Kanata *et al.* 1988).

**10.5.1.2 Metallic multilayers.** In Section 7.4, we have met the recent discovery of multilayers of two kinds of metal, or of a metal and a non-metal, that exhibit the phenomenon of giant magnetoresistance. This discovery is one reason why the preparation and exploitation of such multilayers have recently grown into a major research field.

The original motivation for the preparation of regular metallic multilayers of carefully controlled periodicity was the need for X-ray reflectors, both to calibrate unknown X-ray wavelengths and to function as large and efficient monochromators, especially for 'soft' X-rays of wavelengths of several Å. This was first done by

Deubner (1930) and analysed in detail in a famous paper by DuMond and Youtz (1940). A typical modern multilayer for this purpose would be of W/Si.

The methods of growing such multilayers with rigorously regular spacing, involving especially sputtering methods, and for characterising them, are critically discussed by Greer and Somekh (1991). They also discuss some unexpected uses which have been discovered for such multilayers, in particular, their use for measuring very small diffusion coefficients: here, diffusion of a component from one layer to its neighbour leads to fuzzy interfaces which in turn leads to reduced intensities of reflected X-rays. In this way, diffusivities (for example, in metallic glasses) have been measured much smaller than can be examined by any other technique.

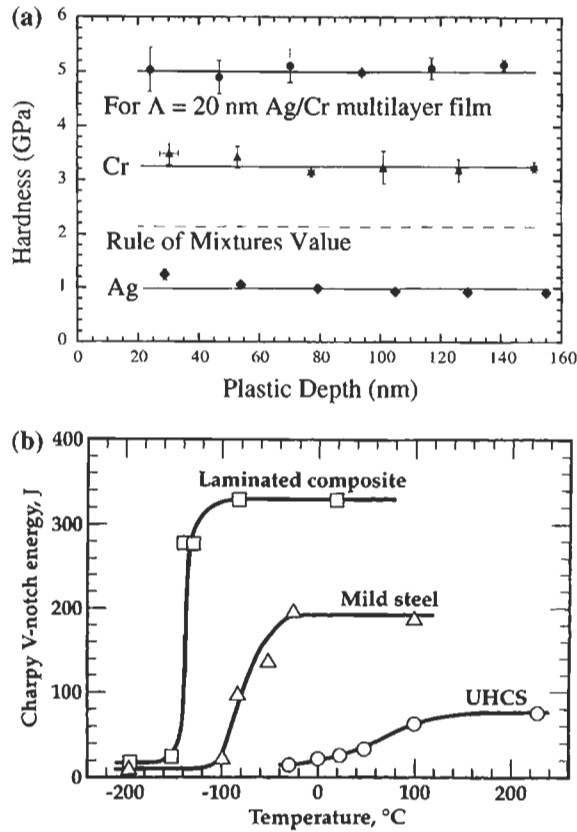
Strength as well as elastic modulus anomalies in multilayers for critical repeat distances caused great excitement a few years ago; it now seems that the elastic anomalies were the result of faulty experimental methods, but the strength enhancement, as well as enhancements of fracture toughness, for very small periodicities seem to be genuine and are beginning to find applications. The motion of dislocations is progressively inhibited as the thickness of individual layers is reduced. Two plots in Figure 10.6 illustrate these trends. In Figure 10.6(a), it can be seen that an Ag/Cr multilayer of wavelength 20 nm is much harder than would be predicted from the rule of mixtures applied to the measured hardnesses of individual layers. Figure 10.6(b) shows a measure of the temperature dependence of fracture toughness (resistance to the spread of cracks) of mild steel, ultrahigh-carbon steel and a laminated (multilayered) composite of the two kinds of steel. Each plot shows a transition temperature from ductile to brittle behavior; this transition is at a very low temperature for the tough composite. The maximum toughness is also much the largest for the multilayered material.

An intriguing recent review of “size effects in materials due to microstructural and dimensional constraints” with a focus on mechanical properties, including those of multilayers, is by Arzt (1998).

## 10.6. EXTREME SYMMETRY

### 10.6.1 *Quasicrystals*

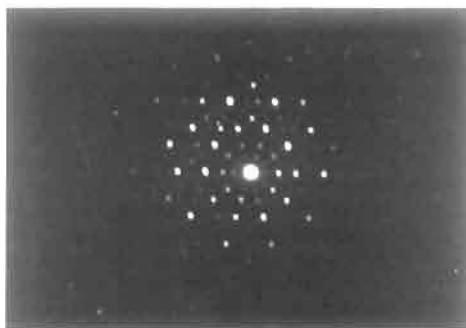
In 1982, at the National Bureau of Standards near Washington, DC, an Israeli crystallographer, Daniel Shechtman, walked in a state of high excitement into the office of his colleague, my namesake John Cahn, to show him a photograph just like the one shown here as Figure 10.7. The pattern was made from an alloy foil (Al–Mn) rapidly quenched from the melt (and in a metastable condition), and shows fivefold symmetry. Every first-year undergraduate of materials science knows that no crystal



**Figure 10.6.** (a) Indentation nanohardness of silver/chromium multilayers and single films of the constituent metals, as a function of depth affected by plastic deformation. (b) Charpy impact energies, a measure of fracture toughness, of three materials, as a function of test temperature: they are mild steel, ultrahigh-carbon steel and a composite of the two kinds of steel (courtesy Dr. J. Wadsworth) (Fig. 10.6(b) is from Kum *et al.* (1983)).

can have fivefold symmetry, because this is incompatible with periodic stacking of atoms. Shechtman claimed this was a new kind of *quasiperiodic* material; the term *quasicrystal* came soon after (Levine and Steinhardt 1984, in a paper entitled *Quasicrystals: a new class of ordered structures*).

John Cahn was irate; what he had been shown was manifest nonsense, and he was sure that a publication making such a claim would relegate both of them, Shechtman and Cahn, to the nether regions of demonstrated crankiness. It took two more years of experimental work, and a good deal of reading of earlier theoretical speculation, before Shechtman and Cahn, together with two French crystallogra-



**Figure 10.7.** Diffraction pattern, prepared in an electron microscope, from a rapidly solidified foil of an Al–Mn alloy containing 14 at.% of manganese. Photograph made in 1984 (courtesy A.L. Greer and the late W.M. Stobbs).

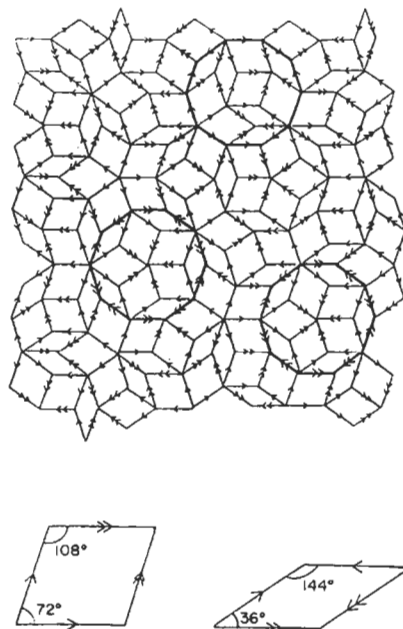
phers who had joined the hunt, took four deep breaths and submitted a paper about their findings (Shechtman *et al.* 1984), under the title *Metallic phase with long-range orientation order and no translational symmetry*. It is perhaps symbolic of the strangeness of this discovery that the preparation method involved another extreme feature, rapid solidification processing. The paper made Shechtman an instant celebrity.

The publication of this paper led to a stampede of research, both experimental and theoretical, and an examination of earlier studies by eminent people like Roger Penrose and Alan Mackay in England about the possibilities of filling space by ‘tiling’ with two distinct populations of tiles, as illustrated in Figure 10.8. This is the basis of quasicrystalline structure.

It took a long time before everyone accepted the reality of quasicrystallinity. No less a celebrity than Linus Pauling took a hard line, and published a paper in *Nature* (Pauling 1985) insisting, erroneously as was finally proved some time later, that the pattern was caused by an array of minute crystals in twinned arrangement.

A great deal of theory was introduced in contemplation of these remarkable materials; the ancient Greek golden section, mathematical Fibonacci series, six-dimensional crystallography... these were three concepts which proved to be relevant to quasicrystals. An early study by Frank and Kasper (1958) – this is the second time that Charles Frank has appeared in this chapter – following the time-hallowed analysis of crystal chemistry in terms of atomic sizes, proved to be important in predicting which alloy systems would generate quasicrystals, and many of the alloys which proved to be convertible to quasicrystals had related Frank–Kasper true crystal structures.

The fivefold symmetry discovered by Shechtman is modelled in terms of the stacking of icosahedra and the term ‘icosahedral symmetry’ is sometimes used.



**Figure 10.8.** Two kinds of rhombi, acute and obtuse, arranged by 'matching rules' to generate a two-dimensional quasiperiodic tiling (courtesy S. Ranganathan).

A little later (Bendersky 1985, Chattopadhyay *et al.* 1985) decagonal (tenfold) symmetry was discovered in other Al-transition metal compounds; quasiperiodic layers are stacked periodically in the third dimension. Since then, one or other of these forms of quasicrystal have been identified in many different compositions. A detailed review of the decagonal type is by Ranganathan *et al.* (1997).

A good, accessible overview of quasicrystals, written only a few years after their discovery, is by Ranganathan (1990); Indian metallurgists played a major part in the early research. Many other published reviews require considerable mathematical sophistication before they can be understood by the reader.

Interest in physical properties of quasicrystals is growing. Thus, a recent comment (Thiel and Dubois 2000) analyses the implications of the fact that decagonal quasicrystals have very much higher electrical resistivity, by orders of magnitude, than do their constituent metals, and moreover that resistivity decreases with rising temperature. For one thing, it seems that the concentration of highly mobile 'free' electrons is much lower in such quasicrystals than in normal metals.

For the first 15 years after the discovery, quasicrystals were studied purely as a compelling scientific issue. Just recently, applications have begun to appear.

According to a recent paper by Shechtman and others (Lang *et al.* 1999) this followed from the first discovery, in Japan, of a thermodynamically stable quasicrystalline phase,  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  (Tsai *et al.* 1987) which could therefore be prepared in bulk, without a need for rapid solidification, so that properties could readily be measured. Such alloys proved to be very hard (and brittle) as well as having a very low coefficient of friction, and this has suggested tribological applications (tribology is the domain of friction and lubrication). The paper by Lang *et al.* reports on systematic studies of the effect of heat-treatment of quasicrystalline alloys, in the form of plasma-sprayed coatings, on tribological properties. It turned out that coatings in the Al-Cu-Fe-Cr and Al-Pd-Mn systems showed the most promising combination of good hardness and low coefficient of friction. Others have proposed such coatings as thermal barrier coatings, and they are being tested on aircraft turbine components. A French metallurgical team that had been studying the fundamentals of quasicrystals for some years came up with an apposite application, non-stick coatings for frying-pans. Most recently, a conference proceedings (Dubois *et al.* 2000) has focused for the first time on technological applications of quasicrystals. One such use is a high-strength steel used for surgical tools and electric shavers; the steel contains quasicrystalline precipitates which are particularly stable against Ostwald ripening (Section 9.1.3), apparently because of the low interfacial energy between precipitates and matrix, and thus resistant to overaging. A range of aluminum alloy strengthened by quasicrystalline precipitates has also been developed.

The many papers in this proceedings are partitioned into very abstruse theoretical analyses of structure and stability of quasicrystals on the one hand, and practical studies of surface structures, mechanical properties and potential applications. The subject shows signs of becoming as deeply divided between theorists and practical investigators, out of touch with each other, as magnetism became in the preceding century.

#### 10.7. EXTREME STATES COMPARED

Virtually every reference at the end of this chapter is to post-war publications, and the majority are to papers published during the past 15 years. This shows, clearly enough, that 'extreme materials' are recent features of materials science and engineering (MSE), and there is every indication that the focus on materials of the kind discussed in this chapter will continue to develop. Individual approaches come and go – thus, rapid solidification processing, the oldest of the approaches discussed here, seems to have passed its apogee – while others go from strength to strength:

thus, a 'nanotechnology initiative' has recently been instituted at the highest level of US government. It is not perhaps too much of an exaggeration to claim that in this chapter, we can see something of the future of MSE.

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## Chapter 11

# Materials Chemistry and Biomimetics

### 11.1. THE EMERGENCE OF MATERIALS CHEMISTRY

Chemistry has featured repeatedly in the earlier parts of this book. In Section 2.1.1, the emergence of physical chemistry is mapped, followed by a short summary of the status of solid-state chemistry in Section 2.1.5. The key ideas of phase equilibria and metastability are set forth in Section 3.1.2, with special emphasis on Willard Gibbs. The linkage between crystal structure, defects in crystals and equilibria in chemical reactions is outlined in Section 3.2.3.5, while crystal chemistry is treated at some length in Section 3.2.4. Chemical analysis features in Sections 6.2.2.3 and 6.3. The chemistry of magnetic ceramics is outlined in Section 7.3, while liquid crystals are presented in Section 7.6. The huge subject of polymer chemistry is briefly introduced in Section 8.2, and the field of glass-ceramics is explained in Section 9.6; this last can be regarded as an expression of high-temperature chemistry. The outline of surface science in Sections 10.4.1 and 10.4.3 includes some remarks about its chemical aspects.

Clearly, chemistry plays as large a part in the evolving science of materials as do physics and metallurgy. Nevertheless, when materials science arrived as a concept in the late 1950s, no chemist would have dreamed of describing himself as a materials chemist, though the term 'solid-state chemist' was just making its appearance at that time. Since then, in the 1980s, materials chemistry has arrived as a recognised category, and the term appears in the titles of several major journals.

We can get an idea of the gradual development of *solid-state chemistry* from a fine autobiographical essay by one of the greatest modern exponents of that science, the Indian Rao (1993). He remarks: "When I first got seriously interested in the subject in the early 1950s it was still in its infancy". He traces it through its stages, including a period of very intense emphasis on the chemical consequences of crystal defects as studied by electron microscopy; he refers to a book (Rao and Rao 1978) he co-authored on phase transitions, a topic which he claims had been neglected by solid-state chemists until then and had perhaps been too much the exclusive domain of metallurgists. He also remarks: "Around 1980, it occurred to me that there was need for greater effort in the synthesis of solid materials, not only to find novel ways of making known solids, but also to prepare new, novel metastable solids by unusual chemical routes". He goes on to point out that "the tendency nowadays is to avoid brute-force methods and instead employ methods involving mild reaction conditions. Soft chemistry routes are indeed becoming popular. . .". This interest led to yet

another book (Rao 1994). His notable book on solid-state chemistry as a whole (Rao and Gopalakrishnan 1986, 1997) has already been discussed in Chapter 2.

So, by the 1990s, Professor Rao had been active in several of the major aspects which, *together*, were beginning to define materials chemistry: crystal defects, phase transitions, novel methods of synthesis. Yet, although he has been president of the Materials Research Society of India, he does not call himself a materials chemist but remains a famous solid-state chemist. As with many new conceptual categories, use of the new terminology has developed sluggishly.

As materials chemistry has developed, it has come to pay more and more attention to that archetypal concern of materials scientists, microstructure. That concern came in early when the defects inherent in non-stoichiometric oxides were studied by the Australian J.S. Anderson and others (an early treatment was in a book edited by Rabenau 1970), but has become more pronounced recently in the rapidly growing emphasis on self-assembly of molecules or colloidal particles. This has not yet featured much in books on materials chemistry, but an excellent recent popular account of the broad field has a great deal to say on self-assembly (Ball 1997). The phenomenon of graphoepitaxy outlined in Section 10.5.1.1 is a minor example of what is meant by self-assembly.

