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# **Mechanical behaviour of ceramics**

**CAMBRIDGE UNIVERSITY PRESS**

Cambridge

London · New York · Melbourne

Published by the Syndics of the Cambridge University Press  
The Pitt Building, Trumpington Street, Cambridge CB2 1RP  
Bentley House, 200 Euston Road, London NW1 2DB  
32 East 57th Street, New York, NY 10022, USA  
296 Beaconsfield Parade, Middle Park, Melbourne 3206, Australia

© Cambridge University Press 1979

First published 1979

Printed in Great Britain at the  
Alden Press, Oxford

*Library of Congress Cataloguing in Publication Data*

Davidge, R. W., 1936–

Mechanical behaviour of ceramics.

(Cambridge solid state science series)

Includes index.

1. Ceramic materials – Testing. I. Title.

TA430.D37 620.1'4 77-90206

ISBN 0 521 21915 9

## Preface

The aims of this book are twofold: first, to present the scientific foundations underlying the mechanical behaviour of engineering ceramics; secondly to show how this theory, together with less rigorous empirical approaches where necessary, can be applied to the engineering use of ceramics. The appeal is thus both to the materials scientist and to the technologist dealing with engineering applications. The links between the materials science and engineering aspects have been insufficiently emphasised in the past. In consequence, the ceramist often regards the engineer as someone who does not know how to handle ceramics, whereas the engineer regards ceramics as fragile materials of variable and unpredictable properties. There is some truth in both of these viewpoints and it is essential that a new type of materials technologist emerges who can both understand ceramic materials and design engineering components from them.

The distinguishing mechanical property of ceramics (as witnessed by any ham-fisted dish-washer) is brittleness – that is, catastrophic failure following an almost entirely elastic deformation. Were it not for this limitation the use of ceramics for general engineering applications would be widespread; other, attractive properties such as hardness, stiffness and refractoriness could be exploited to the full. Brittleness is thus a dominant theme throughout this volume.

The crucial theoretical background stems directly from the basic theory of brittle fracture developed by A. A. Griffith in the early 1920s. It was only some 30–40 years later that these ideas were applied systematically to ceramics – first, in the form of single crystals that exhibited cleavage fracture and subsequently, to more useful ceramics. Over the last decade, however, progress has been spectacular and the science of the mechanical behaviour of ceramics, particularly strength, has now reached a consolidated stage where it is being applied ever increasingly to important engineering applications. Much of this information is still scattered in the literature and it is thus timely that the principles are gathered together in a single volume.

The first part of the subject matter (chapters 1–6) is concerned with the relationship between the mechanical properties of ceramics and their atomic bonding and microstructure. To emphasise the complexity of practical ceramics we summarise first (chapter 1) the definition and use

of ceramics, their bonding and atomic arrangements and their methods of manufacture and resulting microstructures. The general stress/strain behaviour of ceramics is typified by two extremes: brittle failure at low temperatures and ductile failure at high temperatures. The elastic properties of ceramics (chapter 2) are amongst the most fundamental and important and are influenced by the type of bonding and the microstructure of the material. Elastic deformation is, however, limited, generally to  $\sim 0.1\%$ , being followed by either fracture or flow. Fracture in ceramics (chapter 3) is controlled by the stress to propagate small, sharp flaws and can be understood quantitatively by the application of linear elastic fracture mechanics. A consideration of plastic flow in ceramics (chapters 4 and 5) leads to the conclusion that significant plasticity is generally not possible at temperatures useful for engineering purposes and that the limited flow processes available lead to the generation of new flaws. These ideas are then drawn together (chapter 6) through examination of the fracture strength of selected ceramics.

The impact resistance and the development of tough ceramics is discussed in chapter 7 and demonstrates how useful improvements to toughness can be obtained, particularly by the incorporation of fibres into ceramic matrices. At present, however, the key design parameter for engineering ceramics is the useful working strength. Thermal-stress resistance is an important topic for the high-temperature use of ceramics and the background is presented in chapter 8.

