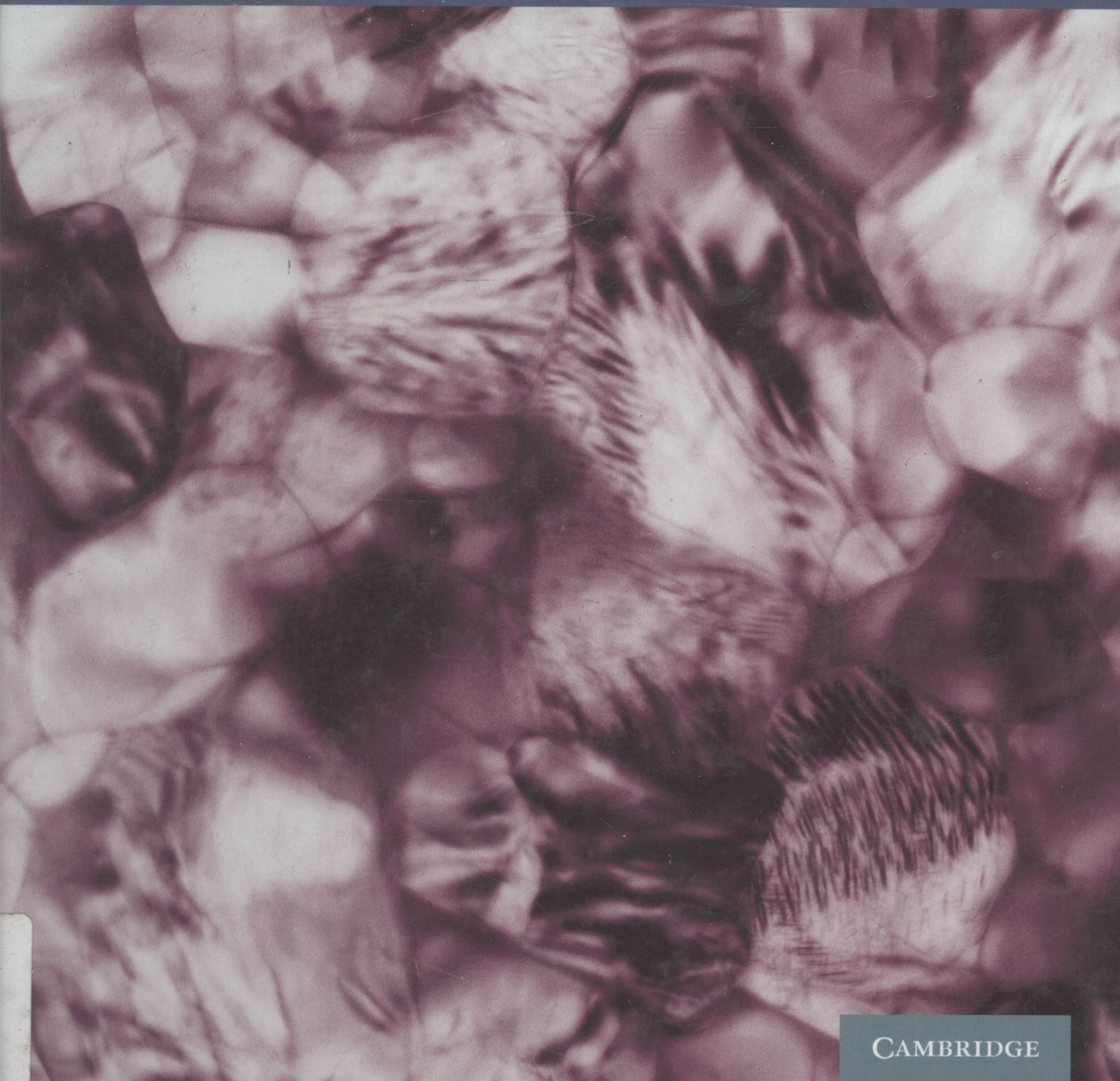
FRANK RILEY

Structural Ceramics

Fundamentals and Case Studies



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STRUCTURAL CERAMICS

Fundamentals and Case Studies

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STRUCTURAL CERAMICS: FUNDAMENTALS AND CASE STUDIES

This book provides an introduction to the structural ceramics, their processing and properties. Five important groups of materials – porcelain, alumina, silicon carbide, silicon nitride and zirconia – are presented as case studies. Historical developments, the properties of constituent components, and relationships between production methods, resulting microstructures, and materials properties, are explained.

The structural ceramics have many commercial applications, ranging from high voltage insulation and fuel cells, to metal machining tools and surgical implants. These applications depend on combinations of chemical, physical and mechanical properties, which include structural stability over wide temperature ranges, strength, hardness, and resistance to wear.