A notable chemist, Peter Day, has recently published an essay under the challenging title *What is a material?* (Day 1997). He makes much of the point that the properties of, say, a molecular material are not determined purely by the characteristics of the molecules but also by their interaction in a continuous solid, and that chemists have to come to terms with this if they wish to be materials chemists. If they do, they can hope to synthesise materials with very novel properties. He also puts emphasis, as did Rao, on the benefits of 'chimie douce', soft chemistry, in which very high temperatures are avoided. For instance, he points out, "to deposit thin films..., selectively decomposing carefully designed organometallic molecules has proved a notable advance over the 'engineering' approach of flinging atoms at a cold surface in ultrahigh vacuum". There is scope for a great deal of discussion in the wording of that sentence.

In the words of a recent paper on MSE education (Flemings and Cahn 2000), "chemistry departments have historically been interested in individual atoms and molecules, but increasingly they are turning to condensed phases". A report by the National Research Council (of the USA) in 1985 highlighted the opportunities for chemists in the materials field, and this was complemented by the NRC's later analysis (MSE 1989) which, *inter alia*, called for much increased emphasis on materials synthesis and processing. As a direct consequence of this recommendation, the National Science Foundation (of the USA) soon afterwards issued a formal call for research proposals in materials synthesis and processing (Lapporte 1995), and by that time it can be said that materials chemistry had well and truly arrived, in the

United States at least. The huge field of inorganic materials synthesis is not further discussed in this chapter, but the interested reader will benefit from reading a survey entitled "Inorganic materials synthesis: learning from case studies" (Roy 1996).

### 11.1.1 Biomimetics

The emphasis on microstructure as a major variable in materials chemistry has been strengthened by the emergence of yet another subdiscipline, that of *biomimetics*. This is simply, in the words of one practitioner, J.F.V. Vincent, retailed by another (Jeronimidis 2000), "the abstraction of good design from nature". (Vincent himself (1997) gave a lecture on "stealing ideas from nature"). Biomimetics seems to have begun as a study of strong and tough materials (skeletons, defensive starfish spines, mollusc shells) in order to mimic their microstructure in man-made materials. Such mimicry necessarily involves chemical methods, to the extent that a recent major text is entitled *Biomimetic Materials Chemistry* (Mann 1996). (In fact, the term 'biomimetic chemistry' was used as early as 1979 as the title of a symposium organised by the American Chemical Society, Dolphin *et al.* 1980.) An exceptionally illuminating presentation of a range of strong and tough biological materials, incorporating both those found in a range of quite distinct creatures and those specific to one taxum, is by Weiner *et al.* (2000). Two examples of the striking features discussed in this paper: echinoderm spines are essentially single crystals of calcite (or dolomite), but their readiness to cleave under stress is obviated by the division of the single crystal into mosaic domains that are very slightly mutually misoriented; this is a highly specific feature. On the other hand, the formation of a very tough structure via a sequence of multilayers in mutually crossed orientations is widespread in zoology: whether the material is based on aragonite in abalone shells, or on chitin in beetle wingcases, the basic principle is the same, and such structures always contain thin layers of biopolymers. As Calvert and Mann (1988) early recognised, "biological mineralisation demonstrates the possibility of growing inorganic minerals locally on or in polymer substrates". A very recent, detailed examination of an ultratough marine shell, that of the conch *Strombus gigas*, which has three hierarchical levels of aragonite lamellae separated by ultrathin organic layers, is by Kamat *et al.* (2000).

Quoting just a few of the chapter headings in Mann's book (a), and also in Elices' (2000) even more recent book (b), conveys the flavour of the subdiscipline: (a) Biomineralisation and biomimetic materials chemistry; biomimetic strategies and materials processing; template-directed nucleation and growth of inorganic materials; biomimetic inorganic-organic composites; organoceramic nanocomposites. (b) Structure and mechanical properties of bone; biological fibrous materials; silk fibres – origins, nature and consequences of structure. These headings indicate several



things: a strong focus on synthesis and preparative methods; self-arrangement; and the thorough mixing of normally quite distinct categories of materials. Biomimetics is succeeding in breaking down almost every historical barrier between fields of MSE. Since 1993, there has been a journal entitled *Biomimetics*.

The book by Ball introduced above includes chapters both on “Only natural: biomaterials” and on “Spare parts: biomedical materials”. The first of these is really about biomimetics (terminology is still somewhat in flux), the second is about the even larger field of artificial materials for use in the human body. This category includes such items as artificial heart-valves (polymeric or carbon-based), synthetic blood-vessels, artificial hips (metallic or ceramic), medical adhesives, collagen, dental composites, polymers for controlled slow drug delivery. There is plainly a link between biomimetics and biomedical materials, but whereas a biomimetic engineer seeks to make materials for non-biological uses under inspiration from the natural world, the biomedical engineer has to work hand-in-glove with surgeons and physicians, and must never forget such crucial considerations as the compatibility of synthetic surfaces with blood or the wear resistance of artificial hip joints. I have no room here for further details, and the interested reader is referred to Williams (1990).

#### ***11.1.2 Self-assembly, alias supramolecular chemistry***

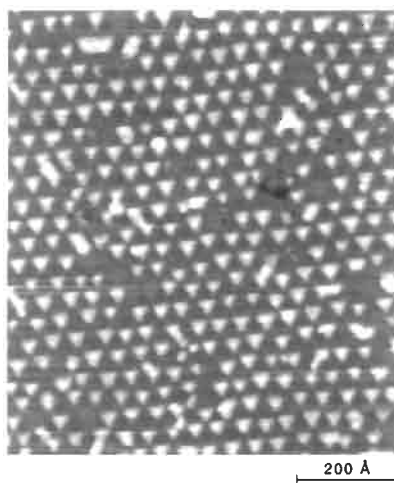
To get a feel for the kind of new issues that weigh on materials chemists nowadays, a brief account of the topic of self-assembly will serve well.

Chemists deal primarily with molecules but, as they concern themselves increasingly with condensed matter, they are brought face-to-face with the means of tying ‘saturated’ molecules, or other small particles, together by weaker bonds, such as hydrogen bonds or van der Waals bonds. This craft was originally dubbed *supramolecular chemistry* by pioneers such as the Nobel-prize-winning French chemist Lehn (1995). But that term seems to be playing hide-and-seek with *self-assembly*. A very recent paper (Nangia and Desiraju 1998) lays it down that “supramolecular chemistry is the chemistry of the *intermolecular* bond and is based on the theme of mutual recognition; such recognition is characterised by chemical and geometrical complementarity between interacting molecules”. A very recent overview of the field from a materials science viewpoint (Moore 2000) emphasises ‘design from the bottom-up’ as the essence of the skills involved here. Whereas ‘supramolecular chemistry’ properly only applies to the assembly of molecules, ‘self-assembly’ can also include the assembly of larger units. . . so I prefer the latter term.

From the way the field has developed during the last few years, two quite distinct kinds of self-assembly are emerging. One kind focuses on the ‘self’ part of the nomenclature and relies entirely on the inherent forces acting between particles. A good example is the formation of colloidal pseudocrystals from small polymeric

spheres, as outlined in Section 2.1.4; a recent set of reviews of this rather mysterious process is by Grier (1998). A subvariant of this is to coat the spheres with nickel and encourage them to align themselves in various configurations by applying a field. Another is the self-organised growth of nanosized arrays of iron crystallites on a copper bilayer deposited on a (1 1 1) face of platinum (Figure 11.1); here the source of organisation is the spontaneously regular array of dislocations resulting from strain-relief between the copper and the platinum which have different lattice constants, defects which in turn act as heterogeneous nucleation sites for iron crystallites when iron is evaporated onto the film (Brune *et al.* 1998). Yet another example of this approach is self-assembly of polymers by relying on interaction between dendritic side-branches (Percec *et al.* 1998).

Special attention has been paid recently to methods of creating 'photonic crystals', microstructured materials in which the dielectric constant is periodically modulated in three dimensions on a length scale comparable to the wavelength of the electromagnetic radiation to be used, whether that is visible light or a UHF radio wave; obviously the periodicity is much greater than that in natural ('real') crystals. One of the many techniques tried out is the use of interfering laser beams sent in four precisely chosen different directions into a layer of photoresist polymer (as used in microcircuit technology); highly exposed photoresist is rendered insoluble, other regions can be etched away, generating a regular array of holes (Campbell *et al.* 2000). An even more intriguing approach is that by Blanco *et al.* (2000) in which an



**Figure 11.1.** Scanning tunnelling microscope image of a periodic array of Fe islands nucleated on the regular dislocation network of a Cu bilayer deposited on a platinum (1 1 1) face (after Brune *et al.* 1998).

opalescent structure of lightly sintered small silica spheres, in regular array, is infiltrated with silicon, followed by removal of the silica template. A very recent survey of the many ways in which photonic crystals can be made, together with an outline of their use in optical communications systems (for instance, in enabling light beams effectively to bend sharply rather than gradually) is by Parker and Charlton (2000).

This takes us to the second type of self-assembly which relies on some form of *template*, a pattern imposed on a surface that will act as a guide to further molecules or particles that are deposited subsequently – so, on a pedantic view, this is aided assembly rather than self-assembly. The current guru of this approach is the chemist George Whitesides of Harvard University: two papers of his illustrate his preferred approaches (Kim *et al.* 1995, Aizenberg *et al.* 1999). In the first paper, moulding in capillaries is described: a pattern, typically of grooves one or two nanometers wide and a fraction of a nanometer in depth, is made by photolithography (as practised in microcircuit fabrication) and then reproduced in negative by casting with an elastomeric polymer. The channel pattern is then filled with a ‘prepolymer’, e.g., some form of monomer solution, relying on capillarity to fill the grooves accurately. The polymer is cured and the elastomeric mould then peeled off. The second paper describes an even more elaborate process: self-assembled monolayers (SAMs) are patterned on a metallic substrate by microcontact printing with an elastomeric ‘stamp’. A suitable chemical is used as “ink”. The unexposed areas are then passivated with an appropriate wash, and the whole immersed in calcium chloride solution. Only the unpassivated SAM regions react to deposit calcite crystals, which thus form an array in regular positions and of regular sizes. In developing this technique, the investigators relied on information from an earlier study of biomineralisation. Neither of these papers proposes a specific use for these patterns; what is done here (as often in self-assembly research up to now) is ‘technology push’, the identification of a sophisticated technique; the market pull of a particular need is confidently expected to arrive later.

Colloidal crystals can be grown by a templated approach too. Thus van Blaaderen and Wiltzius (1997) have shown that allowing colloidal spheres to deposit under gravity on to an array of suitably spaced artificial holes in a plate quickly generates a single ‘crystalline’ layer of colloidal spheres, and a thick crystal will then grow on this basis.

Addadi and Weiner (1999) have concisely and critically reviewed these various strategies and have added their own variant – the use of biological templates, for instance bacterium surfaces to assist self-assembly. Here, self-assembly and biomimetics join forces productively.

One intriguing technique of manufacturing a regular array of sharp electrodes sitting in an insulating matrix, useful for flat-screen displays, relies on a mix between

spontaneous and templated self-assembly. Hill *et al.* (1996) used a regular eutectic array, formed *spontaneously* by directional freezing, of single-crystal tungsten fibres (300–1000 nm in diameter, about  $10^7$  fibres/cm<sup>2</sup>) in an oxide matrix such as UO<sub>2</sub>, the assembly etched so that the fibres stand proud of the surface. Silica evaporated on to the array forms cones that act as shadow-masks for the subsequent deposition of a metallic film on the surface; the silica is then removed and the end-result is an array of free-standing vertical metallic needles in an insulator surrounded by a non-contacting ‘gridded’ superficial ring of metal film. If these conducting rings are made anodic, then 100 volts suffices to induce field-emission of electrons from the nearby electrodes. This is a beautiful example of a combined physical/chemical processing strategy, reminiscent of techniques used in microcircuitry, designed by a group of materials scientists.

Yet another variant of self-assembly relies on the repulsion between blocks of suitably constituted block copolymers, leading to fine-scale patterns of organisation. One very recent description of this approach is by de Rosa *et al.* (2000). Details of this kind of approach as cultivated at Oak Ridge National Laboratory can also be found on the internet (ORNL 2000).

## 11.2. SELECTED TOPICS IN MATERIALS CHEMISTRY

In this Section, I shall briefly exemplify some topics that illustrate how the needs of materials science and engineering have shaped chemists’ approaches to synthesis and processing.

### 11.2.1 Self-propagating high-temperature reactions

In the 19th century, the steel rails of streetcars (trams) were welded in situ by packing a mixture of ferric oxide and aluminium powder between the rails to be joined and initiating a strongly exothermic reaction between the two powders by local heating; the reaction produces molten iron which achieves the weld. This is (gasless) *combustion synthesis*. This approach was generalised by a Russian chemist, A.G. Merzhanov, who began publishing accounts of the synthesis of compounds in this way inside a sealed ‘bomb’; his first account of the synthesis of high-melting carbides, nitrides and borides was published in 1972 (Merzhanov and Borovinskaya 1972). The technique spread rapidly through Soviet industry.

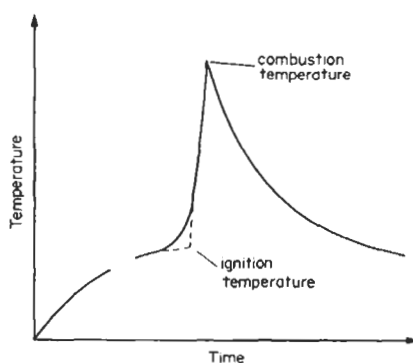
The technique, now named *self-sustaining high-temperature synthesis* (SHS) – on the grounds that long names drive out short ones – was later taken up in the West, and has gradually become more sophisticated. The synthesis of TiC<sub>x</sub> by Holt and Munir (1986) marks the beginning of detailed analysis of heat generation and

disposal, and brought in the practice of the use of inert diluents to limit temperature excursions. Figure 11.2 shows schematically how temperature varies with time in such a process. Much research has been done on the elimination of porosity in the product, often by the application of high pressure for short periods after the reaction is over. The technique, now named XD to mystify the reader, was applied by the Martin-Marietta Corporation in America to create alloys dispersion-hardened by fine intermetallic or ceramic particles; the constituent elements of the ceramic are mixed with a metal or alloy powder (Brubacher *et al.* 1987). The field received a major review by Munir and Anselmi-Tamburini (1989).

A particularly striking recent application was by Deevi and Sikka (1997): they developed an industrial process for casting intermetallics, especially nickel aluminides, so designed (by modifying the furnace-loading sequence) that the runaway temperature rise which had made normal casting particularly dangerous was avoided.

### 11.2.2 Supercritical solvents

In 1873, Johannes van der Waals (1837–1923) presented his celebrated doctoral thesis to the University of Leiden in the Netherlands, under the title “On the continuity of the liquid and gaseous states”: here he established a simple molecular interpretation of the observed fact that a *critical temperature* exists for a particular gas below which a gas can be condensed to a two-phase system of vapour and liquid, whereas above it there can only be a homogeneous fluid phase (‘fluid’ strictly being neither vapour nor liquid). His equation of state for a gas, gradually improved, played a major part in the early understanding of gases and, for instance, helped his countryman Heike Kamerlingh Onnes to work out his method of liquefying helium.



**Figure 11.2.** Schematic representation of the temperature profile associated with the passage of a gasless combustion front.