Finally (chapter 9), the development of engineering design parameters for ceramics is described, including topics of special significance to engineering components: statistical variations in strength, time dependence of strength and the effects of multiaxial stress.

It is hoped that this brief exposure to the mechanical behaviour of ceramics, apart from providing a useful summary of the state-of-the-art, will encourage both the materials scientist to develop better theories and materials, and the engineer to design ceramic components with confidence.

I am indebted to my research collaborators, without whom many of the experimental and theoretical developments described here would not have been possible. Thanks are due to R. W. Cahn for his persistence in persuading me to accept this undertaking and his continued interest and encouragement. I am grateful to a number of colleagues including J. R. McLaren, D. C. Phillips, D. Pooley, P. L. Pratt and G. Tappin, who through discussions and criticism of the text have made valuable contributions.

July 1977

R. W. Davidge

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# 1 Background to ceramics

The properties of ceramics, as of other materials, are highly dependent on their texture, both on the atomic and on the micro- and macrostructural scales. Texture thus represents a key and central feature in the science of ceramics, linking fabrication and properties (fig. 1.1). The raw materials, the way they are processed and fired, can all affect the texture of the material and hence its properties. In addition, a number of external factors, particularly the environment, the temperature and the test conditions, are important in determining properties.



Fig. 1.1. Factors controlling the properties of ceramics.

Ideally, the ceramist attempts not only to explain the properties of interest in terms of the texture of the material but also to adjust the fabrication conditions so as to optimise the important properties. However, consideration must be given also to the form and design of the ceramic component. For traditional ceramics, such as building materials, refractories and pottery, the component is of simple shape and the engineering design aspect is not often of major importance. But for the newer class of engineering ceramics, for example high-strength oxides, carbides and nitrides, and ceramic-based composites, design is of vital importance if the properties of ceramics are to be utilised to the full; furthermore, data on mechanical properties must be expressed in a form relevant to engineering applications.

Although our primary aim is to develop an understanding of mechanical properties under a variety of physical conditions in terms of texture, it is essential to consider how ceramics are fabricated and hence the likely limits to their performance. In this chapter we outline a definition of ceramics, mention the types of atomic bonding and the geometrical arrangements of atoms, indicate briefly the ways in which ceramics are fabricated and their resulting microstructures, and introduce the responses of ceramics to stress.

## 1.1 Definition

The main classes of ceramic material are listed in table 1.1. Included are

Table 1.1. *Definition of ceramics*

Class	Material type	Typical uses	Importance of mechanical properties
Pottery	China, porcelain, earthen-ware, fireclay	Tableware, wall tiles, sanitary ware, electrical insulators	*
Heavy clay	Bulk clayware	Bricks, roof tiles, floor tiles, pipes	**
Abrasives	Alumina, silicon carbide, diamond	Grinding wheels, abrasive pads, polishing powders	***
Refractory	Alumina, silica, aluminosilicate, magnesite, carbon and graphite, zirconia	Furnace linings, molten-metal moulds	**
Glass	Glass, glass ceramics, enamels	Containers, flat glass, glassware, enamelled ware	*
Cement	Portland and alumina cement	Structural cement and concrete	**
Engineering ceramics	Oxides, carbides, nitrides, cermets, ceramic composites	Bearings, seals, dies, engine components	***
Electrical/optical/magnetic	Various	Capacitors, solid-state electrolytes, special windows, magnets	*
Nuclear	Oxides and carbides of fissile metals	Nuclear fuels	**

some common materials of each class and an indication of typical uses. The importance of the mechanical, as opposed to other, properties is denoted by a one- to three-star rating. The mechanical properties of all materials are of some significance in that all components are subjected to certain handling; but this is of minimum importance for, say, a ceramic magnet. At the other extreme the mechanical properties are of major significance for abrasives and engineering ceramics. There is no completely satisfactory and universally accepted definition of ceramics and the table should be regarded only as indicative of the main types and uses. More detailed information is given in Kingery *et al.* (1975) and Norton (1974).

