

# 1

## Fundamentals

### 1.1 What are structural ceramics?

The word “ceramic” is usually associated with images of plates, mugs and cups and saucers, and concepts of brittleness and hardness. While ceramic materials are indeed often very hard, and certainly brittle (and can also be very fine works of art), this is a very narrow picture. Many ceramics have extremely important structural applications that depend on mechanical or thermal stability under a wide range of very demanding conditions. The aim of this book is to present a bigger and more balanced picture of these materials. This is done by taking five materials in the structural ceramics class – the case studies – and subjecting them to systematic and detailed examinations. The materials chosen are either the most widely used of their type, or show in some respect exceptional properties: they can therefore be considered to be the most important of the class. However, all the structural ceramics share their pattern of microstructures and properties to a greater or lesser extent with these five, which means that they are good representatives of the whole class. The small picture developed by these case studies should therefore be an accurate guide to the much larger, and also give the reader a full appreciation of the uses to which the structural ceramics are put.

*Ceramic* materials (which of course include the traditional whitewares) can be defined in very general terms as “high melting-point, inorganic, non-metallic materials” (Kingery, 1976). The word is usually assumed to be derived from the Greek *Keramos*, meaning clay, or ware (pottery) made from clay by heat treatment (Dodd and Murfin, 2006). By extension of meaning the term now includes the products of the silicate industries, thereby bringing in glass and cement. It has been widened further to include all inorganic materials made by the *powder sintering* route. Those materials generally called *structural ceramics* are a large group of ceramic materials with particularly marked properties of high strength, hardness, and resistance to wear. These properties may be retained from room up to high temperature (“white hot”, ~1000 °C or more), over long periods of time, though in



Figure 1.1 A small selection of structural ceramic components, in various types of material. (Reprinted by kind permission of Kyocera Corporation.)

fact most of the materials reviewed here are generally used at much lower temperatures. While some find highly specialised, and restricted, applications, many of these materials are commercially produced on a very large scale. One simple common example of a structural ceramic is the shiny white insulating body of the spark plug used in all petrol engines, which is alumina, and of which millions are produced every week. Another, less obvious, example is silicon carbide (perhaps better known as carborundum), used in the increasingly important filters taking smoke particles out of the exhaust gases of diesel engines. Figure 1.1 is a small selection of the very large number of types of structural ceramic components now produced, illustrating their range of sizes and shapes. At this stage the materials shown in the photograph are not identified, nor are the applications for the components. Some of their applications would in any case be difficult to guess, because the small ceramic component is hidden within a much larger unit.

## 1.2 Compositions

Ceramic materials are based on compounds consisting of metal–non-metal combinations (oxides are common examples), and compounds of the semi-metallic

elements (primarily boron and silicon). Simple two-element (*binary*) compounds form the basis, or major constituents, of four of the case studies (alumina, silicon carbide, silicon nitride, and zirconia). However, many of the chemical compounds (more usually referred to as *phases*) occurring in these materials are compounds of three or more elements (the aluminosilicates, for example, containing at least four elements, two metallic, one semi-metallic, and oxygen), and their crystal structures can be quite complex. Materials constructed entirely from single elements (for example silicon or carbon) are not normally regarded as ceramics, though in many respects they are barely distinguishable in terms of the pattern of their mechanical properties from materials conventionally thought of as ceramics. High-purity single-crystal silicon (in the form of “chips” – actually very thin slices) will be well known for its use in electronic devices and computer memories; carbon may be better known in one form as the transparent single-crystal diamond, and another as the black and much softer polycrystalline graphite (which incidentally provides an important illustration of the influence of the chemical bonding between simple carbon atoms on the physical and mechanical properties of the materials).

It is not possible to discuss any material without some reference to its chemical composition: atoms and ions are fundamental building units, from which all materials are constructed. A material’s stiffness, its hardness, and thermal stability are determined by the strengths and arrangements of the bonds between its constituent atoms and ions. It is also useful to have some appreciation of the chemistry of the processes involving the raw materials from which the basic materials may be produced: this helps with understanding other important aspects of a material such as its purity, and the likely costs of the powders which are normally the starting points for the production of ceramics.