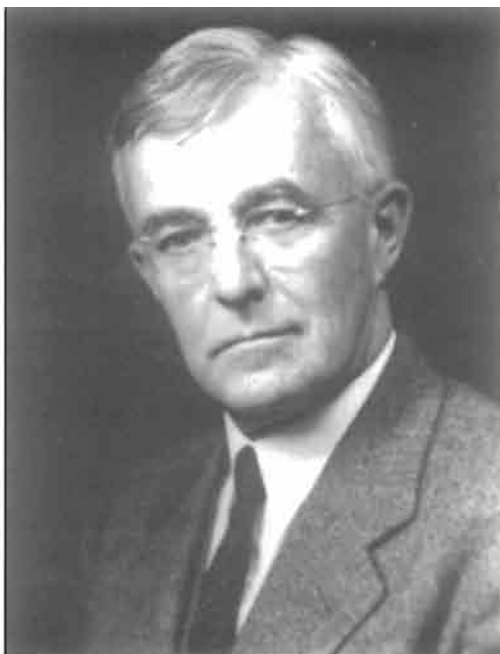
Soon after van der Waals' thesis was published, Hannay and Hogarth (1879) discovered that a *supercritical fluid*, SCF (i.e., a fluid above the critical temperature) can readily dissolve non-volatile solids. Nothing followed from this for a century; it was taken up again only in the 1970s. Now chemical engineers, in particular, are very actively examining the scope for the use of supercritical solvents in dissolving reactants and controlling their reactions in solution. A thorough overview has recently been published (Eckert *et al.* 1996). Supercritical carbon dioxide (critical temperature, 31°C), in particular, is finding growing use as a solvent; the solvent is easily removed, without causing environmental hazards in the way that organic solvents may do. (It is a delightful irony that CO<sub>2</sub>, so often decried as an environmental hazard in its own right, is perceived as benign in its context as a solvent.)

A SCF is highly compressible compared with a normal liquid and accordingly, solubilities (and reaction rates in solution) can change rapidly for small changes in temperature and pressure. In this way, fine control can be exercised in synthesis of products and their physical form. One technique involves rapid depressurisation of a SCF containing a solute of interest; small particles are then precipitated because of the large supersaturation associated with the rapid loss of density in the highly compressible fluid phase. Methods are rapidly being developed to enhance further the solubility of a range of solids in SCF CO<sub>2</sub>, in particular, by addition of co-solvents, surfactants especially.

### 11.2.3 Langmuir–Blodgett films

Benjamin Franklin's observations on the calming effect of oil films on turbulent water (Franklin 1774) has been described as the first recorded experiment in surface chemistry. Franklin noticed that a teaspoonful of oil covered about half an acre of water, which suggests how very thin the surface layer of oil must have been. A century later, Franklin was followed by a remarkable, self-taught German girl, Agnes Pockels, who from the age of 18, in her home, began a series of surface-chemical investigations which finally impressed the great Lord Rayleigh when she drew her work to his attention (Pockels 1891). She introduced, among other techniques, the use of a liquid trough for measuring the properties of thin surface films on liquids. Rayleigh (1899) finally proposed that the films she had studied were monomolecular in thickness.

Enter, now, Irving Langmuir (Figure 11.3), the remarkable American metallurgist/physical chemist whom we have met before in connection with incandescent lamps. During the First World War, he turned some of his attention from metallic surfaces to liquid surfaces, and by 1919, he was ready to read a paper to the Faraday Society in London, describing how he set about making films of fatty acids of



Irving Langmuir (1881–1957)



Katharine Burr Blodgett  
(1898–1979)

**Figure 11.3.** Portraits of Irving Langmuir (1881–1957) and Katharine Blodgett (1898–1979) (after Gaines 1983).

varying molecular weights on water and gave evidence that Rayleigh was indeed correct, and furthermore that the molecules in the surface films were oriented with their chains normal to the surface. (These are 'amphiphilic' molecules, hydrophilic at one end and hydrophobic at the other.) In 1917 (Langmuir 1917), he had invented the film balance which allowed a known stress to be applied to a surface film until it was close-packed and could not be compressed further; in this way, he determined the true diameter of his chain molecules, and incidentally one of his measurements more or less tallied with Agnes Pockels' estimate. Later, in 1933, he published a paper, the very first to be printed in the then new *Journal of Chemical Physics* (see Section 2.1.1) which covered, inter alia, the behaviour of thin films adsorbed on a liquid surface. In the years between 1917 and 1933, Langmuir had been largely taken up with surface studies relevant to radio valves (tubes).

His assistant from 1920 on was a young chemist, Katharine Blodgett (Figure 11.3). In 1934, she published a classic paper on monomolecular fatty-acid films which she was able to transfer sequentially from water to a glass slide, so that multilayer films were thereby created (Blodgett 1934). In a concise historical note on these "Langmuir-Blodgett films", (which served as introduction to a major conference on these films, published in the same issue of *Thin Solid Films*), Gaines (1983) advances evidence that this research probably issued from an interest at GE in lubricating the bearings of electricity meters. The superb fundamental work of this pair was always, it seems, nourished (perhaps one should say, lubricated) by severely practical industrial concerns.

During the remainder of the 1930s, Langmuir and Blodgett carried out a brilliant series of studies on multilayer films of a variety of chemicals, supplemented by studies in Britain, especially at the ill-fated Department of Colloid Science in Cambridge (Section 2.1.4). Then the War came, and momentum was lost for a couple of decades. After that, L-B films came back as a major topic of research and have been so ever since (Mort 1980). It is current practice to refer to *molecular films*, made by various techniques (Swalen 1991), but the L-B approach remains central.

Molecular films are of intense current concern in electronics. For instance, diacetylenes and other polymerisable monomer molecules have been incorporated into L-B films and then illuminated through a mask in such a way that the illuminated areas become polymerised, while the rest of the molecules can be dissolved away. This is one way of making a resistance for microcircuitry. L-B films have also found a major role in the making of gas-sensors (Section 11.3.3).

A review of what has come to be called *molecular electronics* (Mirkin and Ratner 1992) includes many striking discoveries, such as a device based on azobenzene (Liu *et al.* 1990) that undergoes a stereochemical transition, trans-to-cis, when irradiated with ultraviolet light, but reverts to trans when irradiated with visible light. The investigators in Japan found that L-B films of their molecules can be used for a

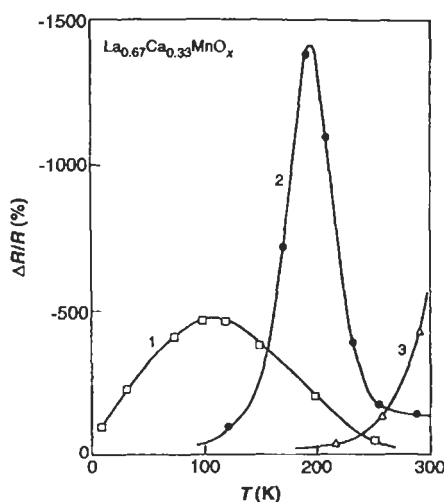


short-term memory system, but a chemical conversion to a related compound generates a film which can serve as a longterm memory. Electrochemical oxidation of the L-B film can erase memory completely, so this kind of film has all the key features of a memory system.

It will be clear that L-B films are intrinsically linked to self-assembly of molecules, and this has been recognised in the title of a recent overview book (Ulman 1991), *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly: An Overview*.

#### 11.2.4 Colossal magnetoresistance: the manganites

In 1993/1994, several papers from diverse laboratories appeared, all reporting a remarkable form of magnetoresistance, that is, a large change of electrical resistivity resulting from the application of a magnetic field, quite distinct from the so-called 'giant magnetoresistance' found in multilayers of metallic and insulating films (Sections 3.3.3, 7.4, 10.5.1.2). Two of the first papers were by Jin *et al.* (1993), reporting from Bell Laboratories, and from von Helmholt *et al.* (1994), reporting from Siemens Research Laboratory and the University of Augsburg, in Germany. The phenomenon (Figure 11.4) required low temperatures and a very high field. The first paper reported on  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_x$ , the second on  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_x$ .



**Figure 11.4.** Three plots of  $\Delta R/R$  curves for a La-Ca-Mn-O film: (1) as deposited; (2) heated to 700°C for 30 min in an oxygen atmosphere; (3) heated to 900°C for 3 h in oxygen (after Jin *et al.* 1993, courtesy of Science).

Such compounds have the cubic perovskite crystal structure, or a close approximation to that structure. Perovskites, much studied both by solid-state chemists and by earth scientists, have an extraordinary range of properties. Thus  $\text{BaTiO}_3$  is ferroelectric,  $\text{SrRuO}_3$  is ferromagnetic,  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  is superconducting. Several perovskitic oxides, e.g.  $\text{ReO}_3$ , show metallic conductivity. Goodenough and Longo (1970) long ago assembled the properties of perovskites known at that time in a wellknown database, but the new phenomenon, which soon came to be called *colossal magnetoresistance* (CMR) to distinguish it from giant magnetoresistance (GMR) of multilayers, came as a complete surprise.

The 1993/1994 papers unleashed a flood of papers during the next few years, both reporting on new perovskite compositions (mostly manganates) showing CMR, and also trying to make sense of the phenomenon. A good overview of the first 4 years' research, already citing 64 papers, is by Rao and Cheetham (1997). The ideas that have been put forward are very varied; suffice it to say that CMR seems to be characteristic of compounds in a heterogeneous condition, split into domains with different degrees of magnetisation, of electrical conductivity, with regions differently charge-ordered. So, though these perovskites are not made as multilayers, they behave rather as though they had been. A relatively accessible discussion of some of the current theoretical ideas is by Littlewood (1999).

The goldrush of research on perovskites showing CMR is reminiscent of similar goldrushes when the rare-earth ultrastrong permanent magnets were discovered, when the oxide ('high-temperature') superconductors were first reported and when the scanning tunnelling microscope was announced – all these within the last 30 years. For instance, the  $\text{Fe}_{14}\text{Nd}_2\text{B}$  permanent-magnet compound discovered in the mid-1980s led to four independent determinations of its crystal structure within a few months. It remains to be seen whether the manganite revolution will lead to an outcome as useful as the other three cited here.

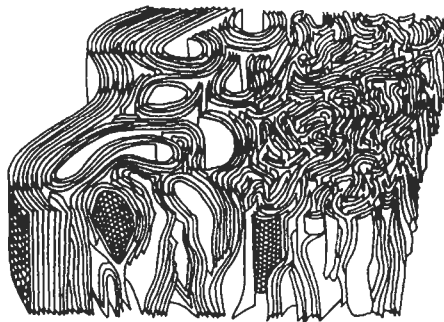
Another feature of this goldrush is instructive. The usefulness of CMR is much reduced by the requirement for a very high field and low temperature (though the first requirement can be bypassed, it seems, with CMR-materials of different crystal structure, such as pyrochlore type (Hwang and Cheong 1997). The original discovery in perovskite, in 1993/1994, was made by physicists, much of the research immediately afterwards was conducted by solid-state chemists; people in materials science departments were rather crowded out. An exception is found in a paper from the Cambridge materials science department (Mathur *et al.* 1997), in which a bicrystal of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ , made by growing the compound epitaxially on a bicrystal substrate, and so patterned that the current repeatedly crosses the single grain boundary, is examined. Such a device displays large magnetoresistance in fields very much smaller than an ordinary polycrystal or monocrystal show, though the peak temperature is still well below room temperature. The investigators express the

view that a similar device using a superconducting perovskite with a high critical temperature may permit room-temperature exploitation of CMR. This is very much a materials scientist's approach to the problem, centred on microstructure.

#### ***11.2.5 Novel methods for making carbon and ceramic materials and artefacts***

At the start of this Chapter, an essay by Peter Day was quoted in which he lauds the use of 'soft chemistry', exemplifying this by citing the use of organometallic precursors for making thin films of various materials used in microelectronics. The same approach, but without the softness, is increasingly used to make ceramic fibres: here, 'ceramic' includes carbon (sometimes regarded as almost an independent state of matter because it is found in so many forms).

This approach was first industrialised around 1970, for the manufacture on a large scale of strong and stiff carbon fibres. The first technique, pioneered at the Royal Aircraft Establishment in Britain, starts with a polymer, polyacrylonitrile, containing carbon, hydrogen and nitrogen (Watt 1970). This is heated under tension and pyrolysed (i.e., transformed by heat) to turn it into essentially pure carbon; one of the variables is the amount of oxygen in the atmosphere in which the fibre is processed. During pyrolysis, sixfold carbon rings are formed and eventually turn into graphitic fragments which are aligned in different ways with respect to the fibre axis, according to the final temperature. Carbonisation in the range 1300–1700°C produces the highest fracture strength, while further heat-treatment above 2000°C maximises the elastic stiffness at some cost to strength. Figure 11.5 shows the structure of PAN-based fibres schematically, with thin graphite-like layers. An alternative source of commercial carbon fibres, used especially in Japan, is pitch made from petroleum, coal tar or polyvinyl chloride; the pitch is spun into fibre, stabilised by a low-temperature anneal, and then pyrolysed to produce a graphitic structure.



**Figure 11.5.** Model of structure of polyacrylonitrile-based carbon fibre (after Johnson 1994).

Similar techniques are used to make massive graphitic material, called *pyrolytic graphite*; here, gaseous hydrocarbons are decomposed on a heated substrate. Further heating under compression sharpens the graphite orientation so that a near-perfect graphite monocrystal can be generated ('highly oriented pyrolytic graphite', HOPG). HOPG is used, inter alia, for highly efficient monochromators for X-rays or thermal neutrons. An early account of this technique is by Moore (1973). A different variant of the process generates *amorphous* or *glassy carbon*, in which graphitic structure has vanished completely. This has proved ideal for one kind of artificial heart valve. Yet another product made by pyrolysis of a gaseous precursor is a carbon/carbon composite: bundles of carbon fibre are impregnated by pyrolytic graphite or amorphous carbon to produce a tough material with excellent heat conduction. These have proved ideal for brake-pads on high-performance aeroplanes, fighters in particular. When one takes these various forms of carbon together with the fullerenes to be described in the next Section and the diamonds discussed elsewhere in this book, one can see that carbon has an array of structures which justify its description as an independent state of matter!

Turning now to other types of ceramic fibre, the most important material made by pyrolysis of organic polymer precursors is silicon carbide fibre. This is commonly made from a poly(diorgano)silane precursor, as described in detail by Riedel (1996) and more concisely by Chawla (1998). Silicon nitride fibres are also made by this sort of approach. Much of this work originates in Japan, where Yajima (1976) was a notable pioneer.

Another approach for making ceramic artefacts which is rapidly gaining in adherents is more of a physical than a chemical character. It is coming to be called *solid freeform fabrication*. The central idea is to deposit an object of complex shape by projecting tiny particles under computer control on to a substrate. In one of several versions of this procedure (Calvert *et al.* 1994), a ceramic slurry (in an immiscible liquid) is ejected by small bursts of gas pressure from a microsyringe attached on a slide which is fixed to a table with x-y drive. The assembly is computer-driven by a stepper motor. The technique has also been used for nylon objects (ejecting a nylon precursor) and for filled polymeric resins. Such a technique, however, only makes economic sense for objects of high intrinsic value. A fairly detailed account of this approach as applied to metal powders has been published by Keicher and Smugersky (1997).

#### 11.2.6 Fullerenes and carbon nanotubes

"Carbon is really peculiar" is one of the milder remarks by Harold Kroto (1997) in his splendid Nobel lecture. The 1996 Nobel Prize for chemistry was shared by Kroto

in Brighton with Richard Smalley and Robert Curl in Texas, for the discovery of (buckminster)-fullerene,  $C_{60}$  and  $C_{70}$ , in 1985. These three protagonists all delivered Nobel lectures which were printed in the same journal issue. Kroto's lecture, which goes most fully into the complicated antecedents and history of the discovery, is entitled "Symmetry, space, stars and  $C_{60}$ ". Stars come into the story because Kroto and astronomer colleagues had for years before 1985 made spectroscopic studies of interstellar dark clouds, had identified some rather unusual carbon-chain molecules with 5–9 carbon atoms, and had then joined forces with the Americans (using advanced techniques involving lasers contributed by the latter) in seeking to use streams of laser-induced tiny carbon clusters to recreate the novel interstellar molecules. They succeeded... but the mass spectra of the molecules also included a mysterious strong peak corresponding to a much larger molecule with 60 carbon atoms, and another weaker peak for 70 atoms. These proved to be the spherical molecules of pure carbon which won the Nobel Prize, called 'fullerenes' for short after Buckminster-Fuller, an architect who was famed for his part-spherical 'geodesic domes'. The discovery was first reported by Kroto *et al.* (1985).