## 1.2      **Bonding and atomic arrangements**

Ceramics are typical solids in which the atoms or ions are arranged in

regular arrays, although in glasses the regularity is only short-range. The type of bonding and the atomic arrangements affect a wide range of mechanical properties including elastic constants, hardness, and plastic properties such as slip by dislocation motion. This is a vast subject but a few relevant basic principles are worth reviewing at this stage.

### Bonding

Bonding in ceramics is mainly of ionic or covalent type, and usually a hybrid of these. The tendency towards ionic bonding between atoms increases with increasing difference in the electronegativity of the atoms. Electronegativity is a qualitative property which is a measure of the

Table 1.2. *Electronegativity values for elements in the first three periods of the periodic table*

H	2.1						
Li	1.0	Be	1.5	B	2.0	C	2.5
Na	0.9	Mg	1.2	Al	1.5	N	3.0
						O	3.5
						P	2.1
						S	2.5
						F	4.0
						Cl	3.0

power of an atom in a molecule to attract electrons to itself (Pauling, 1948). Electronegativity values can be ascribed to each element from a consideration of the bond energies between that element and other elements, and Pauling's values for the elements in the first three periods of the periodic table are given in table 1.2. Note that elements in group I of the periodic table are at opposite ends of the electronegativity scale to elements of group VII with a systematic variation between. It is clear in a qualitative sense that an increase in the difference in the electronegativity values of the two elements in simple compounds leads to an increase in the proportion of ionic bonding. Materials comprising a single group IV element such as carbon or silicon, with zero electronegativity difference, can thus be associated with pure covalent bonding. It would be useful to be able to make quantitative statements for other compounds regarding the proportions of ionic and covalent bonding. The data of the electronegativity scale provide the basis for this but the problem of calculating absolute values is not easy and remains empirical at present. Using reasonably justified assumptions about the amount of ionic bonding in various hydrogen-halogen compounds Pauling produced the curve shown in fig. 1.2. Although the values are not absolute the curve permits an approximate and comparative estimate of the type of bond, and details for selected compounds are included in table 1.3. There is a wide range of bond type, from MgO which is mainly ionic to SiC which is predominantly covalent.

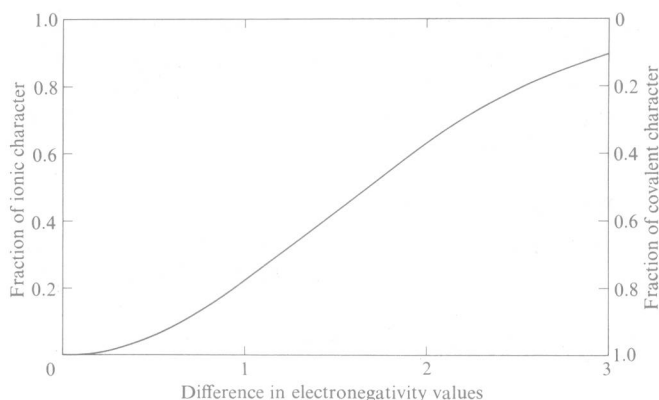


Fig. 1.2. Variation in bond character with difference in electronegativity values of constituent atoms of compounds. (After Pauling, 1948.)

Table 1.3. *Fractions of ionic and covalent bonding for simple compounds*

Compound	LiF	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Si <sub>3</sub> N <sub>4</sub>	SiC	Si
Electronegativity difference	3.0	2.3	2.0	1.7	1.2	0.7	0
Fraction ionic binding	0.89	0.73	0.63	0.51	0.30	0.11	0.00
Fraction covalent bonding	0.11	0.27	0.37	0.49	0.70	0.89	1.00

### Atomic arrangements

The ways in which individual atoms in ceramic compounds are arranged geometrically depends on several factors including (a) the type of bonding, (b) the relative sizes of the atoms, and (c) the need to balance electrostatic charges.