Nonetheless, ceramics certainly cannot be regarded simply as solid inorganic chemicals, although the chemical formula is commonly – and perhaps also misleadingly – used as a shorthand description for a material (for example, “Al<sub>2</sub>O<sub>3</sub>” for aluminium oxide). A simple statement of the types of constituent atom, and their proportions, in the compounds (phases) in a material is only the first step to providing a complete description of the material. The overall chemical composition, the phases and their possible relationships, and the microstructure of a material, are generally inseparable in the development of a material’s properties, and the methods for controlling them.

Table 1.1 lists some of the more common basic chemical compounds making up the structural ceramics, and temperatures at which the pure materials form liquids (by melting or decomposition). While these numbers clearly give some indication of the potential of a material for high-temperature use, they form only a small part of the whole picture (and can by themselves even be misleading). Other factors will

Table 1.1 *Basic components of some common structural materials.*

Component	Chemical formula	Liquid formation temperature / °C
Aluminium oxide	Al <sub>2</sub> O <sub>3</sub>	2054
Calcium oxide	CaO	~2570
Magnesium oxide	MgO	~2800
Silicon dioxide	SiO <sub>2</sub>	1726
Titanium dioxide	TiO <sub>2</sub>	1850
Uranium dioxide	UO <sub>2</sub>	~2880
Zirconium dioxide	ZrO <sub>2</sub>	~2700
Boron carbide	B <sub>4</sub> C	~2450
Silicon carbide	SiC	~2250
Aluminium nitride	AlN	2200
Silicon nitride	Si <sub>3</sub> N <sub>4</sub>	1900 (with decomposition)
Mullite	3Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub>	~1890 (with decomposition)
Iron	Fe	1527
Nickel	Ni	1452
Tungsten	W	~3360

be important. For example it must also (almost always) be possible to produce the material on a profitable commercial scale, in competition with established materials (often metals). Of the large range of inorganic non-metallic materials, very few meet all the requirements for an ideal material.

### 1.3 Microstructure

The internal structure of a material, the patterns provided by the microcrystalline grains and other phases present, their shapes, sizes, orientations, distributions, the types of boundary (or interface) between them is given the broad term *microstructure*. This is the overall physical picture of the material, when examined on the micrometre, or (now more often) the nanometre scale. In a perfect *single crystal* the very regular pattern of the atoms forming the crystal lattice is uninterrupted throughout the piece (though real single crystals usually contain small-scale, local, disruptions to the pattern – the *lattice defects*). *Polycrystalline* materials are constructed from small crystals, microcrystallites – commonly referred to as *grains* – of  $\mu\text{m}$  dimension. The grains have been fused together during the production of the component, normally in the cases of the materials to be discussed here, by *sintering* (that is, heating to a high temperature) compacted fine powder, the particles of which are likely to be small single crystals.

## 1.3 Microstructure

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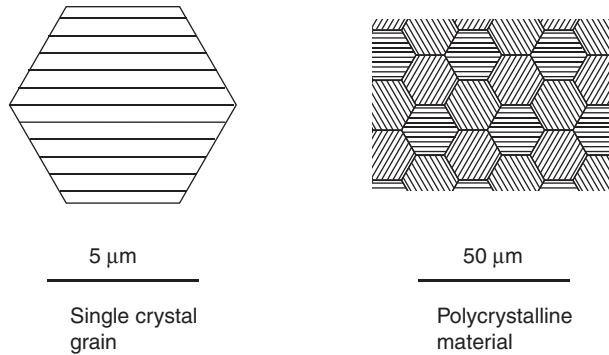


Figure 1.2 Schematic presentations of a single crystal and a polycrystalline material.

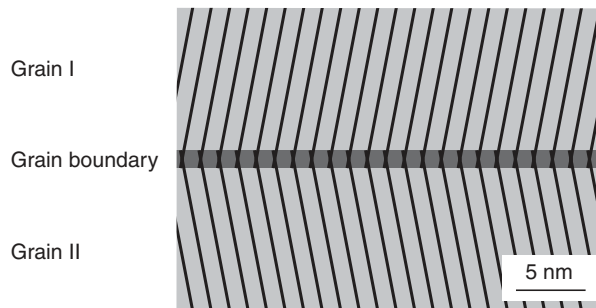


Figure 1.3 Schematic representation of the grain boundary region between two single-crystal grains.