The spherical fullerenes, of which  $C_{60}$  and  $C_{70}$  are just the two most common versions (they go down to 20 carbon atoms and up to 600 carbon atoms or perhaps even further, and some are even spheres within spheres, like Russian dolls), are a new collective allotrope of carbon, in addition to graphite and diamond. The 'magic-number' fullerenes,  $C_{60}$  and  $C_{70}$ , turn out to form strain-free spheres consisting of mixed hexagons (as in graphite sheets) and pentagons, Figure 11.6. Later, Krätschmer *et al.* (1990) established that substantial percentages of the fullerenes were formed in a simple carbon arc operating in argon, and a copious source of the molecules was then available from the soot formed in the arc, leading at once to a deluge of research. Krätschmer succeeded soon after in crystallising  $C_{60}$  from solution in benzene. The crystals are a classic example of a 'rotator phase', so called because molecules (or radicals) in the crystal are very weakly bonded, here by van der Waals forces, and thus rotate freely without moving away from their lattice sites. On severe cooling, the rotation stops. Rotator phases are also known as 'plastic

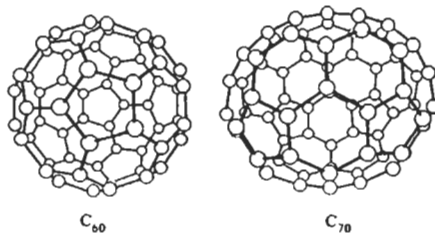


Figure 11.6. Two fullerene molecules,  $C_{60}$  and  $C_{70}$ .

crystals' because they will flow under remarkably small stresses, on account of very high self-diffusivity; the study of this kind of crystal has become a well-established parepisteme of solid-state chemistry (Parsonage and Staveley 1978).

After 1990, the chemistry of fullerenes was studied intensively by teams all over the world; a summary account of what was initially found can be found in a survey by Kroto and Prassides (1994). The internal diameter of a  $C_{60}$  sphere is about 0.4 nm, large enough to accommodate any atom in the periodic table, and a number of atoms have in fact been accommodated there to form proper compounds. Kroto and Prassides describe these 'endohedral complexes' as "superatoms with highly modified electronic properties, opening up the way to novel materials with unique chemical and physical properties". Turning from chemistry to fundamental physics, another striking paper was published recently in *Nature*: Arndt *et al.* (1999) were able to show that a molecular beam of  $C_{60}$  undergoes optical diffraction in a way that clearly demonstrates that these heavy moving 'particles' evince wavelike properties, as originally proposed by de Broglie for subatomic particles. They are the heaviest 'particles' to have demonstrated wave characteristics.

The hoped-for applications of fullerenes have not materialised as yet. A cartoon published in America soon after the discovery shows a hapless hero sinking into a vat full of buckyballs (another name for fullerenes) with their very low friction. It is not known how the hero managed to escape. . .

Applications can be more realistically hoped for from a variant of fullerenes, namely, *carbon nanotubes*. These were discovered, in two distinct variants, on the surface of the cathode of a carbon arc, by a Japanese carbon specialist, Iijima (1991), and Iijima and Ichihashi (1993). These tubes consist of rolled-up graphene sheets (the name for a single layer of the normal graphite structure) with endcaps. Iijima's first report was of multiwalled tubes (Russian dolls again), but his second paper reported the discovery of single-walled tubes, about 1 nm in diameter, capped by well-formed hemispheres with  $C_{60}$  structure. (The multiwalled tubes are capped by far more complex multiwall caps). Printed alongside Iijima's second paper in *Nature* was a similar report by an American team (Bethune *et al.* 1993). It seems that *Nature* has established a speciality in printing adjacent pairs of papers independently reporting the same novelty: this also happened in 1951 with growth spirals on polytypic silicon carbide (Verma and Amelinckx) and earlier, in 1938, with pre-precipitation zones in aged Al-Cu alloys (Guinier, Preston) – see Chapter 3 for details of both these episodes.

Interest has rapidly focused on the single-walled, capped tubes, as shown in Figure 11.7. They can currently be grown up to  $\approx 100\ \mu\text{m}$  in length, i.e., about 100,000 times their diameter. As the figure shows, there are two ways of folding a graphene sheet in such a way that the resultant tube can be seamlessly closed with a  $C_{60}$  hemisphere. . . one way uses a cylinder axis parallel to some of the C—C bonds in

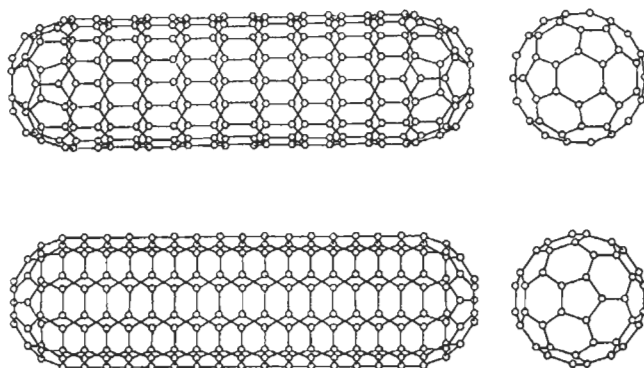


Figure 11.7. Two types of single-walled carbon nanotubes.

the sheet, the other, an axis normal to the first. The distinction is important, because the two types turn out to have radically different electrical properties.

Research on nanotubes has been so intensive that the first single-author textbook has already been published (Harris 1999), following an earlier multi-author overview (Dresselhaus *et al.* 1996). In addition to discussing the mechanism of growth of the different kinds of nanotubes, he also discusses the many precursor studies which almost – but not quite – amounted to discovery of nanotubes. He also has a chapter on ‘carbon onions’, multiwalled carbon spheres first observed in 1992 (and again reported in *Nature*); these seem to be multiwalled versions of fullerenes and the reader is referred to Harris’s book for further details. Just one feature about the onions that merits special attention is that the onions are under extreme internal pressure, as shown by the sharp diminution of lattice spacings in the inner regions of the onion. When such an onion is irradiated at high temperature with electrons, the core turns into diamond (Banhart 1997). For good measure, Harris also provides a historical overview of the spherulitic form of graphite in modified cast irons (see Section 9.1.1). His book also contains a fascinating chapter on chemistry inside nanotubes, achieved by uncapping a tube and sucking in reactants. One promising approach is to use a single-walled nanotube as a template for making ultrafine metallic nanowires.

Harris has this to say on the breadth of appeal of nanotubes: “Carbon nanotubes have captured the imagination of physicists, chemists and materials scientists alike. Physicists have been attracted to their extraordinary electronic properties, chemists to their potential as ‘nanotest-tubes’ and materials scientists to their amazing stiffness, strength and resilience”.

An even more up-to-date account of the current state of nanotube research from physicists’ perspective is in an excellent group of articles published in June 2000

(McEwen *et al.* 2000). One feature which is explained here is the fact that one of the structures in Figure 11.7 has metallic conductivity, the other is a semiconductor, because of the curious energy band structure of nanotubes. The metallic version is beginning to be applied for two purposes: (a) as flexible tips for scanning tunnelling microscopes (Section 6.2.3) (Dai *et al.* 1996), (b) as highly efficient field-emitting electrodes. In this second capacity, arrays of tubes have been used for lamps... electrons are emitted, accelerated and impinge on a phosphor screen. Now the extremely challenging task of using such nanotube arrays for display screens has been initiated, and one such display has been shown in Korea; one of the papers in the recent publication says: "In the extremely competitive display market there will be only a few winners and undoubtedly many losers".

Carbon nanotubes mixed with ruthenium oxide powder, and immersed in a liquid electrolyte, have been shown by a Chinese research group to function as 'supercapacitors' with much larger capacitance per unit volume than is normally accessible (Ma *et al.* 2000).

Nanotubes have also been found to be promising as gas sensors, for instance for  $N_2O$ , and in particular – this could prove to be of major importance – as storage devices for hydrogen. The capacity of both kinds of nanotubes to absorb various gases at high pressure was first found in 1997, and very recently, a Chinese team has established that one hydrogen atom can be stored for every two carbon atoms, using a 'chemically treated' population of nanotubes, a high capacity. Moreover, most of this absorbed gas can be released at room temperature by reducing the pressure; this seems to be the most valuable feature of all. The current position is reviewed by Dresselhaus *et al.* (1999).

The other striking feature of nanotubes is their extreme stiffness and mechanical strength. Such tubes can be bent to small radii and eventually buckled into extreme shapes which in any other material would be irreversible, but here are still in the elastic domain. This phenomenon has been both imaged by electron microscopy and simulated by molecular dynamics by Iijima *et al.* (1996). Brittle and ductile behaviour of nanotubes in tension is examined by simulation (because of the impossibility of testing directly) by Nardelli *et al.* (1998). Hopes of exploiting the remarkable strength of nanotubes may be defeated by the difficulty of joining them to each other and to any other material.

A distinct series of studies is focused on improved methods of growing nanotubes; Hongjie Dai in the 2000 group of papers focuses on this. In a recent research paper (Kong *et al.* 1998) he reports on the synthesis of individual single-walled nanotubes from minute catalyst islands patterned on silicon wafers – a form of templated self-assembly. The latest approach returns towards the 1985 technique: an anonymous report (ORNL 2000) describes an apparatus in which a pulsed laser locally vaporises ('ablates') a graphite target containing metal catalyst. A 'bubble' of



$10^{16}$  carbon and metal atoms streams away through hot argon gas and they then combine to form single-wall nanotubes with high efficiency.

The foregoing is merely a very partial summary of a major field of materials science, into which chemistry and physics are indissolubly blended.

#### 11.2.7 Combinatorial materials synthesis and screening

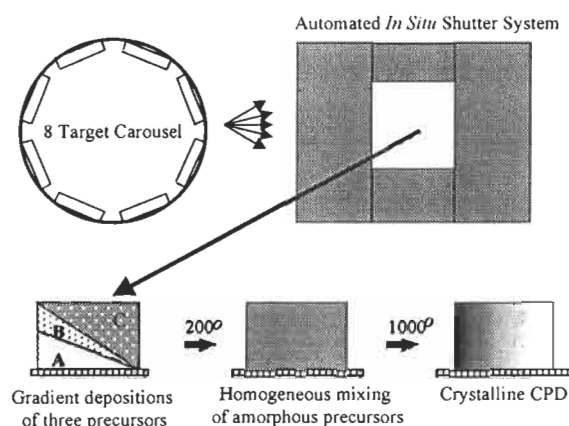
In the early 1990s, a new technique of investigation was introduced in the research laboratories of pharmaceutical companies – combinatorial chemistry. The idea was to generate, by automated techniques, a collection of hundreds or even thousands of compounds, in tiny samples, of graded compositions or chemical structure, and to bioassay them, again by automated techniques, to separate out promising samples. The choice of chemicals was determined by experience, crystallographic information on bond configuration, and inspired guesswork. A little later, this approach was copied by chemists to seek out effective homogeneous and heterogeneous catalysts for specific gas-phase reactions (Weinberg *et al.* 1998); this account cites some of the earlier pharmaceutical papers. Weinberg is technical director of a start-up company called Symys Technologies in Silicon Valley, founded with the objective of applying the above-mentioned approach to solid-state materials. After initial hesitation, the approach is also beginning to be tried by a number of major materials laboratories such as Bell Labs, and by an active group at the Lawrence Berkeley National Laboratory led by Xiao-Dong Xiang.

The main approach of materials scientists who wished to exploit this approach has been to deposit an array of tiny squares of material of systematically varying compositions, on an inert substrate, originally by sequential sputtering from multiple targets through specially prepared masks which are used repeatedly after 90° rotations. The array is then *screened* by some technique, as automated as possible to speed things up, to separate the sheep from the goats. Perhaps the first report of such a search was by Xiang *et al.* (1995), devoted to a search for new superconducting ceramics, with a sample density of as much as 10,000 per square inch. A four-point probe was used to screen the samples. New compositions were found, albeit not with any particularly exciting performance.

A slightly later example of this approach was a search for an efficient new luminescent material (Danielson *et al.* 1997a, b, Wang *et al.* 1998), using about 10 target materials mixed in greatly varying proportions. Screening in this instance was simple, since the entire array could be exposed to light and the ‘winners’ directly identified; in fact an automated light-measuring device was used to record the performance of each sample automatically. In this way,  $\text{Sr}_2\text{CeO}_4$  was identified out of a combinatorial ‘library’ of more than 25 000 members; it gives a powerful blue-white emission and responds well to X-ray stimulation. In the *Science* paper, the

authors show how a consequential test with Ba and Ca oxides was done to see whether a mixed oxide with Sr might perform even better. The array of samples was arranged in an equilateral triangle looking just like a ternary diagram; the pure Sr compound was unambiguously the best. This luminescence search was used as the text of an early survey of the combinatorial approach, under the slightly optimistic title “High-speed materials design” (Service 1997).

Xiang and his many collaborators went on to develop the initial approach in a major way. The stationary masks were abandoned for a technique using precision shutters which could be moved continuously under computer control during deposition; sputtering was replaced by pulsed laser excitation from targets. Figure 11.8 schematically shows the mode of operation. The result is a continuously graded thin film instead of separate samples each of uniform composition; Xiang calls the end-result a *continuous phase diagram* (CPD). Composition and structure at any point can be checked by Rutherford back-scattering of ions, and by an x-ray microbeam technique using synchrotron radiation, respectively, after annealing at a modest temperatures to interdiffuse the distinct, sequentially deposited layers. This approach to making a continuously variable thin film was originally tried by Kennedy *et al.* (1965), curiously enough in the same laboratory as Xiang’s present research. At that time, deposition techniques were too primitive for the approach to be successful. Xiang’s group (unpublished research) has tried out the technique by making a CPD of binary Ni–Fe alloys and testing magnetic characteristics for comparison with published data. More recently (Yoo *et al.* 2000), CPDs were used to locate unusual phase transitions in an extensive series of alloyed perovskite manganites of the kind that show colossal magnetoresistance (Section 11.2.4); this



**Figure 11.8.** Schematic layout of procedure for creating a continuous phase diagram (courtesy X.-D. Xiang, after Yoo *et al.* 2000).

seems to be the first published account of the use of CPDs to examine hitherto unknown phenomena. Moreover, this important study revealed the compositions at which phase changes took place; this implies that 'continuous phase diagrams' can be used to locate the loci of phase transitions in, say, ternary systems at some specified temperature, and thus help to determine isothermal phase equilibria. This would be a considerable technical advance in materials science.

Xiang (1999) has recently published a critical account of the whole field of what he calls *combinatorial materials synthesis and screening*, a phrase which I have chosen to provide the title of this section.

The recent burst of research on the combinatorial approach is not, however, the first. Thirty years ago, a scientist at the laboratories of RCA (the Radio Corporation of America), Joseph Hanak, wrote a precocious paper on what he called the "multiple sample concept" in materials research (Hanak 1970), essentially the same notion. Some 25 papers by Hanak followed during the 1970s, reporting on the application of his concept to a variety of problems, for instance electroluminescence (Hanak 1977) and solar cells. Subsequently, attention lapsed, though a Japanese group in 1988 pursued combinatorial study of oxides. The leader of that group, H. Koinuma, has just published an account of recent Japanese work on the combinatorial approach (Koinuma *et al.* 2000); it includes details of a systematic survey of ZnO doped with variable amounts of transition metals to determine solubility limits and optical properties.

