

Chapter 9

Craft Turned into Science

9.1. METALS AND ALLOYS FOR ENGINEERING, OLD AND NEW

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

9.1.1 Solidification and casting

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

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

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

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

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

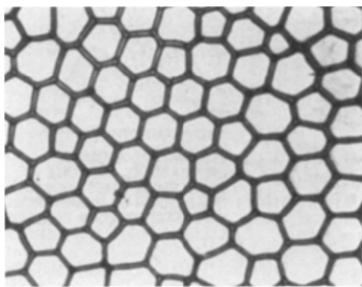


Figure 9.1. Decanted interface of cellularly solidified Pb–Sn alloy. Magnification $\times 150$ (after Chadwick 1967).

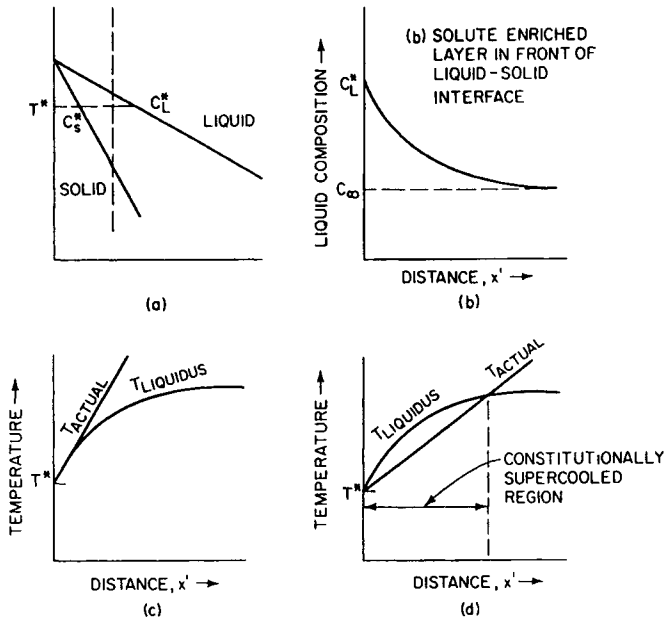


Figure 9.2. Constitutional supercooling in alloy solidification: (a) phase diagram; (b) solute-enriched layer ahead of the solid/liquid interface; (c) condition for a stable interface; (d) condition for an unstable interface.

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

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

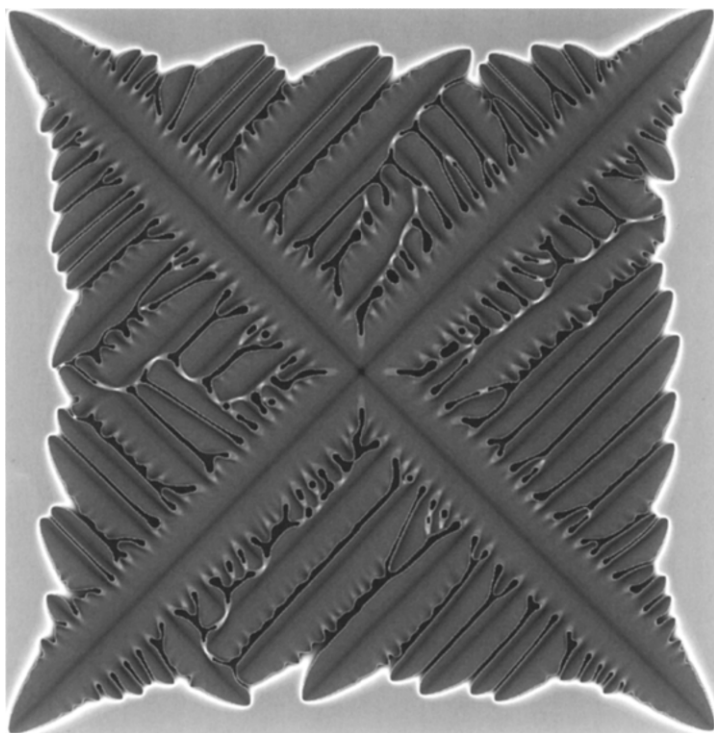


Figure 9.3. Computer simulation of dendrites growing into a Ni–Cu alloy with 41 at.% of Cu. The tints show local composition (courtesy W.J. Boettinger and J.A. Warren).