The interface between two grains is the *grain boundary*, and its structure can be seen using high-resolution electron microscopy. The grains are bonded to each other either directly, or possibly through very thin (nm thickness) films which have a disordered or amorphous structure on the atomic scale. These features are illustrated schematically in Fig. 1.2 and Fig. 1.3. The sizes of the grains, and the grain boundaries, provide these materials with many of their characteristic properties, and further distinguish them from the single-crystal forms. A scanning electron micrograph of the surface of a relatively simple material, solid state sintered alumina, which has been given a heat treatment to show more clearly the boundaries between the grains, is shown in Fig. 1.4. Because the grain boundary is a region where the atoms are to some extent disordered, it also tends to act as sinks for impurity and additive atoms, so that the boundary often has its own distinct chemical compositions and physical properties. Figure 1.5 shows a transmission electron micrograph of a real grain boundary in sintered silicon

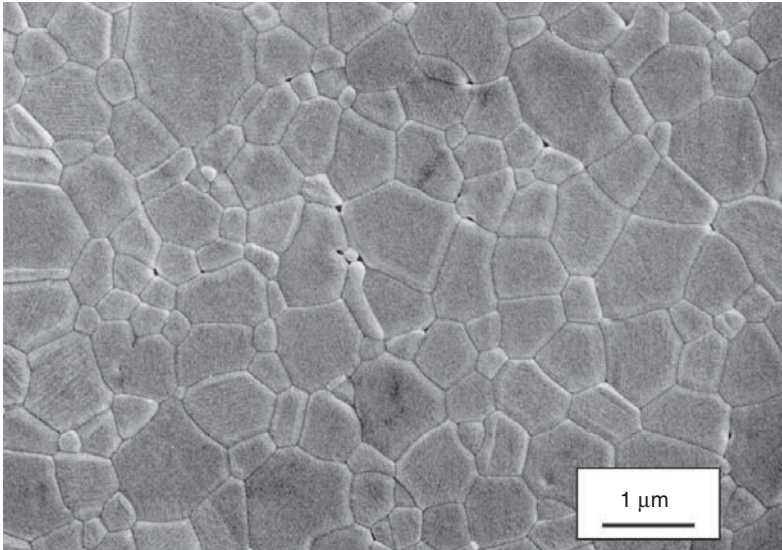


Figure 1.4 The surface of a fine-grain sintered polycrystalline alumina, showing the pattern of grain sizes, and grain boundary curvature.

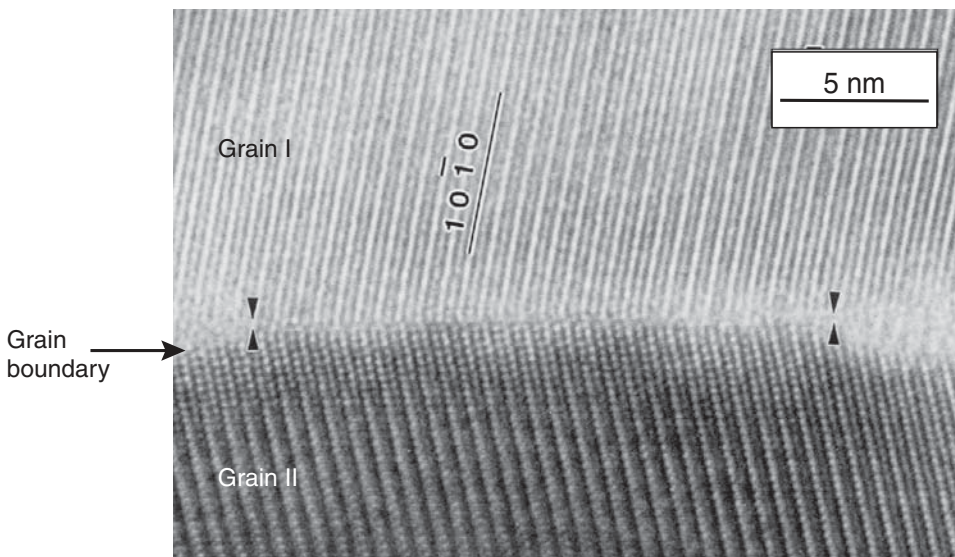


Figure 1.5 A transmission electron micrograph showing a real grain boundary in a silicon nitride ceramic. (Courtesy of Chongmin Wang.)