In covalent crystals the nature of the bond dominates and in  $\beta$ -SiC each atom is surrounded by four neighbours of the other element. This structure, which is similar to that of diamond, is shown in fig. 1.3(a).

In ionic crystals the bond is less directional and the relative atomic sizes and charge-balance factors become of increasing importance. In most oxides the oxygen ions form close-packed arrays and the metallic ions, which are usually smaller, are arranged in the interstices. Thus, the larger the relative difference in the radius of the ions, the smaller the expected coordination number (the number of oxygen ions surrounding each metal ion). The range of radii ratios over which a particular coordination number is likely can be computed from considerations of the packing of hard spheres. For example, six-fold coordination is

expected when the ratio is between 0.73 and 0.41. In MgO the radius ratio (Mg:O) is 0.47 and MgO has the cubic NaCl structure of six-fold coordination, fig. 1.3(b). In  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> the radius ratio (Al:O) is 0.41, the value separating six-fold and four-fold coordination, and in this case a six-fold coordination is also observed but of hexagonal structure, fig. 1.3(c). Although these size rules are a useful guide, other factors like

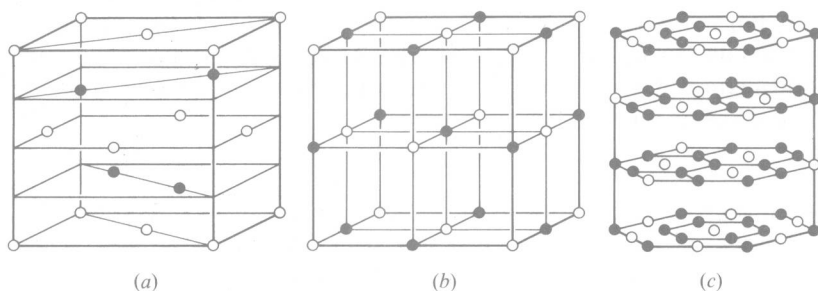


Fig. 1.3. Crystal structures of ceramics: (a)  $\beta$ -SiC (cubic zinc blende structure)  $\circ$ , Si;  $\bullet$ , C; (b) MgO (cubic sodium chloride structure)  $\circ$ , Mg;  $\bullet$ , O; (c)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (hexagonal close packed structure) – only the Al atoms ( $\bullet$ ), which fill two-thirds of the available sites, are shown;  $\circ$  represents the unfilled sites; hexagonal layers of oxygen atoms are sited between the Al layers (see fig. 4.2 for further details).

distortion or polarisation of the ions and tendencies towards covalency play important roles. Further information about the diversity of possible atomic arrangements is given in Kingery *et al.* (1975) and Evans (1964).

### 1.3 Fabrication and microstructure

The fabrication process converts particulate raw materials into useful solid objects. This involves forming the particulate matter into the desired shape, followed by a sintering stage at high temperature. Sintering is a term used to cover the processes whereby the original particles join together, often accompanied by a reduction in volume and in the free spaces between the particles. A variety of processes is available and that chosen depends both on the intricacy of the product shape and the properties required. Our interest in fabrication is not primarily in the precise geometry of the product and how this is formed, but in the texture of the material and how this is related to the manufacturing process. It is, however, essential to appreciate the fundamentals of fabrication, with regard to sizes and shapes possible, because of the relevance to the engineering design process – the optimum design from a stress point of view may be impossible to fabricate. The most widespread

fabrication process is sintering in the presence of a liquid phase but to attain the best mechanical properties it is often necessary to resort to more complicated techniques such as hot-pressing or reaction-sintering.

Fabrication processes other than sintering, which we mention just in passing, are those for glass and cement. Glass is made by melting together the constituent oxides which are then formed into products whilst the glass is in a semiliquid state. Cement is a fired mixture of clay and limestone which is then ground to fine powder; a chemical reaction occurs on mixing with water. Concrete, which is a mix of cement, sand and aggregate, is thus readily formed by pouring a fluid mix into moulds and allowing the mix to set.