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

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

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

Such episodes of empirical discovery, followed only years later by explanation, were a major argument of the 'practical men' against the supposed uselessness of 'metallographists' (Section 3.2.1) but in fact the research leading to an explanation often smooths the way to subsequent, non-empirical improvements. A good recent instance of this was a study of the way in which grain-refining agents work in the casting of aluminium alloys. Fine particles of intermetallic compounds, TiB_2 and Al_3Ti , have long been used to promote heterogeneously catalysed nucleation from the melt of solid grains, on an empirical basis. Schumacher *et al.* (1998) have shown how a metallic glass based on aluminum can be used to permit analysis of the heterogeneous nucleation process: grain-refining particles are added to an Al-Y-Ni-Co composition which is cooled at about a million degrees per second to turn it into a metallic glass (in effect a congealed liquid). This is equivalent to stopping solidification of a melt at a very early stage, so that the interface between the nucleation catalyst and the crystalline Al-alloy nucleus, and the epitaxial fit between them, can be examined at leisure by electron microscopy: it was shown that nucleation is catalysed on particular crystal faces of an Al_3Ti crystallite which is itself attached to a TiB_2 particle. From this observation, certain methods of improving grain refinement were proposed. This is an impressive example of modern physical metallurgy applied to a practical task.

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

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

9.1.2 Steels

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

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

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

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

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

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

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

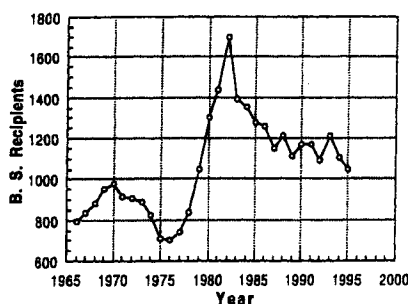


Figure 9.4. US bachelor's degrees in metallurgy and materials, numbers graduating 1966–1995 (after Flemings and Cahn 2000).

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

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

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

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

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

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

9.1.3 Superalloys

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

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

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

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

According to Pfeil's version of events, in Britain in the early 1940s, creep tests were at first made on ordinary commercial nichrome, but the results were not self-consistent; this was traced to differences in titanium and carbon content resulting from the use of titanium as a deoxidiser. A little later, a nickel–titanium additive with some aluminum was tried. The first superalloy, Nimonic 75, was made by 'doping' nichrome with controlled small amounts of carbon and titanium. From there, development continued on the hypothesis (which metallurgists had formulated in the 1930s but had been unable to prove) that creep resistance was conditional on precipitation-hardening. At this stage, in a British industrial laboratory in Birmingham, phase diagram work was thought essential, and the key to all superalloys was established by Taylor and Floyd (1951–1952), at the time of what I have called the 'quantitative revolution': they found that age-hardening in the early superalloys was entirely due to the ordered intermetallic phases Ni_3Al and Ni_3Ti , or rather a mixed intermetallic, $\text{Ni}_3(\text{Al}, \text{Ti})$, a phase they dubbed γ' , gamma prime, as it is still called, dispersed in a more nickel-rich, disordered matrix, called gamma. A little later it became clear that the microstructure (Figure 9.5) was an epitaxial arrangement; both phases were of cubic crystallography and their cube axes were parallel (this was the epitaxial feature); also the structure was extremely fine in scale. The microstructure was reminiscent of the Widmanstätten structures studied by Barrett and Mehl in Pittsburgh in the 1930s (see Section 3.2.2 and Figure 3.16) but finer, and with one important difference: the lattice parameters (length of the sides of the cubic unit cells) of gamma and gamma prime were almost identical. This turned out to be the key to superalloy performance.