### 11.3. ELECTROCHEMISTRY

Electricity and chemistry are linked in two complementary ways: the use of chemical reactions to produce electricity is one, and the use of electricity to induce chemical reactions is the other. The first of these large divisions encompasses primary and secondary batteries and fuel cells; the second includes some forms of extractive metallurgy and of large-scale chemical manufacture and such processes as water purification. In between, there are phenomena which include local electric currents as an incidental; metallic corrosion is the most important of these.

Electrochemistry can be said to have begun with the famous experiments in 1791 by Luigi Galvani (1737–1798): he showed that touching a dissected frog's leg with metal under certain conditions caused the muscle to undergo spasm. Galvani thought his observations pointed to a 'nervous fluid', perhaps a form of 'life force'. His countryman, Alessandro Volta (1745–1827) reexamined the matter and finally concluded that the muscle was merely a detector and that the stimulus could come from two dissimilar metals separated by a poor conductor (Volta 1800). He capitalised on his insight by creating the world's first primary battery, a 'pile' (in

French, a battery is still called 'une pile') of metals and paper disks moistened with brine, in the sequence silver–paper–zinc–silver–paper–zinc etc. Volta's pile only worked for a day or two before the paper dried out, but it marked the beginning of electrochemistry. The next year, William Cruikshank in England designed the first of many variants of a 'trough battery', in which metal plates were dipped into a suitable aqueous solution (ammonium chloride initially). In 1807, Sir Humphry Davy at the Royal Institution in London used three large trough batteries in his famous experiments to separate sodium and potassium from their salts, in the forms of slightly damp, fused soda and potash (Davy 1808). Previously, in 1800, Nicholson and coworkers had been the first to demonstrate chemical reactions resulting from the passage of an electric current when they found that gas bubbles were formed when a drop of water shorted the top of a voltaic pile; they identified the bubbles as hydrogen and oxygen, on the purported basis of smell!

After Cruikshank, there was a steady succession of gradually improving primary batteries (by 'primary', I mean batteries which are not treated as rechargeable): by stages, the power and endurance of such batteries was enhanced, and in 1836, Frederic Daniell designed a battery with two vessels separated by a semipermeable biological membrane, to prevent polarization by gas bubbles. This was the first of a succession of constant-voltage standards. All these are explained and illustrated in a fine historical overview by King (1962). The first dry battery was the 1868 Leclanché cell, using a carbon electrode in a pasty mixture of  $\text{MnO}_2$  and other constituents, with a zinc electrode separated from the rest by a semipermeable ceramic cylinder. In chemical terms, the modern primary dry battery relies on much the same process. The first secondary (or storage) battery was announced in 1859 (Planté 1860): by electrolysing sulphuric acid with lead electrodes, he generated a layer of lead oxide on lead; then the charging primary battery was removed and the lead-acid battery was able to return its charge. 140 years later, after endless improvements to the composition and microstructure of the lead grid (even preferred crystallographic orientation of the lead has recently been found to be vital in improving the longevity of such grids), Planté's approach is still used in every automobile. In 1860, dynamo-generated mains electricity, as primary source of charge for lead-acid batteries, was still two decades away.

Electrochemistry in the modern sense really began with Michael Faraday's experiments in the 1830s, using a giant primary battery made specifically for Faraday's laboratory in London. Williams (1970–1980), in a major essay on Faraday, interprets Faraday's motivation for these experiments as being his desire to prove that electricity from different sources, electrostatic generators, voltaic cells, thermocouples, dynamos and electric fishes was the same entity; Williams estimates that Faraday was successful in this quest. In the process, by establishing quantitative measures for 'quantity of electricity' indifferently from diverse sources, Faraday

established his two laws of electrochemistry: (1) the chemical effect is proportional to the quantity of electricity which has passes into solution, and (2) the amounts of different substances deposited or dissolved by a fixed quantity of electricity are proportional to their equivalent weights. The way Williams puts it, Faraday had proved that “(electricity) was the force of chemical affinity”; Much later, von Helmholtz argued that these experiments of Faraday’s had shown that “electricity must be particulate”. This research, which put electrochemistry firmly on the map, shows Faraday at his most inspired.

In addition to the various early European electrochemists, there was one important American participant, Robert Hare Jr. (1781–1858), whose life is treated by Westbrook (1978). As Westbrook explains, when Hare (who, though largely selftaught, eventually became a professor at the new University of Pennsylvania) began research, science in America was still “in an emergent state”, and the first scientific journal “with national pretensions” had only come into being in 1797. In 1818, he designed his own efficient version of a voltaic trough, which he called the *calorimotor* (not calorimeter), because he was still a believer in the caloric theory of heat and thought of a voltaic trough as accumulating heat as well as electricity, both to be regarded in particulate terms. So, his apparatus was to be seen as a ‘heat mover’. A later, further improved version of his pile was now called a ‘deflagrator’ (he was addicted to curious names) because by striking an arc, he could cause burning, or ‘deflagration’. In 1822, Hare with a friend, made what seem to have been the first demonstrations of electric light from a deflagrator. He also showed clearly, with use of a mercury cathode, the separation of metallic calcium from an aqueous  $\text{CaCl}_2$  solution (Ca was obtained from its amalgam), putting to rest uncertainties remaining from Davy’s earlier attempt (Hare 1841). He went on to design an electric arc furnace with which he achieved a number of ‘firsts’, including  $\text{CaC}_2$  synthesis and metal spot-welding.

### 11.3.1 Modern storage batteries

Batteries, both primary and secondary, have become very big business indeed, which moreover is growing rapidly. Salkind (1998) in a concise overview of the entire domain of battery types and technologies, estimates that in 1996, the world market in the two types of battery combined totalled  $\approx 33$  billion dollars, and that the ratio of secondary to primary battery sales is steadily edging upwards. In spite of its poor charge density per unit mass, the lead-acid battery still accounts for more than a quarter of the total, because it costs so much less than its rivals and lasts well.

Newer batteries can be divided into small rechargeable batteries for consumer electronics, cell-phones and laptop computers primarily, and larger advanced storage systems. The field of research on battery concepts and materials has recently

expanded dramatically. A very detailed overview of battery materials has been published very recently (Besenhard 1999).

Increasing numbers of advanced batteries for all purposes depend on ionically conducting solid electrolytes, so it will be helpful to discuss these before continuing. It should be remembered that any battery can be described as an 'electron pump', and the role of the electrolyte is to block the passage of electrons, letting ions through instead.

**11.3.1.1 Crystalline ionic conductors.** 'Superionic' conductors have already been briefly introduced in Section 7.2.2.2. They have been known for quite a long time, and a major NATO Advanced Study Institute on such conductors was held as early as 1972 (van Gool 1973). Of course, all ionic crystals are to a greater or lesser extent ionically conducting – usually they are cationic conductors, because cations are smaller than anions. Superionic conductors typically have ionic conductivities  $10^{11}$  times higher than do 'ordinary' ionic crystals such as KCl or AgCl.

Certain ionically well-conducting crystals,  $ZrO_2$  for instance, have long been exploited for such applications as sensors (see below) and, long ago, for early electric lamps (Section 9.3.2); nowadays, the compound is stabilised against allotropic transformations by adding yttria,  $Y_2O_3$ . Every mole of the dopant, moreover, brings with it an extra vacancy, which enhances ionic conductivity. This brings zirconia into the domain of ionic *superconductors* which have exceptionally large ionic mobilities, generally because of very high equilibrium vacancy concentrations which permit the ions bordering those vacancies to diffuse very fast, with or without applied electric fields. The materials chemistry of stabilised zirconia, used in the form of thin films less than 100  $\mu m$  in thickness, has become very sophisticated. The interface between the zirconia and the complex electrodes now used affects the ionic conductivity, so that the microstructure of the interface has become a vital variable (Drennan 1998).

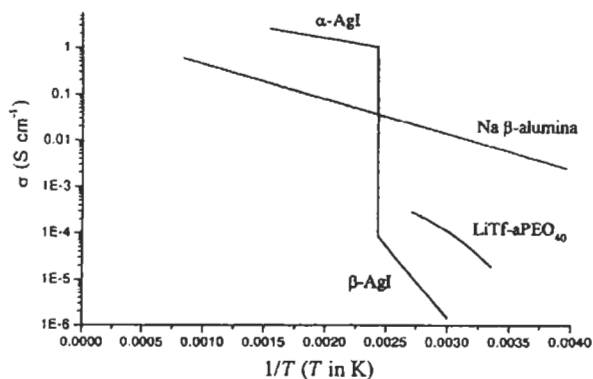
Beta-alumina, mentioned in Section 7.2.2.2, is just the best known and most exploited of this family. They have been developed by intensive research over more than three decades since Yao and Kummer (1967) first reported the remarkably high ionic conductivity of sodium beta-alumina. Many other elements have been used in place of sodium, as well as different crystallographic variants, and various processing procedures developed, until this material is now poised at last to enter battery service in earnest (Sudworth *et al.* 2000).

**11.3.1.2 Polymeric ionic conductors.** One of the most unexpected developments in recent decades in the whole domain of electrochemistry has been the invention of and gradual improvements in ionically conducting polymeric membranes, to the

point where they have become *the* key components of advanced batteries and fuel cells. A comparison between the conductivity of an advanced member of this category and of two ionic superconductors is shown in Figure 11.9.

The original motive for developing such polymers was for the chemical function of ion-exchange membranes, for such purposes as water desalination or softening. This kind of usage was already well established at the beginning of the 1960s. At about that time, the GE Laboratory in Schenectady began research on ionically conducting polymers for use in the fuel cells that were to be used as power sources in the American 'moon shots'; the 'product champion' was a chemist, W. Thomas Grubb who, in the words of Koppel (1999) "got an inspiration from an unlikely source, the common water softener". The story is spelled out in much greater detail in an essay by Suits and Bueche (1967); in 1955, Grubb took out a patent on his sulfonated polystyrene resin and a version of this polymeric electrolyte, in conjunction with an improved way of attaching platinum electrocatalyst developed by Leonard Niedrach, also of GE, eventually was used in the fuel cells for the American Gemini moon shots in the early 1960s. This kind of membrane is now commonly called a PEM, a *proton exchange membrane*, because the ions of interest in this connection are hydrogen ions. Industrially important polymers are cation conductors.

Later, Du Pont in America developed its own ionically conducting membrane, mainly for large-scale electrolysis of sodium chloride to manufacture chlorine, Nafion<sup>®</sup>, (the US Navy also used it on board submarines to generate oxygen by electrolysis of water), while Dow Chemical, also in America, developed its own even more efficient version in the 1980s, while another version will be described below in connection with fuel cells. Meanwhile, Fenton *et al.* (1973) discovered the first of a



**Figure 11.9.** Conductivity vs temperature plot for two ionically conducting crystals and for a polymer electrolyte,  $\text{LiTf-aPEO}_{40}$ , which is based on amorphous poly(ethylene) oxide (after Ratner 2000).

series of polymers suitable specifically for batteries, based on dissolution of a salt in amorphous poly(ethylene) oxide, used in sheets of the order of 100  $\mu\text{m}$  thick. Further development of membranes for battery use is concisely described by Scrosati and Vincent (2000); a number of quite different polymers and polymer composites have been developed; it has become a major branch of materials chemistry.

**11.3.1.3 Modern storage batteries (resumed).** The most advanced batteries to exploit superionic conductors have used beta-alumina. For some years, the sodium-sulphur battery held sway; here the electrodes are of molten sulphur and of molten sodium (the battery only functions at high temperature) and the electrolyte is of beta-alumina with sodium; that is, the electrodes are liquid and the electrolyte solid, standing tradition on its head. For a while, Ford Motor Company hoped to use this approach as a power source for automobiles; in the 1970s and 1980s much research was done on this system, but eventually it was abandoned for what Sudworth *et al.* (2000) call "a variety of technical and economic reasons". It seems that it has been replaced very recently by a sodium/nickel chloride battery, called ZEBRA, again using beta-alumina electrolyte; this well developed concept is peculiar in that the nickel chloride electrode has a liquid electrolyte incorporated, in contact with the solid electrolyte; this seems to be the first system of this type. Sudworth *et al.* indicate that vehicles have covered over 2 million kilometers with this kind of storage battery.

However, the battery system that has caused most excitement in recent years, and an enormous amount of associated research (see, e.g., dozens of papers in a recent MRS symposium, Ginley *et al.* 1998) is the Sony lithium ion battery for consumer electronics, introduced commercially in 1995 after many years of research and development. Without going into extensive details, this consists of a  $\text{LiCoO}_2$  cathode and a Li anode, both intercalated in a specially developed carbon form (the anode consists of 'lithiated graphite',  $\text{LiC}_6$ ; there is no free metallic lithium present). The electrolyte in the latest form of the battery is a newly developed,  $\text{Li}^+$ -conducting polymer, consisting of an amorphous matrix and salt-enriched crystalline regions; the conduction mechanism is still not properly understood. The  $\text{Li}^+$  ions shuttle between two energy states in the two electrodes, and the battery gives a cell voltage of 3.8 V. The electrode chemistry is extremely complex, and alternative electrode strategies are being energetically researched; even computer simulation of electrochemical systems is being extensively applied in the search for improvements (e.g., Ceder *et al.* 1998).

The Sony cell is rapidly outstripping all other batteries for such uses as laptop computers, especially since the electrode design has overcome danger of fire which held back earlier versions of the battery. It has an energy density of  $>200$  watt-



hours/kg, compared with 35 for a modern lead-acid battery (and compared with 12,000 watt-hours/kg for gasoline!) Nevertheless, the Li battery in its latest form is the only one to date which exceeds the minimum battery characteristics officially set for automobile use. For the ZEBRA battery mentioned above, an energy density of 90 watt-hours/kg has been quoted.

It is interesting that one researcher on the lithium batteries, Manthiram (1999) of the University of Texas at Austin, found that to make progress in his group's researches, it was necessary to train students from various relevant disciplines, especially chemistry and physics, in an interdisciplinary materials science course before they acquired the right attitudes to make progress. The way he put it was: "It is difficult to achieve the research goals with graduate students having prior degrees in any of the traditional disciplines".

The great disadvantage of any battery, however advanced, for automobile power trains, is the long time required to charge a battery, and in my view this will be decisive. Here, fuel cells have an enormous advantage over batteries, and so I turn to fuel cells next.

### ***11.3.2 Fuel cells***

A fuel cell is simply a device with two electrodes and an electrolyte for extracting power from the oxidation of a fuel without combustion, converting the power released directly into electricity. The fuel is usually hydrogen. The principle of a fuel cell was first demonstrated by Sir William Grove in London in 1839 with sulphuric acid and platinum gauze as an electrocatalyst, and thereafter there were very occasional attempts to develop the principle, "not all of which were based on sound scientific principles", as one commentator put it.

The father of the modern fuel cell is Francis Thomas Bacon (known as Tom Bacon, 1904–1992), a descendant of Sir Nicholas Bacon, Elizabeth the First's Lord Keeper of the Great Seal and father of the 'original' Francis Bacon. From 1937 onwards, Tom Bacon became fascinated by the potential of fuel cells, and applied his considerable engineering skills to successive designs. He used nickel electrodes, highly pressurised hydrogen and a concentrated potassium hydroxide electrolyte and a temperature typically around 100°C, and the conditions he favoured gradually became more severe. He was faced with endless obstacles in the form of hostile research directors and unreliable financial backers. Fortunately he had a modest private income which throughout his life freed him from the tyranny of the money-men.