### **Solid-state sintering**

In its simplest mechanistic form, the sintering process involves heating a material formed by the compaction at ambient temperatures of fine particles (usually  $< 1 \mu\text{m}$  diameter) of a pure powder. At high temperatures, typically from 0.5 to 0.8 of the absolute melting temperature, the particles sinter together. This is a spontaneous process and must thus be accompanied by a decrease in free energy of the sample. The most important driving force for sintering is the reduction in solid/vapour surface area when the individual particles fuse together and the larger particles grow at the expense of smaller ones. Sintering is thus the reverse of fracture; the creation of new surface area by fracture requires energy as we shall see in detail later.

Idealised solid-state sintering is of restricted practical use for ceramics in that pure materials and fairly high temperatures are involved. Solid-state sintering does, however, have important applications, for example in the preparation of pure uranium dioxide for nuclear fuel, and it is possible to obtain solid material close to theoretical density. The resulting microstructure comprises individual crystallites or grains, separated by grain boundaries, and probably residual porosity. The grain size is usually much greater than the original particle size.

### **Hot-pressing and liquid-phase sintering**

Hot-pressing refers to the simultaneous application of heat and pressure during sintering. The advantages over normal sintering are that higher densities and finer grain sizes may be achieved at lower temperatures. These result from the increased driving force for sintering caused by the stresses set up at the points of particle contact.

The main features of a hot-pressing facility include a refractory die into which is put a finely ground ceramic powder and a means of applying pressure to the die at high temperature. The most common die material

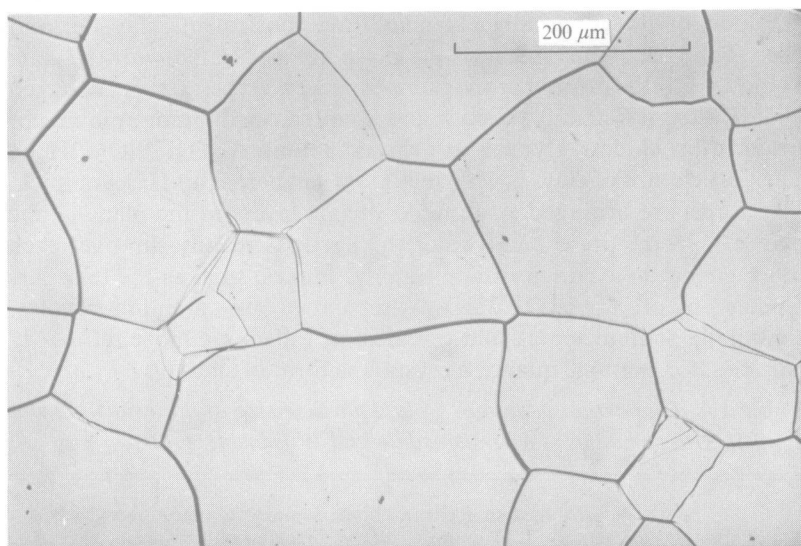


Fig. 1.4. Microstructure of fully dense, transparent magnesia. (After Davidge, 1969.)

is graphite. This needs the protection of an inert atmosphere and the strength of graphite usually limits the available pressures to  $\sim 50 \text{ MN m}^{-2}$ . The times required for pressing are usually quite short (a few minutes) and most of the fabrication time is taken in heating and cooling the assembly.

Because of the expense and difficulty of working at high temperatures, it is often advantageous to include small, controlled amounts of additives that form plastic phases which enable sintering to take place at somewhat lower temperatures. For example, small amounts of magnesia greatly assist the sintering of both alumina and silicon nitride. In some cases a fugitive additive can be used, such as lithium fluoride in magnesia, which can then be removed by a subsequent heat treatment. The microstructure of this hot-pressed magnesia is shown in fig. 1.4. This is a single-phase material with a uniform grain size and virtually no residual porosity. It should be noted that the advantages conferred by controlled chemical additions during hot-pressing may have to be balanced against the disadvantage of a reduction in refractoriness.