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

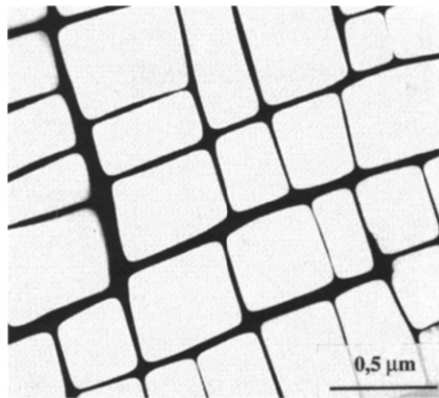


Figure 9.5. Electron micrograph of a superalloy, showing ordered (gamma prime) cuboids dispersed epitaxially in a disordered (gamma) matrix (courtesy of Dr. T. Khan, Paris).

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

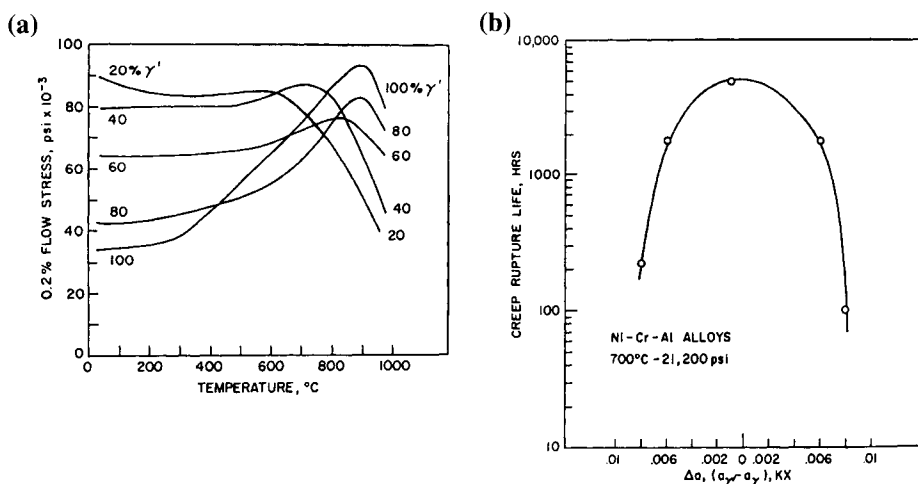


Figure 9.6. (a) The temperature dependence of the flow stress for a Ni-Cr-Al superalloy containing different volume fractions of γ' (after Beardmore *et al.* 1969). (b) Influence of lattice parameter mismatch, in kX (effectively equivalent to Å) on creep rupture life (after Mirkin and Kanchev 1967).

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

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

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

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

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

9.1.4 Intermetallic compounds

In Section 3.2.2, I briefly introduced the family of ordered intermetallic compounds, of which Cu_3Au was the first to be identified, early in the 20th century. We saw in the discussion of superalloys that such phases, Ni_3Al in particular, have a crucial role

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

In the 1950s and 1960s, research focused on 'reversibly ordered' intermetallics, such as Cu_3Au , CuAu , FeCo , Fe_3Al , Ni_4Mo . The idea was to compare the properties, especially mechanical and electrical properties, of the same specimen in fully ordered, imperfectly ordered and disordered states, and these states could be produced by suitable heat-treatment and quenching (e.g., Stoloff and Davies 1966). Of those listed above, only Ni_4Mo has found appreciable use in high-temperature alloys. From the 1970s onwards, attention was drastically transferred to 'permanently ordered' alloys, alloys which are so strongly ordered that they remain so on heating until they melt, such as Ni_3Al , NiAl , FeAl , Ti_3Al , TiAl , Nb_3Al , and investigation focused on creep resistance (closely linked to the magnitude of the ordering energy) and also on the Achilles's heel of the entire family, brittleness at room temperature (Yamaguchi and Imakoshi 1990). The brittleness results partly from the difficulty of driving dislocations through the strongly bonded unlike atom pairs making up the crystal structure, and partly, as we now know, from 'environmental embrittlement' the passage of hydrogen, from water vapour, along grain boundaries. Once again, grain boundaries have proved to be a key concern in determining the behaviour of a new family of metallic materials. In these researches, all the sophisticated techniques of modern characterisation, processing and mechanical analysis are in constant use, and alloying has been systematically used both to reduce the brittleness and to enhance high-temperature strength. This field is unmistakably in the province of the 'new metallurgy'.