After the War, Tom Bacon worked for a while in the ill-fated Department of Colloid Science which we met in Chapter 2. His laboratory space there was taken away from him and he moved to the adjacent metallurgy laboratory and then again to the nearby chemical engineering department. In his own person, Tom Bacon

worked in all the relevant departments in Cambridge University. All these stages are described in a biographical memoir by Williams (1994). Finally, Bacon obtained reasonably steadfast government support and by 1959 he was able to demonstrate a properly engineered 6 kW 40-cell device; the hydrogen electrode was of porous nickel, the oxygen electrode, eventually, of preoxidised nickel. At this stage, British Government support was withdrawn, but Pratt and Whitney in America became very interested, put some 1000 engineers on the project and by the mid-1960s an American fuel cell based on Bacon's design powered the Apollo moonshots, producing copious by-product water as a bonus. President Lyndon Johnson put his arm round Bacon's shoulders and said "Without you, Tom, we wouldn't have gotten to the moon".

The other main approach at the time was a fuel cell based on GE's ionically conducting polymer (Section 11.3.1.2), and this was used in the Gemini moonshots which preceded the Apollo programme. There were many teething troubles but fuel cells proved their worth in the space programme. The stages of this programme are described in Koppel's (1999) book.

Apart from Bacon's 'alkaline' fuel cell and the polymeric membrane cell, other variants are phosphoric acid cell, a molten carbonate cell and (greatly favored by many investigators) the solid oxide fuel cell, using stabilised zirconia as electrolyte and complex compound electrodes. These are all outlined in an encyclopedia article by Steele (1994), and the current design of the oxide fuel cell is described by Singhal (2000). There has been an enormous amount of gradual optimisation and Steele claims that the latest version has operated at  $\approx 900^\circ\text{C}$  with little degradation for more than 32,000 h. Both hydrogen and natural-gas fuels have been used, with very high generation efficiencies. Numerous cells are connected to form an industrial unit.

I suspect that the final competition for large-scale application will be between solid-oxide and polymeric-membrane versions, and that the former may well win out for stationary power sources, while the latter will be the victor for automotive uses, particularly since the operating temperature with polymeric electrolyte is so much lower and very little start-up time is needed. A detailed discussion of the design and merits of the different designs is in a book by Kordesch and Simader (1996), which pays special attention to the phosphoric acid cell. Another detailed review of the alternatives for the "electric option" for powering automobiles is by Shukla *et al.* (1999); they conclude, intriguingly, that a 50 kW polymer electrolyte fuel cell stack, together with a "supercapacitor" or a battery bank for short bursts of extra power, would be a viable arrangement. This takes us naturally to the experience of the most successful company currently active in this field.

The achievements of a small Canadian startup company, Ballard Power Systems, in Vancouver, are the main reason for my view that polymeric-membrane cells have the automotive market at their feet. The stages of the company's achievements,

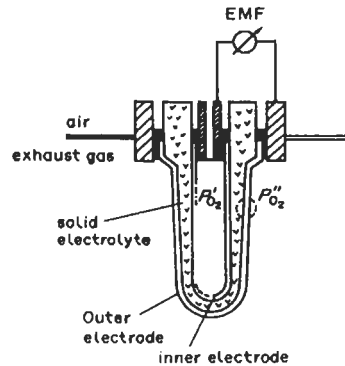
founded by Geoffrey Ballard, are fascinatingly described in Koppel's book, which also goes in considerable detail into the industrial battles between the rival configurations. The Ballard company by degrees improved the polymeric membrane; since the Du Pont and Dow membranes were too expensive and the prices would not come down, the company developed and then began to manufacture its own improved membrane, and also – in collaboration with Johnson Matthey, the precious-metal firm – found ways of using platinum electrocatalyst in ever more efficient physical forms, reducing the amount needed by a factor of ten. Ballard cells, using compressed hydrogen, powered a fleet of municipal buses in Vancouver as early as 1993. Finally, the company made common cause with a major automobile manufacturer and it looks as though a thoroughly practical automobile fuel cell is very close. A recent critical overview strikes an upbeat note (Appleby 1999).

As of 2000, it also looks as though more and more electric utilities are becoming interested in fuel cell stacks as local 'microgenerators' to top up power from large power stations, without the need for long-distance transmission of electricity and its attendant expense and power losses.

Storage of the fuel is the Achilles' heel of all fuel cells. Hydrogen is still the preferred fuel, methanol is another though even here the preference is for an on-board apparatus for 'reforming' the chemical to create hydrogen. Hydrogen can be effectively stored as compressed gas, liquid (here the difficulties are the low density and thus large volume of a supply of LH, and also the large amount of energy irreversibly used in liquefaction) or in the form of a reversibly formed hydride; hydrogen can be released by slight heating. Research on metal hydrides is now a major field of materials chemistry, but as yet the attainable ratio of hydrogen to metal is not quite sufficient and this form of hydrogen storage has to contend with excessive weight. However, magnesium hydride looks distinctly promising (Schwarz 1999), as does the reversible storage of hydrogen in carbon nanotubes (Dresselhaus *et al.* 1999). As with batteries, the speed, simplicity and cost of 'refuelling' will probably be the limiting factor in the development of automobiles driven by fuel cells, but this may not be a major consideration where microgenerators are concerned.

### 11.3.3 Chemical sensors

Electrochemistry plays an important role in the large domain of sensors, especially for gas analysis, that turn the chemical concentration of a gas component into an electrical signal. The longest-established sensors of this kind depend on superionic conductors, notably stabilised zirconia. The most important is probably the oxygen sensor used for analysing automobile exhaust gases (Figure 11.10). The space on one side of a solid-oxide electrolyte is filled with the gas to be analysed, the other side



**Figure 11.10.** Gas sensor to monitor oxygen content of exhaust gases from automobile engines (after Fray 1990).

with a gas of standard composition, and the cell potential is measured. This kind of cell is much more sensitive at low concentrations than at high (Fray 1990). Similar cells can be designed to measure other gases such as  $CO_2$  and  $SO_2$  (Yamazoe and Miura 1999). Hydrogen can be analysed, for instance, by exposing  $SnO_2$ , a conductor, to oxygen, thereby creating a chemisorbed layer of high resistivity; then reducing this by hydrogen: the resistivity is related to the hydrogen concentration. To distinguish between different reducing gases, dopants such as  $La_2O_3$  can be added to the  $SnO_2$ . To show the amount of materials chemistry that has gone into this kind of instrumentation, reference can be made to an overview of the dozens of devices developed to measure just one impurity gas, sulphur dioxide, many using molten salt electrolytes (Singh and Bhoga 1999). Other sensors are based on changes in resistivity or on MOSFET-type transistors, many are used for analysing solutions rather than gases; here the drain current depends on ion concentration. The subject is too vast to attempt any further classification here.

A subset of sensors is designed to function as *smart materials*; these are devices that function both as sensors and as actuators (Newnham 1998). An example is a smart shock absorber for automobiles, designed in Japan; this is a multilayer ferroelectric system in which sensed vibrations lead to a correcting signal acting on another part of the multilayer stack. The ferroelectric mount for the tip of a scanning tunneling microscope also functions as a smart material, in keeping the tip at a predetermined distance from the sample being examined. Magnetostriction and electrostriction are other responses used in certain smart materials. The foregoing are based on sensors for physical rather than chemical properties, but there is no reason why chemical sensors should not come to be incorporated in control systems, for instance to keep constant the concentration of an aqueous solution or of a gas in a gas mixture.

#### 11.3.4 Electrolytic metal extraction

Many metals are extracted from their compounds, as found in ores, by electrolytic processes. By far the most important is the Hall-Héroult process, invented in 1886, for producing aluminium from alumina, itself refined from bauxite ore. Alumina is dissolved in molten cryolite,  $\text{Na}_3\text{AlF}_6$ , and electrolysed, using carbon anodes and the aluminium itself as cathode. While various details are being steadily improved, the basic process is still the same today.

Since 1886, many other metals have been either extracted or else refined by electrolytic means. The latest process to be invented involves titanium metal. This metal is intrinsically cheap in the sense that its ores are plentiful in the earth's crust; the high cost of titanium, a highly reactive metal, is almost entirely due to the very elaborate pyrometallurgical production process used; this is the Kroll process, introduced in 1940. An effective electrolytic process has been sought for decades. Now, it appears, an effective method has been developed (Chen *et al.* 2000):  $\text{TiO}_2$  powder is made the cathode of a bath of molten  $\text{CaCl}_2$  whose cation can form a more stable oxide,  $\text{CaO}$ . The oxygen in the  $\text{TiO}_2$  is ionised and dissolves in the salt, leaving titanium metal behind. The approach is simple, has worked well on a kilogram scale, and may well prove to be cheap. If it is fully proved, it is likely to have a revolutionary effect on the scope of titanium in practical metallurgy.

#### 11.3.5 Metallic corrosion

In economic terms, the study and prevention of metallic corrosion is one of the most important fields of materials science and engineering. Methods of study have been developed throughout the twentieth century. Perhaps the first major text to assemble the many insights gained was that by the Cambridge metallurgist Ulick Evans (1889–1980) (1937, 1945). Evans made it very clear that the operation of localised electrolytic microcells play a dominant role in corrosion. One form of such localised electrolysis was what Evans called “differential aeration”: different rates of supply of oxygen to the centre and periphery of a water drop on metal suffice to set up a potential difference and thus a corrosive current. This particular concept was much discussed and disputed in the 1930s, and a recent overview of corrosion (Schütze 2000) makes no mention of it. This is typical of this disputatious field. However, the centrality of electrochemistry in corrosion is not in doubt, and the first chapter in Schütze's book is devoted to a description of the macroscopic experimental methods used to mimic the localised electrolytic processes in rusting steel and other corroding metals.

Corrosion is fought partly by developing alloys with a built-in proclivity to form protective oxide layers, such as ‘stainless steels’, and partly by designing protective coatings. A form of protection particularly closely linked to electrochemistry is

cathodic or anodic protection. In one form of this strategy, a coating is designed to dissolve preferentially ('sacrificially') instead of the underlying metal: the use of zinc coatings on steel is the most familiar and long-established form of this approach. Another way is to pass an externally sourced current between the item to be protected, whether a ship or a buried pipeline, and an adjacent sacrificial piece of another metal. This form of protection has become a widespread technology; it is fully described by Juchniewicz *et al.* (2000).

Ultramodern techniques are being applied to the study of corrosion: thus a very recent initiative at Sandia Laboratories in America studied the corrosion of copper in air 'spiked' with hydrogen sulphide by a form of combinatorial test, in which a protective coat of copper oxide was varied in thickness, and in parallel, the density of defects in the copper provoked by irradiation was also varied. Defects proved to be more influential than the thickness of the protective layer. This conclusion is valuable in preventing corrosion of copper conductors in advanced microcircuits. This set of experiments is typical of modern materials science, in that quite diverse themes... combinatorial methods, corrosion kinetics and irradiation damage... are simultaneously exploited.

To keep this book in some kind of balance, no further treatment of corrosion and its prevention – or of high-temperature dry corrosion – is feasible here, important though these themes are.

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## Chapter 12

# Computer Simulation

### 12.1. BEGINNINGS

In late 1945, a prototype digital electronic computer, the Electronic Numerical Integrator and Calculator, (ENIAC) designed to compute artillery firing tables, began operation in America. There were many ‘analogue computers’ before ENIAC, there were primitive digital computers that were not programmable, and of course 19th-century computers, calculating engines, were purely mechanical. It is sometimes claimed that ‘the world’s first fully operational computer’ was EDSAC, in Cambridge, England, in 1949 (because the original ENIAC was programmed by pushing plugs into sockets and throwing switches, while EDSAC had a stored electronic program). However that may be, computer simulation in fact began on ENIAC, and one of the first problems treated on this machine was the projected thermonuclear bomb; the method used was the Monte Carlo (MC) approach.

The story of this beginning of computer simulation is told in considerable detail by Galison (1997) in an extraordinary book which is about the evolution of particle physics and also about the evolving nature of ‘experimentation’. The key figure at the beginning was John von Neumann, the Hungarian immigrant physicist whom we have already met in Chapter 1. In 1944, when the Manhattan Project at Los Alamos was still in full swing, he recognised that the hydrodynamical issues linked to the behaviour of colliding shock-waves were too complex to be treated analytically, and he worked out (in Galison’s words) “an understanding of how to transform coupled differential equations into difference equations which, in turn, could be translated into language the computer could understand”. The computer he used in 1944 seems to have been a punched-card device of the kind then used for business transactions. Galison spells out an example of this computational prehistory. Afterwards, within the classified domain, von Neumann had to defend his methods against scepticism that was to continue for a long time. Galison characterises what von Neumann did at this time as “carving out. . . a zone of what one might call *mesoscopic physics* perched precariously between the macroscopic and the microscopic”.

In view of the success of von Neumann’s machine-based hydrodynamics in 1944, and at about the time when the fission bomb was ready, some scientists at Los Alamos were already thinking hard about the possible design of a fusion bomb. Von Neumann invited two of them, Nicholas Metropolis and Stanley Frankel, to try to model the immensely complicated issue of how jets from a fission device might initiate thermonuclear reactions in an adjacent body of deuterium. Metropolis linked

up with the renowned Los Alamos mathematician, Stanislaw Ulam, and they began to sketch what became the Monte Carlo method, in which random numbers were used to decide for any particle what its next move should be, and then to examine what proportion of those moves constitute a “success” in terms of an imposed criterion. In their first public account of their new approach, Metropolis and Ulam (1949) pointed out that they were occupying the uncharted region of mechanics between the classical mechanician (who can only handle a very few bodies together) and the statistical mechanician, for whom Avogadro’s huge Number is routine. The “Monte Carlo” name came from Ulam; it is sometimes claimed that he was inspired to this by a favourite uncle who was devoted to gambling. (A passage in a recent book (Hoffmann 1998) claims that in 1946, Ulam was recovering from a serious illness and played many games of solitaire. He told his friend Vázsonyi: “After spending a lot of time trying to estimate the odds of particular card combinations by pure combinatorial calculations, I wondered whether a more practical method than abstract thinking might not be to lay the cards out say one hundred times and simply observe and count the number of successful plays... I immediately thought of problems of neutron diffusion and other questions of mathematical physics...”).

What von Neumann and Metropolis first did with the new technique, as a try-out, with the help of others such as Richard Feynman, was to work out the neutron economy in a fission weapon, taking into account all the different things – absorption, scattering, fission initiation, each a function of kinetic energy and the object being collided with – that can happen to an individual neutron. Galison goes on to spell out the nature of this proto-simulation. Metropolis’s innovations, in particular, were so basic that even today, people still write about using the “Metropolis algorithm”.

A simple, time-honoured illustration of the operation of the Monte Carlo approach is one curious way of estimating the constant  $\pi$ . Imagine a circle inscribed inside a square of side  $a$ , and use a table of random numbers to determine the cartesian coordinates of many points constrained to lie anywhere at random within the square. The ratio of the number of points that lies inside the circle to the total number of points within the square  $\approx \pi a^2 / 4a^2 = \pi/4$ . The more random points have been put in place, the more accurate will be the value thus obtained. Of course, such a procedure would make no sense, since  $\pi$  can be obtained to any desired accuracy by the summation of a mathematical series... i.e., analytically. But once the simulator is faced with a complex series of particle movements, analytical methods quickly become impracticable and simulation, with time steps included, is literally the only possible approach. That is how computer simulation began.