nitride, where the slightly disordered region, about 1 nm wide and containing in places a separate and amorphous phase, is clearly visible. Most of the materials coming under the heading “structural ceramics” have an internal structure viewed on the micrometre scale that is for the most part polycrystalline (Lee and Rainforth, 1994). The material may be built predominantly from one type of crystalline material (as in a high-purity alumina), or there may be a mixture of several phases (as in porcelain – though porcelain is not normally thought of as a polycrystalline material). Practically all ceramic materials contain more than one phase: most of the major phases will be crystalline, but varying amounts of amorphous (non-crystalline, or glass) material are almost always present. The amorphous phase is usually a silicate, or an aluminosilicate, of composition related to the main phase, or an additive used to accelerate sintering. Some of the material will be in the form of 1 to 2 nanometre thickness silicate films at grain boundaries, as in the case in the silicon nitride boundary shown above, and can be regarded as an intercrystal bonding phase. To put this dimension into perspective, the Si–O bond length is ~162 pm, so that a 1 nm thick silicate grain boundary film will be about six Si–O units across. When the amorphous material is present in large amounts it will exist as small isolated pockets, or as larger volumes of glass, dispersed between and bonded to the crystalline grains. In the porcelains it forms the major phase.

The glass, or amorphous, phases cannot be ignored: in many cases (and particularly at high temperatures) the properties of a multi-phase material may be determined more by the properties of the secondary phases and intergranular grain boundary materials, and particularly if they are amorphous, than they are by those of the major phase.

One more important microstructural feature that cannot be ignored is the *porosity* – the internal void space. This, as with the glass, has a big part in determining properties such as stiffness, strength, and thermal conductivity. The presence of porosity in sintered ceramics is almost inevitable because it is the residual void space in the compacted powder that was not quite completely removed during sintering. Most porosity is *closed*, that is inaccessible to the external environment, and is generally undesirable. Other pores are accessible (*open*), and can be essential for some applications of a material, as a gas or liquid filter, or catalyst support, for example.

To see the internal structures clearly, electron microscopy (scanning and transmission) is generally used. Optical (light) microscopy usually does not provide the necessary magnification. It is the microstructure, with all its finer details, which has a very strong influence on the mechanical and physical properties of the material. The other important influence on property and behaviour is the external environment – that is the temperature, atmosphere, loading conditions and time under load. These relationships are summarised in Fig. 1.6.

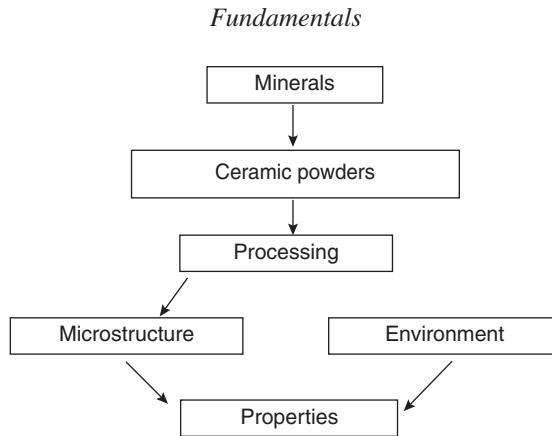


Figure 1.6 The main factors controlling the properties of a ceramic.

## 1.4 Powders

Most forms of the structural ceramics start their lives as fine powders, which are then compacted, shaped and sintered by one method or another. The way in which the microstructure of the final material is developed is strongly dependent on the powder from which it started. It can be said that the ceramic, in its microstructure, tends to retain a memory of its starting powder. For this reason the powder, its properties, and the processing into the ceramic, are crucial aspects of the development of a high-quality microstructure. In fact the quality of the powder processing operations can be as important for the properties, and satisfactory performance, of a ceramic component, as are the intrinsic properties of the material itself.

The main steps in the standard ceramic production process are summarised in Fig. 1.7. These are the production of a fine powder, the formation of the component shape by compaction of the powder, sintering, and any finishing operations required to refine the shape of the component or the quality of its surface. The compaction and final shaping steps can take place simultaneously (as in the *slip-casting* of a mug), or sequentially (as in the case of the spark plug insulator). Sintering is normally a separate production stage, as is indicated (Route I). However, it is also possible to combine the pressing of a powder with the sintering stage, in a process termed *hot pressing* (Route II). While this has the advantages of speed, and that a fine-grain microstructure can be obtained, it is also a more expensive process, and is therefore used only when absolutely necessary. After the sintering has been carried out, grinding and machining operations require the use of tools impregnated or coated with diamond or other ultra-hard powders. Many products, sliding parts for example, will need to be surface ground or polished as a matter of routine, because the as-sintered finish is