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

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

9.1.5 High-purity metals

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

9.3. THE EVOLUTION OF ADVANCED CERAMICS

9.3.1 *Porcelain*

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

9.4. SINTERING AND POWDER COMPACTION

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

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

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

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

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

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

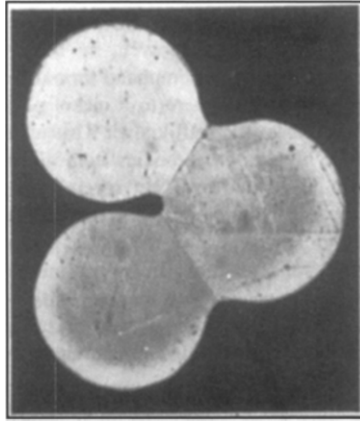


Figure 9.7. Metallographic cross-section through a group of 3 copper particles sintered at 1300 K for 8 h. The necks are occupied by grain boundaries (after Exner and Arzt 1996).

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

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

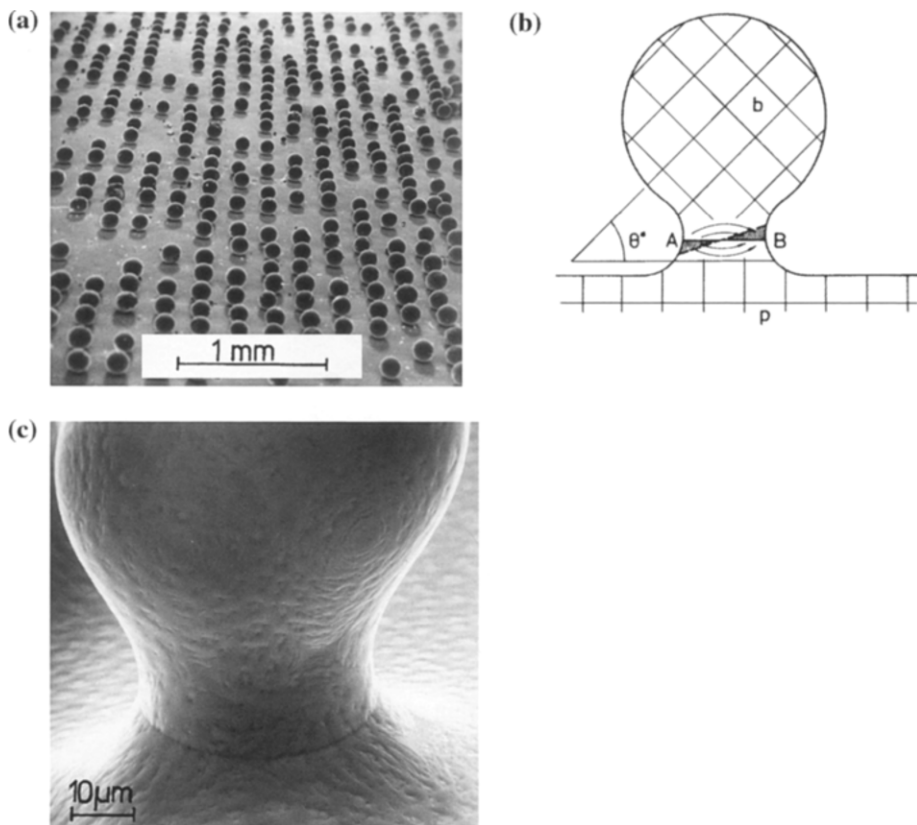


Figure 9.8. Sintering of single-crystal copper spheres to a single-crystal copper substrate. (a) experimental arrangement; (b) mechanism for rotation of an already-sintered sphere; (c) scanning electron micrograph of a sintered sphere (courtesy H. Gleiter).