Among the brilliant mathematicians who developed the minutiae of the MC method, major disputes broke out concerning basic issues, particularly the question whether any (determinate) computer-based method is in principle capable of

generating an array of truly random numbers. The conclusion was that it is not, but that one can get close enough to randomness for practical purposes. This was one of the considerations which led to great hostility from some mathematicians to the whole project of computer simulation: for a classically trained pure mathematician, an approximate table of pseudo-random numbers must have seemed an abomination! The majority of theoretical physicists reacted similarly at first, and it took years for the basic idea to become acceptable to a majority of physicists. There was also a long dispute, outlined by Galison: "What *was* this Monte Carlo? How did it fit into the universally recognised division between experiment and theory – a taxonomic separation as obvious to the product designer at Dow Chemical as it was to the mathematician at Cornell?" The arguments went on for a long time, and gradually computer simulation came to be perceived as a form of experiment: thus, one of the early materials science practitioners, Beeler (1970), wrote uncompromisingly: "A computer experiment is a computational method in which physical processes are simulated according to a given set of physical mechanisms". Galison himself thinks of computer simulation as a hybrid "between the traditional epistemic poles of bench and blackboard". He goes in some detail into the search for "computational errors" introduced by finite object size, finite time steps, erroneous weighting, etc., and accordingly treats a large-scale simulation as a "numerical experiment". These arguments were about more than just semantics. Galison asserts baldly that "without computer-based simulation, the material culture of late-20th century microphysics (the subject of his book) is not simply inconvenienced – it does not exist".

Where computer simulation, and the numerical 'calculations' which flow from it, fits into the world of physics – and, by extension, of materials science – has been anxiously discussed by a number of physicists. One comment was by Herman (1984), an early contributor to the physics of semiconductors. In his memoir of early days in the field, he asserts that "during the 1950s and into the 1960s there was a sharp dichotomy between those doing formal solid-state research and those doing computational work in the field. Many physicists were strongly prejudiced against numerical studies. Considerable prestige was attached to formal theory." He goes on to point out that little progress was in fact made in understanding the band theory of solids (essential for progress in semiconductor technology) until "band theorists rolled up their sleeves and began doing realistic calculations on actual materials (by computer), and checking their results against experiment".

Recently, Langer (1999) has joined the debate. He at first sounds a distinct note of scepticism: "...the term 'numerical simulation' makes many of us uncomfortable. It is easy to build models on computers and watch what they do, but it is often unjustified to claim that we learn anything from such exercises." He continues by examining a number of actual simulations and points out, first, the value of



obtaining *multiscale* information “of a kind that is not available by using ordinary experimental or theoretical techniques”. Again, “we are not limited to simulating ‘real’ phenomena. *We can test theories by simulating idealised systems for which we know that every element has exactly the properties we think are relevant* (my emphasis)”. In other words, in classical experimental fashion we can change one feature at a time, spreadsheet-fashion.

These two points made by Langer are certainly crucial. He goes on to point out that for many years, physicists looked down on instrumentation as a mere service function, but now have come to realise that the people who brought in tools such as the scanning tunnelling microscope (and won the Nobel Prize for doing so) “are playing essential roles at the core of modern physics. I hope” (he concludes) “that we’ll be quicker to recognise that computational physics is emerging as an equally central part of our field”. Exactly the same thing can be said about materials science and computer simulation.

Finally, in this Introduction, it is worthwhile to reproduce one of the several current definitions, in the Oxford English Dictionary, of the word ‘simulate’: “To imitate the conditions or behaviour of (a situation or process) by means of a model, especially for the purpose of study or training; specifically, to produce a computer model of (a process)”. The Dictionary quotes this early (1958) passage from a text on high-speed data processing: “A computer can simulate a warehouse, a factory, an oil refinery, or a river system, and if due regard is paid to detail the imitation can be very exact”. Clearly, in 1958 the scientific uses of computer simulation were not yet thought worthy of mention, or perhaps the authors did not know about them.

## 12.2. COMPUTER SIMULATION IN MATERIALS SCIENCE

In his early survey of ‘computer experiments in materials science’, Beeler (1970), in the book chapter already cited, divides such experiments into four categories. One is the *Monte Carlo approach*. The second is the dynamic approach (today usually named *molecular dynamics*), in which a finite system of  $N$  particles (usually atoms) is treated by setting up  $3N$  equations of motion which are coupled through an assumed two-body potential, and the set of  $3N$  differential equations is then solved numerically on a computer to give the space trajectories and velocities of all particles as function of successive time steps. The third is what Beeler called the *variational approach*, used to establish equilibrium configurations of atoms in (for instance) a crystal dislocation and also to establish what happens to the atoms when the defect moves; each atom is moved in turn, one at a time, in a self-consistent iterative process, until the total energy of the system is minimised. The fourth category of ‘computer experiment’ is what Beeler called a *pattern development*

*calculation*, used to simulate, say, a field-ion microscope or electron microscope image of a crystal defect (on certain alternative assumptions concerning the true three-dimensional configuration) so that the simulated images can be compared with the experimental one in order to establish which is in fact the true configuration. This has by now become a widespread, routine usage. Another common use of such calculations is to generate predicted X-ray diffraction patterns or nuclear magnetic resonance plots of specific substances, for comparison with observed patterns.

Beeler defined the broad scope of computer experiments as follows: "Any conceptual model whose definition can be represented as a unique branching sequence of arithmetical and logical decision steps can be analysed in a computer experiment... The utility of the computer... springs mainly from its computational speed." But that utility goes further; as Beeler says, conventional analytical treatments of many-body aspects of materials problems run into awkward mathematical problems; computer experiments bypass these problems.

One type of computer simulation which Beeler did not include (it was only just beginning when he wrote in 1970) was finite-element simulation of fabrication and other production processes, such as for instance rolling of metals. This involves exclusively continuum aspects; 'particles', or atoms, do not play a part.

In what follows, some of these approaches will be further discussed. A very detailed and exhaustive survey of the various basic techniques and the problems that have been treated with them will be found in the first comprehensive text on "computational materials science", by Raabe (1998). Another book which covers the principal techniques in great mathematical detail and is effectively focused on materials, especially polymers, is by Frenkel and Smit (1996).

One further distinction needs to be made, that between 'modelling' and 'simulation'. Different texts favour different usages, but a fairly common practice is to use the term 'modelling' in the way offered in Raabe's book: "It describes the classical scientific method of formulating a simplified imitation of a real situation with preservation of its essential features. In other words, a model describes a part of a real system by using a *similar* but *simpler* structure." Simulation is essentially the putting of numbers into the model and deriving the numerical end-results of letting the model run on a computer. A simulation can never be better than the model on which it relies.

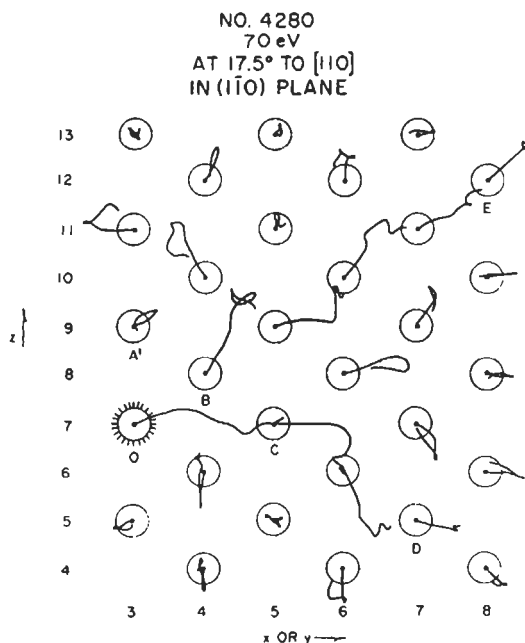
### ***12.2.1 Molecular dynamics (MD) simulations***

The simulation of molecular (or atomic) dynamics on a computer was invented by the physicist George Vineyard, working at Brookhaven National Laboratory in New York State. This laboratory, whose 'biography' has recently been published (Crease 1999), was set up soon after World War II by a group of American universities,

initially to foster research in nuclear physics; because radiation damage (see Section 5.1.3) was an unavoidable accompaniment to the accelerator experiments carried out at Brookhaven, a solid-state group was soon established and grew rapidly. Vineyard was one of its luminaries. In 1957, Vineyard, with George Dienes, wrote an influential early book, *Radiation Damage in Solids*. (Crease comments that this book “helped to bolster the image of solid-state physics as a basic branch of physics”.) In 1973, Vineyard became laboratory director.

In 1972, some autobiographical remarks by Vineyard were published at the front of the proceedings of a conference on simulation of lattice defects (Vineyard 1972). Vineyard recalls that in 1957, at a conference on chemistry and physics of metals, he explained the then current analytical theory of the damage cascade (a collision sequence originating from one very high-energy particle). During discussion, “the idea came up that a computer might be applied to follow in more detail what actually goes on in radiation damage cascades”. Some insisted that this could not be done on a computer, others (such as a well-known, argumentative GE scientist, John Fisher) that it was not necessary. Fisher “insisted that the job could be done well enough by hand, and was then goaded into promising to demonstrate. He went off to his room to work; next morning he asked for a little more time, promising to send me the results soon after he got home. After two weeks... he admitted that he had given up.” Vineyard then drew up a scheme with an atomic model for copper and a procedure for solving the classical equations of state. However, since he knew nothing about computers he sought help from the chief applied mathematician at Brookhaven, Milton Rose, and was delighted when Rose encouragingly replied that ‘it’s a great problem; this is just what computers were designed for’. One of Rose’s mathematicians showed Vineyard how to program one of the early IBM computers at New York University. Other physicists joined the hunt, and it soon became clear that by keeping track of an individual atom and taking into account only near neighbours (rather than all the  $N$  atoms of the simulation), the computing load was roughly proportional to  $N$  rather than to  $N^2$ . (The initial simulation looked at 500 atoms.) The first paper appeared in the *Physical Review* in 1960. Soon after, Vineyard’s team conceived the idea of making moving pictures of the results, “for a more dramatic display of what was happening”. There was overwhelming demand for copies of the first film, and ever since then, the task of making huge arrays of data visualisable has been an integral part of computer simulation. Immediately following his mini-autobiography, Vineyard outlines the results of the early computer experiments: Figure 12.1 is an early set of computed trajectories in a radiation damage cascade.

One other remark of Vineyard’s in 1972, made with evident feeling, is worth repeating here: “Worthwhile computer experiments require time and care. The easy understandability of the results tends to conceal the painstaking hours that went into conceiving and formulating the problem, selecting the parameters of a model,



programming for computation, sifting and analysing the flood of output from the computer, rechecking the approximations and stratagems for accuracy, and out of it all synthesising physical information". None of this has changed in the last 30 years!

Two features of such dynamic simulations need to be emphasised. One is the limitation, set simply by the finite capacity of even the fastest and largest present-day computers, on the number of atoms (or molecules) and the number of time-steps which can be treated. According to Raabe (1998), the time steps used are  $10^{-14}$ – $10^{-15}$  s, less than a typical atomic oscillation period, and the sample incorporates  $10^3$ – $10^9$  atoms, depending on the complexity of the interactions between atoms. So, at best, the size of the region simulated is of the order of  $1 \text{ nm}^3$  and the time below one nanosecond. This limitation is one reason why computer simulators are forever striving to get access to larger and faster computers.

The other feature, which warrants its own section, is the issue of interatomic potentials.

**12.2.1.1 Interatomic potentials.** All molecular dynamics simulations and some MC simulations depend on the form of the interaction between pairs of particles (atoms

or molecules). For instance, the damage cascade in Figure 12.1 was computed by a dynamics simulation on the basis of specific interaction potentials between the atoms that bump into each other. When a MC simulation is used to map the configurational changes of polymer chains, the van der Waals interactions between atoms on neighbouring chains need to have a known dependence of attraction on distance. A plot of force vs distance can be expressed alternatively as a plot of potential energy vs distance; one is the differential of the other. Figure 12.2 (Stoneham *et al.* 1996) depicts a schematic, interionic short-range potential function showing the problems inherent in inferring the function across the significant range of distances from measurements of equilibrium properties alone.

Interatomic potentials began with empirical formulations (empirical in the sense that analytical calculations based on them... no computers were being used yet... gave reasonable agreement with experiments). The most famous of these was the Lennard-Jones (1924) potential for noble gas atoms; these were essentially van der Waals interactions. Another is the 'Weber potential' for covalent interactions between silicon atoms (Stillinger and Weber 1985); to take into account the directed covalent bonds, interactions between three atoms have to be considered. This potential is well-tested and provides a good description of both the crystalline and

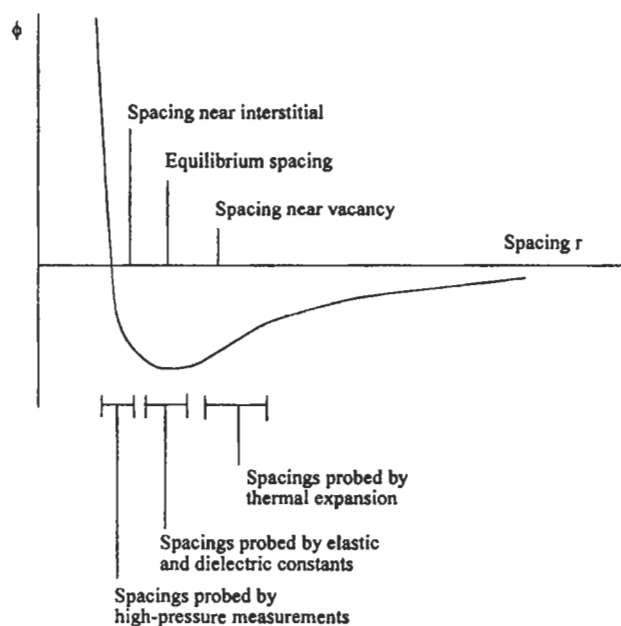


Figure 12.2. A schematic interionic short-range potential function, after Stoneham *et al.* (1996).

the amorphous forms of silicon (which have quite different properties) and of the crystalline melting temperature, as well as predicting the six-coordinated structure of liquid silicon. This kind of test is essential before a particular interatomic potential can be accepted for continued use.

In due course, attempts began to *calculate* from first principles the form of interatomic potentials for different kinds of atoms, beginning with metals. This would quickly get us into very deep quantum-mechanical waters and I cannot go into any details here, except to point out that the essence of the different approaches is to identify different simplifications, since Schrödinger's equation cannot be solved accurately for atoms of any complexity. The many different potentials in use are summarised in Raabe's book (p. 88), and also in a fine overview entitled "the virtual matter laboratory" (Gillan 1997) and in a group of specialised reviews in the *MRS Bulletin* (Voter 1996) that cover specialised methods such as the Hartree-Fock approach and the embedded-atom method. A special mention must be made of density functional theory (Hohenberg and Kohn 1964), an elegant form of simplified estimation of the electron-electron repulsions in a many-electron atom that won its senior originator, Walter Kohn, a Nobel Prize for Chemistry. The idea here is that all that an atom embedded in its surroundings 'knows' about its host is the local electron density provided by its host, and the atom is then assumed to interact with its host exactly as it would if embedded in a homogeneous electron gas which is everywhere of uniform density equal to the local value around the atom considered.

Most treatments, even when intended for materials scientists, of these competing forms of quantum-mechanical simplification are written in terms accessible only to mathematical physicists. Fortunately, a few 'translators', following in the tradition of William Hume-Rothery, have explained the essentials of the various approaches in simple terms, notably David Pettifor and Alan Cottrell (e.g., Cottrell 1998), from whom the formulation at the end of the preceding paragraph has been borrowed.

It may be that in years to come, interatomic potentials can be estimated experimentally by the use of the atomic force microscope (Section 6.2.3). A first step in this direction has been taken by Jarvis *et al.* (1996), who used a force feedback loop in an AFM to prevent sudden springback when the probing silicon tip approaches the silicon specimen. The authors claim that their method means that "force-distance spectroscopy of specific sites is possible – mechanical characterisation of the potentials of specific chemical bonds".