Over 200 diagrams and photographs provide visual aids to learning, and end-of-chapter summaries pull together key points. With numerous review questions to test understanding of the topics covered, and extensive referencing, this book is ideal for those studying materials science and engineering, or starting research in the structural ceramics area.

FRANK RILEY was Professor of Ceramic Processing (and is now Emeritus Professor) at the University of Leeds where he researched and taught for over 30 years. He is a Fellow of the Institute of Materials, Minerals and Mining. He has directed two NATO Advanced Study Institutes, is editor of several conference proceedings, and has authored many research publications and review articles.

For Mary

Preface

The technical ceramics can be divided into *electroceramics*, which, by and large, make use of the materials' electrical or magnetic properties, and the *structural* ceramics, with applications mainly (though not entirely) dependent on mechanical properties. The structural ceramics providing the case studies for this book have been chosen because they illustrate well the characteristic features of the class of structural ceramics as a whole. They have a wide range of properties, and they are of considerable technical importance. The five studies are intended to introduce the reader to this large class of materials, and the rôle they play in today's world. Each of the materials (more precisely, groups of materials) is examined systematically to provide an outline of its history and a simple picture of its development, how it can be fabricated, details of key physical and mechanical properties, and a summary of the principal applications based on these properties.

Because all the ceramics reviewed here have very high melting points, components are normally made by processing powders. Some appreciation of this aspect of the subject will be helpful before any examination of individual materials takes place. Chapter 1 therefore introduces the fundamental features of the powder sintering route to a ceramic, and the development of microstructure. Ceramics have a reputation for brittleness and a rather marked tendency to break if dropped, though in fact the best of the structural ceramics can have strengths comparable with those of the high tensile steels. Aspects of strength, fracture toughness and the general properties of ceramic materials important for the engineer and designer are also introduced here. The following chapters then examine each of the five materials in turn to identify distinguishing features, and those properties which are common to the structural ceramics as a class of material.

The oldest of the structural ceramics, by several thousand years, are the various types of what is usually termed "pottery", originally used for storage of grain, oil, and wine. Development of rudimentary production processes gradually led to refinements in quality, particularly aesthetic appeal, and strength, resulting in the development of the translucent, but strong, materials generally called "porcelain", or "china". Industrial porcelain, a "traditional" ceramic, is reviewed in Chapter 2, and although it is not particularly strong it provides a very useful introduction to some of the important features of the structural ceramics, and a standard by which the property values of the others can be judged. The more modern, or "technical", high-strength ceramics are then examined in the following four chapters. These studies show how limits on a material's properties can be determined by the fundamental nature of the components of the material itself, and assess the extent to which it might be possible to vary the properties or obtain improvements. The alumina, silicon carbide, silicon nitride and zirconia groups of materials have been developed as high-grade structural ceramics only during the last 40 years or so (though their history is actually very much longer). Alumina, discussed in Chapter 3, is by far the most widely used, but silicon carbide discussed in Chapter 4, and silicon nitride in Chapter 5, also have very important and expanding application areas. Zirconia in Chapter 6 is in one way the odd one out, because its markets at present are very much smaller than those of the others. It is included because the zirconia group of materials provides some of the highest strength and toughness ceramics yet seen outside of the ceramic composites area. In this respect therefore zirconia materials might be considered to be the best of the structural ceramics, though, as will be seen, they are not completely perfect. Chapter 7 summarises these case studies, and provides an overview of the development of the five groups of material, and their present areas of application.

This book could not have been written without the stimulus and willing cooperation of a very large number of people, who freely made available illustrations, photographs and technical information. I am particularly indebted to John Bailey, Jake Beatson, John Briggs, Rik Brydson, Francis Cambier, Dusan Galušek, Gren Goldstraw, Christine Hahn, Harry Hodgson, Peter Johnson, Heiner Knoch, Brian Lines, Roger Morrell, Trevor Page, Susan Payne, Günter Petzow, Vladimir Sida, Lance Snead, and Chongmin Wang, for help with background information, photographic illustrations and original diagrams.

January 2009 *Frank Riley*

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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_2O_3" 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_2O_3	2054
Calcium oxide	CaO	~2570
Magnesium oxide	MgO	~2800
Silicon dioxide	SiO_2	1726
Titanium dioxide	TiO_2	1850
Uranium dioxide	UO_2	~2880
Zirconium dioxide	ZrO_2	~2700
Boron carbide	B_4C	~2450
Silicon carbide	SiC	~2250
Aluminium nitride	AlN	2200
Silicon nitride	Si_3N_4	1900 (with decomposition)
Mullite	$3Al_2O_3.2SiO_2$	~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 μm 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.