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

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

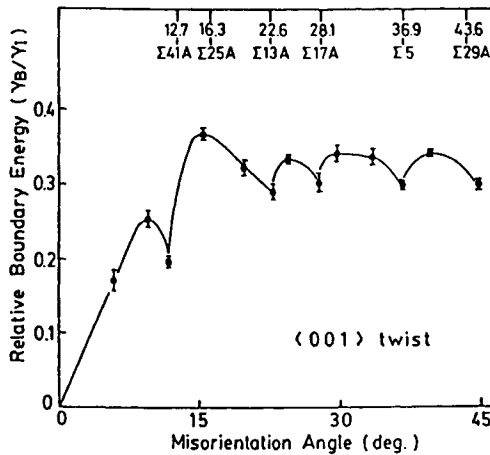


Figure 9.9. Relative boundary energy versus misorientation angle for boundaries in copper related by various twist angles about $[1\ 0\ 0]$ (after Miura *et al.* 1990).

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

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

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

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

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

9.4.1 Pore-free sintering

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

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

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

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

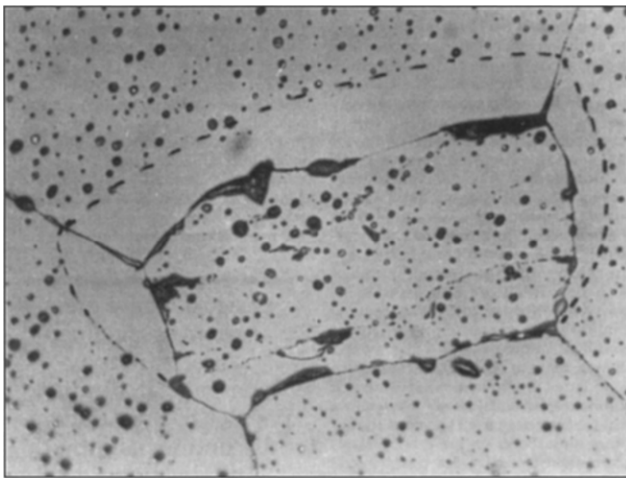


Figure 9.10. Optical micrograph of a powder compact of alumina at a late stage of sintering, showing pore removal along the path of a moving grain boundary. (The large irregular pores are an artefact of specimen preparation.) Grain boundaries revealed by etching. Micrograph prepared at GE in the late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