### 12.2.2 Finite-element simulation

In this approach, continuously varying quantities are computed, generally as a function of time as some process, such as casting or mechanical working, proceeds, by 'discretising' them in small regions, the finite elements of the title. The more

complex the mathematics of the model, the smaller the finite elements have to be. A good understanding of how this approach works can be garnered from a very thorough treatment of a single process; a recent book (Lenard *et al.* 1999) of 364 pages is devoted entirely to hot-rolling of metal sheet. The issue here is to simulate the distribution of pressure across the arc in which the sheet is in contact with the rolls, the friction between sheet and rolls, the torque needed to keep the process going, and even microstructural features such as texture (preferred orientation). The modelling begins with a famous analytical formulation of the problem by Orowan (1943), numerous refinements of this model and the canny selection of acceptable levels of simplification. The end-result allows the mechanical engineering features of the rolling-mill needed to perform a specific task to be estimated.

Finite-element simulations of a wide range of manufacturing processes for metals and polymers in particular are regularly performed. A good feeling for what this kind of simulation can do for engineering design and analysis generally, can be obtained from a popular book on supercomputing (Kaufmann and Smarr 1993).

Finite-element approaches can be supplemented by the other main methods to get comprehensive models of different aspects of a complex engineering domain. A good example of this approach is the recently established Rolls-Royce University Technology Centre at Cambridge. Here, the major manufacturing processes involved in superalloy engineering are modelled: these include welding, forging, heat-treatment, thermal spraying, machining and casting. All these processes need to be optimised for best results and to reduce material wastage. As the Centre's then director, Roger Reed, has expressed it, "if the behaviour of materials can be quantified and understood, then processes can be optimised using computer models". The Centre is to all intents and purposes a virtual factory. A recent example of the approach is a paper by Matan *et al.* (1998), in which the rates of diffusional processes in a superalloy are estimated by simulation, in order to be able to predict what heat-treatment conditions would be needed to achieve an acceptable approach to phase equilibrium at various temperatures. This kind of simulation adds to the databank of such properties as heat-transfer coefficients, friction coefficients, thermal diffusivity, etc., which are assembled by such depositories as the National Physical Laboratory in England.

### ***12.2.3 Examples of simulations of a material***

***12.2.3.1 Grain boundaries in silicon.*** The prolonged efforts to gain an accurate understanding of the fine structure of interfaces – surfaces, grain boundaries, interphase boundaries – have featured repeatedly in this book. Computer simulations are playing a growing part in this process of exploration. One small corner of this process is the study of the role of grain boundaries and free surfaces in the

process of melting, and this is examined in a chapter of a book (Phillpot *et al.* 1992). Computer simulation is essential in an investigation of how much a crystalline solid can be overheated without melting *in the absence of surfaces and grain boundaries* which act as catalysts for the process; such simulation can explain the asymmetry between melting (where superheating is not normally found at all) and freezing, where extensive supercooling is common. The same authors (Phillpot *et al.* 1989) began by examining the melting of imaginary crystals of silicon with or without grain boundaries and surfaces (there is no room here to examine the tricks which computer simulators use to make a model pretend that the small group of atoms being examined has no boundaries). The investigators finish up by distinguishing between mechanical melting (triggered by a phonon instability), which is homogeneous, and thermodynamic melting, which is nucleated at extended defects such as grain boundaries. The process of melting starting from such defects can be neatly simulated by molecular dynamics.

The same group (Kebblinski *et al.* 1996), continuing their researches on grain boundaries, found (purely by computer simulation) a highly unexpected phenomenon. They simulated twist grain boundaries in silicon (boundaries where the neighbouring orientations differ by rotation about an axis normal to the boundary plane) and found that if they introduced an amorphous (non-crystalline) layer 0.25 nm thick into a large-angle crystalline boundary, the computed potential energy is lowered. This means that an amorphous boundary is thermodynamically stable, which takes us back to an idea tenaciously defended by Walter Rosenhain a century ago!

**12.2.3.2 Colloidal 'crystals'.** At the end of Section 2.1.4, there is a brief account of regular, crystal-like structures formed spontaneously by two differently sized populations of hard (polymeric) spheres, typically near 0.5 nm in diameter, depositing out of a colloidal solution. Binary 'superlattices' of composition  $AB_2$  and  $AB_{13}$  are found. Experiment has allowed 'phase diagrams' to be constructed, showing the 'crystal' structures formed for a fixed radius ratio of the two populations but for variable volume fractions in solution of the two populations, and a computer simulation (Eldridge *et al.* 1995) has been used to examine how nearly theory and experiment match up. The agreement is not bad, but there are some unexpected differences from which lessons were learned.

The importance of these pseudo-crystals is that their periodicities are similar to those of visible light and they can thus be used like semiconductors in acting on light beams in optoelectronic devices.

**12.2.3.3 Grain growth and other microstructural changes.** When a deformed metal is heated, it will *recrystallise*, that is to say, a new population of crystal grains will



replace the deformed population, driven by the drop in free energy occasioned by the removal of dislocations and vacancies. When that process is complete but heating is continued then, as we have seen in Section 9.4.1, the mean size of the new grains gradually grows, by the progressive removal of some of them. This process, *grain growth*, is driven by the disappearance of the energy of those grain boundaries that vanish when some grains are absorbed by their neighbours. In industrial terms, grain growth is much less important than recrystallisation, but it has attracted a huge amount of attention by computer modellers during the past few decades, reported in literally hundreds of papers. *This is because the phenomenon offers an admirable testbed for the relative merits of different computational approaches.*

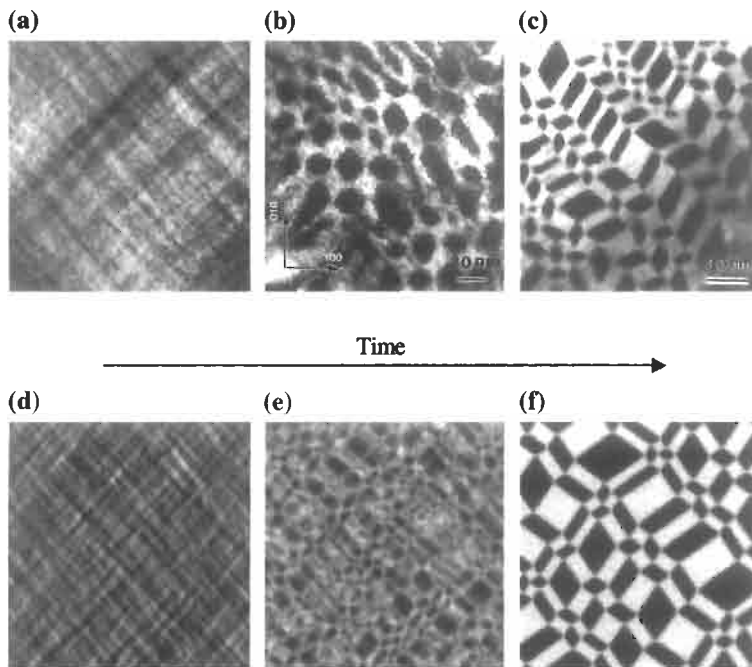
There are a number of variables: the specific grain-boundary energy varies with misorientation if that is fairly small; if the grain-size *distribution* is broad, and if a subpopulation of grains has a pronounced preferred orientation, a few grains grow very much larger than others. (We have seen, Section 9.4.1, that this phenomenon interferes drastically with sintering of ceramics to 100% density.) The metal may contain a population of tiny particles which seize hold of a passing grain boundary and inhibit its migration; the macroscopic effect depends upon both the mean size of the particles and their volume fraction. All this was quantitatively discussed properly for the first time in a classic paper by Smith (1948). On top of these variables, there is also the different grain growth behaviour of thin metallic films, where the surface energy of the metal plays a key part; this process is important in connection with failure of conducting interconnects in microcircuits.

There is no space here to go into the great variety of computer models, both two-dimensional and three-dimensional, that have been promulgated. Many of them are statistical ‘mean-field’ models in which an average grain is considered, others are ‘deterministic’ models in which the growth or shrinkage of every grain is taken into account in sequence. Many models depend on the Monte Carlo approach. One issue which has been raised is whether the simulation of grain size *distributions* and their comparison with experiment (using stereology, see Section 5.1.2.3) can be properly used to prove or disprove a particular modelling approach. One of the most disputed aspects is the modelling of the limiting grain size which results from the pinning of grain boundaries by small particles.

The merits and demerits of the many computer-simulation approaches to grain growth are critically analysed in a book chapter by Humphreys and Hatherly (1995), and the reader is referred to this to gain an appreciation of how alternative modelling strategies can be compared and evaluated. A still more recent and very clear critical comparison of the various modelling approaches is by Miodownik (2001).

Grain growth involves no phase transformation, but a number of such transformations have been modelled and simulated in recent years. A recently published overview volume relates some experimental observations of phase

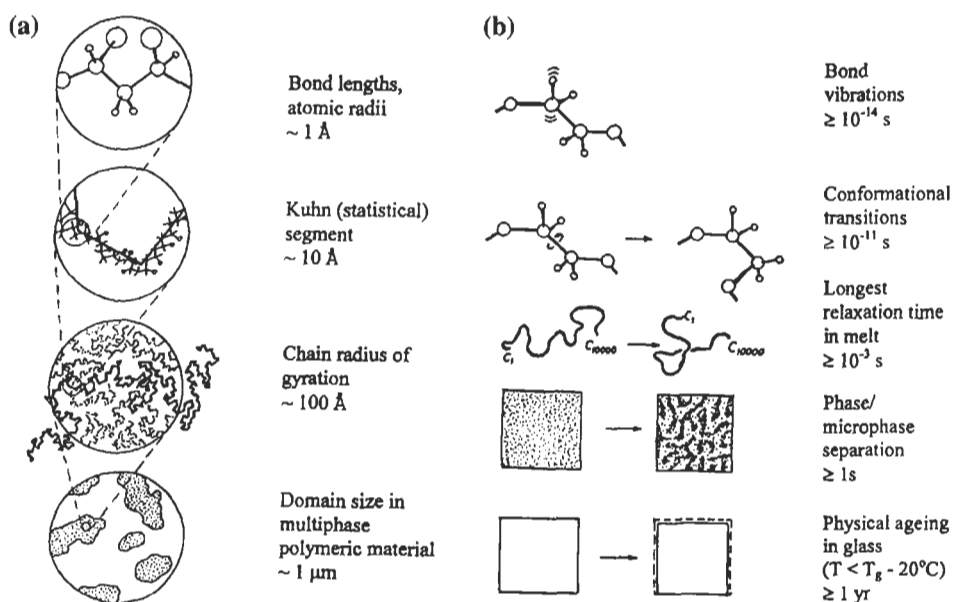
transformations to simulation (Turchi and Gonis 2000). Among the papers here is one describing some very pretty electron microscopy of an order–disorder transformation by a French group, linked to simulation done in cooperation with an eminent Russian-emigré expert on such transformations, Armen Khachaturyan (Le Bouar *et al.* 2000). Figure 12.3 shows a series of micrographs of progressive transformation, in a Co–Pt alloy which have long been studied by the French group, together with corresponding simulated patterns. The transformation pattern here, called a ‘chessboard pattern’, is brought about by internal stresses: a cubic crystal structure (disordered) becomes tetragonal on ordering, and in different domains the unique fourfold axis of the tetragonal form is constrained to lie in orthogonal directions, to accommodate the stresses. The close agreement indicates that the model is close to physical reality... which is always the objective of such modelling and simulation.



**Figure 12.3.** Comparison between experimental observations (a–c) and simulation predictions (d–f) of the microstructural development of a ‘chessboard’ pattern forming in a  $\text{Co}_{39.5}\text{Pt}_{60.5}$  alloy slowly cooled from 1023 K to (a) 963 K, (b) 923 K and (c) 873 K. The last of these was maintained at 873 K to allow the chessboard pattern to perfect itself (Le Bouar *et al.* 2000) (courtesy Y. Le Bouar).

**12.2.3.4 Computer-modelling of polymers.** The properties of polymers are determined by a large range of variables – chemical constitution, mean molecular weight and molecular weight distribution, fractional crystallinity, preferred orientation of amorphous regions, cross-linking, chain entanglement. It is thus no wonder that computer simulation, which can examine all these features to a greater or lesser extent, has found a special welcome among polymer scientists.

The length and time scales that are relevant to polymer structure and properties are shown schematically in Figure 12.4. Bearing in mind the spatial and temporal limitations of MD methods, it is clear that a range of approaches is needed, including quantum-mechanical ‘high-resolution’ methods. In particular, configurations of long-chain molecules and consequences such as rubberlike elasticity depend heavily on MC methods, which can be invoked with “algorithms designed to allow a correspondence between number of moves and elapsed time” (from a review by Theodorou 1994). A further simplification that allows space and time limitations to weigh less heavily is the use of *coarse-graining*, in which “explicit atoms in one or several monomers are replaced by a single particle or *bead*”. This form of words comes from a further concise overview of the “hierarchical simulation approach to



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**Figure 12.4.** Hierarchy of length scales of structure and time scales of motion in polymers.  $T_g$  denotes the glass transition temperature. After Uhlherr and Theodorou (1998) (courtesy Elsevier Science).

structure and dynamics of polymers” by Uhlherr and Theodorou (1998); Figure 12.4 also comes from this overview. Not only structure and properties (including time-dependent ones such as viscosity) of polymers, but also configurations and phase separations of block copolymers, and the kinetics of polymerisation reactions, can be modelled by MC approaches. One issue which has recently received a good deal of attention is the configuration of block copolymers with hydrophobic and hydrophilic ends, where one constituent is a therapeutic drug which needs to be delivered progressively; the hydrophobically ended drug moiety finishes up inside a spherical micelle, protected by the hydrophilically ended outer moiety. Simulation allows the tendency to form micelles and the rate at which the drug is released within the body to be estimated.

The voluminous experimental information about the linkage between structural variables and properties of polymers is assembled in books, notably that by van Krevelen (1990). In effect, such books “encapsulate much empirical knowledge on how to formulate polymers for specific applications” (Uhlherr and Theodorou 1998). What polymer modellers and simulators strive to achieve is to establish more rigorous links between structural variables and properties, to foster more rational design of polymers in future.

A number of computer modelling codes, including an important one named ‘Cerius 2’, have by degrees become commercialised, and are used in a wide range of industrial simulation tasks. This particular code, originally developed in the Materials Science Department in Cambridge in the early 1980s, has formed the basis of a software company and has survived (with changes of name) successive takeovers. The current company name is Molecular Simulations Inc. and it provides codes for many chemical applications, polymeric ones in particular; its latest offering has the ambitious name “Materials Studio”. It can be argued that the ability to survive a series of takeovers and mergers provides an excellent filter to test the utility of a published computer code.

Some special software has been created for particular needs, for instance, lattice models in which, in effect, polymer chains are constrained to lie within particular cells of an imaginary three-dimensional lattice. Such models have been applied to model the spatial distribution of preferred vectors (‘directors’) in liquid-crystalline polymers (e.g., Hobdell *et al.* 1996) and also to study the process of solid-state welding between polymers. In this last simulation, a ‘bead’ on a polymer chain can move by occupying an adjacent vacancy and in this way diffusion, in polymers usually referred to as ‘reptation’, can be modelled; energies associated with different angles between adjacent bonds must be estimated. When two polymer surfaces interpenetrate, a stage is reached when chains wriggle out from one surface and into the contacting surface until the chain midpoints, on average, are at the interface (Figure 12.5). At that stage, adhesion has reached a maximum. Simulation has shown that