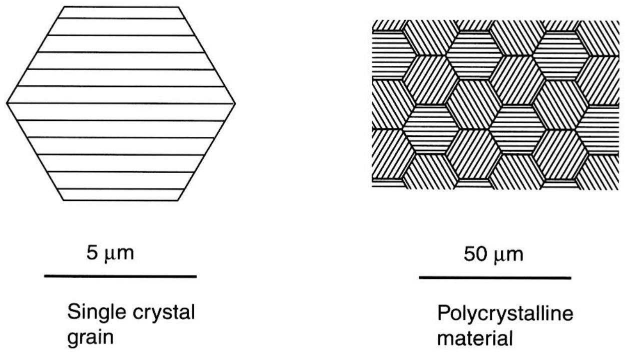

Figure 1.2 Schematic presentations of a single crystal and a polycrystalline material.

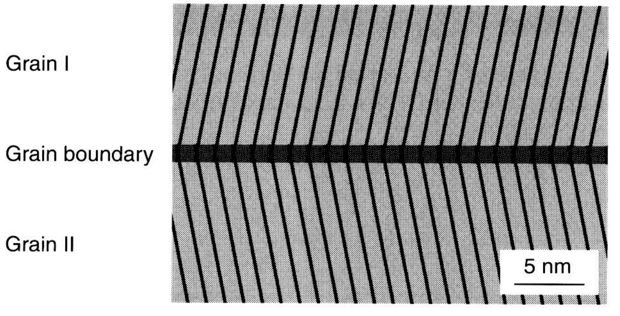

Figure 1.3 Schematic representation of the grain boundary region between two single-crystal grains.

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

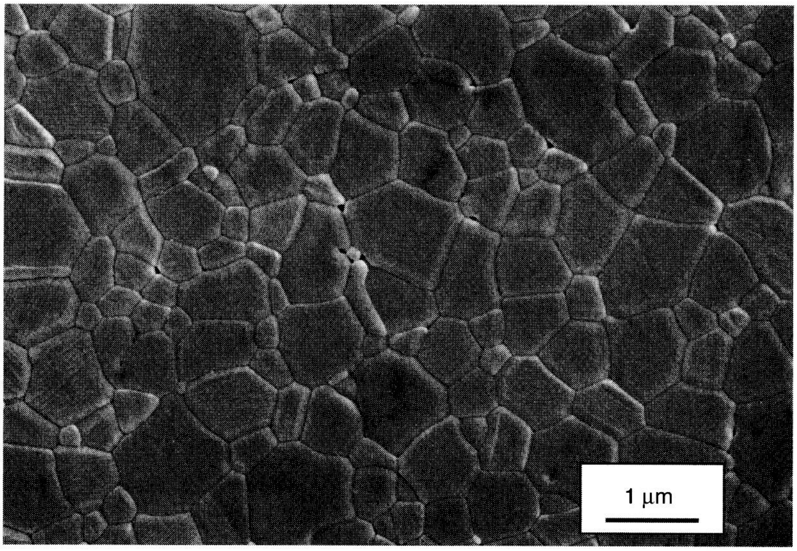

Figure 1.4 The surface of a fine-grain sintered polycrystalline alumina, showing the pattern of grain sizes, and grain boundary curvature.

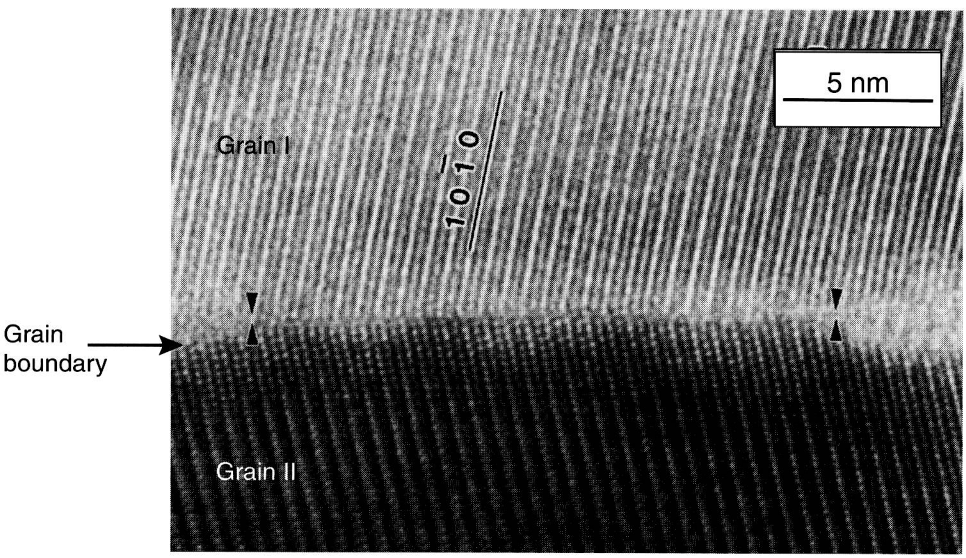

Figure 1.5 A transmission electron micrograph showing a real grain boundary in a silicon nitride ceramic. (Courtesy of Chongmin Wang.)

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.