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

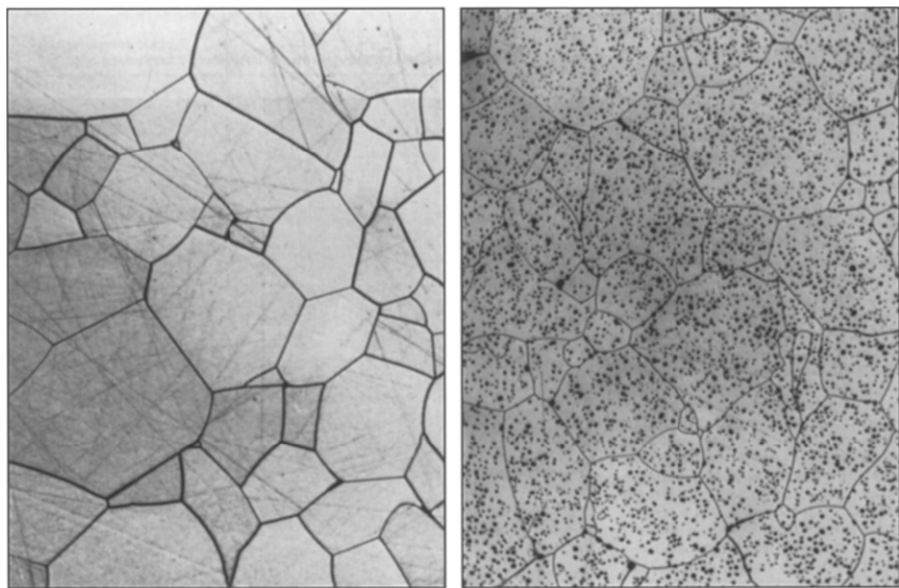


Figure 9.11. Microstructures of porous sintered alumina prepared undoped (right) and when doped with magnesia (left). Optical micrographs, originally 250 \times (after Burke 1996).

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

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

9.5. STRONG STRUCTURAL CERAMICS

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

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

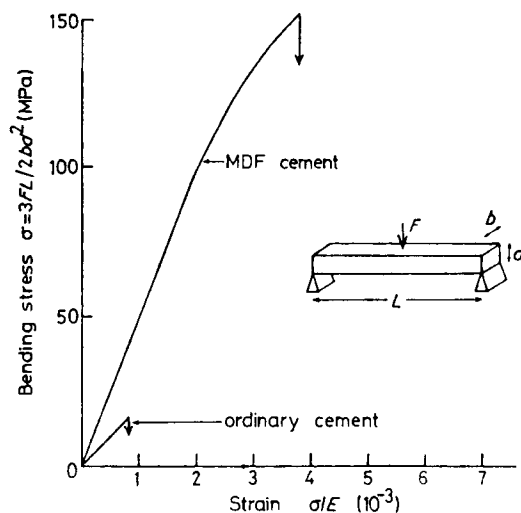


Figure 9.12. Bend strengths of ordinary and MDF cements (after Birchall *et al.* 1982).

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

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

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

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

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

9.5.1 Silicon nitride

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

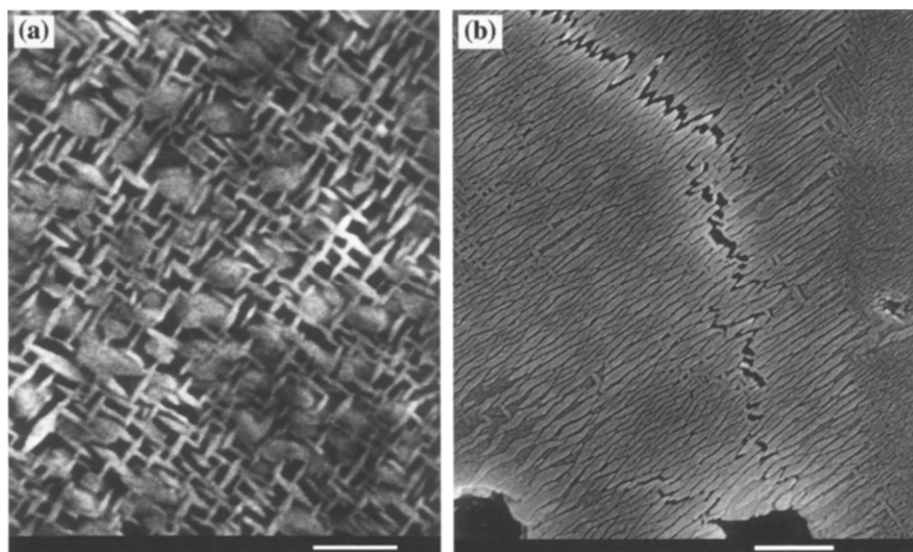


Figure 9.13. (a) Transmission electron micrograph of MgO-stabilised ZrO_2 aged to peak toughness. Tetragonal precipitates on cube planes are shown; the cubic matrix has been etched away with hydrofluoric acid. Bar = 0.5 μm . (b) Scanning electron micrograph of an overaged sample of MgO-stabilised ZrO_2 with coarsened precipitates, subjected to loading. Note the strong crack deflection and bridging. Bar = 2.5 μm (courtesy Dr. R.H.J. Hannink).