#### **Liquid-phase sintering in traditional ceramics**

The traditional pottery and clayware ceramics are shaped by the familiar forming processes, rendered possible by the plasticity of clay. After forming, the ware is dried, and sintered to give a mixture of fused oxides.

Pottery bodies are usually a blend of three constituents: clay, flux and filler. The mix retains much of the plasticity associated with the clay. Table 1.4 gives some mix proportions for several types. Clays are mixed hydrated oxides, mainly of silica and alumina, with minor amounts of several other oxides. A typical pure clay is kaolinite  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . The particle size of clays is very small,  $\sim 1 \mu\text{m}$  across and  $0.1 \mu\text{m}$  thick. The atoms are arranged as aluminosilicate layers in the plane of the platelets. In the presence of water the particles readily slip over each other giving the characteristic plasticity. Fluxes, such as the feldspars typified by  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , are anhydrous aluminosilicates, containing sodium, potassium or calcium. Fillers are more refractory particles, for example quartz, a crystalline form of silica.

Table 1.4. *Proportion (volume %) and particle size of materials in some typical pottery bodies. (After Dinsdale and Wilkinson, 1966)*

Material		Approx. median size ( $\mu\text{m}$ )	Earthen- ware	Bone china	Sanitary fireclay	Sanitary whiteware	Electrical porcelain	Tile
Clay	Ball clay	0.5	25	—	—	23	25	22
	China clay	1.5	25	25	—	24	25	22
	Fireclay	15	—	—	60	—	—	—
Flux	Stone	10	15	30	—	—	—	15
	Feldspar	10	—	—	—	20	25	—
Filler	Flint	10	35	—	—	33	25	41
	Bone	5	—	45	—	—	—	—
	Grog	1000	—	—	40	—	—	—

On heating the blended materials, the water and other volatiles evaporate first. At temperatures  $\sim 1000^\circ\text{C}$  and higher the clay particles and fluxes begin to react together to form a predominantly glassy mass and at this stage sintering and densification occur. This sintering process is complete at typically  $\sim 1200^\circ\text{C}$ . The filler particles being more refractory play a relatively minor chemical role in the sintering process, although some dissolution into the glassy phase occurs. Important aspects of the filler are that it reduces the total shrinkage and imparts rigidity to the body during firing so that the original geometrical form is preserved (albeit on a smaller scale).

The microstructures of traditional ceramics, even relatively simple ones, tend to be complex. Figure 1.5 illustrates that of a simple experimental ceramic made from 50% china clay, 30% alumina (an inert filler) and 20% nepheline syenite (a flux). The white alumina particles are relatively unreacted. The background matrix is mainly glassy but does contain crystalline phases such as mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). Also obvious are the small black regions which are residual porosity.

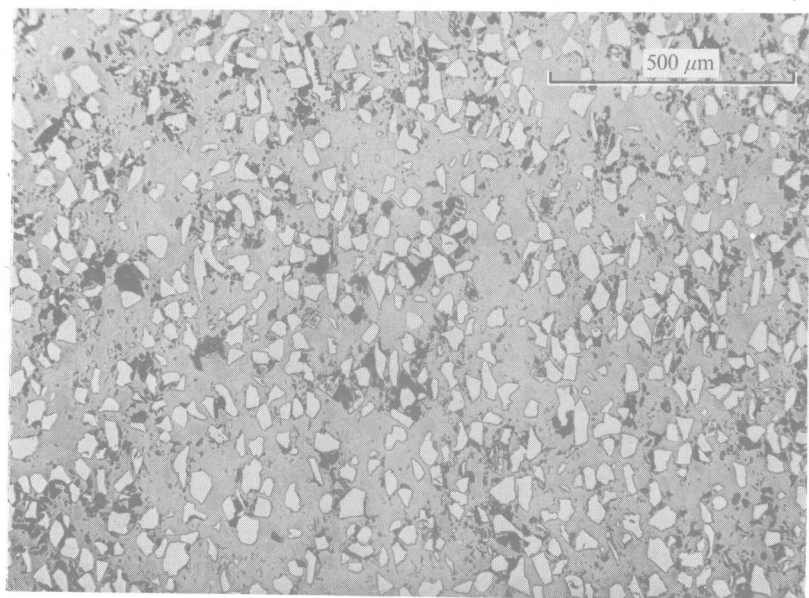


Fig. 1.5. Microstructure of experimental clay-based ceramic showing alumina particles in predominantly glassy matrix.