## 1.4 Powders

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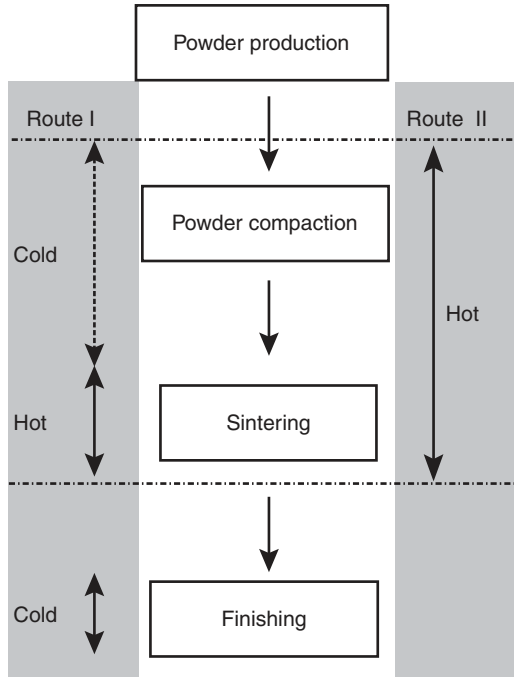


Figure 1.7 Standard ceramic processing routes: I normal pressureless sintering; II hot pressing.

usually not sufficiently smooth. In fact diamond machining of a sintered ceramic can become the most expensive stage of the whole process (although from the point of view of the manufacturer it also represents added value). It is obvious that there can be considerable advantages in trying to obtain the final required shape as closely as possible (sometimes called *near net-shaping*), while the ceramic component is still in the form of its starting powder: afterwards things become very much more difficult, time-consuming, and expensive.

#### 1.4.1 Powder sources

The potter is fortunate in that the clay starting material, which is a major constituent of the blended powders used in the production of what is broadly termed pottery, occurs naturally as a very fine powder, the result of the weathering of igneous rocks over many millions of years. Clay particles usually have sizes of around  $1\ \mu\text{m}$  (though the question of size is not simple because, for reasons to do with the crystallography of the constituent minerals, the shapes of the individual clay particles tend to be thin plates). The other main ingredients of “pottery” (to which the porcelain treated in Chapter 2 comes closest), and those of the

Table 1.2 Typical source minerals.

Material	Typical source minerals
Porcelain	Clays, feldspars, quartz sand
Alumina	Bauxite
Silicon carbide	Quartz sand
Silicon nitride	Quartz sand
Zirconia	Baddeleyite, zircon sand

technical ceramics, are rarely found in nature as fine powders. These starting powders can be produced by grinding and milling minerals or sands. More often, as in the cases of two of the ceramics discussed here, they must be obtained by chemical extraction processes from bulk minerals, leading ultimately to precipitation from a solution of an insoluble hydrated oxide, or hydroxide, followed by dehydration to the oxide. An aqueous suspension (slurry) of the oxide may then be spray-dried, to give soft, free-flowing microspherical agglomerates, which are easier to handle. Very high-purity powders are either difficult to obtain, or are expensive, partly because many materials start out as very impure minerals, and partly because of the difficulties of extracting small amounts of impurity compounds and elements from a chemically rather unreactive material. It is quite feasible to use standard aqueous phase chemistry to prepare many kinds of ultra-high purity (loosely, of chemical “analytical reagent” purity, or >99.9%) ceramic powder, but the cost of these very high-purity powders can be very high and the scale on which they are used is small.

Table 1.2 lists some of the more common minerals used as starting points for the materials treated in this book: the methods by which the prepared starting powders may be obtained from them will be outlined in each chapter. Some knowledge of the powder production process is useful in that it allows the user to be aware of the type, and amount, of impurity to be expected in a commercial powder, and hence the ceramic derived from it. One of the many difficulties faced by manufacturers is that the purity (and indeed other important characteristics) of the powder provided by the supplier tends to vary slightly from batch to batch. It should also be noted that impurities in the powder at the “parts per million” level can have significant effects on the surface chemistry of the particle and thus on the rheology of particle suspensions in water, and consequently on what can very broadly be termed the *processability* of the powder into a ceramic component. Only slightly larger quantities can have detectable and important influences on sintering characteristics, and the high-temperature strength of the finished products, as was clearly shown during the development of sintered silicon nitride materials (Iskoe *et al.*, 1976).