detailed memorandum on advanced structural ceramics and composites, issued by the US Office of Technology Assessment in 1986, remarks: “Ceramics encompass such a broad class of materials that they are more conveniently defined in terms of what they are not, rather than what they are. Accordingly, they may be defined as all solids which are neither metallic nor organic.” I shall restrict myself to just one family of ceramics, the silicon nitrides (Hampshire 1994, Leatherman and Katz 1989); the material was first reported in 1857. Si_3N_4 has two polymorphs, of which one (β) is the stable form at high temperatures. The powder can be prefabricated and then hot-pressed (or hot isostatically pressed), or silicon powder can be sintered and then reacted with nitrogen, which has the advantage of preserving shape and dimensions and being a cheaper process. A range of additives is used to ensure good density and absence of porosity in the final product, and a huge body of research has been devoted to this ceramic since the War. In 1971/1972, two groups, one in Japan (Oyama, Kamigaito) and in England (Jack, Wilson) independently developed more complex variants of silicon nitrides, the ‘sialons’ (an acronym derived from Si–Al–O–N), complex materials some of which can be pressureless-sintered to full density. They are also fully presented in Hampshire’s book chapter.

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

9.5.2 Other ceramic developments

I should add here a mention of a peculiar episode, still in progress, which is based on an attempt to extrapolate from the known properties of silicon nitride to those of a postulated carbon nitride, C_3N_4 , which should theoretically (because of the properties a C—N bond should possess) be harder than diamond. This idea was first promulgated by Liu and Cohen (1989) and led to an extraordinary stampede of research. Within a few years, several hundred papers had been published, but no one has as yet shown unambiguously that the postulated compound exists; however, very high hardnesses have been measured in imperfect approximants to the compound. Two reviews of work to date are by Cahn (1996) (brief) and Wang (1997) (detailed). The theoretically driven search for superhard materials generally has been surveyed by Teter (1998) under the title 'Computational Alchemy'. This whole body of research, squarely nucleated by theoretical prediction, has bounced back and forth

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

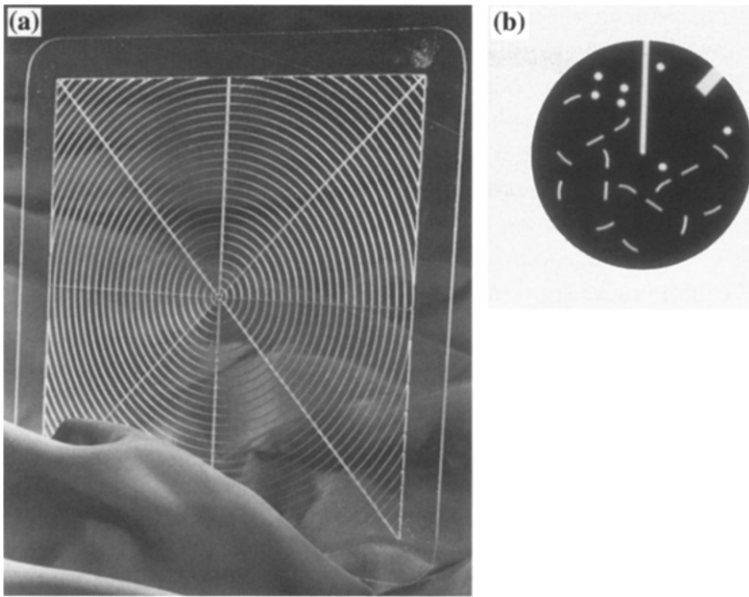


Figure 9.15. Photochemically machined objects made from FOTOFORM™ (after Stookey 1985, and a trade pamphlet, courtesy of the Corning Incorporated Department of Archives and Records Management, Corning, NY).

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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