Although the formulations for other traditional ceramics such as refractories and vitreous-bonded abrasives are very different from those described above, the sintering process is based on the same principles. Refractories are made by firing compacted particles of the major phase(s) which usually contain small amounts of impurities which act as fluxes. Similarly for porous vitreous-bonded alumina abrasives the hard ceramic particles are pressed together with small amounts of clay and flux, which again fuse at high temperatures.

### Reaction-bonding

This process, of increasing technological importance, involves sintering by way of a chemical reaction. This is not a logical route for oxide production because it would require reduction of oxide ores to metal and then oxidation back to the oxide. The technique is used particularly for silicon-based ceramics such as silicon nitride and silicon carbide. The following reactions occur at high temperatures,



and bonding occurs simultaneously.

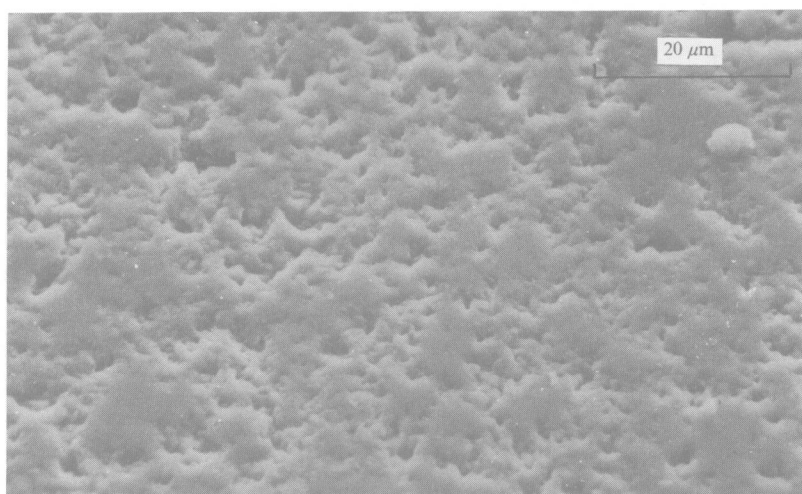


Fig. 1.6. Scanning electron micrograph of polished surface of reaction-bonded silicon nitride revealing porosity. (After Davidge *et al.*, 1972.)

To produce reaction-bonded silicon nitride, the articles are first formed from silicon powders by a variety of processes. These include flame-spraying of silicon on to a former – this process is useful for shells and hollow structures; isostatic pressing of silicon powders; or mixing of silicon powder with plastic binders and then plastic-forming using techniques such as rolling, extruding or pressing. The silicon content at these green stages is  $\sim 50\%$ , the remainder being plastic additives or voids. After burning out the additives where appropriate, at low temperature, the components are then fired in a nitrogen atmosphere. This is generally performed partly below the melting point of silicon ( $1410^\circ\text{C}$ ) and then, once a skeleton of silicon nitride has formed, above the silicon melting point. The total firing schedule is over a few days. The resulting microstructure, fig. 1.6, comprises a pure, fine-grained silicon nitride. The porosity is generally in the range 10–30%. Material containing  $< 10\%$  porosity cannot readily be produced in convenient firing times because the porosity is necessary to allow access of the nitrogen to the centre of the component.

Silicon carbide could be made, in principle, using a similar technique by reacting particles of carbon with liquid or gaseous silicon. However, it has been found advantageous to start with a mixture of silicon carbide particles plus a fine graphite powder before reacting with silicon. The silicon carbide and graphite are blended with plastic binders and formed into shapes in similar ways to those described for silicon nitride. After